

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231369093>

Effect Of The Solvent Used During Preparation On The Properties Of Pt/Al₂O₃ And Pt–Sn/Al₂O₃ Catalysts

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · OCTOBER 2001

Impact Factor: 2.59 · DOI: 10.1021/ie000939t

CITATIONS

16

READS

35

6 AUTHORS, INCLUDING:



G. Pecchi

University of Concepción

83 PUBLICATIONS 1,260 CITATIONS

SEE PROFILE

Effect Of The Solvent Used During Preparation On The Properties Of Pt/Al₂O₃ And Pt–Sn/Al₂O₃ Catalysts

Luciene S. Carvalho,[†] Patricio Reyes,^{‡,§} Gina Pecchi,[‡] Nora Figoli,^{||,⊥}
Carlos L. Pieck,^{||} and Maria do Carmo Rangel^{*,†}

Grupo de Estudos em Cinética e Catalise, Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Federação, 41 820-660 Salvador, Bahia, Brazil, Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 3-C, Concepción, Chile, and INCAPE, Instituto de Investigaciones en Catálisis y Petroquímica (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

The influence of the solvent (water, acetone, and ethanol) used during alumina impregnation on the properties of Pt/Al₂O₃ and Pt–Sn/Al₂O₃ catalysts was studied. Catalysts were characterized by H₂ chemisorption, TEM, temperature-programmed reduction, ammonia temperature-programmed desorption, UV–vis spectroscopy and cyclohexane dehydrogenation, *n*-pentane isomerization, and *n*-octane reforming reactions. It was found that the catalysts prepared in ethanol has the highest metallic dispersion. The results are explained considering the Pt–Sn complex stability in the different solvents used during the preparation. Pt/Al₂O₃ (acetone) is the most active catalyst for isomerization while the activity of Pt–Sn/Al₂O₃ catalysts decreases in the order ethanol > acetone > water. The selectivity to aromatic hydrocarbons is related to isomerization activity, but there also exists a competition between hydrocracking and dehydrocyclization.

Introduction

Catalysts containing both metal and acid functions are often used in naphtha reforming. They catalyze dehydrocyclization, isomerization and dehydrogenation reactions.¹ An adequate balance between both functions is important to achieve high selectivities to aromatic hydrocarbons and a low coke deposition rate. The classical catalyst used is Pt/Al₂O₃. The metallic function can be modified by the addition of a second element (Re, Ir, Sn, W, etc.) thus producing the so-called bimetallic catalysts, in which the second element is mainly present as an oxide. Pt–Sn/Al₂O₃, also used in the dehydrogenation of *n*-paraffins, has been widely studied during the last years because of its increasing importance in low-pressure reforming processes with continuous regeneration.^{2,3} One of the advantages of this type of catalysts is that they do not need pretreatments before being introduced to the reactor. Pt–Re/Al₂O₃, for example, needs a presulfuration step to suppress the excessive hydrogenolytic activity. Borgna et al.⁴ reported that Pt–Sn/Al₂O₃ has the lowest deactivation rate because of its low activity for the production of unsaturated hydrocarbons which are intermediate species for coking. Burch and Garla⁵ reported that there is an electron transfer from tin to platinum, which makes the Pt–C bond weaker, thus increasing the resistance against coke formation. It is possible that Sn modifies the selectivity and stability by an ensemble effect. Sn decreases the number of contiguous Pt atoms by dividing the Pt surface into smaller ensembles. In this way,

the adsorption of hydrocarbon molecules is limited and coke deposition on the metal and hydrogenolysis can be reduced.⁶ Moreover, tin decreases alumina acidity⁷ being the acid sites where dehydrogenated compounds are polymerized to coke. Beltramini and Trimm⁸ pointed out that Pt–Sn systems have a better selectivity to aromatic hydrocarbons compared to Pt and Pt–Re due to the inhibition of hydrocracking, isomerization and coke deposition on the surface of the catalysts.

There are several controversies regarding the oxidation state of Sn. It is related to many factors: the preparation method, the concentrations of Pt and Sn, the metal precursor, the kind and state of the support, the solvent used, etc., leading to the formation of alloys or segregated phases.^{6,9,10} Many authors consider that most part of Sn is present as Sn(II) species stabilized by alumina, and that only a small part is in the metallic state. This metallic species can interact with platinum forming alloys.^{6,9,10} Vásquez-Zabala¹¹ studied Pt–Sn catalysts supported on SiO₂, TiO₂ and Al₂O₃ by HREM and X-ray diffraction and concluded that Pt and Sn tended to be alloyed and that Pt–Sn alloys were easily formed in the bimetallic catalyst. They also observed a decrease in the particle size when Sn was added to Pt. In accordance with this observation, several authors have reported similar results using Mössbauer spectroscopy.^{12–14} They concluded that a part of tin was alloyed with platinum and that the remainder was found as ionic Sn(II) or Sn(IV).

Pt–Sn/Al₂O₃ catalysts are usually prepared by impregnation of the support with metal precursor solutions. Depending on the experimental conditions, different complexes are found in the impregnating solution.^{15,16} Several solvents other than water have been proposed in the literature, such as ethanol⁹ and acetone,^{2,15,17} but a detailed study concerning their effect on the properties of the catalysts is still lacking. In addition the experimental conditions vary widely in

* To whom correspondence should be addressed. Phone: 55 71 237 5784. E-mail: mcarmov@ufba.br

[†] Grupo de Estudos em Cinética e Catalise.

[‡] Facultad de Ciencias Químicas.

[§] Phone: 53 41 245974. E-mail: preyes@udec.cl.

^{||} INCAPE.

[⊥] Phone: 54 342 453 3858. E-mail: nfigoli@fiqus.unl.edu.ar.

these works, and thus one cannot conclude about the effect of the solvent itself. Therefore, a systematic study in which all the variables are kept constant, except the solvent, is necessary.

The objective of this paper is to compare the effect of different solvents used for catalyst preparation on the properties of Pt and Pt–Sn/Al₂O₃ catalysts, in particular on the catalytic activity and selectivity for *n*-octane reforming. The activity of the metallic and acidic functions are followed by test reactions. Only water, acetone, and ethanol were studied because they are the most commonly solvents used in the preparation of Pt and Pt–Sn based catalysts.

Experimental Section

Catalysts' Preparation. γ -Al₂O₃ (Cyanamid Ketjen CK 300, Sg = 180 m² g⁻¹, Vg = 0.50 cm³ g⁻¹), previously 40–80 mesh sieved, was used as support. Pt/Al₂O₃ catalysts containing 0.3 wt % Pt were prepared impregnating with excess liquid (2.0 cm³ g⁻¹ alumina). The impregnating solution was prepared by dissolving 4.0 mg cm⁻³ of H₂PtCl₆ and 0.33 cm³ of HCl (12 mol L⁻¹) in ethanol (e), acetone (a), or deionized water (w). Before impregnation, alumina was wet with the corresponding solvent so that its pores got completely filled. The impregnating solution was then added, and the system was kept in a rotaevaporator for 6 h. No phase separation was observed in all cases. The impregnated solid was separated by vacuum filtration and then dried at 120 °C in an oven for 12 h. The calcination of the solids was carried out in a fixed bed reactor under flowing air (50 cm³ min⁻¹). The catalysts were heated at 20 °C min⁻¹ up to 500 °C and kept at this temperature for 2 h. Sn/Al₂O₃ catalysts were prepared by the same procedure using a solution containing SnCl₂ (2.65 mg cm⁻³) and the same volume of 12 mol L⁻¹ HCl. The bimetallic catalysts (0.3% Pt–0.3% Sn/Al₂O₃) were prepared by the same method using a solution containing SnCl₂ (0.0140 mol L⁻¹), H₂PtCl₆ (0.0098 mol L⁻¹), and 12 mol L⁻¹ HCl. The impregnation time was 16 h, and the catalysts were calcinated for 4 h at 500 °C under flowing air (50 cm³ min⁻¹). Before catalyst evaluation, samples were reduced in situ in a H₂ stream (50 cm³ min⁻¹) for 2 h at 500 °C, heating at 10 °C min⁻¹.

Catalysts' Characterization. Platinum and tin contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES) in an ARL model 3410 equipment, using argon. The selected wave-numbers were 265.917 nm (Pt) and 235.495 nm (Sn). The samples were previously dissolved using a 1:3 HNO₃/HCl molar solution and then heated at 150 °C for 4 h. The liquid obtained was completed to 50 cm³ with HCl 1%. A modified Volhard–Charpentier method was used¹⁸ for the analysis of the chlorine content. About 0.2 g of the sample was dissolved in H₂SO₄, and the HCl produced was transferred under vacuum to a NaOH solution. Chlorine was then determined as chloride by volumetry.

To identify the metal complexes and the ionic species present, the analyses by UV–vis spectroscopy were carried out on impregnating solutions. The analyses were performed using a Varian Cary 1-E equipment, using HCl solutions (0.4 mol L⁻¹) in ethanol, water, or acetone as reference.

Temperature-programmed reduction (TPR) was carried out using a Micromeritics TPD/TPR 2900 system. Samples (0.3 g) were previously heated under nitrogen

(50 cm³ min⁻¹) and then analyzed with a reducing gas (5% H₂/N₂, 50 cm³ min⁻¹), in the temperature range 30–700 °C, heating at 10 °C min⁻¹. Pt dispersion was measured in the same equipment by H₂ chemisorption at room temperature using a pulse method and a mixture of 5% H₂/N₂ (50 cm³ min⁻¹). Before the analysis, samples (0.3 g) were reduced for 2 h at 500 °C and cooled with N₂ until room temperature.

Transmission electronic micrographs (TEM) were obtained in a JEOL model JEM-1200 EXII equipment. The samples were prepared by the extractive replica procedure.¹⁹ The histograms were obtained by measuring the size of about 200–250 particles; the mean particle size was obtained at the maximum of the histograms. The highest error is about 20% for the smallest particles.

The activity of the metallic function was studied by the cyclohexane dehydrogenation reaction.²⁰ The reaction was carried out at 315 °C for 3 h, using a continuous flow reactor and 0.1 g of catalyst. The reactor was fed with a (100 cm³ min⁻¹) H₂ flow saturated in cyclohexane kept at 20 °C (H₂:cyclohexane (molar) = 11). Under such conditions, the process was controlled by the chemical reaction. The activity of the acidic function was studied by *n*-pentane isomerization, a typical reaction of the acidic sites.²¹ The reaction was carried out during 2 h at 500 °C and atmospheric pressure, using 0.15 g catalyst, WHSV = 4.5 h⁻¹, and H₂:*n*-pentane (molar) = 6. Under such conditions there were no external or internal diffusion control, as confirmed by the Weisz–Prater criteria for the internal diffusion and by calculating the gradient of concentrations in the external film. Analysis of reactant and products were performed using a Varian 3400 CX gas chromatograph and a DMS on Chromosorb (1/8 in. × 3 m) column heated at 40 °C.

The acidity of the catalysts was measured by ammonia thermal-programmed desorption using a Micromeritics TPD/TPR 2900 equipment. The sample (0.3 g) was dried for 2 h in flowing air (50 cm³ min⁻¹). At this temperature, ammonia was fed by pulses until saturation. Then, the sample was cooled to room temperature, and it was finally heated at 10 °C min⁻¹ up to 800 °C. The amount of ammonia desorbed was recorded as a function of temperature.

The catalytic activity and selectivity during *n*-octane reforming was evaluated at 500 °C and atmospheric pressure during 6 h. The *n*-octane stream was used as a model feedstock of a naphtha cut that is extensively used in industrial processes in which the BTX (benzene, toluene, and xylene) compounds are desired. The reactor, containing 0.3 g catalyst, was fed with a 12 cm³ min⁻¹ H₂ flow passing over a saturator containing the hydrocarbon kept at 45 °C. Analyses of reactants and products were performed on line using a Varian 3600 CX gas chromatograph equipped with FID detector and a Petro 50 capillary column.

Results and Discussion

When the aqueous solution of stannous chloride was added to the chloroplatinic acid one, a change in color from yellow (typical of the platinum solution) to yellowish-brown was noted, besides the precipitation of a brown solid. After the addition of HCl, the brown solid was completely dissolved and the solution remained yellowish-brown. This color is characteristic of a tin–platinum complex, *trans*-PtCl₂(SnCl₃)₂²⁻, which is stable in acidic medium.^{22–24} It is known²² that this complex

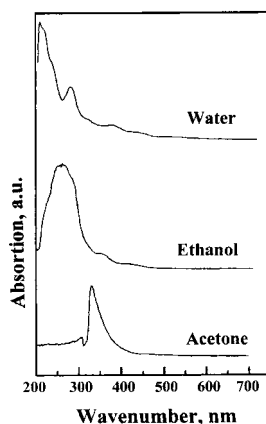


Figure 1. UV-vis curves of the impregnating solution used in the preparation of Pt-Sn/Al₂O₃.

Table 1. Platinum, Tin, and Chlorine Contents of the Samples

catalyst	% Pt	% Sn	% Cl
Pt/Al ₂ O ₃ (w)	0.28	0	0.52
Pt/Al ₂ O ₃ (e)	0.29	0	0.50
Pt/Al ₂ O ₃ (a)	0.28	0	0.70
Sn/Al ₂ O ₃ (w)	0	0.30	0.70
Sn/Al ₂ O ₃ (e)	0	0.29	0.61
Sn/Al ₂ O ₃ (a)	0	0.29	0.80
Pt-Sn/Al ₂ O ₃ (w)	0.20	0.29	0.69
Pt-Sn/Al ₂ O ₃ (e)	0.28	0.28	0.51
Pt-Sn/Al ₂ O ₃ (a)	0.26	0.27	0.73

is slowly transformed into *cis*-PtCl₂(SnCl₃)₂²⁻ as the acidity of the medium decreases and the color of the solution changes to yellow. In the preparation carried out in ethanol, the solution changed from yellow to orange and no solid was produced. In acetone, the solution changed from yellow to orange but immediately came back to yellow. These observations suggest that in aqueous solution the complex is mainly in the *trans* form whereas in ethanol or in acetone solutions it exists mainly in the *cis* form. This can be explained by considering that water is more acidic than ethanol which in turn is more acidic than acetone.

These results were confirmed by the UV-vis experiments carried out with the impregnating solutions, as shown in Figure 1. As it can be seen, the aqueous solution shows a spectrum with absorption bands at 211, 273, 387, and 425 nm. These bands can be assigned to the [PtCl₂(SnCl₃)₂]²⁻ complex being related the Sn(IV) species (211 nm), to the charge transfer of the ligands [SnCl]³⁻ to platinum (273 nm) and to d-d transitions (367 and 425 nm).²³ The spectrum shows bands at 328 and 390 nm, typical of Pt(II) species and another at 220 nm related to Sn(IV) species.²³ The spectrum showed an absorption band at 350 nm which also can be assigned to the platinum-tin complex. This band was shifted to a higher wavenumber probably due to the effect of the solvent, known as solvatochromism.²⁵ These results are in accordance with previous works which claim that surface complexes formed during the impregnation of stannic chloride on alumina are the same independently of the solvent, e.g., ketones, alcohols, etc.²⁶

Table 1 shows the results of the chemical analysis of the catalysts after calcination and reduction. It can be noted that the metal contents are close to the nominal values. On the other hand the amount of chloride changes with the solvent used in the preparation, being acetone the one which led to the highest value. It was

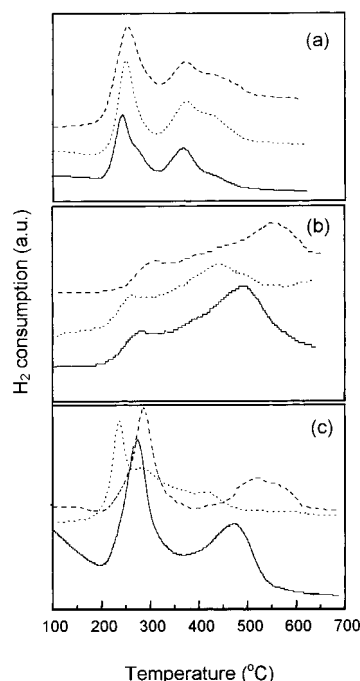


Figure 2. TPR profiles of the samples prepared in (··) ethanol; (- -) water and (—) acetone. (a) Pt/Al₂O₃, (b) Sn/Al₂O₃, (c) Pt-Sn/Al₂O₃.

Table 2. H₂ Consumption and Percentage of Reduced Pt and Sn during the TPR Experiments

catalyst	H ₂ consumption (μmol/g)		% reduced		
	calculated	experimental	Pt	Sn	Pt + Sn
Pt/Al ₂ O ₃ (w)	29.0	29.0	100		
Pt/Al ₂ O ₃ (e)	30.2	30.2	100		
Pt/Al ₂ O ₃ (a)	29.0	20.3	70		
Sn/Al ₂ O ₃ (w)	50.0	13.5		27	
Sn/Al ₂ O ₃ (e)	48.0	13.9		29	
Sn/Al ₂ O ₃ (a)	48.8	24.6		50	
Pt-Sn/Al ₂ O ₃ (w)	69.5	35.0			50
Pt-Sn/Al ₂ O ₃ (e)	76.0	39.8			52
Pt-Sn/Al ₂ O ₃ (a)	72.0	43.0			60

pointed out earlier²⁷ that most of chloride is lost during the steps of calcination and reduction of platinum based catalysts. As acetone has a lower boiling point, as compared to water and ethanol, most of acetone is eliminated at temperatures at which only small amounts of chloride can be eliminated. Ethanol and water are eliminated at temperatures high enough to leach the chloride from the solid.

The TPR profiles of the different catalysts are shown in Figure 2. The three Pt/Al₂O₃ catalysts showed the same profile, independently on the solvent used during preparation: a peak at about 230 °C attributed to the reduction of oxichloride platinum species [Pt(OH)_xCl_y]_s and [Pt O_xCl_y]_s^{16,28,29} and another centered at 370 °C due to the reduction of platinum species in high interaction with the support, generating a surface complex.²⁹ The use of different solvents does not affect significantly the TPR profiles of the Pt/Al₂O₃ catalysts, only slight shifts being observed. The H₂ consumption (Table 2) is the same for the solids prepared in water and ethanol meaning that platinum oxides were completely reduced during the TPR experiments. However, in the case of acetone, the H₂ consumption was lower and this can be assigned to a previous platinum reduction as suggested by the gray color of the solid after calcination, in accordance with previous works.³⁰ For the Sn/Al₂O₃

catalysts, similar profiles were obtained regardless the solvent used. The hydrogen consumption is similar for the catalysts prepared using water and ethanol and higher for the catalyst prepared using acetone. A similar trend is found for bimetallic catalysts. The hydrogen consumption shows no evidence of Pt–Sn interaction because segregated Sn is also reduced during TPR. Figure 2 shows some differences in the TPR profiles for Pt–Sn/Al₂O₃ samples. When acetone or water are used during preparation, two peaks can be observed. The first centered in the 280–300 °C range and the second, smaller and wider, in the 480–520 °C range. The H₂ consumption of the low-temperature peak is higher than the monometallic counterpart (Table 2), which may be attributed to the reduction of Pt and Sn located near Pt species. The second peak includes the partial reduction of segregated Sn,³¹ probably stabilized by the support forming tin aluminates species.^{5,17,30,32,33} The presence of Sn shifts the first peak toward higher temperatures compared with Pt/Al₂O₃, while the second reduction peak of Pt is suppressed. For Pt–Sn/Al₂O₃ (a), there is a shift of the first peak to lower temperatures compared with the material prepared using water. This effect can be attributed to the fact that using acetone, there is a decrease of the interaction of Sn with the support and a part of Sn forms a cluster or is alloyed to Pt. The lower interaction between Sn and Pt in the catalyst prepared with water, can be due to the hydrolysis of stannous chloride which may take place during the impregnation step² and which can lead to the destruction of the bimetallic complex. As pointed out earlier²⁶ the platinum–tin interaction largely depends on the stability of the bimetallic complex. When ethanol is used as solvent, the TPR profiles of Pt–Sn/Al₂O₃ exhibit a peak at 228 °C with shoulders at 276 and 435 °C, suggesting the existence of a strong Pt–Sn interaction, being likely the formation of an alloy. This fact can be assigned to the higher acidity of the ethanol solution as compared to the acetone one, which leads to a more stable bimetallic complex.^{22–24} These results show that different solvents affect only the TPR profiles of the bimetallic catalysts but not of monometallic. Because the solvent was the only variable changed during the catalysts' preparation, the others kept constant, the differences observed can be attributed to a solvent effect.

The particle size distributions of the catalysts evaluated by TEM are shown in Figure 3. It can be noted that the use of ethanol for both Pt/Al₂O₃ and Pt–Sn/Al₂O₃ led to the production of a higher proportion of the smallest particles whereas acetone produces a higher proportion of the biggest particles. This can be explained by considering that alumina in acidic medium adsorbs ions (e.g., PtCl₆^{2–}) as well as polar molecules like water, acetone, and ethanol (1.85, 2.88, and 1.69 D, respectively). The adsorption will be stronger as the dipolar moment increases and the amount of platinum and tin ions in solution will be greater as stronger is the adsorption of the solvent on alumina. Therefore, the drying step will be more important as the dipolar moment of the solvent increases. If this step is fast (e.g., in the case of acetone, BP = 56.2 °C), a fast precipitation of the metal will take place resulting in a low homogeneity of the metal particles on the alumina surface. A fast drying is that in which the rate of evaporation and elimination of steam is greater than the rate of the capillary flux; under these conditions the impregnated species are distributed down to the center of the pellet.³⁴

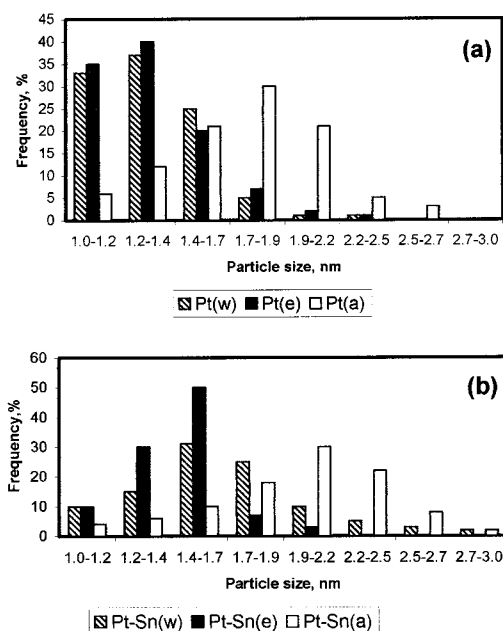


Figure 3. Metal particle size distribution obtained from TEM micrographs: (a) Pt/Al₂O₃, (b) Pt–Sn/Al₂O₃ catalysts.

Table 3. Particle Size Evaluated by TEM and H₂ Chemisorption and Catalytic Activity during Cyclohexane Dehydrogenation over Pt and Pt–Sn/Al₂O₃ Catalysts

catalyst	<i>d</i> (nm) TEM	<i>d</i> (nm) H ₂ chemisorption	conversion (%)
Pt/Al ₂ O ₃ (w)	1.5	1.8	27.0
Pt/Al ₂ O ₃ (e)	1.4	1.3	35.0
Pt/Al ₂ O ₃ (a)	1.9	2.2	20.0
Pt–Sn/Al ₂ O ₃ (w)	1.7		0.7
Pt–Sn/Al ₂ O ₃ (e)	1.5		1.8
Pt–Sn/Al ₂ O ₃ (a)	2.0		2.0

This explanation is in agreement with Boitiaux et al.²⁶ who pointed out that Sn is only physisorbed on chlorided alumina in the presence of acetone. According with such results, Machek et al.³⁵ reported a superior homogeneity of Pt in catalysts prepared using water compared with the catalyst prepared in acetone. It can also noted that the size of the particles produced in ethanol is very close to that of the particles produced in water, which can be due to the similar values of the dipolar moment of both solvents. Moreover, the particle size distribution presents some differences. Pt–Sn/Al₂O₃(e), within Pt–Sn/Al₂O₃ samples, shows a more uniform particle size distribution. The better metallic dispersion of the catalyst prepared in ethanol can be due to the sinterization produced by water during catalyst activation.^{36,37}

Table 3 displays metal particles sizes evaluated from hydrogen uptake and TEM. It can be seen an agreement between both methods for the monometallic samples. Metal particle size obtained by H₂ chemisorption was calculated assuming cubic metal particles in which one face remains on the support and the other five are exposed to H₂, by the equation $d = 5S/\rho$, S being the metal surface area and ρ the metal specific density. A stoichiometry of adsorption H/Pt = 1 was used. However, the pulse chemisorption method is not adequate for bimetallic catalysts due to the interaction of platinum and tin, which decreases the hydrogen adsorption capacity.³⁸ Thus, H₂ adsorption on these catalysts was not measured. Comparing the results of TEM for the monometallic catalysts, it can be seen that the size of

Table 4. Products Distribution (wt %), Conversion (X), and Selectivity to i -C₅ Isomer (S_{i-C_5}) during n -Pentane Reaction at Two Times on Stream on Pt and Pt–Sn/Al₂O₃ Catalysts and Acidity of the Catalysts

catalyst	time (min)	C ₁	C ₃	i -C ₅	n -C ₅	i -C ₆	X (%)	S_{i-C_5} (%)	acidity (meq NH ₃ g ⁻¹)
Pt/Al ₂ O ₃ (w)	5	0.8	2.9	15.0	61.7	13.3	38.3	39.1	0.059
	120	0.4	2.2	7.0	74.6	11.2	25.4	27.4	
Pt/Al ₂ O ₃ (e)	5	0.5	3.0	13.4	62.6	14.0	37.4	35.7	0.062
	120	0.2	1.5	8.7	71.1	15.1	28.9	23.1	
Pt/Al ₂ O ₃ (a)	5	0.9	2.6	17.2	55.4	17.6	44.6	38.4	0.062
	120	0.3	1.6	12.0	64.2	17.8	35.8	33.6	
Pt–Sn/Al ₂ O ₃ (w)	5	0.2	2.6	30.2	43.4	18.9	56.6	53.4	0.061
	120	0.1	1.4	17.6	60.7	17.2	39.3	44.7	
Pt–Sn/Al ₂ O ₃ (e)	5	0.2	2.0	34.9	43.0	16.3	57.0	61.2	0.064
	120	0.1	1.1	29.0	50.0	16.5	50.0	58.1	
Pt–Sn/Al ₂ O ₃ (a)	5	0.2	1.8	33.9	42.0	19.0	58.0	58.4	0.064
	120	0.1	1.1	24.6	54.3	18.3	45.7	54.0	

the particles of the samples prepared using water or ethanol are the same, while there is a small increase in the case of the sample prepared using acetone. The same behavior is noted for the bimetallic catalysts.

Table 3 also shows the catalytic activity for cyclohexane dehydrogenation, which is catalyzed by the metallic sites and is a structure insensitive reaction:³⁹ it does not require a special arrangement of platinum atoms. Therefore, the activity of the catalysts is a function of the exposed platinum atoms and one can consider the dehydrogenating capacity as proportional to the metal function of the catalyst. 100% of selectivity to benzene and stability during the 170 min on stream were found in all cases. All Pt/Al₂O₃ catalysts present a high dehydrogenating activity, being the highest for Pt/Al₂O₃(e), which is the catalyst that showed the platinum particle size distribution shifted to smaller sizes. The TOF (cyclohexane molecules transformed by second and by Pt superficial atom) for the Pt/Al₂O₃ catalyst are 2.2, 2.2, and 2.1 for catalysts prepared using water, ethanol, and acetone, respectively.

The results also show that the activity of the different Pt–Sn/Al₂O₃ catalysts is similar, but lower than those of Pt/Al₂O₃. This indicates geometric and/or electronic interactions between Pt and Sn that produce a drastic decrease in the platinum activity during cyclohexane dehydrogenation.

Table 4 shows the product distribution during the n -pentane reaction for all the studied catalysts at two times on stream as well as the selectivity to i -C₅. The definition of selectivity used in this work considers the number of moles of the i product formed per number of moles of n -C₅ reacted. There is no aromatic hydrocarbons formation using n -C₅ as feed and the main products are isomeric paraffins. It is accepted that the isomerization mechanism for these catalysts is a bifunctional metal–acid one⁴⁰ where the reaction begins with the paraffin dehydrogenation on the metallic sites; then, the olefin so produced is isomerized on the acid sites and the iso-olefin is hydrogenated on the metal sites. The reaction mechanism is controlled by the acid function²¹ and the formation of iso-pentane can be taken as a measure of that function. It has been reported that isomerization can proceed by a metallic monofunctional mechanism through hydrogenolysis of five-member rings.^{1,41,42} However, its contribution is negligible compared to the bifunctional mechanism under the operational conditions used in reforming.¹ By comparing the monometallic catalysts, it can be seen that the catalyst prepared in acetone is the most active and this can be assigned to its high chloride content. It can also be seen that in these catalysts the isomerization activity is

closely related to the amount of chloride. However, these solids showed similar acidity as measured by ammonia thermal programmed desorption (Table 4), and thus, one can conclude that n -C₅ isomerization is a more sensitive method to measure the acidity. This conclusion is confirmed by the high concentration of i -C₆, indicating a high disproportionation activity, typical of the acid sites.

The addition of Sn increased the isomerization activity. The catalyst prepared in ethanol was the most selective to isomerization followed by those prepared in acetone or water. These results cannot be related to the amount of chlorine leading to the conclusion that Sn itself changed the isomerization selectivity of the catalysts, in agreement with Paál et al.⁶ As pointed out earlier,⁷ the presence of tin decreases the acidity of the support, mainly the stronger acids sites, thus decreasing hydrocracking and increasing isomerization through hydrogenolysis of five-member rings.^{41–43} It is possible that Sn decreases the metallic activity leading to a decrease in hydrogenolysis products and to an increase in the selectivity to isomerization products.

Another product of the n -pentane reaction is methane (C₁), which is a typical product of hydrogenolysis on the metallic function,⁴⁴ a demanding reaction.³⁹ The formation of C₁ is higher on the mono than on the bimetallic catalysts, indicating a higher activity of the metallic function of the formers. The lower capacity of Pt–Sn/Al₂O₃ to produce hydrogenolysis products (Table 4) can be explained taking into account that Sn reduces Pt ensembles^{45,46} and decreases hydrogenolytic capacity.

Both monometallic and bimetallic Pt–Sn catalysts exhibit deactivation during reaction, as observed in Table 4 from the values of n -C₅ conversion. This can be due to cracking reactions leading to coke. Both C₁ and i -C₅ decrease with time on stream, depending on the solvent used in the preparation.

Table 5 shows the n -octane conversion, selectivity to C₁, and selectivity to C₈ aromatic hydrocarbons, the most important products in the reforming reaction, at 1 and 6 h time on stream. By comparing the selectivity to C₈ aromatic hydrocarbons on the monometallic catalysts, one can see some differences due to the solvent used in the preparation of the samples. The catalysts prepared in ethanol and acetone showed the highest values followed by that prepared in water. It is well-known that aromatic hydrocarbons are produced by dehydrocyclization of paraffins, which occurs mainly by a bifunctional mechanism under the operational conditions of reforming.¹ The paraffins are first dehydrogenated on the metal to give n -olefins which migrate to a neighboring acid site, where they are protonated,

Table 5. *n*-Octane Conversion (X) and Selectivity to C₁ and C₈ Aromatic Products at Two Time on Stream on Pt and Pt–Sn/Al₂O₃ Catalysts

catalyst	time, h	X, mole %	C ₁ , %	aromatic selectivity %
Pt/Al ₂ O ₃ (w)	1	85.6	0.2	63.8
	6	83.2	0.2	44.7
Pt/Al ₂ O ₃ (e)	1	95.8	0.5	75.4
	6	86.0	0.4	60.8
Pt/Al ₂ O ₃ (a)	1	96.3	0.6	74.3
	6	84.1	0.5	52.6
Pt–Sn/Al ₂ O ₃ (w)	1	97.9	0.1	83.4
	6	97.2	0.1	84.7
Pt–Sn/Al ₂ O ₃ (e)	1	97.9	0.1	86.8
	6	97.8	0.1	85.0
Pt–Sn/Al ₂ O ₃ (a)	1	95.9	0.1	80.7
	6	95.1	0.1	76.4

producing a secondary carbenium ion. This ion is cyclized on the acid function, producing five-carbon-atom ring olefins which are then isomerized on the acid sites, enlarging the ring to six carbons. In this way, cyclohexene and cyclohexadiene (with ramifications or not) are dehydrogenated to aromatic hydrocarbons. The dehydrogenation–hydrogenation reactions on the metal function are rapid enough to be considered in thermodynamic equilibrium, whereas isomerization reactions on the acid function are slower.¹ Therefore, the highest selectivity to aromatic hydrocarbons is expected to take place on catalysts prepared using acetone and water which showed the highest selectivity to *i*-C₅ (Table 4) during the *n*-pentane test reaction. As mentioned before the selectivity to *i*-C₅ is a measure of the acid function. Nevertheless, the high selectivity to C₈ aromatic hydrocarbons is observed on catalysts prepared using ethanol and acetone. This apparent discrepancy can be explained by considering the hydrocracking activity of these catalysts. The selectivity to hydrocracking (C₂–C₆) is 9.7, 7.7, and 6.5 for catalysts obtained using water, acetone or ethanol, respectively. According to previous studies,¹ hydrocracking is catalyzed by the acid function which cracks the paraffin molecule in the middle, resulting in low methane production. It has been found that, in general, the products of hydrocracking are not further cracked within certain reaction contact times, but for high conversions, successive or secondary hydrocracking increase the yield of lower paraffins. In our case, the conversions were high and the distribution of the C₂–C₆ products shows that further hydrocracking took place. Therefore, the acid function of these catalysts is able to catalyze hydrocracking reactions and thus decreases the aromatic hydrocarbons production. Following this reasoning, the catalyst obtained in ethanol was expected to produce more aromatics because it has the lower selectivity to hydrocracking. It means that its acidity is not high enough to prejudice the aromatic production.

The bimetallic catalyst showed a higher selectivity to C₈ aromatic hydrocarbons than the monometallics and this can be assigned to their higher isomerization activity (see Table 4). Moreover, the highest selectivity to C₈ aromatic hydrocarbons among the bimetallics, corresponds to Pt–Sn/Al₂O₃ (e), which showed the highest selectivity to *i*-C₅ during the *n*-pentane test reaction. For the three bimetallics, the selectivity to hydrocracking is almost the same, 1.0%. This is a lower value than those obtained with monometallics, in agreement to the bimetallics weaker acidity. As stated before, Sn affects the alumina strongest acid sites, the most active for hydrocracking reactions.⁴⁷

The production of C₁ is lower on all bimetallic catalysts because, as mentioned above, Sn destroys the Pt ensembles necessary for hydrogenolysis.

All catalysts are deactivated with time, as shown in Table 5. The addition of Sn reduces deactivation, in agreement with previous works which proposed that there is an electron transfer from tin to platinum, which makes the Pt–C bond weaker, thus increasing the resistance against coke formation.⁴⁸ Moreover, it is possible that Sn modifies selectivity and stability by an ensemble effect. Sn decreases the number of contiguous Pt atoms, dividing the Pt surface into smaller ensembles. In this way, limiting the adsorption of hydrocarbon molecules coke deposition on the metal and hydrogenolysis can be reduced.⁶

Conclusions

The use of ethanol, acetone, or water in the impregnation step during the preparation of Pt and Pt–Sn/Al₂O₃ leads to catalysts with different properties and performances during *n*-pentane isomerization, cyclohexane dehydrogenation, and *n*-octane reaction.

The differences can be assigned to the different boiling point and polarity of the solvents. Moreover, the drying step is influenced by the dipolar moment of the solvent.

The selectivity to C₈ aromatic hydrocarbons is related to the acid function, but according to the acidity, there also exists a competition between hydrocracking and dehydrocyclization.

Acknowledgment

L.S.C. acknowledges CAPES. The financial assistance of FINEP, CNPq, CONICET, UNL, SECyT and Vitae Foundation, Antorchas Foundation and Andes Foundation are also acknowledged.

Literature Cited

- (1) Parera, J. M.; Fígoli, N. S. Reactions in the Commercial Reformers. In *Catalytic Naphtha Reforming: Science and Technology*; Antos, G. J., Aitani, A. M., Parera, J. M.; Eds.; Marcel Dekker: New York, 1995.
- (2) Li, Y. X.; Klabund, K. L.; Davis, B. H. Alloy Formation in Supported Pt–Sn Catalysts: Mossbauer Studies. *J. Catal.* **1991**, *128*, 1.
- (3) Srinivasan, R.; Rice, L.; Davis, B. H. Electron Microdiffraction Study of Pt–Sn–Alumina Reforming Catalysts. *J. Catal.* **1991**, *129*, 257.
- (4) Borgna, A.; Garetto, T. F.; Apesteguía, C. R. Simultaneous Deactivation by Coke and Sulfur of Bimetallic Pt–Re(Ge, Sn)/Al₂O₃ Catalysts for *n*-Hexane Reforming. *Appl. Catal., A* **2000**, *197*, 11.
- (5) Burch, R.; Garla, L. C. Platinum–tin Reforming Catalysts II: Activity and Selectivity in Hydrocarbons Reactions. *J. Catal.* **1981**, *71*, 360.
- (6) Paál, Z.; Györy, A.; Urzkurat, I.; Olivier, S.; Ghérin, M.; Kappenstein, C. Pt/Al₂O₃ Catalysts Prepared by Two Different Methods: Hydrogen Pressure Effects in the Reactions of *n*-Hexane. *J. Catal.* **1997**, *168*, 164.
- (7) Shen, J.; Cartright, R. D.; Chen, Y.; Dumesic, J. A. Microcalorimetric and Infrared Spectroscopic Studies of γ -Al₂O₃ Modified by Tin Oxides. *Catal. Lett.* **1994**, *26*, 247.
- (8) Beltramini, J. N.; Trimm, D. Catalytic Reforming of *n*-Heptane on Platinum, Tin and Platinum–Tin Supported on Alumina. *Appl. Catal.* **1987**, *31*, 113.
- (9) Weishen, Y.; Liwu, L.; Yining, F.; Jingling, Z. Surface Structure and Catalytic Performance of Supported PtSn Catalysts. *Catal. Lett.* **1992**, *12*, 267.
- (10) Barías, O.; Holmen, A.; Blekkan, E. A. Propane Dehydrogenation over Supported Pt and Pt–Sn Catalysts: Catalyst

Preparation, Characterization and Activity Measurements. *J. Catal.* **1996**, 158, 1.

(11) Vázquez-Zavala, A.; Ostoa-Montes, A.; Acosta, D.; Gómez-Cortés, A. Characterization of Structure and Catalytic Activity of Pt–Sn Catalysts Supported in Al_2O_3 , SiO_2 and TiO_2 . *Appl. Surf. Sci.* **1998**, 136, 62.

(12) Vértés, Cs.; Tálas, E.; Czako-Nagy, I.; Vértés, A.; Margitfalvi, J. Mössbauer Spectroscopy Studies of Pt–Sn/ Al_2O_3 Catalysts Prepared by Controlled Surface Reactions. *Appl. Catal.* **1991**, 68, 149.

(13) Hobson, M. C., Jr.; Goresh, S. L.; Khare, G. P. A Mössbauer Spectroscopy Study of Platinum–Tin Reforming Catalysts. *J. Catal.* **1993**, 142, 641.

(14) Kuznetsov, V. I.; Belyi, A. I.; Yurchenko, E. N.; Smolikov, M. D.; Protasova, M. T.; Zatulokina; Duplyakin, V. K. Mössbauer Spectroscopic and Chemical Analysis of the Composition of Sn-Containing Components of Pt–Sn/ Al_2O_3 (Cl) Reforming Catalysts. *J. Catal.* **1986**, 99, 159.

(15) Srinivasan, R.; Davis, B. H. X-ray Diffraction and Electron Microscopy Studies of Platinum–Tin–Silica Catalysts. *Appl. Catal., A* **1992**, 87, 45.

(16) Lieske, H.; Völter, J. State of Tin in Pt–Sn/ Al_2O_3 Reforming Catalysts Investigated by TPR and Chemisorption. *J. Catal.* **1991**, 90, 96.

(17) Balakrishnan, K.; Schwank, J. A Chemisorption and XPS Study of Bimetallic Pt–Sn/ Al_2O_3 . *J. Catal.* **1991**, 127, 287.

(18) Figoli, N. S.; Sad, M. R.; Beltrami, J. N.; Jablonski, E. L.; Parera, J. M. Influence of the Chlorine Content on the Behavior of Catalysts for *n*-Heptane Reforming. *Ind. Eng. Chem. Prod. Dev.* **1980**, 19, 545.

(19) Gallezot, P.; Leclercq, C. Characterization of Catalysts by Conventional and Analytical Electron Microscopy. In *Catalyst Characterization*, Imelik, B., Vedrine, J., Eds.; Plenum Press: New York, 1993.

(20) Ayo, D. B.; Susu, A. A. Platinum–Rhenium/Alumina Catalysts. III. Mechanism of C_6 Ring Hydrogenation/Dehydrogenation Reactions. *Appl. Catal.* **1988**, 40, 1.

(21) Querini, C. A.; Figoli, N. S.; Parera, J. M. Hydrocarbons Reforming on Pt–Re–S/ Al_2O_3 –Cl Coked in a Commercial Reactor. *Appl. Catal.* **1989**, 52, 249.

(22) Young, J. F.; Gillard, R. D.; Wilkinson, G. Complexes of Ruthenium, Rhodium, Iridium, and Platinum with Tin (II) Chloride. *J. Chem. Soc.* **1964**, 5176.

(23) Baronetti, G. T.; de Miguel, S. R.; Scelza, O. A.; Fritzler, M. A.; Castro, A. A. Pt–Sn/ Al_2O_3 Catalysts: Studies of the Impregnation Step. *Appl. Catal.* **1985**, 19, 77.

(24) Jin, L. Y. Platinum–Tin Complexing and its Application to Catalysis. *Appl. Catal.* **1991**, 72, 33.

(25) El Seoud, O. A.; Novaki, L. P. Effects of Solvent Polarity on Chemical Processes: A Brief Review. *An Assoc. Bras. Quim.* **1996**, 45, 10.

(26) Boitiaux, J. P.; Deves, J. M.; Didillon, B.; Marcilly, C. R. Catalyst Preparation. In *Catalytic Naphtha Reforming: Science and Technology*; Antos, G. J., Aitani, A. M., Parera, J. M., Eds.; Marcel Dekker: New York, 1995; Chapter 4, pp 79–111.

(27) Bishara, A.; Murad, K. M.; Stanislaus, A.; Ismail, M.; Hussain, S. S. Chlorine Leaching and Replenishing Studies on a Bimetallic Reforming Catalyst. *Appl. Catal.* **1983**, 7, 337.

(28) Garetto, T. F.; Borgna, A.; Benvenuto, E.; Apesteguía, C. R. Mecanismos de Sinterización de Catalizadores de Pt Soportado. Influencia de las Especies Intermedias. *XII Simp. Iberoam. Catal.* **1990**, 1, 585.

(29) Augustine, S. M.; Sachtler, W. M. H. On the Mechanism for the Platinum-Catalyzed Reduction of Rhenium in PtRe/ γ - Al_2O_3 . *J. Catal.* **1989**, 116, 184.

(30) Lieske, H.; Lietz, G.; Spindler, H.; Völter, J. Reactions of Platinum in Oxygen- and Hydrogen-treated Platinum-Alumina

Catalysts I: Temperature Programmed Reduction, Adsorption and redispersion of Platinum. *J. Catal.* **1983**, 81, 8.

(31) Stagg, S.; Alvarez, W.; Resasco, V.; Parera, J. M.; Querini, C. A. Influencia del Estaño en Catalizadores de Pt Soportado para Dehidrogenación de Isobutano. *XV Simp. Iberoam. Catal.* **1996**, Vol II, p 1061.

(32) Huang, Y. J.; Fryer, C.; Park, D.; Stirling; Webb, G. Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy Studies of Pt–Sn. *J. Catal.* **1996**, 159, 340.

(33) Völter, J.; Jurschner, U. Deactivation of Supported Pt and Pt–Sn Catalysts in the Conversion of Methylcyclopentane. *Appl. Catal.* **1983**, 8, 167.

(34) Komiyama, M. Design and Preparation of Impregnated Catalysts. *Catal. Rev.—Sci. Eng.* **1985**, 27, 341.

(35) Machek, V.; Hanika, J.; Sporka, K.; Ruzicka, V.; Kunz, J.; Janacek, L. The Influence of Solvent Nature of Chloropaltinic Acid Used for Supports Impregnations on the Distribution, Dispersity and Activity of Platinum Hydrogenation Catalysts. In *Scientific Bases for the Preparation of Heterogeneous Catalysts*, Proceedings of the 3rd International Symposium, Louvain-la-Neuve, Belgium, Elsevier: Amsterdam, 1982.

(36) Inui, T.; Miyake, T. Influence of Water in the Reaction Stage of Oxygen-Adsorbed Platinum Supported on γ -Alumina. *J. Catal.* **1984**, 86, 446.

(37) Huang, Y. J.; Fung, S. C. The Effect of the Chloride and Water Vapor on the Pt–Ir Reforming Catalysts. *J. Catal.* **1991**, 131, 378.

(38) Völter, J.; Lieske, H.; Lietz, G. Dehydrogenation of Cyclohexane and Chemisorption of H_2 and O_2 on Supported Pt–Pb and Pt–Sn Catalysts. *React. Kinet. Catal. Lett.* **1981**, 16, 87.

(39) Boudart, M.; Aldag, A.; Benson, J. E.; Dougharty, N. A.; Harkins, C. G. On the Specific Activity of Platinum Catalysts. *J. Catal.* **1966**, 6, 92.

(40) Mills, G. A.; Heinemann, H.; Milleken, T. H.; Oblad, A. G. Catalytic Mechanism. *Ind. Eng. Chem.* **1953**, 45, 134.

(41) Sparks, D. E.; Srinivasan, R.; Davis, B. H. Paraffin Dehydrocyclization. Part 8. Conversion of *n*-octane with Mono and Bifunctional Pt– Al_2O_3 Catalysts at 100 psig. *J. Mol. Catal.* **1994**, 88, 325.

(42) Srinivasan, R.; Davis, B. H. Paraffin Dehydrocyclization. Part 9. Conversion of *n*-octane with Pt–Sn Catalysts at Atmospheric Pressure. *J. Mol. Catal.* **1994**, 88, 343.

(43) Sparks, D. E.; Srinivasan, R.; Davis, B. H. Paraffin Dehydrocyclization. Part 10. Conversion of *n*-octane with Supported Pt–Sn Catalysts at 100 psig. *J. Mol. Catal.* **1994**, 88, 359.

(44) Sinfelt, J. H. Supported Bimetallic Cluster Catalysts. *J. Catal.* **1973**, 29, 308.

(45) Dautzenberg, F. M.; Helle, J. N.; Biloen, P.; Sachtler, W. M. H. Conversion of *n*-Hexane over Monofunctional Supported and Unsupported Pt Sn Catalysts. *J. Catal.* **1980**, 63, 119.

(46) Cartright, R. D.; Dumesic, J. A. Microcalorimetric, Spectroscopic, and Kinetic Studies of Silica Supported Pt and Pt/Sn Catalysts for Isobutane Dehydrogenation. *J. Catal.* **1994**, 148, 771.

(47) Wojciechowki, B. W.; Corma, A. *Catalytic Cracking Catalysis, Chemistry and Kinetics*; Marcel Dekker: New York, 1986.

(48) Burch, R. Platinum–tin Reforming Catalysts I: The Oxidation State of Tin and the Interaction Between Platinum and Tin. *J. Catal.* **1981**, 71, 348.

Received for review November 1, 2000
 Revised manuscript received May 29, 2001
 Accepted July 9, 2001

IE000939T