

H₂ reduction behaviors and catalytic performance of bimetallic tin-modified platinum catalysts for propane dehydrogenation

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Abstract

Bimetallic Pt–Sn/MgAl₂O₄ catalysts with different metal concentrations, used for propane dehydrogenation, were prepared by the impregnation, coprecipitation–impregnation and sol–gel methods. Pore size distribution and surface acidity of the catalysts were studied by N₂ physisorption and temperature programmed desorption of ammonia (TPD–NH₃), respectively. Reduction behaviors of the catalysts were characterized by temperature programmed reduction (TPR) technique. In the catalysts containing 0.6 wt.% Sn, some platinum-modified by tin crystals were produced by association with acid sites of the support, where hydrogen reduction took place above 500 °C. These tin-modified platinum species were found to be favorable for propane dehydrogenation reaction and also to be responsible for the improvement of the activity as tin content increases from 0.3 to 0.6 wt.%. Metal dispersion, pore size distribution and acidity of the support strongly impact the selectivity and stability of the catalysts. The sol–gel catalyst showed better selectivity but lower stability compared to other catalysts that can be explained by its very narrow pore size distribution and relatively stronger acidity as well as more homogeneous metal distribution on the support. When the catalysts were pretreated with oxygen and then hydrogen, their catalytic activities were significantly enhanced largely due to a better metal distribution on the support. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Propane dehydrogenation; Pt–Sn/MgAl₂O₄ catalysts; Tin effects; TPR; Catalytic stability; Acidity

1. Introduction

Catalytic dehydrogenation of light alkanes has great industrial importance because it represents an alternative for obtaining alkenes for polymerization and other organic synthesis from low cost saturated hydrocarbon feed stocks. Propane dehydrogenation is such an interesting research topic due to the potential use of the propane as a source of propene, which

is an important starting material in the petrochemical industries. Some processes such as OLEFLEX, Phillips STAR, CATOFIN, Linde BASF, etc. have been developed and well documented [1–3].

Bimetallic tin-modified platinum supported on different supports like Al₂O₃, ZrO₂, SiO₂, which are believed to be the promising catalysts used in the propane dehydrogenation process have been extensively investigated [4–7]. Tin is believed to inhibit hydrocracking, isomerization and coke formation [8–10]; addition of tin improves platinum dispersion due to favorable size ensemble formation based on geometric effects [11]. Also it was suggested that Pt–Sn alloy is formed at the

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ratio of Pt to Sn 1:1, that increases hydrogen mobility on the catalysts [4,12–14].

Most of the propane dehydrogenation catalysts are Pt–Sn supported on alumina. Owing to the very strong interaction between the metals and alumina support, that affects the reduction behaviors and stability of the catalysts; a few work have been focused on the use of some solid spinels such as magnesium aluminate or zinc aluminate, instead of alumina, as new support [15–17]. Under operation promoted platinum catalysts supported on magnesium-aluminate spinel have a good activity and stability. So far studies about dehydrogenation, in particular, propane dehydrogenation over Pt–Sn/MgAl₂O₄ catalysts, showed that a significant activity increase was obtained upon the introduction of various amounts of tin through several preparation methods [18,19].

It is the purpose of the present work to study the catalytic performance of bimetallic Pt–Sn/MgAl₂O₄ catalysts prepared by using different methods in the propane dehydrogenation reaction. For this kind of support, several questions arise: for instance, effects of the structures of the supports on the catalytic properties and the action of tin addition including the reduction behavior as well as interaction between the metal and support and different crystal phases located on the support need to be further clarified.

2. Experimental

2.1. Supports preparation

MgAl₂O₄ was prepared by coprecipitation of parents salts (Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O) with (NH₄)₂CO₃ as precipitating agent at a pH value of 10. The fresh sample was dried at 120 °C and calcined at 600 °C in air for 8 h. X-ray diffraction analysis showed that the calcined sample has spinel structure.

2.2. Catalysts preparation

2.2.1. Impregnation

The monometallic catalysts were prepared at 80 °C by impregnating a solution of SnCl₂·4H₂O or H₂PtCl₆·H₂O with ethanol as solvent on the calcined magnesium-aluminate spinel support in a rotatory

vacuum evaporator. The dried samples were calcined at 600 °C in a flow of air for 8 h.

The bimetallic Pt–Sn catalysts were prepared by a double impregnation of the support: firstly with an alcoholic solution of SnCl₂·4H₂O, dried at 120 °C and followed by an alcoholic solution of H₂PtCl₆·H₂O, finally dried at 120 °C for 4 h and calcined at 600 °C for 8 h in an air flow. The nominal compositions were for platinum 0.5 wt.% and for two tin compositions 0.3 and 0.6 wt.%.

2.2.2. Coprecipitation–impregnation

By using (NH₄)₂CO₃ as precipitating agent and Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, SnCl₂·4H₂O as precursors, three solutions were, respectively, prepared by dissolving the above three precursors in deionized water. The amount of SnCl₂·4H₂O was controlled to acquire 0.3 and 0.6 wt.% of metal tin. The above solutions, drop by drop, were simultaneously added into a container with a continuous stirring. The pH value of the mixture was fixed at about 10. After the addition, the mixture was aged for 10 h followed by washing, drying and finally calcined at 600 °C in a flow of air for 8 h. Afterwards, the calcined sample was impregnated with H₂PtCl₆·H₂O to obtain Pt–Sn/MgAl₂O₄ catalysts with 0.5 wt.% of metal platinum.

2.2.3. Sol–gel method

As an example, 0.5 wt.% Pt/MgAl₂O₄ sol–gel catalyst was synthesized by using metallic-organic compounds as precursors and alcohols as solvent. Magnesium ethoxide (Mg(OC₂H₅)₂) and aluminum *sec*-butoxide (Al(OC₄H₁₁)₃) were added into a container with 100 ml ethanol, the solution was stirred for 2 h. And then, H₂PtCl₆·H₂O was slowly dropped into the above solution to form a sol. Water was slowly added into the sol in a mole ratio of alcohols/H₂O of 10. The mixture was stirred and a gel was formed, afterwards the solvent was eliminated in a rotatory vacuum evaporator for 12 h. Finally, the sample was dried at 120 °C for 4 h and calcined at 600 °C in flowing of air for 8 h.

2.3. Pretreatment

Before the catalytic test, the catalysts were pre-treated with different methods:

He treatment. The samples were heated in the reactor at 550 °C for 2 h with a increasing temperature rate by 5 °C/min in a He flow for eliminating the adsorbed impurities.

H₂ reduction in situ. After the He treatment, the samples were treated with a stream of 99.99% H₂ in the reactor at 550 °C for 2 h in order to reduce metal oxide to metal particles.

Oxidation–reduction in situ. After treatment with He, the catalysts were first pretreated in the reactor in an air flow of 40 ml/min at 550 °C for 1 h and then flowing He was introduced into the reactor to purge out the oxygen from the reaction system. Finally a stream of 99.99% H₂ was introduced to the reactor to reduce the catalyst at the same temperature for 2 h.

2.4. Temperature programmed reduction (TPR)

The catalysts were first pretreated in a flow of He (30 ml/min) at 550 °C for 1 h, and then they were cooled to room temperature in He atmosphere. After the thermal treatment, the catalysts were reduced in a mixture of 10% H₂ in He at increasing temperature programmed to a rate of 10 °C/min up to 700 °C. Catalyst weight used for TPR measurements was about 0.1 g. The TPR experiments were carried out on a Zeton Altamire Model AMI-3 equipment.

2.5. Temperature programmed desorption of ammonia (TPD-NH₃)

To measure acidity of the catalysts, TPD-NH₃ experiments were carried out in a Zeton Altamire Model AMI-3 equipment. The samples were first treated in a He flow (30 ml/min) at 550 °C for 2 h, and then cooled to 100 °C. Ammonia (20 vol.%) was introduced in an He flow into the reactor for 30 min. Finally the samples were heated with increasing the temperature rate by 10 °C/min in a He flow to 700 °C.

2.6. Surface area and pore size distribution

The specific surface area and pore size distribution of the samples were measured in a Digisorb 2600 equipment by analyzing N₂ physisorption isotherms.

2.7. Catalytic test

Catalytic performance in propane dehydrogenation was tested at 550 °C and 590 Torr. In all the cases, 0.1 g of catalyst (80–120 mesh) and a total flow rate (v_0) of 4.8 l/h were used. An equimolar blend of propane and hydrogen was fed to the reactor. The total reaction time is 180 min. Before each reaction test, catalysts were pretreated under different conditions as described above.

The conversion of propane (X_A) is defined as the percentage of propane converted to all different products. The selectivity to propene (S) is defined as the amount of propene divided by the amount of reactant converted to all products. The main by-products observed were methane, ethane and ethylene. To describe deactivation curves, an overall first-order parallel deactivation mechanism was assumed. In most cases, the propane reaction was carried out at a low conversion. Based on the first-order for deactivation and the surface reaction kinetics, the following model can be derived from which the deactivation constants (k_d) were obtained [20]:

$$\ln \left[\frac{1 - X_A}{X_A} \right] = k_d t + \ln \left[\frac{1 - X_{A0}}{X_{A0}} \right]$$

where X_{A0} is the initial conversion of propane. The stability of the catalyst (E) was defined as

$$E = \frac{\text{conversion after 180 min of reaction}}{\text{conversion after 5 min of reaction}}$$

3. Results

3.1. Textural properties

The specific surface area and textural properties of the various catalysts were measured by low temperature physisorption of N₂ (Table 1). The specific surface area (A) increases and the mean pore diameter (D) of the catalysts decreases in following orders (1) and (2):

$$A_{\text{impregnation}} < A_{\text{cop-impregnation}} < A_{\text{sol-gel}} \quad (1)$$

$$D_{\text{impregnation}} > D_{\text{cop-impregnation}} > D_{\text{sol-gel}} \quad (2)$$

The pore size distribution profiles of the various catalyst samples are shown in Figs. 1–3. The pore diameters of the catalysts prepared by using sol–gel

Table 1

Amount of ammonia adsorbed and textural properties of various samples of Pt–Sn/MgAl₂O₄ catalysts

Catalyst	Preparation method	NH ₃ (μmol/g catalyst)	Surface area (m ² /g)	Pore diameter (Å)
0.5% Pt–0.3% Sn/MgAl ₂ O ₄	Impregnation	1041.8	132	480
0.5% Pt–0.6% Sn/MgAl ₂ O ₄	Impregnation	905.5	133	485
0.5% Pt–0.3% Sn/MgAl ₂ O ₄	Coprecipitation–impregnation	1179.6	170	350
0.5% Pt–0.6% Sn/MgAl ₂ O ₄	Coprecipitation–impregnation	863.1	149	200
0.5% Pt–0.3% Sn/MgAl ₂ O ₄	Sol–gel	1355.7	192	30
0.5% Pt–0.6% Sn/MgAl ₂ O ₄	Sol–gel	816.1	197	40

technique are very small, ranging between 30 and 50 Å (Fig. 3a and b), which is only one-tenth of the pore size of the catalysts prepared by using impregnation method (Fig. 1a and b). These results clearly

show that the preparation methods strongly affect the textural properties of the samples that must produce important effect on catalytic activity which will be discussed in the following section.

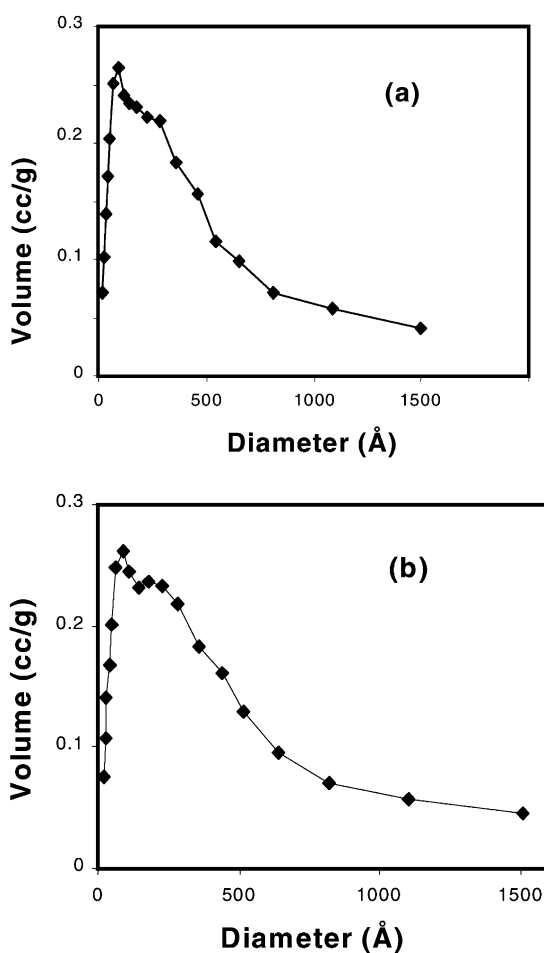


Fig. 1. Pore size distribution of the catalysts prepared by impregnation: (a) 0.5% Pt–0.3% Sn/MgAl₂O₄; (b) 0.5% Pt–0.6% Sn/MgAl₂O₄.

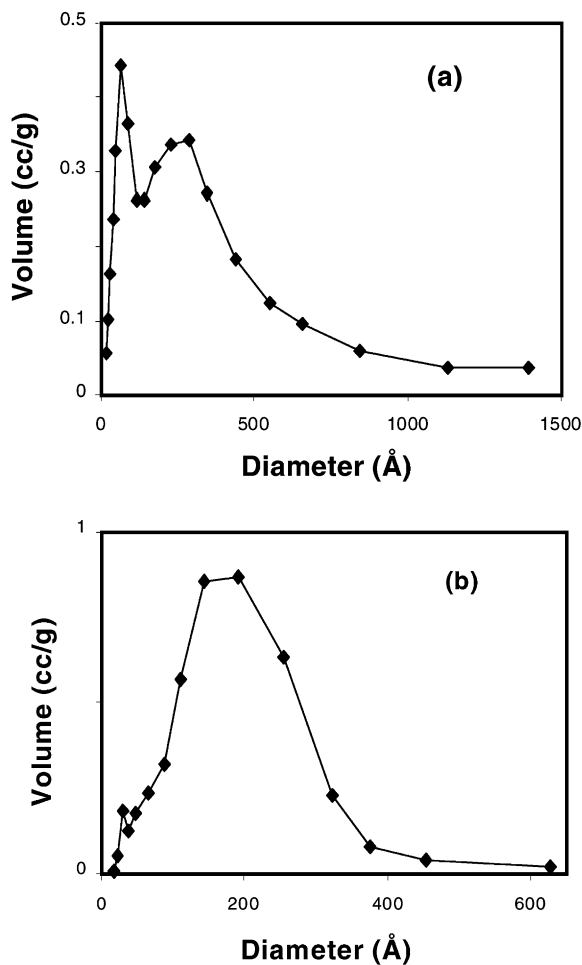


Fig. 2. Pore size distribution of the catalysts prepared by coprecipitation–impregnation: (a) 0.5% Pt–0.3% Sn/MgAl₂O₄; (b) 0.5% Pt–0.6% Sn/MgAl₂O₄.

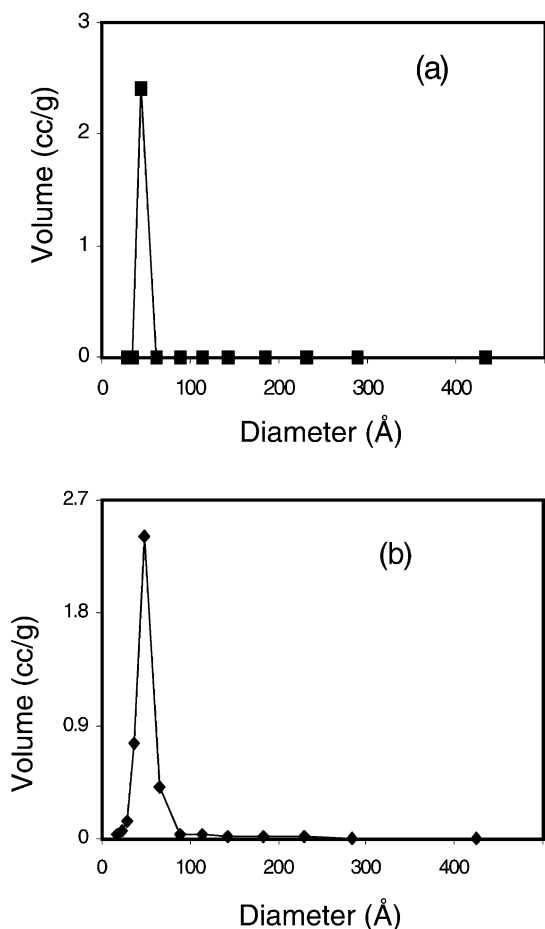


Fig. 3. Pore size distribution of the catalysts prepared by sol-gel: (a) 0.5% Pt–0.3% Sn/MgAl₂O₄; (b) 0.5% Pt–0.6% Sn/MgAl₂O₄.

3.2. Catalysts activation

It is observed in Fig. 4a that the catalysts pretreated with He showed the lower activity (<6% conversion). When the catalysts were reduced by hydrogen, the conversion of propane increased by 40% in comparison with the simple He pretreatment (Fig. 4b). When the catalyst was first oxidized with oxygen and then reduced by hydrogen (Fig. 4c), the propane conversions and stability were significantly increased. The stability (E) of the catalysts after different treatments increases in the following order:

$$E_{\text{oxidation-reduction}} > E_{\text{H}_2 \text{ reduction}} > E_{\text{He pretreatment}} \quad (3)$$

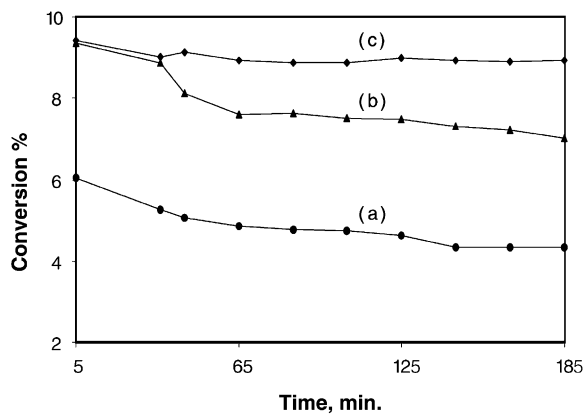


Fig. 4. Pretreatment effects on the catalytic activity of 0.5% Pt–0.3% Sn/MgAl₂O₄ catalyst: (a) He pretreatment; (b) H₂ reduction in situ; (c) oxidation and reduction in situ.

Enhancement of the catalytic activity after oxygen pretreatment is probably due to the formation of homogeneity of platinum and tin oxide phases that are completely reduced in the following H₂ reduction step compared with the catalysts with only H₂ pretreatment. In the latter case, the catalysts might contain other metal species like mixed oxicom-pounds related to the precursors used, their reduction mechanism could differ from that of pure oxide phases.

3.3. Effects of tin content

The activity of the catalysts was strongly affected by tin addition. Increasing tin content from 0.3 to 0.6 wt.%, results in about 30% increment in propane conversion for the catalyst prepared by the impregnation technique (Fig. 5a). Tin content, however, almost does not affect catalysts activity when coprecipitation–impregnation method was used (Fig. 5b). These results indicate that tin addition is favorable to enhance the catalytic activity but depends on catalyst preparation technique.

Tin content also affects catalyst stability. Table 2 reports the data concerning catalysts deactivation constants and catalytic stability. Increasing tin content from 0.3 to 0.6 wt.%, leads to a decrease in stability from 0.95 to 0.84 for the impregnated catalysts. However, for the coprecipitation–impregnation sample, the stability increases from 0.90 to 0.95.

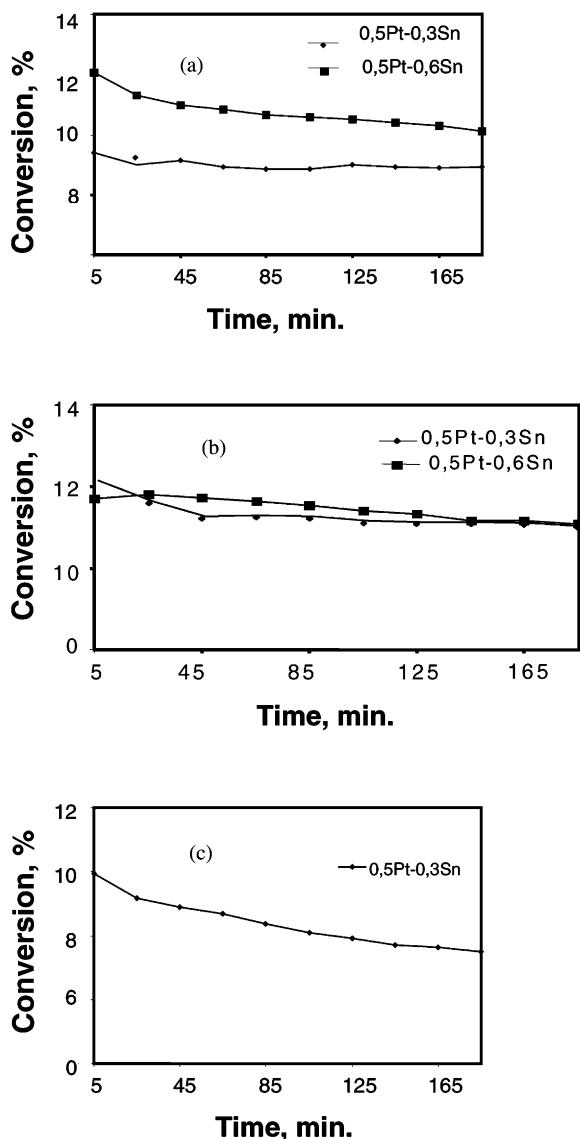


Fig. 5. Effects of tin addition on the catalytic activity. The 0.5% Pt–0.3% Sn/MgAl₂O₄ and 0.5% Pt–0.6% Sn/MgAl₂O₄ catalysts synthesized by: (a) impregnation; (b) coprecipitation–impregnation; (c) sol–gel.

3.4. Effect of catalysts preparation technique

In order to clarify the effect of the preparation techniques on the catalytic activity, Fig. 6 exhibits the conversion of propane over the 0.5% Pt–0.3% Sn/MgAl₂O₄ catalysts prepared by different meth-

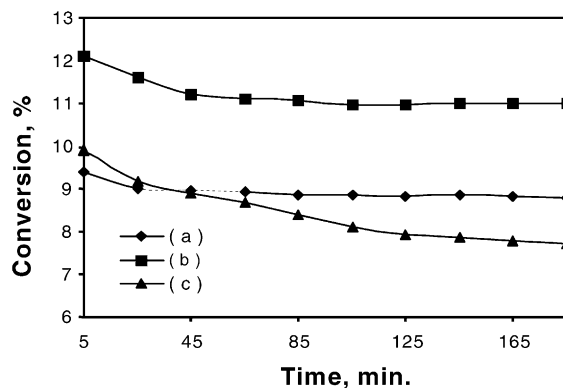


Fig. 6. Effects of preparation methods on propane conversion. The 0.5% Pt–0.3% Sn/MgAl₂O₄ synthesized by: (a) impregnation; (b) coprecipitation–impregnation; (c) sol–gel.

ods. Under the same reaction conditions, the catalysts prepared by coprecipitation–impregnation method (Fig. 6b) shows higher activity than the catalysts prepared with impregnation (Fig. 6a) and sol–gel (Fig. 6c) methods. Worthy of mention is that propane conversion rapidly decreased in the first 30 min of the reaction, indicating that this catalyst was easily deactivated on the fresh surface. After 30 min of reaction, the catalytic activities of impregnation and coprecipitation–impregnation samples almost remained unchanged in the following 150 min. However, the activity of the sol–gel sample decreased continuously. These results show that the different catalysts have different deactivation behavior. The deactivation constants of the different catalysts are shown in Table 2. The catalyst prepared by the sol–gel technique showed the bigger deactivation constant, leading to catalytic instability. For the catalysts with 0.6% tin, the deactivation rate (k_d) decreases in the following order:

$$k_{d\text{cop-impregnation}} < k_{d\text{impregnation}} < k_{d\text{sol-gel}} \quad (4)$$

The catalyst preparation techniques also have impact on selectivity of the reaction. All catalysts show a relatively stable selectivity to propene higher than 90% (Fig. 7). The sol–gel sample 0.5% Pt–0.3% Sn/MgAl₂O₄ exhibits the highest selectivity, 97% (Fig. 7e). The selectivity to propene (S) over the different catalyst are shown in sequences (5) and (6).

Table 2

Deactivation constants and stability of the catalysts

Catalyst	Preparation method	Deactivation constants ($k_d \times 10^{-4}$, min^{-1})	Stability (E^a , %)
0.5% Pt–0.3% Sn/MgAl ₂ O ₄	Impregnation	2.4	0.95
0.5% Pt–0.6% Sn/MgAl ₂ O ₄	Impregnation	8.9	0.84
0.5% Pt–0.3% Sn/MgAl ₂ O ₄	Coprecipitation–impregnation	4.1	0.90
0.5% Pt–0.6% Sn/MgAl ₂ O ₄	Coprecipitation–impregnation	1.54	0.95
0.5% Pt–0.3% Sn/MgAl ₂ O ₄	Sol–gel	15.5	0.76

^a E = activity measured at 180 min/activity measured at 5 min.

For the catalysts system of 0.5% Pt–0.3% Sn/MgAl₂O₄:

$$S_{\text{sol-gel}} > S_{\text{cop-impregnation}} > S_{\text{impregnation}} \quad (5)$$

For the catalysts system of 0.5% Pt–0.6% Sn/MgAl₂O₄:

$$S_{\text{cop-impregnation}} > S_{\text{impregnation}} \quad (6)$$

The observed difference in selectivity could be explained by the different Pt/Sn ratios due to the nature of the different preparation methods used. It is well known that it is not easy to achieve uniform Sn distribution across the support crystals by using impregnation preparation technique. Therefore, a part of the impregnated Pt remain separated from tin atoms, catalyzing cracking and other side reactions, which results in a lower propene selectivity.

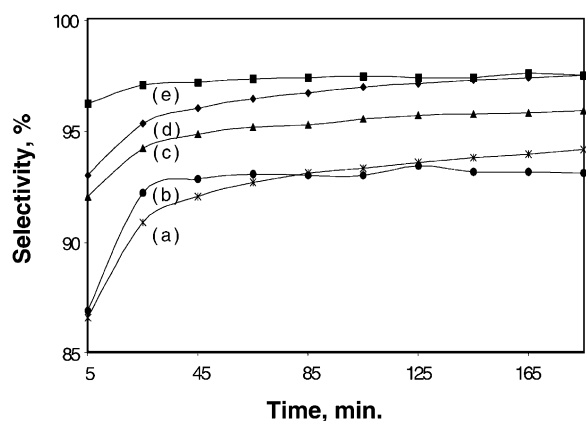


Fig. 7. Propene selectivity of Pt–Sn/MgAl₂O₄ catalysts: (a) 0.5% Pt–0.3% Sn/MgAl₂O₄ (impregnation); (b) 0.5% Pt–0.6% Sn/MgAl₂O₄ (impregnation); (c) 0.5% Pt–0.3% Sn/MgAl₂O₄ (coprecipitation–impregnation); (d) 0.5% Pt–0.6% Sn/MgAl₂O₄ (coprecipitation–impregnation); (e) 0.5% Pt–0.3% Sn/MgAl₂O₄ (sol–gel).

Coprecipitated–impregnated and sol–gel catalysts may have more uniform tin distribution involving higher degree of Pt–Sn alloy formation and therefore less side reactions.

3.5. Reduction behaviors of the catalysts

Fig. 8 shows the TPR spectra of the monometallic 0.5% Pt/MgAl₂O₄ catalysts prepared by impregnation and sol–gel methods. Two peaks were observed in TPR profiles for both samples: the first one ranging from 30 to 150 °C was centered at about 80 °C, it was assigned to the reduction from Pt(IV) to Pt(II). The second one centered at 330 °C corresponds to the reduction of Pt(II) ions to Pt⁰ atoms. However, it is noted that the second peak area is much bigger than the first one, indicating that in the second reduction stage more hydrogen was consumed. This is mostly due to the reduction occurring in the first stage is not complete. Therefore, it is suggested herein that in the first reduction stage, the PtO₂ crystals were only reduced

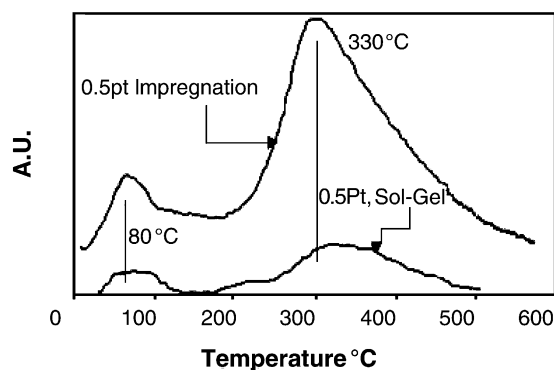


Fig. 8. TPR spectra of the catalysts 0.5% Pt/MgAl₂O₄ prepared by impregnation and sol–gel.

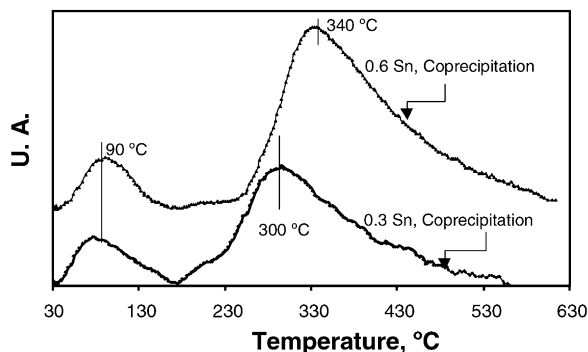
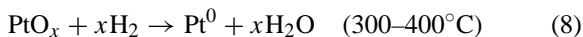
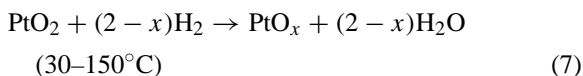


Fig. 9. TPR spectra of the catalysts 0.3% Sn/MgAl₂O₄ and 0.6% Sn/MgAl₂O₄ prepared by coprecipitation.

to PtO_x (1 < x < 2). These reduction steps can be illustrated in Eqs. (7) and (8):



Since some Pt atoms may be possibly buried in the bulk during the sol–gel procedure, the number of exposed Pt crystals is therefore less than that of the impregnation sample, resulting in smaller TPR area of the sol–gel sample in comparison with the impregnation one.

Fig. 9 shows the TPR spectra of two monometallic catalysts 0.3% Sn/MgAl₂O₄ and 0.6% Sn/MgAl₂O₄ prepared with coprecipitation method. There are also two peaks appearing in Fig. 9. The first one with smaller area ranging from 30 to 150 °C and the second with higher area is in between 150 and 550 °C. These two hydrogen consumption peaks, which are very similar to that observed in Fig. 8, were also caused by the reductions of SnO₂ to SnO_x (1 < x < 2) and SnO_x to Sn⁰. The only difference between the two profiles shown in Fig. 9 is the peak maxima of the second H₂ consumption peak slightly shifts 40 °C towards higher temperature when tin content increases from 0.3 to 0.6 wt.%.

The above results indicate that the reduction behaviors of monometallic platinum and tin-supported on magnesium-aluminate spinel are very similar. Their hydrogen consumption peaks are almost overlapped.

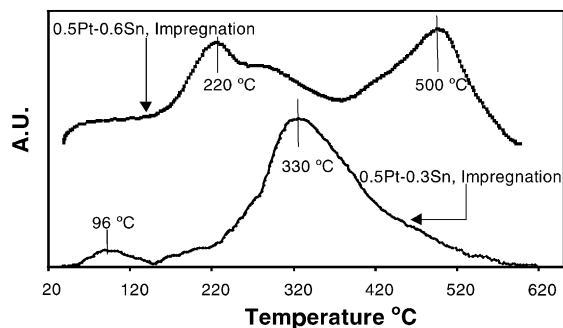


Fig. 10. TPR spectra of the catalysts 0.5% Pt–0.3% Sn/MgAl₂O₄ and 0.5% Pt–0.6% Sn/MgAl₂O₄ prepared by impregnation.

This produces difficulty in distinguishing the reduction properties of Pt–Sn bimetallic catalysts.

The TPR spectra of bimetallic Pt–Sn catalysts 0.5% Pt–0.3% Sn/MgAl₂O₄ and 0.5% Pt–0.6% Sn/MgAl₂O₄, prepared by impregnation method are shown in Fig. 10. For the sample with 0.3 wt.% tin, two peaks were observed: one centered at about 100 °C and the other at 330 °C, similar to the reductions of single metal-supported catalysts shown in Figs. 8 and 9. Because the similar reduction temperature regions of monometallic platinum and tin catalysts, we according to the above analysis assigned these two hydrogen consumption peaks in Fig. 10 to the coreduction of SnO₂ (PtO₂) to SnO_x (PtO_x) and of SnO_x (PtO_x) to Sn⁰ (Pt⁰).

When tin content increases to 0.6 wt.%, the TPR spectrum consists of three peaks (Fig. 10); the first two are similar to those shown in Fig. 9, they appear between 30 and 150 °C as well as between 150 and 400 °C, originated from the reductions of platinum and tin oxides to metal platinum and tin crystals. The third one corresponded to a reduction temperature between 400 and 620 °C and centered at 500 °C. Since this high temperature peak is related to tin content, it may be produced by the reduction of a platinum-tin oxide species, which will be further discussed in the following section.

The TPR spectra of the bimetallic catalysts prepared by sol–gel are shown in Fig. 11. An additional hydrogen consumption peak appearing at higher temperature range in the catalyst with 0.6 wt.% Sn was also clearly observed.

Fig. 12 shows the TPR spectra of the catalysts prepared by coprecipitation–impregnation technique. If

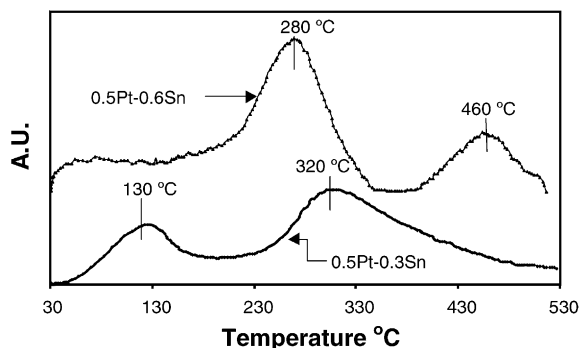


Fig. 11. TPR spectra of the catalysts 0.5% Pt–0.3% Sn/MgAl₂O₄ and 0.5% Pt–0.6% Sn/MgAl₂O₄ prepared by sol–gel.

one compares Figs. 10 and 11, some differences can be found with respect to Fig. 12: first, the low temperature peak shifts to about 200 °C; second, both catalysts have a third reduction peak with larger area. These differences can be explained by the different preparation techniques. These two catalysts were prepared by first introducing tin into the support by using coprecipitation method and then impregnating platinum on the support containing tin. Tin might strongly interact with the support by anchoring in the structure of the support. When platinum was supported on this kind of coprecipitation–impregnated support the interactions between platinum and tin oxides as well as metals and support are stronger than those shown by the catalysts prepared by impregnation and sol–gel. This alters their reduction properties, thus leading to a shift of reduction temperature of SnO₂ (PtO₂) to SnO_x (PtO_x) to higher values.

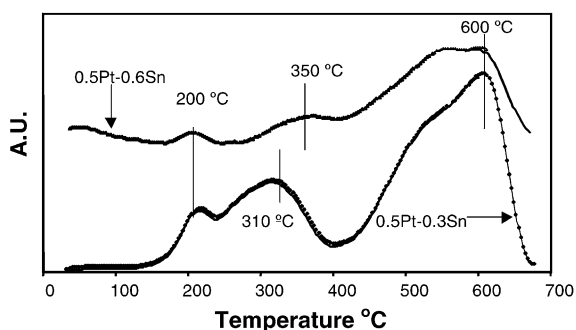


Fig. 12. TPR spectra of the catalysts 0.5% Pt–0.3% Sn/MgAl₂O₄ and 0.5% Pt–0.6% Sn/MgAl₂O₄ prepared by coprecipitation–impregnation.

4. Discussion

Several groups [6,18] report that in bimetallic Pt–Sn supported on Al₂O₃ catalysts, only one TPR peak was observed because most of tin exist in a form of SnO_x (0 < x < 2) and only a small part of tin is in zerovalent state forming alloys with platinum. This is due to the very strong interaction of tin and the support, which results in tin oxide stabilized on alumina. However, existence of tin oxide was not found in our catalysts since two or three reduction stages were observed after the H₂ reduction. This is also an indication of a weak interaction between metal oxides and magnesium-aluminate spinel, particularly in the cases of low tin content on the catalysts prepared with impregnation or sol–gel techniques.

The Pt–Sn alloy phases can be formed in Pt–Sn catalyst containing a 1:1 Pt/Sn ratio [4]. These Pt–Sn alloy particles are homogeneously distributed on the surface of the support. At lower Pt/Sn ratio, Pt₃Sn or PtSn metal species can also be formed [12–14]. Therefore, in the 0.5% Pt–0.3% Sn/MgAl₂O₄ catalysts, the observation of two peaks in the TPR spectra indicates that they are not only probably caused by the reduction of platinum or tin oxide to form metal particles but to form Pt–Sn alloyed phases also.

An important information revealed from the TPR measurements is found in the sol–gel and impregnation samples, only two peaks were formed in the TPR spectra in the sample containing 0.3% tin but three peaks in the samples with 0.6 wt.% of tin (Figs. 10 and 11). This may be responsible for the difference of propane dehydrogenation between catalysts with different tin content. As mentioned above, in the catalysts prepared by using sol–gel and impregnation methods, the activity was improved as tin content increased from 0.3 to 0.6 wt.%. The appearance of the third peak in the TPR spectra of the catalysts containing 0.6 wt.% Sn strongly indicates that some stable tin crystal structure that is reduced at high temperature could be responsible for the activity enhancement.

The above suggestion regarding the effect of tin on activity is also supported by the results obtained from the catalysts prepared by coprecipitation–impregnation method. As shown in Fig. 5b, the conversions of propane on the 0.5% Pt–0.3% Sn/MgAl₂O₄ and 0.5% Pt–0.6% Sn/MgAl₂O₄ catalysts prepared by coprecipitation–impregnation, are very similar and

they are much higher than that performed on the 0.5% Pt–0.3% Sn/MgAl₂O₄ catalyst synthesized by sol–gel and impregnation techniques (Figs. 5 and 6). This can be explained by their TPR behaviors. In the coprecipitation–impregnation samples, the TPR spectra show three peaks (Fig. 12). The first one is in the temperature region lower than 250 °C, the second is in between 250 and 400 °C and the third is in between 400 and 700 °C. In these three peaks, the relative area of the third is the largest, which reveals that the metal crystals reduced at higher temperature are the main component for these two samples. In comparison with the TPR spectra of the impregnation and sol–gel samples (Figs. 10 and 11), the third peak in both coprecipitation–impregnation samples are much bigger. Therefore, the activities of these coprecipitation–impregnation samples are higher and due to the similar area of the third H₂ consumption peak, their catalytic activity is also very similar on the catalysts prepared by coprecipitation–impregnation.

One question arises: what structure corresponds to the metallic crystals produced by reduction temperature above 500 °C? One is confirmed that these crystals must relate to high tin content. However, it is difficult to understand why in the mono-tin-supported catalysts with 0.6% tin, the TPR peak at above 500 °C was not observed (Fig. 9). This also indicates that the metal crystals reduced at high temperature are not only related to tin content but to platinum also. It may correspond to a metallic Sn modified by metallic platinum, similar to the suggestion made by Arteaga et al. [19], that in the tin-rich Pt–Sn/Al₂O₃ catalyst, after being reduced, some Pt atoms were covered with Sn atoms. This result is also similar to the work reported by Humblot et al. [21], who postulate that there exist many platinum crystals surrounded by tin atoms on the Pt surface, forming so-called “sites isolation platinum crystals” in the bimetallic Pt–Sn/SiO₂ catalyst, that are responsible for the extremely selective dehydrogenation process of isobutane to isobutene.

TPD–NH₃ measurements show that in the tin-rich samples, the acidity of the catalysts decreased (Table 1) when tin content increases from 0.3 to 0.6%, the amount of adsorbed ammonia, respectively, decreases for the impregnation sample from 1041.8 to 905.5 μmol NH₃/g, for the coprecipitation–impregnation sample from 1179.6 to 863.1 μmol

NH₃/g and for the sol–gel sample from 1355.7 to 816.1 μmol NH₃/g.

It seems from the acidity data that increasing tin concentration poisons acid sites (Table 1). It is well-known that many acidic sites exist on the support, since the relatively low metal concentration applied in our catalysts, most surface of the support is not occupied by the metals. Therefore, some of tin species in the tin-rich case, might be directly located on the acid sites in the support, diminishing their number. This is also in agreement with the other claims that deactivation of acidic sites on the alumina support is caused by the spreading of tin species over the alumina surface [22–25]. From this, we assumed that the crystals which could be reduced by hydrogen at higher temperature were produced by platinum-modified tin species in association with the acidic sites in the support.

The reduction of a number of acid sites can suppress acid catalytic cracking reactions, which implies an improvement of selectivity to dehydrogenation products. Since tin addition reduces the number of the acid centers, the selectivity to propene can hence be enhanced as shown in Fig. 7. However, the factors influencing the selectivity of propane dehydrogenation are very complex. It is a function of preparation methods, acidity and metal loading, and it is also sensitive to catalysts textural structure. As shown in Fig. 1, the catalysts prepared by the impregnation show a much wide pore size distribution ranging from 10 to 1000 Å and for coprecipitation–impregnation catalysts, it was doubly distributed in relatively wide range between 10 and 700 Å (Fig. 2). However, for the sol–gel sample with 0.3% Sn, the pore size was uniformly distributed in a very narrow range between 10 and 40 Å and it was centered at about 30 Å (Fig. 3a). In another sol–gel sample with 0.6% Sn, also single pore size distribution was observed in a very narrow range between 10 and 80 Å. Generally, the narrow pore size distribution has the function for shape-selection of the reactant and products. In other words, it favors the dehydrogenation but not the cracking reactions. Thus the propene selectivity is higher on the sol–gel catalysts. It is concluded from this result that propane dehydrogenation to propene is a catalyst textural-sensitive reaction.

On the other hand, sol–gel catalysts present a stronger acidity than the others, due to the acidic catalyzing action, more coke is formed on both the

metallic crystals and support. In the very narrow pore channels in sol–gel catalysts, coke is easily accumulated in the channel and is difficult to move out of the sample. The coke might cover the active sites or block the pore mouth, resulting in a rapid deactivation. This is reasonable to explain why the catalytic activity of the sol–gel catalysts is unstable.

It is also noteworthy that in the initial stage of the reaction, all the catalysts show a decrease in activity but an increase in selectivity to propene as the reaction time increases to 30 min. This is most likely due to the rapid coking occurring in the metallic sites that are active for cracking reaction in the beginning of the reaction. The produced coke or carbon deposit may preferentially covers these sites and poison the cracking activity, leading to reduction of the total conversion, as a result, it relatively enhances the selectivity to propene.

5. Conclusions

The H₂ reduction behaviors of bimetallic Pt–Sn/MgAl₂O₄ catalysts are related to tin content and preparation techniques, in the samples with 0.3 wt.% Sn, when the sol–gel and impregnation techniques were applied, there are two hydrogen consumption peaks, respectively, centered at about 100 and 330 °C, corresponding to the reduction steps of PtO₂ and SnO₂ to PtO_x and SnO_x (1 < x < 2) and then to Pt⁰ and Sn⁰. In the samples with 0.6 wt.% Sn, besides the platinum and tin phases present, a new kind of tin species were produced, which strongly interacted with the support in the presence of platinum, it could only be reduced up to 500 °C. This kind of platinum-modified tin crystals are responsible for the improvement of the catalytic activity of tin-rich samples.

Tin content showed very important effects on the catalyst acidity. Increasing tin content results in a remarkable reduction of acidity of all the catalysts prepared by different methods, this is a strong indication that some of tin species in the tin-rich samples poison the acid sites on the support by tin interaction with these acid centers.

Metal distribution, pore size distribution and acidity, shows that they strongly depend on the different preparation methods, affecting the selectivity and stability of the catalysts. The sol–gel catalyst shows very narrow

pore size distribution and a larger number of acid sites as well as higher metal distribution, which benefit not only the dehydrogenation reaction but coke formation also, therefore the sol–gel catalyst shows higher selectivity to propene but lower catalytic stability.

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