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Development of an industrial characterisation method for naphtha reforming bimetallic Pt-Sn/Al_2O_3 catalysts through *n*-heptane reforming test reactions

M.P. González-Marcos [a,c,*], B. Iñarra [a,c], J.M. Guil [b,c], M.A. Gutiérrez-Ortiz [a,c]

[a] *Dpto. Ingeniería Química, Facultad de Ciencia y Tecnología, Universidad del País Vasco/E.H.U., P.O. Box 644, E-48080 Bilbao, Spain*
[b] *Instituto de Química Física "Rocasolano", CSIC, c/Serrano, 119, E-28006 Madrid, Spain*
[c] *Unidad Asociada al CSIC "Grupo de Tecnologías Químicas para la Sostenibilidad Ambiental", Spain*

Abstract

Test reactions are proposed as a quick, cheap and reliable characterisation method that can be useful for evaluating catalytic deactivation during an industrial reforming process. In this work, *n*-heptane reforming is evaluated as a test reaction for the characterisation of Pt-Sn/Al_2O_3 catalysts. The reaction has been studied using purposely prepared catalysts and the results compared to those obtained using industrial catalysts subjected to different ageing treatments. On the other hand, all catalysts have been characterised by classical methods: surface acidity has been measured by ammonia–TPD and metallic particle size has been determined by hydrogen chemisorption, and the results compared to those of test reaction. It can be concluded that the analysis of activity and selectivity in *n*-heptane reforming allows evaluation of the state of the catalyst, and the results are more reliable than those of classical characterisation methods.

Keywords: Pt-Sn/Al_2O_3; Bimetallic catalysts; Naphtha reforming catalysts; Characterisation; Ammonia–TPD; Chemisorption; Physisorption; Test reaction; *n*-Heptane reforming

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1. Introduction

Naphtha reforming is usually called "platforming" due to the use of catalysts based on platinum supported on alumina, nowadays modified with a second metal, such as Re, Sn or Ir. Bimetallic platinum-tin supported on alumina catalysts have been widely employed in industrial naphtha reforming processes since Kluksdahl discovered, at the end of the sixties, the improvement in catalytic performance when a second metal, rhenium, was added to Pt/Al_2O_3 [1]. This discovery led to an intense research focused on addition of a second metal to the monometallic catalyst, the use of trimetallic catalysts, or the inclusion of promoters such as chlorine or fluorine [2–6].

Industrially, Pt-Re and Pt-Ir are used in semi-regenerative or cycling reforming processes. Due to the easy regeneration of Pt-Sn catalysts, they are preferred for continuous regeneration systems (CCR) [5,7].

In reforming processes, addition of tin to monometallic Pt/Al_2O_3 catalysts provides better stability, mitigates the sintering effect, improves selectivity by inhibition of the hydrogenolytic effect of platinum, and decreases isomerisation and coke deposition, while aromatisation is increased [5,8–12].

Two different effects caused by tin addition are suggested in the literature: one geometrical, in which a physical dilution of platinum by tin takes place, and one electronic, where the formation of alloys causes a change in bond strength between the chemisorbed hydrocarbon and the active metal [13–17].

Despite the intense research effort, some aspects of these catalysts are still the subjects of discussion. Most authors agree with the easy reducibility of platinum to Pt^0, but the oxidation state of tin remains unclear, being a function of support, loading, preparation method and pretreatment [18,19]. While some studies point out that platinum–tin

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* Corresponding author. Tel.: +34 946015412; fax: +34 946015963.
E-mail address: mp.gonzalezmarcos@ehu.es (M.P. González-Marcos).

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alloys containing more than 25% of tin are catalytically inactive [20–22], some authors prove that no proper alloys are formed between platinum and tin [23], whereas others show the existence of a part of tin as a Pt–Sn alloy [24,25]. On the other hand, the bimetallic phases obtained seem to depend on the particle size for a given preparation technique [18,26].

This problem also affects the measurement of the active metal particles accessibility. H_2 and O_2 chemisorption, or H_2/O_2 titration, are normally employed for the evaluation of metallic dispersions and are well established for monometallic Pt/Al_2O_3, but they show some difficulties with bimetallic $Pt\text{-}Sn/Al_2O_3$ [12,27,28].

Other characterisation techniques, such as HREM, XRD, XPS or Mössbauer, present a limited utility, due to the low metallic contents of industrial catalysts (around 0.3%) and to the high dispersion of these catalysts [2,29]. Thus, industrial characterisation of the catalysts is carried out by a complicated analysis of catalytic results of reactions carried out in pilot plants, what is time consuming and expensive.

Therefore, the development of new characterisation methods is needed, which combine quickness and cheapness with interesting and reliable information of the studied samples. The standardisation of test reactions appears as a straight way to evaluate the performance of $Pt\text{-}Sn/Al_2O_3$ catalysts in the process.

In a previous work, the study of cyclohexane dehydrogenation and methylcyclopentane reforming reactions showed that the former can be used to estimate platinum dispersion in the catalysts, whereas the distribution of products in the latter gives indications on the degree of deactivation of a catalyst and how it will perform in the industrial process [30].

The aim of this work is to demonstrate the usefulness of *n*-heptane reforming for its use as a test reaction and hence for the characterisation of $Pt\text{-}Sn/Al_2O_3$. Reforming of *n*-heptane has been chosen for comparison with the previous test reactions and to progress in the study with a reaction which is closer to the industrial naphtha reforming process.

Reforming of *n*-heptane shows several reaction mechanisms involving different kind of active centres. In this reaction, there is a competition between cracking, hydrogenolysis, dehydrogenation, dehydrocyclisation, isomerisation and aromatisation. Some of these reactions occur over metallic sites, others over acid sites, while others require a bifunctional mechanism [31]. A series of alumina-supported platinum and/or tin catalysts with various metal contents has been prepared, characterised and catalytically tested. Industrial catalysts have been also studied in order to compare the results.

2. Experimental

2.1. Preparation of catalysts

A number of catalysts has been prepared for this work, with platinum and/or tin content varying around the industrial metallic loading (0.3% of Pt and 0.3% of Sn).

All catalysts have been prepared by impregnation of the metallic salt on a SPH-512-C alumina, provided by Repsol-YPF. It is a γ-alumina of 220 $m^2\,g^{-1}$, a pore volume of 0.60 $cm^3\,g^{-1}$ and an average pore diameter of 10.3 nm. Alumina pellets were 1 mm diameter, 0.5–1 cm length cylindrical extrudates.

The active phase has been deposited on the support by successive impregnation from hydrated hydrogen hexachloroplatinate(IV) ($H_2PtCl_6\cdot 2H_2O$, Aldrich, 99.995%), dissolved in distilled water, and tin dichloride dihydrated ($SnCl_2\cdot 2H_2O$, Aldrich, 99.999%), dissolved in 1 M hydrochloric acid. In bimetallic catalysts, platinum was added by impregnation on the Sn/Al_2O_3 precursor with an intermediate drying step.

Then, the catalytic precursors were dried in stove at 389 K for 16 h. Finally, they were activated by successive calcination at 723 K for 2 h and reduction in H_2 flow at 723 K for 2 h.

2.2. Catalysts characterisation

Specific surface areas of support and catalysts, evaluated by the BET method, were determined from the nitrogen adsorption isotherms carried out at the normal boiling point of N_2, using a Micromeritics ASAP 2010 equipment. The samples were previously outgassed at 573 K for 16 h.

Metallic dispersion was evaluated by H_2 chemisorption in a Micromeritics ASAP 2010 instrument. The sample was outgased for 16 h at 573 K, and then reduced in H_2 flow at 723 K during 4 h. Afterwards, hydrogen was removed by a dynamic vacuum system at the same temperature during 2 h and then the sample was cooled down to room temperature. The chemisorption measurements were carried out at 303 K.

A chemisorption measurement performed to a catalyst containing only tin (1% Sn/Al_2O_3) showed that hydrogen does not chemisorb on tin, and then chemisorption over bimetallic $Pt\text{-}Sn/Al_2O_3$ catalysts is assumed to occur only on platinum. This is generally accepted, as well as the H/Pt ratio of unity [2,17].

Acidity of the catalysts was evaluated by TPD of ammonia and was carried out in a Micromeritics Autochem 2910 instrument. The sample was dried and reduced in a 50 ml min^{-1} flow of 5% H_2 in Ar at 723 K during 1 h. Adsorption of NH_3 was conducted by admitting 0.5 cm^3 pulses until saturation at 373 K. TPD experiments were carried out with a thermal ramp of 10 K min^{-1} from 373 K to 723 K.

2.3. n-Heptane reforming conditions

Before all runs, in situ pretreatments were carried out; the catalysts were reduced in a 150 $cm^3\,min^{-1}$ hydrogen flow at 723 K for 5 h. Partial pressure of the hydrocarbon was kept always below its vapour pressure, in order to prevent condensation in the experimental equipment.

The composition of the effluent was measured by an online gas chromatograph equipped with a capillary HP–1 column. The detectors were: an AED, used for quantification, and a mass spectrometer, for identification of the compounds.

n-Heptane reforming was performed in a flow reactor operating in the differential mode (conversion below 10%) and with high linear gas space velocity in order to avoid internal and external diffusion controls. The reactions were carried out with a hydrogen/*n*-heptane ratio of 20 with a catalyst bed of ca. 0.7 g.

Temperature was varied from 558 K to 693 K and pressure was kept at one atmosphere. A noticeable deactivation was observed for the catalysts without tin. In these cases, studies were carried out in several stages, keeping temperature constant.

Conversion has been calculated from the molar amount of *n*-heptane reacted. The properties of the catalysts have been evaluated through selectivity. As the number of products is very large, they have been grouped regarding their mechanism of formation. Selectivity to isomerisation takes into account 2-methylhexane, 3-methylhexane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane and 3-ethylpentane. Selectivity to cyclisation comprises 1,2-dimethylcyclopentane, 1,3-dimethylcyclopentane and ethylcyclopentane formation. Selectivity to dehydrogenation includes C7 olefins formation. Toluene is the only aromatic product generated and included in aromatisation selectivity. Finally, selectivity to cracking includes all products with less than seven carbons.

It must be pointed out that selectivity to cracking products is over-evaluated, as the number of moles produced per mole of *n*-heptane is two for the first cracking step and increase rapidly for further steps. In order to avoid this effect, selectivity has been calculated as the number of moles of *n*-heptane necessary to produce each group per total amount of *n*-heptane reacted.

Reforming of *n*-heptane involves different pathways which need different active centres. Metallic sites take part in reactions where hydrogen is removed or added, while acid sites are involved in reactions with skeletal rearrangement steps [32,33]. In the industrial process, dehydrogenation and hydrogenolysis are supposed to occur over metallic sites, while isomerisation occurs over acid sites. Dehydrocyclisation and aromatisation reactions present a bifunctional mechanism [10]. However, in the experimental conditions of this work, an important contribution of metallic sites to isomerisation, cyclisation and aromatisation must be taken into account [32,34]. Over metallic sites, isomers can be produced by a bond shift mechanism or through a 1–5 ring closure and ulterior hydrogenolysis of the cycle (cyclic mechanism). Two main mechanisms are proposed for the aromatisation: a 1–6 ring closure of *n*-heptane followed by dehydrogenation, or a 1–5 ring closure followed by ring enlargement; the former being the most frequent for hydrocarbons of more than six carbons [34–36]. Other mechanisms are proposed for aromatic production: cyclisation of the alka-triene, or 1–7 ring closure followed by a bond shift with formation of methylcyclohexane and then dehydrogenation [34,36].

3. Results

3.1. Catalysts properties

The catalyst properties are summarized in Table 1 and have been discussed in a previous work [30]. Prepared catalysts have been named with two numbers indicating the nominal platinum content in a per thousand basis followed by a letter, an S (from Sn), and two other numbers indicating the nominal tin content in a per thousand basis; then 10S03 refers to the 1%Pt-0.3%Sn/Al_2O_3 catalyst. Industrial catalysts have been labelled using the following code: the first letter is I (of industrial), followed by an S (of tin) and, finally, either an F for the fresh catalysts or an R for the industrial catalysts with a certain number of regeneration cycles.

Table 1 shows that all catalysts have the same specific surface area except the industrial aged catalyst, which presents an important loss of surface due to the industrial use and regeneration. The catalysts show a high dispersion of the metal, evaluated through chemisorption, with similar values for all the samples.

Table 1
Catalysts properties, nomenclature and *n*-heptane reforming reaction rate at 648 K

Catalyst code	Surface area ($m^2\,g^{-1}$)	Metallic content (wt.%)		Dispersion (H/Pt ratio)		Acidity ($\mu mol_{NH_3}\,g^{-1}$)		*n*-Heptane reaction rate ($\mu mol\,min^{-1}\,g^{-1}$)
		Pt	Sn	(Chem.)	(CH)	Total	S/W	
Al_2O_3	228	–	–	–	–	817	2.18	<1
10S00	181	0.91	–	0.56	0.56	788	2.28	146[a]
10S03	183	0.90	0.32	0.63	0.33	800	2.29	127
03S00	180	0.25	–	0.70	0.7	690	2.29	59
03S03	194	0.29	0.33	0.55	0.11	727	2.29	23
03S10	177	0.27	1.02	0.60	<0.01	804	2.18	7
00S10	178	–	1.08	–	–	629	1.97	<1
IS–F	170	0.23	0.24	0.53	0.11	752	2.10	39
IS–R	127	0.24	0.24	0.61	~0.01	586	2.47	17

[a] Except catalyst 10S00, evaluated at 603 K.

The values of metal accessibility evaluated through cyclohexane dehydrogenation test reaction are also shown in Table 1. It can be noticed that an important decrease of active metallic sites is produced by tin addition, which is not reflected by hydrogen chemisorption. Hydrogen chemisorption results can be affected by spillover, effect which is increased by tin addition [18,37].

All NH_3–TPD curves presented the same shape with two maxima at 435 K and 630 K. These peaks have been assigned to weak and strong acidity, respectively. Acidity values are mainly related to the alumina surface, but a slight increase of acidity with metallic loading can be noticed, probably related to the presence of chlorine in the catalysts due to the preparation method. Also, a decrease of strong/weak acidity ratio (S/W) with the increase of Sn/Pt ratio is observed, related to the poisoning or coverage of strong acid sites by unreduced tin (tin oxide) [38], effect particularly noticeable in 00S10 catalysts.

It should be noticed that the industrial fresh catalyst shows a similar value of total acidity than the prepared catalysts, but with a strong/weak acidity ratio somewhat smaller, while the aged catalyst shows an important loss of acidity, related to the loss of alumina surface, as well as an increase in strong/weak acidity ratio.

3.2. Reforming of *n*-heptane

The rate of *n*-heptane reforming has been determined for all the samples and only those results accomplishing the differential reactor assumption have been used. Neither the support nor the monometallic 00S10 catalyst present significant activity in the studied conditions.

The reaction rate of the catalysts, expressed in moles per minute and per gram of catalyst, present the following order: 10S00 > 10S03 > 03S00 > IS–F ~ 03S03 > IS–R > 03S10 (Table 1). For a constant amount of platinum, addition of tin diminishes catalyst activity. Both industrial fresh catalyst and the laboratory catalyst with the same metallic loading present the same reaction rate. Industrial aged catalyst shows a loss of activity around 50% or, in other words, a shift of 15 K to higher temperature to reach the same rate in the studied conditions, value similar to that proposed as a “normal temperature cycle” in a semi-regenerative reforming [5].

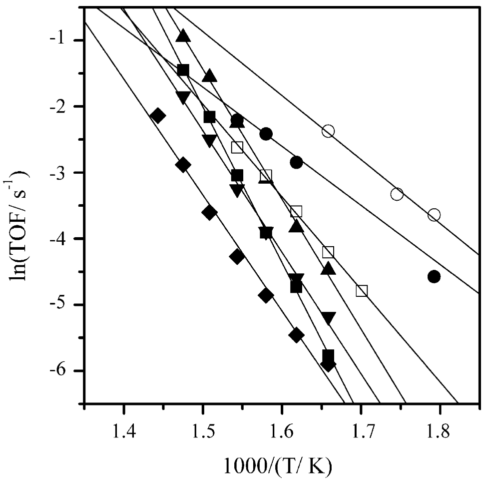

Fig. 1. Effect of temperature in TOF of catalysts in *n*-heptane reforming: ○, 10S00; ●, 03S00; □, 10S03; ■, 03S03; ◆, 03S10; ▲, IS–F; ▼, IS–R.

If we evaluate the turn over frequency (TOF) through the dispersion values obtained with chemisorption measurements, a slight change can be pointed out. Fig. 1 shows the natural logarithm of TOF values versus the inverse of absolute temperature, to evaluate the apparent activation energy and to compare catalyst activity. The order of activity at 648 K is 10S00 > 03S00 > IS–F > 10S03 > 03S03 > IS–R > 03S10.

As *n*-heptane reforming involves mono and bifunctional mechanisms, changes in TOF values were expected, as only structure-insensitive reactions are supposed to maintain TOF values constant. Addition of tin, as well as ageing of the industrial catalysts, produces a clear decrease in TOF values.

Table 2 shows the calculated values of apparent activation energy for each catalyst in *n*-heptane reforming and in its different pathways. Concerning the apparent activation energy in *n*-heptane reforming, shown in the third column of Table 2, catalysts can be arranged in two groups: one corresponding to monometallic and 10S03 catalyst, and the second group including all the rest. This trend is also noticeable in all the different pathways involved in this reaction.

Table 2

Estimated apparent activation energies (kJ mol^{-1}) in *n*-heptane reforming (*n*-H) and the different pathways: dehydrogenation (DH); isomerisation (Isom); cyclisation (Cyc); cracking (Crack); aromatisation (Ar)

	Sn/Pt (atomic ratio)	*n*-H	DH	Isom	Cyc	Crack	Ar	
							First step	Second step
10S00	0	80	–	100	57	61	–	120
10S03	0.58	116	118	122	91	84	–	135
03S00	0	83	133	122	57	28	–	111
03S03	1.87	196	132	175	93	179	65	233
03S10	6.21	146	113	154	89	198	22	182
IS–F	1.71	164	134	154	133	150	93	237
IS–R	1.64	153	134	171	98	146	77	157

Table 3
Product distribution at 648 K

	10S00[a]	10S03	03S00	03S03	03S10	IS–F	IS–R
Cracking	19.0	18.5	10.6	4.5	1.2	6.1	8.0
Dehydrogenation	1.5	4.3	17.9	23.2	30.0	15.3	27.1
Isomerisation	28.7	47.0	35.8	63.7	47.0	69.9	56.5
Cyclisation	32.1	11.1	22.1	4.1	19.3	4.1	3.3
Aromatisation	18.7	19.2	13.5	4.5	2.5	4.6	5.1

[a] Except catalysts 10S00, evaluated at 603 K.

These changes in apparent activation energy reveal modifications in the limiting step in the reaction and are due to the selectivity of these catalysts as will be shown below. The variation of relative rates of the different pathways can be related to the active sites that take part in the catalytic reaction. The study of selectivity can therefore bring information on the catalysts state by studying the active sites involved in each set of products [32,34].

In Table 3, selectivity of each catalyst has been reported. All values correspond to 648 K except for catalyst 10S00, whose values correspond to 603 K.

Product distribution shows that the main reaction is isomerisation. The only catalyst showing a difference is catalyst 10S00, which leads primarily to cyclisation products, but this change is mainly related to the low temperature of evaluation of this sample because isomerisation selectivity increases with temperature as shown in Fig. 2. Monometallic catalysts are, however, those presenting the lowest selectivity to isomerisation products, followed by catalyst 10S03, IS–R and 03S10. Catalysts 03S03 and IR–F are the most selective toward isomerisation.

Therefore, the presence of tin improves selectivity to isomers when Sn/Pt ratio is small, while selectivity decreases again for values greater than 1.87. Concerning industrial catalysts, IS–F presents the same selectivity to isomers than the prepared catalysts of the same composition, while the industrial aged catalyst behaves as 03S10.

Concerning dehydrogenation, the selectivity order is opposite, catalysts IS–R and 03S10 being the most selective to dehydrogenation, followed by 03S03, IS–F and, finally, 03S00 and 10S03. In this case, the evolution of selectivity with temperature is more interesting: while all catalysts present the same apparent activation energy for the formation of dehydrogenated products, see Table 2 column 4, most catalysts present a decrease in selectivity toward dehydrogenated products with temperature (IS–R, 03S03, 03S10, IS–F), whereas the level is maintained for 10S03 and increased for 03S00. The evolution and apparent activation energy of monometallic 10S00 catalyst has not been evaluated, as only one temperature presents a significant level of dehydrogenated products. However, as its evolution is similar to monometallic 03S00 catalyst, its trend in dehydrogenation can be predicted to be similar.

The change of evolution is again related to tin addition and Sn/Pt ratio, and a maximum of selectivity is attained at Sn/Pt ratio equal to 1.87. Ageing of the industrial catalyst produces an effect similar to the increase in Sn loading.

Fig. 3 shows the evolution of selectivity toward aromatisation products as a function of temperature, where three different behaviours can be distinguished. Catalysts 10S00, 10S03 and 03S00 increase their selectivity with temperature, while IS–F and 03S03 present a minimum around 650 K. Finally, IS–R and 03S10 present a decrease of aromatisation selectivity with temperature in the studied interval.

This evolution is related to a change in the mechanism, or in the active site, involved in the production of toluene. This change can also be observed if we evaluate the apparent activation energy of aromatics production. Fig. 4 shows the Arrhenius plot for toluene formation, where an important change in slope can be noticed in most bimetallic catalysts. In Table 2, the apparent activation energy of aromatisation has been separated in two steps: the first one related to aromatisation over metallic sites and the second one related to a bifunctional pathway. As monometallic and 10S03

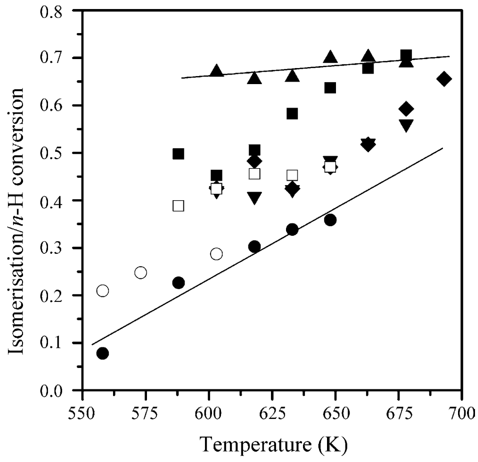

Fig. 2. Evolution of isomerisation pathways with temperature: ○, 10S00; ●, 03S00; □, 10S03; ■, 03S03; ◆, 03S10; ▲, IS–F; ▼, IS–R.

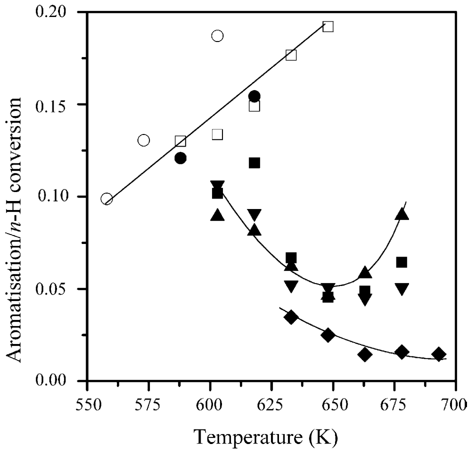

Fig. 3. Evolution of aromatisation pathways with temperature: ○, 10S00; ●, 03S00; □, 10S03; ■, 03S03; ◆, 03S10; ▲, IS–F; ▼, IS–R.

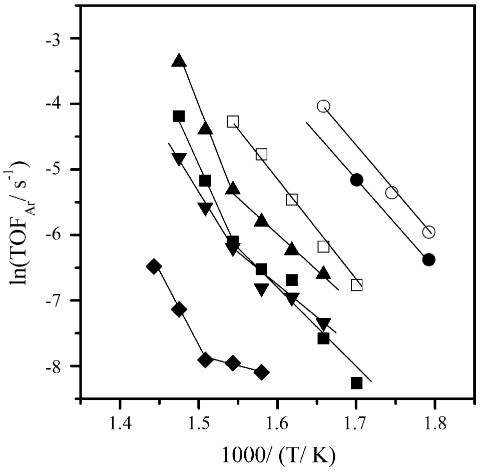

Fig. 4. Change of apparent activation energy in the production of aromatics: ○, 10S00; ●, 03S00; □, 10S03; ■, 03S03; ◆, 03S10; ▲, IS–F; ▼, IS–R.

catalysts do not present a change in the apparent activation energy and their values are closer to those of the second step, it has been assumed that, in the studied range, these catalysts produce toluene mainly by the bifunctional pathway, probably affected by an important production of aromatics in metallic sites as the low apparent activation energies reflect.

Selectivity to cyclisation products decreases with temperature for all catalysts. However, three different trends can be distinguished: the decrease is linear but keeping the highest values in the studied interval of temperatures for monometallic and 03S10 catalysts; 10S03 catalyst presents a softer decrease; the other catalysts seem to reach an equilibrium value of 3% at 650 K.

Regarding the cracking products, selectivity is decreased by tin addition as well as by temperature. Ageing in the industrial catalysts produces a decrease in the formation of cracked products but a slight increase in the selectivity toward them.

4. Discussion

The activity results show that an important loss of activity is caused by tin addition. These changes can be explained in several ways: formation of inactive alloys, tin coverage of platinum sites or a general poisoning by tin. These suppositions would also explain the decrease in activity with increasing the Sn/Pt ratio.

Regarding the industrial catalysts, the decrease in activity with ageing can be due either to the loss of acidity related to the diminution of specific area of the catalyst or to a change in tin distribution causing an effect similar to an increase of Sn/Pt ratio.

The study of selectivity in reforming of *n*-heptane shows that the addition of tin increases selectivity toward isomers for Sn/Pt ratios smaller than 1.87. On the other hand, tin addition produces a decrease in the selectivity to cyclisation with a minimum value for Sn/Pt ratio equal to 1.87. Tin addition also leads to a decrease in aromatisation and cracking selectivity, and an increase in the selectivity to dehydrogenated products. Also, tin addition improves stability of the catalysts. These results are similar to those obtained by Passos et al. [31].

Regarding the industrial catalysts, ageing produces an effect close to the increase of Sn/Pt ratio between catalysts 03S03 and 03S10. However, two main differences can be pointed out. First, while cracking and aromatisation slightly increase with ageing, a slight decrease is observed with the increase of Sn/Pt. This difference is related to the changes in the strong/weak acidity ratio, as cracking is promoted by the strong acid sites and aromatics are formed through a bifunctional pathway. Second, the selectivity of 03S10 catalyst toward cyclisation products is higher than that of IS–R.

In order to study the catalyst properties through *n*-heptane reforming, the bifunctional character of these catalysts during the industrial process must be kept in mind.

If we suppose that all reactions are occurring only over metallic sites, TOF values should only depend on metallic particle size. As all catalysts present similar H/Pt ratio when measured by chemisorption, that is, analogous particle size, one would expect all catalysts to present similar TOF values. However, the differences are very important and the decrease of TOF values with tin loading cannot be taken as an experimental error. On the other hand, in a previous paper [30] the accessibility of metallic sites was corrected according to the TOF values obtained in cyclohexane dehydrogenation text reaction, obtaining the dispersion values reflected in Table 1. Fig. 5 shows the Arrhenius plot with TOF values calculated with the corrected dispersions (TOF*). The figure shows that catalysts of similar behaviour get closer but the differences remain clear. Then, the participation of acid sites cannot be ruled out, and the

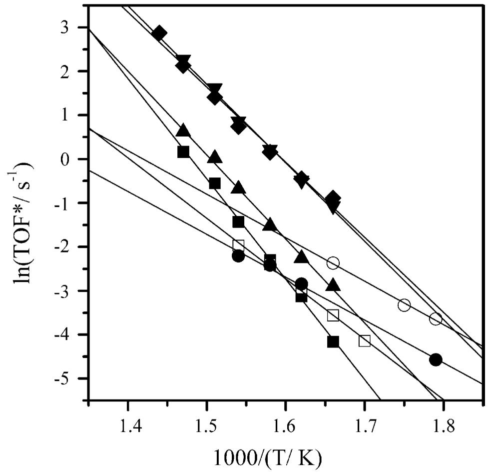

Fig. 5. Effect of temperature in TOF* of catalysts in *n*-heptane reforming: ○, 10S00; ●, 03S00; □, 10S03; ■, 03S03; ◆, 03S10; ▲, IS–F; ▼, IS–R.

involvement of acid sites in reactions such as aromatisation must be weighed up.

Assuming that hydrogenolysis, included in cracking selectivity, and dehydrogenation take place over metallic sites, it remains clear that at the lowest temperatures in the studied interval the reaction is controlled by the metallic function of the catalysts. As the temperature increases, the contribution of acid sites of the alumina becomes more important. Acid sites are involved in reactions where a skeletal rearrangement step takes place; therefore, the activation of acid sites at higher temperatures explains the increase in isomerisation and aromatisation. The decrease of selectivity toward cycles can be related to the isomerisation of the cycles, producing toluene, or their hydrogenolysis, producing isomers as well as a simple change in selectivity due to the participation of alumina in the formation of isomers.

The change in predominant mechanism can bring very interesting information related to the acid strength of the catalyst. The study of the selectivity to aromatisation allows the estimation of this evolution. If, in Fig. 3, we estimate the temperature at which these variations take place, IS–F and 03S03 present a minimum around 650 K, while IS–R and 03S10 reach a stability around 660 K. Monometallic and 10S03 catalysts do not present a minimum in the studied range. On the other hand, if we look at the apparent activation energy for each step (Table 2), the values of the first step are smaller than those of the second that, moreover, are similar to the values of the monometallic catalysts.

This loss of acid-site activity is in accordance with the poisoning of acid sites by tin [25,39]. Thus, the study of that change in aromatisation selectivity gives important information of the acidity of the catalysts. Moreover, this evolution agrees with cracking selectivity, and with the deactivation observed in monometallic catalysts related with coke formation. Both, cracking and coke formation, are usually related to acid sites.

Fig. 6 shows the evolution of dehydrogenation/aromatisation ratio (D/A) versus temperature. As dehydrogenation can only occur over metallic sites and aromatisation, at higher temperatures, needs both acid and metallic sites, the ratio between dehydrogenation and aromatisation can give an idea of the metallic/acid sites ratio.

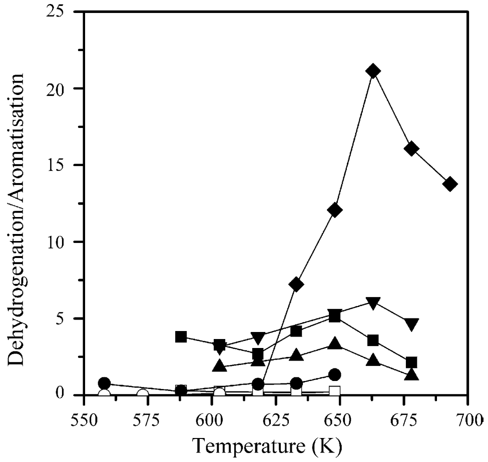

Fig. 6. Evolution of dehydrogenation/aromatisation ratio with temperature: ○, 10S00; ●, 03S00; □, 10S03; ■, 03S03; ◆, 03S10; ▲, IS–F; ▼, IS–R.

Again, monometallic and 10S03 catalysts show a very low D/A ratio, smaller than unity on the studied interval. The ratio increases in the following order at all temperatures, IS–F < 03S03 < IS–R < 03S10. Moreover, the change in the evolution of D/A ratio is parallel to that observed in aromatisation, and maximum values in D/A ratio appear around 660 K for 03S10 and IS–R catalysts and around 650 K for 03S03 and IS–F.

If we study the apparent activation energy of each pathway, it remains clear that catalysts with low Sn/Pt ratio present values somewhat smaller, except for dehydrogenation, where all values are similar.

On the other hand, it must be pointed out that industrial fresh catalyst and prepared catalyst with the same metal content (03S03) present similar values, especially in the second step of aromatisation, as well as IS–R and 03S10. This effect is related to the formation of Pt–Sn alloys, as reported in a previous work [30].

In the laboratory catalysts, the increase of Sn/Pt ratio leads to the formation of active sites formed by Pt–Sn alloys which, for ratios smaller than 1.87, present similar behaviour to those of monometallic, while for higher ratios there is a structural modification of the active sites causing a loss of activity [20,21,40,41].

Concerning the industrial catalysts, a similar effect can be expected. In this case, there is no change in metal content but a change in tin distribution. During the industrial process, or during regeneration, a migration of tin to the surface of platinum clusters is possible, leading to an effect similar to an increase in Sn/Pt ratio, as well as the formation of Pt–Sn alloys due to the industrial process [18,25,30].

5. Conclusions

The study of Pt-Sn/Al_2O_3 catalysts in *n*-heptane reforming has been carried out with catalysts purposely prepared for this work and with two industrial catalysts, one fresh and another one used and regenerated. The catalysts have been also characterised using classical techniques such as H_2 chemisorption and NH_3–TPD.

The results have shown that *n*-heptane reforming can be used to evaluate the state of naphtha reforming catalysts. The study of activity and selectivity of the catalysts in this reaction allows the evaluation of the state of the different kind of sites present in those catalysts.

The study of activity in the reaction gives a direct idea of the state of the catalysts, while the change in aromatisation selectivity evaluates the strength of acids sites. The ratio of metallic to acid sites can be evaluated through the dehydrogenation/aromatisation rate.

These results confirm also those obtained in a previous work, showing that the deactivation of industrial catalysts is related to a segregation of tin to the surface of metallic particles.

We have shown that *n*-heptane reforming is a useful test reaction to characterise Pt-Sn/Al_2O_3 catalysts and can be used as a cheap, easy, quick and reliable way for the evaluation of naphtha reforming catalysts. However, despite the additional information given by this test reaction, the lack of knowledge of the mechanisms involved in each pathway and the diversity of products obtained make the standardisation of *n*-heptane reforming more difficult than would be interesting to be used as an industrial characterisation method.

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