

Preventing self-poisoning in [Pt/Al₂O₃ + SO₄²⁻-ZrO₂] mixed catalysts for isomerization-cracking of heavy alkanes by prereduction of the acid function

Javier Mario Grau, Carlos Román Vera, José Miguel Parera*

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

Received 25 June 2001; received in revised form 25 October 2001; accepted 26 October 2001

Abstract

The activity and stability of composite catalysts obtained by mixing Pt/Al₂O₃ with SO₄²⁻-ZrO₂, were studied in the reaction of hydroisomerization-cracking of *n*-octane (300 °C, 1.5 MPa, WHSV = 4 h⁻¹, H₂/*n*-C₈ = 6) obtaining light isoalkanes (isobutane, isopentane, isohexane), very important components of the pool of reformulated gasoline. Both components of the composites were pretreated in H₂ before mixing. Prereduction eliminated the fraction of SO₄²⁻ reducible at low temperature, thought to produce SO₂ during reaction, a poison for the metal function. A reduction in the poisoning of the metal, produced by adsorption of S compounds, was tried in order to get a higher metal activity for the production of atomic H, needed for the hydrogenation of coke precursors and the prevention of deactivation.

The pretreatment temperature was adjusted between 300 and 500 °C in order to keep a suitable amount of sulfate, needed for a sustainable isomerizing-cracking activity and for the stabilization of the tetragonal crystal phase of ZrO₂, the most catalytically active crystal phase. When compared to non-reduced catalysts, composites reduced at 300–350 °C displayed improved activity and stability for benzene hydrogenation, a metal-catalyzed reaction, and the results were addressed to a decrease in S poisoning. In the pretreated composites the SO₄²⁻-ZrO₂ active tetragonal phase was maintained in spite of the loss of S. For isomerization-cracking of *n*-octane, the pretreated catalysts showed a higher selectivity to isobutane and a fairly longer stability than non-pretreated catalysts, like Pt/SO₄²⁻-ZrO₂ and SO₄²⁻-ZrO₂ mixed with Pt/Al. TPO tests showed that the catalysts were essentially free of coke. This fact was addressed to a lower coking rate on prereduced sites and to a higher metal activity for hydrogenation of coke precursors. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: SO₄²⁻-ZrO₂; Pt/Al₂O₃; Composite catalysts; *n*-Octane hydroisomerization-hydrocracking; Hydrogen pretreatment

1. Introduction

Environmental restrictions have put a stress on refiners for replacing high octane aromatics by other additives of similar high octane number and lower polluting effect. The option of choice in the recent

past used to be the addition of MTBE. However, recent concerns about the contamination of water natural sources by water-soluble MTBE coming from spills of stored tanks may lead to a gradual banning of this additive. The attention of the refiners has therefore changed to other sources of octane points, e.g. alkylate and branched alkanes. In the case of the latter, the usual route for obtaining C₅–C₆ branched alkanes is the isomerization of the unbranched compounds over an acidic catalyst.

* Corresponding author. Tel.: +54-342-4533858;

fax: +54-342-4531068.

E-mail address: incape@fiqus.unl.edu.ar (J.M. Parera).

Alternatively they can also be obtained by the isomerization and cracking of long-chain normal alkanes. In this case inexpensive feedstocks like long-chain paraffinic cuts can be valorized by means of their conversion to mixtures of high RON branched shorter alkanes.

Isomerization-cracking of long-chain *n*-alkanes is thus a suitable route for providing high octane number branched alkanes for the gasoline pool. The reaction has been studied by several research groups using different feedstocks. Weitkamp and co-workers reacted C₈–C₁₀ long-chain alkanes over Pt/Y zeolites [1,2] and over Pt/H-ZSM-5 zeolites [3]. Martens et al. used Pt/H-ZSM-22 zeolites for the conversion of decane [4]. Alvarez et al. studied the conversion of C₁₀ on Pt/HY zeolites [5]. Isomerization-cracking of long-chain alkanes can be performed over other strong acid catalysts, like H-MOR zeolites, WO₃-ZrO₂ (WZ) or SO₄²⁻-ZrO₂ (SZ). Recently, Zhang et al. have published an article on the hydroisomerization of *n*-C₁₆ on Pt/WZ [6]. Grau and co-workers have also published several papers on the hydroisomerization-cracking of *n*-C₈ over Pt promoted oxoanion promoted superacids [7–10].

Sulfate promoted zirconia is a specially attractive catalyst due to its high activity at low temperatures and its high selectivity to isomers. The addition of Pt improves the activity and diminishes the coking [8,11]. In the case of Pt/SZ catalysts a large portion of Pt is however found in an anomalous state. The dehydrogenation capacity is highly inhibited and the same occurs with the adsorption of H₂. This might be the reason why the catalyst needs to be operated at a high hydrogen partial pressure in order to be stable (molar H₂/paraffin > 6). It has been stated [8] that during the reduction of the catalyst and during the reaction in the presence of H₂, part of the sulfate is decomposed and sulfur products poison the Pt particles. Ebitani et al. [12] have shown by means of XPS experiments that Pt remains in an oxidized state even after reduction at 400 °C. The authors have suggested [13] that Pt is in the form of PtO and PtS and that the metal fraction is low. However other results obtained by X-ray diffraction (XRD) indicate that Pt⁰ metal is present. Shishido et al. [14] on the basis of XANES and EXAFS measurements of Pt/SZ (oxidized and reduced), PtO₂ and Pt foil, have found that Pt/SZ has mixed properties intermediate between

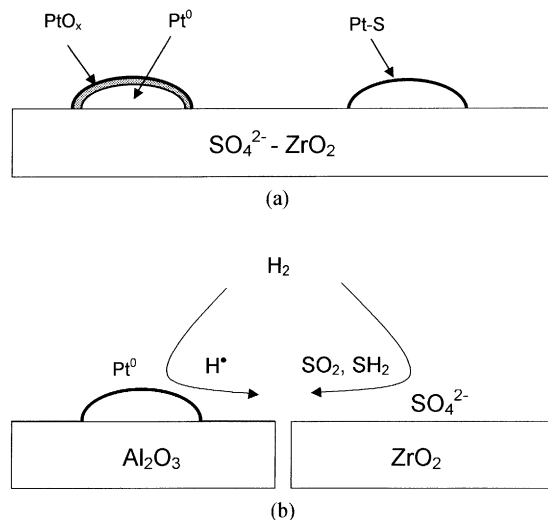


Fig. 1. (a) Two different models that explain the inhibition of metal properties in Pt supported over SZ [14,15]. (b) Migration of species over a [Pt/Al + SZ] composite catalyst, in the presence of hydrogen.

those of metal Pt⁰ and PtO₂. The results have been reconciliated by the authors by supposing the existence of Pt particles with a metallic core and an oxidized surface layer, as shown in Fig. 1a [14]. Paál et al. [15] firstly stated that Pt on the surface is in the form of PtS. On the basis of new data, Paál and co-workers [16,17] have recently postulated that Pt particles are almost completely encapsulated in the SZ matrix and that the anomalous properties are a result of a special case of strong metal support interaction. Ivanov and co-workers [18,19] on the basis of DRIFTS spectroscopic studies consider that over acidic Pt/SZ and in the presence of H₂, delocalized protons migrate to the surface of Pt and produce electron deficient Pt^{δ+}, as a result of the formation of [H–Pt]⁺ surface adducts. In any case, most of the authors agree that poisoning of the Pt surface by sulfur is present to some extent. Some other phenomena which are still a matter of debate (encapsulation, formation of Pt^{δ+} or PtO_x) could be responsible for the electron deficiency of the metal.

One way to increase the fraction of Pt non-affected by SZ and therefore the hydrogenating and hydrogen activation capacity is to separate the metal and acid

functions by using composite catalysts. Composites are formed by intimately mixing the acid catalyst (SZ, H-ZSM-5, H-MOR, etc.) with Pt/Al₂O₃ or Pt/SiO₂. The use of these hybrid catalysts has proved effective in producing active, stable and selective catalysts in acid catalyzed reactions [20–22]. In the case of the [(Pt/support) + SZ] system, an increase in conversion can be got depending on the working process conditions [21,22]. In some reported more complex preparations and with the same purpose of separating the metal and acid functions, the metal has been selectively deposited on the inert fraction of supported SZ/Al₂O₃ and SZ/SiO₂ [9]. But even when Pt and SZ are present on different particles and the effects of the strong interaction between SZ and Pt are prevented, Pt poisoning by S species seems also to be present when working in a hydrogen atmosphere [9]. This is seemingly due to the migration of SO₂ species and its further reduction to SH₂ onto Pt particles [23].

A possible solution to the problem of S poisoning in composite catalysts has been tried in this work. Composites of SZ and Pt/SZ mixed with Pt/Al₂O₃ were prepared by mixing the single components previously reduced with hydrogen. The object of the pretreatment was to eliminate labile SO₄²⁻ groups responsible for poisoning. Though less important the reduction pretreatment could also decrease the Pt mobility in Pt/Al₂O₃ and prevent its displacement over SZ. The extent of the pretreatment was optimized in order to preserve the structure of the active site. It is known that the presence of SO₄²⁻ promotes the stabilization of the catalytically active tetragonal phase of zirconia [24,25]. SZ with a monoclinic structure has much lower or almost null catalytic activity. The monoclinic phase is the thermodynamically stable phase at 620 °C (usual temperature of activation of the Pt/SZ catalyst). Partial elimination of sulfate by prereluction may generate changes in the active crystalline structure of ZrO₂ [26] and thus decrease the activity of the catalyst by decreasing the number of acid sites. A trade-off solution was pursued in this work, in order to improve the stability of the catalyst while retaining a good level of activity. The studied composite catalysts were used in the *n*-C₈ isomerization-cracking reaction and were further characterized by temperature programmed reduction

(TPR), XRD and temperature programmed oxidation (TPO).

2. Experimental

2.1. Catalyst preparation

The γ -Al₂O₃ (CK300 pellets provided by Ketjen, 180 m² g⁻¹) were used as inert support for the preparation of Pt/Al₂O₃ catalysts. The support was first calcined for 4 h at 400 °C and finally ground to 35–80 mesh ([Al] support). Zr(OH)₄ gel [ZH] was obtained by hydrolysis and precipitation of ZrOCl₂ (Strem, 99.9998%) [27]. Sulfated Zr(OH)₄ [SZH] was prepared by dipping the dried gel in H₂SO₄ 1 N for 2 h (10 ml g⁻¹), filtering and drying for 8 h at 110 °C. SO₄²⁻-ZrO₂ [SZ] was obtained by calcining SZH in air (3 h, 620 °C). Samples of SZ were treated in H₂ (21 g⁻¹ h⁻¹) at different temperatures (300, 400 and 500 °C) for 2 h in order to eliminate part of the sulfate groups. Then they were reoxidized at 620 °C in air for 1 h to ensure that S was in its maximum oxidation state (samples [SZ³⁰⁰], [SZ⁴⁰⁰] and [SZ⁵⁰⁰]).

2.1.1. Single catalysts

[Al] and [SZ], both ground to 35–80 mesh, were impregnated by incipient wetness with a solution of chloroplatinic acid in order to get materials with a 0.15 or 0.3% Pt. The impregnated supports were dried at 100 °C for 8 h. Then they were calcined in air at 300 °C (21 g⁻¹ h⁻¹, 2 h, sample [Pt/Al]) and 500 °C (21 g⁻¹ h⁻¹, 1 h, sample [Pt/SZ]). Both catalysts were further reduced in H₂ (21 g⁻¹ h⁻¹, 2 h) at 300 °C.

2.1.2. Composite catalysts

Composites containing 0.15% Pt were prepared by mixing powders sieved to 120–200 mesh. The sulfated supports [SZ, SZ³⁰⁰, SZ⁴⁰⁰, SZ⁵⁰⁰] were mixed with [Pt/Al] (0.3% Pt) in a 1:1 mass ratio. Another composite was prepared by mixing [Pt/SZ] (0.15% Pt) with [Pt/Al] (0.15% Pt). All the mixtures were suspended in *n*-hexane and stirred for 20 min. Then they were dried, pressed into a 6 mm diameter disk at 6 ton cm⁻² and ground to 35–80 mesh. Catalysts thus prepared were denoted as [(Pt/Al) + SZ], [(Pt/Al) + SZ³⁰⁰], [(Pt/Al) + SZ⁴⁰⁰], [(Pt/Al) + SZ⁵⁰⁰] and [(Pt/Al) + (Pt/SZ)].

2.2. Catalyst characterization

2.2.1. Chemical analysis

Sulfur content (before and after pretreatment) was determined by IR absorption in a LECO equipment. Pt content was measured by ICP-AES.

2.2.2. TPR

Reducibility of sulfate on pretreated and non-pretreated sulfated supports was assessed by TPR. An Ohkura TP2002S apparatus was used, a H₂:Ar reducing mixture (1.8%), a heating rate of 1 °C min⁻¹ and 0.15 g of catalyst per test.

2.2.3. XRD

X-ray diffraction spectra were recorded in a Shimadzu XD-1 spectrometer. Radiation was Cu K α filtered with Ni and the scanned angle was $2\theta = 20\text{--}80^\circ$.

2.2.4. Hydrogenation activity of the metal function

The hydrogenation capacity of supported Pt was assessed with the catalytic test of hydrogenation of benzene. An adequate mass of catalyst in order to obtain a constant mass of 0.15 mg of Pt was loaded in a glass reactor and heated in H₂ (1 h, 300 °C, 10 ml min⁻¹). Then the temperature was lowered to 100 °C and benzene was injected (0.51 ml h⁻¹) in a stream of H₂ (30 ml min⁻¹). The amount of cyclohexane formed was chromatographically monitored during 60 min.

2.2.5. Catalytic activity of the acid function

It was tested with the reaction of isomerization-cracking of *n*-octane (Carlo Erba RPA). It must be remarked that even though isomerization and hydrocracking can proceed through a bifunctional mechanism in which the formation of olefins on the metal sites enhances the overall reaction rate, the controlling reaction step takes place on the acid site, and the initial and overall conversion are supposed to be related mainly to the activity of the acid function. The metal function is thought to influence mainly the stability by means of the generation of activated hydrogen, an effective hydrogenating agent for coke precursors. For the isomerization-cracking reaction an amount of catalyst in order to maintain a constant mass of 0.5 g of SZ was used in each test. A plug-flow reactor was used [28]. Reaction conditions were: 300 °C, 1.5 MPa, WHSV = 4 h⁻¹ (with respect to SZ mass), molar

ratio H₂/*n*-C₈ = 6, length of the run = 10 h. The catalyst was kept at 300 °C for 1 h before the reaction was started. From chromatographic data, *n*-C₈ conversion and yields to the different products (on a carbon basis) were calculated.

2.2.6. Characterization of coke deposits

The coke deposited on the catalysts during the reaction was characterized by means of TPO using intermediate methanation [29]. The carrier was 6% O₂:N₂, the flow rate was 60 ml min⁻¹ and the heating rate was 12 °C min⁻¹.

3. Results

3.1. Reducibility of sulfate

The sulfur content of all the SZ supports used and the Pt content of the catalysts, are included in Table 1. The TPR plots are displayed in Fig. 2. The plots of the SZ supports, either prerduced or without prerduction showed a common pattern. A big broad signal due to sulfur reduction started at about 480 °C and had a maximum at about 600 °C. Prerduction produced a decrease in the amount of sulfate either if measured by ICP-AES or estimated by calculating the area of the TPR peak (see Table 1), in accordance with the elimination of surface sulfate groups. Prerduction also produced a shift of the maximum of the reduction peak to about 615 °C (same for all prerduced catalysts). The shift is thought to be linked to a process of elimination of weakly bound sulfur during reduction and stabilization of the remaining sulfur with stronger bonds upon reoxidation to sulfate. The TPR plot of the SZ sample without reduction showed a shoulder at 550 °C, not present in the other samples. Since the samples were recalcined after the reduction treatment these are not likely related to sulfur species with different oxidation states. The presence of both a small group of labile sulfates reducible at low temperature and a major group of sulfates reducible at higher temperatures, is more likely. For the samples prerduced at the lowest temperature used, 300 °C (also the temperature of reaction in the catalytic test of isomerization-cracking), the labile sulfate group is seemingly completely eliminated. At this temperature also a big percentage of the original sulfate groups reducible at higher temperature

Table 1
Intensity of the XRD peaks of the crystalline phases of zirconia^a

Catalysts	I^M/I^T (cps)	T^{PR} (°C)	S (%)	Pt (%)	SO ₄ ²⁻ reduction peak (°C)		
					Start	Maximum	Area (a.u.)
[SZ]	10/520 (0.019)	–	1.83	–	400	600	100
[SZ ³⁰⁰]	20/575 (0.035)	300	1.42	–	450	615	39
[SZ ⁴⁰⁰]	25/700 (0.036)	400	1.28	–	475	615	34
[SZ ⁵⁰⁰]	50/655 (0.076)	500	0.45	–	500	615	14
[Pt/Al]	–	300	–	0.29	–	–	–
[Pt/SZ]	–	300	1.32	0.31	280–300	550–600	–
[(Pt/Al) + SZ] ^b	–	–	0.91	0.14	380–400	580–620	–
[(Pt/Al) + (Pt/SZ)] ^c	–	–	0.76	0.15	380–400	550–600	–

^a Pt (%) and S (%) retained by SZ prereduced at different temperatures (T^{PR}). Starting and maximum temperature and area of the SO₄²⁻ reduction peak, as determined by TPR. I^M : intensity of the monoclinic phase; I^T : intensity of the tetragonal phase; T^{PR} : temperature of prereduction.

^b Pt/Al in this composite catalyst was reduced before mixing (2 h, 300 °C), SZ was not.

^c Both Pt/Al and Pt/SZ were reduced before mixing (2 h, 300 °C).

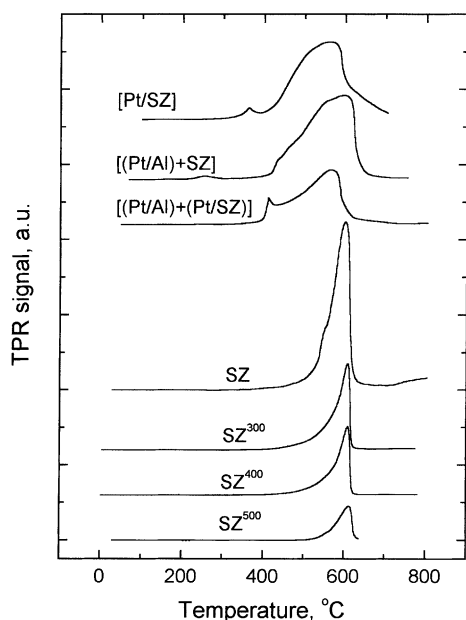


Fig. 2. Temperature programmed reduction plots. Reducing mixture: 1.8% H₂ in Ar; heating ramp: 1 °C min⁻¹; [SZ]: sulfated zirconia reoxidized 1 h at 620 °C in air; [SZ^x]: sulfated zirconia treated 2 h in H₂ (21 g⁻¹ h⁻¹) at different temperatures ($x = 300, 400, \text{ or } 500$ °C) and reoxidized 1 h at 620 °C in air; [Pt/SZ]: 0.3% Pt supported on sulfated zirconia calcinated 1 h in air at 500 °C; [(Pt/Al) + SZ]: composite containing sulfated zirconia reoxidized 1 h at 620 °C in air and 0.3% Pt supported on alumina reoxidated 1 h a 300 °C in a 1:1 mass ratio; [(Pt/Al) + (Pt/SZ)]: 1:1 (mass ratio) composite containing 0.15% Pt supported on sulfated zirconia (calcined 1 h in air at 500 °C) and 0.15% Pt supported on alumina (reoxidated 1 h at 300 °C).

was eliminated. The total amount of sulfate removed was 22% for the SZ³⁰⁰ support. For the other samples reduced at higher temperatures there was an increase in the amount of sulfate eliminated: 30% for SZ⁴⁰⁰ and 75% for SZ⁵⁰⁰, respectively.

A comparison of the data of Table 1 shows that at increasing prereduction temperatures the amount of sulfur estimated by the TPR peak area is lower than that measured by ICP-AES. If both data are taken as reliable it could be posed that part of the prereduced sulfate is not completely reoxidized to S⁶⁺ during the calcination in air at 620 °C for 1 h before the TPR test. This is not likely because for SZ catalyst XPS measurements have always reported a full coverage of S in the +6 oxidation state after calcination in air. Another possibility is that during reduction in the TPR test different reduced sulfur species are generated and variable amounts of H₂ are consumed depending on the pretreatment of the sample. In this sense Xu and Sachtler [23] by means of TPR-MS have shown that sulfate on SZ is decomposed to SO₂ upon reduction and that only a 50% of the original sulfur is removed. The rest remains as S²⁻ on the surface of the catalyst. Taking this fact into account it seems that for catalysts with a high percentage of S in the fresh state not all the sulfate species are removed as SO₂ but a big fraction remains as S²⁻. Reduction of sulfate to SO₂ consumes less hydrogen than reduction to S²⁻. For samples prereduced at successively higher temperatures the fraction of sulfate decomposed to SO₂

increases and therefore the amount of H_2 consumed in the TPR test decreases.

The addition of Pt, directly on SZ or by mixing with Pt/Al, produced a broadening and a shift of the TPR sulfate reduction peak to lower temperatures. Sulfur reduction started at about $300^\circ C$ for [Pt/SZ] (non-prerduced) and at about $380^\circ C$ for the composites [(Pt/Al) + SZ] and [(Pt/Al) + (Pt/SZ)] (Table 1, Fig. 2, non-prerduced). The maximum of the peak was located at about 550 – $580^\circ C$ for the catalysts containing Pt/SZ and at 600 – $620^\circ C$ for the one containing only Pt/Al. This result indicates that sulfur reduction in the TPR test is more effective when Pt is directly deposited over SZ. This was expected because in the case of [(Pt/Al) + SZ] activated hydrogen must spill over alumina before reaching SZ by surface diffusion while in the case of [Pt/SZ] sulfate groups are reached more directly.

3.2. XRD

The spectra of samples SZ, SZ^{300} , SZ^{400} and SZ^{500} recalcined (1 h at $620^\circ C$ in air) after the prerduction step were very similar (not shown). Though there were important sulfate losses produced by the hydrogenation, the tetragonal structure (T) was always the main crystalline phase (peaks at $2\theta = 30.3$, 50.5 – 51 and 60.5°). The signals at $2\theta = 28.2$ and 31.5° , typical of the monoclinic phase (M), increased with the temperature of prerduction, i.e. with the decrease of S content on the support (see Table 1). The intensity ratio I^M/I^T of the main peaks of the M ($2\theta = 28.2^\circ$) and T ($2\theta = 30.3^\circ$) phases was about 0.02 for SZ and about 0.08 for SZ^{500} . Comparing the I^T and I^M values for SZ and SZ^x it can be seen that from no prerduction to $T^{PR} = 400^\circ C$ there is a small growth of the tetragonal phase (from 520 to 700 cps) and an even much smaller growth of the monoclinic one (from 10 to 25 cps). In both cases the supposed process taking place is the crystallization of amorphous material. Conversely at $T^{PR} = 500^\circ C$ there is a net tetragonal to monoclinic transition because I^T decreases 6–7%, while I^M increases two-fold.

3.3. Activity in hydrogenation of benzene

The results of this test reaction are shown in Fig. 3, for measurements taken at 60 min time-on-stream

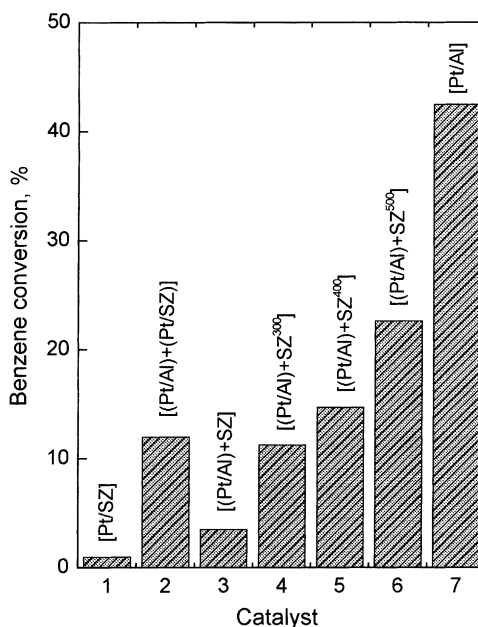


Fig. 3. Conversion of benzene into cyclohexane over Pt loaded catalysts after 1 h TOS. Experimental conditions: $100^\circ C$, 0.1 MPa, catalyst mass in order to obtain 0.15 mg of Pt, $H_2/Bz = 4.6$ (molar ratio). Labels are as in Fig. 2. All catalysts were prerduced 1 h in H_2 at $300^\circ C$ before the reaction.

(TOS). The sulfur-free [Pt/Al] catalyst had the highest conversion to cyclohexane. Conversely, the catalytic activity of [Pt/SZ] was the lowest, with a total conversion of benzene of about 1%. For the composites the conversion was intermediate between that of [Pt/Al] and [Pt/SZ]. In the case of the [(Pt/Al) + SZ^x] family there was a clear beneficial effect of prerduction on the conversion of benzene to cyclohexane. For the prerduced mixtures ($x \geq 300^\circ C$) an increment in the hydrogenation activity was observed as compared to [(Pt/Al) + SZ] (non-prerduced). The increase in the hydrogenating activity correlated with the higher temperature of prerduction and the corresponding decrease in the sulfate content. In the case of [Pt/SZ] and the non-prerduced composite catalyst [(Pt/Al) + SZ], during the heating in H_2 ($300^\circ C$, 1 h) before the catalytic test H_2S was detected in the exhaust gases of the reactor. H_2S was thought to be responsible for the poisoning of the metal function.

An outlier of the previous set of catalysts was the composite [(Pt/Al) + (Pt/SZ)]. It was not prereduced and its conversion was similar to that of [(Pt/Al) + SZ³⁰⁰].

3.4. Isomerization-cracking of *n*-octane

The results of Fig. 4 allow us to compare the activity levels and the stabilization patterns of the samples. The activity level is thought to be mainly related to the amount of acid sites capable of cracking and isomerization. The stabilization is supposed to be related to the capacity of Pt for generating activated hydrogen that spills over the surface and hydrogenates coke precursors. It is also linked to the surface concentration of acid sites of high acid strength that participate in the coking mechanism.

Table 2 contains conversion values of [Pt/Al], [SZ] and [Pt/SZ] in the reaction of *n*-C₈ at 0.1, 1 and 10 h TOS. For [Pt/Al] the conversion throughout the run decreased from 12.1% at 0.1 h to 6.9% at 10 h. Deactivation was addressed to coking on the metal sites. The catalyst had the highest selectivity to (C₆ + C₇) indicating the presence of cracking of octane, very likely due to hydrogenolysis. The sites responsible for hydrogenolysis were rapidly deactivated during the run. For the Pt-free [SZ] catalyst deactivation was important during the first hour of TOS, and the slope corresponding to the conversion drop was maximum (Fig. 4). For [SZ] the selectivity to isomers was

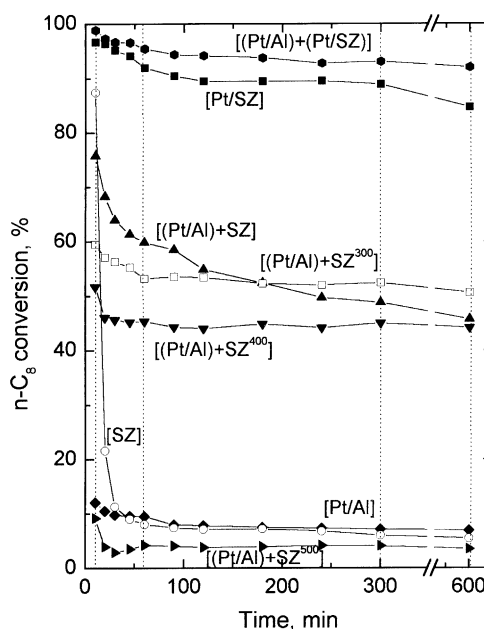


Fig. 4. Total conversion of *n*-octane on the different catalysts as a function of TOS. Experimental conditions: 300 °C, 1.5 MPa, WHSV = 4 h⁻¹ and molar ratio H₂/*n*-C₈ = 6. Labels are as in Fig. 2.

important and in contrast with [Pt/Al], the formation of (C₆ + C₇) was negligible indicating that highly asymmetric cracking was not favored. Conversely *i*-C₄, *i*-C₅ and C₃ were formed with good yield indicating the high selectivity to cracking of the bonds

Table 2

Total conversion, selectivities to each product and coke deposited on [Pt/Al], [SZ] and [Pt/SZ] catalysts, in hydroisomerization-cracking of *n*-C₈ at three values of TOS (0.1, 1.0 and 10.0 h)^a

Selectivity	[Pt/Al]			[SZ]			[Pt/SZ]		
	0.1 h	1.0 h	10.0 h	0.1 h	1.0 h	10.0 h	0.1 h	1.0 h	10.0 h
Conversion (%)	12.1	9.5	6.9	87.5	8.1	5.4	96.7	93.0	84.7
S _{C₂}	0.1	–	–	2.9	2.3	1.6	1.1	0.5	0.3
S _{C₃}	3.5	6.2	7.3	14.9	7.9	6.9	17.1	16.3	15.6
S _{<i>i</i>-C₄}	7.4	11.7	17.2	34.6	29.4	23.4	36.3	36.4	37.2
S _{<i>n</i>-C₄}	5.6	6.0	8.2	17.7	12.6	9.3	19.4	19.3	18.7
S _{<i>i</i>-C₅}	6.3	7.0	9.1	16.0	14.6	10.2	16.2	16.9	16.8
S _{<i>n</i>-C₅}	2.0	2.1	2.6	6.8	5.3	3.4	8.5	8.3	7.2
S _{<i>i</i>-C₆₋₇}	18.7	12.2	0.8	0.6	–	–	0.4	0.4	1.4
S _{<i>n</i>-C₆₋₇}	26.2	17.3	1.9	0.3	–	–	0.2	0.1	0.3
S _{<i>i</i>-C₈}	30.2	37.5	52.9	6.2	27.9	44.8	0.8	1.8	2.5
C%	–	–	0.26	–	–	1.80	–	–	0.29

^a Reaction conditions of *n*-C₈: 300 °C; 1.5 MPa; molar ratio H₂/*n*-C₈ = 6 and WHSV = 4 h⁻¹. S_{C₂}: selectivity to ethane; S_{C₃}: selectivity to propane; S_{*i*-C_{*m*}}: selectivity to *i*-alkane of *m* carbon atoms; S_{*n*-C_{*m*}}: selectivity to *n*-alkane of *m* carbon atoms.

connecting the fourth carbon of the adsorbed C₈ species.

The metal addition over [SZ] produced an increase in the initial catalytic activity (at 0.1 h). It also produced a decrease in the deactivation rate and this effect can be confirmed by the higher catalytic activity at 1 h TOS. The proportion of C₃ and C₅ in the products of reaction increased, indicating the increase in the contribution of the cracking reactions. The *iso*/normal ratio for the C₄ and C₅ alkanes was higher than the corresponding thermodynamic equilibrium value for the isomerization reaction [27], indicating the cracking of isoalkanes of C₆, C₇ and C₈. The presence of Pt on SZ reduced the amount of carbon deposited (values in Table 2 correspond to the end of the run) with respect to the support alone (SZ). Table 2 shows that during the run, at 0.1, 1.0 and 10, the total selectivity to isomers increased, due to the deactivation of the cracking reaction. For [SZ] the values are 57.4, 71.9 and 78.4, respectively, and for [Pt/SZ] 53.7, 55.5 and 57.9. The greater deactivation of [SZ] produced a great increase in the selectivity to the intermediate product *i*-C₈ and a decrease for the light isomers *i*-C_{4–7} to 51.2, 44.0 and 33.6 at the before-mentioned times. Meanwhile on [Pt/SZ] due to the lower deactivation there was a smaller increase in the intermediate *i*-C₈ and a small increase in each one of the light isomers, sum of which is 52.9, 53.7 and 55.4.

The high yields of *i*-C₄ and *i*-C₅ resemble the suggested bimolecular mechanism for isomerization of *n*-butane on SZ [30–33]. The reaction is initiated by small amounts of olefins, either in the feed or produced by the catalyst [30,31]. The propagation steps involve oligomerization of adsorbed C₄ species to form adsorbed C₈ intermediates, rearrangement and β-scission of this intermediate, and hydride transfer from gas phase paraffins to the reactive intermediates, leading to isomerization products and reactive surface intermediates. The termination steps involve coke formation, as well as hydride transfer between paraffin and the higher molecular weight intermediates to form, for example, C₆ and C₈ alkanes.

In our reaction system, *n*-C₈ might be firstly adsorbed and dehydrogenated to an *n*-C₈ alkene on a metal site, and then transformed into a C₈ carbenium ion on an acid site. This carbenium ion could then be isomerized and cracked as described in the above paragraph. The presence of C₈ olefins was detected in our

experiments at low values of conversion on the [SZ] catalyst. Oligomerization of olefins could be the origin of the coke deposits that caused the deactivation of the catalysts. No C₈ oligomers were detected in the reaction products, indicating that heavier products, if formed, are not desorbed.

Some other facts can be inferred from the values of *n*-C₄, *i*-C₄ and *i*-C₈ relative abundance. If the *i*-C₈ intermediate had been monobranching, similar amounts of *n*-C₄ and *i*-C₄ would have been produced. The *i*-C₄ was produced in higher proportion and therefore the *i*-C₈ intermediate was multibranching. Sometimes when the acid site is too strong cracking rapidly takes place and before enough branching has been produced. As a consequence little *i*-C₈ appears in the products and its concentration increases when the strong acid sites are deactivated by coke. Tables 2 and 3 indicate that the percentage of *i*-C₈ always increases with TOS (due to coking). This increase is steep and starts from a low level of conversion in the case of the non-prerduced catalysts and is smoother and starting from a high level in the case of the prerduced ones. This fact clearly indicates that strong acid sites responsible for coking are removed by prerduction.

It can also be seen that for most catalysts the selectivity to *i*-C₈ was lower than the selectivity to (*i*-C₄ + *i*-C₅). If desired, the cracking/isomerization ratio could be decreased by lowering the reaction temperature, but then the total conversion and the yield to isomers would also decrease.

It must be stressed that there is a great increase in the stability when Pt is added. However, one aspect to be noted is that after 10 h TOS the conversion of the [Pt/SZ] catalyst is still decreasing, i.e. stabilization is not complete. There is a drop in conversion of 10% if compared with the value at 1 h and the slope of the curve in Fig. 4 indicates a trend of continuous decline.

Plots of the conversion of *n*-C₈ as a function of TOS for the prerduced composites are also included in Fig. 4. Selectivity values can be found in Table 3. The conversion values of *n*-C₈ on [(Pt/Al) + SZ⁵⁰⁰] were very small and for this reason were not included in the table. The low conversion was addressed both to sulfur poisoning of the metal (lower activity than [Pt/Al]) and removal of acid sites in SZ⁵⁰⁰ (much lower activity than SZ). All composites displayed the beneficial action of Pt: they had a greater stability than Pt-free SZ under the same conditions of reaction. On the other

Table 3

Catalytic activity in hydroisomerization-cracking of *n*-C₈ on composite catalysts (non-prerduced and prerduced)^a

Selectivity	[(Pt/Al) + SZ]			[(Pt/Al) + SZ ³⁰⁰]			[(Pt/Al) + SZ ⁴⁰⁰]		
	0.1 h	1.0 h	10.0 h	0.1 h	1.0 h	10.0 h	0.1 h	1.0 h	10.0 h
Conversion (%)	75.8	59.9	45.7	59.5	53.2	50.6	51.7	45.4	44.2
S _{C₂}	–	–	–	–	–	–	–	–	–
S _{C₃}	16.3	15.4	14.3	13.5	12.4	12.0	11.0	10.6	10.4
S _{<i>i</i>-C₄}	39.5	39.9	33.7	34.2	33.3	31.6	28.7	27.9	27.0
S _{<i>n</i>-C₄}	18.6	18.1	15.1	16.2	15.6	15.1	13.4	13.3	12.1
S _{<i>i</i>-C₅}	16.1	16.0	16.5	15.0	14.8	14.3	15.0	14.1	13.2
S _{<i>n</i>-C₅}	5.3	5.6	5.9	4.9	4.3	4.0	3.1	2.8	2.1
S _{<i>i</i>-C₆₋₇}	0.5	0.3	0.3	0.5	0.4	1.4	0.4	–	–
S _{<i>n</i>-C₆₋₇}	0.2	0.1	0.2	0.2	0.2	0.3	0.1	–	–
S _{<i>i</i>-C₈}	3.5	4.6	14.6	15.5	19.0	21.3	28.3	31.3	35.2
C%	–	–	0.35	–	–	0.14	–	–	0.12

^a Total conversion and selectivity at three values of TOS and C% at the end of the test.

side, all composite catalysts had a lower catalytic activity than Pt/SZ. The results of catalytic activity of the prerduced catalysts, at 10 h TOS confirmed the improvement in stability produced by the prerduction.

The decrease in sulfate content produced a decrease in activity of the composite catalysts and hence a lower production of coke precursors. Both this fact and the higher hydrogenating capacity of the metal may be responsible for the increase in stability of the catalyst.

The inspection of Figs. 4 and 5 reveals that activity, selectivity to *i*-C₄ and stability for the composite catalyst [(Pt/Al) + (Pt/SZ)] are the best of all catalysts tested. Specially the conversion, which dropped in [Pt/SZ], remained stable in [(Pt/Al) + (Pt/SZ)] at 10 h TOS. With respect to the yield of *i*-C₄ (Fig. 5), prerduction greatly affected the yield values and the following order was approximately found:

$$[(\text{Pt}/\text{Al}) + (\text{Pt}/\text{SZ})] > [(\text{Pt}/\text{SZ})] \gg [(\text{Pt}/\text{Al}) + \text{SZ}] > [(\text{Pt}/\text{Al}) + \text{SZ}^{300}] > [(\text{Pt}/\text{Al}) + \text{SZ}^{400}] \gg [\text{SZ}]$$

The relative order was not modified during the run due to deactivation except for [(Pt/Al) + SZ]. For this composite the isobutane yield declined continuously and at the end of the run was lower than [(Pt/Al) + SZ³⁰⁰].

A bar plot in Fig. 6 shows the values of total conversion, global selectivity to *iso*- and *n*-alkanes and the selectivity to each isoalkane for the most important catalysts (isomerization-cracking of *n*-octane, 10 h TOS). The conversion for non-prerduced

[(Pt/Al) + SZ] was high at the beginning of the run and much higher than that of [(Pt/Al) + SZ³⁰⁰] (see Fig. 4). At 10 h TOS this trend was however reversed and the prerduced composite had more activity than [(Pt/Al) + SZ]. This fact must have been due to the lower deactivation rate of [(Pt/Al) + SZ³⁰⁰]. The

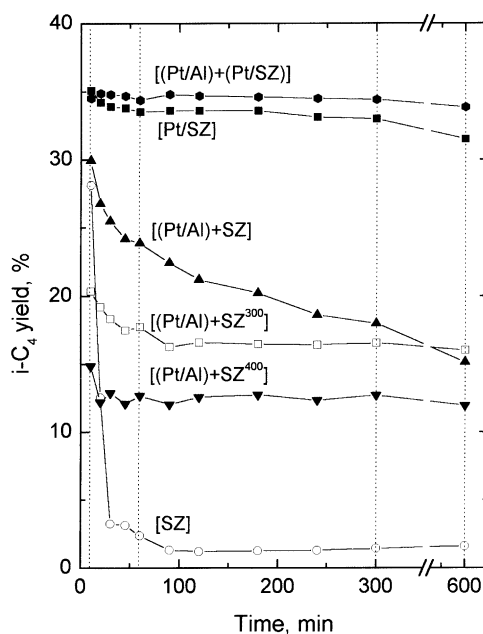


Fig. 5. Yield of isobutane in the isomerization-cracking of *n*-octane as a function of time. Experimental conditions and labels are as in Fig. 4.

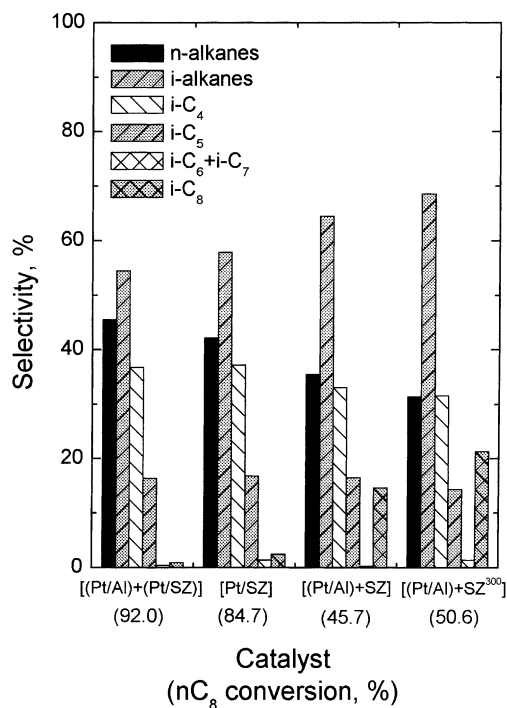


Fig. 6. Total conversion and selectivity to different products in the reaction of isomerization-cracking of *n*-octane, at 10 h TOS; *i*-C₄: isobutane; *i*-C_y: C_y isoalkanes.

acid sites of this catalyst seemed to have a lower acid strength than those present in [(Pt/Al) + SZ] as revealed by the higher yield to *i*-octane (see Fig. 6). If we accept that the acid strength was lower then the higher conversion at longer times must be related to the presence of a higher fraction of coke-free sites.

With regard to the case of [(Pt/Al) + (Pt/SZ)] and [Pt/SZ] it can be seen (Fig. 6) that both catalysts have an almost equal selectivity pattern. The activity is however higher for the first one, indicating that for the same amount of Pt on the catalyst, the overall performance is improved by distributing the metal on the acid and neutral support. It must be recalled that all catalysts have the same average concentration (0.15% Pt).

Fig. 7 contains results of the total conversion of *n*-octane and the yield to isomers (*i*-C₄, *i*-C₅ and *i*-C₈) as a function of the catalyst sulfur content of the composite catalysts [(Pt/Al) + SZ^x], *x* = 25, 300, 400, 450 and 500 °C, fresh (at 0.1 h TOS) and at the end of the run (10 h time-on-stream). Under reaction conditions

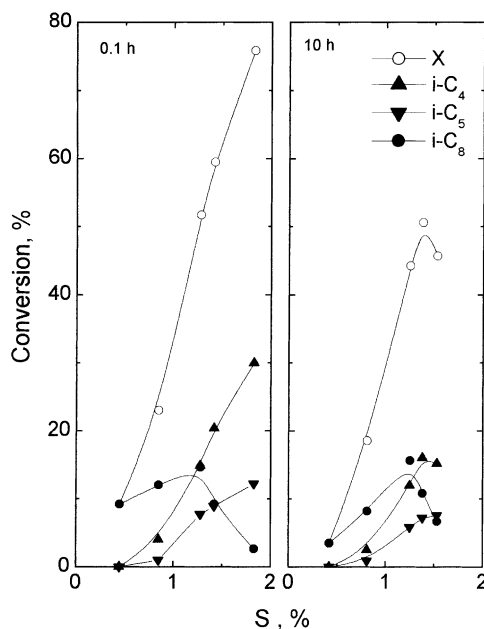


Fig. 7. Total conversion (*x*) and yield to different isoalkanes in the reaction of isomerization-cracking of *n*-octane as a function of the sulfur content at 0.1 and 10 h TOS.

(H₂, 300 °C, 1.5 MPa), the catalysts suffered of sulfate decomposition and removal and their sulfur content decreased. The sample without prerduction has the highest sulfur content, the highest initial total conversion, the highest yield to *i*-C₄ and *i*-C₅, and the lowest yield of *i*-C₈. After 10 h in the reaction medium it is no longer the most active sample (now 46%), the yield to *i*-C₄ and *i*-C₅ drops (50% for *i*-C₄ and 40% for *i*-C₅), and the yield to *i*-C₈ increases (15%). Conversely the sample prerduced at 300 °C has only a small activity drop during the run (60% total conversion at the beginning and 51% at the end). Its total yield of isomers at the end of the run is the highest of all composite catalysts. If we analyze the yield of isooctane for all catalysts it can be seen that the yield plots have a volcano shape. The maximum yield either at the beginning or the end of the run corresponds to S% of 1.25% approximately.

3.5. TPO of coke deposit

Fig. 8 shows the results of oxidation at programmed temperature of the carbonaceous deposit formed over

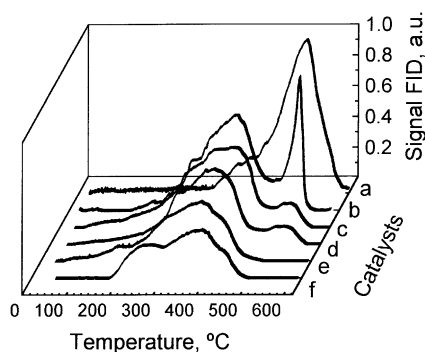


Fig. 8. Temperature programmed oxidation plots: (a) [SZ]; (b) [(Pt/Al) + SZ]; (c) [(Pt/Al) + SZ³⁰⁰]; (d) [(Pt/Al) + SZ⁴⁰⁰]; (e) [(Pt/Al) + SZ⁵⁰⁰]; (f) [Pt/Al].

simple and composite catalysts. Over SZ (curve a) desorption and burning of heavy adsorbed hydrocarbons started at about 300 °C and the TPO plot had a maximum at 540 °C. In the case of [Pt/Al] (curve f) we can identify two peaks. The burning of a fairly hydrogenated coke, adjacent or covering the metal sites, occurs with a maximum at 300 °C. A second big and broad peak at about 380 °C would correspond to the burning of carbon deposits over alumina.

In the case of the composite catalysts the peak related to the burning of hydrogenated coke on metal sites (300 °C) was not present or was much smaller. Two important peaks can be seen on these catalysts, one big and broad in the zone of combustion of coke on alumina (380–400 °C) and another smaller corresponding to the burning of highly polymerized coke on the strong acid sites of SZ, at about 530–540 °C. The magnitude of this last signal varied with the temperature of pretreatment of the composite, being smaller for composites pretreated at higher temperatures. This fact may be related to two different things: (i) a higher hydrogenating activity of the metal, preventing the formation of carbonaceous deposits over the acid sites; (ii) a lower polymerizing activity of the catalyst, related to a lower amount of sulfate and hence a lower acidity.

Comparing curve (f) with curves (b–e), we can see that the amount of coke on the metal was highest for the sulfate-free catalyst. This is not surprising. Coke on Pt particles is due to dehydrogenation and polymerization and in the case of the composites sulfur poisoning reduces the dehydrogenation activity.

4. Discussion

An increase in the hydrogenating capacity of the metal in composite catalysts prepared with pre-reduced SZ was thoroughly demonstrated by the results of Fig. 3. The increase in hydrogenating capacity goes parallel with the increase in temperature of pre-reduction. An improvement in the stability of these composite catalysts in hydroisomerization-cracking of *n*-octane (Fig. 4) was also found. At 10 h TOS, the activity of [(Pt/Al) + SZ³⁰⁰] was higher than that of the non-pre-reduced composite, though the sulfate content of the former was much lower.

In the case of Pt loaded SZ catalysts used in *n*-C₄ isomerization, it has been reported that minimum contents of SO₄²⁻ (approximately 1% for catalysts of 100 m²/g) are sufficient for the production of an activity level similar to that of catalysts with half a monolayer of SO₄²⁻ or more [34]. It has also been suggested [35] that the activity of SZ catalysts may be related to the presence of a small number of surface crystalline defects (anionic vacancies) in active tetragonal samples. Over surface defects sulfate anions would be very strongly chemisorbed due to the electrophilic nature of the sulfate group and the greater electronic availability of anionic vacancies. Activity could then be mainly related to a small group of sulfates, relatively strongly grafted and of hard reducibility. If we recall the TPR results of this work, the presence of these active sulfate sites could be linked to the high temperature TPR peak found in the pre-reduced composites at about 600 °C (Fig. 2). Though total elimination of these active sites would take place at 600 °C it seems that were also partially eliminated at 300, 400 and 500 °C, as revealed by the decreasing activity in *n*-octane hydroisomerization. The rest of the area of the TPR plot between 600 and 800 °C could correspond to other strongly grafted sulfate groups not related to catalytically active sites.

At high temperatures of pre-reduction an increase in the hydrogenating capacity of the metal was seen, but also the concentration of active SO₄²⁻ groups diminished and total activity dropped. Therefore an optimum was found, when a catalyst with a high activity (though less than that of [(Pt/Al) + SZ]) and enhanced stability was produced, e.g. the [(Pt/Al) + SZ³⁰⁰] composite.

There was clearly a negative effect of labile sulfate groups. Sulfur species would migrate toward the Pt particles during the reduction of Pt loaded SZ catalysts, poisoning it and decreasing its dehydrogenating properties. The migration of these sulfur species was attenuated by prereducing the acid function (SZ) and eliminating the weakly bound sulfate ions. The elimination of sulfate groups with reduction up to 400 °C did not reduce the catalytic activity to a great extent, indicating that only a fraction of these groups is related to active sites. The increase in stability of the composite catalyst may have been related both to the elimination of non-active sulfate and to a higher metal activity.

Despite the good results found for [(Pt/Al)+SZ³⁰⁰] activity and stability were maximum for [(Pt/Al) + (Pt/SZ)]. For this catalyst higher benzene conversion values were obtained in the hydrogenation test and an activity loss of only 8% after 10 h TOS was found in the *n*-C₈ isomerization-cracking reaction. A 12% loss of activity was found for the [Pt/SZ] catalyst with the same total amount of Pt. The reasons for such improved performance can be speculated. The selectivity of [(Pt/Al) + (Pt/SZ)] was similar to that of [Pt/SZ] for all products and therefore no new reaction mechanism is supposed to operate on the composite catalyst (Table 4). The higher stability must be related to a higher production of activated hydrogen that first spills from Pt over alumina and then moves by surface diffusion onto the SZ particles, thus keeping free of coke the acid sites responsible for isomerization and cracking.

Table 5 contains results of this work and other reported results of hydroisomerization on several catalysts of the Pt/zeolite type. A direct comparison is not easy, because the TOS, the reaction conditions and the Pt content of the catalysts vary widely. Under the same conditions, a comparison of our results with those of Grau and Parera [7] for hydroisomerization on H-MOR, indicates that both the activity and selectivity of [Pt/SZ + Pt/Al] are higher. The yield to isomers of zeolite HY and H-ZSM-5 is reported in [1,3] to be 60% or higher. This is much higher than the 50.1% of [Pt/SZ + Pt/Al], but the results were obtained at H₂/HC = 17–100 as compared to H₂/HC = 6 (this work) and the Pt content of those catalysts was 3.3 times higher. The same occurs in the case of the results of Martens et al. [4]. The performance of the zeolite is better, but it could be related to the high Pt content (1.0%) and different working conditions. On the other side, the results of Steijns et al. [2] and Alvarez et al. [5], corresponding to a long-term reaction and a low-pressure reaction, respectively, indicate a much worse performance of the Pt/zeolite catalyst. For a more fair comparison with industrial catalysts, particularly a Pt/Y zeolite catalyst, it would be appealing to study the hydroisomerization of long-chain alkanes over a [Pt/SZ + Pt/Al] catalyst of higher Pt content and under a higher H₂ partial pressure. Such experiments are currently under way and will be the subject of a next article.

The results of Fig. 4 were regressed with a simple first-order deactivation model in order to obtain

Table 4
Catalytic activity in hydroisomerization-cracking of *n*-C₈ on [Pt/SZ], [(Pt/Al) + SZ³⁰⁰] and [(Pt/Al) + (Pt/SZ)]^a

Selectivity	[Pt/SZ]			[(Pt/Al) + SZ ³⁰⁰]			[(Pt/Al) + (Pt/SZ)]		
	0.1 h	1.0 h	10.0 h	0.1 h	1.0 h	10.0 h	0.1 h	1.0 h	10.0 h
Conversion (%)	96.7	92.0	84.7	59.5	53.2	50.6	98.9	95.5	92.0
S _{C₂}	1.1	0.5	0.3	–	–	–	1.2	0.6	0.5
S _{C₃}	17.1	16.3	15.6	13.5	12.4	12.0	20.2	17.7	16.9
S _{i-C₄}	36.3	36.4	37.2	34.2	33.3	31.6	34.9	36.0	36.8
S _{n-C₄}	19.4	19.3	18.7	16.2	15.6	15.1	20.1	21.2	20.8
S _{i-C₅}	16.2	16.9	16.8	15.0	14.8	14.3	15.8	16.0	16.4
S _{n-C₅}	8.5	8.3	7.2	4.9	4.3	4.0	7.6	7.6	7.2
S _{i-C₆₋₇}	0.4	0.4	1.4	0.5	0.4	1.4	–	0.4	0.4
S _{n-C₆₋₇}	0.2	0.1	0.3	0.2	0.2	0.3	–	0.1	0.1
S _{i-C₈}	0.8	1.8	2.5	15.5	19.0	21.3	0.2	0.4	0.9
C%	–	–	0.29	–	–	0.14	–	–	0.02

^a Total conversion and selectivity at three values of TOS and C% at the end of the test.

Table 5

Comparison of current results with other reported results for hydroisomerization on zeolites^a

Catalysts	Feed	<i>T</i> (°C)	<i>P</i> _{HC} (kPa)	<i>P</i> _{H₂} (MPa)	<i>W/F</i> _{HC} (g h mol ⁻¹)	TOS (h)	Conversion (%)	Selectivity to isomer (%)	Yield to isomer (%)	Reference
Pt (0.5%)/CaY	<i>n</i> -C ₈	275	230	3.7	292	n.a.	82.6	81.1	67.0	[1]
Pt (0.5%)/CaY	<i>n</i> -C ₈	225	220	3.7	96	n.a.	1.1	≈100	1.1	[1]
Pt (0.3%)/H-MOR	<i>n</i> -C ₈	300	210	1.3	60	5	67.9	24.2	16.4	[7]
Pt (0.15%)/SZ + Pt (0.15%)/Al	<i>n</i> -C ₈	300	210	1.3	60	10	92	54.5	50.1	This work
Pt (0.3%) + SZ ³⁰⁰	<i>n</i> -C ₈	300	210	1.3	60	10	50.6	68.6	34.7	This work
Pt (0.5%)/H-ZSM-5	<i>n</i> -C ₉	240	20	2.0	130	n.a.	30.6	90.5	27.7	[3]
Pt (0.5%)/H-ZSM-5	<i>n</i> -C ₉	260	20	2.0	130	n.a.	81.6	74.3	60.6	[3]
Pt (0.5%)/HY	<i>n</i> -C ₁₀	130–250	n.a.	0.5–10	20–700	700	60.0	66.7	≈40.0	[2]
Pt (1.0%)/H-ZSM-22	<i>n</i> -C ₁₀	180–280	700	1.8	68	>1	80.0	78.7	63.0	[4]
Pt (1.5%)/HY	<i>n</i> -C ₁₀	200	11	0.1	<400	n.a.	70.0	66.6	46.6	[5]
Pt (0.35%)/HY	<i>n</i> -C ₁₀	200	11	0.1	<400	n.a.	60.0	62.5	37.5	[5]
Pt (0.5%)/WZ	<i>n</i> -C ₁₆	300	700	1.4	75	6	95.0	37.0	35.0	[6]

^a The values of activity and selectivity taken from the articles were chosen for conditions of maximum yield of isomers. In the case of [6] the chosen results correspond to the experiment with the *W/F* value closest to ours (n.a., not available).

information on the deactivation rate constants. The model used was

$$\frac{dX}{dt} = -kX \quad (1)$$

$$\ln\left(\frac{X}{X^0}\right) = -kt \quad (2)$$

where *t* is the TOS, *X* the conversion of *n*-octane, *X*⁰ = *X* the value extrapolated to *t* = 0, and *k* can be directly related to the initial slope of the curve of the natural logarithm of conversion as a function of TOS. The value of *k* for each catalyst was regressed with a minimum squares algorithm and it was found that it varied between 0.004 and 0.08 min⁻¹. Only the first points corresponding to the fast deactivation period were taken into account in the regression, because at longer times the coke removal effect could not be disregarded. This effect is not included in the model of Eqs. (1) and (2).

In the case of the [SZ] catalyst, *k* = 0.075 min⁻¹. For [(Pt/Al) + SZ], *k* = 0.023 min⁻¹. For [Pt/SZ] and [(Pt/Al) + SZ³⁰⁰], *k* = 0.007 min⁻¹, and for [(Pt/Al) + (Pt/SZ)], *k* = 0.004 min⁻¹. The *k* values follow the order: [SZ] > [(Pt/Al) + SZ] > [Pt/SZ] > [(Pt/Al) + SZ³⁰⁰] > [(Pt/Al) + (Pt/SZ)]. The *k* value of [(Pt/Al) + (Pt/SZ)] clearly shows the enhanced stability achieved by distributing the same amount of Pt over alumina and sulfate-zirconia.

5. Conclusions

A treatment of prerduction of both components of [(Pt/Al) + SZ] composite catalysts, in hydrogen and at the temperature of reaction (300 °C), greatly increases the metal activity as assessed by the test of hydrogenation of benzene. It also enables a stable operation of the catalyst during isomerization-cracking of *n*-octane, with a conversion level of about 80% that of the non-prerduced composite. At prerduction temperatures higher than 400 °C the activity level is too low. The activity drop is mainly related to an excessive removal of sulfate and hence of acid active sites. At a reduction temperature of 300 °C, the amount of remaining sulfate (1.4% in the SZ particle) is enough for sustaining a moderate level of conversion.

The composite catalysts obtained from components prerduced at 300–400 °C display a level of conversion of *n*-C₈ that decays no more than 2% in 10 h of reaction. The enhanced stability can be rationalized in terms of two factors. Metal particles suffer a lower poisoning by sulfur and can effectively generate activated hydrogen that spills over the support and hydrogenates coke precursors. Removal of sulfate by reduction also decreases an important amount of acid sites of high acid strength responsible for coking.

No significant changes in the crystal structure of the catalysts (fully tetragonal) are produced by the prerduction treatment, but at reduction temperatures

higher than 400 °C XRD signals related to the monoclinic phase increase more noticeably. Catalysts reduced at these high temperatures show negligible activity in isomerization-cracking.

For the same amount of Pt, when the metal is distributed on both supports, alumina and $\text{SO}_4^{2-}\text{-ZrO}_2$, the best performance in isomerization-cracking of long-chain alkanes is obtained. [(Pt/Al) + (Pt/SZ)] composites display the highest values of activity, stability and yield of isobutane.

Acknowledgements

This work was financially supported by Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Nacional del Litoral (UNL, Santa Fe, Argentina). We are specially indebted to Prof. C.A. Querini who performed the TPO tests.

References

- [1] J. Weitkamp, *Ind. Eng. Chem. Prod. Res. Dev.* 21 (1982) 550.
- [2] M. Steijns, G. Froment, P.A. Jacobs, J.B. Uytterhoeven, J. Weitkamp, *Ind. Eng. Chem. Prod. Res. Dev.* 20 (1981) 654.
- [3] J. Weitkamp, P.A. Jacobs, J.A. Martens, *Appl. Catal.* 8 (1983) 123.
- [4] J.A. Martens, R. Parton, L. Uytterhoeven, P.A. Jacobs, G.F. Froment, *Appl. Catal.* 76 (1991) 95.
- [5] F. Alvarez, F.R. Ribeiro, G. Perot, C. Thomazeau, M. Guisnet, *J. Catal.* 162 (1996) 179.
- [6] S. Zhang, Y. Zhang, J.W. Tierney, I. Wender, *Appl. Catal. A: Gen.* 193 (2000) 155.
- [7] J.M. Grau, J.M. Parera, *Appl. Catal. A* 106 (1993) 27.
- [8] J.M. Grau, J.M. Parera, *Appl. Catal. A* 162 (1997) 17.
- [9] J.M. Grau, C.R. Vera, J.M. Parera, *Appl. Catal. A* 172 (1998) 311.
- [10] J.M. Grau, J.C. Yori, J.M. Parera, *Appl. Catal. A* 213 (2001) 247.
- [11] R.A. Comelli, S. Canavese, S. Vaudagna, N.S. Figoli, *Appl. Catal. A* 135 (1996) 287.
- [12] K. Ebitani, T. Tsuji, H. Hattori, H. Kita, *J. Catal.* 135 (1992) 609.
- [13] K. Ebitani, H. Konno, T. Tanaka, H. Hattori, *J. Catal.* 143 (1993) 322.
- [14] T. Shishido, T. Tanaka, H. Hattori, *J. Catal.* 172 (1997) 24.
- [15] Z. Paál, M. Muhler, R. Schlögl, *J. Catal.* 143 (1993) 318.
- [16] Z. Paál, U. Wild, M. Muhler, J.-M. Manoli, C. Potvin, T. Buchholz, S. Sprenger, G. Resofszki, *Appl. Catal. A* 188 (1999) 257.
- [17] J.-M. Manoli, C. Potvin, M. Muhler, U. Wild, G. Resofszki, T. Buchholz, Z. Paál, *J. Catal.* 178 (1998) 338.
- [18] A.V. Ivanov, L.M. Kustov, T.V. Vasina, V.B. Kazanskii, P. Zeuthen, *Kinet. Catal.* 38 (1997) 403.
- [19] A.V. Ivanov, L.M. Kustov, *Russ. Chem. Bull.* 47 (1998) 1061.
- [20] A. Zhang, I. Nakamura, K. Aimoto, K. Fujimoto, *Ind. Eng. Chem. Res.* 34 (1995) 1074.
- [21] K. Tomishige, A. Okabe, K. Fujimoto, *Appl. Catal. A* 194 (2000) 383.
- [22] J.C. Yori, M.A. D'Amato, G. Costa, J.M. Parera, *J. Catal.* 153 (1995) 218.
- [23] B.-Q. Xu, W.M.H. Sachtler, *J. Catal.* 167 (1997) 224.
- [24] R.A. Comelli, C.R. Vera, J.M. Parera, *J. Catal.* 151 (1995) 96.
- [25] C.R. Vera, J.M. Parera, *J. Catal.* 166 (1997) 254.
- [26] F.R. Chen, G. Coudurier, J.-F. Joly, J.C. Viedrine, *J. Catal.* 143 (1993) 616.
- [27] J.M. Parera, *Catal. Today* 15 (1992) 481.
- [28] M.R. Sad, N.S. Figoli, J.N. Beltramini, E.L. Jablonski, R.A. Lazzaroni, J.M. Parera, *J. Chem. Tech. Biotechnol.* 30 (1980) 374.
- [29] S.C. Fung, C.A. Querini, *J. Catal.* 138 (1992) 240.
- [30] V. Adeeva, H.-Y. Liu, B.-Q. Xu, W.M.H. Sachtler, *Top. Catal.* 6 (1998) 61.
- [31] H. Liu, V. Adeeva, G.D. Lei, W.M.H. Sachtler, *J. Mol. Catal. A: Chem.* 100 (1995) 35.
- [32] M.-T. Tran, N.S. Gnep, G. Szabó, M. Guisnet, *Appl. Catal. A* 171 (1998) 207.
- [33] M.-T. Tran, N.S. Gnep, M. Guisnet, P. Nascimento, *Catal. Lett.* 47 (1997) 57.
- [34] J.C. Yori, J.M. Parera, *Appl. Catal. A* 129 (1995) L151.
- [35] C.R. Vera, J.C. Yori, J.M. Parera, *Appl. Catal. A* 167 (1998) 75.