Pt–Sn/Al$_2$O$_3$ sol–gel catalysts: catalytic properties

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Abstract

Platinum–tin supported catalysts at various tin and platinum contents were prepared by the sol–gel method by adding tetrabutyltin to a homogeneous solution containing aluminum tri-sec-butoxide (TBA). After gelation, the solids were dried, calcined and then impregnated with an aqueous solution of hexachloroplatinic acid. Catalysts prepared by this method show specific BET areas around 270 m^2/g and platinum dispersion up to 90%. Ammonia adsorption shows that there are less acidic sites in tin–alumina sol–gel preparations than in sol–gel alumina. Activity measurements for n-heptane dehydrocyclization show that Pt–Sn sol–gel catalysts are more active than catalysts prepared by successive impregnation of a commercial alumina. Moreover, selectivity to benzene formation was found 54% lower with sol–gel catalysts than with commercial based catalysts. A high tolerance to thiophene poisoning during n-heptane dehydrocyclization was also found. Additional catalytic tests for cyclohexane dehydrogenation, isopropanol dehydration and toluene dealkylation were performed. High selectivity to acetone in the dehydration reaction and very low activity for toluene dealkylation were found for sol–gel preparations. The high activity in n-heptane dehydrocyclization and the high selectivity to acetone in Pt–Sn–alumina sol–gel catalysts was interpreted as a result of the modification by tin of the support acidity. Nevertheless, the tolerance to thiophene poisoning and the low dealkylation rate observed for sol–gel preparations can only be explained by an important tin–alumina support effect on platinum activity.

Keywords: Sol–gel catalysts; Platinum–tin catalysts; n-Heptane; Dehydrocyclization; Cyclohexane; Dehydrogenation; Toluene; Dealkylation; Coke deactivation; Thiophene poisoning

1. Introduction

Highly dispersed platinum catalysts and platinum-containing bimetallic catalysts are widely used for the naphtha reforming in the petroleum industry. In the 60's the first Pt–Re promoted catalysts appeared [1]. Since then, numerous other bi- or multimetallic catalysts have been developed and used industrially [2]. A distinc-

tion can be made between two groups of bimetals catalysts used for reforming processes. Pt–Re and Pt–Ir are placed in the first group as their activity is comparable to that of platinum monometallic catalyst. Bimetallic catalysts are more stable and can thus be used at lower pressures than conventional monometallic ones. In the second group (Sn, Ge, Pb) tin is the more widely used [3], it is less active than catalysts containing Pt–Re or Pt–Ir. However, tin provides increased stability and produces the same

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octane number gasoline in comparison to monometallic catalysts without the need to increase the operating temperature. A large amount of work has been devoted to understand the role of tin in reforming catalysts. The formation of alloys, tin–aluminates and presence of unreduced tin has been demonstrated using a variety of techniques [4–10], however, their role is still controversial.

Burch and Garla [11,12] tested a series of Pt–Sn/Al$_2$O$_3$ catalysts in the conversion of n-hexane, methylcyclopentane and cyclohexane. They concluded that tin modifies both the acidity of the support and the electronic properties of platinum, the main effect being to reduce the activity in cracking/coking reactions.

Dautzenberg et al. [13] reported the catalytic activity for n-hexane conversion of Pt–Sn supported on alumina and silica. Their results show a drastic lowering of the reaction rate in the case of silica supported catalysts. The formation of Pt–Sn alloys were suggested on silica while tin oxide instead of metallic alloys were proposed in the case of the alumina support.

The properties of the catalyst are strongly dependent on the preparation techniques used. Important changes in catalytic activity are obtained by a two-step impregnation, first tin and then platinum [13,14]. The use of organic solvents [4,15,16] is also reported as a good method to obtain better performing Pt–Sn catalysts. However, if formation of platinum–tin alloys is the goal of the preparation, then co-impregnation with H$_2$PtCl$_6$ and SnCl$_2$ or the use of a soluble Pt–Sn complex are recommended [17].

Alternative methods of preparation close to industrial ones [3] i.e., addition of tin to an alumina gel must be sought. In this respect, the sol–gel method seems to be the most promising [18]. Briefly, it consists in the addition of tetrabutyltin to a n-butanol solution containing aluminum tri-sec-butoxide. The resultant gel is dried and treated in air at 300°C and later impregnated with hexachloroplatinic acid. Precursor and support interactions during the synthesis steps were characterized by UV–Vis and FT-IR spectroscopies [19]. A strong interaction between the Pt precursor and the support is reported. As a consequence of such interaction, platinum dispersions up to 90% are obtained [20]. Moreover, catalyst characterization by energy dispersive X-ray microanalysis (EDX) transmission electron microscope technique shows that only Pt emission was detected in the sol–gel preparations. On the contrary, both platinum and tin were detected in samples prepared by successive impregnation of a commercial alumina. The absence of tin emission in sol–gel catalysts was interpreted as an evidence of the formation of bulk tin–aluminates [20].

The advantages of the sol–gel catalysts must be sustained by their improved catalytic properties. In this regard, this paper shows results for n-heptane dehydrocyclization, cyclohexane dehydrogenation, toluene dealkylation and isopropanol dehydration. Side reactions like thiophene poisoning and coke deactivation were also studied.

2. Experimental

2.1. Preparation of catalysts

Catalysts were prepared by gelling tetrabutyltin and aluminum tri-sec-butoxide in n-butanol. The mixture was refluxed until a gel was formed. The resultant solid was dried at 70°C for 12 h and then treated at 300°C for 3 h. This thermally treated sol–gel support (Sn/Al$_2$O$_3$ sol–gel) was later impregnated by an incipient wetness technique using hexachloroplatinic acid. Concentration of Sn and Pt were calculated to obtain samples with metal content between 0.3 and 1.0 wt.-%. Sol–gel catalysts are labeled as Pt–Sn-0-0-0-0, where the figures indicates the Pt and Sn concentrations respectively. In addition to the sol–gel samples, as reference, monometallic and bimetallic catalysts were prepared using commercial alumina. Wet impregnation was used to impregnate commercial alumina (used as re-

ceived) Rhone Poulenc SCS 250, BET 250 m^2/g; hexachloroplatinic acid was used for the platinum impregnation. For the bimetallic catalyst, an n-butanol solution of tetrabutyltin was used to impregnate the support, the solid was dried and treated at 300°C in air and later impregnated with the hexachloroplatinic solution. These catalysts were labeled Pt-I-0.3 and Pt-Sn-0.3-0.3 where the figures indicate metal content.

After hexachloroplatinic impregnation, all sol–gel and commercial impregnated samples were dried at 70°C, later calcined at 500°C in air and finally reduced at 500°C in flowing hydrogen for 3 h prior to characterization.

2.2. Characterization techniques

Surface areas were evaluated by the BET method using nitrogen as an adsorbent (Micromeritics ASAP 2000). Values of platinum metal dispersion (percentage exposed) were calculated from CO uptakes measured at 70°C and 100 Torr of gas pressure in a Cahn Electrobalance as described elsewhere [20].

Ammonia pulse chemisorption analysis was performed using a conventional static adsorption system. Samples were evacuated at 500°C for 1 h and then exposed to ammonia gas at 200°C. A 'total acidity' was then calculated from the amount of adsorbed ammonia.

Temperature-programmed desorption (TPD) profiles were also recorded in flowing He using a thermal conductivity detector. The position of the temperature maximum of such curves is a qualitative indication of the relative acid strength of the particular site.

2.3. Catalytic tests

The n-heptane dehydrocyclization, cyclohexane dehydrogenation, isopropanol dehydration and toluene dealkylation reactions were performed in flowing hydrogen in a conventional continuous flow microreactor system coupled to a gas chromatograph. Typically, tests were done

with 10–20 mg of catalyst sample reactivated in situ at 500°C in flowing hydrogen. The hydrogen subsequently feed the reactant by a saturator system. The n-heptane conversion was performed using a partial pressure equal to 11.0 Torr at 475°C. In the case of cyclohexane the partial pressure of the hydrocarbon was 57.9 Torr and the temperature 400°C. Isopropanol reaction was done with a partial pressure of 22.4 Torr at 200°C and lastly, the toluene reaction was carried out at 6.5 Torr and 500°C.

2.4. Deactivation study

Some deactivation was observed in the course of time for several reactions studied Deactivation was studied using the deactivation law previously reported for platinum [21], rhodium [22] palladium [23] and ruthenium [24]. Briefly, the deactivation constant was calculated using the equation proposed by Levenspiel [25] and modified by López et al. in their study of deactivation by coke on ruthenium sol–gel catalysts [26].

The activity decay obeys a hyperbolic law, from which the homographic decay is of second order. According to Levenspiel [25], the rate constant of deactivation can be obtained, since the hyperbolic law is a particular form of a more general rate law proposed by Levenspiel.

2.5. Nomenclature

The activity a is defined as the ratio of the reaction rate at time t to the reaction rate at time zero, $-r_A$ the rate of reaction of A, r_0 the initial rate of reaction of A, k_h the rate constant for A, C_A the reactant concentration (mol/L), n the reaction order for the main reaction, and W the weight of the catalysts (g). F_{A0} is the feed rate of reactant A (mol/s), C the fractional conversion of A, C_0 the initial conversion, k_d the rate constant for deactivation, and $k_d = k_e k_h$; m is the order of deactivation, t the time, and k_e

the experimental rate constant deactivation. For the reaction rate we can write:

$$-r_A = r_0 a \tag{1}$$

where r_0 is expressed by

$$r_0 = k_h C_A^n \tag{2}$$

taking an experimental order of zero ($n = 0$), Eq. 2 becomes

$$-r_A = k_h a \tag{3}$$

A differential reactor at low conversion can be considered, as well as mixed reactors, therefore the reaction rate is,

$$\frac{W}{F_{A0}} = \frac{C}{-r_A} \tag{4}$$

substituting Eq. 4 into Eq. 3 yields

$$k_h = \frac{C F_{A_0}}{a W} = \frac{F_{A_0} C_0}{W} \tag{5}$$

where C_0 is the initial conversion $(C/a)_{t=0}$ the deactivation law is given by

$$-da/dt = k_d a^m \tag{6}$$

since the hyperbolic law gives an order of 2 ($m = 2$)

$$1/a = k_d t + 1 \tag{7}$$

from Eqs. 5 and 7

$$\frac{1}{C} = \frac{k_d F_{A_0} t}{k_h W} + k'_e \tag{8}$$

$$1/C = k_e t + k'_e \tag{9}$$

with

$$k'_e = \frac{F_{A0}}{k_h W} \tag{10}$$

and

$$k_e = \frac{k_d F_{A0} t}{k_h W} \tag{11}$$

By plotting the reciprocal of the conversion as a function of time, we obtain a k_e slope. Considering that the feed rate and the weight of the catalysts are constant, we can write:

$$k'_d = k_h k_e \tag{12}$$

However, to maintain the mass and feed rate constant to compare the behavior of various catalysts is difficult. To avoid this problem in the graphic representation, we propose the following equations. From Eqs. 5 and 7

$$\frac{1}{C} = \frac{F_{A_0}}{W k_h} + \frac{F_{A_0}}{W k_h} k_d t \tag{13}$$

$$\frac{1}{C} = \frac{1}{C_0} + \frac{1}{C_0} k_d t \tag{14}$$

and then

$$C_0/C = 1 + k_d t \tag{15}$$

By the use of Eq. 14, the k_d values can be obtained directly.

Deactivation by thiophene was performed by adding 50 ppm of thiophene to the reactant mixture. The deactivation with thiophene in n-heptane dehydrocyclization was observed as a first order reaction. The model proposed by Levenspiel [25] can be used which assumes separability of the rate equations. The reaction scheme may be written:

$$n\text{-heptane} \xrightarrow{k} \text{products}$$

$$\text{thiophene} \xrightarrow{k_{ds}} \text{S (adsorbed) butane}$$
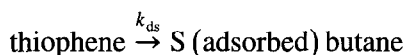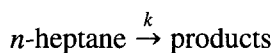
where n-heptane dehydrocyclization and thiophene conversion proceed side by side. The rate equation can be written as:

$$r = k C_A^n a \tag{16}$$

$$r_d = -\frac{da}{dt} = k_{ds} C_p^m a^n \tag{17}$$

with $a = r/r_0$. The values of the exponents m and n were determined and are respectively equal to 0 and 1.

$$r/r_0 = \exp(-k_{ds} t) \tag{18}$$

where k_{ds} represents the rate constant for the deactivation in the presence of thiophene and r and r_0 represent the reaction rate at time t and time zero respectively [27]. From the graph of the logarithm of conversion versus time, a

Table 1
Characterization of Pt and Pt–Sn/Al$_2$O$_3$ catalysts

Catalysts	BET area (m^2/g)	Dispersion [a] (%)	Particle [b] size (Å)	Acidity (meq/g)
Pt–Sn-0.3-0.3	264	90	10	0.34
Pt–Sn-1.0-0.3	277	50	20	0.26
Pt–Sn-0.3-1.0	280	90	10	0.29
Pt–Sn-I-0.3-0.3	230	50	20	0.30
Pt-I-0.3	230	63	16	0.29
Al$_2$O$_3$ sol–gel	231	–	–	0.32
Commercial Al$_2$O$_3$	250	–	–	0.37
Sn/Al$_2$O$_3$ sol–gel	265	–	–	0.23

[a] Determined by CO chemisorption.
[b] From CO dispersion.

straight line is obtained whose slope is the deactivation constant.

3. Results

BET surface areas, platinum dispersion and mean platinum particle size diameter are summarized in Table 1. As can be seen, BET areas for the various sol–gel catalysts are between 264 and 280 m^2/g and close to 230 m^2/g for the commercial alumina sample. The mean pore diameter corresponds to pores of 60–80 Å, very close to that shown by the commercial alumina support used for impregnated catalysts (85 Å).

Concerning the calculated metallic dispersion values for the sol–gel catalysts, the results show a Pt metal content effect in dispersion.

Catalysts at low platinum content (0.3 Pt wt.-%) show high dispersion value (90%) while in sample with 1.0 wt.-% Pt dispersion is only 50%. An effect of Sn in Pt dispersion cannot be detected if one compares samples with 0.3 and 1.0 Sn wt.-%. At high metal platinum content 1.0 wt.-% a positive tin effect can be speculated if one compares the dispersion of 50% with the low one dispersion obtained in catalysts at 0.3 wt.-% Pt prepared by impregnation of the commercial alumina support.

Dispersion values of 63 and 50% have been obtained for the commercial alumina (Pt-I-0.3 and Pt–Sn-I-0.3-0.3) impregnated catalysts, respectively (Table 1). Literature data for Pt/Al$_2$O$_3$ commercial alumina impregnated catalysts reports Pt dispersions of 90%. However, such dispersion must depend of the commercial support used for impregnation. It seems then, this is not the case when SCS alumina is used as received and impregnated under the same conditions used for the sol–gel catalysts.

The effect of tin during the gelation of the TBA can be observed in Table 1. The sol–gel alumina support shows an acidity value of 0.32 meq NH$_3$/g, while in the sol–gel tin–alumina support the acidity is 0.23 meq NH$_3$/g. This result show that co-gelation of tetrabutyltin and TBA modifies the total acidity. For the sol–gel Pt–Sn samples the acidity is between 0.28 and 0.34 meq NH$_3$/g. Moreover, one observes differences in the TPD profiles between the case of the sol–gel Pt–Sn catalysts and the alumina sol–gel (Fig. 1) or Sn–alumina sol–gel preparation. In sol–gel platinum–tin catalysts weak and

Table 2
Isopropanol dehydration on Pt and Pt–Sn/Al$_2$O$_3$ catalysts

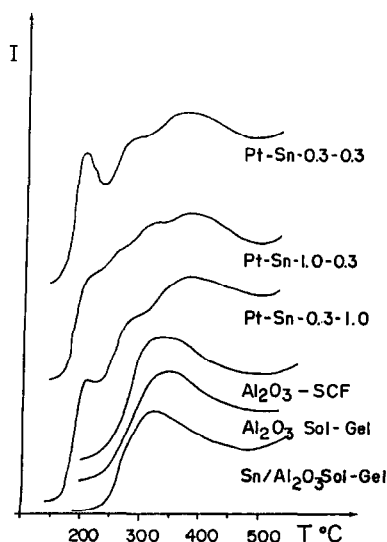| Catalysts	Conversion (%)	Rate mol/g · s (10^6)	Selectivity (% mol)	
			propene	acetone
Pt–Sn-0.3-0.3	3.9	1.9	40.9	50.1
Pt–Sn-1.0-0.3	33.8	135.6	25.6	74.4
Pt–Sn-0.3-1.0	20.2	56.6	20.1	79.9
Pt–Sn-0.3-0.0	14.7	39.2	58.8	41.2
Pt–Sn-I-0-3-0.3	10.3	4.1	10.5	89.5
Pt-I-0.3	25.2	33.5	51.4	49.6
Al$_2$O$_3$ sol–gel	1.5	0.1	77.2	22.8
Commercial Al$_2$O$_3$	11.0	5.2	86.0	14.0
Sn/Al$_2$O$_3$ sol–gel	1.0	0.4	32.0	68.0

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Fig. 1. Ammonia thermodesorption for Pt–Sn/Al$_2$O$_3$ sol–gel catalysts.

strong sites are noted. The modification of the TPD support profile is certainly caused by the effect of hexachloroplatinic acid impregnation.

To study the extent of the modification produced by tin on the alumina support, the isopropanol dehydration was performed with the various catalysts. The results of Table 2 show that the effect of tin on the support acidity is of importance, since both activity and selectivity are largely affected. In tin–alumina sol–gel preparation the main product is acetone, while on the alumina sol–gel or commercial alumina the main product was propene.

The results obtained in the catalytic conversion of n-heptane dehydrocyclization are shown in Table 3. The activity per site (TOF) for the

various Pt–Sn/Al$_2$O$_3$ catalysts must be analyzed as a function of the metal content: (i) effect of platinum content at constant tin loading (ii) effect of tin content at constant platinum loading. For the first case, Table 3 shows that for sol–gel catalysts the activity per Pt site does not change substantially when the platinum content varies from 0.3 to 1.0 wt.-%. The TOF values of 26 and 21 molec/site · s, shown by the sol–gel catalysts at 0.3 wt.-% and 1.0 wt.-% of platinum are of the same order as reference catalysts Pt-I-0.3 (TOF = 29). However, a major decrease in the TOF can be observed in catalyst prepared by successive impregnation of tin and platinum. The TOF of 7.0 shows for this catalyst is four times lower than TOFs of the sol–gel catalysts Thus the preparation method has an important effect in the catalytic properties of platinum–tin catalysts. The negative effect of tin content in platinum catalysts at 0.3 wt.-% Pt can be noted in Table 3. TOF diminishes in sol–gel catalysts from 26 to 9.0 as the tin content increases from 0.3 to 1.0 wt.-%. Note that the tin content effect is of the same order of the successive impregnation effect; the TOF (7.0) of the impregnated catalysts Pt–Sn-I-0.3-0.3 is close to the value obtained with the sol–gel catalyst at 1.0 wt.-% Sn (TOF = 9.0).

The selectivity (mol %) to C$_1$–C$_4$, C$_5$–C$_7$, toluene and benzene for the n-heptane dehydrocyclization is reported in Table 4. The selectivity values for the catalysts at high tin content are quite different from those observed in catalysts at low tin content. Table 4 shows an important decrease of the aromatic compounds

Table 3
n-Heptane dehydrocyclization on Pt and Pt/Sn–Al$_2$O$_3$ catalysts

Catalysts	Conversion (%)	Rate mol/g · s (10^6)	TOF molec/site · s (10^2)	k_d [a] (10^{10})	k_{ds} [b] (10^{10})
Pt–Sn-0.3-0.3	28	3.4	26	2.5	23
Pt–Sn-1.0-0.3	18	5.5	21	15.0	80
Pt–Sn-0.3-1.0	18	1.4	9	1.2	–
Pt–Sn-I-0.3-0.3	13	0.5	7	1.2	21
Pt-I-0.3	24	2.9	29	21.0	120

[a] Coke deactivation constant.
[b] Thiophene deactivation constant.

Table 4
Selectivity pattern (% mole) for n-heptane dehydrocyclization on Pt and Pt–Sn/Al$_2$O$_3$ catalysts

Catalysts	C$_1$–C$_4$	C$_5$–C$_7$	Toluene	Benzene
Pt–Sn-0.3-0.3	7.6	14.7	71.7	6.0
Pt–Sn-1.0-0.3	9.1	14.2	69.9	6.8
Pt–Sn-0.3-1.0	4.1	17.9	62.1	6.5
Pt–Sn-I-0.3-0.3	10.5	24.3	52.1	13.1
Pt-I-0.3	13.3	8.3	68.1	10.3

and an increase of the C$_1$–C$_4$ and C$_5$–C$_7$ fractions in catalysts at 1.0 wt.-% Sn. The effect of the preparation method can also be seen on the selectivity for benzene. For this reaction, sol–gel catalysts are less selective to benzene formation in 54% than the commercial alumina impregnated catalysts.

Industrial applications of heterogeneous catalysts depend on their ability to tolerate coke as well as to tolerate sulfur. Therefore, coke deactivation and thiophene tolerance were studied in the Pt–Sn/Al$_2$O$_3$ catalysts.

The values of k_d obtained for the various catalysts are reported in Table 2. It can be seen that tin in both sol–gel or commercial alumina platinum impregnated catalysts has a positive effect; small values of the deactivation constant of 2.5 and 1.2 instead of that of 21 observed for the monometallic platinum catalysts can be seen in Table 3. The positive effect diminishes when the platinum content is increased to 1.0 wt.-%, in this case the tin effect is of less importance ($k_d = 15.0$). This positive effect of tin on the constant deactivation for coke tolerance is also observed when the reaction is carried out with n-heptane flowing contaminated with thiophene. In Table 3 is observed that the deactivation by thiophene (k_{ds}) is of less importance in Pt–Sn catalysts (k_{ds} from 21 to 80) than in the monometallic preparation ($k_{ds} = 120$).

4. Discussion

Platinum dispersion is a function of the interaction between the platinum precursor and hydroxylation of the support [28–30]. The extent of the exchange occurring between the surface hydroxyls and the platinum precursor gives low mobility to the platinum complex along the support and hence a high dispersion. The surface hydroxylation as well as the extent of the interaction Pt–Cl–OH in the Pt–Sn sol–gel catalysts have been studied by FTIR and UV–Vis spectroscopies [19]. The results show that, both hydroxylation and Pt–Cl–OH interaction is more important in sol–gel preparations than in the commercial alumina impregnated catalyst. Comparing catalysts at the same platinum content, it can be observed in Table 1, that sol–gel catalysts are more dispersed than the impregnated preparations. This high dispersion (D 90%) then, can be interpreted as an effect of the strong interaction occurring between the support and the metallic precursor during the impregnation step. At high platinum content (1.0 wt.-%) the dispersion decreases as a consequence of the metal content. Some hydroxylation occurs during the impregnation of commercial alumina, but this does not occur to the same extent as that observed in sol–gel samples. Weak interaction is produced and hence a low dispersion is obtained even when the platinum content is 0.3 wt.-%.

Total acidity for the various catalysts is of the same order in either of the Pt–Sn sol–gel preparations, Table 1. However, the effect of tin on the alumina gelation has been observed when the total acidity of the sol–gel alumina sample is compared with that of the tin–alumina sol–gel preparation. Low total acidity is observed for the latter. The TPD pattern of the NH$_3$ chemisorbed at 200°C for the various samples can be seen in Fig. 1. Low acidity sites and few strong ones which desorb at 200°C and 450°C respectively are identified for the Pt–Sn sol–gel samples. Thus the impregnation with hexachloroplatinic acid of tin–alumina sol–gel supports allows a different acidic sites distribution compared with the impregnated tin commercial alumina catalyst. Changes in acidic site distribution must produce changes in the alcohol's dehydration reactions.

Alcohol dehydration was used as a test reaction to evaluate the support acidity [31–35]. If isopropanol dehydration is used, the main reaction occurring in solids of strong acidity is the alcohol dehydration to propene. In contrast, in solids of weak acidity the dehydrogenated product, acetone, became the main product. In sol-gel preparations high selectivity to acetone can be observed in Table 2, whereas propene is the main product when the catalysts were prepared by coimpregnation. Unfortunately, the effect of platinum chloride in alcohol dehydrogenation cannot be easily separated from the acidic properties of the support. Hexachloroplatinic acid modifies substantially the NH_3 TPD pattern and hence, the role of tin in the acidity developed by platinum chloride cannot be quantified in this paper. Additional work on this is in progress.

To understand the role of the support acidity on platinum performance, it is useful to study the selectivity patterns obtained when the catalysts are tested in reactions such as n-heptane dehydrocyclization. This reaction was reported either as bifunctional or monofunctional [12]. The nature of the reaction depends on the support acidity (bifunctional) or the metal content (monofunctional occurring on the metal particles). Identification of which function is operative during the dehydrocyclization can be obtained from the study of the side reactions like coke deactivation or thiophene poisoning.

The formation of coke during n-heptane dehydrocyclization was reported by Barbier [36] as a bifunctional reaction, due to the activities of both support and metal. The results of Table 3 show that the monometallic catalyst deactivates faster than a bimetallic preparation. In Fig. 2 it can be noted that the Pt–Sn sol–gel catalysts at D 90% deactivate less than the sol–gel catalysts at D 50% i.e., small particles produce less coke than larger ones [37]. Note that the Pt–Sn commercial alumina catalysts show the lower constant deactivation even when the dispersion is only 50%. However, in such catalysts we can postulate that a dilution of the platinum clusters by tin could produce an effect similar to
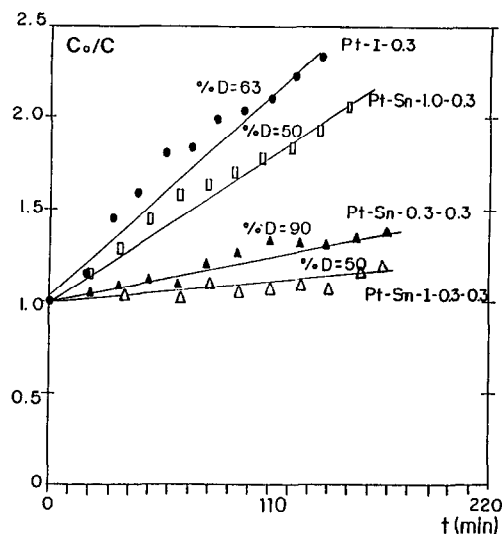

Fig. 2. Coke deactivation constant (k_d) in the n-heptane dehydocyclization for Pt and Pt–Sn/Al_2O_3 catalysts.

a diminution of the particle size. Thus, it seems then in the Pt–Sn catalysts studied in the present work the metal function plays the must important role during the deactivation by coke.

Metal thiophene poisoning occurs at high temperature by hydrodesulfurization. Thiophene decomposes to butane and adsorbed sulfur [27]. Hydrodesulfurization has been reported to be controlled by the electronic properties of the catalyst [38,39]. On supported platinum, thiophene is reported to be an electron acceptor [40]. On the other hand, small metal particles are reported to be electron deficient for metals like rhodium, platinum and palladium [27,40,41].

The results of Table 3 show that Pt–Sn catalysts are more resistant to thiophene poisoning than the monometallic catalyst. This result suggests an electronic or structural modification of platinum [27,40,41]. It can be caused by the support in Pt–Sn sol–gel catalysts or by platinum clusters dilution in Pt–Sn commercial alumina. Thus different effects operate in different preparations. In Fig. 3, the deactivation constant k_{ds} for the n-heptane dehydrocyclization poisoned with thiophene for various Pt–Sn catalysts is illustrated.
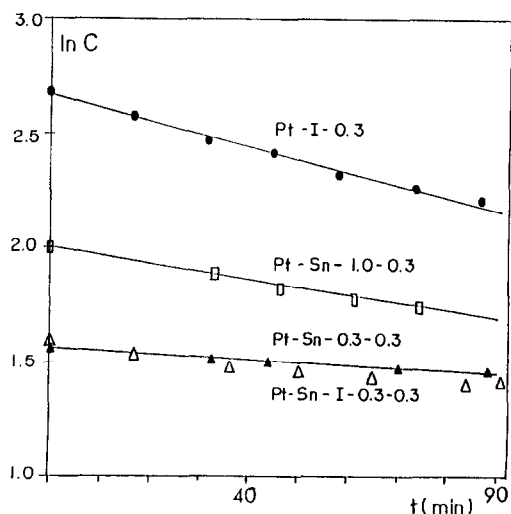
Unfortunately, coking (k_d) or deactivation by

Fig. 3. Thiophene constant deactivation (k_{ds}) in n-heptane dehydrocyclization for Pt and Pt–Sn/Al$_2$O$_3$ catalysts.

thiophene (k_{ds}) are complex functions which can be modified by the presence of sulfur and coke, respectively. In a flow reactor system like the used in the present work, it is not possible to separated both functions. Hence, some modifications of k_d and k_{ds} can occur. Coking increases the sulfur tolerance and sulfur increases the coke resistance [42]. SCF-250 alumina is a support not totally free of sulfur ($>$ 1000 ppm), then in the impregnated catalysts one can speculate that there is some diminution of the constant deactivation rate (k_d) by sulfur effect. Thus, assuming this support–sulfur content effect, the real differences between the sol–gel and the impregnated catalysts concerning the sulfur resistance must be larger than those reported in Table 3.

The effect of tin in platinum activity can be also observed in the cyclohexane dehydrogenation, a monofunctional reaction. The results of Table 5 show that the activity per site is largely affected in Pt–Sn commercial alumina impregnated catalyst.The large effect in the dehydrogenation activity observed for the impregnated bimetallic catalyst may be due to the tendency of such preparations to the formation of alloys. EDX studies of Pt–Sn commercial alumina impregnated catalysts show that tin and platinum co-exist on the support surface and probably as some alloy [20]. On the contrary, in sol–gel preparations the EDX analysis show that on this catalysts only platinum can be detected i.e., little or non alloy formation. The absence of tin EDX signal in Pt–Sn sol–gel preparations was interpreted as an evidence of homogeneous tin distribution in surface and bulk alumina, i.e., a bulk tin–aluminate. The EDX study has been made in a Microscope JEOL JEM-100 CX equipped with ASID and EDX analysis. In this equipment the EDX detection limit is 0.1 wt.-% in bulk, and the penetration depth was 0.5 mm.

Deactivation by coke during cyclohexane dehydrogenation was studied (Fig. 4). The results show that deactivation is more important in the monometallic catalyst than in the Pt–Sn preparations. The sol–gel catalysts highly dispersed (D 90%) and the Pt–Sn commercial alumina preparations deactivate lesser than the sol–gel catalysts at low dispersion (D 50%) and much lower than the monometallic platinum commercial alumina catalyst. A particle size effect for sol–gel preparations and platinum clusters dilu-

Table 5
Cyclohexane dehydrogenation on Pt and Pt–Sn/Al$_2$O$_3$ catalysts

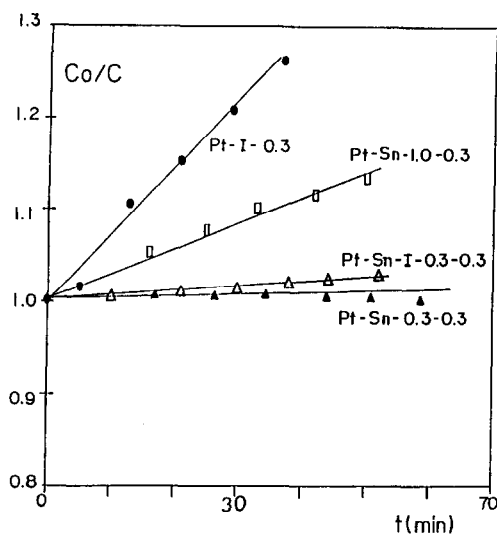| Catalysts	Conversion (%)	Rate mol/g · s (10^7)	TOF molec/site · s (10^2)	k_d [a] (10^9)
Pt–Sn-0.3-0.3	18	36	28	1
Pt–Sn-1.0-0.3	44	196	75	60
Pt–Sn-0.3-1.0	16	26	17	28
Pt–Sn-I-0.3-0.3	7	2	3	4
Pt-I-0.3	23	56	57	82

[a] Coke deactivation constant.

Fig. 4. Coke deactivation constant (k_d) in the cyclohexane dehydrogenation for Pt and Pt–Sn/Al$_2$O$_3$ catalysts.

tion by tin in impregnated Pt–Sn catalysts operates here. This result is in agreement with that observed for deactivation during the n-heptane dehydrocyclization where it is shown that the metallic function is the main responsible for coke deactivation in the Pt–Sn catalysts studied in this paper.

Side reactions like dealkylation can be analyzed from the study of the selectivity patterns shown in Table 4. An important modification on selectivity due to the presence of tin is illustrated by the benzene formation. Some of the benzene produced can be formed during the dealkylation of toluene. Toluene dealkylation was reported by Barbier [36], as a monofunctional reaction, which occurs on the metallic phase. In sol–gel catalysts, the formation of benzene is about 54% smaller than that ob-

served for the Pt or Pt–Sn commercial alumina catalysts. The very low dealkylation rate observed in sol–gel catalysts, Table 6, show that toluene dealkylation is strongly inhibited in Pt–Sn sol–gel catalysts.

Dealkylation must occur preferentially on the metallic phase [36], however, additional effects due to the acidity of the support can be produced. Note that in the catalysts studied (Table 6), the higher dealkylation rate corresponds to the catalyst showing the higher activity in the isopropanol dehydration (Table 2). In spite of the probable role of the acidity support in the dealkylation rate, the activity of the supports were found negligible and non dialkylated products like xylene were detected in Pt–Sn catalysts. Dealkylation must produce coke and some deactivation was detected during the reaction. The deactivation by coke during the toluene dealkylation is shown in Fig. 5. Coke deposition is dramatically diminished in Pt–Sn sol–gel catalysts. The decrease of the dealkylation rate is an important result, because the gasoline product will contain less benzene [43].

The low dealkylation rate and the thiophene resistance observed on Pt–Sn catalysts, show that additionally to the support acidity effects, tin–alumina support effects in the metal activity must be take into account. The nature of such effects has not been established. However, some modification of the platinum properties other than those involving alloy formation can be advanced. Metallic particles and especially small particles deposited on support oxides can be structurally [27] and or electronically modified [40]. In our case it seems that the modification must occur preferentially on the particle struc-

Table 6
Toluene dealkylation on Pt and Pt–Sn/Al$_2$O$_3$ catalysts

Catalysts	Conversion (%)	Rate mol/g · s (10^{10})	TOF molec/site · s (10^4)	k_d [a] (10^{10})
Pt–Sn-0.3-0.3	0.03	2	0.16	0.4
Pt–Sn-I-0.3-0.3	1.19	143	19.00	7.0
Pt-I-0.3	23.1	2209	225.00	19.3

[a] Coke deactivation constant.
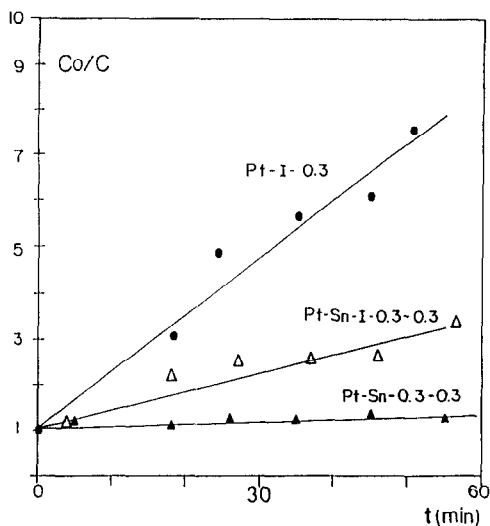
Fig. 5. Coke deactivation constant (k_d) in the toluene dealkylation for Pt and Pt–Sn/Al$_2$O$_3$ catalysts.

low rate of toluene dealkylation is observed in sol–gel catalysts.

4. The deactivation rate by thiophene or coke in n-heptane dehydrocyclization and cyclohexane dehydrogenation are smaller in Pt–Sn/Al$_2$O$_3$ catalysts than in Pt/Al$_2$O$_3$ catalyst. Tin can play a dual role in coke tolerance; (a) a dilution effect of the platinum clusters, and (b) a structural effect on platinum particles induced by the interaction platinum–tin–alumina. The dilution effect can be observed in catalysts prepared by the successive impregnation (first tin and second platinum) of a commercial alumina. The tin–alumina support effect in platinum activity is the phenomenon observed in supports prepared by the cogelation of aluminum tri-sec-butoxide and tetrabutyltin (sol–gel method).

ture than with the electronic properties, since the latter are only observed on supports showing strong acidity [44]. The improved stability as well as the coke or sulfur tolerance shown by the Pt–Sn/Al$_2$O$_3$ sol–gel catalysts i.e., addition of tetrabutyltin to an alumina gel and impregnation with hexachloroplatinic acid, are promising properties of industrial applications.

5. Conclusions

The conclusions emerging from this study are the following:

1. Tin has an important role on the support acidity. The impregnation of tin–alumina sol–gel supports with hexachloroplatinic acid, forms weak and strong acid sites increasing the selectivity to acetone in the isopropanol conversion.

2. Catalytic activity test for n-heptane dehydrocyclization shows that the principal role of tin in platinum catalysts is related to modification of the selectivities. Sol–gel preparations result in catalysts which produce low benzene.

3. Benzene formation is suggested to be mainly produced by toluene dealkylation. A very

Acknowledgements

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