

Catalytic activity of Pt-Re-Pb/Al₂O₃ naphtha reforming catalysts

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Abstract

BACKGROUND: The main purpose of the naphtha reforming process is to obtain high octane naphtha, aromatic compounds and hydrogen. The catalysts are bifunctional in nature, having both acid and metal sites. The metal function is supplied by metal particles (Pt with other promoters like Re, Ge, Sn, etc.) deposited on the support. The influence of the addition of Pb to Pt-Re/Al₂O₃ naphtha reforming catalysts was studied in this work. The catalysts were prepared by co-impregnation and they were characterized by means of temperature programmed reduction, thermal programmed desorption of pyridine and several test reactions such as cyclohexane dehydrogenation, cyclopentane hydrogenolysis and n-heptane reforming.

RESULTS: It was found that Pb interacts strongly with the (Pt-Re) active phase producing decay in the metal function activity. Hydrogenolysis is more affected than dehydrogenation. Part of the Pb is deposited over the support decreasing the acidity and the strength of the most acidic sites.

CONCLUSION: The n-heptane reforming reaction shows that Pb modifies the stability and selectivity of the Pt-Re catalysts. Small Pb additions increase the stability and greatly improve the selectivity to C₇ isomers and aromatics while they decrease the formation of low value products such as methane and gases.

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Keywords: Naphtha reforming catalysts; Pt-Re-Pb/Al₂O₃

INTRODUCTION

Since World War II the catalytic reforming of naphtha has acquired a growing importance among the processes of the petrochemical industry. Currently, there are more than 700 commercial installations of catalytic reforming units worldwide, with a total capacity of about 11.0 million barrels a day. About 40% of this capacity is located in North America followed by 20% each in Western Europe and the Asia–Pacific region.¹ The objective of the process is to obtain a high octane fuel for its use in vehicles with spark ignition engines and airplanes, and the production of aromatic compounds such as benzene, toluene and xylene, which are raw materials for the plastics industry, nylon fibers, solvents, polyester fibers, etc.

In order to promote the desired reactions, naphtha reforming catalysts must have two functions: an acid function to promote isomerization and cyclization and a metal function with dehydrogenation properties. Normally the acid function is supplied by the support (γ -alumina), which is chlorinated in order to promote its acidity. The activity of the metal function – which is supplied by metal particles – is modified by promoters added in small quantities. These are metals and non-metals with suitable properties, such as Ge, Re, Sn, etc. The first bimetallic catalyst of commercial interest was Pt-Re/Al₂O₃, patented in 1968.² This catalyst had better resistance to deactivation by coking than the monometallic Pt/Al₂O₃ catalyst. This enabled the use of more severe conditions in the reformer (higher temperatures and lower pressures) that led to a higher yield of high octane compounds and hydrogen and longer operating cycles. The Pt-Re metal function has the

drawback that it has a higher activity for the hydrogenolysis of hydrocarbons, producing methane and other light hydrocarbons of low value.³ For this reason, the catalyst needs to be sulfided. The success of the Pt-Re/Al₂O₃ catalyst boosted the interest of industry and laboratories to develop new catalysts with greater activity, selectivity and stability. From the 1990s trimetallic catalysts thus appeared on the scene. In order to protect their competitive edge catalyst manufacturers keep the formulation of these catalysts highly secret. Therefore little information is available in the open literature.

Although information on trimetallic catalysts is scarce, some data related to the synthesis, characterization and use of Pt-Ir-Sn⁴, Pt-Sn-M (M: Bi, Te, Au, Pd, In),^{5–7} Pt-Ir-Ge,⁸ Pt-Re-Sn^{9,10} and Pt-Re-Ge¹¹ catalysts can be found. The most recently developed catalysts have favored increasing the isomer/aromatics ratio in order to satisfy environmental regulations restricting the aromatics content in fuels. The best additives for the Pt-Re metal function are elements of the IVA group (IUPAC 14) of the periodic table: Ge, Sn and Pb. The oxides of these elements are partially reduced to the metal state at reaction conditions. However only a fraction of the promoters can be alloyed to Pt or interact with it. The remaining fraction remains as oxidized species on the support

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and their effect is to alter its acidity.^{9,10} Very few publications in the open literature have been devoted to the influence of Pb on the catalytic properties of naphtha reforming catalysts.^{12,13} Völter *et al.*¹³ reported that Pb has the same effect as Sn on the catalytic properties of Pt/Al₂O₃; i.e. it affects the distribution (both strength and number) of acid sites, decreases hydrogenolysis, and improves the aromatization of paraffins.

The objective of this work is to determine the influence of Pb addition on the properties of the acid and metal functions of Pt-Re/Al₂O₃ naphtha reforming catalysts.

EXPERIMENTAL

Catalyst preparation

Pt-Re-Pb/Al₂O₃ catalysts were prepared using alumina supplied by Ketjen (CK-300, 200 m² g⁻¹, 0.55 cm³ g⁻¹, mean pore radius: 60 Å, impurities: Na=5 ppm, Fe=150 ppm, S=50 ppm). The supports were crushed and sieved to the size range 0.25–0.40 mm and then they were calcined in flowing air at 650 °C for 4 h. The trimetallic catalysts were prepared by coimpregnation. First HCl 0.2 mol L⁻¹ was added to the support and was left for 1 h without stirring. Then solutions of H₂PtCl₆, NH₄ReO₄ and (NO₃)₂Pb were added. The slurry was stirred gently for 1 h at room temperature. Then it was dried in a water bath at 70 °C until a dry solid was obtained. Drying was completed on a stove at 120 °C. The concentration of the impregnating solutions was adjusted in order to obtain 0.3% (w/w) Re and Pt in the final catalysts and variable amounts of Pb (0.1, 0.3 and 0.6% (w/w) Pb). Then the catalysts were activated by calcination in air at 400 °C for 4 h, followed by cooling to room temperature in nitrogen. Finally, the catalysts were reduced in hydrogen (60 cm³ min⁻¹) at 500 °C for 4 h. A heating rate of 10 °C min⁻¹ was employed in all cases.

Measurement of the Pt, Re and Pb contents

The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkim Elmer, Optima 2100 DV) after digestion of the sample in an acid solution and dilution. Levels of chlorine on catalysts in their final state, i.e. after activation, were measured by the Volhard method,¹⁴ in which the sample was dissolved in concentrated sulfuric acid and Cl ions were precipitated with silver nitrate solution. Excess silver solution was back titrated with a thiocyanate solution to give the amount of chlorine on the original sample.

Temperature-programmed desorption of pyridine

The amount and strength of acid sites of the catalysts were assessed by means of temperature-programmed desorption of pyridine. In this way, both Brønsted and Lewis acid sites were probed. 200 mg of the catalyst to be tested were first immersed in a closed vial containing the base for 4 h. Then the vial was opened and excess base 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 rate of nitrogen (40 mL min⁻¹) was used. A first step of desorption of weakly adsorbed base and stabilization was performed by heating the sample at 110 °C for 1 h. Then the temperature of the stove 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 units) was sampled at 1 Hz.

Cyclopentane hydrogenolysis (CP)

The reaction was performed in a glass reactor (length 10 cm, diameter 1 cm) under the following conditions: catalyst mass 150 mg, temperature 350 °C, pressure 0.1 MPa, H₂ flow rate 40 cm³ min⁻¹, cyclopentane flow rate 0.483 cm³ h⁻¹. Cyclopentane was fed to the reactor using a Sage Instruments 341B syringe pump. Before the reaction was started, the catalysts were treated in H₂ (60 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed by online gas chromatography using a ZB-1 capillary column. The cyclopentane hydrogenolysis rate was determined from the conversion value according to expression (1). The error in the conversion value in the CP hydrogenolysis test is about 8%. Only values of initial conversion at 5 min time-on-stream are reported.

Cyclohexane dehydrogenation (CH)

The reaction was performed in a glass reactor (length 10 cm, diameter 1 cm) under the following conditions: catalyst mass 50 mg, temperature 300 °C, pressure 0.1 MPa, H₂ flow rate 36 cm³ min⁻¹, cyclohexane flow rate 0.727 cm³ h⁻¹. The CH was introduced into the reactor using a Sage Instruments 341B syringe pump. Before the reaction was started, the catalysts were treated in H₂ (60 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed by online gas chromatography using a ZB-1 capillary column. All points reported are mean values obtained by averaging 12 consecutive measurements equally spaced along the run. No significant catalyst deactivation was observed in any run. The average error was less than 3%.

n-heptane reforming

The reactions were performed using a fixed bed tubular reactor at the following reaction conditions: 0.1 MPa, 450 °C, H₂/n-C₇ = 4, WHSV=7.3 h⁻¹. The catalysts were first reduced in H₂ (12 cm³ min⁻¹) for 1 h at 500 °C. The analysis of the reaction products was made using a ZB-1 capillary column and a flame ionization detector. The conversion of n-C₇ was defined as:

$$n - C_7 \text{ conv.} = \frac{n - C_7^i - n - C_7^0}{n - C_7^i} \quad (1)$$

where n-C₇ⁱ is the number of n-C₇ molecules at the reactor inlet and n-C₇⁰ is the number at the reactor outlet. The selectivity to each product *i* was defined as:

$$S_i = \frac{\text{yield of } i}{n - C_7 \text{ conv.}} = \frac{\frac{A_i \cdot f_i \cdot n_i / M_i}{\sum \frac{A_j \cdot f_j \cdot n_j}{M_j}}}{n - C_7 \text{ conv.}} 100 \quad (2)$$

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.

The absence in mass transfer limitations was assessed by calculating the modulus of Weisz-Prater and the Damköhler number for all the reactions involved: CH dehydrogenation, CP hydrogenolysis and n-C₇ reforming. In all cases the Weisz-Prater modulus was found to be much smaller than 0.1 while the Damköhler number was smaller than 0.01. Mass transfer could thus be neglected.

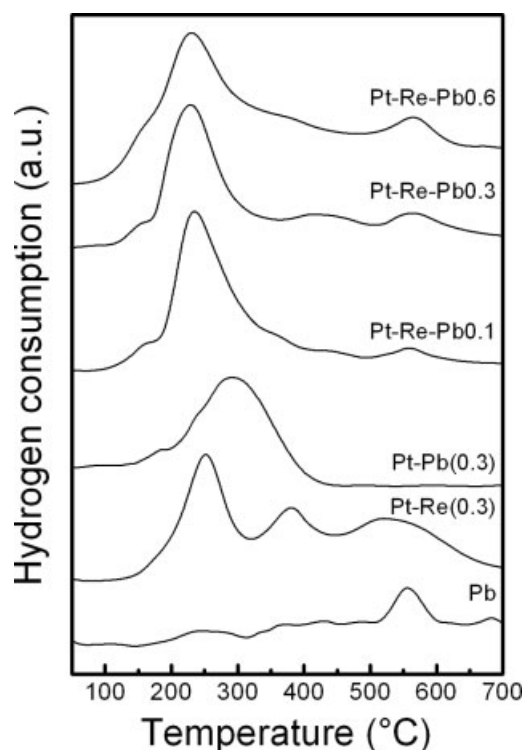


Figure 1. TPR traces of catalysts.

Temperature programmed oxidation

Carbon deposits formed on the surface of the catalysts during the $n\text{-C}_7$ reaction were studied by means of temperature programmed oxidation (TPO). 40–60 mg of the coked catalyst were first charged to a quartz microreactor. Then the carbon was burned in an oxidizing stream ($40\text{ cm}^3\text{ min}^{-1}$ of diluted oxygen, 5% O_2 in N_2). The temperature of the cell was increased from $30\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The outlet gases were fed to a methanation reactor where CO_2 and CO were quantitatively transformed into CH_4 over a Ni/Kieselgur catalyst in the presence of H_2 . The $\text{N}_2\text{:CH}_4$ stream was connected to a flame ionization detector (FID) and the signal produced was continuously recorded in a computer. The carbon concentration of the catalysts was calculated from the area of the TPO trace (FID signal as a function of the temperature of the cell) by reference to calibration experiments performed with catalysts of known carbon concentration.

RESULTS AND DISCUSSION

Chemical analyses of catalysts showed that metal contents were in close agreement with the expected theoretical values for all samples, while chlorine contents were about 0.9% for all the catalysts.

TPR results are reported in Fig. 1. TPR data for the Pt and Re monometallic catalysts supported on alumina have been reported previously.⁹ Pt oxides reduce in the range $240\text{--}260\text{ }^\circ\text{C}$, with a smaller peak at $300\text{ }^\circ\text{C}$ corresponding to the reduction of oxychlorinated species in strong interaction with alumina. The total hydrogen consumption (TPR area) corresponds to the total reduction of Pt(IV) to Pt(0). The TPR trace of Re oxide (results not shown) has a peak centered at about $590\text{ }^\circ\text{C}$ with a small shoulder at a lower temperature that may correspond to the reduction of particles that – due to their larger size – display a weak interaction

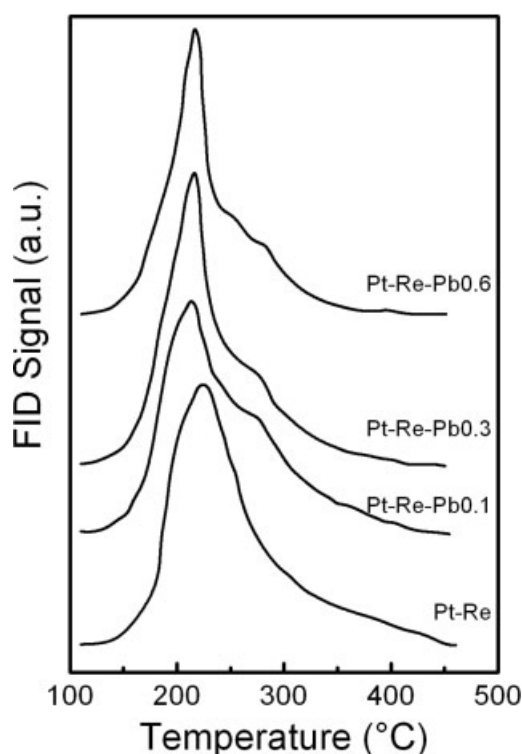


Figure 2. Pyridine TPD traces of bimetallic Pt-Re and trimetallic Pt-Re-Pb catalysts.

with the support. The area under the peaks indicates that about 90% of Re oxide is reduced to metallic Re(0). It can be seen in Fig. 1 that Pb has a small reduction peak at about $560\text{ }^\circ\text{C}$. This reduction pattern is similar to that reported by Lieske and Völter.¹⁵ Bimetallic Pt-Re shows three reduction peaks. The first at $250\text{ }^\circ\text{C}$ can be assigned to the reduction of Pt oxide species, the second at $380\text{ }^\circ\text{C}$ to the reduction of Re oxides in interaction with Pt, and the third peak at $530\text{ }^\circ\text{C}$ to the reduction of segregated Re oxides. The TPR trace of bimetallic Pt-Pb shows that Pb shifts the reduction peak of Pt to higher temperatures ($300\text{ }^\circ\text{C}$). The size of this peak indicates that part of Pb is reduced by the catalytic action of Pt. In the case of the trimetallic catalysts increasing the Pb content does not shift the position of the Pt reduction peak. The peak is, however, broadened, indicating that Pb is interacting with Pt. Moreover, it is possible to observe that a shoulder appears between 140 and $180\text{ }^\circ\text{C}$, which increases with Pb content. This shoulder could be due to the reduction of large PtO_x particles in weak interaction with the support, as reported by Carnevillier *et al.*¹⁶ Also observed is a peak at $580\text{ }^\circ\text{C}$ that can be attributed to the reduction of segregated oxides of Re and Pb. The TPR results thus indicate that Pb is anchored on the surface in close interaction with Pt. A reduction peak is observed around $200\text{ }^\circ\text{C}$, which is probably due to the reduction of Pt oxides with weak interaction with the support. This peak can be observed in the samples with Pb. This effect could be due to Pb deposition on the strongest acid sites forcing the Pt oxides to occupy the remaining weaker acid sites with lower Pt–support interaction. In this way Pt oxides can be reduced at lower temperatures.

The pyridine TPD traces shown in Fig. 2 indicate that the addition of Pb mainly decreases the concentration of the strong acid sites, while the concentration of mild and weak acid sites is less affected. The width of pyridine desorption peaks decreases as Pb

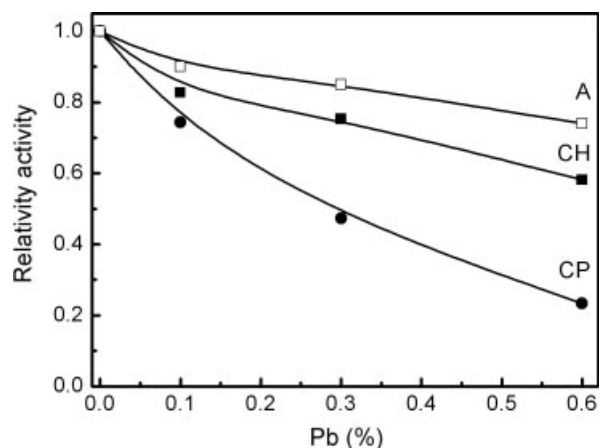


Figure 3. Results of cyclohexane dehydrogenation, cyclopentane hydrogenolysis and pyridine TPD. Data presented with reference to the base Pt-Re catalyst and as a function of the Pb percentage. CH: cyclohexane dehydrogenation, CP: cyclopentane hydrogenolysis, A: acidity determined by TPD of pyridine.

content increases. Pb oxide particles have a basic character and neutralize the acid sites of the support. When Pb is added the strongest acid sites are preferentially neutralized while the weak acid sites remain almost unaltered. This phenomenon probably causes this observed decrease in peak width. Therefore, during the impregnation step, these basic oxides are selectively deposited on the strong acid sites by means of electrostatic attraction.

Figure 3 shows conversions of a function of Pb content in the reactions of cyclohexane hydrogenation, cyclopentane hydrogenolysis and results of the pyridine TPD tests. The results are presented on a relative basis, with reference to the Pt-Re base catalyst and as a function of the Pb content. It can be seen that the acidity is decreased as the Pb content is increased. This can be attributed to the basic nature of the Pb oxides. The results related to the activity of the metal function indicate that Pb decreases both the dehydrogenation and hydrogenolysis activities. This occurs because Pb is inactive for these reactions and therefore when it is present on the metal function, it decreases its overall activity. Cyclopentane (CP) hydrogenolysis is a metal-catalyzed demanding reaction^{17,18} while the dehydrogenation of cyclohexane is a typical metal-catalyzed, non-demanding reaction;^{17,19} i.e. it does not require the presence of special atom ensembles.¹⁹ Therefore, hydrogenolysis is evidently more affected than dehydrogenation by the incorporation of Pb.

n-heptane reforming is a very useful test for evaluating catalysts because it comprises a series of elementary reactions that are acid-and/or metal-catalyzed. The main catalytic reactions occurring during the whole reforming process are: isomerization, dehydrocyclization, hydrocracking, dehydrogenation, hydrogenolysis, and coke deposition. The results of many studies show that the isomerization can be considered to be controlled by the acid function of the catalyst.²⁰ It is accepted that the isomerization of n-paraffins proceeds through a bifunctional metal-acid mechanism.¹⁸ The reaction starts on the metal sites with the dehydrogenation of the paraffins. Olefins then migrate to a neighboring acid site where they are converted to alkene isomers. These alkenes are finally hydrogenated on a metal site. The reaction mechanism is controlled by the slowest elementary step on the acid function.¹⁹ This statement is in agreement with the conclusions of Sinfelt²¹ and Sterba and Haensel,²² who stated that under commercial reform-

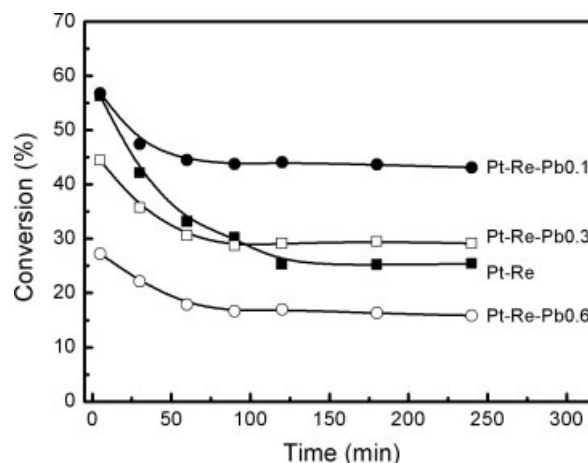


Figure 4. Conversion of n-C₇ as a function of time-on-stream for the Pt-Re-Pb catalysts.

ing conditions the rate of isomerization on metal sites is negligible compared with that of the bifunctional mechanism. Furthermore, trace amounts of sulfur are enough to poison the active sites responsible for isomerization on the metal function.

Aromatic hydrocarbons are produced by dehydrocyclization of paraffins, a reaction that occurs mainly by a bifunctional mechanism at industrial catalytic reforming conditions.^{23,24} The paraffins are first dehydrogenated on the metal to give n-olefins, which migrate to a neighboring acid site, where they are protonated, producing a secondary carbenium ion. This ion is cyclized on the acid function, producing five-carbon-atom ring olefins, which are then isomerized on the acid sites, enlarging the ring up to six carbons. In this way cyclohexene and cyclohexadiene (with and without branches) are dehydrogenated to aromatic hydrocarbons.

The bifunctional hydrocracking of n-paraffins produces paraffins of lower molecular weight and is also considered to be controlled by the acid function of the catalyst.^{23,24} Regarding the acid controlled reactions, cracking requires stronger acid sites than isomerization.²⁵

The dehydrogenation-hydrogenation reactions on the metal function are rapid enough to be considered in thermodynamic equilibrium, whereas isomerization reactions on the acid function are much slower.^{23,24} The hydrogenolysis is produced on the metal particles and requires large ensembles of Pt atoms, this reaction is prevented when the number of these ensembles is reduced by dilution of Pt with a second element (Sn, Ge, ReS). As a conclusion, toluene is produced by dehydrocyclization, heptane isomers by skeletal branching and light paraffins (C₂-C₆) by cracking. Methane is mainly also produced by metal catalyzed hydrogenolysis.²³

Figure 4 shows the evolution of the conversion of n-C₇ as a function of time for the bimetallic catalyst Pt-Re and the trimetallic Pt-Re-Pb catalyst. Pt-Re-Pb0.1 has the same initial activity as the Pt-Re catalyst. The addition of 0.1% (w/w) Pb affects the acidity by only 5%, the dehydrogenation activity by 17% and the hydrogenolysis activity by 25%. The amount of metals is in excess while the main reactions (dehydrocyclization, isomerization, and hydrocracking) are controlled by the acid function. The more important effect of the addition of 0.1% (w/w) of Pb is to change the selectivity and the rate of coke formation. These changes are due to the selective elimination of strong acid sites responsible for coke formation

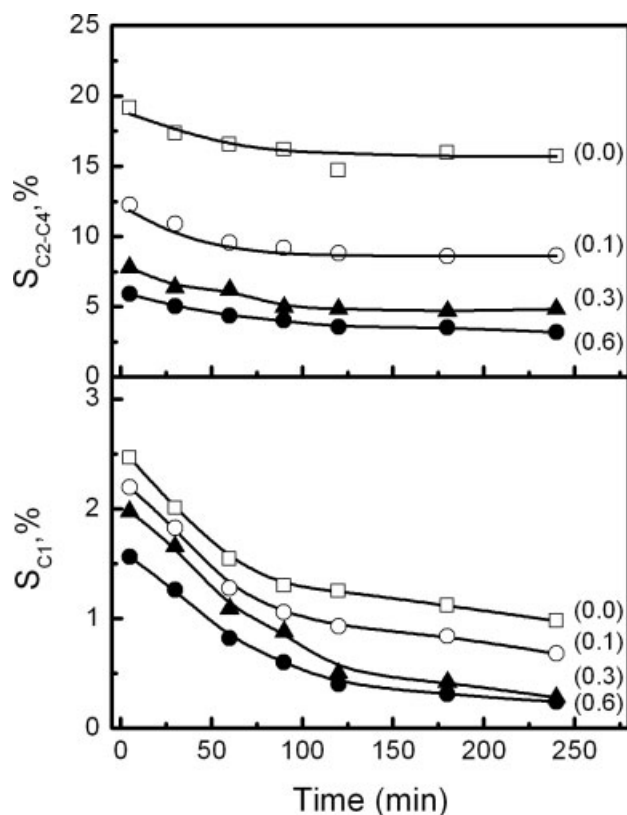


Figure 5. Selectivity to C₂+C₃+C₄ and C₁ as function of time-on-stream. Values between brackets are the percentages of Pb of the catalysts.

and hydrocracking. In all cases, deactivation of the catalyst occurs due to the formation and accumulation of coke on the surface. This coke is present both on the acid and metal functions.^{26–28} Addition of Pb produces an increase in the stability, while the initial activity is decreased as the Pb content increases. This is related to the loss of acid sites by neutralization with basic Pb species and to the decrease in the metal activity by Pb addition. The best formulation is that with 0.1% (w/w) Pb.

Figure 5 shows the results of selectivity to methane and light hydrocarbons (C₂+C₃+C₄) as a function of time-on-stream. It should be recalled that the formation of methane is mainly due to hydrogenolysis of the C–C bond on the metal function while the formation of C₂, C₃ and C₄ is due to cracking on strong acid sites.^{23,24} The Pt-Re catalyst has the highest selectivity to methane and this decreases with time as a consequence of coke deposition. The addition of Pb produces a decrease in hydrogenolysis activity. This correlates with the results of Fig. 3. However, the hydrogenolysis inhibition by Pb addition is not as marked as that indicated in Fig. 3. The lower formation of light gases at growing Pb contents can be explained by a decrease in the acidity of the catalyst (Fig. 3). The reduction of the concentration of strong acid sites accordingly decreases the rate of hydrocracking occurring on these sites.

Figure 6 shows values of selectivity to i-C₇ and aromatics as a function of the content of Pb at two values of time-on-stream (5 min and 240 min). It can be seen that Pb addition improves the selectivity to isomers and aromatics. In spite of these, both the selectivity to aromatics and heptane isomers passes through a maximum. Because of coke deposition both selectivities are decreased at high values of time-on-stream. As mentioned pre-

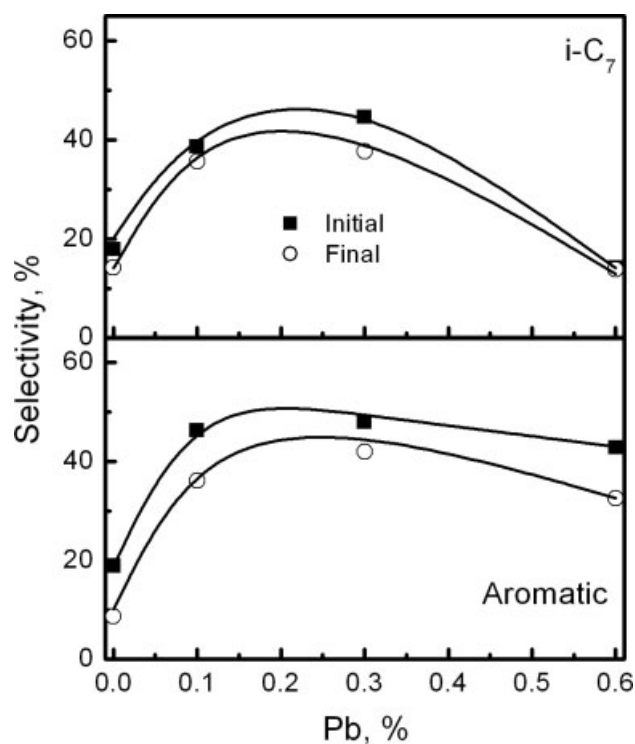


Figure 6. Selectivity to aromatics and C₇ isomers at 5 and 240 min time-on-stream, as a function of the Pb content.

viously, both the isomerization and dehydrocyclization reactions are bifunctional but the rate is controlled by the acid function of the catalyst.^{23,24,29,30} Therefore, the improvement in the selectivity of both reactions when adding Pb could be due to a decrease in cracking, which produces mainly C₂, C₃ and C₄. According to the results of Fig. 5, Pb addition produces a drastic decrease in the production of light gases. Therefore the formation of olefins (intermediates in the bifunctional mechanism) is followed by the formation of isomers or aromatics and not by the formation of smaller fragments (C₂, C₃, C₄). The addition of Pb decreases both the hydrogenolytic activity and the amount of strong acids sites. As a consequence a lower C₁ selectivity and hydrocracking activity (production of C₂–C₄ light gases) is observed. On the other hand, the selectivity of products associated with intermediate strength acid sites is improved (aromatics and C₇ isomers). In other words, the addition of Pb improves the metal/acid function balance. As pointed out by Prins³¹ and Parera *et al.*³² the naphtha reforming catalyst requires an adequate balance between the acid and metal functions in order to obtain the desired products.^{31,32} Contrary to expectations, at high Pb content (0.6% (w/w)) the selectivity to aromatics has a minor decrease while the selectivity to isomers is much more affected. The high Pb content (≥0.3% (w/w)) could be causing this effect and making the metal/acid function balance inadequate.

It is important to point out that commercial Pt-Re/Al₂O₃ catalysts are normally presulfided in the commercial units at the start of the run because the catalyst has high initial hydrogenolytic activity that needs to be suppressed for proper operation and product quality. If the catalyst is not passivated by this procedure at start-up, temperature runaways in the reactor can be expected to occur. The poor selectivity to aromatic and i-C₇ isomers found for these catalysts is mainly due to the absence of presulfidation. As a consequence, the metal and acid functions are not properly

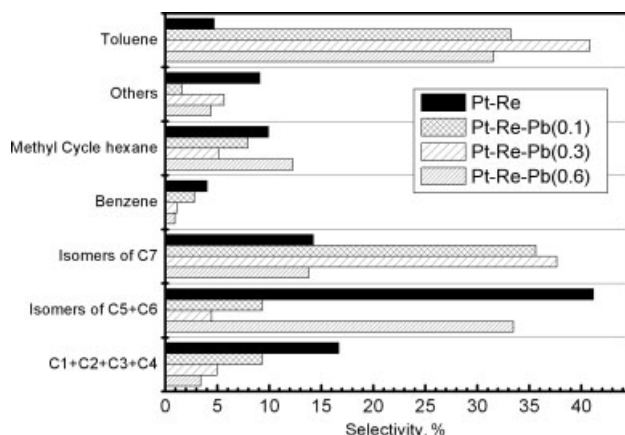


Figure 7. Selectivity to all products at the end of n - C_7 reforming grouped by number of carbon atoms. C_5 and C_6 isomers group include C_{5-6} paraffins and naphthenics and the group named 'others' includes some paraffin and naphthene isomers of C_8 .

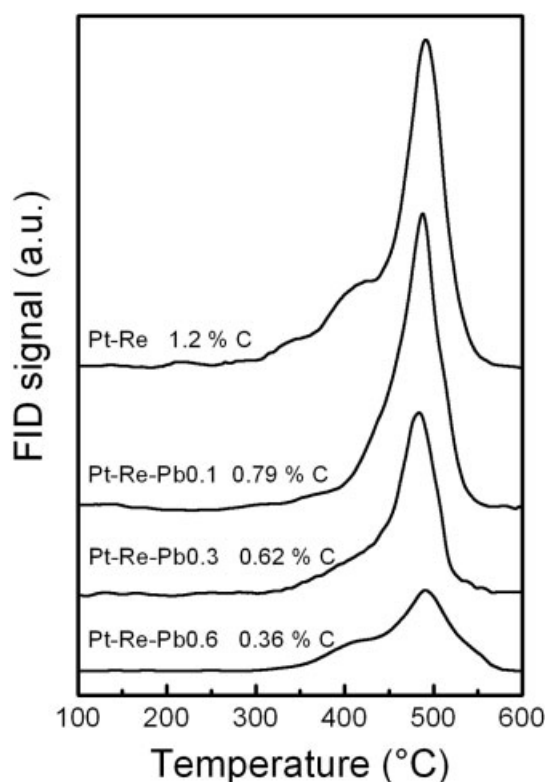


Figure 8. TPO traces of the catalysts coked in the reaction of n - C_7 reforming.

balanced, the hydrogenolysis produces methane and the high acidity (compared with catalysts containing Pb) promotes cracking reaction (C_2 – C_4 formation).

Figure 7 shows the selectivity to all products at the end of n - C_7 reforming for the studied catalysts. For the sake of simplicity the products were grouped. C_5 and C_6 isomers group include C_{5-6} paraffins and naphthenics and the group named 'others' includes some paraffin and naphthene isomers of C_8 . It can be seen that the main differences between the Pb-free catalyst and the catalyst

with Pb are the selectivities to i - C_5 and i - C_6 isomers. There is a pronounced decrease in this parameter at 0.3 Pb content.

Figure 8 shows the TPO traces of the carbon deposits formed on the Pt-Re and Pt-Re-Pb catalysts at the end of the reaction of n - C_7 . The coke on the PtRe catalyst after the n - C_7 reaction exhibits a combustion peak at about 490°C attributed to the burning of carbon on the support. The TPO of the Pt-Re catalyst run in n - C_7 displays a shoulder at 400°C that could be due to the coke deposited on the support, in the vicinity of the metal.³³ When a third metal is added to the metal function a remarkable decrease in the coke content occurs. Coke deposition on the metal demands larger ensembles with a size similar to those needed for the hydrogenolysis reaction.³⁴ This is due to the fact that coking is a structure-sensitive reaction and that Pb atoms decrease the effective size of Pt and Re ensembles thus inhibiting the formation of coke on the metal function. In the case of the trimetallic catalysts the lower coking rate in comparison with the Pt-Re catalyst is related to a lower formation rate of coke precursors. These are dehydrogenated, olefinic compounds that undergo polymerization on acid sites. The CH dehydrogenation tests show that the addition of Pb decreases the dehydrogenation activity of the Pt-Re catalyst. Another factor influencing the deposition of coke is the nature of the acid function. Sites of strong acidity are responsible for polymerization reactions leading to the formation and accumulation of coke. Therefore, the lower coking rate in the Pb-doped catalysts can be attributed to the lower formation rate of coke precursors and to the lower acidity of the coking sites.

CONCLUSIONS

According to the TPR results Pb is in interaction with the Pt-Re active phase. As a consequence the activity of the metal function is decreased. Hydrogenolysis is more affected than dehydrogenation. Pb is partly deposited on the support, decreasing its acidity and the strength of the most acidic sites.

The n -heptane reforming results show that Pb modifies the stability and selectivity of the Pt-Re catalysts. The addition of a small amount of Pb improves the stability and increases the selectivity to aromatics and C_7 isomers while the production of low value methane and other hydrocarbons gases is decreased.

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