Ph.D. THESIS

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THESIS OF THE DOCTORAL (Ph.D.) DISSERTATION

SURFACE CHEMISTRY STUDIES OF SnO_2-Pt/Al_2O_3 CATALYST FOR ENVIRONMENTALLY IMPROVED CATALYTIC OXIDATION OF CARBON MONOXIDE, PROPYLENE AND FOR CYCLOPROPANE ISOMERIZATION

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DOKTORI (PH.D.) ÉRTEKEZÉS TÉZISEI

SZÉN-MONOXID ÉS POLIPROPILÉN KÖRNYEZETVÉDELMI SZEMPONTBÓL JAVÍTOTT OXIDÁCIÓJÁRA, VALAMINT CIKLOPROPÁN IZOMERIZÁCIÓJÁRA HASZNÁLT SnO_2-Pt/Al_2O_3 KATALIZÁTOR FELÜLETKÉMIAI VIZSGÁLATA

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Készült a Pannon Egyetem
Vegyészmérnöki Tudományok Doktori Iskola Keretében

Témavezető: Dr. Rédey Ákos

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Veszprém
2007

Szén-monoxid és polipropilén környezetvédelmi szempontból javított oxidációjára, valamint ciklopropán izomerizációjára használt SnO_2-Pt/Al_2O_3 katalizátor felületkémiai vizsgálata

Értekezés doktori (Ph.D.) fokozat elnyerése érdekében

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Témavezető: Dr. Rédey Ákos
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THESIS OF THE DOCTORAL (Ph.D.) DISSERTATION

SURFACE CHEMISTRY STUDIES of SnO_2-Pt/Al_2O_3 CATALYST FOR ENVIRONMENTALLY IMPROVED CATALYTIC OXIDATION OF CARBON MONOXIDE, PROPYLENE AND FOR CYCLOPROPANE ISOMERIZATION

ABSTRACT

The knowledge on the chemical nature of the surface of supported metals and metal oxides is crucial for understanding their catalytic behaviour. Tin containing catalysts having acidic properties can be effectively used for catalytic oxidation of carbon monoxide to carbon dioxide, for propylene oxidation as well as for cyclopropane isomerization. Tin oxide supported on alumina oxide was dopped with platinum (<1%) using mechanical mixing in order to enhance the catalytic activity of sample in oxidation, isomerization reactions.

The investigation of the surface properties of samples by different methods (BET, ICP, XRD, XPS, FTIR, TPR, microcalorimetry and electrical conductivity) and catalytic reactions were correlated in order to detect the source of catalytic activity and the nature of the active sites formed during the activation procedure.

The work consists of two main parts:

I. The surface chemistry of the newly prepared SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 catalyst and Pt(0.28%)/Al_2O_3; SnO_2(2.83%)/Al_2O_3; SnO_2(3.10%)/Al_2O_3; Al_2O_3; SnO_2 catalyst samples, which were used for comparison purposes.

II. The catalytic activity on cyclopropane isomerization and carbon monoxide oxidation of oxygen and hydrogen treated catalyst samples and in propylene oxidation of oxygen treated catalysts.

The catalytic activity of supported catalysts stems from interactions between the physico-chemical, acidic and electronic properties of supported tin or/ and platinum oxide and the support. SnO_2, known as n-type semiconductor, changed the electronic density in the bulk by transmitting electrons to the PtO (p-type semiconductor) and Al_2O_3 (weak n-type semiconductor), and thus decreases the acidic strength of some of the corresponding Lewis sites.

Catalytic activities for cyclopropane isomerization, CO and propylene oxidation were higher for platinum containing samples among oxidized samples. The catalyst

combining both platinum and tin oxides was found to be promising catalyst for total oxidation of CO, hydrocarbons since it showed high selectivity for CO_2 formation and was recommended for using at industrial level.

Cyclopropane isomerization was additionally studied over samples pretreated in hydrogen. Pt(0.28%)/Al_2O_3 was only active catalyst among of reduced samples.

From cyclopropane isomerization studies can be concluded that tin can exists in different forms in SnO_2(2.94%)-Pt(0.28%)/Al_2O_3, depending on the pretreatment conditions of the catalyst (i) in oxidized form, Sn^{4+} (SnO_2), resulting in promoting effect; (ii) in reduced form, tin resulting in poisoning effect “ligand-effect” due to blocking of the sites responsible for cyclopropane isomerization by formation an alloy.

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DOKTORI (PH.D.) ÉRTEKEZÉS TÉZISEI

SZÉN-MONOXID ÉS POLIPROPILÉN KÖRNYEZETVÉDELMI SZEMPONTBÓL JAVÍTOTT OXIDÁCIÓJÁRA, VALAMINT CIKLOPROPÁN IZOMERIZÁCIÓJÁRA HASZNÁLT SnO_2-Pt/Al_2O_3 KATALIZÁTOR FELÜLETKÉMIAI VIZSGÁLATA

KIVONAT

A hordozóra felvitt fémek és fémoxidok kémiájának ismerete katalitikus viselkedésük megértése szempontjából kulcsfontosságú. A savas tulajdonságú, óntartalmú katalizátorok hatékonyan felhasználhatók a szén-monoxid szén-dioxiddá való oxidálására, a propilén oxidálására, valamint a ciklopropán izomerizációjára. A korund hordozóra felvitt ón-oxidot mechanikus keveréssel 1 %-nál kisebb mennyiségben platinával adalékoltuk az oxidációs, izomerizációs reakciókban mutatott katalitikus aktivitás fokozása érdekében.

A katalitikus aktivitás forrásának és az aktiválási folyamat alatt képződött aktív helyek jellegének felderítése érdekében a minták felületi tulajdonságainak vizsgálatára alkalmazott különféle módszerek (BET, ICP, XRD, XPS, FTIR, TPR, mikrokalorimetria és elektromos vezetőképesség-mérés) eredményeit összevetettük a katalitikus reakciók eredményeivel.

A munka két fő részből áll:

I. Az újonnan készített SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 katalizátor és az összehasonlítás céljára használt SnO_2(2.83%)/Al_2O_3, SnO_2(3.10%)/Al_2O_3, Pt(0.28%)/Al_2O_3, Al_2O_3, SnO_2 katalizátor minták felületi kémiája

II. Az oxigénnel és hidrogénnel kezelt katalizátor minták ciklopropán izomerizációval és szén-monoxid oxidációval mutatott katalitikus aktivitása, valamint az oxigénnel kezelt katalizátorok propilén oxidációval mutatott aktivitása.

A hordozóra felvitt katalizátorok katalitikus aktivitása a hordozó és a hordozóra felvitt ón- vagy/és platina-oxid fizikai, kémiai és elektronos tulajdonságai közötti kölcsönhatásokból ered. Az n típusú félvezetőként ismert SnO_2 a szilárd anyagban megváltoztatta az elektronsűrűséget azáltal, hogy elektronokat adott át a PtO (p típusú félvezető) és az Al_2O_3 (gyenge n típusú félvezető) számára, így csökkentette a megfelelő Lewis helyek közül néhánynak a savas erősségét.

A ciklopropán izomerizációjában, a CO és a propilén oxidációjában az oxidált minták között a platina tartalmúak nagyobb aktivitást mutattak. A platina- és ón-oxidot kombináló katalizátor ígéretesnek mutatkozott a szén-monoxid és a szénhidrogének teljes oxidálásában, mivel a CO_2 képződésében nagy szelektivitású. Ez a katalizátor ipari léptékű alkalmazásra ajánlható.

Kiegészítésképpen megvizsgáltuk a ciklopropán izomerizációját hidrogénben előkezelt mintákon. A redukált minták közül egyedül a $Pt(0.28\%)/Al_2O_3$ volt aktív katalizátor.

A ciklopropán izomerizációjának vizsgálatából arra a következtetésre jutottunk, hogy az $SnO_2(2.94\%)$-$Pt(0.28\%)/Al_2O_3$ rendszerben az ón a katalizátor előkezelési körülményeitől függően különböző formákban fordul elő: (i) oxidált, Sn^{4+} (SnO_2) formában, ami a folyamatot elősegítő hatású, valamint (ii) redukált formában, fém ón formájában, ami az ötvözetképződés révén mérgező hatást, „ligandum hatást" fejt ki azáltal, hogy blokkolja a ciklopropán izomerizációért felelős helyeket.

ТЕЗИС ДОКТОРСКОЙ (Ph.D.) ДИССЕРТАЦИИ

ИССЛЕДОВАНИЯ ХИМИЧЕСКИХ СВОЙСТВ ПОВЕРХНОСТИ SnO_2-Pt/Al_2O_3 КАТАЛИЗАТОРА ДЛЯ ИЗОМЕРИЗАЦИИ ЦИКЛОПРОПАНА И ДЛЯ ЭКОЛОГИЧЕСКОГО УЛУЧШЕНИЯ КАТАЛИТИЧЕСКОГО ОКИСЛЕНИЯ МОНООКСИДА УГЛЕРОДА, ПРОПИЛЕНА

АННОТАЦИЯ

Знание о химических свойствах поверхности нанесенных металлов и металлических оксидов является важным в определении их каталитического поведения. Катализаторы, содержащие оксид олова, имеют кислотные свойства и могут эффективно использоваться для каталитического окисления монооксида углерода, для окисления пропилена, а так же для изомеризации циклопропана. Для того, чтобы увеличить каталитическую активность в реакциях окисления, изомеризации, нанесенный на Al_2O_3 образец оксида олова был механически смешан с платиной (<1%).

Результаты исследований поверхностных свойств образцов различными методами (ИСП, РД, РФЭС, ИКС, ТПВ, микрокалориметрии и электрической проводимости) и результаты каталитических реакций были проанализированы и сопоставими между собой для того, чтобы идентифицировать характер и тип поверхностых активных участков, сформированных при предварительной тренировке образцов.

Работа состояла из двух основных частей:

I. Исследование поверхностных свойств SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 нового образца и Pt(0.28%)/Al_2O_3; SnO_2(2.83%)/Al_2O_3; SnO_2(3.10%)/Al_2O_3; Al_2O_3; SnO_2 образцов использованных для сравнения;

II. Исследование каталитической активности образцов, отренированных в кислороде и водороде, в изомеризации циклопропана и в окислении монооксида углерода, так же образцов, отренированных в кислороде, в окислении пропилена.

Взаимодействие между физико-химическими, кислотными и электронными свойствами оксидов олова или / и платины и носителя определило каталитическую активность катализатора. SnO_2, известен как полупроводник n-

типа, повлиял на электронную плотность SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 образца путем передачи своих электронов к PtO (полупроводник p-типа) и Al_2O_3 (слабый полупроводник n-типа), и таким образом уменьшил кислотную силу некоторых Льюисовских участков на поверхности образца.

Каталитическая активность при изомеризации циклопропана, при окисление CO и пропилена была выше для окисленных образцов, содержащих платину. Образец SnO_2(2.94%)-Pt(0.28%)/Al_2O_3, содержащий и оксид платины и оксид олова, показал себя обещающим катализатором для полного окисления углеводородов, CO, так как он проявил высокую селективность в формирование CO_2 и был рекомендован для использования в промышленности.

Изомеризация циклопропана была дополнительно исследована в присутствии образцов, отренированных в водороде. При этом только Pt(0.28%)/Al_2O_3 был активным катализатором среди восстановленных образцов.

Исследования изомеризации циклопропана показали, что в зависимости от условий тренировки катализатора, олово было обнаружено в различных формах в SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 образце, а именно: (i) в окисленной форме, Sn^{4+} (SnO_2), олово действовало как промотор; (ii) в восстановленной форме, олово действовало как ингибитор, образуя сплав с платиной и блокируя активные участки участвующие в изомеризации циклопропана.

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I. INTRODUCTION

The catalytic approach for hydrocarbon oxidation is a subject of special attention during the last years due to the improved efficiency of catalysts and reduced emissions of pollutants like CO, hydrocarbons. A catalytically enhanced combustion system operates at much lower temperatures than an open flame burner, and lower temperature also means reduced emission of CO and NO_x.

Semiconductor oxides (SnO_2, V_2O_5) are known to exhibit oxidizing activity and can be considered as potential catalysts for isomerization and total or selective oxidation of C_1-C_3 hydrocarbons and for CO oxidation to CO_2. The application of pure semiconductor catalysts is very limited due to their low surface area (10-20 m^2/g) and poor thermal stability. Supported semiconductor oxides and particularly those doped with platinum exhibit improved catalytic properties, since noble metals are the most active catalysts for hydrocarbons or CO oxidation (Baldwin et al., 1990).

The physico-chemical properties and catalytic activity of the solid sample containing several oxides are generally different from that of composed oxides alone. This is due to the fact that the activity of the „mixed oxides" could be the result of various interactions. In case of sample containing different types of metal oxides, electronic effect should also be considered. According to the electronic theory of catalysis, the rate and activation energy of reaction depend upon the a Fermi level of the catalyst, and thus it can be expected that electronic interaction between metal oxides or metal and the support can modify the Fermi level of the catalyst. Therefore this interaction can influence the catalytic activity of sample.

At the same time the acid-base properties of the catalysts are also important for activation of the reactants. The strong or weak Lewis acid or basic sites of the catalyst will determine the strength of interaction of the reactants with the active sites of the catalysts and interaction of the reaction (oxidation, isomerization) products with the solid surface (Ai and Ikawa, 1975), which in turn determines whether a reactant and/or reaction products can readily be adsorbed (and presumably activated) or the products can readily be desorbed (preventing its further transformations).

1.1. Acid-Base Properties of Supported Catalysts on Alumina

Pure alumina is widely used as catalyst for several reactions where it activates hydrogen-hydrogen, carbon-hydrogen and carbon-carbon bonds. The C-H bond activation in isomerization reaction happens near to room temperature and C-C bond activation in skeletal isomerization occurs at 600 K on alumina (Knözinger and Rantnasamy, 1978). The alumina surface contains basic and acidic OH groups as well as Lewis acid sites. The Lewis acid sites are provided by multiple defects sites: Al^{3+}_{tet} or Al^{3+}_{oct}. Basic OH groups are coordinated end-on to an Al^{3+} ion (HO-Al_{oct}, HO-Al_{tet}). The protons acidic OH groups are bonded to bridging oxygen atoms. Their acidity depends on how and how many Al^{3+} ions the bridging oxygen atoms interconnect: Al_{oct}-HO-Al_{tet}, Al_{oct}-HO-Al_{oct}, HO-$(Al_{oct})_3$ (for more details see 3.2.1 p.36). The removal of water and/or hydroxyl groups from alumina surfaces is important for the development of it catalytic activity. As a consequence of the removal of water and/or hydroxyl groups (surface ligands), coordinatively unsaturated anions (oxygen ions) and cations (Al^{3+}) are created (Kirszenszejn et al., 1993). Those sites are participating in catalytic transformations. Hence active sites of alumina can be directly involved in catalytic process in presence of supported metal / metal oxides attaining not total monolayer coverage.

Tin (IV) oxide surface is rather complex containing different surface sites: hydroxyl groups, oxide species (which may be ever terminal or bridging) and Lewis acid Sn^{4+} species. The relative ratio of these particular sites depends on the thermal pretreatment. Surface properties of SnO_2 make tin oxide containing materials to be able to act as catalysts in quite a wide range of different reactions including oxidation of CO, sulphur dioxide, saturated and unsaturated hydrocarbons and other volatile organic compounds; tin oxide is also used in composition of the catalysts for ammoxidation and isomerization of alkenes or for dehydroxylation of alcohols (Harrison, 1987). Pure SnO_2 has a small surface area (9-20 m^2/g). Its area can be increase by deposition on supports of much higher surface area such as Al_2O_3, TiO_2, SiO_2 (Caldararu et al, 2002). In this case the catalytic activity of tin containing materials is derived from the subtle interactions between the physico-chemical, acid-base and electronic properties of supported tin oxide and support.

1.2. Interaction between Compounds in Supported Catalyst

Tin (IV) oxide itself is mildly oxidizing catalyst. The significant changes in behavior of tin oxide material may be induced after appropriate doping carried out by impregnation, mechanical mixing, cohydrolysis or ion exchange (Irving and Tylor, 1978). The resulted materials should usually be calcinated in order to activate as a catalysts. Dopants may act in at least two different ways: (i) either by providing "active" sites on the oxide surface for the dissociative adsorption and spillover of reactance (e.g Pt, Pd and other noble metals) and (ii) by influence an electron properties of support material (e.g. Ag or Sb) (Harrison, 1987).

At the same time the addition of tin to Pt/γ-Al_2O_3 catalyst showed high stability inhibiting the coke formation (Siri et al., 2005). The presence of tin can modify platinum dispersion by an ensemble effect (i.e. by the redistribution of Pt on the surface into smaller ensembles). In absence of large Pt clusters coke formation is not preferred. On the other hand isomerization can occur on single isolated atoms (Spivey and Roberts, 2004).

The alloy formation between noble metal and reducible oxide can occur on SnO_2/Pt-Al_2O_3 under reduction condition. XPS results obtained for PtSn/γ-Al_2O_3 hydrogen treated catalysts show that significant portion of tin is present in ionic state while on silica-support mainly Sn(0) is formed (Balakrishnan and Schwank, 1991). The influence of the preparation procedure is well described in a paper of Vértes and co-authors who studied by Mössbauer spectroscopy a series of PtSn/γ-Al_2O_3 catalysts prepared via surface organometallic chemistry on metals technique using $Sn(C_2H_5)_4$ reagent and via conventional procedure by impregnating Pt/γ-Al_2O_3 with a $SnCl_2$ solution (Vértes et al., 1991). In former case $PtSn_x$ alloy formation in catalyst was observed and later case major part of tin was detected in an ionic state. PtSn/C catalysts were studied by EXAFS (Román-Martínez et al., 2000) and the presence of bimetallic PtSn phases, Pt particles, and Pt-O-Sn^{2+} species were observed, suggesting that the catalytic activity of bimetallic catalysts is determined by the relative concentration of these surface species and their distribution on the support.

1.3. Electronic Properties of Semiconductors

According to the electronic theory of catalysis, the rate and activation energy of reaction depend upon the a Fermi level of the catalyst, and thus it was expected that electronic interaction between metal and oxide modifies the position of the Fermi level of the metal of active component and support oxide in contact with it (Szabó and Kalló, 1976).

In semiconductors the Fermi level lies in the forbidden zone. It is the electrochemical potential intermediate between the highest filled (valence Nv) and the lowest empty (conduction Nc) band. The energy band structure, Fermi probability function of a p-type and a p-type semiconductors are shown in Fig.1.a and 1.b respectively. An electron from donor band enters on heating to conduction band in case of n-type semiconductor and positive charge remains on donor level. An electrons from the valence band enters on heating to the acceptor level and remains there then a positive hole is generated in the valence band in case of p-type semiconductor (Hagen, 1999). If a semiconductors come into contact then at thermodynamic equilibrium the Fermi level much be the same at interface. The electrons will pass from the semiconductor having higher Fermi level to semiconductor of lower Fermi level until equilibrium is reached. The same rule is valid for metal-semiconductor contact (Szabó and Kalló, 1976). The Fermi level of n-type semiconductor is much higher than that for p-type semiconductor (Fig.1.a,1.b). Therefore if two types semiconductors come into a contact that electron flow should occur from n-type to p-type semiconductor.

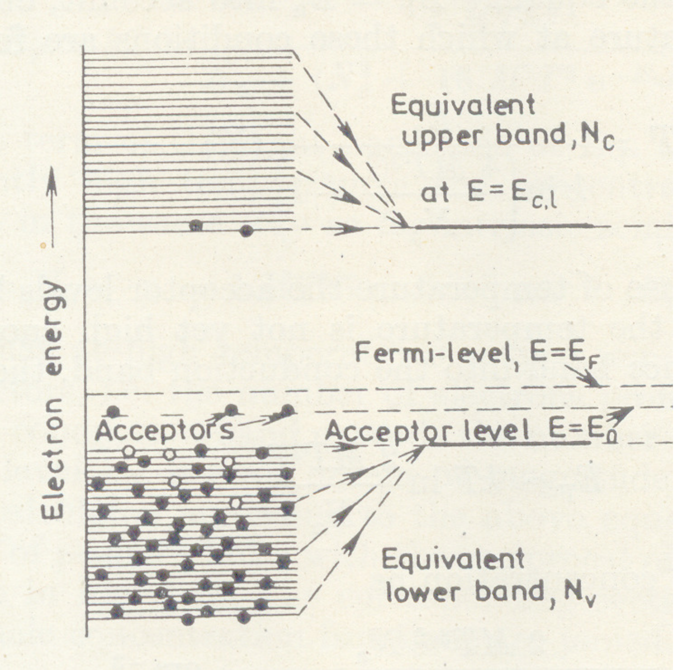


Fig. 1.a. The energy band structure of a p-type semiconductor and Fermi probability function where Nc, Nv are conduction and valence bands (Szabó and Kalló, 1976).

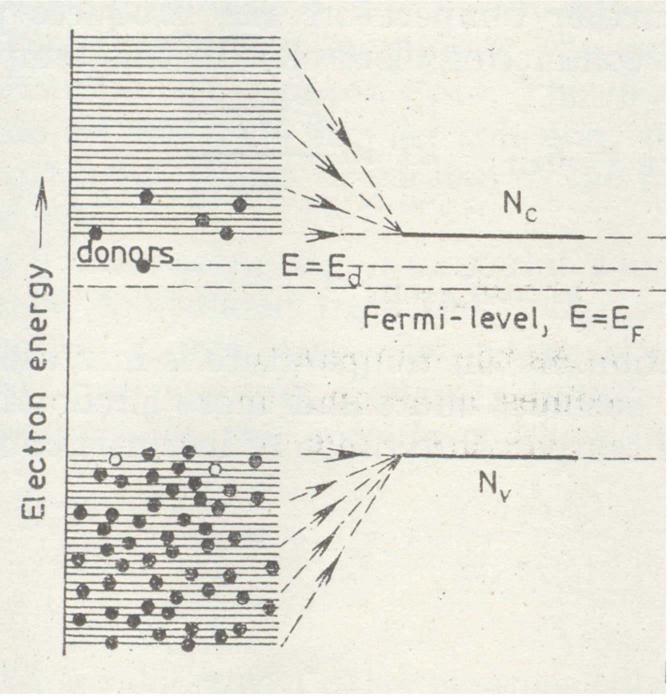


Fig. 1.b. The energy band structure of a n-type semiconductor and Fermi probability function (Szabó and Kalló, 1976).

There are several possibilities for measuring the semiconductor properties of a substance. On of these is to determine the conductivity of the solid at various temperature. The solid–state catalysts can be classified according to their electronic conductivity and electron-transfer properties as shown in Table 1 (Hagen, 1999).

Table 1. Classification of the metal oxides according to their electronic properties.

	Conductors	Semiconductors	Insulators
Conductivity range,nS	10^6 - 10^4	10^3 -10^{-9}	10^{-9} – 10^{-20}
Electron transfer	Electron exchange between Metal-Adsorbate	Electron transfer at high temperature	no
Studied material	Pt^0	PtO p-type SnO_2 n-type	Al_2O_3 (RT)*

* On heating alumina acts as weak n-type semiconductor (Caldararu, 2001).

Nonstoichiometric semiconductor oxides play an important role. On heating, their crystal lattices tend to release or take up oxygen. When oxygen is adsorbed on an n-type semiconductor, electrons flow from the donor level to adsorbate, and O^- and O^{2-} ions can be formed (Caldararu, INCO report, 2002). The surface of the solid becomes negatively polarized, and the adsorption of further oxygen requires more and more energy. Therefore the adsorption of oxygen on n-type semiconductors is subject to very rapid auto-inhibition. If n-type semiconductor like SnO_2 has it exact stoichiometric composition then it cannot chemisorb oxygen. If there is oxygen deficiency (SnO_{2-x}), it can chemisorb precisely the amount of oxygen required to fill the anionic defect and reoxidize the tin atoms.

Metals of p–type semiconductors that favor the adsorption of oxygen have five, seven, eight, or ten d electrons. The order of preference is (Hagen, 1999):

$$Cu^+ \approx Ag^+ > Pt^{2+} > Mn^{2+} > Rh^{2+} > Ir^{2+} > Co^{2+} > Hg^{2+}$$

Therefore the corresponding p-type semiconductors are highly effective catalysts for the activation of oxygen. Generally metals that form p-type oxides are those exist at several oxidation states. The oxides contain the lower oxidation state form (e.g. Pt^{2+}), which can then enter the higher oxidation state (Pt^{4+}) during interaction with oxygen. The n-type oxides, in contrast, are those usually exist in the highest oxidation state (e.g. Sn^{4+}).

1.4. Chemisorption and Oxidation of CO on Semiconductors

Reducing gas, carbon monoxide, is strongly adsorbed on surface of semiconductors. On n-type semiconductors, CO almost totally cover the surface, whereas chemisorption on p-type semiconductors is less extensive. In this strong chemisorption a free electron or positive hole from the lattice is involved in the chemisorptive bonding.

The activity of the catalyst increases when different multi-component oxides (n and p-type semiconductors) are present in sample. Addition of small amount of platinum to transition metal catalyst (e.g. Pt/SnO_2) can synergistically increases hydrocarbon oxydation (Carata et al., 2004), CO oxidation to CO_2 (Herz, 1989). Chemisorption of CO usually occurs initially on metal cations (PtO), after which it reacts with an with oxygen of n-type semiconductor (SnO_2) followed by desorption of CO_2 from surface according to Equation (1). This reaction can eventually lead to complete reduction of the oxide to the metal.

$$CO\cdots M^{2+} + O^{2-} \rightarrow M + CO_2 \qquad (1)$$

In a case of competitive adsorption (Hagen, 1999) if the supported nobel metal oxides catalyst (Pt or Pt) is first exposed to O_2, then atomic adsorption of oxygen on the surface occurs. CO is then introduced at room temperature and the reaction proceeds rapidly by the Eley-Rideal mechanism (Eq. 2):

$$O^* + CO \rightarrow CO_2 \quad \text{fast} \qquad (2)$$

If CO is first adsorbed and then oxygen is introduced then no reaction occurs (Eq. 3):

$$CO^* + 0.5\, O_2 \not\rightarrow CO_2 \qquad (3)$$

Finally, if a nobel metal oxide (Pd or Pt) surface partially covered with CO is allowed to react with O_2, then the latter is adsorbed at the free sites. Only at the boundary layers of the two adsorbed reactants reaction takes place and proceeds slowly according to the Langmuir-Hinshelwood mechanism (Eq. 4):

$$CO^* + O^* \rightarrow CO_2 \ \text{slow} \qquad (4)$$

It was note that at low temperatures CO blocks the surface and the reaction is slow (Eq.4). With increasing temperature, above ~373 K, CO is partially desorbed, and O_2 is chemisorbed on the surface. The reaction rate passes through a maximum around 473 K, after which it falls again. The reaction is structure-insensitive in case of noble metal catalysts (Hangen,1999).

1.5. Oxidation of Propylene on Semiconductors

The knowledge obtained about chemisorption on semiconductor oxides makes possible a better understanding of the behavior of these materials as oxidation catalysts. An oxidation reaction consists of several steps (Hagen, 1999):

1) Formation of an electron bond between the starting material to be oxidized (e. g., a hydrocarbon) and the catalyst; chemisorption of the starting material;
2) Chemisorption of oxygen;
3) Transfer of electrons from the molecule to be oxidized (the donor) to the acceptor (O_2) by the catalyst;
4) Interaction between the resulting ion, radical, or radical ion of the starting material and the oxygen ion with formation of an intermediate (or the oxidation product);
5) Possible rearrangement of the intermediate;
6) Desorption of the oxidation product.

Hence the oxidation catalyst must be capable of forming bonds with the reactants and transferring electrons between them. Oxides of the p-type, with their tendency to adsorb oxygen up to complete saturation of the surface, are more active than n-type oxides. Unfortunately, activity and selectivity mostly do not run parallel, and the p-type semiconductors are less selective than the n-type semiconductors. The p-type semiconductors can often cause complete oxidation of hydrocarbons to CO_2 and H_2O, while the n-type semiconductor oxides often allow controlled/selective oxidation of the same hydrocarbons to be performed.

The ratio of adsorbed oxygen to hydrocarbon on p-type semiconductor oxides is generally high and is difficult to control even at low partial pressures of oxygen. The result is often complete oxidation of the hydrocarbon. In contrast the amount of adsorbed oxygen on n-type semiconductors is generally small and can readily be controlled by means of the nature and amount of dopant (nobel metals, Sb), making selective hydrocarbon oxidation possible.

Simple two-step oxidation/reduction mechanisms are often used to explain industrial reactions. The oxidation of a molecule X (e.g. hydrocarbons) can proceed by two mechanism (Hagen, 1999):

$$\begin{array}{ll} \frac{1}{2}\,O_{2\,(G)} \rightarrow O^{*} & (5) \\ X^{*} + O^{*} \rightarrow \text{products} & \end{array}$$

$$\begin{array}{ll} X^{*} + O\ (\text{lattice}) \rightarrow \text{products} + \text{lattice} & (6) \\ \frac{1}{2}\,O_{2(G)} + \text{lattice vacancy} \rightarrow O\ (\text{lattice}) & \end{array}$$

In case of (Eq. 5), O_2 is more rapidly adsorbed than X, and X* reacts to remove this „excess” oxygen. Oxidation then proceeds through to the final products: CO_2 and H_2O.

In case (Eq. 6), adsorbed molecules of the starting material react with lattice oxygen. The result is selective oxidation, as is observed for partially oxidized molecules such as carbonyl compounds and unsaturated species in particular. Selective catalysts that react according to this Mars-van Krevelen mechanism (Krenzke and Keulks, 1980, ***64***) formally contain a cation with an empty or filled d orbital, for example:

$$\begin{array}{cccc} Mo^{6+} & V^{5+} & Sb^{5+} & Sn^{4+} \\ 4d^{\circ} & 3d^{\circ} & 4d^{10} & 4d^{10} \end{array}$$

Those metals in their highest oxidation states readily release lattice oxygen, formally as O^{2-}. The pathway involving lattice oxygen is commonly referred to as the redox mechanism because the catalyst itself acts as the oxidizing agent. Gas-phase oxygen then serves only to reoxidize the reduced catalyst. There is a considerable amount of data which support the redox concept (Krenzke and Keulks, 1980, ***61***). Peacock and co-authours (Peacock et al.,1969) have shown that a bismuth molybdate catalyst can oxidize propylene in the absence of gas-phase oxygen and that the oxygen appearing in the products is from the lattice. The amount of oxygen removed during reduction corresponds to the participation of many sublayers of oxide ions. Report involving other oxide systems such as Bi-W-O, Sn-Sb-O, and Sn-P-O (Niwa and Murakami, 1972) have also concluded that these catalysts have the capacity to act as a source of active oxygen. Although these result strongly support the redox mechanism, the most compelling evidence for the participation of lattice oxygen comes from studies of propylene oxidation in the presence of isotopic oxygen, $^{18}O_2$ (Krenzke and Keulks, 1980, ***61***), (Ciuparu and Pfefferle, 2002), (Ciuparu et all., 2001).

Keulks (Keulks,1970) reported that during the oxidation of propylene over bismuth molybdate at 753 K in the presence of gas-phase $^{18}O_2$, only 2 to 2.5% of the oxygen atoms in the acrolein and carbon dioxide produced were isotopically labeled. This lack of extensive incorporation of $^{18}O_2$ into the reaction products implies the participation of lattice oxide ions in both the selective and nonselective oxidation reactions (Krenzke and Keulks, 1980, ***64***).

The heterogeneously catalyzed gas-phase oxidations of unsaturated hydrocarbons (e.g propylene) are large-scale industrial processes (Bettahar et al., 1996). Economic operation of these processes requires a selectivity of at least 60%. In the selective oxidation of propylene, metal oxides are mainly used as catalysts and many different products are obtained (Fig. 2), depending on the catalyst used. The catalytic oxidation of propylene leads preferentially to formation of acrolein (Bettahar *et al.*, 1996):

$$H_2C{=}CH\text{-}CH_3 + O_2 \rightarrow H_2C{=}CH\text{-}CHO + H_2O$$

Carbon dioxide, acetaldehyde, and acrylic acid are formed as side products

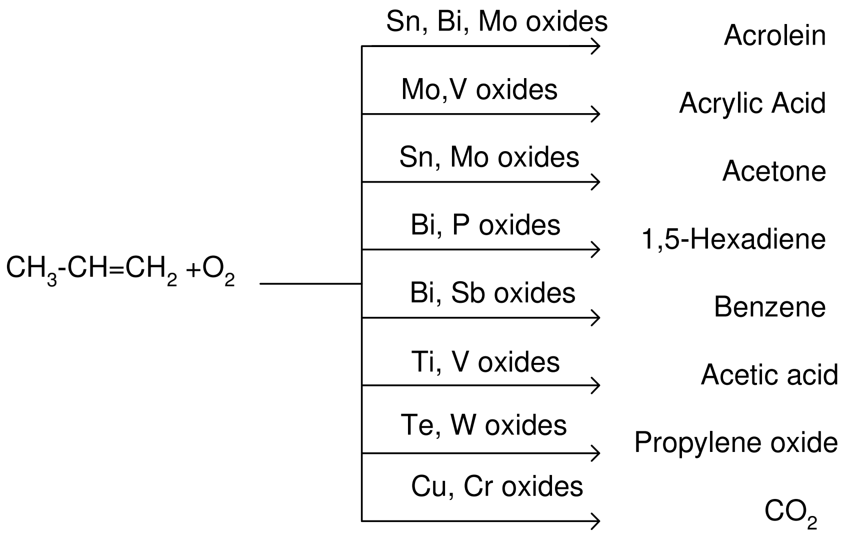


Fig. 2. Oxidation of propylene on various metal oxide catalysts (Hagen, 1999), (Bettahar *et al.*, 1996).

The mechanism of selective oxidation of propylene to acrolein can be summarized as a succession of redox and acid-base steps (Burrington et. al., 1984),

(Fig.3). The π-allyl anion should be first formed by proton abstraction on a basic active site and then oxidized to the π-allyl cation on a redox active site. Through a nucleophilic attack by a lattice O^{2-} anion, the latter species forms the σ-allylic species which, in turn, gives rise to acrolein by a hydride abstraction in a redox step. The intervention of a σ-allylic species is invoked to explain the obtaining of 1-d_1 and 3,3-d_2, acrolein molecules from 1,1-d_2, propylene (Fig.3) in the same proportions (30% and 70% respectively), (Fig.3). These results suppose that the interconversion between π and σ species takes a place (Burrington *et. al.,* 1984), (Bettahar *et al.,* 1996).

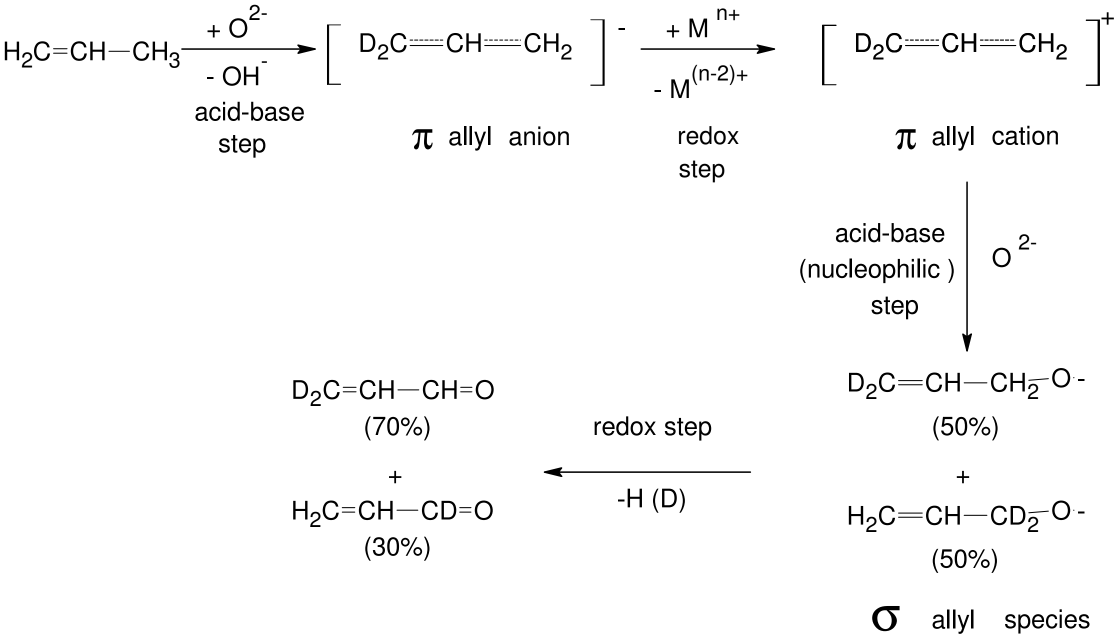


Fig.3. Mechanism of the catalytic oxidation of propylene to acrolein on metal oxides through allylic surface species (Bettahar *et al.,* 1996).

1.6. Cyclopropane Isomerization

1.6.1. General Consideration of Mechanism

The isomerization of cyclopropane has been widely used as test reaction in catalytic research. It is well known that cyclopropane isomerization is an acid catalyzed reaction at relatively low temperatures (Hightower and Hall,1968, ***90***). The overall reaction is of first order in cyclopropane. Consequently it can be a test-reaction for the investigation of acidic catalysts supplying information on hydrocarbon reactions in general (Fejes et al., 1978). Conventional catalysts for cyclopropane isomerization include acids such as solutions (Baird and Aboderin, 1964), oxides (Hightower and Hall,1968, ***90***), and zeolites (Kiricsi et al., 1980). Some transition metal oxides have also been reported to be active catalysts (Oliveros et al., 1997), (Dyne et al., 1972), (Wang et al., 1983).

The rate of isomerization of cyclopropane increases with degree of reduction (Jacono and Hall, 1976), (Lombardo et al., 1978) over molybdena-alumina further the rate of the reaction measured in microcatalytic system increased with the extent of dehydroxylation of the surface; this fact disagrees with early studies over known acidic systems, e.g. SiO_2-Al_2O_3 (Hall et al., 1964), where added-back water inhances the isomerization reaction. The isomerization of cyclopropane has also been studied over non-acidic catalysts such as chromia (Dyne et al., 1972) and metal containing system (Ebitani at el., 1991). Some authors (Goldwasser, 1981), (Segawa and Hall, 1982) showed evidence of the presence of Brönsted acidity for the oxidized but not for the reduced molybdena-alumina system. These results cast serious doubts on the isomerization of cyclopropne being acid-catalyzed over reduced system. A hydride insertion mechanism, which was identified using the $H_2Os_3(CO)_9PPh_2C_2H_4$ – silica catalyst, provided an alternative explanation for the facts observed (no detectable acidity by pyridine adsorption etc) with reduced molybdena-alumina catalyst (Goldwasser, 1981). In an another work (Oliveros et al., 1997) is mentioned that ring opening over reduced molybdena-alumina catalyst takes place through metallocyclobutane intermediates (MCB) by direct insertion of the coordinatively unsaturated transition metal ion into the cyclopropane ring.

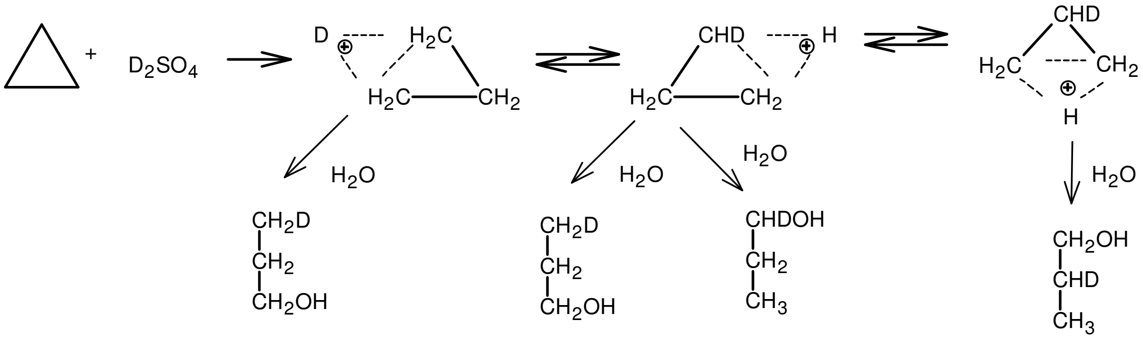
As can be seen from mentioned above, cyclopropane isomerization provides useful information for the characterization of active intermediates.

1.6.2. Homogeneous Reaction

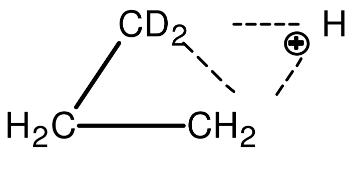
The bonds between the carbon atoms are much weaker than in a typical carbon-carbon bond. This is the result of the 60° angle between the carbon atoms, which is far less than the normal angle of 109.5°. The cyclopropane molecule is thus said to be "strained." This strain has to be subtracted from the normal C-C bond energy, making the resultant compound more reactive than acyclic alkanes and other cycloalkanes such as cyclohexane and cyclopentane. Many reactions of cyclopropane involve breaking one of the carbon-carbon bonds in the ring, which opens the ring and relieves the strain.

Thermal isomerization of cyclopropane does not proceed below 773 K (Jacono and Hall, 1976). The homogeneous gas phase isomerization to propylene take place through trimethylene radical intermediate and has been characterized (Benson, 1961) as unimolecular reaction having an activation energy of about 272 kJ/mol. It was immeasurably slow below about 698 K.

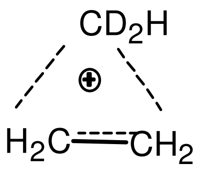
During the solvolysis of cyclopropane in D_2SO_4 (Baird and Aboderin, 1964) deuterium was bound to any of three carbon atoms of the 1-propanol (the only product obtained) and scrambling of deuterium did not occur either before or after solvolysis of the cyclopropane. These results were interpreted in terms of an equilibrium among the following three edge-protonated species (Baird and Aboderin, 1964):



Since the tracer atom was not localized in the methyl group, but was distributed over all three carbon atoms in a way which could be explained if the carbonium ion intermediate was a nonclassical hydrogen-bridged, rather than the n-propyl or a methyl-bridged, ion (Baird and Aboderin, 1964):



Nonclassical hydrogen-bridged
carbonium ion



Methyl-bridged
carbonium ion

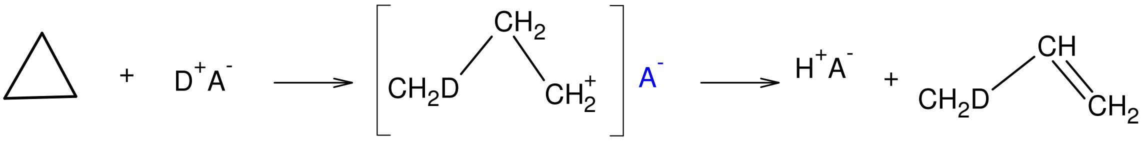
Another conclusion of this study was that cyclopropane hydrogen atoms can exchange for deuterium without ring opening

1.6.3. Catalytic Reaction

1.6.3.1. Cyclopropane Isomerization over Acid Catalyst Sites

1.6.3.1.1. Mechanism on Brönsted Acid Sites

Roberts (Roberts, 1959) studied cyclopropane isomerization over a large number of solid acids at 408 K using a flow system. It was concluded that c-C_3H_6 isomerization is one of the fastest hydrocarbon reactions catalyzed by solid acids. When completely deuterated catalyst is contacted with cyclopropane, the initial product propylene should contain nearly one deuterium atom per molecule; moreover, deuterium does not appear in the unreacted cyclopropane since the ring was opened when a catalyst proton attached to a ring carbon thus forming a n-propyl carbenium ion. Since the added proton forms a methyl group, the isomerization is completed by loss of another proton to the catalyst surface (Roberts, 1959):



Good correlation was found (Hall et al., 1964) between the rate of isomerization of cyclopropane and the hydrogen contents of alumina and silica-alumina.

Unisomerized cyclopropane was extensively exchanged with deuterium atom of catalysts over deuterated silica-alumina and alumina (Larson et al., 1965). This fact disagreed with the simple picture presented earlier by Roberts (Roberts, 1959).

Later kinetic studies by Hightower and Hall (Hightower and Hall, 1968, ***72***) showed that during isomerization cyclopropane in presence of proton on surface becomes activated to a nonclassical carbonium ion, similar to that proposed by Baird and Aboderin (Baird and Aboderin, 1964), and either isomerizes or returns to the ground sate as shown on reaction scheme below:

$$c\text{-}C_3H_6\ (g) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} c\text{-}C_3H_6\ (ads) \underset{-H^+\ k_{-1}}{\overset{+H^+\ k_1}{\rightleftharpoons}} c\ \text{-}C_3H_7^+ \xrightarrow[k_2]{-H^+} CH_3CH{=}CH_2$$

where k_{-1} was found to be similar to k_2.

Using isotopic tracers George and co-worker (George and Habgood, 1970) came to the same conclusion, that in the chemisorption step the non-classical carbonium ion so called edge-protonated cyclopropane is formed.

1.6.3.1.2. Effect of Hydrogen on the Activity of Protonic Sites

It was noted that reduction of nickel up to metallic form increases c-C_3H_6 isomerization rate over Ni/NaX zeolites (Simon et al., 1994). In this case upon reduction with H_2 a significant increase of Brönsted acidity is observed according to the reaction:

$$Ni^{2+} + H_2\,(g) \rightarrow Ni^0 + 2H^+_{zeolites}$$

Promoting effect of hydrogen pretreatment on acid-catalyzed reactions have been reported, as well, for the Ag ion exchanged Y zeolite (Baba and Ono, 1987). In the system of Ag-Y zeolite, a proton was produced by the reaction of Ag^+ with hydrogen molecule accompanied by the formation of Ag^0, where proton acts as the active site for acid-catalyzed reactions:

$$Ag^+ + \frac{1}{2}H_2 \rightarrow Ag^0 + H^+$$

Hydrogen effects in catalysis are strongly connected with dissociateive adsorption in presence of noble metal oxides (Stoica et al., 2000), (Herz,1989). Heterolytic process of absorption has positive effect on the acid-catalyzed reaction, for example, over platinum containing catalyst (Ebitani et all., 1991). Study of Pt/SO_4^{2-}-ZrO_2 catalytic system showed that hydrogen molecule adsorbed on the platinum particle is dissociated into two H ions:

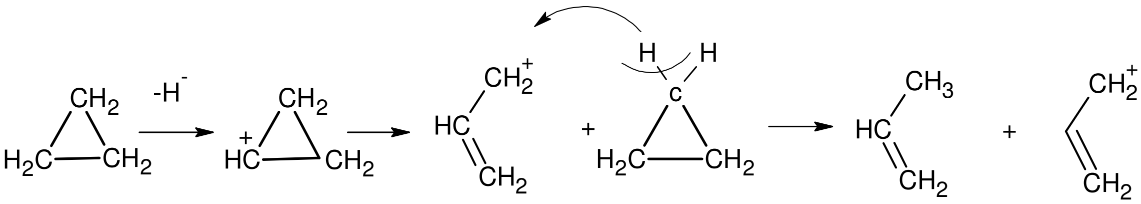
$$H_2 \rightarrow H^+ + H^-$$

The H^+ is localized on an O^- ion near the Lewis acid sites, and acts as an active (Brönsted) site for acid-catalyzed reaction. Lewis acid sites accepted an H^- became weaker.

As it have been mentioned (Ai and Ikawa, 1975) that the surface having active sites with moderate strength on which basic reactants such hydrocarbons, e.g. during oxidation or isomerization reaction, can be easily adsorbed (and presumably activated) and the products can be easily desorbed. As hence reaction proceeds faster over those sites.

1.6.3.1.3. Mechanism on Lewis Acid Sites

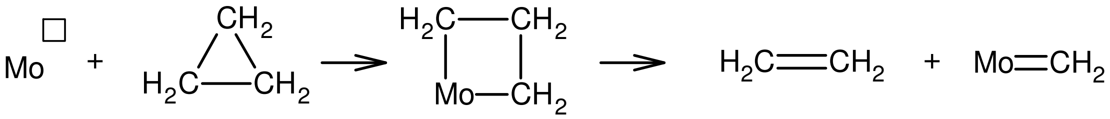
Protonic mechanism of cyclopropane isomerization has been accepted by Larson and coworker (Larson et al., 1965) nevertheless, they did not exclude the possibility of a different mechanism on silica-alumina catalysts which have been calcined at high temperatures and the therefore might contain Lewis acid sites as well. In case of a mechanism involving Lewis sites the first reaction step is H^- ion abstraction producing allyl cation ($C_3H_5^+$) intermediate. They act as molecular chain carriers by interaction with cyclopropane leading to propylene and reproducing the allyl cation (Fejes et al., 1978). Accordingly, the following scheme can be considered:



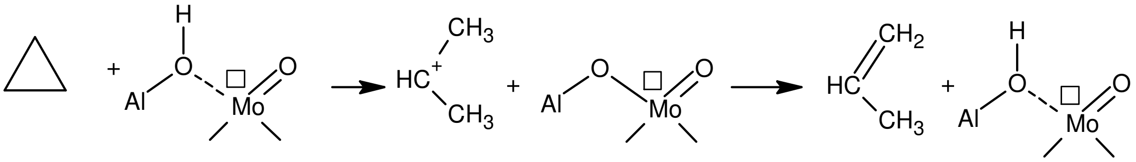
1.6.3.2. Cyclopropane Ring Opening Reaction over Transition Metal Oxides

1.6.3.2.1. Metathesis Mechanism

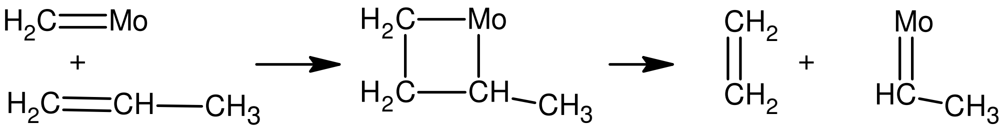
In case of absence or at low concentration of Brönsted acid sites on the surface (reduced molybdena-alumina) the presence of anion vacancies (transition metal ion sites) must play significant role in cyclopropane ring opening reaction (Segawa and Hall, 1982). This could be traced by cyclopropane transformation in other pathways, for example through formation of a metallocyclobytane by insertion of the Mo ion (Mo^{+4}) of molybdena-alumina catalyst into cyclopropane ring, according to Gasman and Johnsom (Gasman and Johnsom, 1977), (Jacono and Hall, 1977), (Lombardo et al., 1978), (Oliveros et al., 1997). This leads to formation of ethylene (C_2H_4) and a surface carbene ($Mo=CH_2$) which then acted as a center for olefin metathesis (Lombardo et al., 1978):

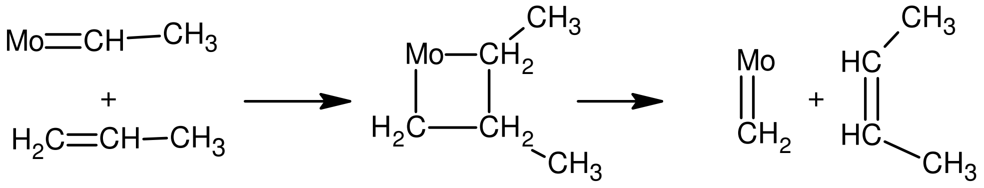


In addition to ethylene the propylene can be also formed from cyclopropane isomerization over reduced molybdena-alumina where c-C_3H_6 ring opening occurs on Brönsted acid sites of Al-OH with a neighboring Mo(cus) (thus making OH groups of alumina more acidic) (Lombardo et al., 1978):



And finally metathesis of propelyne can take place (Jacono and Hall, 1977):

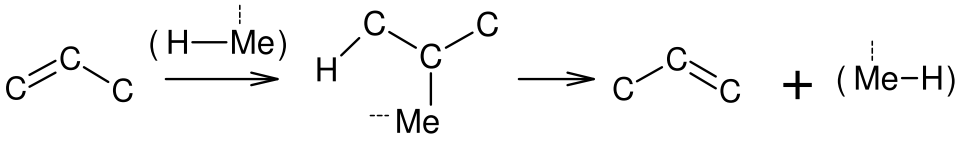




It was suggested that mechanism of this reaction involves the carbene complex of the transition metal with formation of four member metallocycle as an intermediate (Gassman, Johnson, 1976)

1.6.3.2.2. Hydride-Insertion Mechanism

Cycloalkanes often have reactivity similar to alkenes therefore here is shown mechanism isomerization of olefins. Isomerization of olefins occurs via alkyl intermediates-hydride insertion mechanism (Tanaka and Okuhara, 1980). (Goldwasser, 1981). Hydride (H^-) insertion mechanism is, like the proton catalyzed reaction, an "add-on" mechanism. In this case transition metal ions are active sites and hydrogen, as a cocatalyst for the formation of the half-hydrogenation state, are required. In this case the isomerization reaction occurs on the entirely isolated active sites having two degrees of coordinative unsaturation to which one hydrogen atom is bound as shown on scheme below (Tanaka and Okuhara, 1980):



1.7. Aims of Work

This research work has been started in the frame of an international research INCO COPERNICUS project entitled "Semi-conductor metal oxides as high performance catalysts for energetically and environmentally improved catalytic combustion of C_1-C_3 hydrocarbons" ERBIC 15 CT 98 05 15. The present study is part of the mentioned project and is focused mainly on the characterization of acidic properties, electronic characteristic, reducibility, electrical conductivity and catalytic activity of semiconductor tin oxide (~3 %) supported on alumina. In order to enhance the catalytic activity (oxidation, isomerization) this oxide was dopped with platinum (<1%) using mechanical mixing. $Pt(0.28\%)/Al_2O_3$, $SnO_2(2.83)/Al_2O_3$, $SnO_2(3.10\%)/Al_2O_3$, Al_2O_3, SnO_2 samples were also studied for comparison.

The surface active sites (hydroxyl groups, anion sites and surface cations) formed during pretreatment procedure (oxidation or reduction) were investigated by FTIR CO adsorption spectroscopic technique at room temperature (RT); these sites could directly be involved in adsorption and/ or in oxidation of hazardous carbon monoxide to less hazardous carbon dioxide through carbonate and bicarbonate intermediates.

Propylene oxidation was selected as a model reaction to obtain primary relevant information about the surface behaviour and activity of the catalysts under real operation conditions, i.e. under atmospheric pressure in propylene gas flow and in presence of oxygen. The aim of the primary study was to check the catalyst samples for selective oxidation of propylene to acrolein using of a mixture (C_3H_6 : air) equal to 1:10. The activity of samples containing platinum were also tested for total oxidation of propylene (main products water and CO_2) using of a mixture (C_3H_6 : air, 1:22).

Cyclopropane isomerization was chosen as a test reaction, since it could help to establish the correlations between the catalytic activity and the nature of the active sites formed / modified during the different activation (oxidation, reduction) procedures of the supported catalysts, or generated in presence of platinum. The isomerization of cyclopropane to propylene was studied at 473 K and 523 K in a static reactor. The mechanism of cyclopropane isomerization was studied.

Finally the correlation between surface chemistry and catalytic properties was investigated.

2. EXPERIMENTAL

2.1. Catalyst Preparation

All samples (except Sn/Al) were received for investigation from Rompetrol Vega Refinery, Romania (partner of joint INCO COMPERNUCUS project). The aim of the catalyst preparation were the following:

a) to improve the catalytic property of tin oxide containing catalysts by doping a small amount of platinum, less than 1 % (w/w);[1]

b) to obtain a high dispersion of deposited supported oxides with a minimum decrease of the surface area in the resulting material with respect to the support;

The main steps of catalysts preparation are summarized below. More detail information about prepation of Rompetrol Vegas' samples are given in INCO COPERNICUS report (Manoiu D., Ionescu M., INCO report 2002).

The Pt(0.28 %)/Al_2O_3 (designated as Pt/Al) catalyst was prepared by impregnation of alumina with the corresponding amount of H_2PtCl_6 solution (0.43 % (v/v)). The mixture obtained was dried overnight at 393 K followed by calcination in oxygen flow for 8 h at 823 K.

The preparation of SnO_2(2.94%)-Pt(0.28 %)/Al_2O_3 (designated as Sn-Pt/Al) sample was modified. Mechanical mixing was used in order to provide the requested amount of tin oxide in Pt doped catalysts (during the second step of impregnation some of tin precursor was lost).

For the preparation of the Sn-Pt/Al catalyst sample the Pt/Al was mixed with the requested quantity of SnO_2 (> 99%, Vega) in a mortar for 30 min. The mixture obtained was homogenized by adding of small portions of nitric acid solution (HNO_3 10 % (v/v)) up to formation of mixture exhibiting paste consistence. The obtained paste was kept for 30 min at room temperature followed by drying at 393 K for 4 h and calcination procedure was carried out at 823 K for 8 h in air flow.

SnO_2(3.10 %)/γ-Al_2O_3 sample (designated as Sn/Al(Deg)) was received from Institut de Recherches sur la Catalyse, Villeurbane, France, from French partner of the joint INCO COPERNICUS project. The sample was prepared by impregnation of γ-alumina (supplied by Degussa Co.) with the corresponding amount of solution

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[1] %– abbreviation, according the international system of unit, is used for expression of the quantities and expresses the percentage by mass (w/w) or by volume (v/v) or by atomic mass (at/at).

$SnCl_4 \cdot 5H_2O$ (99.99 %, Aldrich). The requested quantity of the tin salt was dissolved in deionized water at room temperature. The resulting mixture was evaporated to dryness and the powder further was dried overnight at 373 K followed by calcination in oxygen flow for 6 h at 423 K and for 8 h at 773K. For more detailed information on the sample preparation see reference (Auroux D., INCO report 2000).

In order to have better understanding on the nature of interaction between tin and platinum elements in the Sn-Pt/Al sample, SnO_2(2.83 %)/Al_2O_3 catalyst (designated as Sn/Al) was prepared by using mechanical mixing method as well (the same method of deposition of tin oxide as for Sn-Pt/Al sample), where the corresponding amounts of $SnCl_2 \cdot 2H_2O$ powder (>99%, Interkémia) and Al_2O_3 were mixed together for 30 min. The mixture obtained was homogenized by adding of a small portion of nitric acid solution (HNO_3 10 % (v/v)) up to the formation of mixture having paste consistence. The paste was kept for 30 min at RT followed by drying at 393 K for 4 h and calcination procedure at 823 K for 8 h was carried out in air flow.

The alumina support used for Sn/Al, Pt/Al, Sn-Pt/Al catalyst samples was Al_2O_3 and was supplied by Vega Co. (designated as Al) having a surface area of 363 m^2/g. It had pore volume of 0.440 cm^3/g with pore diameters between 1.7 and 300 nm and contains Fe_2O_3 impurity in amount of 0.008 % (w/w).

The alumina Degussa support was used for preparation of Sn/Al(Deg) sample having surface area of 110 m^2/g. The alumina Degussa had 97 % of purity, the particle size was 20 nm, powder density of 60 g/l; it has pore volume of 0.294 cm^3/g with pore diameters between 1.7 and 300 nm and contains trace of impurities of $Fe_2O_3 < 2000$ ppm; $SO_4^{2-} < 6$ppm; $SiO_2 < 1000$ ppm; $TiO_2 < 1000$ ppm; HCl < 5000 ppm.

SnO_2 (>99%, Vega and designated as Sn) sample had surface area 9 m^2/g and was studied for comparison.

It is generally accepted that for most catalytic applications, solid materials with high specific surface areas are desirable. Experience has shown that low temperature processes are necessary to obtain oxides with high surface areas, poor crystallinity and small particle sizes (Kung, 1989). Usually calcination temperature at 773-823 K is high enough to achieve the complete removal/decomposion of water and the chlorides (Cl^-), nitrates (NO_3^-), carbonates (CO_3^{2-}) from the bulk of a sample which accumulated during the preparation and under ambient condition of storing (Yuzhakova et al., 2007). The studied catalysts and their symbpls are shown in Table 2.

Table 2. The list of catalysts studied

Symbol	S_{BET}	ICP(bulk)	Number of atoms in bulk $\cdot 10^{18b}$	XPS (surface)[c]	Micro calorimetric (surface)	Catalyst
	m^2/g	Sn^{4+}/Pt^{n+} % (w/w)	$\frac{N_{Sn}}{g} / \frac{N_{Pt}}{g}$	Sn^{n+} % (w/w)	Pt^{n+} % (w/w)	composition
Al	363	-	-	-	-	Al_2O_3
Sn	9	-	-	-	-	SnO_2
Sn/Al	259	2.83/ -	143.56/ -	5.80	-	SnO_2/Al_2O_3
Sn/Al(Deg)[a]	108	3.10/ -	157.26/ -	-	-	SnO_2/Al_2O_3
Pt/Al	210	- /0.28	- /8.64	-	0.04	Pt/Al_2O_3
Sn-Pt/Al	234	2.94/0.28	149.14/8.64	0.80	0.16	SnO_2-Pt/Al_2O_3

[a] – alumina support was γ-Al_2O_3 Degussa with low surface area of110 m^2/g.

[b] – Number of atoms of active compounds in 1 g of solid sample was calculated, as example for Sn/Al sample, using the following equation:

$$N_{Sn} = n \times N_A = \frac{g}{Mr} \times N_A = \frac{0.0283}{118.71} \times 6.022 \cdot 10^{23} = 143.56 \cdot 10^{18} \frac{atom}{g}$$

where n - is number of Sn mole on the surface of 1 g of catalyst, mol/g;

N_A – is Avogadro number, 6.022×10^{23} mol^{-1};

Mr- is molecular mass, g/mol.

[c] – approximate value of tin population on the surface

2.2. Characterization Methods

The prepared materials were fully characterized in order to get a maximum of relevant information concerning their surface composition and catalytic activity.

The structural and surface properties of catalyst samples including the acidic characteristics, reducibility and electrical features were studied using different techniques:

Inductively Coupled Plasma (ICP) analysis. Chemical compositions (metal ion content) were determined using AES-ICP technique (Spectroflame-ICP instrument). The measurements were carried out on two parallel samples.

Platinum containing samples were dissolved in a mixture of mineral acids (HCl and HNO_3) under heating up to 573 K. Tin containing samples were melt with Li tetraborate in a Pt-Au cell with heating up to 1373 K and addition of 20% (v/v) HCl.

The obtained values of tin ion were close to the calculated amount (~3% w/w) used for preparation of catalysts and summarized in Table 2.

Low-temperature nitrogen adsorption (BET). Pretreatment of samples was performed for 4 h at 673 K under vacuum before adsorption of nitrogen at 77 K. The surface areas were determined by the BET method on the basis of the obtained isotherms. The BET surfaces areas are presented in Table 2.

X-ray diffraction (XRD). The crystalline structure was examined using XRD method. XR diffractograms were recorded for calcined samples in O_2 at 773 K and for reduced samples after TPR experiment in H_2 at 1073 K. Well ground sample powder was examined using a Phillips PW 1710 diffractometer at room temperature using Cu Kα radiation source (0.154 nm) from 3° to 80° by 0.02° step per 1 s.

X-ray Photoelectron Spectroscopy (XPS). The composition of the surface layer and oxidation states of tin were determined by X-ray Photoelectron Spectroscopy (XPS), using a VG Escalab 200R spectrometer including a hemispherical analyzer adjusted at 50 eV pass energy. An Al anode (Al K=1486.6 eV) was used as the X-ray source. Charging effect was corrected by using the carbon 1s line at 284.8 eV as the reference energy. XPS analysis depth was around 5-10 nm. The XPS spectra of Al (2p), O (1s), Sn ($3d_{5/2}$) and C (1s) were recorded and evaluated. XPS peak intensities, proportional to the relative population of elements on the surface, were estimated by calculating the integrated area of each peak after fitting the experimental peak with a Lorentzian/Gaussian curve using deconvolution.

The acidity of solid catalysts is an important factor that determines their applications as industrial catalysts and consequently, many of their catalytic properties can be directly related with their acidity. Acidic properties were studied using the adsorption of probe molecules (CO, Py and NH_3) by means of two appropriate methods: FTIR spectroscopy and adsorption microcalorimetry. The information obtained from these investigations can be considered to supplement each other, rather then as a basis for comparison of results, since the values determined by the two experimental techniques (microcalorimetric and FTIR) are different. Microcalorimetry offers to obtain the precise information on the total concentrations of base or acid, while FTIR technique enable to differentiate the types of sites (Brönsted or Lewis).

Fourier Transform Infrared (FTIR) Spectroscopic studies were carried out in Bio-Rad FTS 175 spectrometer using an air cooled DTGS detector of 8 cm^{-1} resolution and 128 scans for self-supported wafers having a density of around 20 mg/cm^2. The quartz cell (Fig.4) suitable for high temperature treatment was connected with a gas inlet and ultrahigh vacuum system (Fig.5). Dry oxygen, hydrogen of ultrahigh purity and carbon monoxide of 99.99% purity were used for the experiments. The liquid pyridine of analytical purity was additionally purified before spectroscopic adsorption study in order to eliminate the contaminants.

Adsorption of CO was studied at the same partial pressure (4 kPa) on Al, Pt/Al and Sn-Pt/Al samples, therefore, the qualitive and quantitative analysis, i.e., the type and density of acidic sites present on the catalytic surface were possible to be calculated. Approximately 0.1 kPa of pyridine (Py) pressure was set for the adsorption studies.

The experimental program was carried out for oxidized and reduced samples as follows:

1. Heating in O_2 flow (100 ml/min) up to 473(573, 673, 773) K with 5 K/min heating rate;
2. Flushing of samples with O_2 (100 ml/min) at 473(573, 673, 773) K for 2 h;
3. Evacuation of samples at 473(573, 673, 773) K for 0.5 h;
    3.1. Introduction of the H_2 ($P=1.01\cdot10^5$ Pa) into the cell at 473 K (823 K for Py adsorption) for 0.5 h *;
4. Cooling the catalyst sample to room temperature in vacuum;
5. FTIR spectra recording;
6. Adsorption of CO (P= 4 kPa) or Py (P=0.1 kPa) was carried out at RT for 0.5 h;
7. Evacuation of catalyst samples at RT;
8. FTIR spectra recording at RT.

* additional pretreatment step for the reduced samples.

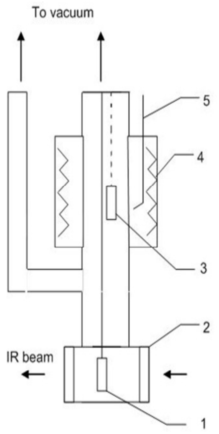
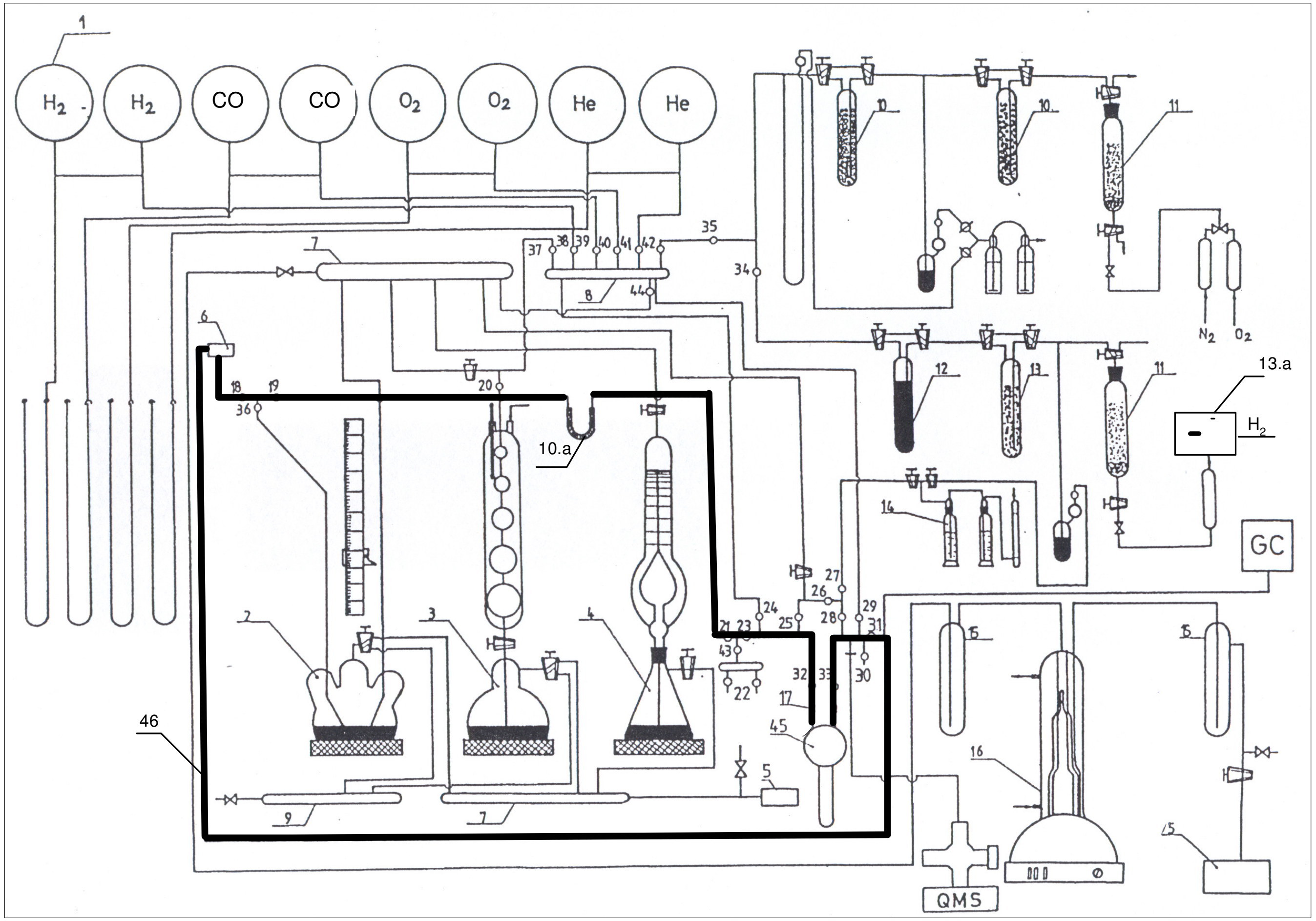


Fig. 4. FTIR cell: 1) position of catalyst sample during FTIR measurement; 2)KRS-5 windows; 3) position of sample during pretreatment; 4) furnace; 5) thermocouple



1 - gas flasks vessel;
2 - mercury differential manometer;
3 - mercury burette for volume measuring;
4 - McLeod vacuum gauge;
5 - oil pump;
6 - circulation pump;
7 - vacuum distributor vessel;
8 - gas distributor vessel;
9 - air distributor vessel;
10,13 - vessels for gas purification;
10.a – loop for gas purification;
11 - $CaCl_2$ ($MgClO_4$) drying cartridge;
12 - active carbon cartridge;
13.a - H_2 purifier;
14 - gas flow controller;
15 - mercury trap;
16- mercury diffusion pump;
17 - glass-metal joints for IR cell/ static reactor;
18 - 44 stopcocks;
45 - static reactor;
46 - recirculation system (bold line).

Fig. 5. Schematic representation of high - vacuum / gas handling system

Microcalorimetry. This method was used for obtaining accurate information on number, strength and strength distribution of the surface acid sites. Acidity was studied by using the adsorption of NH_3 probe molecule at 423 K. CO chemisorption at 303 K was applied to determine the Pt dispersion on the surface. Microcalorimetric studies were carried out in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus equipped with a Barocel capacitance manometer for pressure measurements. The samples were pretreated in a quartz cell by heating overnight under vacuum at 673 K with a heating rate of 0.6 K/min in order to remove the adsorbed molecules (mainly water and carbon containing compounds) adsorbed during contact of samples with environment under storing condition. The differential heats of adsorption were measured as a function of coverage by admitting a small doses of the gas doses onto the sample until the surface was saturated by adsorbed species. The saturation of sample took place when the gas pressure in the system reached about 67 Pa (0.5 Torr). The time required for the pressure to equilibrate in the calorimeter after each does was approximately 20-25 min.

The adsorption amount (V) of n_a moles of gas is accompanied by liberation of the total (integral) heat of adsorption (Q_{int}). If heats are measured isothermally at particular coverage (θ) values, in such a way that no external work is transferred to the calorimeter as heat during the adsorption, the true differential heat of adsorption Q_{diff} is obtained as defined by $Q_{diff} = dQ_{int}/dn_a$. The data, obtained directly from the calorimetric measurements, the pressure, integral heat, and amount adsorbed, can be determined in several ways (Fig.6):

(a) The volumetric isotherms (V vs. P) for a cycle of adsorption ($V_{ad,}$), desorption by pumping at the same temperature for 30 min and then readsorption (V_{read}). The irreversibly adsorbed volume (V_{irr}), which characterizes the strong active sites of the catalyst, can then be calculated as the difference between the adsorption volume and the readsorption volume at a given equilibrium pressure, P = 27 Pa;

(b) On the basis of corresponding calorimetric isotherms (Q_{int} vs. P);

(c) On the basis of integral heats (Q_{int}) as a function of the adsorbed quantities (V). This representation leads to the detection of coverage values with constant heat of adsorption. In this case the evolved heat is a linear function of the coverage;

(d) On the basis of differential heat $Q_{diff} = dQ_{int}/dn_a$ as a function of n_a. The ratio of the amount of heat evolved for each increment relates to the number of moles adsorbed in the same period and is equal to the average value of the differential enthalpy of adsorption in the interval of the adsorbed quantity considered. The curve showing the differential heat variations in relation to the adsorbed amount is traditionally represented by histograms. However, for simplification, the histogram steps are often replaced by a continuous curve connecting the centers of the steps. Differential heats of chemisorption usually decreases with increasing volume adsorbed. The way in which the heat of chemisorption decreases with increasing coverage varies both with the adsorbate and with the adsorbent. Sharp heat decrease at low values should in general be regarded as indication of the surface heterogeneity.

Differential heats of absorption was used for graphical representation of microcalorimetric data in this work.

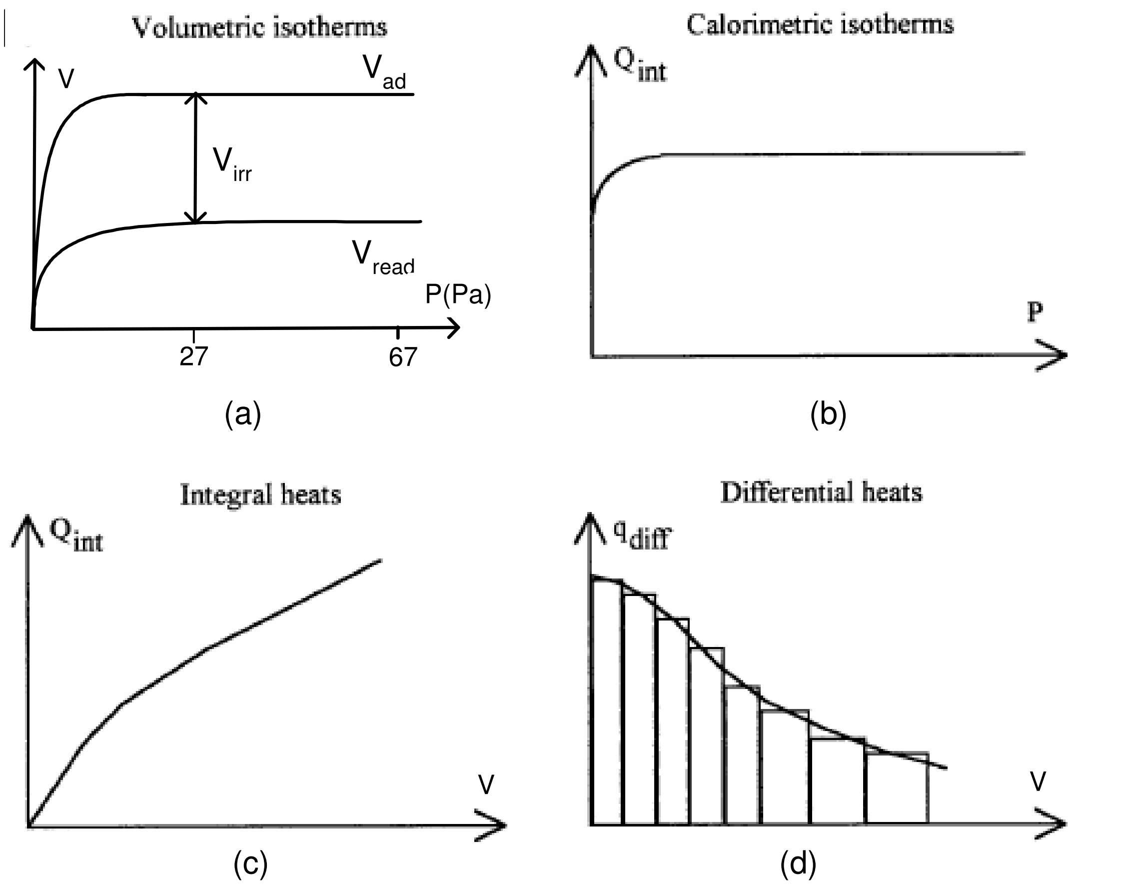


Fig. 6. Interpretation of obtained microcalorimetric data (Auroux, 1997)

Temperature programmed reduction (TPR). Temperature programmed reduction studies can give information on stability of catalyst under reduction atmospheres and at different temperatures. TPR method is frequently applied for studies of metal dispersion, surface composition, reducibility and oxidation state of metal components in mono- and bimetallic supported catalysts (Spivey and Roberts, 2004), (Wallin et al., 2004). The position of TPR peaks can also be used for characterization of the type of interaction between metal-metal, metal-support species in the catalysts (Lieske and Völter, 1984).

The sample of about 0.1 g was used for TPR and was held on the frit in a U-shape quartz reactor, allowing the reducing gas stream to pass through the sample. Prior the TPR experiment, the sample was heated up to 723 K in air flow and kept at the same temperature for 1 h following by cooling down to room temperature. TPR was performed *in situ* up to 1073 K in H_2 flow (5%/Ar). The flow rate of the gas was 1.3 L/h and the heating rate was 5 K/min. The hydrogen consumption was monitored using thermal conductivity detector (TCD).

Electrical conductivity (EC). EC indicates the transport of the electric charges. The EC measurements performed "in situ", in operando conditions allow to get information about surface changes connected with processes occurring with charge transfer (gas adsorption, desorption, surface reaction) in conditions similar to those encountered in catalysis (Caldararu et al., 1996), (Stoica et al., 1999), (Stoica et al., 2000), (Caldararu et al., 2001), (Caldararu et al., 2003, ***207***), (Caldararu, et al., 2003, ***211***).

The conductivity of polycrystalline semiconductor metal oxides reflects to a combination of bulk, grain-boundary and surface properties (McAleer et al., 1987). The bulk conductivity and conductivity across grain-boundaries in the polycrystalline substances is also thermally activated. The surface conductivity may be increased or decreased by a chemisorbate. Generally, in the case of n-type semiconductors, the surface conductivity is increased by electron transfer from a chemisorbed species to the solid (leading to a positively charged adsorbate) and decreased by electron transfer from solid surface to the adsorbate (leading to a negatively charged adsorbate as in the case of oxygen adsorption, as O_2^- and O^-) (Caldararu, INCO partner report, 2002). The electrical conductivity studies, combined with other methods of investigation, allow to understand better the type and the strength of adsorption of the reactive species and thus the mechanism of reactions

Electrical conductivity (G), capacity (C) and catalytic activity were measured simultaneously “in situ”, in alternating current (AC at 1592Hz) and under operando conditions on granulated powder (the fraction between 0.25 and 0.5 mm) with using a special reaction cell (Caldararu et al., 1996):

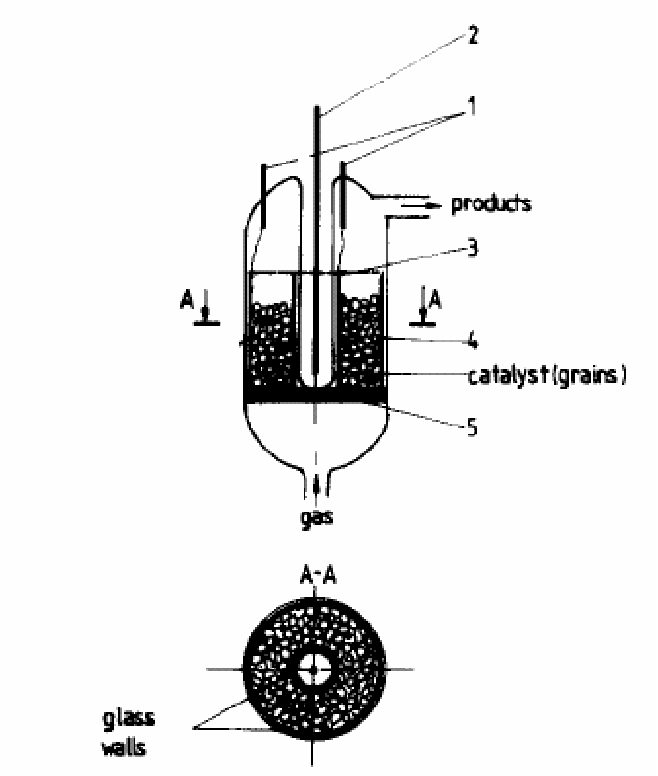


Fig.7. Dynamic reactor for electrical conductivity, capacity and catalytic activity measurements on powder: l-tungsten contacts; 2-thermocouple; 3-tantalum cylinder (inner electrode); 4-tantalum cylinder (external electrode); 5-Pyrex glass frit.

The cell is made of Pyrex glass with two embedded cylindrical coaxial tantalum electrodes connected by tungsten wires to a precision RLC bridge - TESLA BM 484 (Fig. 7). The RLC bridge allows simultaneous measurements of G and C with a resolution of 0.02 nS and 0.02 pF respectively. The catalyst powder ($1.5 cm^3 = 0.8–0.9 g$) was placed between the electrodes and supported on a frit. The temperature in the powder bed was monitored with a thermocouple located in the center of the cell. The grain fraction, between 0.25 and 0.5 mm, was obtained by pelleting the powder (the applied pressure was around 50 kg/cm^2) followed by crushing and sieving to separate the particles with desired fraction size. Under these preparation conditions (crystalline structure and surface area of powder cannot be damaged by applying an appropriate low pressure) the sample is considered to be slightly pre-sintered powder and the conductivity can be described as controlled by Schottky barriers, very sensible to changes of morphology in inter-grain boundary areas (Harrison, 1987), (Mc Aleer 1987).

The protocol of the experiments consisted of successive heating-cooling cycles from 293 to 623 (673) K and back, with a heating rate of 2 K/min followed by fast cooling (about 10 K/min). The sequence of the cycles was: DHe-1 (first cycle), DHe-2 (second cycle), CHe (third cycle) where DHe is the abbreviation for dry helium and CHe denotes the mixture used for cyclopropane isomerization, i.e., c-C_3H_6 : He of 1:20 ratio of atmospheric pressure (101 kPa).

Dry gases were obtained by passing the helium through molecular sieve beds. The outlet gases during CT cycle were permanently monitored by using on-line gas chromatography with TC detector and a column with packed celite impregnated by 20% BMEA (bis/2-metoxi-ethyl-adipate). Each heating run starts with flushing for 30 min at room temperature with the corresponding gas (He) or gas mixture (c-C_3H_6 : He). The overall flow rate of used gas/ gas mixture in all cases was 69.3 cm^3/min.

Propylene oxidation. Propylene oxidation was studied in flow reaction cell (the same cell was used as for EC study, Fig.7) over oxidized samples pretreated in O_2 at 773 K. The gas mixture used for the catalytic test had a ratio of C_3H_6 : air equal to 1:10 for selective oxidation or equal to 1:22 for total oxidation of propylene, mass of sample was ~0.9 g, gas flow rate was 69.3 cm^3/min, contact time was $\tau = 1.3$ s (C_3H_6:air 1:10) or $\tau = 1.1$ s (C_3H_6 : air 1:22).

Cyclopropane isomerization. The isomerization of cyclopropane to propylene was studied over 0.1 g of catalysts with particle size of 0.4-0.5 mm at 473 K and 523 K in a static reactor attached to a glass gas-circulation system with manual sampling of gas doses for GC analysis. The gas-circulation system is shown in Fig.5. Its volume including the reactor was 365.3 cm^3. Cyclopropane isomerization was studied over: (i) oxidized samples pretreated in O_2 at 773 K ($P=1.01\cdot10^5$ Pa); (ii) reduced samples pretreated in O_2 at 773 K followed by hydrogen pretreatment at 823 K ($P=1.01\cdot10^5$ Pa). After the pretreatments carried out in static reactor the sample was cooled to 473 K in vacuum ($P=1.33\cdot10^{-2}$ Pa).

The mixture of cyclopropane and helium gases was introduced into the reaction space (reactor and recirculation system) and the reaction was carried out for 2 h at 473 K. The initial pressures of c-C_3H_6 (99.9% purity) and He (99.99% purity) were 4.0 kPa and 13.3 kPa, respectively. Helium was added for increasing the efficiency of the gas circulation.

After 2 h (first reaction run) the reactor was evacuated to $1.33 \cdot 10^{-1}$ Pa and N_2 (99.996 %) was introduced at atmospheric pressure to remove the residues from the catalyst surface with a flushing rate of 70 ml/min while the temperature in the reactor was raised from 473 K up to 523 K. Nitrogen was evacuated from the reactor to $1.33 \cdot 10^{-2}$ Pa and the system was set up for the second run of cyclopropane isomerization at 523 K for 2 h.

In order to check the stability and the efficiency of catalysts regeneration, the same catalyst sample was used for three regeneration cycles. Each cycle included two reaction runs of cyclopropane isomerization at two temperatures (473 K and 523 K) followed by evacuation overnight and regeneration in oxidizing or/and in reduction atmospheres.

Reaction products were analyzed by gas chromatography (GC). The solid support of packed column was celite modified by 20% BMEA (bis/2-metoxi-ethyl-adopate). Gas samples were analyzed in every 10 min during 2 h experiments.

3. RESULTS

It is well known that during the catalytic transformation the first step is the adsorption of the reactant followed by surface reaction. Therefore it is necessary to investigate surface properties of catalysts.

3.1. Chemical Composition, Structure and Morphology of Catalysts

Table 2. presents the list of the samples studied. Their chemical compositions obtained by ICP technique, the surface concentrations of tin measured by XPS method, the Pt dispersion measured by microcalorimetric method and surface areas determined by BET are summarized in Table 2.

The substanstial decrease in the surface area of alumina support occurs upon the deposition of metal oxides (SnO_2 or/and PtO). The decrease in the surface area is probabily due to the blocking of alumina pores (average pore diameter of Al_2O_3-Vega is between of 3-5 nm and that of Al_2O_3-Degussa is between 10-12 nm) by the supported elements (the atomic diameter of Pt is 0.27 nm and that of Sn is 0.29 nm).

XRD pattern of alumina (Vega) sample exhibits characteristic peaks of two crystalline phases: bayerite ($Al(OH)_3$) and boehmite ($AlO(OH)$). At the same time in Pt/Al, Sn/Al, Sn-Pt/Al samples only γ-Al_2O_3 phase was detected (Fig. 8).

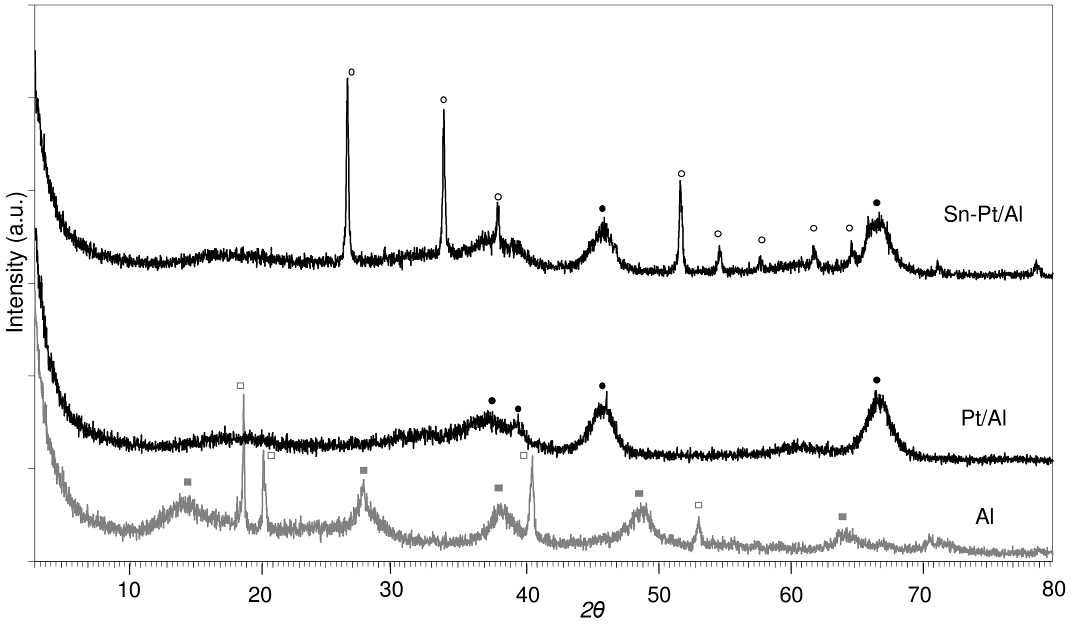


Fig. 8. XRD patterns of samples calcined in O_2 at 773 K where : °- cassiterite structure (SnO_2); and • - γ-Al_2O_3; □-bayerite ($Al(OH)_3$); ▪- boehmite ($AlO(OH)$) crystalline phases of aluminum oxide

There are different crystallographic structures of alumina. The dehydration scheme according to which the various alumina phases can be transformed from one to another under thermal condition is shown below (Rosynek, 1972), (Linsen, 1970):

$$Bayerite \xrightarrow{453K} Boehmite \xrightarrow{573-723K} \gamma - Al_2O_3 \rightarrow$$

$$\xrightarrow{873-1173K} \delta - Al_2O_3 \xrightarrow{1273-1323K} \theta - Al_2O_3 \xrightarrow{1473K} \alpha - Al_2O_3$$

The absence of boehmite and bayerite peaks of XRD patterns for Pt/Al, Sn/Al, Sn-Pt/Al samples (Fig. 8) can be explained by transforming the boehmite and bayerite to γ-Al_2O_3 during calcination at 773 K during 8 h, (see scheme above) (Morterra et al., 1992). Pure alumina support is hydroxylated in higher extent than in supported samples.

No characteristic peaks assigned to tin oxide structure were observed for Sn/Al. This indicates high dispersion, perhaps amorphous structure of tin oxide in Sn/Al. However, the presence of platinum influences the crystal structure of Sn-Pt/Al sample. In this case the XRD pattern showed the characteristic line of formation of some tin oxide crystals having cassiterite structure (Fig. 8), (Harrison and Guest, 1987). A close interaction between Pt and Sn elements occurs in Sn-Pt/Al sample, where chloroplatinic acid was used as impregnation agent. This interaction can be achieved after calcination pretreatment at 773 K (Lieske and Völter, 1984). This could be the reason of attraction of several Sn atoms by Pt, and formation a tin cluster having crystalline structure.

The absence of diffraction peaks of platinum is to be noted. Based on XRD results it is possible also to assert that the methods used for the preparation provide a good dispersion of platinum on the surface of Pt/Al and in Sn-Pt/Al samples.

XPS investigation was carried out on oxidized form of samples. It is known that the XPS gives information on the composition of active surface layer of catalysts, distribution and electronic state of the supported elements. Since there is significant uncertainty in the XPS atomic percentages due particularly to the Scofield intensity factors, which are average values, only the relative atomic ratios in each catalyst series are considered (Scofield, 1976). In addition very small regions of surface were analyzed (analysis depth 5-10 nm) therefore quantitative and qualitative parameters obtained by XPS analysis on the surface composition have informative character and should be considered as approximate values.

Table 3. shows the surface layer composition of samples expressed in atomic percent and the binding energy of the identified elements (BE O1s for O; BE C1s for C; BE Sn3d$_{5/2}$ for Sn; BE Al2p for Al) in XPS spectra. Platinum was not detected on the surface by XPS due to the fact that the concentration of Pt was under the detection limit.

Table 3. XPS binding energies (eV) and population of O, C, Sn, Al elements in atomic percent on the surface of catalysts

Sample	O		C		Sn		Al		Sn/Al
	BE O1s	O (%)	BE C1s	C (%)	BE Sn3d	Sn (%)	BE Al2p	Al (%)	
Sn/Al	530.9	62.2	284.6	5.8	486.8	0.98	73.9	31.0	0.031
Pt/Al	531.0	64.0	284.7	3.3	-	-	74.0	32.6	-
Sn-Pt/Al	531.1	65.3	284.6	2.2	485.2/ 486.8	0.14	74.2	32.4	0.004

Sn/Al ratio was determined from the Sn3d$_{5/2}$ and Al2p peak areas. As it can be seen from Sn/Al values in Table 3, the dispersion of Sn atoms on the surface was relatively higher for Sn/Al than for Sn-Pt/Al sample. It could be explained by the aggregation of the tin species in clusters around Pt (possibly due to the preparation method and calcination) which leads to a lower dispersion of the tin ions on the surface of Sn-Pt/Al, but higher dispersion of platinum in this sample in comparison with Pt/Al which was proved by calorimetric study (section 3.3.2).

The tin species showed the doublet Sn3d$_{5/2}$ - Sn3d$_{3/2}$ (spin-orbit coupling) in XPS spectra with the intensity ratio 1.5:1 (Fig. 9). For the determination of the oxidation states of tin, the peak of Sn3d$_{5/2}$ exhibing a higher intensity was taken into account. Deconvolution of the higher intensity peak from Sn3d$_{5/2}$ – Sn3d$_{3/2}$ doublet of Sn-Pt/Al sample showed that tin is present in two types of species: the first type of tin species having the binding energy centered around 485.2 eV was assigned to SnO with oxidation state of Sn(II) and the second was assigned to SnO$_2$ with the binding energy centered at 486.2 eV corresponding to Sn(IV) (Serrano-Ruiz et al., 2006). For Sn/Al only Sn(IV) species were detected (Table 4). In should be noted that for Sn-Pt/Al catalyst sample the X-ray diffraction spectra did not show any line corresponding to a lower oxidation state of tin. The presence of Sn(II) can mainly be attributed to the removal of surface hydroxyl groups and oxygen from SnO$_2$ during exposure of the samples in ultra high vacuum chamber (UHV), i.e., under mild reduction conditions (Reddy et al., 2003), (Yuzhakova et al., 2007). The reduction might be initiated by platinum (Herz, 1989), which could enhance oxygen mobility and provoked reduction of tin oxide.

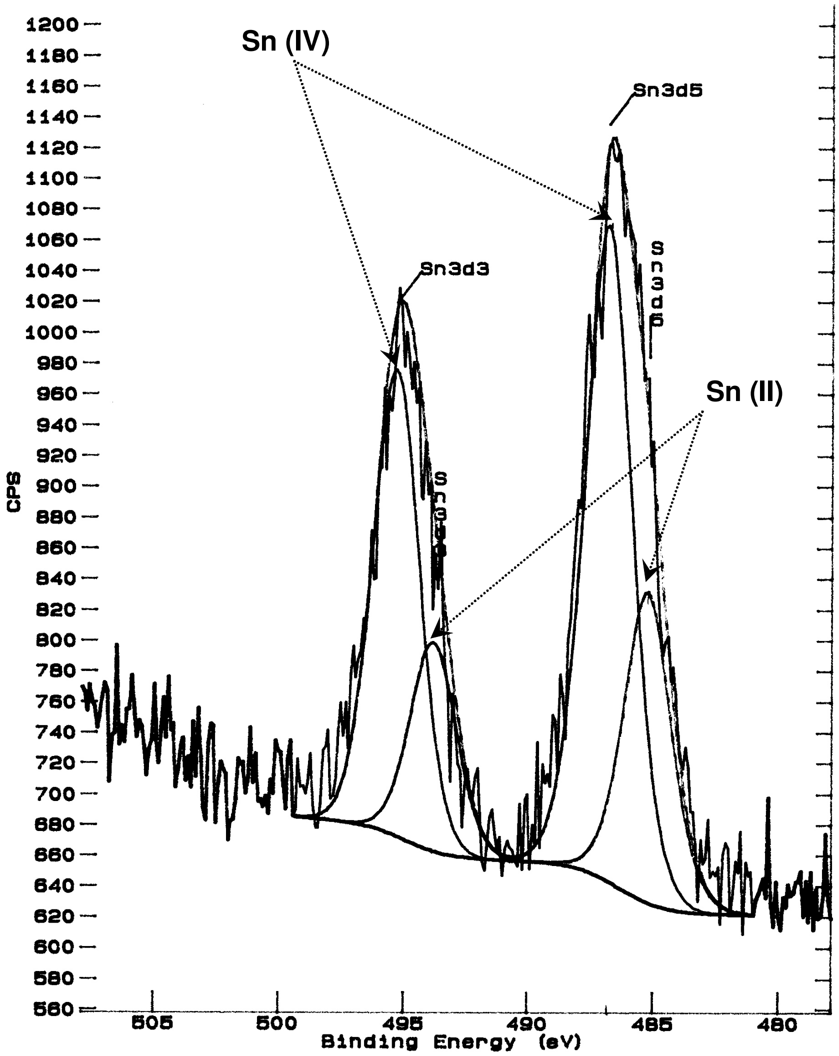


Fig. 9. XPS spectra of $Sn3d_{5/2}$ –$Sn3d_{3/2}$ doublet of Sn-Pt/Al sample after oxygen pretreatment at 773 K

Table 4. Oxidation states of tin oxide on the surface of Sn/Al, Pt-Sn/Al catalysts

Sample	BE 485.2 eV- Sn(II), %	BE 486.8 eV- Sn (IV), %
Sn/Al	-	100
Sn-Pt/Al	32	68

There are shifts in binding energies of O, Sn and Al atoms depending on the composition of the samples (Table 3), and this indicates a different interactions between the same elements (O, Sn and Al) in samples having different compositions. The cation of the oxide support, Al^{3+}, was detected in all samples. According to the literature (Thomas and Sherwood, 1992) the Al2p band appears at 74.2 eV. Addition of a second metal oxide to alumina has a slight reducing impact on support by decreasing of the BE of Al2p from 74.2 to 73.9 eV (in agreement with FTIR results). At the same time Sn-Pt/Al sample containing both supported metal and oxide has the same value of Al2p binding energy as for pure alumina (74.2 eV).

The presence of carbon was also studied since the catalysts surface is capable to absorb the carbon compounds from air under ambient conditions (Table 3). The highest concentration of carbon on the catalyst surface was observed for Sn/Al. The ability to adsorb carbon-containing compounds from the environment after the oxidation pretreatment decreases in the presence of platinum in the following order: Sn/Al > Pt/Al > Sn-Pt/Al.

3.2. Fourier Transform Infrared Spectroscopy

3.2.1. Study on the Effect of Temperature on Dehydroxylation

The surface of metal oxides are usually covered by OH-groups at ambient condition which are connected to the active sites (M^{n+}, O^{2-}). OH groups are formed as a result of dissociative H_2O adsorption, which reduces the number of CUS (coordinative unsaturated of the surface sites) (Caldararu et al, 2003, ***207***). The CUS cations (M^{n+}) and oxide anions (O^{2-}) are formed during the thermal dehydroxylation of catalyst surface which might act as Lewis acid or Lewis base sites respectively. Surface OH groups can have basic, acidic or neutral character depending on the surface structure. The behavior and properties of hydroxyl groups can easily be studied by IR spectroscopy (Zaki at el., 2001), (Tsyganenko and Mardilovich, 1996).

FTIR spectra were recorded for Al, Sn/Al (Deg), Pt/Al and Sn catalyst samples after dehydroxylation in a temperature range from 473 to 773 K. After outgassing of all samples in temperature range 473-773 K five O-H bands can be resolved at about 3790, 3775, 3730, 3680 and 3580 cm^{-1} and results are summarized in Table 5.

The optical transmittance of pure SnO_2 in 3000-3500 cm^{-1} region was very poor and it was not possible to resolve peaks attributed to different types of OH groups present on the surface. Only one broad and noisy peak centered at 3670 cm^{-1} has been recorded and can be assigned to terminal groups of SnO_2 (Sn-OH) (Harbeck et al., 2003), (Amalric-Popescu and Bozon-Verduraz, 2001).

Table 5. Relative band intensity of different types of surface hydroxyl groups

$T_{dehydroxilation}$ K	Isolated hydroxyl groups								Associated Hydroxyl groups	
	Basic OH groups				Acidic OH groups					
	Al_{oct}-OH		Al_{tet}-OH		Al_{oct}-OH-Al_{tet}		OH-$(Al_{-oct})_3$			
	ν, cm^{-1}	I^3	ν, cm^{-1}	I	ν, cm^{-1}	I	ν, cm^{-1}	I	ν, cm^{-1}	I
Al (ox)[1]										
473	-	-	-	-	-	-	3681	0.033	-	-
573	-	-	-	-	3728	0.222	3681	0.029	3581	0.226
673	3790	0.066	3777	0.066	3727	0.163	3697	0.190	-	-
773	3791	0.038	3777	0.039	3729	0.088	3696	0.108	-	-
Al (red)[2]										
773	3785	0.027	-	-	3728	0.074	3692	0.094	3580	0.093
Sn/Al (Deg) (ox)										
473	-	-	-	-	-		3670	0.181	-	-
573	3789	0.015	-	-	3727	0.065	3681	0.114	3596	0.085
673	3789	0.016	-	-	3727	0.052	3681	0.088	3596	0.049
773	3784	0.023	-	-	3727	0.062	3684	0.080	-	-
Pt/Al (ox)										
473	3790	0.008	-	-	3723	0.111	3666	0.168	3583	0.180
573	3790	0.013	-	-	3728	0.090	3668	0.131	3584	0.102
673	3791	0.012	3773	0.026	3731	0.073	3684	0.095	3584	0.050
773	3790	0.015	3773	0.025	3730	0.071	3684	0.075	-	-
Pt/Al (red)										
773	3790	0.013	-	-	3730	0.169	3685	0.189	3571	0.230
Sn-Pt/Al (ox)										
473	-	-	-	-	3729	0.152	3680	0.195	3588	0.162
573	-	-	-	-	3728	0.151	3679	0.194	3587	0.162
673	3788	0.017	-	-	3731	0.149	3682	0.139	3582	0.060
773	3790	0.019	3774	0.031	3731	0.149	3684	0.110	-	-
Sn-Pt/Al (red)										
773	3790	0.012	-	-	3738	0.210	3683	0.215	3579	0.269

[1] - Pretreatment of samples in O_2 in temperature region 473 -773 K;

[2] - Pretreatment samples at 773 K in O_2 followed by reduction in H_2 at 473 K;

[3] -Band intensity (arbitrary units)

At the same time five bands were resolved on pure alumina in 3000-3500 cm^{-1} region. Therefore, the IR bands were assigned to hydroxyl groups bound to surface aluminum having different coordination (tetrahedral or octahedral) (Ballinger and Yates, 1991), (Knözinger and Ratnasamy, 1978), (Sohlberg et al., 2000). Resolved O-H stretching bands have been refered to four isolated OH groups and one associated hydroxyl group. Their configurations, wavenumbers and net charges at a surface OH groups are summarized in Figure 10 (Knözinger and Ratnasamy, 1978)

Isolated OH groups:

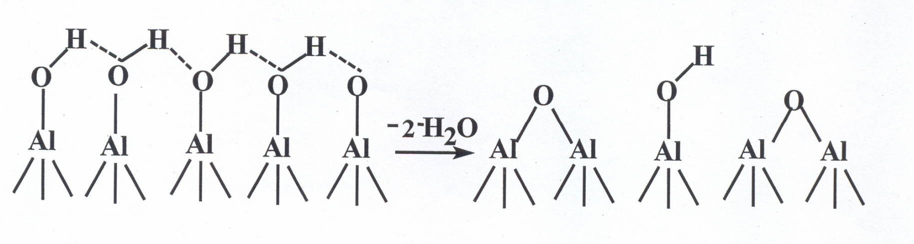
HO-Al$_{oct}$; 3784-3790 cm^{-1}; Net charge at OH -0.5

HO-Al$_{tet}$; 3773-3777 cm^{-1}; Net charge at OH -0.25

Al$_{oct}$-OH -Al$_{tet}$; 3723-3738 cm^{-1}; Net charge at OH +0.25

HO–(Al$_{oct}$)$_3$; 3666-3697 cm^{-1}; Net charge at OH +0.5

Associated hydroxyl groups:



3571-3596 cm^{-1}

Fig.10. Configuration of surface hydroxyl groups of alumina, their wavenumbers and net charges

The net charges at a surface OH groups were obtained as the sum of the negative charge of the anion and the sum of the strengths of the electrostatic bonds (equal to cation charge divided by coordination number) to the anion from adjacent cations (Knözinger and Ratnasamy, 1978). For example the net charge at the surface OH group for HO-Al$_{oct}$ is:

$$1\cdot(H) - 2\cdot(O) + 3\cdot(Al)/6 = -0.5$$

The hydroxyl group is coordinated to three aluminum cations in an octahedral interstice in HO-(Al_{oct})$_3$ configuration. In this position OH group is the most acidic one with a net positive charge +0.5 (Knözinger and Ratnasamy, 1978) in comparison with the different types of hydroxyl groups which might be present in the surface layer of alumina (Fig.10). As a consequence the OH-(Al_{oct})$_3$ sites might be responsible for Brönsted acidic character of the sample with high probability. The protonic acidity of the OH groups will decrease as the net charge on them becomes more negative (Fig.10).

Changes in the bands' adsorption intensity can be taken as a measure of the changes in the concentration of the particular OH group of alumina due to the increase of dehydroxylation temperature of catalyst samples and due to Sn, Pt doping (Table 5). It be assumed that hydroxyl groups of support are interacting with deposited tin or platinum on catalyst surface during impregnation. This interaction diminished the population of alumina OH groups. (Margitfalvi et al., 1984), (Lietz et al., 1983). Catalysts containing platinum have a higher affinity to dissociatively adsorb water molecule; as a sequence a higher band intensity of hydroxyl groups was observed on Sn-Pt/Al and Pt/Al surface of samples in comparison with that of Sn/Al. An example of the variation of population of acidic hydroxyl groups, HO-(Al_{oct})$_{3,}$ with increasing dehydroxylation temperature for oxidized sample is shown in Fig.11.

After heating the samples, except Sn/Al (Deg), up to 673 K band at about 3775 cm^{-1} assigned to more basic group could be resolved. At the same time lower frequency band of associated hydroxyl groups (at 3580 cm^{-1}) diminishes for studied samples (Table 5). It could mean that associated hydroxyl groups (hydrogen-bonded OH groups) during increasing dehydroxylation temperature break their association and fraction of them increases the density of basic OH groups.

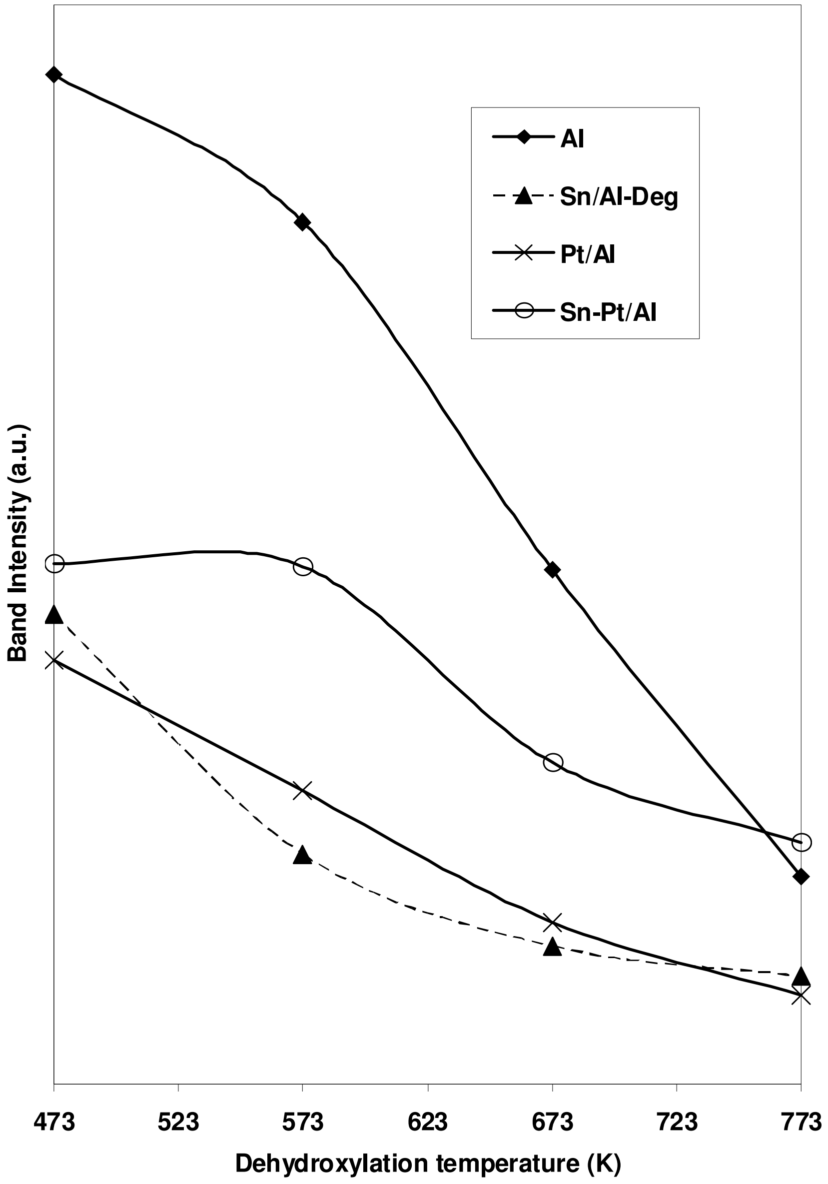


Fig.11. Variation of the intensity of acid hydroxyl groups, HO-$(Al_{oct})_3$, as a function of pretreatment temperature from 473 K to 773 K in oxygen atmosphere

Dehydroxylation at 773 K followed by pretreatment in hydrogen at 473 K has the impact on population of hydroxyl groups (in comparison with bands of hydroxyl groups of the same calcined sample) namely:

1) diminishes the population of basic hydroxyl groups;

2) restores the population of associated hydroxyl groups;

3) slightly decreases the population of acidic groups of alumina and increases population of same groups for samples containing platinum.

It can be concluded that increase of population of acid hydroxyl groups after hydrogen pretreatment for Pt/Al and Sn-Pt/Al samples is due to heterolitically dissociation of hydrogen molecule in presence of platinum followed by interaction of formed proton with surface oxygen ion:

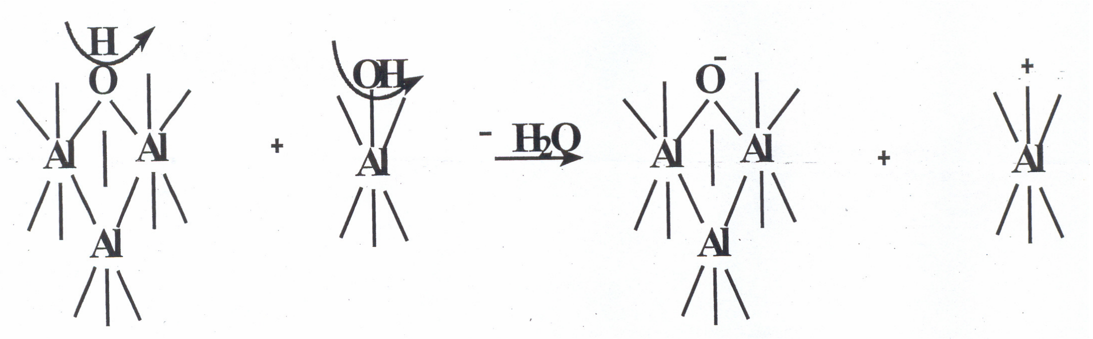
$$1)\ H_{2\,(Gas)} \xrightarrow{Pt} H^+ + H^-$$

$$2)\ O^-_{(surface)} + H^+ \rightarrow O\text{-}H$$

The population of hydroxyl groups was higher for Sn-Pt/Al sample pretreated in hydrogen (Table 5) which has better dispersion of noble metal on the surface proved by microcalorimetric study (Table 8).

3.2.2. Carbon Monoxide Adsorption on Alumina

As it was mentioned above the removal of protons and OH groups from the alumina surface (catalytic surface) during dehydroxylation leads to the formation of surface defects – oxygen and anion vacancies. The oxygen bears a negative charge (Lewis base site) and the anion vacancy a positive one (Lewis acid site):



$HO\text{-}(Al_{oct})_3$ $HO–Al_{oct}$ Lewis base site Lewis acid site

CO is known as a soft basic probe molecule and can be used for identification of acid sites of the solid material (Knözinger & Ratnasamy, 1978), (Anderson & Rochester, 1991). Lewis acidity of alumina is represented by two different coordinatively unsaturated Al^{3+} sites: Al^{3+} octahedral (Al^{3+}_{oct}) and Al^{3+} tetrahedral (Al^{3+}_{tet}). Due to their geometry, aluminum ion with tetrahedral coordination has a stronger Lewis acidic character. Therefore the band generated by chemisorption of CO on Al^{3+}_{tet} sites is located at a higher wavenumber (at about 2230 cm^{-1}) in comparison with CO bonded to

Al^{3+}_{oct} (at about 2200 cm^{-1}) (Fig.12), (Ballinger and Yates, 1991), (Gordimova and Davidov,1979), (Caldararu et al, 2003, ***211***).

Since the deposited metal oxides do not covered completely of the support, Lewis acid sites of alumina were detected on the supported catalysts, as well. It is worth-while to mention that the increase of dehydroxylation temperature increases the population of alumina Lewis sites and hence the intensity of IR bands belonging to them increases. The IR band of CO-Al^{3+}_{oct} can be resolved for all samples after dehydroxylation at $\geq$ 573 K. Carbon monoxide adsorption on stronger Al $^{3+}_{tet}$ acid sites was detected on Pt/Al sample after dehydroxylation at 673 K and on Al, Sn/Al and at 773 K Sn-Pt/Al.

Deposition of semiconductor oxide (strong n-type semiconductor) diminishes population of the stronger acidic sites of alumina (Al^{3+}_{tet}). At the same time platinum (PtO p-type semiconductor) increases the number of stronger sites of Al_2O_3 (Fig.12). The explanation of this difference may be found in the first case by transition of n-type conduction electrons from the SnO_2 to the Al_2O_3 (week n-type semiconductor) which decreases absorption ability of Al^{3+}_{tet} towards CO. In case of Pt/Al electron flow occurs from Al_2O_3 n-type to the PtO p-type semiconductors, thereby facilitating the development of Al^{3+}_{tet} –CO sites.

Lower absorption ability of carbon monoxide on Al^{3+}_{tet} was detected for Sn-Pt/Al than for Pt/Al sample and it is due to the presence of SnO_2 (Fig.12). The presence of both Sn and Pt metal oxides influences the acidity of the support making the strength of acid sites more uniform.

CO adsorption on alumina Lewis acid sites was not observed after hydrogen pretreatment of the samples at 473 K. This treatment suppresses the ability of alumina acid sites to adsorb carbon monoxide by increasing the population of hydroxyl group on the surface (Table 5).

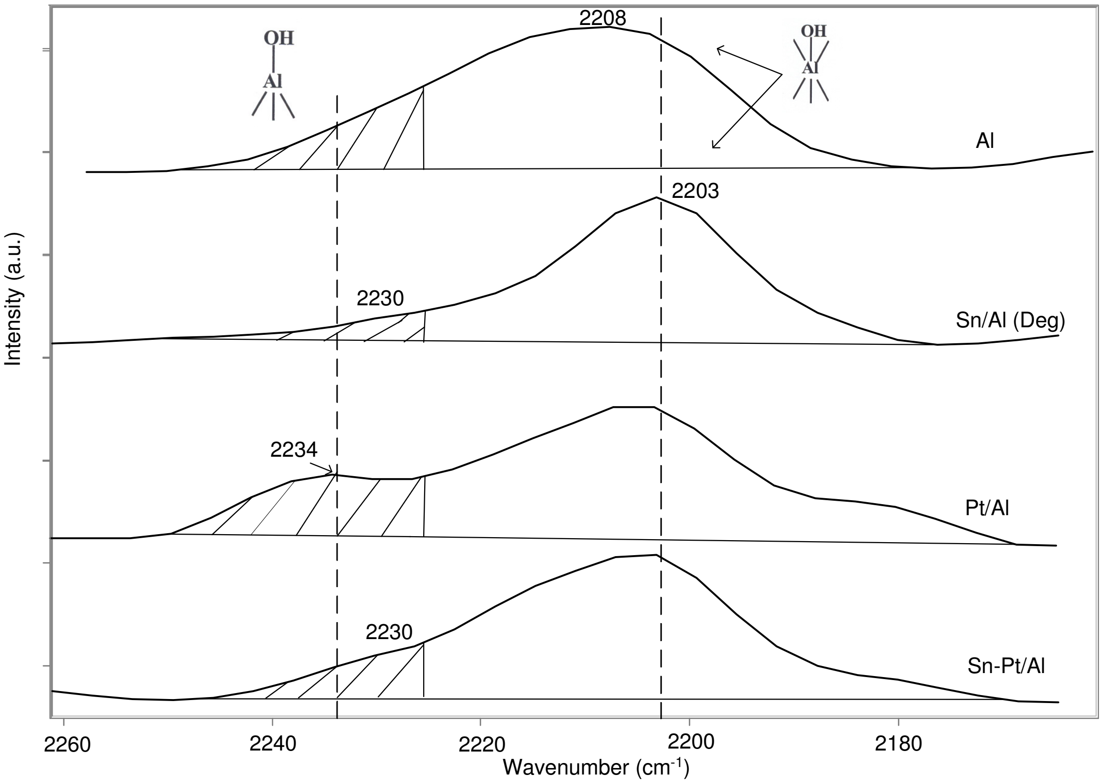


Fig.12. FTIR spectra of CO adsorption at room temperature on alumina Lewis sites after pretreatment of catalysts in O_2 at 773K

3.2.3. Carbon Monoxide Adsorption on Platinum

Oxidized Pt/Al, Sn-Pt/Al samples showed CO adsorption broad band at 2132 cm^{-1} (Fig.13). The band higher than 2100 cm^{-1} was attributed to ($Pt^{n+}O$-CO) complex in platinum containing catalysts (Barshad et al., 1985), (Anderson and Rochester, 1991), (Anderson, 1992). More precisely assignment of band at 2132 cm^{-1} was done by Davidov (Davidov, 1984) and it was attributed to Pt^{1+}-CO.

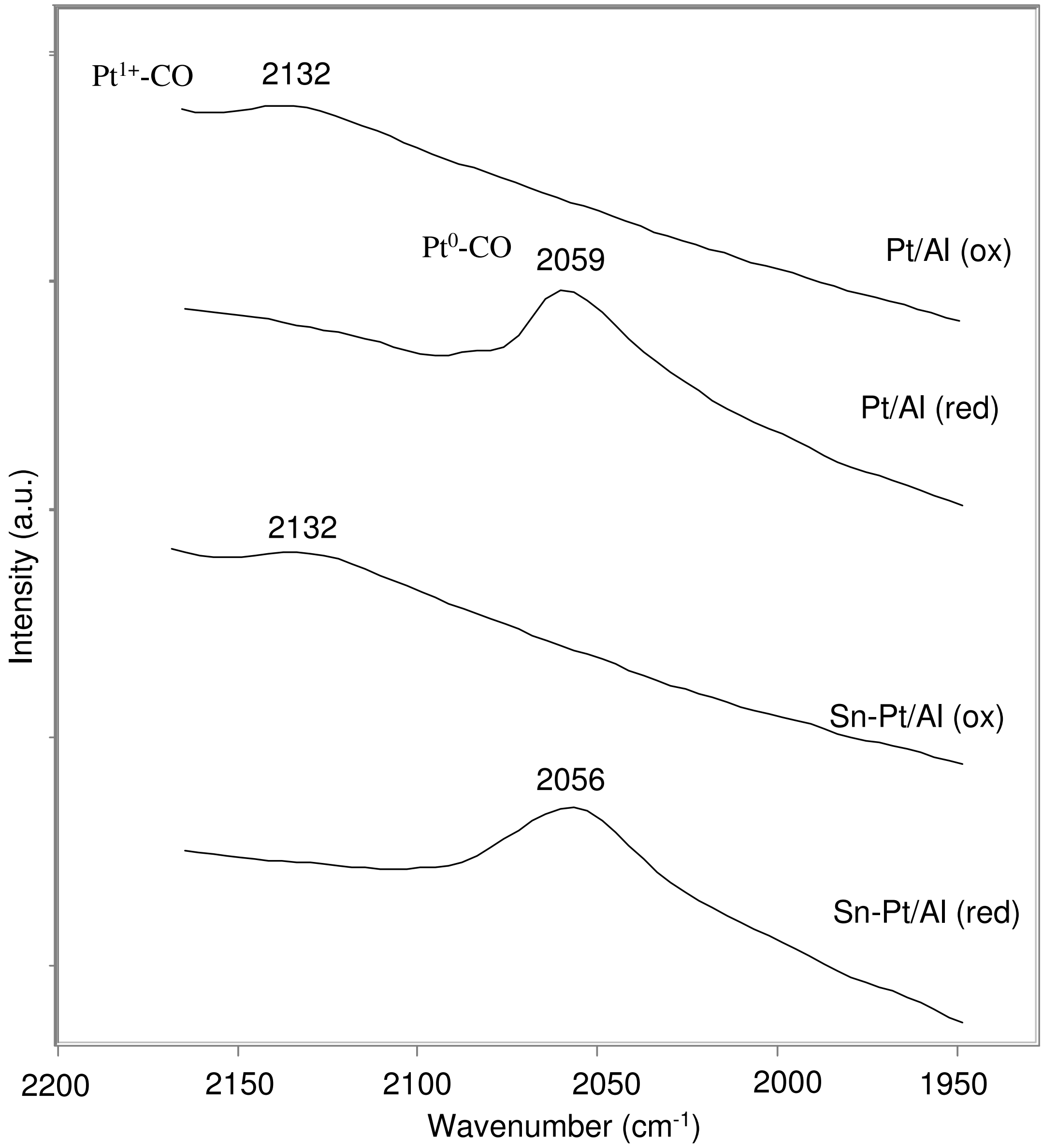


Fig.13. FTIR spectra of CO adsorption at RT on platinum sites on Pt/Al and Sn-Pt/Al pretreated in oxygen (ox) or in hydrogen (red)

The reasons of reduction of platinum oxide, Pt(II or/and IV), to low oxidation state, Pt(I), after pretreatment in oxygen can be the followings: (i) presence of reducing gas CO; (ii) occurrence of electron flow from Al_2O_3 (week n-type semiconductor) or from SnO_2 (strong n-type semiconductor) to platinum oxide (p-type semiconductor).

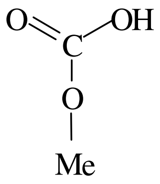
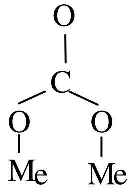
The formation of IR band at around 2059 cm^{-1} was detected after reduction of Pt/Al, Sn-Pt/Al samples at 473 K. This band characterizes linear CO adsorption on platinum particles (Pt^0-CO) (Fig.13) that have poor crystalline structure and hence well dispersed on support (Blyholder, 1964), (Anderson and Rochester, 1991) which is in agreement with XPS and XRD data.

Bridge bonded CO on platinum ($Pt^{0}{}_{2}CO$) which would be characterized by IR band in region 1780-1860 cm^{-1} was not detected (Barth et al., 1989), (Sullivan et al., 1992).

The intensities of 2132 cm^{-1} band for oxidized samples and of 2059 cm^{-1} band for reduced samples increase with the increasing the dehydroxylation temperature. This is due to increase of the number of Pt^{n+} sites (oxidized samples) and consequentially to increasing number of Pt^{0} sites (reduced samples) on elevating the dehydroxylation temperature (in accordance with the pretreatment procedure applied section 2.2. p.24).

3.2.4. Carbon Monoxide Adsorption on Surface Oxygen Containing Species

CO was adsorbed on surface oxygen species followed by formation of bicarbonate and carbonate. They have characteristic bands in wavenumber range 1200-1800 cm^{-1}(Thornton and Harrison, 1975), (Turek et al., 1992), (Shen et al., 1994):

Bicarbonate group: 1227-1235 cm^{-1}- δ(COH) 1480-1490 cm^{-1}- $\nu_1(CO_3H)$ 1640-1656 cm^{-1} -$\nu_4(CO_3H)$  	Bridging carbonate group: 1780-1792 cm^{-1} -ν(C=O) 

Carbonate formation on the oxidized alumina Vega support (having mainly boehmite and bayerite phases before calcinations) was not observed presumably due to the higher degree of hydroxylation of the surface than for supported samples, having less hydrated γ-Al_2O_3 crystalline structure (Fig.11).

Depositing of tin oxide and platinum oxide increases the extent of formation of carbonate and bicarbonate species on the surface: the presence of these compounds increases the activity of the catalyst for CO oxidation to CO_2 (Harrison and Guest, 1989), (Amalric-Popescu and Bozon-Verduraz, 2001).

Carbonate and bicarbonate bands were observed after the pretreatment of samples in oxygen at $\geq$ 573 K.

The pretreatment in hydrogen suppressed the formation of carbonate groups on the surface (Fig.14) since hydrogen has been adsorbed on active oxygen species.

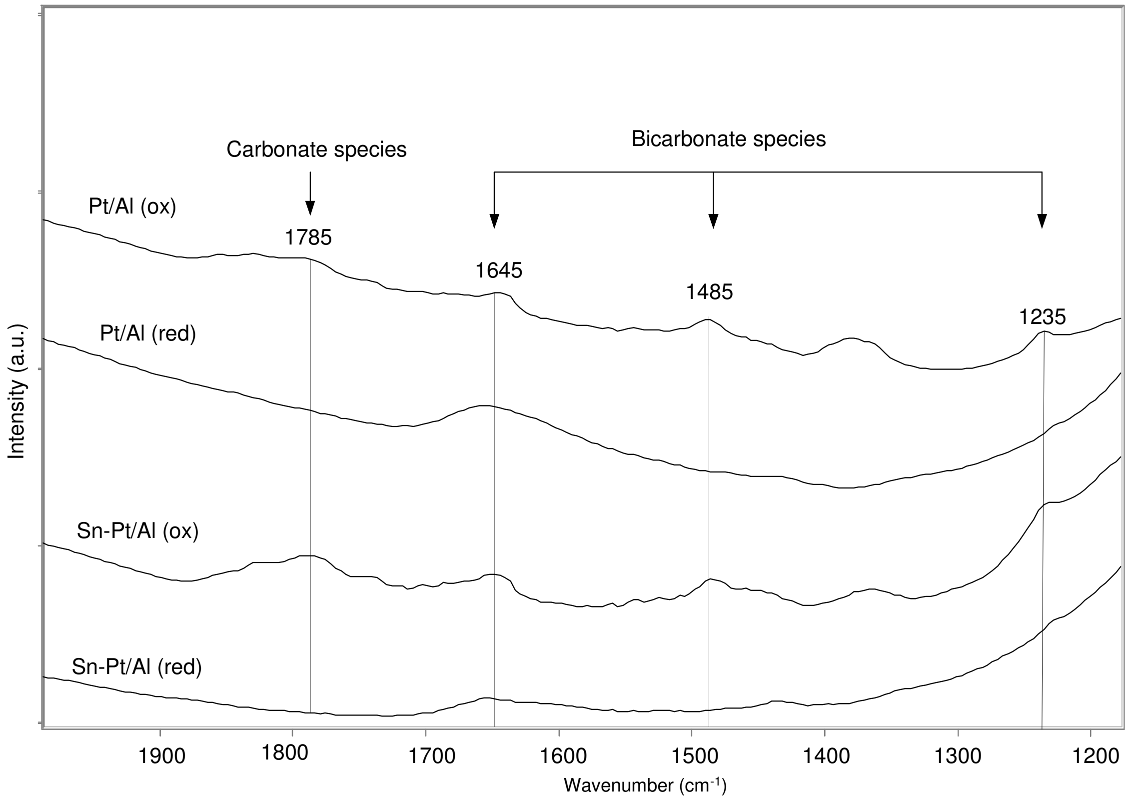


Fig. 14. FTIR spectra of CO adsorption at RT on oxygen and hydroxyl species of Pt/Al and Sn-Pt/Al samples pretreated in oxygen (ox) or in hydrogen (red)

3.2.5. Pyridine (Py) Adsorption

Lewis (coordinatively unsaturated metal atoms) and Brönsted (proton donor OH groups) acid sites on solid surfaces influence the sorption properties of samples and hence their utilization in catalysis. FTIR spectroscopy of adsorbed base molecules, such as NH_3, pyridine, CH_3CN, NO or CO, has been well evaluated as a powerful surface analytical technique for characterization of nature, strength and relative concentration of acid sites (Kustov, 1997). The principle of the IR method is the detection of surface active sites via determination of changes of characteristic IR absorption features (frequency and intensity) of probe molecules adsorbed thereon and of associated functional groups (e.g. OH groups) of the surface (Blyholder, 1964), (Zaki et al., 2001), (Ryczkowski, 2001), (Skoog and Leary, 1992).

In addition to investigation of acidic properties of catalysts Py probe molecule was applied. FTIR measurements of Py adsorption allows to determine the presence of both Lewis cus (coordinatively unsaturated sites) and Brönsted (proton donor) acid sites on the catalyst surface as well as to better understand the mechanism of cyclopropane isomerisation (section 4.3.3.) (Segawa and Hall, 1982), (Ryczkowski, 2001).

Pyridine has been preferred as a FTIR probe molecule on metal oxide surfaces at room temperature since it is (i) more selective and stable than NH_3; (ii) much more strongly adsorbed than CO and CH_3CN; (iii) relatively more sensitive to the strength of Lewis acid sites than NO (Zaki et al., 2001); and (iv) its IR band intensities are higher then that of NH_3.

The chemisorption of Py on Lewis (LPy) sites results in bands at about 1446, 1490 and 1613 cm^{-1} for all samples after different pretreatments (O_2 at 773 K and H_2 at 823 K) (Fig. 15.a and 15.b).

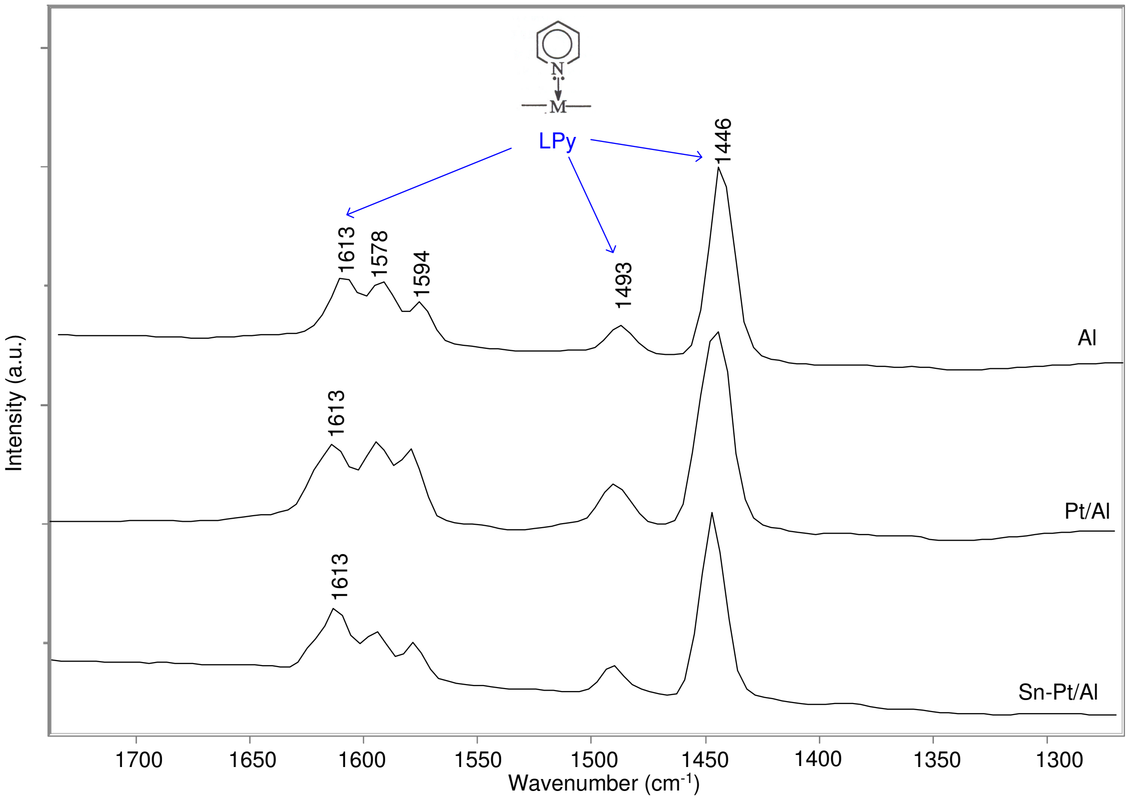


Fig. 15.a. FTIR spectra of Py adsorption at RT after pretreatment of samples in O_2 at 773K

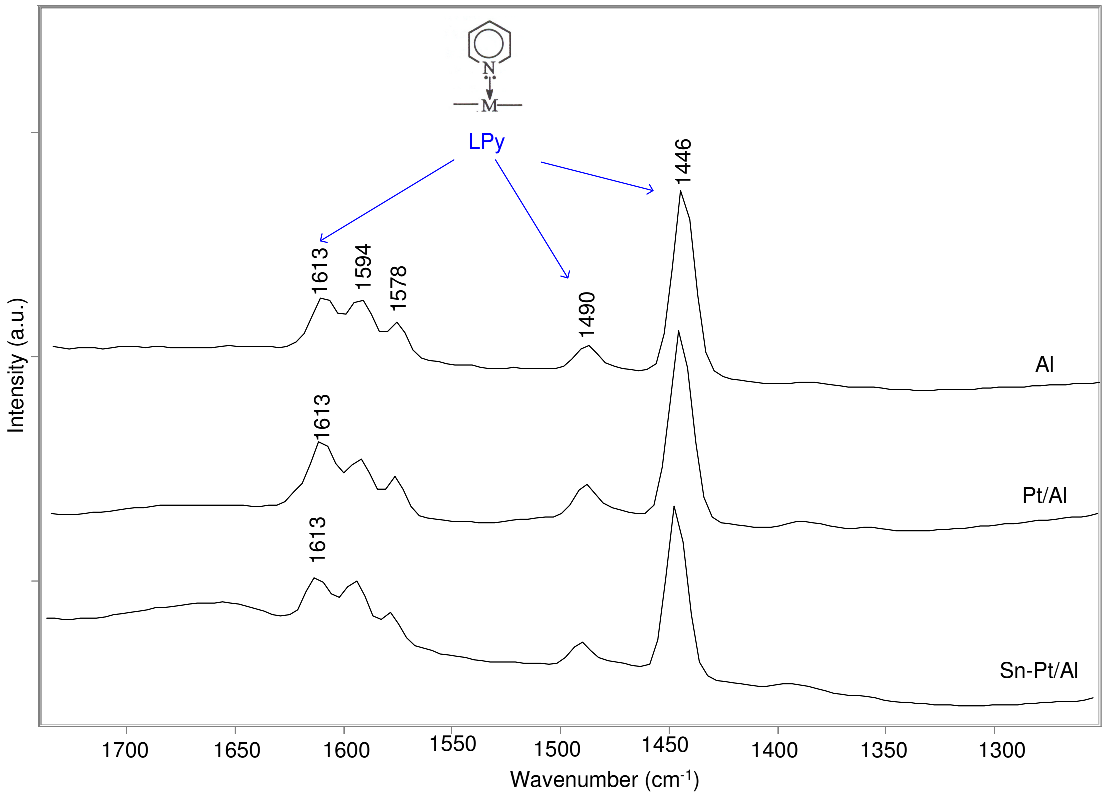


Fig.15.b. FTIR spectra of Py adsorption at RT after pretreatment of samples in O_2 at 773K followed by pretreatment in H_2 at 823 K

Adsorption bands at 1540 cm^{-1} assigned to Brönsted acid sites were not observed in spectra of any sample either after hydrogen or oxygen pretreatment. At the same time acidic hydroxyl group of alumina were well resolved (indirect indication of protonic acidity) (Table 5, Fig.10). This phenomena can be explain that before Py adsorption samples were treated at higher temperature (773 K in O_2) which drastically decreases the population of hydroxyl group. As sequences the high extent of dehydroxylation of the surface decreases Brönsted acidity (Kirszensztejn et al., 1993).

3.3. Microcalorimetry

As it has already been shown in Table 2 that BET surface areas of investigated samples are highly different in values and may significantly influence the catalytic properties The higher the surface area the better the interaction between reagents and catalysts can occur due to better dispersion of active sites. For more reliable comparison of acidic character of samples, adsorption heats, were related either to micromole per gram of catalyst (µmol/g) or micromole per unit surface area of catalyst (µmol/m^2) (Table 6).

3.3.1. Total Acidity

Microcalorimetric data in Table 6 display the amount of ammonia adsorbed per gram or per unit surface area. Ammonia has a strong base character (p*K*a of ammonia = 9.25) and therefore can interact with week, medium and stronger acidic sites (Guimon et al., 2001). The V_t columns in Table 6 show the total amount of gas adsorbed under pressure of 27 Pa and it corresponds to the total number of acidic sites (combining acid sites of support and supported compounds) present on the surface (Gergely et al., 1999). The V_{read} represents the physisorbed amount of gas determined under equilibrium pressures of 27 Pa by readsorption after pumping. Number of the strongest sites corresponding to the irreversibly adsorbed gas amount (V_{irr}) calculated by subtracting the secondary (V_{read}) isotherm from the primary (V_t) one. The integral heat, Q_{int}, shows the heat evolved during adsorption of total amount of gas, V_t, at pressure of 27 Pa and it corresponds to the average strength of acidic sites participating in adsorption (Auroux, 1997). For more detail information see experimental section 2.2 p.32.

Fig. 16. displays the differential heats of NH_3 adsorption on investigated oxides. The profiles, differential heats *vs* uptake of the gas probe, are multi-indicative; they give the data concerning the amount, strength, and distribution of the active sites. Besides, the values of initial heats of adsorption characterize the strongest sites (195-140 kJ/mol for studied samples) active in adsorption process.

Table 6. Calorimetric data for NH_3 adsorption at 423 K

Sample	S_{BET} m^2/g	NH_3 amount adsorbed µmol/**g**			Q_{int} J/g	NH_3 amount adsorbed µmol/**m^2**			Q_{int} J/m^2
		V_t	V_{read}	V_{ir}		V_t	V_{read}	V_{ir}	
Al (Deg)	110	188.24	83.31	104.93	22.46	1.71	0.76	0.95	0.20
Sn/Al(Deg)	108	216.47	93.34	123.13	25.65	2.00	0.86	1.14	0.24
Al	363	325.59	162.98	162.61	36.96	0.90	0.45	0.45	0.10
Sn/Al	259	375.30	174.63	200.67	44.21	1.45	0.67	0.78	0.17
Pt/Al	210	331.80	n/a	n/a	37.80	1.58	n/a	n/a	0.18
Sn-Pt/Al	234	260.83	108.02	152.79	29.31	1.11	0.46	0.65	0.13

The deposition of SnO_2 and platinum alone enhances the number of total acid sites (combining acid sites of support Al^{3+} and supported compound Sn^{4+} or Pt^{n+}, where $n+ \leq 4$) and their strength and this is valid for both Sn/Al variants, Table 6.

The simultaneous presence of platinum and tin oxide on alumina surface (S_{BET} =363 m^2/g) makes strength of strongest acidic sites, in amount of ~0.28 µmol/m^2, more uniform on the support and it results in decrease of initial differential heat from 195 (for Al and Sn/Al) to 150 kJ/mol (for Sn-Pt/Al), (Fig.16). Sn-Pt/Al exhibits higher differential heats than for Al and lower than for Sn/Al for ammonia adsorption in higher gas coverage region (more than 0.28 µmol/m^2).

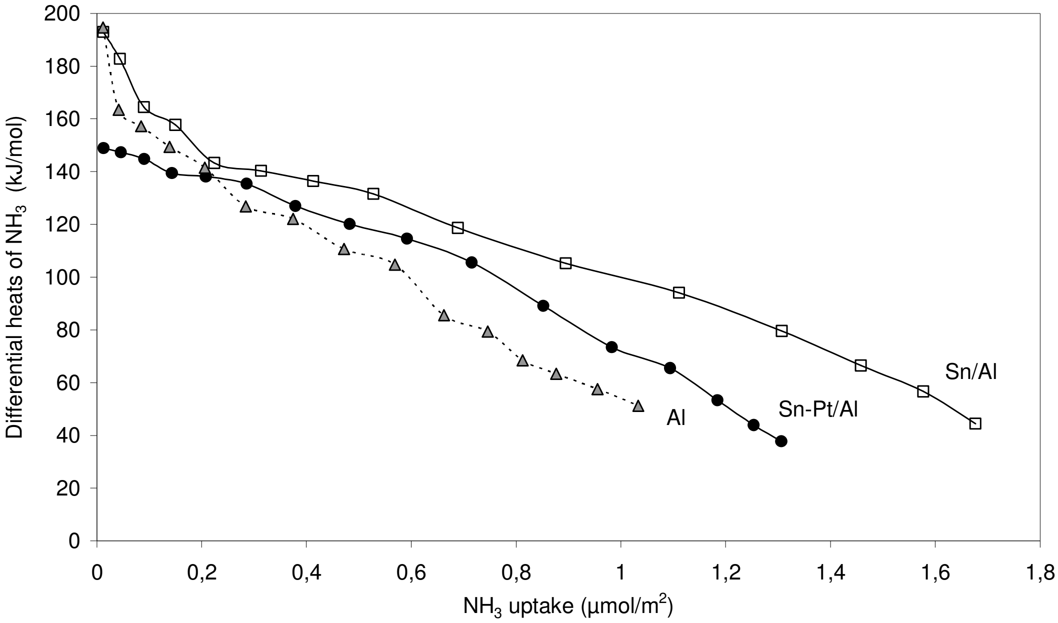


Fig.16. Differential heats of NH_3 adsorption at 423 K versus coverage

3.3.2. Dispersion of Platinum

The configuration and strength of the carbon monoxide chemisorption on a metal surface is expected to depend on the nature of metallic (metal ion) adsorbent and also on its surface structure. To obtain information on the heterogeneity of the surface very small doses of gas at constant temperature are introduced to measure the adsorption heat (Q_{dif}) and as a function of the coverage the adsorbate amount. On a heterogeneous surface, first the strongest sites are covered, because the adsorption proceed fastest on them. Thus, as the coverage increases, weaker sites will be covered so that the heat of adsorption continuously decreases. The uptake at unimolecular coverage is reached when the heat evolved falls in the range of physisorption (P≅ 67 Pa) (Guerrero-Ruiz et al., 2002), (Dragoi et al., 2004). The heat of adsorption of a basic molecule on an acid site is claimed to be characteristic of the strength of the site. During chemisorption evolved heat can be in the range between 40-800 kJ/mol and for physorption it is significantly lower, up to 20 kJ/mol (Szabo and Kallo, 1976).

Table 7. summarizes the results obtained from microcalorimetric CO adsorption at RT on samples preatreated in oxygen by giving the total number of active sites capable to absorb carbon monoxide, V_t (in µmol CO per gram of sample), at the given pressure of 27 Pa; the number of stronger sites, V_{irr}, corresponding to the irreversibly chemisorbed gas amount, calculated by subtracting the secondary isotherms (V_{read}) from the primary ones (V_t); the integral heat, $Q_{int,}$ was measured at 27 Pa.

Table 7. Microcalorimetric data for CO adsorption at 303 K

Sample	S_{BET} m^2/g	V_t , µmol/g	V_{read}, µmol/g	V_{irr}, µmol/g	Q_{int} J/g
Sn/Al	259	0.60	0.56	0.04	0.01
Pt/Al	210	3.41	1.99	1.42	0.11
Sn-Pt/Al	234	5.90	1.19	4.71	0.53

Fig.17. of microcalorimetric profiles represent the differential heats of CO adsorption as a function of surface coverage. CO was physically adsorbed on Sn/Al (V_{irr} is close to zero and maximum value of Q_{dif} ≅ 20 kJ/mol) and carbon monoxide uptake showed a very low population (V_t) of absorption sites on Sn/Al sample (Fig.17, Table 7). In this case adsorption of CO on $Sn^{4+,2+}$ is considered as negligible since absorbed CO-$Sn^{4+,2+}$ species were not detected at room temperature by FTIR and CO adsorption. Adsorbed amount and evolved heat during adsorption of carbon monoxide gas probe molecule significantly increases in the presence of platinum oxide and it is even higher for Sn-Pt/Al sample (Table 7). In addition to mentioned above taking in to consideration of differential heat of CO adsorption (Fig.17) can be concluded that CO chemisorption at 303 K occurs with high extent on platinum ionic sites (Q_{dif} ≅142-64 kJ/mol) and CO physisorption occurs on alumina and tin oxide sites (Q_{dif} ≅ 20 kJ/mol)

in these conditions. Hence the obtained value of chemisorbed volume of CO can be used for determining the platinum ion dispersion on the surface.

The amount of carbon monoxide used for calculation of metal ion dispersion is the value of CO chemisorbed on the platinum sites having strongest character among of the active sites on surface. The chemisorption on those sites for Pt/Al and Sn-Pt/Al samples resulting differential heat values 64-59 kJ/mol and 142-60 kJ/mol respectively (Fig.17).

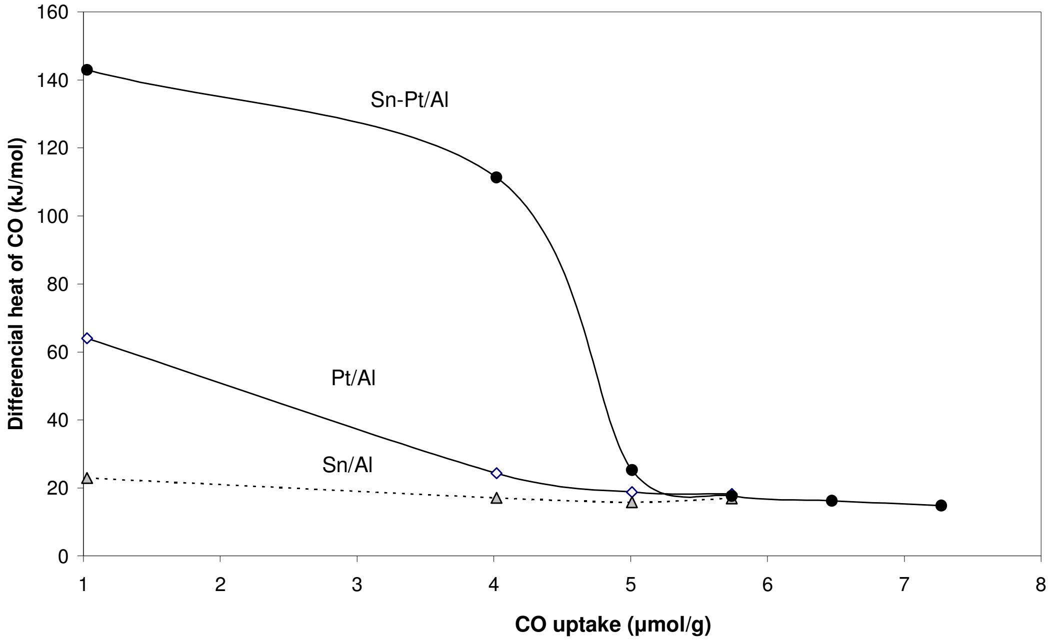


Fig. 17. Differential heat of CO adsorption at RT versus coverage

The Pt dispersion was calculated from the chemisorbed amount of CO using stoihiometric relation of one chemisorbed carbon monoxide molecule to one platinum surface atom, Pt^{n+}:CO 1:1 since FTIR spectra showed adsorption of one carbon monoxide molecule on one platinum ion, Pt^{1+}-CO, for both Pt/Al and Sn-Pt/Al catalysts (Fig.13).

The comparison between the weight percent of platinum in the bulk obtained by ICP and on the surface of catalysts determined by microcalorimetric CO chemisorption is resented in Table 8.

Table 8. Content of platinum in the bulk (ICP) and on the surface (microcalorimetric measurement) of the catalysts

Sample	BET m^2/g	ICP (bulk)		Microcalorimetric measurements (surface)	
		Pt, % (w/w)	Pt, µmol/g	$V_{irr,}$ µmol/g	$Pt_{dispersion,}$ %
Pt/Al	210	0.28	14.36	1.42	9.89
Sn-Pt/Al	234	0.28	14.36	4.71	32.80

The equation (7), which was used for estimation of percent of platinum dispersion on the surface (Table 8), are presented below and calculation was done as an example for Pt/Al sample.

$$Pt_{dispersion\,\%} = \frac{V_{irr\,CO}\,(\mu mol) * 100\%}{Pt_{bulk}\,(\mu mol)} = \frac{1.42 * 100\%}{14.36} = 9.89\% \qquad (7)$$

Since the amount of chemisorbed CO on strongest sites was higher for Sn-Pt/Al (V = 4.71 µmol/g) in comparison with Pt/Al (V=1.42 µmol/g) with the same deposition of the Pt during preparation procedure it is suggested that a Sn-Pt/Al catalyst has a higher amount of platinum ions on the surface (supposing that tin and alumina compounds are only participate in physisorption of CO). A higher dispersion of Pt in Sn-Pt/Al probably is the result of the dilution of platinum particles into smaller ensembles in presence of tin (Spivey and Roberts, 2004).

3.4. Temperature Programmed Reduction

TPR investigation was focused on reduction ability of active components, mostly of platinum and tin oxide. Pt or SnO_2 can completely be reduced at lower temperatures up to 753 K or up to 1073 K (Lieske and Völter, 1984), respectively then Al_2O_3 being stable up to 1473 K (Rosynek, 1972), (Linsen, 1970).

Fig.18 shows the hydrogen consumption as a function of temperature (293-1073 K) for the tin and/or platinum containing samples as well as for pure tin oxide and alumina support. As it can be seen, SnO_2 bulk was relatively stable toward reduction with H_2 up to 673 K. The major reduction of bulk tin oxide occurred at 933 K and almost accomplished at 1073 K (Fig.18).

TPR profile of Sn/Al (Deg) showed a very small hydrogen consumption starts at 593 K and finishs at 813 K with formation of broad peak of low intensity centered at 703 K . Position of this peak is lower than peak position attributed to metallic tin at 933 K. Therefore the peak at 703 K can be assigned to the formation of tightly bonded Sn(II) to alumina support (Fig.18). The tin-support interaction between hinders reduction of SnO to metallic tin (Lieske and Völter, 1984), (Muller et al., 1979), (Serrano-Ruiz, 2006).

Pt/Al shows one peak (Fig.18) which is centered at 693 K and can be attributed to reduction of platinum oxide species to metallic platinum and / or to a reduction of oxychlor-platinum surface complex, $[PtO_xCl_y]$, to metallic platinum (Lieske et al., 1983), (Damyanova and Bueno, 2003).

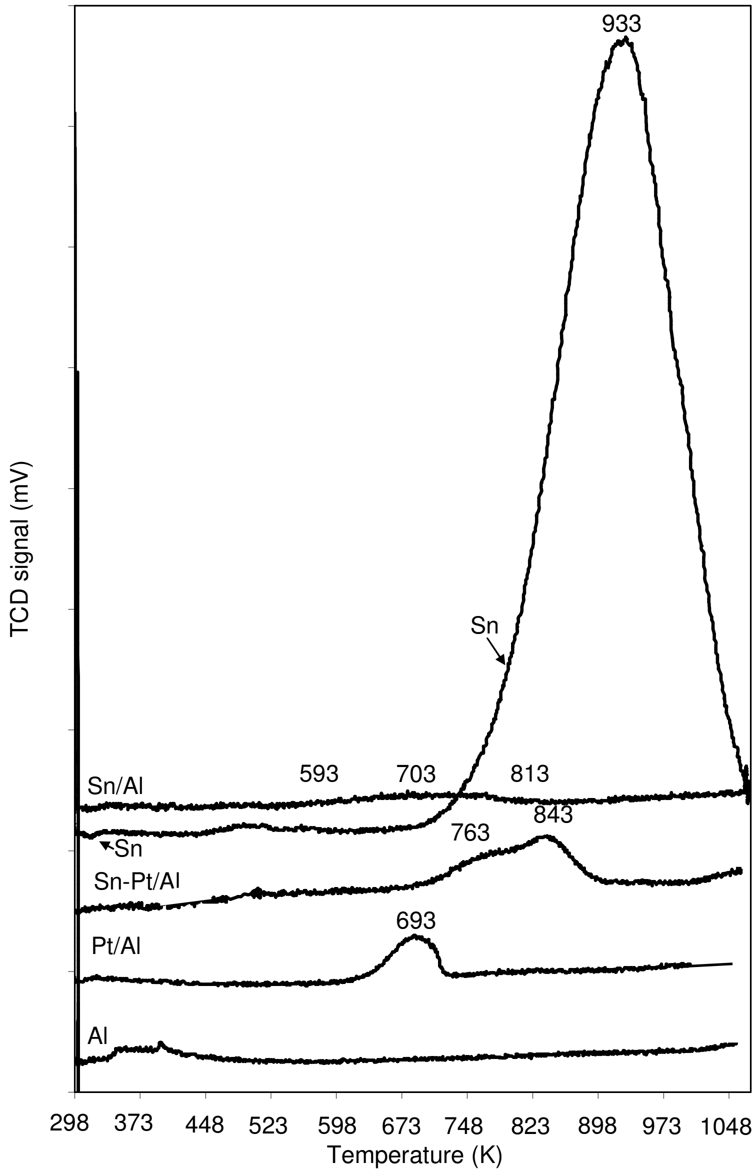


Fig. 18. TPR profiles of samples reduced in hydrogen atmosphere up to 1073 K

TPR curve of Sn-Pt/Al catalyst is shown in Fig.18. The hydrogen consumption peak appeared at 843 K with a shoulder at about 763 K. In relation with TPR profiles for bulk SnO_2 and Pt/Al the high temperature peak can be attributed to hydrogen consumption for tin dioxide reduction, while the shoulder could be assigned to a co-reduction of both platinum and SnO_2 with formation of Pt-Sn alloy (Lieske and Völter, 1984).

3.5. Electrical Conductivity (EC)

EC measurements provide useful information about surface dynamics in heterogeneous catalysis. In situ measuring electrical properties of oxide powder can be used for answering questions like: (i) the adsorption ability of the surface layer and the mobility of surface dipoles; (ii) the "quality" of the deposited active phase layer and its behavior in operating conditions; (iii) the reciprocal influence of the active phase and of the support and the important role of the electrical/dielectrical properties of the latter. In addition, the increase of the concentration of the free charge carriers/mobile lattice dipoles (Q) for a given electrical potential (V) on the catalytic surface is reflected by the increase of the electrical capacitance (C).

γ-Alumina support is basically an insulator at room temperature. However, in presence of humidity it behaves as a proton conductor (Stoica, et al., 2000). There exist several charged species (H^+, O^-, OH^-, OH^+, OH^0) on alumina surface (Knözinger and Ratnasamy, 1978) which theoretically might transport the electric charge. Data published in literature on "in situ" EC measurements (Caldararu et al., 2001), (Caldararu et al., 2003, ***207***), (Caldararu et al., 2003, ***211***) prove that between room temperature (RT) and 673 K the surface conductivity of γ-Al_2O_3 and of a boehmite / bayerite type precursor of alumina (support used for the studied catalysts) is dominated by protonic (H^+) conduction. Up to about 473 K proton movement occurs by ''vehicle'' mechanism, facilitated by the presence of molecular water species:

$$H_2O + H^+ \rightarrow H_3{}^+O$$

The loss / gain of mobile molecules of water (proton ''vehicle'' at low temperature) is accompanied by a sharp decrease/increase of conductivity, and thus, this method was proposed as a tool for investigation of the dynamics of physically adsorbed water on γ-Al_2O_3 surface. The decrease of conductivity accompanied by the loss of weakly adsorbed water is the result of two combined effects: (i) the progressive loss of proton ‘‘vehicles’’ and (ii) the loss of mobile dipoles able to reorient themselves in the AC electric field (Stoica et al.,1996), (Caldararu et al., 2003, ***207***). This mobilization /reorientation of dipoles corresponds to the increase of capacitance, while their progressive desorption is associated with the loss of vehicles, thus with the decrease of capacity.

Above 473 K as most of the physically adsorbed water species are removed, the mobile protons of acidic OH groups move most probably by hopping/jumping between neighbouring OH groups according to Grotthuss mechanism (Grotthuss, 1806), (Kreuer, 1996):

$$OH \cdot OH \cdot OH \rightarrow OH \overset{\curvearrowright}{\cdot} OH \overset{\curvearrowright}{\cdot} OH \rightarrow O^{-} \cdot HO \cdot HO \cdot H^{+}$$

The electrical properties of Pt/Al, Sn-Pt/Al samples are expected to be a combination of ionic, i.e. protonic (facilitated by the support) and electronic (facilitated by the tin oxide phase) conductivity (Stoica et al., 2000). It was noticed that the support controls the behavior of the supported catalyst in case when the loading of the active component on alumina does not form a uniform (or complete) monolayer coverage (Caldararu, INCO report, 2002).

The electrical conductivity and capacity measurements in inert atmosphere and in presence of c-C_3H_6, were carried out with pure alumina support and platinum containing samples, namely for Pt/Al and Sn-Pt/Al samples active in isomerization in order to obtain information on the reaction mechanism.

3.5.1. Electrical Conductivity at Room Temperature

The values of capacity C and electrical conductivity G obtained for Al, Pt/Al and Sn-Pt/Al samples at room temperature are presented in Table 9. The difference between samples is evidenced by measuring C and G at RT in all runs. The capacity and conductivity values for dry helium of cycle 1 (DHe-1) were much higher for the Al and Pt/Al and they decrease sharper than in the case of Sn-Pt/Al (Fig.19, 20). This is an indication on the much higher ability of the former samples to adsorb molecules from the ambient.

Table 9. Capacity (C) and electrical conductivity (G) at room temperature

Cycle	Sample	C_i-C_f (pF) [a]	G_i –G_f (nS) [a]
Cycle 1: Dry Helium	Pt/Al	95.03-66.71	293.10-314.9
(DHe-1)	Sn-Pt/Al	24.76-21.37	52.90-47.33
	Al	139.51-102.38	427.10-435.60
Cycle 2: Dry Helium	Pt/Al	5.10-5.11	0.10-0.10
(DHe-2)	Sn-Pt/Al	5.41-5.43	0.30-0.30
	Al	5.44-5.47	0.30-0.40
Cycle3: c-C_3H_6:He (1:20)	Pt/Al	5.09-6.48	0.10-4.30
(CHe)	Sn-Pt/Al	5.41-5.86	0.30-2.90
	Al	5.42-5.78	0.30-1.80

[a] -C_i (G_i) initial capacity (electrical conductivity) and C_f (G_f) final capacity (electrical conductivity) after 30 min of flushing in the corresponding gas;

Higher C and G values were kept for Al sample in DHe-2 as well. On the other side, the measured values of capacitance C and electrical conductivity G in dry helium of cycle 2 (DHe-2) for Sn-Pt/Al sample were higher than those obtained for Pt/Al sample. C and G values for all samples were rather constant in time in DHe-2 cycle.

The increases of C at RT in third cycle under contacting with cyclopropane : helium mixture with ration 1:20 (CHe) are accompanied by identical increases of G for all samples. The adsorption ability was higher for Pt/Al during CHe cycle at temperature close to RT and was decreasing in the following order: Pt/Al > Sn-Pt/Al > Al. It indicates that the interaction with / adsorption of cyclopropane was smaller for pure γ-alumina than for the alumina supported samples.

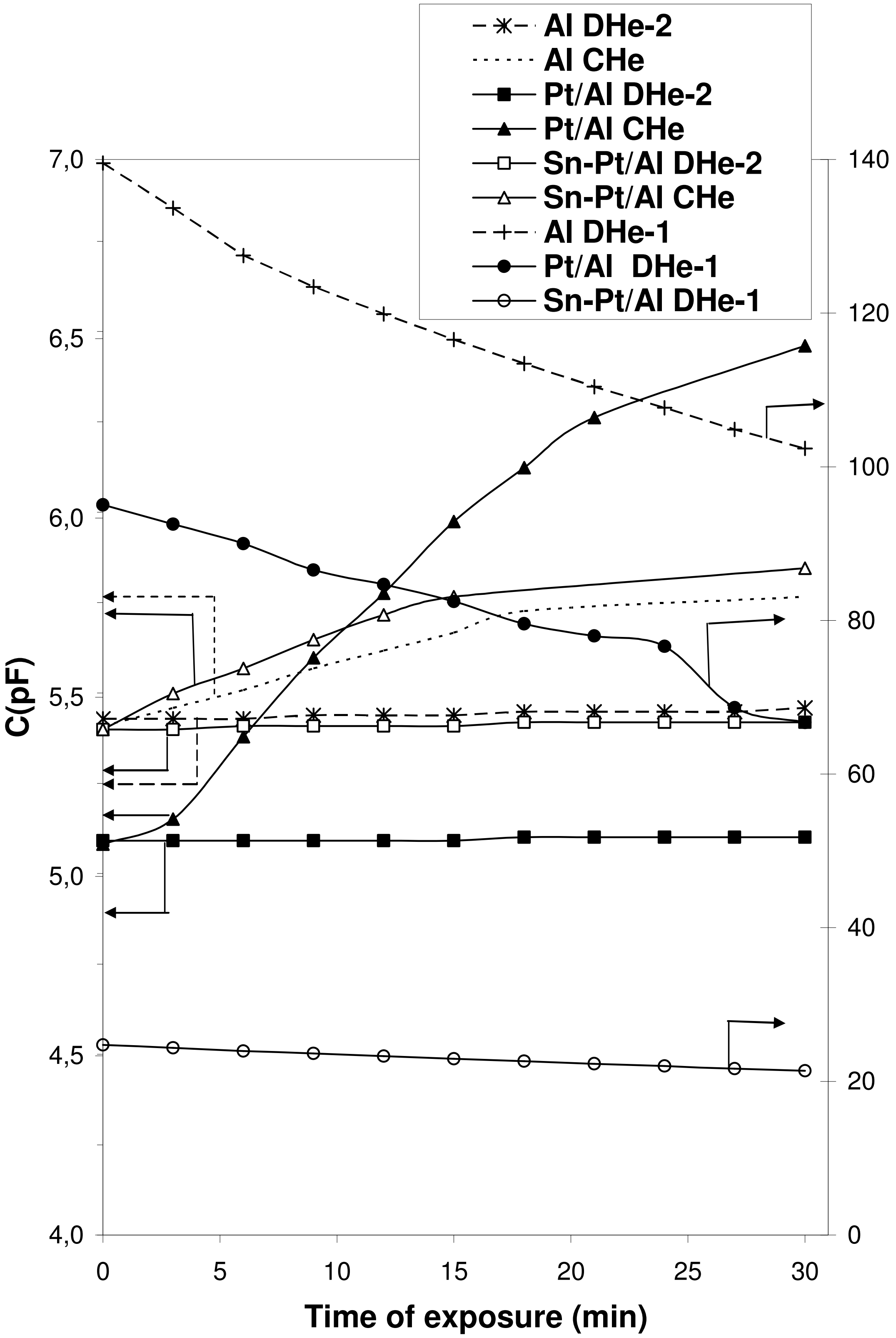


Fig. 19. Comparison of capacity (C) variation at room temperature in different atmospheres for Al, Pt/Al and Sn-Pt/Al samples

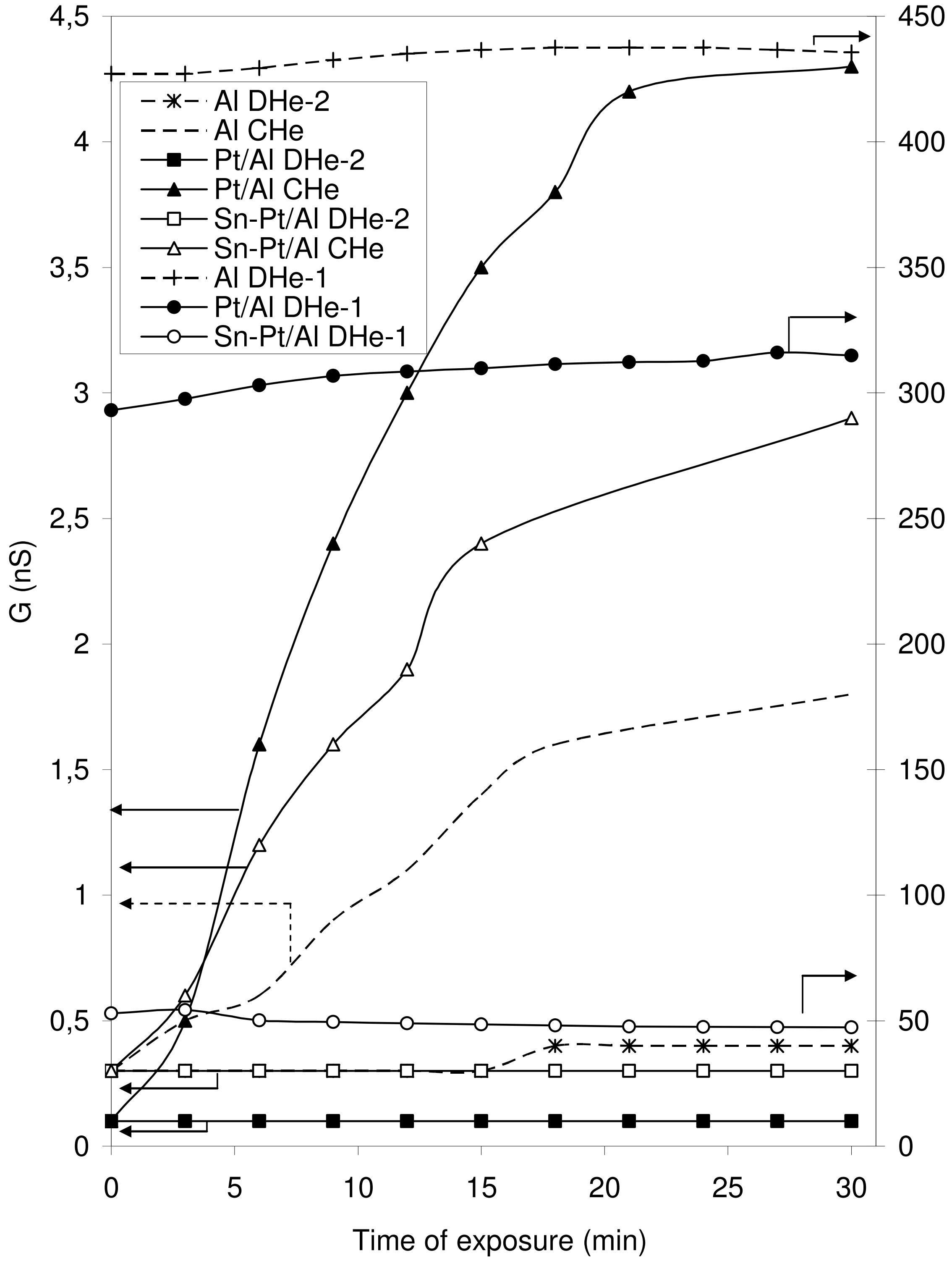


Fig. 20. Comparison of conductivity (G) variation at room temperature in different atmospheres for Al, Pt/Al and Sn-Pt/Al samples

3.5. 2. Low Temperature (LT) Region of Electrical Conductivity

The plot of conductivity, Ln (G) vs 1000/ T (K) , for Al, Pt/Al and Sn-Pt/Al samples in cycle 1: Dry Helium (*DHe-1*); cycle 2: Dry Helium (*DHe-2*); and cycle 3: c-C_3H_6:Dry Helium 1:20 (*CHe*) is shown on Fig.21.

The pattern of Al in DHe-1 cycle decreases down to 383 K then slightly increases up to 403 K followed by the stabilization of LnG values up to 623 K due to higher extent of hydroxylation of the pure alumina support. Patterns of Pt/Al, Sn-Pt/Al samples at the DHe-1 cycle have an U-shape: the decrease in the low temperature range (down to 458 K for Sn-Pt/Al and down to 483 K for Pt/Al respectively) is followed by the increase of lnG up to 623 K. As shown by the analysis of the effluent, the decrease of conductivity / capacity on heating in inert atmosphere is accompanied by the loss of physically adsorbed water. The weakly adsorbed water is a vehicle for the mobilization of proton, which generates the proton conductivity on the surface (Caldararu et al., 2001), (Caldararu et al., 2003, ***207***), (Caldararu et al., 2003, ***211***). This is in agreement with FTIR data on the physisorbed water and it was stable on the surface up to 473 K during the pretreatment in oxygen atmosphere. It was noted (Caldararu et al., 2001) that the differences in data published by the various authors about the range of the thermal stability of physically adsorbed water molecule on the γ-alumina surface (which varies from 373 - 473 K) are correlated with the initial water content, the flow rate of the flushing gas and on the rate of heating. The reason of increase of conductivity at ~ 400 K is discussed later in section 3.5.3.

It is obvious that the major loss of water occurs in the first cycle (DHe-1) and consequently the EC parameters are starting to be lower values at low temperature (see DHe-2 values in LT region in Fig.21). This clearly indicates an essentially lower of surface coverage of adsorbed water species (Baldwin et al., 1962). Similar behavior was observed for water-alumina system (Caldararu et al., 2001), (Caldararu et al., 2003, ***211***). The samples lose the characteristic U-shape of the plot in the second cycle in inert atmosphere. An increase of temperature results in proton movement by hopping between neighbor OH groups on the surface (Grotthus mechanism) requiring an activation energy which is expressed by a monotonous increase of lnG of the plot.

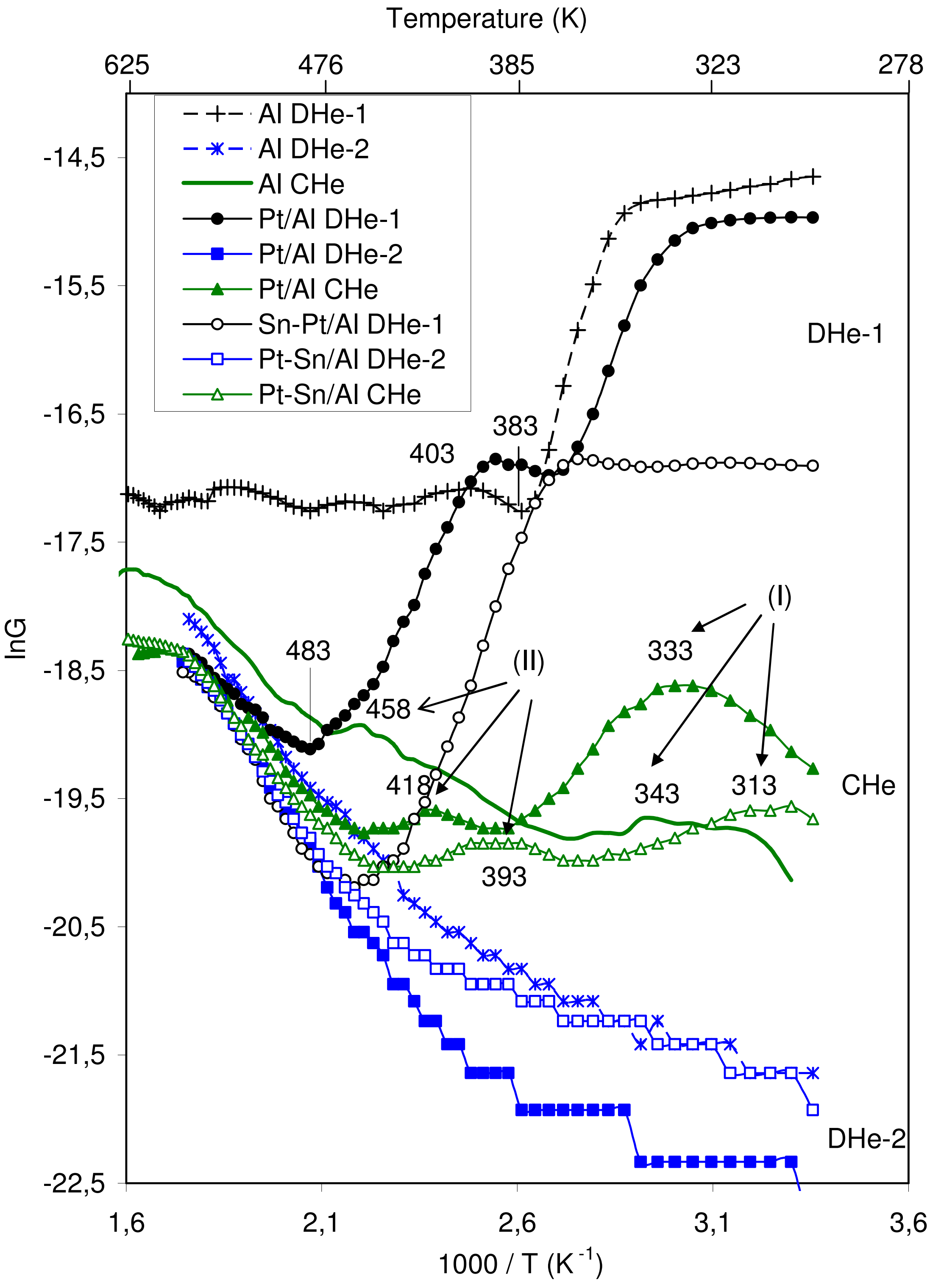
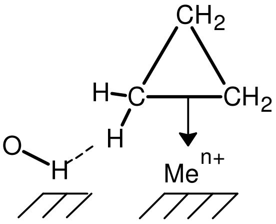


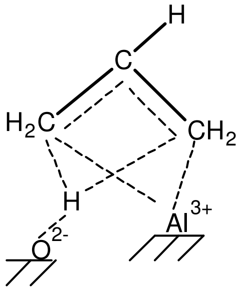
Fig. 21. Conductivity (G) as a function of temperature for Al, Pt/Al and Sn-Pt/Al samples

Adsorption of cyclopropane takes place at room temperature (sites (I) in Fig.21) and the evidence for this statement is represented by the increase of lnG values in the CT cycle in comparison with analogues values at RT in DHe-2 cycle (Fig.21). The simple cycloalkanes, like cyclopropane, often have the reactivity similar to that of the alkenes. Cyclopropane has acid dissociation constant (pKa) 46 of ion-pair acidity scale mesuared in dimethyl sylfoxide solvent and can be considered as basic molecule (for comparison: pKa of ethylene is 50; pKa of propylene 43) (Bordwell, 1988). The adsorption of c-C_3H_6 may proceed in a similar way as observed for propylene adsorption (Gordimova and Davydov,1979), (Caldararu et al., 2003, ***211***). Cyclopropane molecule is stabilized on two centers of active sites: on Me^{n+} (Al_{oct}^{3+} or Pt^{n+} or Sn^{4+}) cation by donating its electron pair and on basic hydroxyl site of the surface :



This Me^{n+}-OH surface of pair sites keeps the gas molecules on the surface up to 343 K on Al, up to 333 K on Pt/Al and up to 313 K on Sn-Pt/Al (Fig.21). The presence of Al^{3+} and Pt^{n+} and OH basic groups on the surface of the samples after the dehydroxylation treatment at about 573 K were confirmed by FTIR study (Table 5 and Fig.12,13) The bands belonging to tin cation sites were not resolved in our case but the existence of these sites was reported in literature (Amalric-Popescu et al., 2001), (Spivey and Roberts, 2004), (Harrison, 1987).

Cyclopropane was absorbed on second type of surface sites (II) in LT region and peak at 458 K for Al, at 418 K for Pt/Al and at 393 K for Sn-Pt/Al were resolved (Fig.21). These sites have a stronger adsorption ability and the interaction of c-C_3H_6 with them can be described in a similar way as for propylene adsorption on Al_{tet}^{3+}– O^{2-} pair (Caldararu et al., 2003, **211**), (Gordimova and Davidov, 1979):



where instead of Al^{3+} can be Pt^{n+} or Sn^{4+} active metal cations in the case of studied catalysts.

Should be mentioned that cyclopropane are adsorbed more strongly on alumina than on Pt/Al, Sn-Pt/Al samples therefore positions of adsorbed peaks in CHe cycle were shifted to lower temperature for supported samples (e.g. adsorption maximum of c-C_3H_6 on second type of surface sites occurs at about 458 K for Al, at 418 K for Pt/Al and at 393 K for Sn-Pt/Al). Therefore it can be concluded that combined platinum with tin decreases the strength of the acidic sites of surface in comparison with Al and Pt/Al. This effect has been noted by FTIR spectroscopic (Fig.12) and microcalorimetric (Table 6, Fig.16) studies as well.

3.5.3. High Temperature (HT) Region of Electrical Conductivity

The desorption from a third type of sites involved in cyclopropane adsorption is accompanied with increasing of LnG patterns in the high temperature range: HT > 473 K for Al, HT > 453 K for Pt/Al and HT > 448 K for Sn-Pt/Al (Fig.21) in parallel with the appearance of the isomerization product – propylene. Around this temperature the bulk proton movement is described by Grotthuss mechanism (Caldararu et al., 2001). It can be supposed that these mobile protons could be involved in adsorption of cyclopropane species on the catalytic surface with formation of $C_3H_7^+$ carbocation as an intermediate species during isomerization reaction.

The electrical conductivity data in DHe-1, DHe-2 and CHe cycles (except Al DHe-1; CHe cycles) start to match each other in the high temperature range (above 503 K) which is indicative for the reproducible surface behavior (Fig.21). It can be concluded that most of cyclopropane adsorbed species were removed above 503 K. Similar features were observed for γ-alumina during the interaction with propylene (Caldararu et al., 2003, ***211***) where the mobile species (water and propylene) were desorbed above 473 K.

During EC study in inert atmosphere was observed that the alumina support influences on electrical properties of supported components, namely the samples had conductivity values (0.3-10.5 nS) similar to support (0.4-13.8 nS): close to room temperature samples behavior as insulator and with increasing of temperature as semiconductor (Hagen, 1999).

3.6. Catalytic Activity

3.6.1. Propylene Oxidation in Flow Reactor

In primary study (not knowing the behaviour of the supported catalyst) samples ability was checked for propylene selective oxidation to acrolein using mixture C_3H_6 : air with ratio 1:10.

In this case was supposed that the oxygen consumption is much lower (than for total oxidation), as for each propylene molecule only one molecule of oxygen is theoretically used ($C_3H_6 + O_2 = C_3H_4O + H_2O$) and the extra oxygen keeps the coke formation at low level (the redox or so called Mars van Krevelan mechanism) (Krenzke and Keulks, 1980, ***64***), (Hagen, 1999). Theoretically the lattice oxygen acts as the main active oxygen species, and the gas oxygen is estimated to re-oxidize the reduced oxide phase. The experimental procedure of propylene oxidation is described in section 2.2. p.30.

The results obtained in catalytic test oxidation of propylene are presented in Table 10.

Table 10**.** Propylene oxidation at 673 K in C_3H_6-air mixture 1:10, contact time τ =1.3 s.

Sample	BET, m^2/g	Propylene conversion, %	Selectivity to CO_2, %	Selectivity to CO,%	Other carbon containing compounds, % [b]
Al	363	26.7	78.1	19.6	0.3
SnO_2	9	30.0	83.6	16.4	-
Sn/Al (A1) [a]	108	11.0	72.5	22.6	4.9
Pt/Al	210	61.3	78.6	0.01	21.39
Sn-Pt/Al	234	43.8	100.0	-	-

a- alumina support was γ-Al_2O_3 Degussa of low surface area 110 m^2/g
b- acrolein, acetone, acetaldehyde and oligomerization products

The deposition of the low surface area SnO_2 on γ-alumina produced a catalyst with higher surface area but lower oxidation activity than pure bulk SnO_2 (Table 10). Beside CO_2, CO and water the other products of selective oxidation (acrolein, acetone, acetaldehyde, and oligomerization products) were formed in very small amounts so precise selectivity for each product was not possible to determine.

Platinum containing samples were of highest activity in hydrocarbon conversion. At the same time Sn-Pt/Al sample showed the highest selectivity towards CO_2 formation under oxidation conditions. The propylene conversion was limited by the presence of oxygen amount in reactive mixture (C_3H_6:air ratio 1:10). This is indication on partial coke deposition which blocks some of the active site.

Thus, testing of higher active Pt/Al, Sn-Pt/Al samples and Al support (for comparison) was performed in mixture with higher content of air (propylene:air as 1:22). In this case activity of samples were checked for total oxidation where water and carbon dioxide were formed as main products (Table 11). The 1:22 ratio was chosen according the stoichiometry:

$$C_3H_6 + 4.5\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$$

$$1 + 4.8 \cdot 4.5\ \text{air} = 1:21.6 \cong 1:22$$

(20.94 % (v/v) of oxygen in air (Whitten et al., 1992))

Table 11. Propylene oxidation at 673 K in C_3H_6:air 1:22, τ =1.1 s

Sample	Propylene conversion, %	Selectivity to CO_2, %	Selectivity to CO, %	Other carbon containing compounds, % [a]
Al	24.2	96.4	1.3	2.3
Pt/Al	100	52.66	-	47.34
Sn-Pt/Al	94.30	99.90	0.01	-

a - acrolein, acetone, acetaldehyde and oligomerization products

The conversion over platinum containing samples during total oxidation propylene was much higher (95-100 %) than for selective oxidation (44-62%) over the same samples. Therefore could be concluded that platinum containing samples are applicable for total oxidation with high selectivity (99.9%) of Sn-Pt/Al for CO_2 formation.

3.6.2. Cyclopropane Isomerization

3.6.2.1. Catalyst Samples Pretreated in Oxygen

Cyclopropane isomerization was chosen as test reaction for catalyst samples pretreated in oxygen and hydrogen with the formation of propylene as a main product at 473 K and 523 K reaction temperatures (Fig. 22):

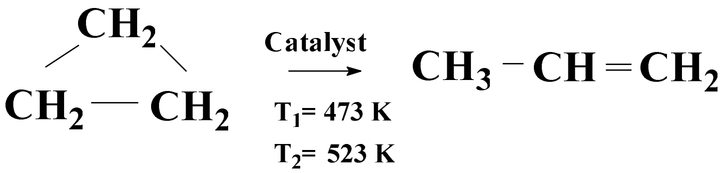
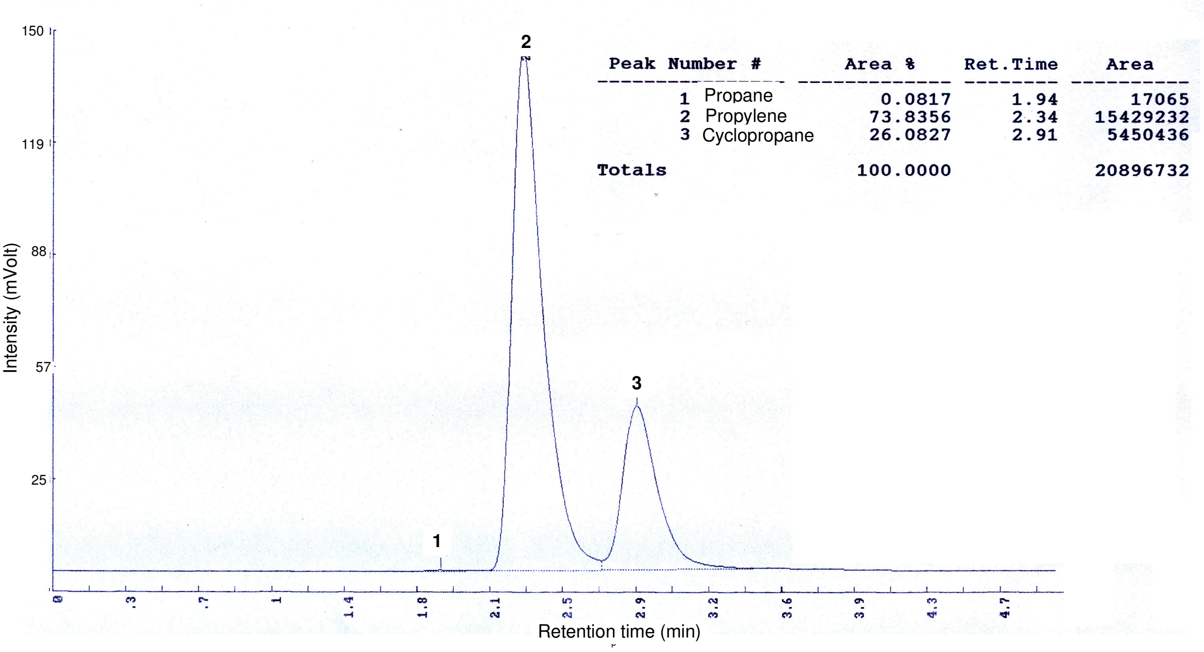


Fig. 22. Schematic representation of cyclopropane isomerization reaction

The experimental procedure of cyclopropane isomerization is described in section 2.2. p.30.

In absence of catalyst, isomerization does not proceed at 473 K. A very low (2 %) cyclopropane conversion to propylene was observed at higher temperature, at 523 K. The homogeneous gas phase isomerization of cyclopropane to propylene was characterized as a unimolecular reaction with an activation energy of about 14.11 kJ/mol and it was slow below ~ 698 K (Jacono and Hall, 1976), (Goldwasser, 1981).

Cyclopropane conversion to propylene was defined as the ratio of the amount of cyclopropane transformed and its amount introduced since product of cyclopropane isomerization determined by GC over Al and Sn/Al oxidized / reduced and over reduced Sn-Pt/Al samples was propylene only. Besides propylene a very small amount of by-product (max 0.3 %), with high probability of propane, was detected over Pt/Al oxidized and reduced and over Sn-Pt/Al oxidized samples. The presence of C_1 or C_2 in a product mixture was not observed. An example of gas probe chromatogram of isomerization reaction products is presented for Sn-Pt/Al sample in Fig.23. This GC analysis was performed after 2 h of cyclopropane isomerization reaction at 473 K.



```
Peak Number #          Area %    Ret.Time      Area
----------------- -------------- -------- ----------
      1 Propane          0.0817     1.94      17065
      2 Propylene       73.8356     2.34   15429232
      3 Cyclopropane    26.0827     2.91    5450436

Totals                 100.0000             20896732
```

Fig.23. Gas probe chromatogram of cyclopropane isomerization reaction products for Sn-Pt/Al catalyst pretreated in oxygen (T_{reaction} = 473 K, reaction time was 2 h or 120 min)

Addition of platinum to the support increases the extension of cyclopropane conversion to propylene, while adding tin oxide to the support diminishes conversion with respect to the pure support (Al sample) (Fig.24). The simultaneous presence of Pt and Sn results a little increase of the reaction rate in comparison with Pt/Al and significant increase of the catalytic activity in comparison with Sn/Al. The conversion of cyclopropane to propylene after 2 h of reaction duration was 98 % over Sn-Pt/Al; 96 % over Pt/Al; 68 % over Al; 6 % over Sn/Al at 523 K.

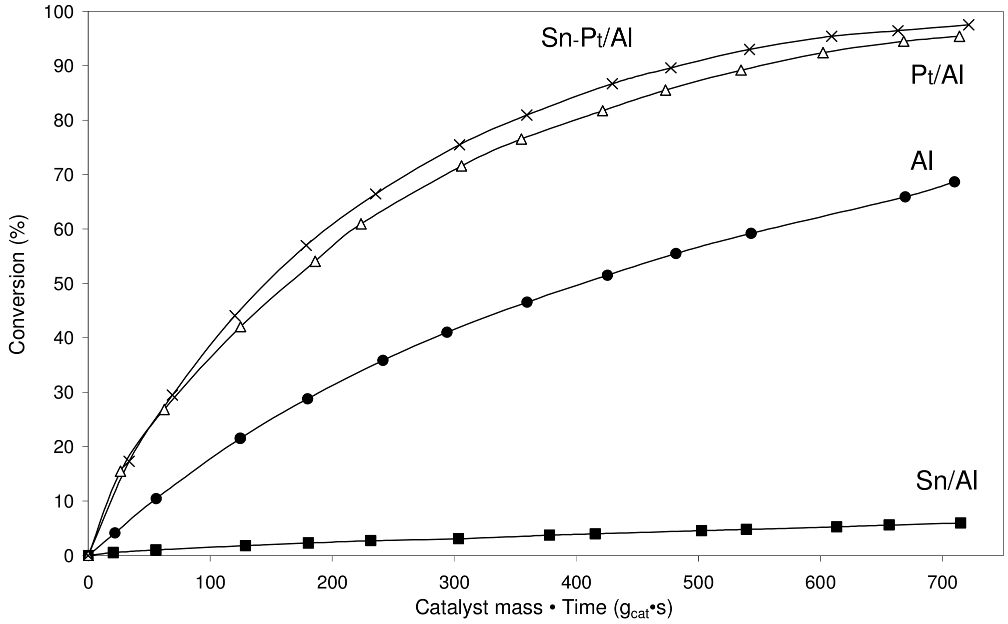


Fig. 24. Conversion at 523 K of c-C_3H_6 over samples pretreated in O_2 (reaction time was 2 h or 7200 s, mass of sample was ~0.1g)

3.6.2.2. Catalyst Samples Pretreated in Hydrogen

The changes of activity were studied after pretreatment in hydrogen (Fig.25). The conversion of cyclopropane to propylene increases for Pt/Al, Al and decreases for Sn/Al, Sn-Pt/Al samples in comparison with the oxidized form of catalysts.

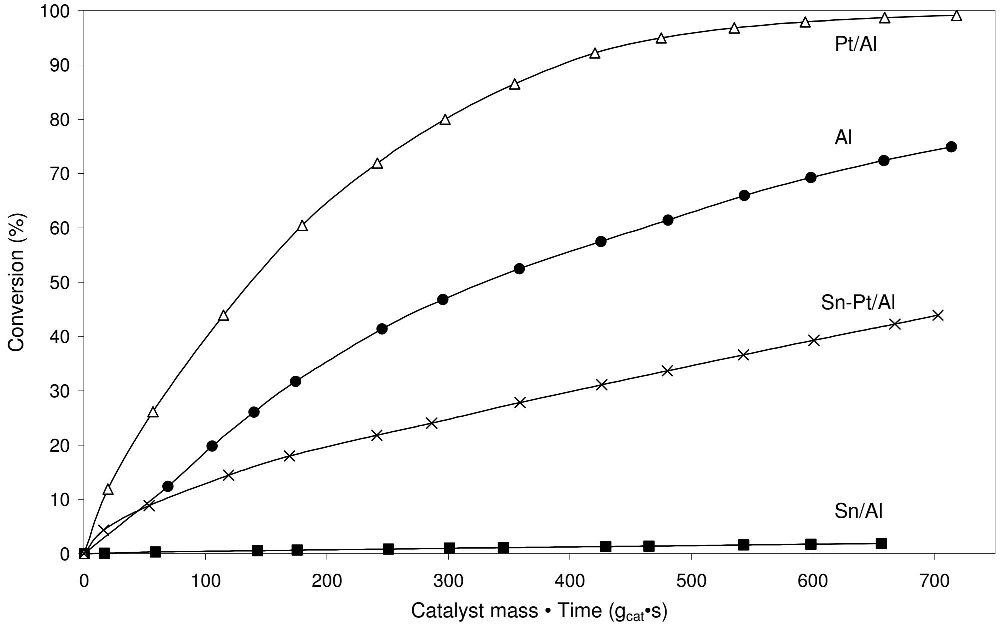


Fig. 25. Conversion at 523 K of c-C_3H_6 over sample pretreated in H_2 (reaction time was 2 h or 7200 s, mass of sample was ~0.1g)

4. DISCUSSION

4.1. Acidic Properties

This study was focused on investigation of the acidic character of catalysts since alumina and tin oxide supported on alumina are known to exhibit acidic properties.

Lewis acid sites are formed on catalytic surface after pretreatment at ≥573 K. FTIR results of carbon monoxide adsorption showed presence of two types of Lewis acid sites on alumina support: Al^{3+}_{oct} and Al^{3+}_{tet} (having stronger acidic character than octahedral coordinated alumina) (Gordimova and Davidov, 1979). The population of these acid sites increases with increasing dehydroxylation temperature. Deposition of tin semiconductor oxide diminishes the population of stronger alumina acid sites (Al^{3+}_{tet}). Addition of small amount of platinum increases the number of stronger sites of Al_2O_3. The presence of both Sn and Pt metal oxides influences the acidity of the support making the strength of acidic sites more uniform (Fig.12).

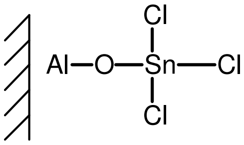
At the same time microcalorimetric study demonstrated that the deposition of SnO_2 and platinum oxide alone enhances the number of the total acid sites (combining acid sites of support Al^{3+} and supported compounds Sn^{4+} and/or Pt^{n+}) and their strength on catalytic surface. However, the simultaneous presence of platinum and tin oxide decreases the strength of stronger acid sites possibly due to the electron transfer from tin to platinum (Fig.16). Tin oxide, known as n-type semiconductor, can change the electronic density in the bulk, by transmitting electrons to the PtO_x-alumina phases and thus decreasing the acidic strength of some of the corresponding Lewis sites. This is in agreement with other published data (Roman-Martínez, 2000), (Sprivey and Roberts, 2004).

The presence of surface hydroxyl groups, $OH\text{-}(Al_{oct})_3$, having well-defined acidic character (Knözinger and Ratnasamy, 1978), was found on all samples after oxidizing and reduction pretreatments (Table 5, Fig.11) and can be considered as a proof of presence of Brönsted acidic sites on catalyst samples. One explanation why Brönsted acidic sites were not detected by Py adsorption at room temperature may be that in case of oxidized (773 K) / reduced (823 K) samples their surfaces are highly dehydroxylated and therefore mobilization of bulk/surface protons higher temperature than RT.

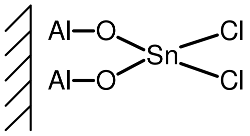
4.2. Reducibility

4.2.1. Influence of Chloride on Reduction of Tin and Platinum

Chloride, which is an essential component during preparation of industrial catalysts, was found to have a crucial influence on the catalytic properties (Liske et al., 1983), (Lietz et al., 1983). The Pt/Al or Sn/Al studied samples were prepared by impregnation of support with a solution of H_2PtCl_6 or mixing of support with $SnCl_2$ respectively. Literature data showed that using tin chloride salt for preparation of catalysts results in strongly bound ionic forms of tin on the alumina support such as (Margitfalvi et al., 1984):



(I)



(II)

Tin in forms (I) or (II) cannot be reduced to Sn^0 in hydrogen even at high temperature, (Lieske and Völter, 1984), (Muller et al., 1979), (Serrano-Ruiz, 2006). Similar effect was observed for Sn/Al (Deg) investigated sample: deposited tin oxide on alumina formed Sn(II)-alumina surface complex under reduction condition at around 703 K (Fig.18).

There is surface interaction between supported platinum and support in the chlorinated Pt/Al catalyst as well. It results in reduction of platinum species at higher temperature than that of chloride-free Pt/Al system where α-$[PtO_2]$ species usually is reduced around 373 K (Liske et al., 1983). In accordance with Lietz and co-authors' observation (Lietz et al., 1983) impregnation of Al_2O_3 with H_2PtCl_6 produced a surface complex, $[PtCl_6]^{2-}$. The saturation for $[PtCl_6]^{2-}$ on support can reach of 10^{14} sites/cm^2 being in the same order of magnitude as OH group density on alumina (Knözinger and Ratnasamy, 1978). The proposed surface interaction is an chloride anion replacement in $[PtCl_6]^2$ on OH groups of the alumina support, forming $[Pt(OH)_4Cl_2]^{2-}$. The OH ligands can be transformed into O^{2-} and water at 773 K temperature of calcination used and complex $[PtO_2Cl_2]^{2-}$ appeared. In this work the reduction of platinum containing surface complex starts at around 600 K and completely accomplished by 753 K with formation of metallic Pt (Fig.18).

4.2.2. Effect of Platinum on Reduction of Tin

A close contact between Pt and Sn elements in Sn-Pt/Al sample, where chloroplatinic acid was used as impregnation agent, can be achieved after calcination pretreatment at 773 K (Lieske and Völter, 1984). This could be a reason of attraction of several Sn atoms by Pt and as a sequence a higher degree of alloy formation under reduction atmosphere (section 3.1.) (Lieske and Völter, 1984). The alloy formation between noble metal and reducible tin oxide was detected at 763 K on surface of Sn-Pt/Al catalyst studied under reduction condition (Fig.18).

In addition microcalorimetric measurements indicated that platinum is better dispersed in Sn-Pt/Al than in Pt/Al, therefore adsorption of hydrogen theoretically should be at least 3 times higher than on the latter one (Table 8). Nevertheless, practically no increase of hydrogen consumption was observed for Sn-Pt/Al (Fig.18), however the reduction occurred at higher temperature than with Pt/Al (Fig.18). This can be attributed to the strong interaction between tin and platinum and reduction of all Pt together with part of tin forming Pt-Sn alloy particles at 763 K (Fig.18) (Lieske and Völter, 1984).

It has been shown (Verbeek and Sachtler, 1976), (Serrano-Ruiz, 2006), (Guerrero-Ruiz et al., 2002) that Pt-Sn alloy formation inhibits chemisorption of hydrogen (deuterium), carbon monoxide and ethene on platinum. An explanation of the hydrogen adsorption behavior of sintered platinum-tin particles was given by Verbeek and Sachtler (Verbeek and Sachtler, 1976), namely, there is a strong tin-ligand effect (under reduction condition) resulting in drastic lowering of the heat of adsorption of hydrogen on the platinum atoms on the alloy surface. This extremely lowers the adsorption of hydrogen on alloy.

Obviously the reduction of Sn(IV) is provoked by Pt. The mechanism of this process can be explained by the following ways:

I) Cluster model (Lieske and Völter, 1984): Pt(II, IV) and Sn(IV) species are concentrated and well mixed in small clusters on the support surface. The reduction of such a cluster starts with the formation of metallic platinum from the Pt(II, IV) species inside of the cluster. Metallic platinum activates hydrogen which reduces in the next step the Sn(IV) species of the cluster. In this way the Sn(IV) reduction is provoked and the reduction behavior of tin is governed by Pt. The main part of stabilized tin on alumina-support is only reduced to Sn(II) species, forming the outer region of the reduced clusters (Serrano-Ruiz et al., 2006). Since tin loading (2.94% w/w Table 2) used for preparation was higher than platinum (0.28%) therefore can be supposed that only a minor part of the Sn is taken up by the Pt^0 clusters as Sn^0.

II) Electron transfer: in this way Pt (II,IV) species are reduced first to metallic platinum followed by electron transfer from metallic platinum to Sn(IV). Electronegativity in Pauling scale (with decreasing of atomic radius ionization energy and ectronegativity increases) of Sn (1.96 eV) is higher than for Pt (2.28 eV) (Emsley, 1991). Therefore difference in electronegativity values can generate electron flow from Pt to Sn with possible formation Sn(II) and Pt (0<x<II) surface sites.

Summarized mentioned above Pt-Sn, Sn(II), Pt (0<x<II) sites can be formed on Pt-Sn/Al surface during reduction. In order to examine the influence of reduction on the structure of the studied samples, XR diffractograms were recorded after TPR at 1073 K (Fig.26). All samples showed the presence of γ-Al_2O_3 phase. It should be noted, that there is no evidence for peak corresponding to Pt^0, PtO_x or / and $PtSn_x$ (sintered particles) in reduced Pt/Al and Sn-Pt/Al samples. That means that the reduction in H_2 converts platinum oxide species into highly dispersed metallic platinum in Pt/Al or/ and tin-platinum alloy in Sn-Pt/Al sample. Similar effect of undetectable by XRD alloy formation at 623 K in hydrogen was observed for low doping platinum and tin sample, Pt(1%)-Sn(1%)/Al_2O_3, due to high dispersion of alloy on alumina support (Dautzemberg et al.,1980).

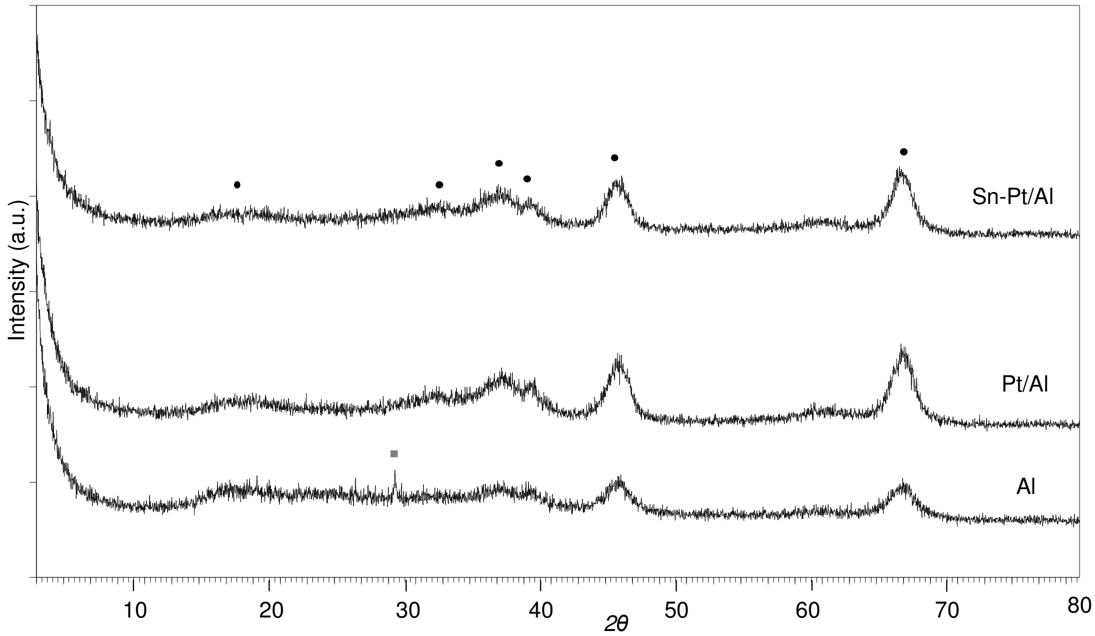


Fig. 26. XRD patterns for samples reduced in hydrogen atmosphere up to 1073 K, where ● - γ-Al_2O_3 and ■ - boehmite (AlO(OH)) crystalline phases of aluminum oxide

The disappearance of cassiterite crystallites of SnO_2 in Sn-Pt/Al sample after reduction at 1073 K indicates changes in crystalline structure of sample but formed SnO phase or Sn^0 was not observed by XRD. Based on cluster model mentioned above it seems that cassiterate crystalline structure is destroyed during reduction by interaction of a part of tin atoms with platinum forming Pt-Sn alloy clusters. Unreacted part of tin forms amorphous Sn(II). The coexistence of an unalloyed metallic tin or Sn(II) phase can be confirmed taking into consideration the quantity of Sn and Pt in bimetallic catalyst. The obtained Sn^{4+}/Pt^{n+} (149.14 /8.64; at/at, Table 2) atomic ratio determined by ICP analysis is 17.26. Maximum four atoms of tin can be involved in alloy formation with one atom of platinum $PtSn_4$ (Speller and Bardi, 2002). The obtained atomic ratio (17.26) is higher than four therefore unalloyed tin is present on the surface.

4.3. Catalytic Activity

4.3.1. CO Oxidation

Analysis of the collected data on CO adsorption has shown that CO oxidation takes place on surface of the supported samples (section 3.2.4.) and it was confirmed by the presence of lower frequency (below 1900 cm^{-1}) bands assigned to bridging type of carbonate and / or bicarbonate species (Fig.14).

Bicarbonate and carbonate species are formed as a result of carbon monoxide adsorption on surface oxygen and hydroxyl group or on oxygen species, respectively (Parkyns, 1967), (Amalric-Popescu and Bozon-Verduraz, 2001), (Thornton and Harrison, 1975). Adsorption of CO on oxide surface can be illustrated as shown in Fig.27:

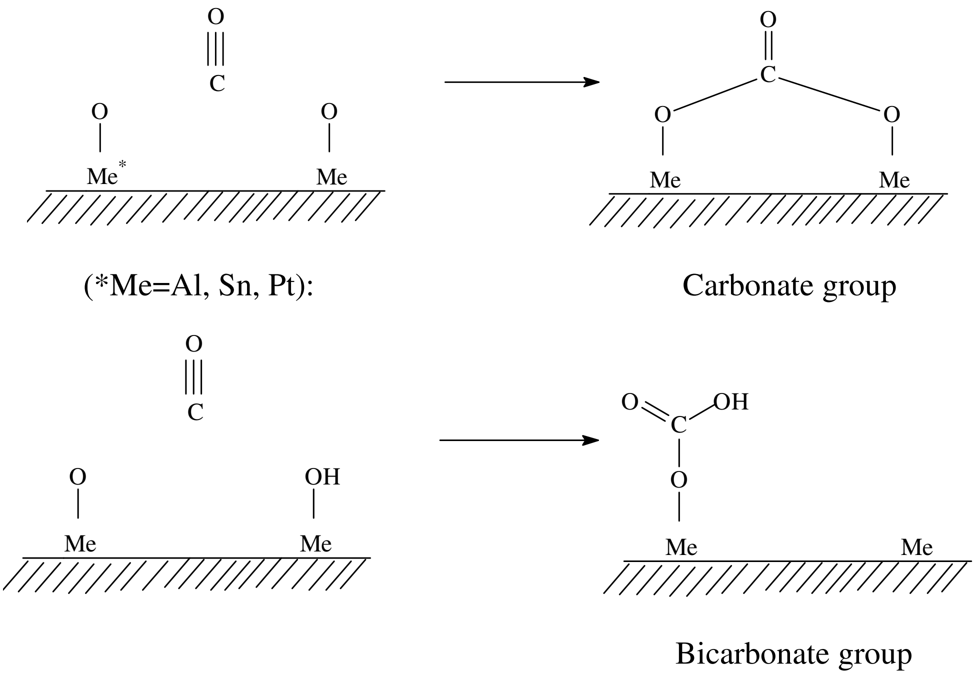
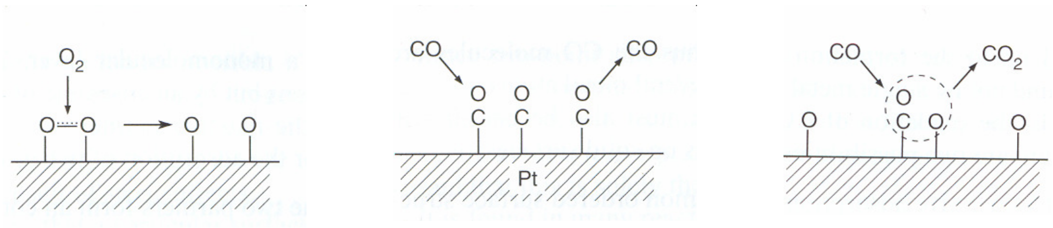


Fig. 27. Schematic representation of CO adsorption with formation of carbonate and bicarbonate groups (Thornton and Harrison, 1975).

Moderately higher number of carbonate and bicarbonate species was observed on Sn-Pt/Al than on Pt/Al sample (Fig.14) due to higher dispersion of platinum on the surface proved by microcalorimetric measurements. Platinum cation can also participate in carbon monoxide oxidation in the following way (Hagen, 1999):



(a) (b) (c)

Fig.28. Oxidation of CO with involvement the platinum cation species (Hagen, 1997)

Thus the molecular adsorption of CO occurs initially on platinum metal cations after it reacts with an oxygen on the surface followed by desorption of CO_2 from surface (Fig.28). O_2 is dissociatively adsorbed during pretreatment procedure (Fig.28.a). The low degree of oxygen coverage allows adsorption of CO between the O atoms (Fig.28.c), and the reaction proceeds by the Langmuir-Hinshelwood mechanism. The CO_2 product is only weakly bound on the surface and is rapidly desorbed into the surrounding gas phase (Fig.28.c).

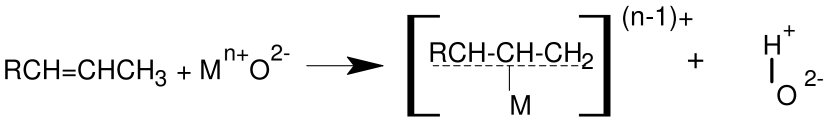
4.3.2. Mechanism of Propylene Oxidation

Electrical conductivity / capacity data reported indicate that platinum has the ability to activate the tin oxide lattice and the activated oxygen plays an important role in the oxidation process (Carata et al., 2004). The contribution of the lattice oxygen in total oxidation of methane over PdO-based catalysts using a reaction mixture labeled with $^{18}O_2$ was mentioned by Ciuparu and co-authors (Ciuparu and Pfefferle, 2002), (Ciuparu et al., 2001). They observed that surface hydroxyls resulting from methane oxidation inhibit the surface reoxidation, leading to a certain degree of catalyst depletion of oxygen and formation of bulk oxygen vacancies. This can be responsible for the lower temperature of thermal reduction for pure PdO as compared to supported PdO particles. For the supported catalyst, oxygen vacancies in the PdO phase are refilled with oxygen from the support, consistent with the larger amounts of ^{16}O observed in the reaction products resulting from PdO on zirconia. This oxygen transfer may be responsible for the lowering thermal decomposition rate of PdO particles supported on ceria–zirconia and as hence, increasing stability of active phase, PdO.

Apparently, as shown in Table 10. and 11., the presence of platinum oxide together with the tin oxide produces higher catalytic activity in hydrocarbon oxidation than Sn/Al. This can be an indication that platinum has the ability to activate the tin oxide lattice. Increased oxygen mobility / higher reducibility of tin oxide in presence of platinum was indicated by the XPS (Fig.9, Table 4) and TPR results (Fig.18).

It was proposed that propylene is dissociatively adsorbed on pair of Me^{n+}-O^{2-} sites where the allyl anion is formed on Lewis acid sites and the proton abstracted by Lewis basic sites (Caldararu et al., 2003), (Kung, 1989), (Gordimova and Davydov, 1979).

Unlike alkanes, the C=C bond of alkenes can interact comparatively strongly with the cations of the catalyst surface. The strong bonding makes possible the charge delocalization between the adsorbate and the cation. Since the charge on the cation in the solid can be much better stabilized by electrostatic forces in the solid than charges on the adsorbate outside the solid, it becomes possible that the allylic C-H bond breaking in this step is achieved with charge transfer between the π-allyl and the surface cation (Kung, 1989):



$$RCH{=}CHCH_3 + M^{n+}O^{2-} \longrightarrow \left[\underset{M}{RCH\text{-}CH\text{-}CH_2}\right]^{(n-1)+} + \overset{H^+}{O^{2-}}$$

Formed propyl cation is oxidized in to carbon dioxide in oxygen reach atmosphere. In case of limited number of oxygen in reacting mixture partial oxidation of propylene takes place. Mechanism of selective oxidation of propylene to acrolein is shown in Fig.3.

It may be supposed that the presence of platinum ion not only increases the mobility of the surface lattice oxygen but facilitates the dissociative adsorption of propylene. At the same time the simultaneous presence of both platinum and tin oxide diminishes the strength of the acidic sites of the catalytic sample (Table 6) and hence can affect the propylene adsorption on the catalyst surface. The higher the number of site of moderate strength, the higher the oxydation activity of the catalyst. Additionally, FTIR results showed that the formation of Lewis acidic sites which might be responsible for hydrocarbon oxidation are developing at dehydroxylation temperature ≥ 573 K consequently relatively high activation reaction temperature is needed.

4.3.3. Cyclopropane Isomerization

4.3.3.1. Kinetics

First order reaction was considered and characterized by the rate constant determined using linear regression from measured data for sample pretreated in oxygen (Fig.29) and for catalyst samples pretreated in hydrogen (Fig.30) using equation (8) for closed system (Szabó and Kalló, 1976):

$$\ln [A] / [A_0] = -k\ [t \cdot m] \qquad (8)$$

where, A_0 – initial concentration of cyclopropane (mol), at starting time t=0 (s);

A –concentration of cyclopropane (mol), at some later time, t (s);

k – rate constant of the heterogeneous transformation of cyclopropane to propylene, ($mol \cdot g^{-1} \cdot s^{-1}$);

m- mass of catalyst used (g).

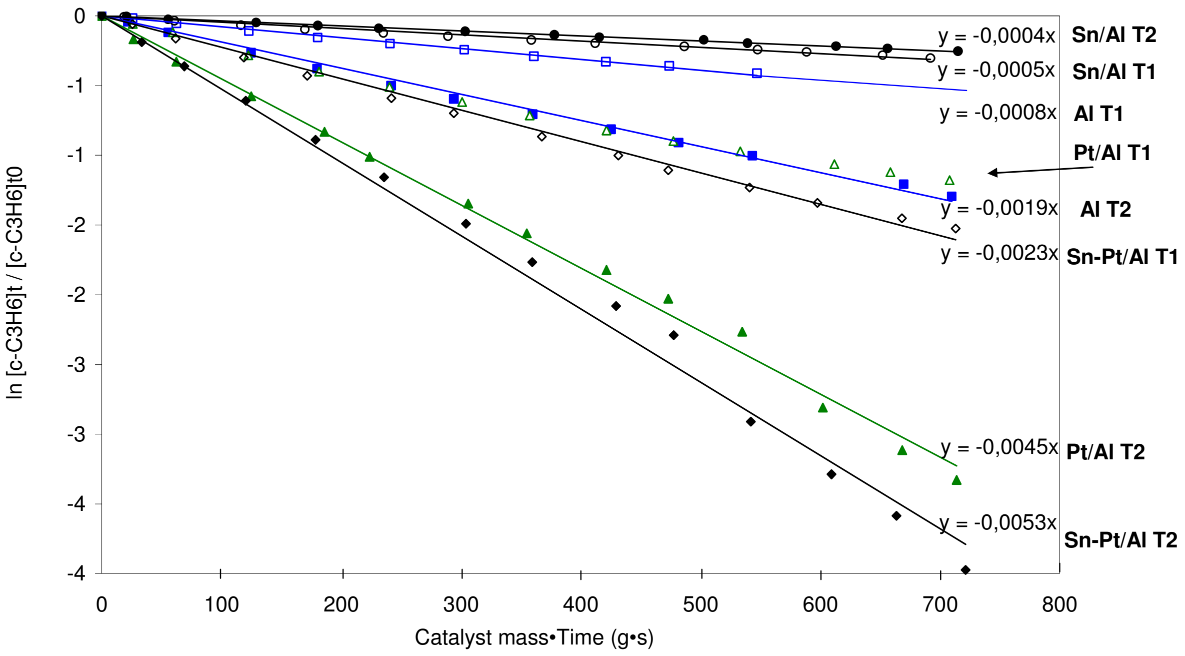


Fig. 29. Determination of rate constant of cyclopropane isomerization reaction over oxidized form of catalysts at T_1=473 K and at T_2=523 K (reaction time was 2 h or 7200 s, mass of sample ~0.1g)

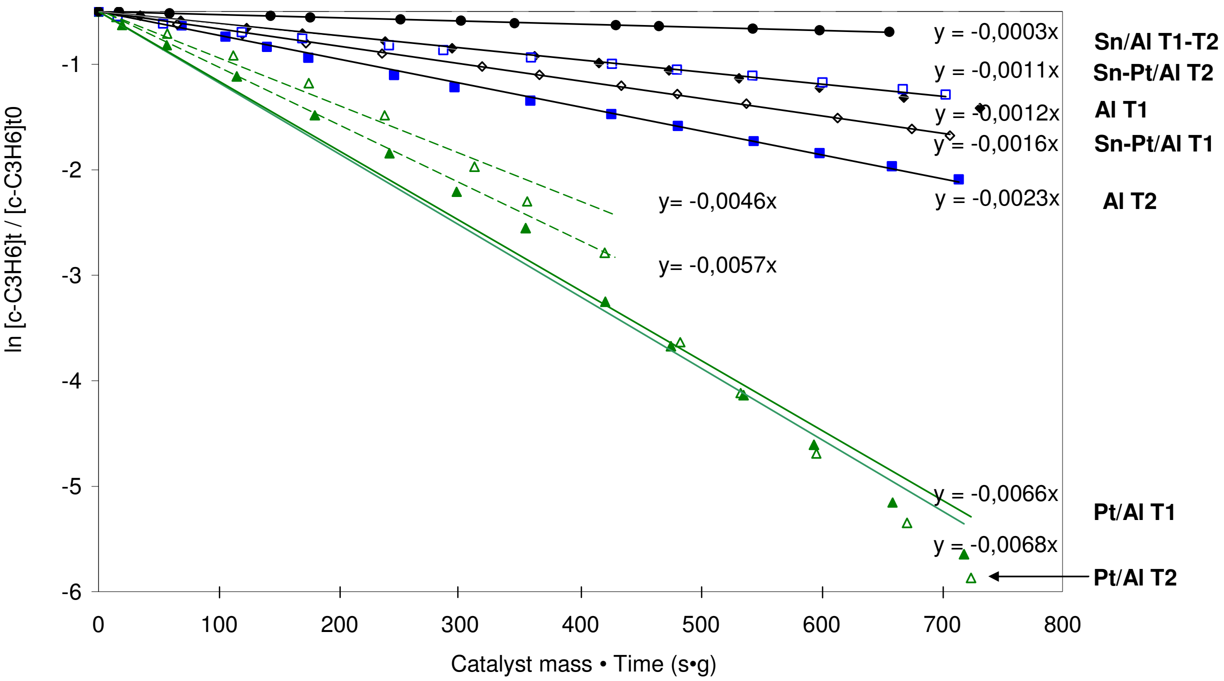


Fig. 30. Determination of rate constant of cyclopropane isomerization reaction over reduced form of catalysts at T_1= 473 K and at T_2 =523 K, where interrupted line is for determination of rate constant after one hour of reaction over Pt/Al

Rate constants determined over reduced and oxidized forms of samples are summarized in Table 12.

Table 12. Rate constants of cyclopropane isomerization to propylene (over samples pretreated in O_2 773 K and in H_2 at 823 K) recorded for 2 h of reaction runs at 447 K and at 523 K

Catalyst	Rate constant, $k\cdot10^{-3}\cdot mol\cdot g^{-1}\cdot s^{-1}$		Rate constant, $k\cdot10^{-3}\cdot mol\cdot g^{-1}\cdot s^{-1}$		**Rate constant,** $k\cdot10^{-3}\cdot mol\cdot g^{-1}\cdot s^{-1}$	
	Run 1st		Run 2nd		**Run 3rd**	
	T_1 = 473K	T_2 = 523K	T_1 = 473K	T_2 = 523K	**T_1 = 473K**	**T_2 = 523K**
reaction without catalyst					-	**0.03**
oxygen treated samples						
Al	0.70	1.90	0.80	2.20	**0.80**	**1.90**
Pt/Al	1.60	4.00	1.60	7.10	**1.80**	**4.50**
Sn/Al	0.50	0.40	0.50	0.40	**0.50**	**0.40**
Sn-Pt/Al	2.30	5.30	1.80	3.90	**2.30**	**5.30**
hydrogen treated samples						
Al	1.20	2.40	1.20	2.20	**1.20**	**2.30**
Pt/Al	5.80 (4.90) [a]	8.30 (7.20) [a]	6.60 (4.80) [a]	7.20 (6.10) [a]	**6.60** **(4.60)** [a]	**6.80** **(5.70)** [a]
Sn/Al	0.30	0.30	0.30	0.30	**0.30**	**0.30**
Sn-Pt/Al	1.80	1.20	1.60	1.20	**1.60**	**1.10**

[a] -rate constant recorded for 1h of reaction run

In order to check the stability and regeneration ability of the catalysts, the same catalyst sample was used for 3 runs when reaction was followed by regeneration. The rate constant (k) increases with the increasing reaction temperature from 473 to 523 K for samples in all the three reaction runs, except Sn/Al sample in its oxidized and reduced forms and Sn-Pt/Al in reduced form (Table 12). After each reaction run the oxygen treatment at 773 K (followed by reduction in H_2 at 823 K for reduced samples) was applied for burning off the carbonaceous residues containing compounds adsorbed on the surface after the former reaction run. The original activity was restored for all samples. This is an indication of the good of catalysts' stability. Experimental values for catalysts catalyst samples after 3rd run of isomerization reaction were used for comparison of catalytic activity, rate constants (Table 12), activation energies (Table 13) for the catalyst samples as well as for presentation of data in graphic forms (Fig.24, 25, 29, 30, 32).

For oxidized Sn/Al sample the same rate constant ($k = 0.5\cdot10^{-3}$, $mol\cdot g^{-1}s^{-1}$) was obtained during three reaction cycles; it decreased ($k = 0.4\cdot10^{-3}$, $mol\cdot g^{-1}\cdot s^{-1}$) with increase of reaction temperature. With high probability the deactivation of Sn/Al catalyst with the increase of reaction temperature is a results in increased coke formation on the surface (Margitfalvi et al., 1984). The addition of platinum to alumina increases the reaction rate, while addition of tin oxide to the alumina support diminishes the reaction rate. The simultaneous presence of Pt and Sn in oxidized forms results in a little bit higher rate constant ($k = 5.3\cdot10^{-3}$, $mol\cdot g^{-1}\cdot s^{-1}$) than for Pt/Al ($k = 4.5\cdot10^{-3}$, $mol\cdot g^{-1}\cdot s^{-1}$) and significantly higher for Sn/Al ($k = 0.4\cdot10^{-3}$, s^{-1}) hence some synergetic effect can be considered.

The reduction pretreatment decreases the reaction rate on Sn-Pt/Al and increases on Al, Pt/Al samples. The highest value of rate constant ($k = 6.8\cdot10^{-3}$, $mol\cdot g^{-1}\cdot s^{-1}$) was formed for reduced Pt/Al among studied the catalysts samples. It should be noted that the increase of reaction temperature from 473 K to 523 K has little effect on catalytic activity of Pt/Al during first hour of reaction run and almost no effect during second hour of reaction run (Fig.30, Table 12). This is indication on partial coke deposition which blocks some of the active site. Reduced form of Sn/Al sample (as well as its oxidized form) was least active for cyclopropane isomerization and showing the lowest rate constant ($k = 0.3\cdot10^{-3}$, $mol\cdot g^{-1}\cdot s^{-1}$).

The approximate value of activation energy, Ea, of cyclopropane isomerization to propylene was determined over active oxidized and reduced catalysts using Arrhenius equation (Eq.9):

$$\ln k = -Ea / RT + \ln A \tag{9}$$

The value of Ea was estimated from the slope of ln k vs. 1/T determined by two points only at 473 K and at 523 K, at which the reaction was carried out. Obtained approximate Ea values are summarized in Table 13. The decrease of activation energy indicates lower energy barrier of catalyst reaction.

Table 13. Approximate values of activation energy, Ea, of cyclopropane isomerization to propylene over oxidized and reduced forms of catalysts

Catalyst	Ea, kJ/mol
oxygen pretreatment	
Al	35.58
Pt/Al	37.69
Sn-Pt/Al	34.34
hydrogen pretreatment	
Al	26.76
Pt/Al	1.23 (8.82)[a]

[a] -Ea after 1h of reaction run.

4.3.3.2. Effect of Oxygen Pretreatment

The oxygen treated catalyst samples showed the following order of activity for cyclopropane isomerization: Sn-Pt/Al > Pt/Al > Al > Sn/Al (Table 12).

The supported tin oxide on alumina was not active catalyst for isomerization. However SnO_2 has promoter effect on catalytic activity in Sn-Pt/Al sample pretreated in oxygen. The slight promoter effect of Sn may be ascribed either to an electronic and/or to geometric effect due to the dilution of the platinum atoms resulting in decrease of the its cluster size (Roman-Martínez, 2000), (Sprivey and Roberts, 2004).

In our case both effects were detected for Sn-Pt/Al catalyst. Electron transfer from Sn to support was detected by FTIR for CO adsorption study on Sn-Pt/Al (section 3.2.2. Fig.12). It results in a decrease of the bonding strength of stronger Al^{+3}_{tet} Lewis acid sites of alumina support to carbon monoxide. Total acidity of Pt/Al (combining acidity of all metal cations) and its strength determined by calorimetric NH_3 adsorption decrease with adding SnO_2 to this catalyst due to electron transfer from Sn to the bulk (section 3.3.1. Table 6).

In the view of Davis and co-authors (Davis et al.,1976) an electron transfer from tin to platinum is not only responsible for enhancement of the selectivity for isomerization but for increase of stability of Sn-Pt/Al catalyst by decreasing coke deposition. The electron enrichment of platinum weakens the Pt-C bond and increases their resistance to self-poisoning by coke (Coq and Figureras, 1983). This is in agreement with XPS in our study (section 3.1. Table 3) where Sn-Pt/Al was less active than Pt/Al and Sn/Al in adsorption of carbon containing compounds from the environment and was keeping high activity and stability for a long time (2 h) in cyclopropane isomerization reaction (section 4.3.3.1, Table 12).

XRD patterns did not show crystalline platinum particle due to higher dispersion of platinum in samples (section 3.1. Fig.8). In addition, microcalorimetric measurement shows a high dispersion of Pt in Sn-Pt/Al probably is the result of the dilution of platinum particles into smaller ensembles in presence of tin (section 3.3.2. Table 8). This fact should be taken into account while explaining the higher activity of Sn-Pt/Al sample.

4.3.3.2.1. Proposed Mechanisms over Oxygen Treated Samples

The proposed mechanism which might prevail in cyclopropane isomerization over samples pretreated in oxygen is based mainly on the electrical conductivity (EC) data (section 3.5.) and the acidic properties of the catalytic surface (section 3.2., 3.3.1). As shown in EC section, the conduction occurs mainly by protonic mobility on catalytic surface (combined with the electronic conductivity for SnO_2 containing samples) at higher temperature (section 3.5.3. and Fig. 21). The presence of mobile protons indicates the existence of Brönsted acid sites on the surface. Based on this statement, the mechanism of cyclopropane isomerization over oxidized catalysts involving Lewis acid sites, where the hydride ion transfer should occur, is less probable in our case (Fejes et al., 1978), (section 1.6.3.1.3.). The catalytic results may be interpreted in terms of a nonclassical carbonium ion mechanism, making repeated use of a small number of catalyst protons of basic hydroxyl groups, which are involved in the formation of $C_3H_7^+$ carbocation or propyl cation as intermediate species during the isomerization reaction (Goldwasser, 1981).

The FTIR band intensity assigned to acidic OH groups of alumina, having Brönsted acidic character, for Sn-Pt/Al was higher at 473 K than for Pt/Al, Sn/Al and this difference is preserved at 773 K (Table 5, Fig.11). This suggests that the presence of both Pt and Sn elements facilitate the formation / stabilization Brönsted acid groups, considered as active sites in cyclopropane transformation to propylene. It should be mentioned however that Brönsted acidity was not detected by adsorption of Py at room temperature (Fig.15.a.) as indicated by FTIR spectroscopy. This fact can be explained that the dehydroxylation of surface at 773 K before adsorption diminishes drastically the density of surface Brönsted acid sites and their number became therefore below the detection limit of FTIR method. Consequently higher temperature is needed in order to initiate the movement of surface and / or migration of bulk proton to the surface. It was shown by EC measurements that the higher the temperature the higher the mobility of proton by hopping /jumping mechanism (section 3.5. and Fig.21) and hence the conversion percent of cyclopropane to propylene over active samples increases with increasing of the reaction temperature (Fig.24, Table 12). In case when the temperature is raised up to 523 K the release of the proton from the surface becomes easier and its interaction with cyclopropane occurs without strong pre-adsorption of c-C_3H_6 on the surface, which increases the catalyst efficiency (by increasing the reaction rate, Table 12).

The possible reaction steps summarized from literature review (Baird and Aboderin, 1964), (Hightower and Hall, 168, ***72***), (Fejes et al., 1978) of mechanism of cyclopropane isomerization involving Brönsted acid site of surface are shown on Fig.31.

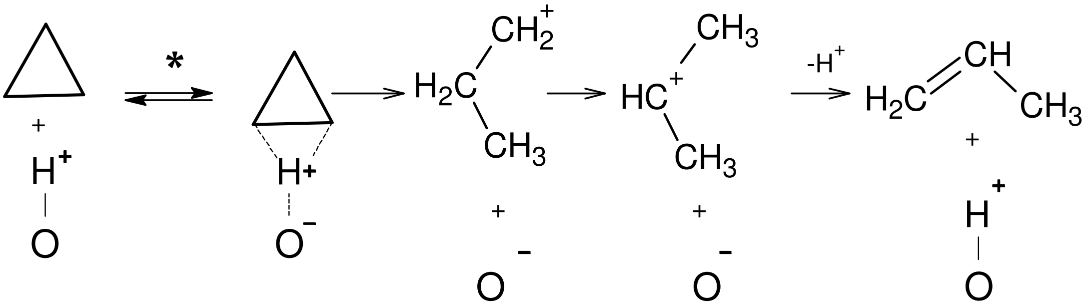


Fig.31. Schematic presentation of mechanism of cyclopropane isomerization involving of Brönsted acid sites

The non-classical carbonium ion (so called edge-protonated cyclopropane) is produced during adsorption on the surface (Baird and Aboderin, 1964), (Hightower and Hall, 1968, ***72***). This cation is transformed into a classical propyl cation by C-C bond rupture of the ring which desorbs as propylene while regenerating the acidic center is regenerated (Fejes et al., 1978). The first step (marked as *) of the catalytic transformation is a relatively fast adsorption step being a weak chemisorption with an adsorption heat of 34.69 kJ/mol (Fejes et al., 1978). The physisorption should be taken into consideration because the adsorbed amount of cyclopropane exceeds the number of acidic sites (Fejes et al., 1978). For example, only a small number of protons ≤ 10^{12} Brönsted sites/cm^2 of co-catalytic hydroxyl groups were involved in isomerization of cyclopropane over silica-alumina (Larson et al., 1965). For comparison pure alumina has OH groups from 12.6 to 5.5·10^{14} sites/cm^2 within dehydroxylation range from 373 to 673 K (Knözinger and Ratnasamy, 1978).

Besides propylene over platinum containing samples the formation of very small amount (max 0.3%) of propane was observed, which can be formed after some molecules of propylene-product react with surface protons and hydrogenation of propylene occurs (Fejes et al., 1978).

On the other hand, the mechanism of cyclopropane isomerization on Lewis acid sites proceeding over oxidized catalysts, where hydride ion transfer should occur, can not be denied at least for supported catalysts having higher number of electron pair excepting sites like platinum and tin cations which can attract and easier subtract (than alumina cation) H^- from cyclopropane ring. The steps of this mechamsim were discussed in more details in introduction part (section 1.6.3.1.3).

4.3.3.3. Effect of Hydrogen Pretreatment

Reduced Pt/Al is highest activity in isomerization of cyclopropane to propylene among catalysts studied having an activity 1.3 times higher at 523 K than in oxidized form at the same temperature (Table 12, Fig.32). The pretreatment of Pt/Al in hydrogen at 823 K results in reduction of platinum oxide to Pt^0 (proved by TPR) and this allows to stipulate that metallic platinum sites are of highest activity for cyclopropane isomerization.

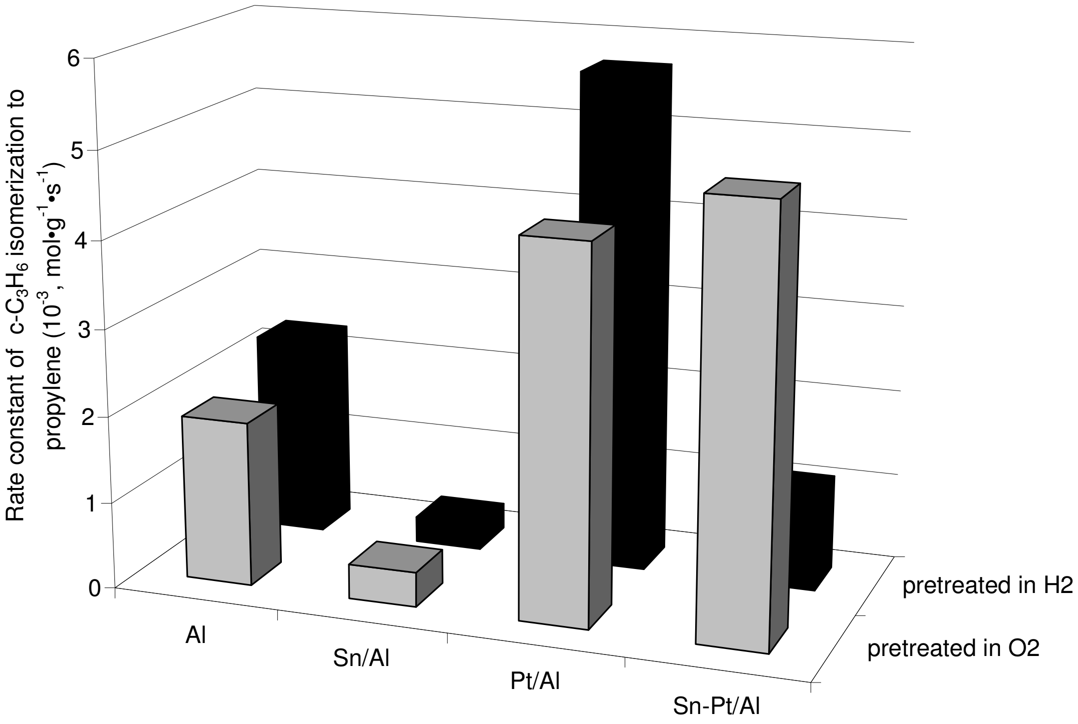


Fig. 32. Comparison of rate constants (10^{-3}, mol·g^{-1}·s^{-1}) of cyclopropane isomerization to propylene at 523 K for samples treated in oxygen and hydrogen atmospheres

However, after reduction a considerable decrease of activity was observed in case of Sn-Pt/Al catalyst containing both platinum and tin in comparison with its activity in oxidized form (Fig.32). The measurement was repeated three times (Table 12) and results were similar, namely, Sn-Pt/Al showed low activity after reduction at 823 K in hydrogen. Moreover, decreasing rate constant was observed for this sample with increase of reaction temperature possibly because of coke formation on the surface. The low activity of reduced form of Sn-Pt/Al can be explained by the PtSn alloy formation under hydrogen atmosphere treatment proved by TPR. Sintered PtSn particles are supposed to be responsible for inhibition of the reaction by decreasing the adsorption ability of platinum sites (Liske and Völter, 1984), (Verbeek and Sachtler, 2004), (Serrano-Ruiz, 2006).

Sn/Al remains inactive catalyst after reduction pretreatment where tin is present as Sn(II) confirmed by TPR. Rate constant of Sn/Al reduced catalyst was $0.3 \cdot 10^{-3}$(mol·g^{-1}·s^{-1}) and did not change with increasing of reaction temperature.

4.3.3.3.1. Proposed Mechanism over Hydrogen Treated Samples

Pt metal sites play an important role in cyclopropane isomerisation since the highest activity was observed for reduced Pt/Al among the catalysts studied. The isomerization of cyclic hydrocarbon over metal sites requires hydrogen as a co-catalyst (Du et al., 2005), (Bond and Newhan, 1960). It has been reported that hydrogenation of cyclopropane over platinum catalysts proceeds most probably in terms of Eley-Rideal mechanism when gas-phase or physically adsorbed cyclopropane reacts with chemisorbed hydrogen around or above 473 K (Bond and Newhan, 1960), (Addy and Bond 1957), (Bond and Sheridan, 1952).

Based on above mentioned the radical mechanism of cyclopropane isomerization over platinum metallic sites can be proposed over reduced Pt/Al catalyst. The schematic presentation of this mechanism is shown in Fig.33:

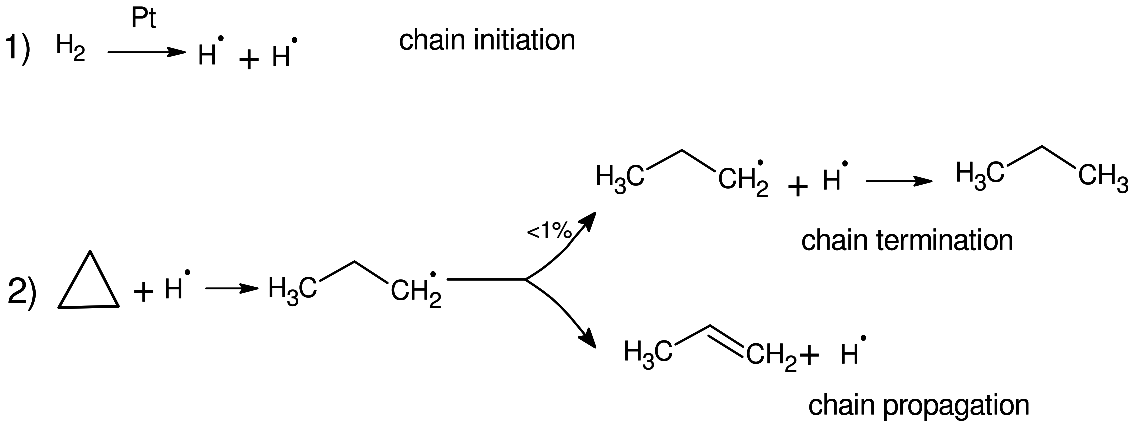


Fig. 33. Schematic presentation of radical mechanism of isomerization of cyclopropane over samples containing metallic platinum species

The first step is the formation of active hydrogen species during pretreatment in H_2 by homolytical adsorption of hydrogen molecule in presence of metallic platinum. In second step cyclopropane is physically adsorbed on metal, which then reacts with chemisorbed hydrogen in push-pull manner (Du et al., 2005) to produce adsorbed alkyl radical. The adsorbed propyl radical may then either lose one hydrogen atom (isomerization process) and form propylene-product or attach a hydrogen atom (hydrogenation process) to form propane by-product. In our case the main product was propylene (99.3%) since the further hydrogenation of C_3H_6 was limited by presence of hydrogen (hydrogen was used for pretreatment of the surface before reaction starts and was absent in reacting mixture during reaction run). The situation could change with excess of hydrogen, when H_2 is present in reacting mixture. In this case hydrogenation of cyclopropane (Bond and Sheridan, 1952) could be the dominat reaction with formation of propane as the main product.

5. CONCLUSION

Addition of small amount of platinum (0.28 %) strongly influences the physico-chemical characteristics of tin containing catalyst with consequences on its catalytic behavior.

The deposition of SnO_2 or platinum oxide alone enhances the number of the total acid sites (combining acid sites of support Al^{3+} and supported compounds Sn^{4+} and/or Pt^{n+}) and their strength on catalyst surface. However, the simultaneous presence of platinum and tin oxides decreases the strength of stronger acid sites possibly due to the electron transfer from tin to platinum. This effect can be explained by Sn-Pt electronic interaction: SnO_2, known as n-type semiconductor, can change the electronic density in the bulk by transmitting electrons to the PtO (p-type semiconductor) and Al_2O_3 (weak n-type semiconductor), and thus decreases the acidic strength of some of the corresponding Lewis sites.

Microcalorimetric study of CO adsorption showed that platinum ions are better dispersed on the surface of Sn-Pt/Al than for Pt/Al catalyst sample. A higher dispersion of Pt in Sn-Pt/Al is probably the result of the dilution of platinum particles into smaller ensembles in presence of tin element.

FTIR study showed that Pt/Al and Sn-Pt/Al are promising catalysts for oxidation of carbon monoxide to carbon dioxide through carbonate and bicarbonate intermediates formation on the catalyst.

It was concluded that the studied catalysts were not active in selective oxidation (propylene : air ratio mixture 1:10) since CO_2 (CO) and water were formed as a main products.

The deposition of the low surface area SnO_2 on γ-alumina produced a catalyst with higher surface area but lower oxidation activity then pure bulk SnO_2. Platinum containing catalysts showed good catalytic activity for total propylene oxidation (conversion of 95-100% at 673 K). Sn-Pt/Al sample showed the highest selectivity (99.9%) for CO_2 formation under oxidation conditions. The presence of Pt facilitates the dissociative propylene adsorption and mobility of the surface lattice oxygen, as consequence it increases the rate of oxidation reaction. Additionally, FTIR results showed that the formation of Lewis acidic sites responsible for hydrocarbon oxidation proceeds at dehydroxylation temperature $\geq$ 573 K therefore relatively high activation reaction temperature is needed for oxidation of hydrocarbons.

In agreement with electrical conductivity results it was concluded that the c-C_3H_6 isomerization proceeds probably over Brönsted acid sites (via formation of $C_3H_7^+$ intermediate) of oxidized samples. Since Lewis acidity was detected on the samples studied the possible involvement of the Lewis acid sites (via formation of $C_3H_5^+$ intermediate) in cyclopropane isomerization could also be considered. Cyclopropane isomerization started at around 473 K and the increase of the reaction temperature (523 K) increased the reaction rate. The temperature increase up to 473 K for isomerization increased the proton mobility, i.e., the surface/bulk proton or hydride movement and thus reduced the strong adsorption of hydrocarbon species. The oxidized samples showed the following catalytic activity sequence for c-C_3H_6 isomerization at 523K:

Sn-Pt/Al > Pt/Al > Al > Sn/Al.

Only the Pt/Al exhibited high catalytic activity (k= $6.8\cdot10^{-3}$ mol$\cdot$g$^{-1}\cdot$s^{-1}) and selectivity (nearly 100% of reacted cyclopropane was transformed to propylene) from reduced catalysts where isomerization probably takes place via the formation of the allyl radical intermediates.

From cyclopropane isomerization studies concluded that tin exists in different forms in Sn-Pt/Al, depending on the pretreatment conditions of the catalyst (i) in an oxidized form, Sn^{4+} (SnO_2), resulting in a promoting effect; (ii) in reduced form, tin resulting poisoning effect “ligand-effect” due to blocking of the sites responsible for cyclopropane isomerization by formation an alloy.

This research work has been started in the frame of an international research INCOCOPERNICUS research project ERBIC 15 CT 98 05 15. Within this project the Sn-Pt/Al was recommended as a catalyst for total oxidation of lower hydrocarbons (C_1-C_3) and also for environmental purposes (CO elimination). As an outcome the catalyst system has been scaled up at industrial level at ROMPETROL, VEGA Refinery, Romania.

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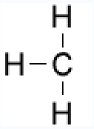
APPENDIX

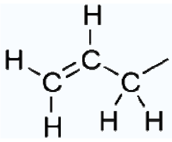
Definitions

1. Alkyl is a univalent radical containing only carbon and hydrogen atoms arranged in a chain. The alkyls form a homologous series with the general formula C_nH_{2n+1}. Examples include *methyl*, $CH_3\cdot$ (derived from *methane*) and *propyl* $C_3H_7\cdot$ (derived from *propane*). On their own they are free radicals and therefore extremely reactive. The structure of an alkyl is the same as its straight chained alkane counterpart but with one less hydrogen atom. For example, this is the structure of methyl, the smallest alkyl:



Alkyls are radicals since only three out of four valency electrons are used in bonding on one of the carbon atoms.

2. Allyl group - is an alkene hydrocarbon group with the formula $H_2C=CH-CH_2-$. It is made up of a vinyl group, $CH_2=CH-$, attached to a methylene $-CH_2$. Compounds containing the allyl group are often referred to as being allylic. Allylic carbons are sp^3 hybridized. Chemical structure of the allyl group:



3. Allyl cation has a chemical structure $CH_2=CH-CH_2^+$

4. **Carbonium ion** is a carbocation of the penta- or tetracoordinated nonclassical type such as an ion of the type R_5C^+. In older literature a carbocation of the type R_3C^+ may still be referred to as a carbonium ion.

5. Cyclopropane is a cycloalkane molecule with the molecular formula C_3H_6 consisting of three carbon atoms linked to each other to form a ring, with each carbon atom bearing two hydrogen atoms. The bonds between the carbon atoms are much weaker than in a typical carbon-carbon bond. This is the result of the 60° angle between the carbon atoms, which is far less than the normal angle of 109.5°. This strain has to be subtracted from the normal C-C bond energy, making the resultant compound more reactive than acyclic alkanes and other cycloalkanes such as cyclohexane and cyclopentane. However, cyclopropanes are more stable than a simple angle strain analysis would suggest. Cyclopropane can also be modeled as a three-center-bonded orbital combination of methylene carbenes. This results in the walsh orbital description of cyclopropane, where the C-C bonds have mostly π character. This is also why cyclopropanes often have reactivity similar to alkenes. This is also why carbenes can easily add into alkenes to produce cyclopropanes.

6. Carbenium ion is a carbocation of the trivalent and classical type R_3C^+.

7. Propyl is a three-carbon alkyl substituent with chemical formula **$-C_3H_7$**. There are two isomeric forms of propyl:

- with the substituent attached to one of the end carbons (called 1-propyl in the IUPAC nomenclature, or **n-propyl** in the old naming system); and
- with the substituent attached to the middle carbon (called 2-propyl in the IUPAC system, or isopropyl in the old system).

8. Propyl cation has a chemical formula CH_3-CH_2-CH_2^+

9. **Propylene**, also known by its IUPAC name **propene**, is an organic compound having the chemical formula C_3H_6.

Thesis of the Doctoral (Ph.D.) Dissertation

Surface Chemistry Studies of SnO_2-Pt/Al_2O_3 Catalyst for Environmentally Improved Catalytic Oxidation of Carbon Monoxide, Propylene and for Cyclopropane Isomerization

1. INTRODUCTION

The catalytic approach for hydrocarbon oxidation is a subject of special attention during the last years due to the improved efficiency of catalysts and reduced emissions of pollutants like CO, hydrocarbons. A catalytically enhanced combustion system operates at much lower temperatures than an open flame burner, and lower temperature also means reduced emission of CO and NO_x. Semiconductor oxides (SnO_2, V_2O_5) are known to exhibit oxidizing activity and can be considered as potential catalysts for isomerization and total or selective oxidation of C_1-C_3 hydrocarbons and for CO oxidation to CO_2. The application of pure semiconductor catalysts is very limited due to their low surface area (10-20 m^2/g) and poor thermal stability. The surface area can be increased by deposition of active components on the supports (Al_2O_3, TiO_2, SiO_2) having much higher surface areas (100-400 m^2/g). Tin (IV) oxide is a mild oxidizing catalyst, but its catalytic properties can significantly be modified by incorporation of other elements (noble metals, Sb) by impregnation, cohydrolysis, ion exchange or mechanical mixing. Supported semiconductor oxides and particularly those doped with platinum exhibit improved catalytic properties, since noble metals are the most active catalysts for hydrocarbons or CO oxidation. The prepared materials should be usually calcined in order to be active as catalysts.

The physico-chemical properties and catalytic activity of the solid sample containing several oxides are generally different from that of composed oxides alone. This is due to the fact that the activity of the „mixed oxides" could be the result of various interactions. In case of sample containing different types of metal oxides, electronic effect should also be considered. According to the electronic theory of catalysis, the rate and activation energy of reaction depend upon the a Fermi level of the catalyst, and thus it can be expected that electronic interaction between metal oxides or metal and the support can modify the Fermi level of the catalyst. Therefore this interaction can influence the catalytic activity of sample.

At the same time the acid-base properties of the catalysts are also important for activation of the reactants. The strong or weak Lewis acid or basic sites of the catalyst will determine the strength of interaction of the reactants with the active sites of the catalysts and interaction of the reaction (oxidation, isomerization) products with the solid surface, which in turn determines whether a reactant and/or reaction products can readily be adsorbed (and presumably activated) or the products can readily be desorbed (preventing its further transformations).

2. EXPERIMENTAL

Tin oxide supported on alumina sample was prepared by two methods: impregnation and mechanical mixing. Pt(0.28%)/Al_2O_3 was prepared by impregnation, and doping of SnO_2 to Pt(0.28%)/Al_2O_3 was done by mechanical mixing. The prepared materials were fully characterized in order to obtain maximum amount of relevant information concerning their surface composition and catalytic activity. The physico-chemical characteristics of the catalysts were studied by BET, ICP, XRD, XPS methods. Acidic properties of the catalysts were studied using the adsorption of probe molecules (CO, Py and NH_3) by means of two appropriate methods: FTIR spectroscopy and adsorption microcalorimetry. Microcalorimetric CO chemisorption at 303 K was applied to determine the Pt dispersion on the surface as well. Temperature programmed reduction (TPR) method was used for studying of the reducibility and stability of catalyst under reduction atmosphere. The electrical conductivity (G) and capacity (C) measurements were performed "in situ" under inert atmosphere and under cyclopropane-helium mixture (1:20 ratio) in the temperature range of 293- 623 K in order to obtain information on the adsorption ability of the surface layer and the mobility of surface dipoles and to have better understanding on the mechanism of cyclopropane isomerization.

The surface active sites (hydroxyl groups, anion sites and surface cations) formed during pretreatment procedure (oxidation or reduction) were investigated by FTIR CO adsorption spectroscopic technique at room temperature (RT); these sites could directly be involved in adsorption and/ or in oxidation of hazardous carbon monoxide to less hazardous carbon dioxide through carbonate and bicarbonate intermediates.

Propylene oxidation was selected as a model reaction to obtain primary relevant information about the surface behaviour and activity of the catalysts under real operation conditions, i.e. under atmospheric pressure in propylene gas flow and in presence of oxygen. The aim of the primary study was to check the catalyst samples for selective oxidation of propylene to acrolein using of a mixture (C_3H_6 : air) equal to 1:10. The activity of samples containing platinum were also tested for total oxidation of propylene (main products water and CO_2) using of a mixture (C_3H_6 : air, 1:22).

Cyclopropane isomerization was chosen as a test reaction, since it could help to establish the correlations between the catalytic activity and the nature of the active sites formed / modified during the different activation (oxidation, reduction) procedures of the supported catalysts, or generated in presence of platinum. The isomerization of cyclopropane to propylene was studied at 473 K and 523 K in a static reactor attached to a glass gas-circulation system with manual sampling of gas doses for GC analysis. The mechanism of cyclopropane isomerization was studied.

3. NEW SCIENTIFIC RESULTS

The catalytic activity of supported catalysts stems from interactions between the physical, chemical and electrical properties of supported tin or/ and platinum oxide and support. The obtained results is of particular importance for possible application of catalysts in cyclopropane isomerization and in the environmental catalysis, e.g. for carbon monoxide and hydrocarbon oxidation. Main conclusions of investigation are summarized below for the newly prepared SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 catalysts and, SnO_2(2.83%)/Al_2O_3, SnO_2(3.10%)/Al_2O_3, Pt(0.28%)/Al_2O_3, Al_2O_3, SnO_2 catalyst samples were used for comparison purposes:

1) It was concluded that the deposition of SnO_2 or platinum oxide alone enhances the number of the total acid sites (combining acid sites of support Al^{3+} and supported compounds Sn^{4+} and/or Pt^{n+}) and their strength on catalyst surface. However, the simultaneous presence of platinum and tin oxides decreases the strength of stronger acid sites possibly due to the electron transfer from tin to platinum. This effect can be explained by Sn-Pt electronic interaction: SnO_2, known as n-type semiconductor, can change the electronic density in the bulk by transmitting electrons to the PtO (p-type semiconductor) and Al_2O_3 (weak n-

type semiconductor), and thus decreases the acidic strength of some of the corresponding Lewis sites. Microcalorimetric study of CO adsorption showed that platinum ions are better dispersed on the surface of SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 than for Pt(0.28%)/Al_2O_3 catalyst sample. A higher dispersion of Pt in SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 is probably the result of the dilution of platinum particles into smaller ensembles in presence of tin element.

2) It was stated that Sn-Pt interaction supports of alloy formation under reduction condition. The alloy formation between noble metal and reducible tin oxide was detected at 763 K on the the surface of SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 catalyst under hydrogen atmosphere. Pt-Sn alloy inhibits the chemisorption of hydrogen, cyclopropane on platinum.

3) It can be concluded that the alumina support influences the electrical properties of the supported components, namely the samples had conductivity values (0.3-10.5 nS) similar to that of support (0.4-13.8 nS). The samples exhibit an insulator like behavior around room temperature and with increasing the temperature those act as semiconductors. The propylene formation (as the product of cyclopropane isomerization) was detected at ~ 473 K. Around this temperature the bulk proton movement occurs by Grotthuss mechanism. It can be supposed that these mobile protons could be involved in adsorption of cyclopropane species on the catalytic surface with formation of $C_3H_7^+$ carbocations as intermediate species during the isomerization reaction.

4) It was observed that the addition of small amount of platinum to transition metal catalysts synergistically increases the CO oxidation to CO_2. Moderately higher number of carbonate and bicarbonate species was observed on SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 catalyst sample than on Pt(0.28%)/Al_2O_3 sample probably due to higher dispersion of platinum on the surface.

5) It was concluded that the studied catalysts were not active in selective oxidation (propylene : air ratio mixture 1:10) since CO_2 (CO) and water were formed as a main products. Platinum containing catalysts showed good catalytic activity for total propylene oxidation (conversion of 95-100% at 673 K). SnO_2(2.94%)-

$Pt(0.28\%)/Al_2O_3$ sample showed the highest selectivity (99.9%) for CO_2 formation under oxidation conditions. The presence of Pt facilitates the dissociative propylene adsorption and mobility of the surface lattice oxygen, as consequence it increases the rate of oxidation reaction.

6) In agreement with electrical conductivity results it was concluded that the $c-C_3H_6$ isomerization proceeds probably over Brönsted acid sites (via formation of $C_3H_7^+$ intermediate) of oxidized samples. Since Lewis acidity was detected on the samples studied the possible involvement of the Lewis acid sites (via formation of $C_3H_5^+$ intermediate) in cyclopropane isomerization could also be considered. Cyclopropane isomerization started at around 473 K and the increase of the reaction temperature (523 K) increased the reaction rate. The temperature increase up to 473 K for isomerization increased the proton mobility, i.e., the surface/bulk proton or hydride movement and thus reduced the strong adsorption of hydrocarbon species. The oxidized samples showed the following catalytic activity sequence for $c-C_3H_6$ isomerization at 523K:
$SnO_2(2.94\%)-Pt(0.28\%)/Al_2O_3 > Pt(0.28\%)/Al_2O_3 > Al_2O_3 > SnO_2(2.83\%)/Al_2O_3$.

7) It was observed that only the $Pt(0.28\%)/Al_2O_3$ exhibited high catalytic activity ($k= 6.8 \cdot 10^{-3}$ $mol \cdot g^{-1} \cdot s^{-1}$) and selectivity (nearly 100% of reacted cyclopropane was transformed to propylene) from reduced catalysts where isomerization probably takes place via the formation of the allyl radical intermediates.

8) It was concluded from cyclopropane isomerization studies that tin exists in different forms in $SnO_2(2.94\%)-Pt(0.28\%)/Al_2O_3$, depending on the pretreatment conditions of the catalyst (i) in an oxidized form, Sn^{4+} (SnO_2), resulting in a promoting effect; (ii) in reduced form, tin resulting poisoning effect “ligand-effect” due to blocking of the sites responsible for cyclopropane isomerization by formation an alloy.

9) SnO_2-Pt/Al_2O_3 was recommended as a catalyst for total oxidation of lower hydrocarbons (C_1-C_3) and also for environmental purposes (CO elimination). As an outcome the catalyst system has been scaled up at industrial level at ROMPETROL, VEGA Refinery, Romania.

Doktori (PhD) Értekezés Tézisei

Szén-monoxid és polipropilén környezetvédelmi szempontból javított oxidációjára, valamint ciklopropán izomerizációjára használt SnO_2-Pt/Al_2O_3 katalizátor felületkémiai vizsgálata

1. BEVEZETÉS

A katalizátorok jobb hatékonysága és a csökkentett káros anyag (például CO, szénhidrogén) kibocsátás miatt a szénhidrogének katalitikus oxidációját az utóbbi években különös figyelem kíséri. A katalitikus égetőrendszer a nyílt lángos égőnél kisebb hőmérsékleten működik, és a kisebb hőmérséklet egyúttal csökkentett CO- és NO_x kibocsátással jár. A félvezető oxidok (SnO_2, V_2O_5) oxidáló aktivitása közismert, és ezek az izomerizáció, valamint a C_1-C_3 szénhidrogének teljes vagy szelektív oxidálása és a szén-monoxid szén-dioxiddá való oxidálása lehetséges katalizátorainak tekinthetők. A tiszta félvezető katalizátorok alkalmazását kis (10-20 m^2/g) fajlagos felületük és rossz termikus stabilitásuk korlátozza. A fajlagos felület az aktív komponensek nagyobb (100-400 m^2/g) fajlagos felületű hordozóra (Al_2O_3, TiO_2, SiO_2) való felvitelével növelhető. Az ón (IV) oxid enyhén oxidáló katalizátor, de katalitikus tulajdonságai jelentős mértékben módosíthatók, ha impregnálással, együttes hidrolízissel, ioncserével vagy mechanikus keveréssel egyéb elemeket (nemesfémeket, antimont) építünk be a szerkezetbe. A hordozóra felvitt félvezető oxidok és különösen azok, amelyek platina adalékot tartalmaznak jobb katalitikus tulajdonságúak, mivel a szénhidrogének vagy a CO oxidálásának legaktívabb katalizátorai a nemesfémek. Az elkészített anyagot a katalitikus aktivitás elérése érdekében rendszerint kalcinálni kell.

A néhány oxidot tartalmazó szilárd minták fizikai-kémiai tulajdonságai és katalitikus aktivitása nagymértékben különbözik a csak összetett oxidok tulajdonságaitól. Ez annak tulajdonítható, hogy a „kevert oxidok” aktivitása különféle kölcsönhatások eredménye lehet. A különböző fémoxidokat tartalmazó minták esetén figyelembe kell venni az elektron hatásokat is. A katalizátorok elektron elmélete szerint a reakciók sebessége és aktiválási energiája a katalizátor Fermi szintjétől függ, így várható, hogy a fémoxidok vagy fémek és a hordozó közötti elektron kölcsönhatások módosíthatják a katalizátor Fermi szintjét. Ezért ez a kölcsönhatás befolyásolhatja a minta katalitikus aktivitását.

A katalizátorok sav-bázis tulajdonságai a reagensek aktiválása szempontjából szintén fontosak. A katalizátor erős vagy gyenge Lewis sav vagy bázis helyei határozzák meg a reagensek és a katalizátor aktív helyei közötti kölcsönhatások erősségét és az oxidációs, izomerizációs reakciótermékek kölcsönhatásait a szilárd anyag felületével, ami viszont meghatározza, hogy a reagens és/vagy a reakciótermékek könnyen adszorbeálódnak (és valószínűleg aktiválódnak) vagy a termékek könnyen deszorbeálódnak (megakadályozva a további átalakulásokat).

2. KÍSÉRLETI RÉSZ

A korund hordozóra felvitt ón-oxid mintát kétféle módszerrel, impregnálással és mechanikus keveréssel állítottuk elő. A Pt(0.28%)/Al_2O_3 impregnálással készült, és a Pt(0.28%)/Al_2O_3–hoz az SnO_2–t mechanikus keveréssel adtuk hozzá. Az elkészített anyagokat a felületi összetételre és katalitikus aktivitásra vonatkozó maximális mennyiségű releváns információ összegyűjtése érdekében részletesen megvizsgáltuk. A katalizátorok fizikai-kémiai tulajdonságait BET, ICP, XRD, XPS módszerekkel vizsgáltuk. A katalizátorok savas tulajdonságait tesztmolekulák (CO, Py és NH_3) adszorpciójának felhasználásával két alkalmas módszerrel, FTIR spektroszkópiával és adszorpciós mikrokalorimetriával vizsgáltuk. A felület Pt-eloszlásának meghatározására is a CO 303 K hőmérsékletű mikrokalorimetriás kemiszorpcióját alkalmaztuk. A katalizátor redukálhatóságát és stabilitását programozott hőmérsékletű redukciós (TPR) módszerrel redukáló atmoszférában tanulmányoztuk. A felületi réteg adszorpciós képességével és a felületi dipólusok mozgékonyságával kapcsolatos információ összegyűjtése, valamint a ciklopropán izomerizáció mechanizmusának jobb megértése érdekében „in situ” mértük az elektromos vezetőképességet (G) és kapacitást (C) inert atmoszférában ciklopropán – hélium 1:20 arányú elegye alatt méretük 293 – 623 K közötti hőmérsékleten.

Az előkezelés (oxidáció vagy redukció) alatt képződött felületi aktív helyeket (hidroxil csoportokat, anionos helyeket és felületi kationokat) CO-adszorpciós FTIR módszerrel vizsgáltuk szobahőmérsékleten; ezek a helyek közvetlenül részt vehetnek az adszorpcióban és/vagy karbonát vagy bikarbonát intermediereken keresztül a veszélyes szén-monoxid kevésbé veszélyes szén-dioxiddá oxidálásában.

A propilén oxidációt választottuk modellreakciónak ahhoz, hogy a katalizátor felületi viselkedéséről és aktivitásáról valós üzemi körülmények között, vagyis légköri nyomáson propilén gázáramban és oxigén jelenlétében elsődleges és releváns információt szerezzünk. Az elővizsgálat célja a katalizátor minták ellenőrzése a propilén akroleinné való szelektív oxidációja közben, 1:10 arányú (C_3H_6 : levegő) eleggyel. 1 : 22 arányú (C_3H_6 : levegő) eleggyel vizsgáltuk a platinát tartalmazó mintáknak a propilén teljes oxidációja (a fő termék víz és szén-dioxid) közben mutatott aktivitását is.

A ciklopropán izomerizációját választottuk tesztreakciónak, mert ez segítheti a katalitikus aktivitás és a különböző aktiválások (oxidáció, redukció) során képződő/módosított aktív helyek fajtája közötti korreláció meghatározását. A ciklopropán propilénné való izomerizációját 473 és 523 K hőmérsékleten, szakaszos reaktorban vizsgáltok. A reaktorhoz üveg gázkeringető rendszer kapcsolódott, amelyből kézi módszerrel vettünk mintákat a GC elemzéshez. Tanulmányoztuk a ciklopropán izomerizációjának mechanizmusát.

3. ÚJ TUDOMÁNYOS EREDMÉNYEK

A hordozóra felvitt katalizátorok katalitikus aktivitása a hordozó és a hordozóra felvitt ón- vagy/és platina-oxid fizikai, kémiai és elektronos tulajdonságai közötti kölcsönhatásokból ered. A kapott eredmények különösen fontosak a katalizátor ciklopropán izomerizációra és környezetvédelmi katalízisre, például szén-monoxid és szénhidrogének oxidációjára való lehetséges felhasználása szempontjából. Az újonnan készített SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 katalizátorral kapott vizsgálati eredmények fő következtetéseit az alábbiakban foglaljuk össze. Az SnO_2(2.83%)/Al_2O_3, SnO_2(3.10%)/Al_2O_3, Pt(0.28%)/Al_2O_3, Al_2O_3, SnO_2 katalizátor mintákat az összehasonlítás céljára használtuk:

1) Megállapítottuk, hogy önmagában az SnO_2 vagy platina-oxid felvitele fokozza az összes savas helyek számát (összeadódnak a hordozó Al^{3+} és a felvitt vegyületek Sn^{4+} és/vagy Pt^{n+} helyek) és erősségüket a katalizátor felületén. Ugyanakkor a platina- és ón-oxidok együttes jelenléte csökkenti az erősebb savas helyek erősségét, valószínűleg az ónból a platinába végbemenő elektronátadás következtében. Ez a hatás az Sn-Pt elektron kölcsönhatással magyarázható: az n típusú félvezetőként ismert SnO_2 a szilárd anyagban meg

tudja változtatni az elektronsűrűséget azáltal, hogy elektronokat ad át a PtO (p típusú félvezető) és az Al_2O_3 (gyenge n típusú félvezető) számára, így csökkenti a megfelelő Lewis helyek közül néhánynak a savas erősségét. A CO adszorpció mikrokalorimetriás vizsgálata azt mutatta, hogy a platina ionok az SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 felületén jobban eloszlanak, mint a Pt(0.28%)/Al_2O_3 katalizátor mintán. A platina SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 katalizátoron való jobb eloszlása valószínűleg a platina részecskék ón jelenlétében végbemenő, kisebb csoportokká való feloldódása.

2) Megállapítottuk, hogy az Sn-Pt kölcsönhatás redukáló körülmények között az ötvözetképződésnek kedvez. A nemesfém és a redukálható ón-oxid közötti ötvözetképződést 763 K hőmérsékleten észleltük hidrogén atmoszférában az SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 katalizátor felületén. A Pt-Sn ötvözet megakadályozza a hidrogén és ciklopropán kemiszorpcióját platinán.

3) Arra következtethetünk, hogy a korund hordozó befolyásolja a rávitt komponensek elektromos tulajdonságait, nevezetesen a minták vezetőképessége (0.4-13.8 nS) hasonló volt a hordozó vezetőképességéhez (0.3-10.5 nS). A minták szobahőmérsékleten elektromosan szigetelőként viselkednek, növekvő hőmérsékleten pedig félvezető tulajdonságokat mutatnak. A propilén képződését (a ciklopropán izomerizációjának termékét) ~ 473 K hőmérsékleten mutattuk ki. Ezen a hőmérsékleten a proton mozgás a Grotthuss mechanizmust követi. Feltételezhető, hogy ezek a mobil protonok az izomerizációs reakció alatt $C_3H_7^+$ karbokationok képződése mellett részt vehetnek a ciklopropánnak a katalizátor felületén való adszorpciójában.

4) Megfigyeltük, hogy az átmeneti fém katalizátorokhoz adott kis mennyiségű platina szinergikusan fokozza a szén-monoxid szén-dioxiddá való oxidációját. Az SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 katalizátor mintákon valamelyest nagyobb mennyiségű karbonát- és bikarbonát vegyületet észleltünk, mint a Pt(0.28%)/Al_2O_3 mintán, valószínűleg a platinának a felületen való nagyobb diszperziója miatt.

5) Arra a következtetésre jutottunk, hogy a vizsgált katalizátorok a szelektív oxidációra (propilén : levegő 1 : 10 arányú elegye) nem aktívak, mivel fő termékként CO_2 (CO) és víz képződött. A platina tartalmú katalizátor a teljes propilén oxidációra jó katalitikus aktivitást mutatott (95-100% konverzió 673 K hőmérsékleten). Oxidáló körülmények között a CO_2 képződésre az SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 minta mutatta a legnagyobb (99.9%) szelektivitást. A platina jelenléte megkönnyíti a disszociatív propilén adszorpciót és fokozza a felületi rács oxigének mozgékonyságát, aminek következménye az oxidációs reakció sebességének növekedése.

6) Az elektromos vezetőképességi eredményekkel összhangban arra következtettünk, hogy a c-C_3H_6 izomerizáció valószínűleg az oxidált minták Brönsted sav helyein halad előre ($C_3H_7^+$ intermedier képződésén keresztül). Mivel a vizsgált mintákon Lewis savasságot detektáltunk, a Lewis savas helyek lehetséges részvételét ($C_3H_5^+$ intermedier képződésén keresztül) a ciklopropán izomerizációjában szintén figyelembe lehet venni. A ciklopropán izomerizáció körülbelül 473 K hőmérsékleten indult meg és a reakcióhőmérséklet emelése (523 K) növelte a reakciósebességet. 473 K értékig a hőmérséklet növelése az izomerizáció esetében növelte a protonok mozgékonyságát, vagyis a felület és az anyag belseje közötti proton vagy hidrid mozgást, így csökkentette a szénhidrogén vegyületek erős adszorpcióját. Az oxidált minták 523 K hőmérsékleten a c-C_3H_6 izomerizációjára a következő katalitikus aktivitási sorrendet mutatták:
SnO_2(2.94%)-Pt(0.28%)/Al_2O_3>Pt(0.28%)/Al_2O_3>Al_2O_3 > SnO_2(2.83%)/Al_2O_3.

7) Megfigyeltük, hogy a redukált katalizátorok közül csak a Pt(0.28%)/Al_2O_3 mutatott nagy katalitikus aktivitást ($k= 6.8\cdot10^{-3}$ $mol\cdot g^{-1}\cdot s^{-1}$) és szelektivitást (a reagált ciklopropánnak csaknem 100%-a propilénné alakult); itt az izomerizáció valószínűleg allil gyök intermedierek képződésén keresztül megy végbe.

8) A ciklopropán izomerizációjának vizsgálatából arra a következtetésre jutottunk, hogy az SnO_2(2.94%)-Pt(0.28%)/Al_2O_3 rendszerben az ón a katalizátor előkezelési körülményeitől függően különböző formákban fordul elő: (i) oxidált, Sn^{4+} (SnO_2) formában, ami a folyamatot elősegítő hatású, valamint (ii)

redukált formában, fém ón formájában, ami az ötvözetképződés révén mérgező hatást, „ligandum hatást” fejt ki azáltal, hogy blokkolja a ciklopropán izomerizációért felelős helyeket.

9) Az SnO_2-Pt/Al_2O_3 a kisebb rendszámú (C_1-C_3) szénhidrogének teljes oxidációjára, valamint környezeti célokra (CO eliminálására) ajánlott. A kutatás hozadéka, hogy a katalizátor rendszer ipari szintű bevezetése folyamatban van a ROMPETROL Vega Finomítójában, Romániában.

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1. Rédey, Á., **Yuzhakova T.,** Lakó Janós: *Fenntartható Fejlődés és a Környezetgazdálkodás*, Balatonfüredi Környezetvédelmi Konferencia, Balatonfüred, Magyaroszág, október 24, 2006
2. Nasser, H., Rédey, Á., **Yuzhakova, T.:** *Környezetvédelmi Felhasználású Cézium Tartalmú Mo/*Al_2O_3 *Katalizátorok Struktúrája és Termikus Stabilitása*, Országos Környezetvédelmi Konferencia kiadványa pp. 285-233, Siófok, 2006. szeptember 19-21.
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