Trimetallic naphtha reforming catalysts
II. Properties of the acid function and influence of the order of addition of the metallic precursors on Pt-Re-Sn/$\gamma$-Al$_2$O$_3$-Cl

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Abstract

Mono, bi- and trimetallic catalysts were prepared by successive impregnation of $\gamma$-Al$_2$O$_3$ with Pt, Re and Sn precursors, with intermediate drying, calcination and reduction steps. The catalysts were tested in the reactions of $n$-pentane (500°C, WHSV = 4.5, H$_2$:n-C$_5$ = 6) and $n$-octane (500°C, WHSV = 1.8, H$_2$:n-C$_8$ = 10).

Concerning the preparation parameters it was found that the addition of Sn first favorably affects the catalytic acid function, increasing the activity for alkane isomerization and cyclization and decreasing cracking and coking. The addition of Re first has opposite effects. It increases the rates of undesirable reactions which require strong acidity, i.e. cracking and coking. Basic SnO$_x$ species are responsible for a decrease in the number and strength of acid sites while highly dispersed ReO$_x$-AlO$_y$ surface species increase the relative concentration of strong acid sites. These facts have been confirmed by pyridine TPD and TPO of coke deposits.

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Keywords: Trimetallic catalysts; Acid function; Successive impregnation

1. Introduction

The naphtha reforming process was developed during World War II due to the need of high octane gasolines. Since then the process has had continuous improvements which have mainly involved the introduction of new catalysts. In the last years and due to environmental regulations the composition of gasolines has been continuously reformulated. As the composition of the reformate mainly depends on the catalyst, the fine-tuning of the catalyst properties has grown in importance in order to manipulate the composition. One way is to add elements that modify the properties of the metal function and alternatively also the properties of the acid one. The new catalysts are not only required to produce naphtha reformate with a more appropriate composition for reformulated gasoline but also to produce energy savings by allowing the process to be run at lower temperatures and hydrogen pressures, for longer times and with less power consumption for recycling and separation. In this sense the naphtha reforming catalyst is one of the most complicated ones in today’s process technologies. It has two catalytic functions: metal and acid, and both are promoted by the addition of other elements. One of the improvements of the last years has been the introduction of the so-called trimetallic catalysts, about which not much information is found in the open literature.

The study of the formulation of trimetallic catalysts and of their metal-catalyzed reactions has been the subject of a former paper [1]. In this report trimetallic catalysts with Pt, Re and Sn supported on chlorided $\gamma$-Al$_2$O$_3$ were prepared by successive impregnation of their salts in such a concentration that catalysts of constant chemical composition (0.3% Pt, 0.3% Re, 0.3% Sn, 1% Cl) were produced. All possible combinations of one, two and three of these elements and all possible orders of addition were tried in the preparation procedure. A big number of catalyst formulations was
produced in this way. The catalytic properties of the metal function and the influence of the preparation procedure were thus studied [1]. It was concluded that the metal additives decreased the catalytic activity of Pt and that trimetallic catalysts were very sensitive to sulfur poisoning. Although the metallic function does not control the rate of the bifunctional reactions of naphtha reforming its modification influences both the selectivity and stability of the catalyst. During the reduction treatment Pt is reduced to Pt(0) but a great part of Re and Sn remain in an oxidized state. Re(0) and Sn(0) interact or get alloyed with Pt(0) while their oxides greatly influence the properties of the support.

In this paper we undertake the study of the catalytic activity in acid-demanding reactions and the assessment of the amount and strength of the acid sites of trimetallic naphtha reforming catalysts. The samples studied are those prepared in our previous paper [1]. Our purpose in this work is two-fold: (i) to elucidate the influence of the preparation method, particularly the order of addition of the promoters, on the properties of the acid function of trimetallic catalysts; (ii) to assess the individual effect of each promoter on the catalytic and acid-related properties of these materials.

2. Experimental

2.1. Preparation of catalysts

The catalysts are the same of Ref. [1], where their preparation method is detailed. The metal precursor compounds used were H2PtCl6, NH4ReO4 and SnCl2 which were added by successive impregnation to chlorided alumina followed by steps of calcination and reduction. The concentration of promoter salts during impregnation was regulated in order to have a 0.3% (w/w) of each element in the final catalyst. The support was commercial γ-Al2O3 (Ketjen CK300, 180 m² g⁻¹, average pore radius 5.4 nm) and the final chlorine content of the catalysts was 0.9%, as determined by the Volhard-Charpentier method. All catalysts were used in the form of ground particles sieved to 35–80 meshes.

We have kept the naming convention of the referenced work: the catalyst name is a string containing the names of the metal promoters (Pt, Sn, Re) separated by hyphens (-), and in the order in which they were impregnated. For example, Pt-Sn is a bimetallic catalyst prepared by successive steps of: (i) impregnation of chlorided alumina with a solution of the Pt precursor; (ii) drying, calcination and reduction; (iii) impregnation with the Sn precursor; (iv) drying, calcination and reduction. The catalysts to be used in n-octane reforming were previously sulfided. 2.5 g of catalyst were sulfided in each batch. They were treated in a stream composed of H2 (60 ml min⁻¹) and CS2 (0.042 ml h⁻¹) during 30 min at 500 °C. Then the feed of CS2 was stopped and H2 was allowed to continue flowing for 8 h at the same temperature. In this way the excess of sulfur (reversible sulfur) was eliminated.

2.2. Temperature programmed desorption of pyridine

The amount and strength of the acid sites of the catalysts were assessed by means of temperature programmed desorption of pyridine. An amount of 150–250 mg of the catalyst to be tested were first immersed in a closed vial containing pure pyridine (Merck, 99.9%) for 4 h. Then the vial was open and excess pyridine was allowed to evaporate in a ventilated hood at room conditions until the surface of the particles was dry. The sample was then loaded into a quartz tube microreactor and supported over a quartz wool plug. A constant flow of nitrogen (40 ml min⁻¹) was made to flow over the sample. A first step of desorption of weakly adsorbed pyridine and stabilization was performed by heating the sample at 110 °C for 2 h. Then the temperature of the oven was raised to a final value of 450 °C at a heating rate of 10 °C min⁻¹. The reactor outlet was directly connected to a flame ionization detector. The detector signal (in mV) was sampled at 1 Hz and recorded in a computer device. The total amount of adsorbed pyridine was determined by comparing the area of the TPD traces with the area produced by calibrated pyridine pulses (1–2 μl) injected to the empty reactor.

2.3. Reaction of n-pentane

The reaction was carried out for 4 h in a continuous flow glass reactor at atmospheric pressure, 500 °C, WHSV = 4.5 and molar ratio H2:n-C5 = 6. n-C5 was supplied by Merck (99.9%). According to the Merck catalogue the sulfur upper level was 0.005%. In order to assure a negligible S content in the reactant was kept in contact with a suitable mass of sulfur adsorbent, Pt/Al2O3. Under the reaction conditions chosen there were no internal or external mass transfer limitations in the catalyst particles, as confirmed by the calculation of the Weiss–Prater modulus (Φ < 0.01) and the Damköhler number (Da ≈ 0). For the calculation, kinetic parameters were conservatively estimated from maximum initial reaction rate values by assuming first-order kinetics and transport coefficients were estimated from known correlations. The analysis of reactants and products was performed using a Varian 3400 CX gas chromatograph equipped with a flame ionization detector. A packed column of dimethyl sulfolane on Chromosorb P (i.d. 3 × 10⁻³ m, 3 m length) maintained at 40 °C was used for the chromatographic separation of the products.

The conversion of n-C5 was defined as

\[
n_{n-C_5, conv} = \frac{n_{C_5}^{\text{inlet}} - n_{C_5}^{\text{isoutlet}}}{n_{C_5}^{\text{inlet}}} \times 100
\]

where \( n_{C_5}^{\text{inlet}} \) is the number of n-C5 molecules at the reactor inlet and \( n_{C_5}^{\text{isoutlet}} \) is the number at the reactor outlet.
The selectivity to each product \( i \) was defined as

\[
S_i = \frac{nM_i}{nC} \times 100
\]

where \( A_i \) is the area of the chromatographic peak of product \( i \), \( f_i \) is its response factor, \( n_i \) is the number of carbon atoms of \( i \) and \( M_i \) is its molecular weight.

### 2.4. Reaction of n-octane

n-Octane was supplied by Merck (99.9%). As it was the case with n-pentane, the reactant was kept in contact with Pt/Al\(_2\)O\(_3\) in order to decrease the S content to negligible values. The glass reactor used was loaded with 0.18 g of catalysts and maintained at 1 atm and 500 °C for 6 h during the test. The feed consisted of 10.7 cm\(^3\) min\(^{-1}\) of H\(_2\) (WHSV = 1.8) which was presaturated in a glass chamber containing n-C\(_8\) at 56.5 °C (vapor pressure 69.1 mmHg, molecular ratio H\(_2\):n-C\(_8\) = 10). Analyses were performed on line with a Varian 3400 CX gas chromatograph equipped with a Petro 50 capillary column and a flame ionization detector.

### 2.5. Analysis of carbon deposits

The coke deposited on the catalysts at the end of the n-C\(_5\) and n-C\(_8\) reaction tests was analyzed by means of temperature programmed oxidation (TPO). An amount of 50–100 mg of the coked catalyst were placed in a quartz cell. Then the carbon deposits were continuously oxidized with 50–100 mg of the coked catalyst were placed in a quartz cell. The cell was heated from room temperature to 650 °C with a heating rate of 10 °C min\(^{-1}\). The gases issuing from the cell were fed to a methanation reactor where CO\(_2\) and CO were quantitatively transformed into CH\(_4\) over a Ni catalyst connected to a flame ionization detector and the signal was continuously sampled and recorded. The carbon concentration on the catalysts was calculated from the TPO diagram area by calibration with TPO tests of standard samples of known carbon content.

### 3. Results and discussion

#### 3.1. Temperature programmed desorption of pyridine

When a base like pyridine is adsorbed on an acid surface, strong bonds occur between the molecules adsorbed and the acid sites and high temperatures are needed in order to desorb the base. In the case of pyridine molecules adsorbed on weak acid sites desorption occurs at lower temperatures. The measurement of the amount of base evacuated as a function of programmed heating temperature gives a measure of the acid strength distribution.

Fig. 1 is a TPD trace of the chlorided alumina support. The plot has been deconvoluted into four peaks, located at about 175 °C (peak I), 220 °C (peak II), 295 °C (peak III) and 410 °C (peak IV). These acid sites of different strength are produced by the replacement of different families of OH groups by Cl and the displacement of water coordinated to Al surface atoms of different chemical environment. Peri[2] early noted that five different types of OH groups are detected by infrared absorption and developed a surface model of alumina. Due to their increasing temperatures of desorption, the order of acid strength of the sites of the Cl-Al\(_2\)O\(_3\) sample goes: IV > III > II > I. The amount of each kind of sites and the total amount of sites were determined from the area of the deconvoluted peaks and the total area for this and most of the other catalysts used. The results are included in Table 1. The TPD traces of some of the catalysts can be found in Figs. 2 and 3.

The pyridine TPD traces were fitted with Elovich’s equation [3]:

\[
\frac{dA}{dT} = \psi \left( \frac{dT}{d} \right) = \psi \theta^{\beta} \exp \left( \frac{-E_A}{RT} \right)
\]

\[
r_d = \frac{dA}{dT} = \psi \theta^{\beta} \exp \left( \frac{-E_A}{RT} \right)
\]

\[
E_A = E_A(\theta) = E_A^0 - \alpha T
\]

where \( r_d \) is the rate of desorption = (d\(N_A\)/dt) (mol min\(^{-1}\) g\(^{-1}\)), \( N_A \) the number of desorbed moles of pyridine (mol g\(^{-1}\)), \( \sigma_A \) the density of adsorption sites (mol g\(^{-1}\)), \( \theta = \theta / \theta_{Sat} \) = relative coverage (0 < \( \theta \) < 1), \( \beta = dT/dt \) = heating rate (°C min\(^{-1}\)), \( R \) the ideal gas constant = 1.9872 cal mol\(^{-1}\) K\(^{-1}\), \( E_A \) the desorption activation energy (cal mol\(^{-1}\) K\(^{-1}\)), \( \psi \) the adsorbate–adsorbate interaction parameter (cal mol\(^{-1}\) K\(^{-1}\)), \( \nu_A \) the desorption frequency factor (rate constant) (min\(^{-1}\)), \( n \) the order of desorption, \( \psi = TPD = \)
Table 1: Quantification of the acid sites on the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid concentration (pyridine adsorbed) (µmol/g)</th>
<th>Relative TPD area</th>
<th>Pyridine desorption activation energy (kcal mol⁻¹)</th>
<th>Distribution of acid strength (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I, 150–180 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>II, 200–250 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>III, 280–320 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV, 390–430 °C</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>235</td>
<td>0.48</td>
<td>28.1</td>
<td>57</td>
</tr>
<tr>
<td>Cl-Al₂O₃</td>
<td>684</td>
<td>1.39</td>
<td>30.6</td>
<td>119</td>
</tr>
<tr>
<td>Pt</td>
<td>491</td>
<td>1.00</td>
<td>31.2</td>
<td>105</td>
</tr>
<tr>
<td>Re</td>
<td>486</td>
<td>0.99</td>
<td>32.2</td>
<td>80</td>
</tr>
<tr>
<td>Sn</td>
<td>433</td>
<td>0.88</td>
<td>31.1</td>
<td>84</td>
</tr>
<tr>
<td>Pt-Re</td>
<td>503</td>
<td>1.03</td>
<td>31.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt-Sn</td>
<td>203</td>
<td>0.41</td>
<td>30.6</td>
<td>12</td>
</tr>
<tr>
<td>Pt-Sn-Re</td>
<td>310</td>
<td>0.63</td>
<td>–</td>
<td>0.0</td>
</tr>
<tr>
<td>Sn-Pt-Re</td>
<td>186</td>
<td>0.38</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Re-Pt-Sn</td>
<td>207</td>
<td>0.42</td>
<td>–</td>
<td>95</td>
</tr>
<tr>
<td>Pt-Re-Sn</td>
<td>403</td>
<td>0.82</td>
<td>–</td>
<td>226</td>
</tr>
</tbody>
</table>

The error of the method was estimated by running three different tests on samples of the same catalyst, deconvoluting the TPD trace and comparing the areas. This was found to be lower than 5% for peaks I and II and lower than 7% for peaks III and IV.

*Calculated from the position of the main peak, taking n = 1, heating rate β = 10 °C min⁻¹ and ν₀ = 10¹³ min⁻¹ [4].

Fig. 2: Pyridine TPD traces of monometallic (a) and bimetallic catalysts (b).

Fig. 3: Pyridine TPD profiles of trimetallic catalysts.
with no adsorbate–adsorbate interaction ($\alpha = 0$). Therefore any dependence of the energy of desorption of pyridine on coverage was finally disregarded.

It can be seen (Table 1) that the total amount of acid sites is increased by a factor of 2.9 by doping $\gamma$-alumina with chlorine. The amount of low strength acid sites is more than doubled. These sites were 83% of the total acid sites of alumina and become 66% of the total acid sites of chlorided alumina. The amount of high strength acid sites is increased, and medium strength acid sites have a great increase. Previously they were practically absent (3%) and now they are 26% of the population of Cl-Al$_2$O$_3$ sites. A further addition of Pt, Re or Sn produces a decrease in the total amount of acid sites. The decrease specially affects the newly formed medium strength acid sites, while the sites of low acid strength associated to peaks I and II remain seemingly unaltered, because there is no meaningful variation in their amount. In the case of Re, new sites of high acid strength are created and they probably come from the modification of the originally medium and low (peak I) strength sites. No modification to the amount of strong sites of Cl-Al$_2$O$_3$ or only a small one occurs in the case of the Pt and Sn addition, indicating that only a blocking or neutralization of medium strength sites occurs in this case.

Looking at the Pt-Sn catalyst and considering an additive effect, it turns out that the addition of Sn while decreasing the total population of acid sites of the Pt catalyst, it mainly affects the fraction of the weak ones. This change in Sn behavior can be explained if we consider that the original medium strength acid sites have been partly blocked by Pt and that now Sn is mainly adsorbed over low acid strength sites of greater availability. Most probably Sn-Cl$_x$(OH)$_y$ species compete with Cl for the bonding to Al atoms related to these sites.

In the case of Pt-Re and in comparison to Pt or Re the total amount of sites is practically constant. Mainly affected are the weakest acid sites (peak I), which disappear and merge into the population of peak II sites. The size of peak IV (medium strength) is decreased, probably because the weakest groups, which are converted to sites of lower acid strength as associated to peaks I and II remain seemingly unaltered, because there is no meaningful variation in their amount. In the case of Re, new sites of high acid strength are created and they probably come from the modification of the originally medium and low (peak I) strength sites. No modification to the amount of strong sites of Cl-Al$_2$O$_3$ or only a small one occurs in the case of the Pt and Sn addition, indicating that only a blocking or neutralization of medium strength sites occurs in this case.

If we look closely at the degree of decrease of acid sites produced by metal addition we see that it follows the order: Sn > Re ≈ Pt. Sn species have a net effect of neutralizing the surface while Re mostly enhances the acid strength. Another interesting fact is that the fraction of sites of Cl-Al$_2$O$_3$ which were changed by the addition of the first metal is less affected by the addition of the second metal, which only has the other remaining sites for modifying.

In the case of the trimetallic catalysts some of the previous features are repeated. Addition of Re to Pt-Sn finishes depleting the weakest groups, which are converted to sites of higher acid strength. New sites are also created, specially of the strong type. Conversely the addition of Sn to Pt-Re or Re-Pt produces a decrease in the population of high and low acid strength sites (peaks II and IV). Some of them are neutralized and others are converted into sites of weaker strength (size of peaks I and III is increased).

Some information on the absolute concentrations of surface groups of supports and catalysts, taken from experimental results and from literature, is included in Table 2. During impregnation chlorine incorporated into the $\gamma$-alumina support first neutralizes all basic sites, which correspond to 4.5% of all surface OH groups of a fully hydroxylated $\gamma$-alumina surface calcined at 1000°C [5]. As depicted in Scheme 1(a), Cl is not an acid site itself but it produces acid sites by polarizing the bonds of the Al cation it is linked to. After removal of surface adsorbed water and excess chlorine by calcination, 0.25 mmol Cl/g remain on the surface (Table 2) and the acidity increases 0.45 mmol/g (Table 1). This means that 1.8 new acid sites are generated per unit Cl atom. Since the amount of Cl retained on the surface after calcination at 500°C is practically the same for all catalysts (0.9%) the decrease in the amount of acid sites by metal addition can only be explained by a displacement of Cl atoms from Al sites that generate neighboring acid sites, to other Al sites where Cl becomes an spectator. Addition of 0.025 mmol Sn/g to Cl-Al$_2$O$_3$ produces a decrease in acidity of 0.25 mmol/g, seemingly neutralizing 10 acid sites per added Sn atom. This is equivalent to say that Sn inhibits the effect of roughly 5.6 Cl atoms. In the case of Re and Pt,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Groups</th>
<th>Concentration (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Alumina$^a$</td>
<td>OH groups $T = 100$°C</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>OH groups $T = 300$°C</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>OH groups $T = 500$°C</td>
<td>1.3</td>
</tr>
<tr>
<td>$\gamma$-Alumina$^b$</td>
<td>Surface Al$^{14+}$ groups, coordinately unsaturated and hydroxylated</td>
<td>4.1</td>
</tr>
<tr>
<td>$\gamma$-Alumina$^c$</td>
<td>Total basicity</td>
<td>0.210</td>
</tr>
<tr>
<td>$\gamma$-Alumina$^d$</td>
<td>Total acidity</td>
<td>0.215</td>
</tr>
<tr>
<td>Cl-$\gamma$-alumina$^e$</td>
<td>Total acidity</td>
<td>0.24</td>
</tr>
<tr>
<td>Cl-$\gamma$-alumina$^f$</td>
<td>Cl groups after calcination at $T = 500$°C</td>
<td>0.25</td>
</tr>
<tr>
<td>Cl-$\gamma$-alumina$^g$</td>
<td>Re</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Results of this work and reference values from literature: $^a$ Calculated from OH surface density for a 200 m$^2$/g alumina. Taken from Ref. [5]. $^b$ Surface Al density (12.5 Al nm$^{-2}$) taken from Boehm [6] transformed to mmol/g for a 200 m$^2$/g sample. $^c$ Desorption of CO$_2$ from ALO-1 reference alumina of Catalysis Society of Japan [7]. $^d$ Desorption of pyridine from ALO-1 reference alumina of Catalysis Society of Japan [7] (100–500°C). $^e$ This work. Desorption of pyridine from 100 to 500°C. $^f$ This work. Calculated for an equilibrium 0.9% Cl on alumina. $^g$ This work. Calculated for 0.3% of each metal.
the competition with Cl ions for specific adsorption sites (Scheme 1(b)) produces on average similar but less strong effects.

It is important to try to correlate these results with known models of acidity generation. Pt, Re and Sn in their metal state do not have acid properties and therefore the possibility must be explored that unreduced particles do. Since we are interested in exploring the effects of combinations between the elements, the acidity of mixed oxides of Al, Pt, Re and Sn is to be studied. A model on the acidity of binary oxides has been proposed by Tanabe et al. [8]. According to this model, the generation of acid sites is caused by an excess of negative or positive charge in the lattice. The theory rests upon two postulates: (i) the coordination numbers of the positive elements of metal oxides are maintained even if mixed; (ii) the coordination number of all oxygen in the binary oxide have the coordination number of the oxygen of the major component. In the case of Pt, Re and Sn, if they associate to form binary mixed oxides, between them or with Al, many possibilities arise depending on the combinations and the kind of oxide components involved. In most of their oxide forms Pt, Re and Sn have the coordination number (CN) six and therefore this was the only CN used in the calculations. Results for many oxide combinations are included in Table 3. When Pt and Sn are the major oxide cations, oxygen has a CN = 3 and when Re is the major component, oxygen’s CN = 1.7−2. When a negative surface charge is developed, Bronsted acidity is expected to appear because protons adsorb onto the surface and keep the electric neutrality of the solid. Pt is supposed to be completely reduced and as the concentrations of Re and Sn are very low compared to that of Al, Re-Al and Sn-Al species are considered to be dominant. Therefore we can expect that only Al-Sn and Al-Re give significant contributions to the acidity change while minor contributions like that of Re-Sn species, if they exist, are considered negligible. Of the two Al-X combinations, Sn mixed oxides provide the lowest excess charge while Re gives the highest. It is difficult to say whether Al is in excess or not in mixed oxide particles because Re oxide particles are dispersed on the surface. It can be supposed that Bronsted acid sites should concentrate on Al atoms near Re oxide particles while Lewis sites concentrate on Re atoms of the Re-Al interface. For example, inside a ReO3 particle the coordination number of oxygen is different from that of Al2O3. In the close neighborhood of this particle if the coordination geometry of the Re oxide is maintained, there will be a perturbation and the Al-O bonds next to the Re particle will carry an extra negative charge. The charge imbalance will be compensated by proton abstraction to keep electroneutrality and a Bronsted acid site will be formed.

Tanabe’s model has been found to be about 90% correct in predicting acidity increases in a great number of mixed oxide systems in which the resulting acidity per unit area is greater than the weighted average of the acidities of the component oxides. This model is one of acidity generation and

![Scheme 1](image-url)

### Table 3

<table>
<thead>
<tr>
<th>System</th>
<th>Charge*</th>
<th>Acidity</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtO2-ReO3</td>
<td>(7/6 − 2/3) × 6 = 3.0</td>
<td>Lewis 14.4</td>
<td></td>
</tr>
<tr>
<td>PtO2-Re2O7</td>
<td>(44/6 − 2/1.7) × 6 = −3.06</td>
<td>Bronsted 24.15</td>
<td></td>
</tr>
<tr>
<td>PtO2-ReO3</td>
<td>(64/6 − 6/6) × 6 = 2.0</td>
<td>Lewis −</td>
<td></td>
</tr>
<tr>
<td>PtO2-ReO3</td>
<td>(44/6 − 2/2) × 6 = −2.0</td>
<td>Bronsted −</td>
<td></td>
</tr>
<tr>
<td>PtO2-SnO2</td>
<td>(48/6 − 3/6) × 6 = 0</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>PtO2-SnO2</td>
<td>(44/6 − 2/1.7) × 6 = −3.06</td>
<td>Bronsted 23.05</td>
<td></td>
</tr>
<tr>
<td>Re2O3-Sn2O3</td>
<td>(7/6 − 2/2) × 6 = 3.0</td>
<td>Lewis 23.05</td>
<td></td>
</tr>
<tr>
<td>Re2O3-Sn2O3</td>
<td>(64/6 − 6/6) × 6 = −2.0</td>
<td>Bronsted 21.15</td>
<td></td>
</tr>
<tr>
<td>ReO2-SnO2</td>
<td>(48/6 − 2/3) × 6 = 2.0</td>
<td>Lewis 21.15</td>
<td></td>
</tr>
<tr>
<td>ReO2-SnO2</td>
<td>(44/6 − 2/2) × 6 = −2.0</td>
<td>Bronsted 19.9</td>
<td></td>
</tr>
<tr>
<td>ReO2-Al2O3</td>
<td>(7/6 − 2/1.7) × 6 = −4.06</td>
<td>Bronsted 19.9</td>
<td></td>
</tr>
<tr>
<td>ReO2-Al2O3</td>
<td>(44/6 − 2/2) × 6 = −3.0</td>
<td>Bronsted 18.0</td>
<td></td>
</tr>
<tr>
<td>ReO2-SnO2</td>
<td>(48/6 − 2/3) × 6 = −1.0</td>
<td>Lewis 18.0</td>
<td></td>
</tr>
<tr>
<td>Al2O3-SnO2</td>
<td>(44/6 − 2/2) × 6 = 1.0</td>
<td>Bronsted 14.4</td>
<td></td>
</tr>
</tbody>
</table>

Average electronegativity of the cation of an equimolar mixed oxide taken as a measure of its acidity [9]. Electronegativity of the individual cations calculated with Tanaka and Osaki’s estimation [10].

* Charge = (X1(CN1) − X2(CN2))/2 × CN2, where X1 is the charge of the cation of the minor component; X2 the charge of the oxygen of the minor component; CN2 the coordination number of the cation of the minor component; CN1 the coordination number of the oxygen of the major component.
duced states of Pt-Sn/Al₂O₃ [11,12] , Re/Al₂O₃ [13] and catalyst agrees with the literature on the oxidized and re-
metal on alumina and the formation of strong acid sites. Acidity of metal ions in-
creases with charge and decreases with radius. In conclusion acidity increase due to mixing of different cations should theoretically appear mostly when Re is present. In all other combinations with no Re present, either the charge would be null or low, or the electronegativity of the species would be too low. Both ReO₃-Al₂O₃ and Re₂O₇-Al₂O₃ have the highest average cationic electronegativities of Table 3 and would produce sites of high acid strength. This is in fact confirmed by the high Ea of the main sites of peak II of the Re catalyst and the high proportion of strong acid sites (size of peak IV).

According to the data of Table 3 Sn-Al species are also theoretically capable of increasing the acidity. The exper-
imental results however indicate that rather than forming mixed cation oxide species with Al, Sn cations bond mostly between themselves and hence the basic character of SnO₂ oxides dominates. The property of Re of forming stable species with Al is responsible for the high dispersion of this metal on alumina and the formation of strong acid sites.

The great influence of Re and Sn on the acidity of the catalyst agrees with the literature on the oxidized and re-
duced states of Pt-Sn/Al₂O₃ [11,12], Re/Al₂O₃ [13] and Pt-Re/Al₂O₃ [14] and with the amphoteric nature of Al₂O₃. According to Bacaud et al. [11] tin poisons the strong acid sites of the support. After calcination of the catalyst, tin is reported to be mainly present as Sn(II). After reduction most Sn is present as Sn(II) while a minor part would be reduced to Sn(0) that combines to Pt(0) to form alloy clus-
ters [12]. Some Sn(II) forms tin aluminate with the support, (Al₂O₃)₂Sn, which is stable on reduction conditions. Nava et al. [15] in a Mossbauer study of Pt-Sn supported on alu-
mina found that after reduction there is an increase in the interaction between SnO₂ and alumina and that the presence of Sn(II) modifies the electronic states of alumina. Electron diffraction (ED) has allowed the identification of Sn oxi-
dized species [1]. The Sn oxides appear in aggregates of sufficient size to be easily identified while Re species, how-
ever present, cannot be detected. Several authors [14,16–18] have stated that Re and its oxides are not detected by ED unless highly sophisticated equipment are used. After calci-
nation of the catalyst, rhenium would be present as Re(VII) in the form of ReO₅ monomers coordinated to the alumina support. Al-(O-ReO₅)₅ [13] Upon reduction with H₂ a frac-
tion would be converted to highly dispersed Re(0) particles which interact with Pt(0) producing very small Pt and Pt-Re particles [14]. The rest remains oxidized and in interaction with the support in a highly dispersed form. As we can see, the so-called “metallic promoters” are also great support acidity modifiers, as demonstrated by the current pyridine TPD results.

3.2. Reactions of n-pentane

The n-pentane reactions occurring on the naphtha reform-
ing catalyst are useful for having an insight on the properties of the acid and metal functions of the catalyst [19]. Typical reactions, in decreasing order of n-pentane conversion, are the following:

isomerization : \[ n-C₅H₁₂ → i-C₅H₁₂ \] (6)
hydrocracking : \[ n-C₅H₁₂ + H₂ → C₂H₆ + C₃H₈ \] (7)
hydrogenolysis : \[ n-C₅H₁₂ + H₂ → CH₄ + n-C₄H₁₀ \] (8)
dehydrocyclization : \[ n-C₅H₁₂ → C₃H₁₀ + H₂ \] (9)

Isomerization can take place either by a “bond shift” mech-
anism [20] involving only the metal function of the catalyst or by a bifunctional mechanism where the n-alkane is first dehydrogenated by the metal function, the formed alkene is then isomerized by the acid function to an i-alkene and finally the i-alkene is hydrogenated to the i-alkane on the metal function [21]. The results of many studies show [19] that the isomerization can be considered to be controlled by the acid function of the catalyst. This agrees with the conclusions of Stinfelt [22] and Sterba and Haensel [23] who stated that under commercial reforming conditions the rate of isomerization on the metal sites was negligible compared to that of the bifunctional mechanism. Furthermore, trace amounts of sulfur are enough to poison the active sites res-
ponsible for isomerization on the metal function. The bi-
functional hydrocracking of n-pentane producing C₂H₆ is also controlled to be controlled by the acid function of the catalyst. Reactions (8) and (9) occur by a monofunctional metallic mechanisms [24]. Regarding the acid controlled re-
actions, cracking requires stronger acid sites than isomer-
ization [25].

Table 4 contains the results of the reactions of n-pentane over the metal promoted catalysts: initial conversion at 5 min time-on-stream, drop in conversion between the start (5 min) and end of the reaction (240 min), average product selectiv-
ities during the run (calculated with Eq. (20) and percentage of carbon deposited on the catalyst at the end of the test (from the TPO analysis). The selectivity to i-pentane (i-C₅) can be taken as representative of the acid function of intermediate strength, the selectivity to propane (C₃) as representative of the strong acid sites, the selectivity to methane (C₁) as rep-
resentative of the metal function activity (hydrogenolysis). The ratio C₃/C₁ is an estimate of the activity ratio between the metal and acid functions.

Comparing the results of monometallic Pt with those of the bimetals, the advantages of the addition of Sn to Pt are
There is an increase in the total conversion of \( n-C_5 \), the selectivity to \( i-C_5 \) and the stability (smaller conversion drop and carbon deposition). There is a great decrease in the selectivity to gaseous products, \( C_1 \) and \( C_3 \), and in the \( C_1/C_3 \) ratio, indicating that the activity of the metal and the activity of the strong acid sites are decreased, the activity decrease of the metallic function being proportionally higher. The metal activity decrease upon the addition of Sn to Pt has been also observed when studying the metal function [1]. The great improvement in selectivity produced by Sn can be attributed to the formation of clusters of Sn oxide during the calcination step, which are only partially reduced during the hydrogen reduction step. As proposed by Bacaud et al. [11] and shown in our pyridine TPD results, these clusters interact with the acid sites of alumina, decreasing their acid strength. In this way, some strong acid sites responsible for the cracking of \( n-C_5 \) are neutralized in a higher extent than the sites of lower strength with mainly isomerizing properties.

The addition of Re to the Pt catalyst produces a small decrease in conversion and an increase in stability (smaller conversion drop and carbon deposition) and selectivity to \( i-C_5 \). The amount of strong acid sites on Pt-Re is greater than the amount on Pt-Sn as it can be seen from the higher production of \( C_1 \) over Pt-Re and the different size of the pyridine TPD traces of Fig. 2 (acid strength distribution described in Table 1). The activity of the metal function of Pt-Re is greater than that of Pt-Sn (more \( C_1 \) is produced).

The trimetallic catalysts are grouped in Table 4 according to the order of addition of Re and Sn during the preparation procedure. A similar ordering was used in our previous paper on trimetallic catalysts [1]. The great influence of the preparation procedure does not need to be overemphasized. The catalysts prepared adding Sn before Re are, on average, more active, stable and selective to \( i-C_5 \) than the catalysts prepared adding Re before Sn. The selectivities to \( C_1 \) and \( C_3 \) and the \( C_1/C_3 \) ratio are smaller when Sn is added before Re, indicating that in this case Sn affects the metallic function of Pt and the strong acid sites of the support much more than Re does. In general the advantages of the trimetallic catalysts over the bimetallic ones are the higher stability and the higher selectivity to \( i-C_5 \).

It is interesting to compare the results obtained with the reaction of \( n-C_5 \), which is a test of the acid function, with the reaction of dehydrogenation of cyclohexane [1], a typical reaction of the metallic function. Pt-Sn is a better catalyst than Pt-Re for the \( n-C_5 \) reaction, but the opposite occurs in dehydrogenation where Pt-Re performs better than Pt-Sn. In the case of the trimetallic catalysts two clear effects can be rationalized: (i) the non-noble metal precursor added first interacts with the support affecting its acidity; (ii) the non-noble metal precursor added last interacts more with Pt, likely because the sites of the support with affinity for the promoters have already been partly blocked by the first one.

The catalytic activity and selectivity values of the \( n \)-pentane and \( n \)-octane reaction tests indeed showed only minor variations between the three catalysts (X-Y-Pt, X-Pt-Y, Pt-X-Y) and the average values of Table 4 are good overall descriptors of the properties of the series.
When Sn is added first it favorably affects the acid function, as it happens in the case of the Pt-Sn catalyst. When Re is added last, it interacts more with Pt, affecting its activity to a smaller extent than Sn and producing metal active sites resembling those of Pt-Re. Then the best trimetallic catalyst, with improved properties of both the metal and acid function, is Sn-Pt-Re. Among the trimetallics and according to the metal function characterization data of Ref. [1], Sn-Pt-Re has the highest catalytic activity for dehydrogenation of cyclohexane, it has low sulfur poisoning and has one of the highest values of activity recovery (by hydrogenation of sulfur deposits produced during poisoning). Regarding the n-C5 reactions, Sn-Pt-Re is among the catalysts with highest catalytic activity. It also has the lowest conversion drop, the highest selectivity to i-C5 and the lowest selectivity to C1 and C3. The opposite occurs with the catalyst Re-Pt-Sn and the causes can be easily derived from rules (i) and (ii) rationalized above.

3.3. Reactions of n-octane

The reforming of n-octane produces mainly C8 aromatic hydrocarbons: ortho-, meta- and para-xylene and ethylbenzene. Other aromatic hydrocarbons, benzene and toluene are also produced. The results corresponding to the tests of the different catalysts are shown in Table 5: conversion of n-octane at 30 min time-on-stream, conversion drop between 30 and 360 min, average values of selectivity to C8 aromatics, to total (C6-C8) aromatics and to low value gases (C1-C4) (calculated with an equation similar to (2)) and amount of carbon deposited at the end of the test (TPO). The catalysts are grouped according to the order of addition of the metal precursors, similarly to Table 4.

The addition of Re or Sn to Pt produces bimetallic catalysts which exhibit an increase in activity, stability and selectivity to aromatics. The selectivity to gases (C1-C4) is decreased. Regarding the trimetallics catalysts, those prepared adding Sn before Re are the best catalysts. If we compare them to the catalysts prepared by impregnating Re before Sn, we can see that they exhibit a greater conversion of n-C8, a smaller conversion drop, a lower deposition of carbon during the run, a greater selectivity to C9 and C7-C8 aromatics and a lower production of gases. These results are similar to those found in the case of the n-C5 reaction, but now the differences among the groups of catalysts are bigger. For n-C7 reforming, the best catalyst is Sn-Pt-Re and the worst is Re-Pt-Sn. The same criteria (i)–(ii) discussed in the n-C5 section can be recalled to explain the results. The dehydrocyclization reactions of n-C6 are bifunctional and are controlled by the acid function of the catalyst [24]. The cyclization of the alkenes produced on Pt sites is a special isomerization reaction, it occurs on the acid sites and is affected by the metal oxide promoters that change the amount and strength of the acid sites. In this sense the beneficial effect of Sn on the acidity of the support for n-C5 isomerization is expected to take place also in the case of the reactions of n-C8 aromatization.

The preparation of the Sn-Pt-Re catalyst starts with the impregnation of the chlorided alumina with a solution of the Sn salt. Sn ions are adsorbed electrostatically on specific sites of the support. Then, the catalyst is calcined and reduced. Whichever the Sn precursor, SnO2 is produced during calcination. This oxide is heterogeneously bonded to the Al2O3 surface as it can be deduced from the TPR data presented in [1]. The TPR profile of the freshly calcined catalyst shows that reduction of SnO2 to SnO occurs in a wide temperature range, 170-550 °C [1]. SnO covers part of the Al2O3 surface and interacts strongly with it, partly forming tin aluminate (SnAl2O4). Then Pt is added and the catalyst is again dried, calcined and reduced. Reduction produces the transformation of PO2 into Pt(0). Freshly formed Pt crystals also catalyze the reduction of neighboring SnO species

<table>
<thead>
<tr>
<th>Catalyst (metal phase)</th>
<th>Conversion (%)</th>
<th>Conversion drop (%)</th>
<th>Selectivity to C8 aromatics (%)</th>
<th>Selectivity to total aromatics (%)</th>
<th>Selectivity to gases (%)</th>
<th>E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>89.5</td>
<td>24.0</td>
<td>43</td>
<td>49</td>
<td>23.0</td>
<td>1.68</td>
</tr>
<tr>
<td>Pt-Re</td>
<td>99.2</td>
<td>14.0</td>
<td>73</td>
<td>79</td>
<td>11.0</td>
<td>0.96</td>
</tr>
<tr>
<td>Pt-Sn</td>
<td>99.3</td>
<td>2.2</td>
<td>89</td>
<td>92</td>
<td>3.0</td>
<td>1.01</td>
</tr>
<tr>
<td>Sn added before Re</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn-Re-Pt</td>
<td>99.8</td>
<td>3.9</td>
<td>86</td>
<td>89</td>
<td>3.6</td>
<td>0.83</td>
</tr>
<tr>
<td>Sn-Pt-Re</td>
<td>99.6</td>
<td>3.0</td>
<td>87</td>
<td>91</td>
<td>3.2</td>
<td>0.97</td>
</tr>
<tr>
<td>Pt-Sn-Re</td>
<td>99.5</td>
<td>2.2</td>
<td>87</td>
<td>91</td>
<td>3.9</td>
<td>0.90</td>
</tr>
<tr>
<td>Average</td>
<td>99.6</td>
<td>3.0</td>
<td>87</td>
<td>90</td>
<td>3.6</td>
<td>0.90</td>
</tr>
<tr>
<td>Re added before Sn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re-Sn-Pt</td>
<td>98.4</td>
<td>17.0</td>
<td>80</td>
<td>83</td>
<td>6.2</td>
<td>1.60</td>
</tr>
<tr>
<td>Re-Pt-Sn</td>
<td>81.8</td>
<td>10.0</td>
<td>74</td>
<td>77</td>
<td>6.5</td>
<td>1.59</td>
</tr>
<tr>
<td>Pt-Re-Sn</td>
<td>91.5</td>
<td>9.2</td>
<td>72</td>
<td>75</td>
<td>6.1</td>
<td>0.57</td>
</tr>
<tr>
<td>Average</td>
<td>87.1</td>
<td>12.0</td>
<td>75</td>
<td>78</td>
<td>6.3</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Conditions: 500 °C, 1 atm, WHSV = 1.8 and molar H2/n-C8H18 = 10. Hydrogen pre-reduction: 2 h at 500 °C.
to Sn(0) which is then alloyed to Pt. In this way the metal species expected to be found on the catalyst surface are: metallic Pt-Sn alloys supported on alumina, metallic Pt supported on alumina and metallic Pt supported on SnO. The subsequent addition of the Re precursor, followed by drying, calcination and reduction, produces a catalyst which is more stable than the bimetallic one. During reduction and according to their degree of hydration, surface Re oxide clusters become mobile and are able to migrate to Pt crystals where they are reduced. As a result both Pt-Re and Pt-Sn-Re aggregates are formed. Re oxide clusters interact with Al₂O₃ and with SnO species and they are stabilized on them. Therefore the catalyst surface is supposed to be formed by crystallites of Pt, Pt-Sn, Pt-Re, Re-Sn and Pt-Sn-Re supported on Al₂O₃.

In the case of the worst performing catalyst, Re-Pt-Sn, the preparation starts with the addition of Re to the bare chlorided support surface. After calcination a catalytic surface is produced in which the Re oxide species are the only ones interacting with the support. Afterwards, when Pt and Sn precursors are added, the most active sites for adsorption on the alumina surface have already been partly blocked by Re species and Pt and Sn mainly interact between themselves. After calcination and reduction a catalytic surface is produced in which Sn and Pt interact strongly and in which Sn has only slightly modified the acidity of the acid function. In this way the acid function of this trimetallic catalyst resembles that of Pt-Re and the metal function that of Pt-Sn.

The addition of Sn before Re affects the acid function of the catalyst favoring isomerization and cyclization and decreasing cracking. An interesting question for reformulated gasoline is how to favor the isomerization of alkanes over cyclization. It is accepted [24] that paraffin isomerization is a very rapid reaction and that cracking and cyclization are slower. Scheme 2 describes a simple reaction network for n-C₈ on a reforming catalyst. n-C₈ is rapidly isomerized (IS) and n-C₈ and the produced C₈ isomers are slowly dehydrocyclized (DHC) to C₈ aromatics. n- and i-C₈ are also slowly hydrocracked (HC) to lower n- and i-alkanes. Gases (C₁–C₄) and C₅ are final products and C₆–C₇ can be dehydrocyclized to aromatics. When Sn is added before Re the HC reactions are decreased. As i-(C₆–C₈) are interme-diate products, one way to increase them over aromatics is to decrease the reaction contact time or the activity of the catalysts.

3.4. Study of the coke deposits

During the reaction of hydrocarbons on bifunctional metal-acid catalysts a carbonaceous deposit is produced on their surface. This deposit, commonly named coke, deactivates the catalyst and is the reason why costly regeneration schemes must be implemented in order to recover catalytic activity. During regeneration coke is burned-off in an oxidizing atmosphere.

The amount of coke produced, expressed as the percentage of carbon deposited on the catalysts and calculated from the area of the TPO diagrams, is shown in the last column of Tables 4 and 5. When comparing bimetallic catalysts with monometallic Pt we can see that the addition of the second metal decreases the coking rate. In the case of the trimetallic catalysts prepared adding Sn before Re the coking activity and the residual amount of deposited carbon are even lower, clearly indicating that this kind of trimetallic catalysts is the most stable one.

Fig. 4 shows the TPO profiles of coked Pt and of three representative coked trimetallic catalysts after being used in the n-C₅ reaction (left) and in the n-C₈ reaction (right). According to literature [26,27], the oxidation of coke on Pt supported on chlorided alumina occurs in two distinctive temperature zones. The low temperature zone at about 300–350 °C corresponds to the burning of a small fraction of the coke, which is deposited on Pt or nearby and is poorly polymerized. This coke is burned first because it is rich in hydrogen and because of the catalytic action of Pt. The high temperature peak, located at about 450–500 °C, corresponds...
to the burning of coke deposits on alumina, which are more polymerized and cannot benefit from Pt-aided oxidation. There also exists an intermediate zone of burning of coke, which is attributed to the existence of coke deposits of intermediate degree of polymerization and deposits located in the neighborhood of Pt. If we inspect the TPO profiles of the trimetallic catalysts, we can see that all of them have the low and high temperature peaks. On the trimetallic catalysts the fraction of coke on the metal function and around it is however smaller than the fraction on monometallic Pt. Compared to Pt, a great decrease of coke on the metal function was found in Pt-Re [28] and in Pt-Sn [29,30]. The phenomenon has been attributed to the smaller dehydrogenation capacity of Pt in bimetallic catalysts: a smaller amount of unsaturated coke precursors are formed and polymerized on the metal. In bimetallic catalysts the capacity of Pt to catalyze the oxidation of coke is decreased and higher temperatures are necessary to burn the coke on the metal function and its surroundings. In the case of the trimetallic catalysts, the low temperature peak could be expected to be very small or non-existing. The peak is however always present and it is possible that the coke on the metal function is mainly produced on isolated Pt particles not interacting with Sn and/or Re.

The catalysts prepared adding Re before the other two have, on average, more coke than those prepared adding Sn first of all. The greater amount of coke found on the catalysts prepared adding Re first of all agrees with the high deactivation suffered by these catalysts in both the α-C5 and α-C8 reactions. However in some cases there exists a great mismatch or disproportion between the amount of carbon formed and the drop in conversion. This is likely due to differences between the metal and acid functions of the catalysts and on the different distribution of coke deposits on them. For instance for both reactions the drop in conversion for Re-Pt-Sn and for Pt-Re-Sn are similar but the amount of coke on Re-Pt-Sn is three times the value on Pt-Re-Sn, indicating that there are coke deposits of different deactivation capacity. The differences are smaller when other catalysts are compared.

Re produces two opposite effects on coke formation: (i) it increases the concentration and strength of the acid sites; therefore it increases the condensation reactions of unsaturated hydrocarbons producing coke; (ii) when in good interaction with Pt, it decreases the size of the Pt crystals, as shown in [1]; in this case the deep dehydrogenation of big coke precursor molecules should be decreased, because this reaction needs big ensembles of Pt atoms. This would justify the very little coke produced on Pt-Re-Sn when compared to all other catalysts.

When using α-C5 as feed, the amount of coke formed is lower than in the case of α-C8 although the WHSV is higher and the H2/HC ratio lower. The difference in test length is not very important because most of the coke is formed at the beginning of the tests [15]. The total TPO area and the temperature of the maximum coke burning rate are higher when the coke content is higher. It is generally considered that during the reaction over a bifunctional catalyst there is a short initial period of great coking deposition, mainly on the metal function followed by a deposition on both functions. After this period, the coke is only deposited on the support and its degree of polymerization increases continuously [31]. It is interesting to note that the Pt catalyst has a TPO profile with a zone of coke burning at intermediate temperature which is bigger than that of the trimetallics. Very likely the high metallic activity of Pt allows the burning of neighboring coke which is not directly covering the Pt particles but can be reached by split-over atomic oxygen previously activated over the Pt surface [32]. In this way the low temperature peak would be enlarged. Fig. 5 compares the TPO profiles of coke formed on Pt-Re-Sn, produced in the α-C5 (0.20% C) and α-C8 (0.90% C) reactions. The α-C5 signal was multiplied by 5 when plotting the profiles in order to compare them better.

As compared to α-C5, the use of α-C8 not only decreased the coking rate, but also the coke deposits were less condensed and located in a greater proportion near the metallic function.

4. Conclusions

The catalytic properties of trimetallic naphtha reforming catalysts containing Pt, Re and Sn, prepared by successive impregnations are greatly influenced by the order of addition of the promoters. Activity, selectivity and stability results indicate that some of these catalysts have many advantages.

The so-called “metal” promoters of Pt, i.e. Re and Sn, affect also the “acid” function of the catalyst. Only a fraction of their oxides is reduced to the metallic state and has a specific action on Pt. The rest remains oxidized and affects
mainly the acidity of the support. During the catalyst preparation, if Sn is added first, the acid function is modified with positive consequences for the catalyst properties. It must be recalled that the acid function controls the most important reforming reactions: paraffins isomerization and cyclization. Sn addition decreases the total acidity, particularly blocking some strong acid sites responsible for cracking and coking, while milder sites suitable for isomerization and cyclization remain. Sn-Pt-Re is the most convenient catalyst for n-C₅ isomerization and for n-C₈ dehydrocyclization from the point of view of activity, selectivity and stability. When adding Sn first, it interacts strongly and partly irreversibly with the Cl-Al₂O₃ surface, displaying all the catalytic advantages already described. The addition of Re after Sn and Pt, mainly influences the metallic activity of Pt. A great advantage of introducing Re in the catalyst formulation is that the effective size of Pt crystals is reduced [1]. Re-Pt-Sn is the opposite to Sn-Pt-Re. The addition of Re at the beginning increases the strength of the acid sites of the support, in such a way that the activity, selectivity and stability are lower.

Both catalytic functions of Pt/Cl-Al₂O₃ are favorably affected by the promoters. The selectivity of the acid function to isomerization products is increased. The selectivity of the metal function to coke precursors and cracking products (gas) is decreased.

The metallic activity of Pt follows the order: monometallic > bimetallics > trimetallics. Even so, the controlling function of the main reforming reactions is always the acid function and its tuning by the addition of promoters is still a challenge to researchers. The main technological advantage of trimetallic catalysts is the increase in selectivity and stability.

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References


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