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Influence of Time and Temperature on the Regeneration of PtReIn/Al₂O₃ Naphtha Reforming Catalysts

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Abstract The influence of temperature (450–500 °C) and time (1–4 h) of coke combustion on the catalytic properties of PtReIn/Al₂O₃ were studied. The results of the cyclohexane dehydrogenation and cyclopentane hydrogenolysis reactions show that the regeneration treatment with diluted oxygen can fully recover the activity of the metal function despite some observed segregation of Re and In. In the case of the *n*-heptane reforming reaction, the regenerated catalysts had lower activity and stability than the fresh ones. The experiments at high temperature in air showed that In prevents the sintering of Pt and Re but at 650 °C a segregation of Re from the Pt–Re phase occurs.

Keywords PtReIn/Al₂O₃ catalysts · Naphtha reforming · Regeneration

1 Introduction

On the basis of volume, catalytic naphtha reforming is one of the largest processes of the petroleum industry used to upgrade the octane number of gasoline. It does so by increasing the amount of branched paraffins and aromatics. In the petrochemical industry, the process is also an important source of high value aromatic compounds such

as benzene, toluene and xylenes. The process is also one of the major sources of hydrogen in petroleum refineries [1].

The formation of carbonaceous deposits on a catalyst surface is an undesirable reaction because it gradually deactivates the catalyst by blocking the active sites. To compensate this activity decay, increasing the operation temperature is the common industrial practice. However, after a certain time it becomes necessary to regenerate the catalyst so as to restore its original properties [2]. In order to decrease deactivation, bimetallic and trimetallic naphtha reforming catalysts were introduced [3–9]. Composition and preparation routes of the metal function are crucial in determining the activity and stability of these catalysts. Recently, Liu et al. [10] reported that the use of polyacrylic acid metal templates produces Pt–Re naphtha reforming catalysts with low coke deposition and high liquid yield.

The main reaction variables affecting the formation of coke are the partial pressure of hydrogen and hydrocarbon, space velocity, reaction temperature and feed composition [11]. On the catalyst side, the rate of coke deposition depends on the nature of the metal, the metal particle size, and the kind of promoters and support, among other factors [12]. In bifunctional catalysts, the properties of the metal function are particularly responsible for the formation of coke [11] because: (i) olefins are precursors of coke formation produced on the metal by dehydrogenation; (ii) polymers formed on the support can be stabilized by dehydrogenation through reverse spillover of hydrogen; (iii) coke precursors can be destroyed on the metal particles by hydrogenolysis. In addition, the support acid sites promote the polymerization reactions leading to coke deposition. The coke formed on the catalyst pore walls during naphtha reforming shows that the coke deposition reaction is the slow controlling step of coking while the mass transfer rate of the coke ingredients into the pores is fast [13].

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Coke removal in the industry is carried out by combustion using a diluted mixture of oxygen in nitrogen. Despite the use of a low concentration of oxygen, the active metal component of the catalyst becomes sintered due to the high exothermicity of the combustion reaction which causes an increase in temperature ($>500\text{ }^{\circ}\text{C}$). High temperature conditions and the presence of oxygen not only produce the sintering of the metal particles but also the segregation of different metals [2]. The water produced during coke combustion enhances the removal of chlorine. Thus, the acidity of the catalyst is decreased.

Lacombe and coworkers [14] studied Pt–Sn–In/Al₂O₃–Cl catalysts and found that indium addition decreases the catalyst overall conversion and the selectivity to C₁ and C₃–C₄ paraffins and increases the isomerization selectivity. Moreover, they proposed an original approach for stabilizing Pt_xSn alloyed clusters with an elevated Sn⁰/Pt ratio, highly dispersed on γ -alumina, using indium as “third element” by adding In³⁺ on the support [15]. To improve the efficiency of catalytic reforming catalysts, some patents claim the incorporation of In. Wilhelm [16] reported that the addition of indium markedly improves activity, selectivity and stability. Antos [17] proposed the use of catalysts containing indium in order to obtain rich aromatic cuts that would be adequate for petrochemical use. They also reported that the addition of indium improves the resistance to deactivation by coke formation [17]. In agreement with these authors, Bogdan and Imai [18, 19] reported that indium improves the aromatization/cracking ratio of the reforming reaction and increases the production of gasoline. More recently, Peltier et al. [20] proposed the use of various catalysts containing Pt and other metals (Re, In, Sn, W). The formation of Pt_xSn alloys at higher indium loading produces a decrease of the conversion and selectivity to C₁ and C₃–C₄ paraffins and an increase of the isomerization selectivity [21].

In a previous work we studied the influence of the indium content on the properties of Pt–Re/Al₂O₃ naphtha reforming catalysts [22]. In order to improve our knowledge of the PtReIn/Al₂O₃ catalysts, in this paper we study the influence of the regeneration conditions (temperature and time) on the properties of PtReIn(x)/Al₂O₃ catalysts for naphtha reforming. It is important to point out that there are no references in the open literature regarding the regeneration of PtReIn(x)/Al₂O₃ catalysts.

2 Experimental

2.1 Catalysts Preparation

All catalysts were prepared using a commercial γ -alumina as support (Cyanamid Ketjen CK-300, pore volume = $0.5\text{ cm}^3\text{ g}^{-1}$, specific surface area = $180\text{ m}^2\text{ g}^{-1}$, impurities:

Na = 5 ppm, Fe = 150 ppm, S = 50 ppm). The alumina pellets were ground to 0.500–0.177 mm diameter and then they were calcined in air at $650\text{ }^{\circ}\text{C}$ for 3 h. Then, 0.2 M HCl solution ($1.5\text{ cm}^3\text{ g}^{-1}$) was added to the support and the slurry was left unstirred for 1 h at room temperature. Afterwards, H₂PtCl₆, NH₄ReO₄ and In(NO₃)₃ impregnating solutions were added to the system and the slurry was shaken gently for 1 h at room temperature. Then, it was dried at $70\text{ }^{\circ}\text{C}$ until a dry solid was obtained. Drying was completed in an oven at $120\text{ }^{\circ}\text{C}$ for 12 h. The concentration of the impregnating solutions was adjusted in order to obtain 0.3 % Pt, 0.3 % Re and 0.3 or 0.1 % In on the final catalysts. Then, the catalysts were activated by calcination in air at $450\text{ }^{\circ}\text{C}$ for 4 and cooled down to room temperature in nitrogen. The samples were reduced in hydrogen ($60\text{ cm}^3\text{ min}^{-1}$) at $500\text{ }^{\circ}\text{C}$ for 4 h. Heating ramps were programmed at $10\text{ }^{\circ}\text{C min}^{-1}$. The catalysts were named with reference to the composition of the metal function only (Pt, PtRe, etc.) because the support is the same for all of them. For example, PtReIn(0.1) means trimetallic catalyst with 0.3 wt% of Pt and Re and 0.1 wt% of In supported on Al₂O₃.

2.2 Measurement of the Pt, Re and In Contents

The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin–Elmer, Optima 2100 DV) after digestion in an acid solution and dilution.

2.3 Temperature-Programmed Reduction

TPR tests were performed in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. Prior to reduction, the calcined catalysts (ca. 0.1 g loaded in a U-shaped reactor) were heated at $120\text{ }^{\circ}\text{C}$ and kept at that temperature for 1 h in a stream of argon to remove water. The samples were then cooled to room temperature under this atmosphere and once the base line was restored, a flow of argon was switched to $50\text{ cm}^3\text{ min}^{-1}$ of a 5 % H₂/Ar mixture. The catalyst was heated from room temperature to $850\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The effluent gas was passed through a cold trap before thermal conductivity detector (TCD) in order to remove water from the exit stream.

2.4 Temperature-Programmed Pyridine Desorption

The quantity and strength of the surface acid sites of the catalysts were assessed by means of temperature-programmed desorption of pyridine. 0.2 g of the reduced catalyst were immersed into a closed vial containing pure pyridine (Merck, 99.9 %) for 4 h. Then the catalyst was taken out from the vial and excess pyridine was removed by evaporation at room temperature under a fumes hood.

The sample was then charged to a quartz micro reactor with a constant nitrogen flow ($40 \text{ cm}^3 \text{ min}^{-1}$). Weakly adsorbed pyridine was first desorbed in a first stage of stabilization by heating the sample at $110 \text{ }^\circ\text{C}$ for 2 h. The temperature of the oven was then raised to $600 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The reactor outlet was directly connected to a flame ionization detector (FID) to measure the desorption rate of pyridine.

2.5 Transmission Electron Microscopy

Transmission electron micrographs (TEM) were obtained in a Jeol JEM 1200 EXII microscope. The supported catalysts were ground in an Agatha mortar and dispersed in ethanol. A diluted drop of each dispersion was placed on a 0.102 mm copper grid coated with carbon. Average particle sizes were determined by measuring a minimum of 140 particles for each sample analyzed.

2.6 Dynamic Chemisorption of CO

This technique was used to estimate the dispersion of the Pt metal particles on the surface of the catalyst. Calibrated pulses of the adsorbate were injected to a stream of inert gas that flowed over the sample. These pulses were sent to the reactor until the sample was saturated. At the beginning of the experiment, the sample (400 mg) was reduced at $500 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C min}^{-1}$) for 1 h. Then, a nitrogen flow was passed over the sample for 1 h at $500 \text{ }^\circ\text{C}$ in order to eliminate adsorbed hydrogen. Finally, the sample was cooled down to room temperature under nitrogen flow and $0.6 \text{ } \mu\text{mol}$ of CO were sent to the reactor. Non-chemisorbed CO was quantitatively transformed into CH_4 over a Ni/Kieselguhr catalyst and detected in a FID connected on-line. The error of the method was estimated by means of nine chemisorption tests with a Pt/ Al_2O_3 catalyst with a dispersion of 40 %. The average deviation was found to be 4.3 %. The stoichiometry for CO adsorption assumed for dispersion calculations was $\text{CO/Pt} = 1$.

2.7 Regeneration by Coke Burning-off

Regeneration treatments were performed in a quartz reactor loaded with 0.3 g of deactivated catalyst. The catalyst sample was heated in nitrogen from room temperature to the coke burning temperature (450 or $500 \text{ }^\circ\text{C}$). Once the temperature was stabilized, coke burning was started by feeding the $\text{O}_2:\text{N}_2$ mixture (5 % O_2) at $40 \text{ cm}^3 \text{ min}^{-1}$. The span of the treatment was fixed at 30, 60 or 240 min.

2.8 Accelerated Deactivation by Coking

Accelerated deactivation treatments were performed in order to study the influence of the deposition of carbon

deposits and the regeneration on the performance of the catalyst. Cyclopentane (CP), a well-known important coke precursor [23], was reacted over the catalyst at a low hydrogen partial pressure in order to increase the coking rate. One gram catalyst samples were loaded to a fixed bed reactor and reduced in situ for 1 h at $500 \text{ }^\circ\text{C}$ in H_2 ($30 \text{ cm}^3 \text{ min}^{-1}$). Then, CP was fed to a reactor at $1.2 \text{ cm}^3 \text{ h}^{-1}$ while keeping the hydrogen flow rate and reaction temperature for 7 h. The WHSV was 0.90 h^{-1} .

2.9 Cyclopentane Hydrogenolysis

Before the reaction, catalysts were reduced for 1 h at $500 \text{ }^\circ\text{C}$ in H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$). Then, they were cooled in H_2 to the reaction temperature ($350 \text{ }^\circ\text{C}$). Reaction conditions were: catalyst mass = 150 mg , pressure = 0.1 MPa , H_2 flow rate = $40 \text{ cm}^3 \text{ min}^{-1}$, CP flow rate = $0.483 \text{ cm}^3 \text{ h}^{-1}$, WHSV = 2.42 h^{-1} . The reaction products were analyzed in an on-line gas chromatograph equipped with FID detector and a Phenomenex ZB-1 capillary column (30 m length and 0.25 mm internal diameter).

2.10 Cyclohexane Dehydrogenation

The reaction was performed in a glass reactor with the following conditions: catalyst mass = 100 mg , temperature = $300 \text{ }^\circ\text{C}$, pressure = 0.1 MPa , $\text{H}_2 = 80 \text{ cm}^3 \text{ min}^{-1}$, cyclohexane = $1.61 \text{ cm}^3 \text{ h}^{-1}$, WHSV = 12.5 h^{-1} . Before the reaction was started, the catalysts were treated in H_2 ($80 \text{ cm}^3 \text{ min}^{-1}$, $500 \text{ }^\circ\text{C}$, 1 h). The reaction products were analyzed in an on-line gas chromatograph equipped with FID detector using a Phenomenex ZB-1 capillary column (30 m length and 0.25 mm internal diameter).

2.11 Temperature-Programmed Oxidation (TPO)

Carbon deposits formed on the catalysts surface were studied by means of temperature-programmed oxidation (TPO). $40\text{--}60 \text{ mg}$ of the coked catalyst were first charged in a quartz reactor. Then, the carbon was burned in an oxidizing stream ($60 \text{ cm}^3 \text{ min}^{-1}$ of diluted oxygen, 5 % O_2 in N_2 vol:vol). The temperature of the cell was increased from 30 to $650 \text{ }^\circ\text{C}$ 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 catalyst in the presence of H_2 . The CH_4 stream was connected to a 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 profiles (FID signal as a function of the temperature of the cell) by reference to calibration experiments performed with catalysts with known carbon amounts.

2.12 *n*-Heptane Reforming

The reaction was performed in a fixed-bed tubular reactor under the following conditions: 0.1 MPa, 500 °C, $H_2/n-C_7 = 6$, $WHSV = 4 \text{ h}^{-1}$. The catalysts were first reduced in H_2 ($12 \text{ cm}^3 \text{ min}^{-1}$) for 1 h at 500 °C. The analysis of the reaction products was performed using a Phenomenex ZB-1 capillary column (30 m length and 0.25 mm internal diameter) and a flame ionization detector. The conversion of *n*- C_7 was defined as:

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

$n - C_7^i$ is the number of *n*- C_7 molecules at the reactor inlet and $n - C_7^0$ is the number at the reactor outlet. The selectivity to each product *i* was defined as:

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

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.

2.13 Thermal Treatments

In order to study the thermal stability of the catalysts i.e., metal sintering and segregation, samples were treated in flowing air ($60 \text{ cm}^3 \text{ min}^{-1}$) at 550 or 650 °C for 4 h.

3 Results and Discussion

In a previous work some characterization results of PtReIn(*x*)/ Al_2O_3 catalysts were reported [22]. The analysis of the TPR profiles showed the presence of indium species interacting with Re and Pt. It was also found that the addition of indium to a PtRe/ Al_2O_3 catalyst produces a marked decrease in acidity, the effect being greater at increasing indium loads. It also causes an inhibition of the metal function properties, namely, dehydrogenation and hydrogenolysis.

Table 1 shows the conversion values of cyclohexane dehydrogenation and cyclopentane hydrogenolysis for fresh, coked and regenerated catalysts. Only Pt surface atoms are active for dehydrogenation of cyclohexane to benzene and the Pt–Re ensembles are the most active ones in the hydrogenolysis reaction [24]. Therefore, the drastic decrease of the metal activity of the coked catalysts shows that a fraction of coke is deposited on the metallic phase. The hydrogenolysis activity is more affected than the dehydrogenation activity because hydrogenolysis is a demanding reaction while dehydrogenation is a structure

Table 1 Conversion values obtained in the reactions of cyclopentane hydrogenolysis (HCP) and cyclohexane dehydrogenation (DCH)

	Catalysts			
	PtReIn (0.1)/ Al_2O_3		PtReIn (0.3)/ Al_2O_3	
	DCH	HCP	DCH	HCP
Fresh	37.7	8.9	34.1	4.5
Coked	1.1	0.0	1.4	0.0
Regenerated ^a	7.1	0.8	5.5	0.8
Regenerated ^b	17.2	3.3	12.7	2.1
Regenerated ^c	40.5	8.6	37.2	4.0

Fresh, coked and regenerated catalysts

^a Regeneration for 1 h at 450 °C

^b Regeneration for 1 h at 500 °C

^c Regeneration for 4 h at 500 °C

insensitive reaction [25–27]. The dehydrogenation activity of the PtReIn(0.1) coked catalyst is lower than the activity of the PtReIn(0.3) coked catalyst. This could be related to indium destroying ensembles of the metal phase. As a consequence, less coke is deposited because coke deposition on the metal function is a demanding reaction [28, 29]. As expected, the metal function activity is recovered as coke is eliminated. It is important to note that the dehydrogenation activity levels of the catalysts regenerated at 500 °C for 4 h are higher than those of the fresh catalysts. The higher metal activity of the regenerated catalysts could be the result of two opposite phenomena: (i) sintering of the metal phase due to the higher regeneration temperature (exothermal reaction, hot spot) and (ii) segregation of In and Re of the active metal phase.

Figure 1 shows profiles of coke combustion of PtReIn(0.1) and PtReIn(0.3) catalysts which were deactivated in the reaction of cyclopentane. It is known that the plots of TPO of coke deposited on naphtha reforming catalysts have two burning zones [30, 31]. The burning zone at low temperatures (300–350 °C) can be ascribed to the burning of coke deposited on the metallic function. This coke is richer in hydrogen. The burning zone at higher temperatures can be addressed to the burning of coke deposited on the acid function (support) which is more polymerized. The temperatures of these peaks depend on the amount of coke and its composition, and on the operating conditions of the TPO experiments (heating rate, oxygen concentration, gas flow-rate, etc.) [30, 32–35]. There is also an intermediate zone of coke combustion attributed to the existence of coke with intermediate degrees of polymerization and located in the vicinity of Pt particles [36]. The ratio between the amount of coke deposited on the metal and coke deposited on the support depends on the type of metal, support, reaction conditions,

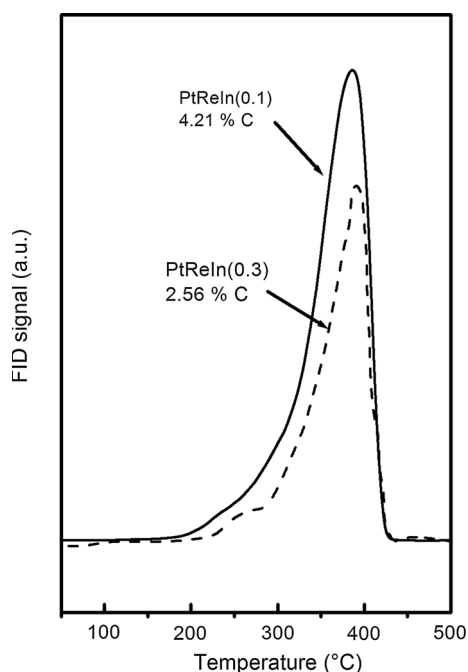


Fig. 1 TPO profiles of the coked PtReIn(0.1) and PtReIn(0.3) catalysts

nature of hydrocarbon and reaction time [37]. It can be seen that under the conditions of accelerated deactivation, the PtReIn(0.1) catalyst has a higher rate of coke deposition than the PtReIn(0.3) catalyst since it has a final carbon content of 4.21 wt% while PtReIn(0.3) has only 2.56 wt%. Taking into consideration the coking mechanism, the metal sites are responsible for two rate limiting steps: (i) the formation of dehydrogenated compounds; these are coke precursors that polymerize over the acid sites of the catalyst [32, 38, 39]; (ii) the destruction of coke precursors by hydrogenolysis [37, 40, 41]. The relative magnitude of these two processes and the amount and strength of the acid sites determines the final coking rate and coke content of the catalyst. As shown in Table 1, the catalyst with 0.3 % of In (fresh) has less dehydrogenation activity than the catalyst with 0.1 % of indium. Therefore, the reduced formation of coke on the catalyst with 0.3 wt% of indium can be due to this catalyst producing a smaller amount of dehydrogenated compounds (olefins) which are recognized coke precursors. Another factor affecting the deposition of coke is the nature of the acid function. The strong acid sites are responsible for the polymerization reactions leading to the formation of coke [42–45]. The catalyst with 0.3 % of indium has lower acidity [22]. Thus, not only less coke precursors are formed on this catalyst but also a lower polymerization rate takes place on its acid sites. Moreover, it can be seen in Fig. 1 that the amount of coke deposited on the metal is very low in both catalysts. This is due to coke deposition being a structure sensitive reaction. Indium

Table 2 Carbon percentage (%wt) of the used catalysts after regeneration

Regeneration temperature (°C)	Regeneration time (h)	Coke (wt%)	
		PtReIn(0.1)	PtReIn(0.3)
Coked			
–	–	4.21	2.56
Regeneration			
450	1	2.48	0.69
500	1	0.20	Not detected
500	4	0.01	Not detected

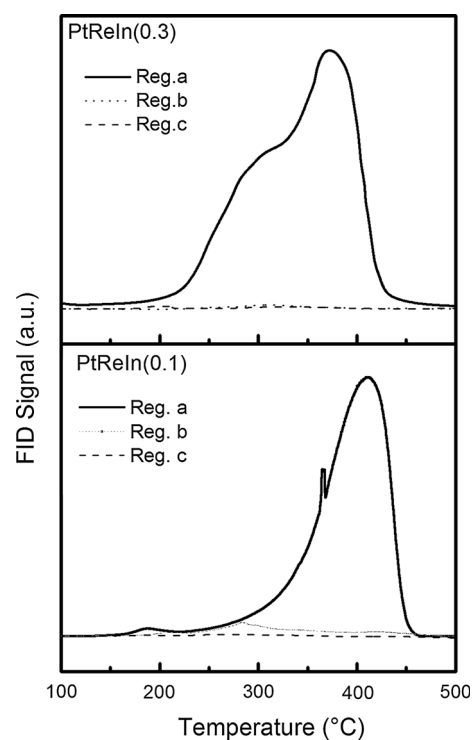


Fig. 2 TPO profiles of the PtReIn(0.1) and PtReIn(0.3) catalysts partially regenerated under different conditions

atoms decrease the amount of Pt and Re ensembles thus inhibiting the formation of coke on the metal function. The TPO of the coke formed during the reaction of CP confirms that the coke is preferably deposited on the acid sites.

Table 2 shows the values of the carbon content on the deactivated and partially regenerated catalysts under different conditions (as obtained by TPO). It can be seen that the regeneration procedure at low temperature (450 °C) and short burning-off time (1 h) only partially removed coke while treatments at high temperature (500 °C) resulted in the almost complete removal of coke. The

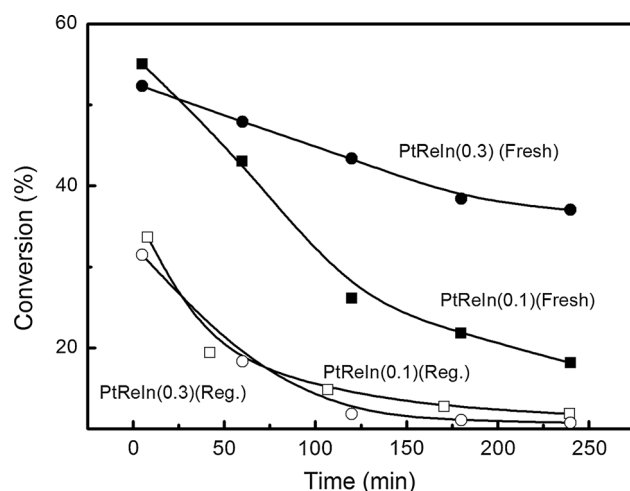


Fig. 3 Conversion of n -C₇ as a function of time for the fresh and totally regenerated PtReIn(0.1) and PtReIn(0.3) catalysts

regeneration of the PtReIn(0.3) catalyst was more effective due to its low content of coke.

Figure 2 shows the coke burning patterns of the PtReIn(0.1) and PtReIn(0.3) catalysts that were coked and regenerated at different temperatures: regenerated 1 h at 450 °C (a), regenerated 1 h at 500 °C (b) and regenerated 4 h at 500 °C (c). In a previous work, using bimetallic Pt–Re/Al₂O₃ catalysts, we reported that the burning of coke is produced by a selective mechanism at low combustion temperature where the coke deposited over the metal is first eliminated. Combustion at higher temperatures is not selective because both the coke deposited on the metal and the support are burned simultaneously [31, 46]. The only partial elimination of the coke deposited on the metal function shows that indium impedes the catalytic action of Pt for burning-off the coke on the metal.

The regenerated catalysts (500 °C, 4 h) and fresh catalysts were tested in the reforming of n -C₇. The reforming of n -heptane is a very useful test for evaluating catalysts because it involves a series of reactions requiring both catalytic functions, i.e. the acid and metal function. The principal reactions that occur during the reforming process are: isomerization, dehydrocyclization, hydrocracking, dehydrogenation, hydrogenolysis and coke deposition [47]. Figure 3 shows the values of n -C₇ conversion as a function of time. During the reaction of n -C₇ reforming, coke is deposited over the catalyst. At the reaction conditions used (atmospheric pressure), coking is important and in a short time a significant decrease of the catalytic activity takes place. It can be seen that all the catalysts suffer deactivation by coke formation. At the beginning of the reaction (5 min), the two fresh catalysts display practically the same activity. However, at the end of the test the catalyst with 0.3 % indium is the most active. The lower deactivation of

the PtReIn(0.3) catalyst correlates with its lower acidity and lower formation of dehydrogenated compounds (coke precursors). The dehydrogenated olefinic compounds undergo polymerization on acid sites. The cyclohexane dehydrogenation tests showed that the addition of a non active metal (In) decreases the activity of dehydrogenation of the Pt–Re catalyst (Table 1). Another factor affecting the deposition of coke is the nature of the acid function. The strong acid sites are responsible for polymerization reactions leading to the formation and accumulation of coke. Therefore, the lower coking rate in the case of the catalyst with high In content can be attributed to the lower rate of formation of coke precursors and the lower acidity of the coking sites.

The same deactivation pattern for coke deposition during the CP reaction is valid for justifying the higher stability of the catalyst with 0.3 % of indium, i.e., low formation of dehydrogenated coke precursors and low catalyst acidity. Moreover, the low initial conversion and the low stability of the regenerated catalysts are remarkable. This can be attributed to the fact that during the regeneration process, the chlorine of the support was removed and even though the metal function was regenerated, the acid function of the catalyst was adversely changed. As a consequence, the reactions catalyzed by the acid function such as isomerization and dehydrocyclization are inhibited.

Table 3 shows the selectivity values to i -C₇ isomers and aromatics obtained in the reforming reaction of n -C₇ at 5 and 240 min of time-on-stream of fresh and regenerated catalysts at 500 °C for 4 h. It can be noticed that neither the selectivity to aromatics nor the selectivity to C₇ isomers is recovered by the regeneration treatments used. The results of numerous studies show that isomerization and dehydrocyclization can be considered controlled by the acidic function of the catalysts [47]. It is accepted that the isomerization of n -paraffins proceeds via a bifunctional metal–acid mechanism [48]. The reaction starts on the metal site where paraffins are dehydrogenated to olefins. These olefins migrate to neighboring acid sites which

Table 3 Selectivity to aromatics and isomers of C₇ at 5 and 240 min time-on-stream. PtReIn(0.1)/Al₂O₃ and PtReIn(0.3)/Al₂O₃ catalysts, fresh and regenerated at 500 °C for 4 h

Catalyst	Selectivity to i -C ₇ (%)		Selectivity to aromatic (%)	
	5 min	240 min	5 min	240 min
PtReIn(0.1) fresh	6.2	2.2	69.9	46.1
PtReIn(0.1) regenerated	3.7	1.4	41.4	29.9
PtReIn(0.3) fresh	1.02	0.1	44.7	31.7
PtReIn(0.3) regenerated	0.61	0.03	26.8	9.25

transform them to isoolefins. Finally, this alkene is hydrogenated over the metal. The reaction is controlled by the slowest step on the acid function [49]. The aromatic hydrocarbons are produced by dehydrocyclization of paraffins which occur by a metal–acid bifunctional mechanism [47]. The paraffins are firstly dehydrogenated over the metal to provide the corresponding olefins that migrate to acid sites where they are protonated to secondary carbenium ions. These ions are converted to cycles on the acid function, producing cyclic olefins of 5 carbon atoms which are then isomerized on the acid sites, enlarging the ring to 6 carbon atoms. Reactions of de/hydrogenation on the metal function are fast enough to be considered in thermodynamic equilibrium while isomerization reactions are slow [47]. A conclusion to be drawn from the results of Table 3 is that the acid function of the regenerated catalyst is weaker than that of the fresh catalysts. For this reason, regenerated catalysts have a lower selectivity to aromatics and C₇ isomers.

In order to explain the higher metal activity and the poor activity in *n*-C₇ reforming of the regenerated catalysts, additional experiments were performed. The fresh catalysts were treated in flowing air at 550 or 650 °C for 4 h.

The analysis of the metal content is reported in Table 4. It can be seen that during the treatments there is no loss of the metal. Even after the treatments at high temperature the metal composition of the catalysts does not change significantly; consequently, the formation of volatile oxides can be ruled out.

Figure 4 shows the TPR patterns of the fresh and the treated at high temperature PtReIn(0.1) and PtReIn(0.3) catalysts. Previous reported results [42, 50] indicate that Pt displays a large reduction peak at 240–260 °C attributed to the reduction of most of the Pt oxides and a small reduction peak at 300 °C, corresponding to the reduction of oxychlorinated platinum species in strong interaction with alumina. Supported Re has a broad reduction peak centered at approximately 590 °C, with a small shoulder at low temperatures due to the reduction of species with a lower interaction with the support [24]. A reduction peak centered at ca. 360 °C was found in the case of the

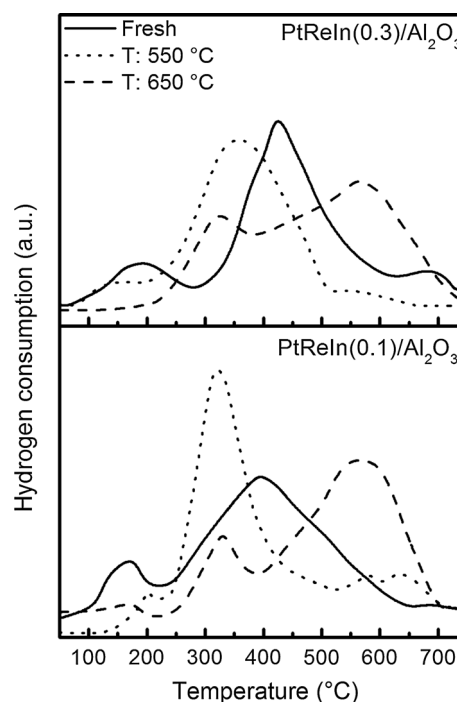


Fig. 4 TPR profiles of the fresh and thermally treated (550 and 650 °C for 4 h in air) PtReIn(0.1) and PtReIn(0.3) catalysts

monometallic (0.35 % In) catalyst while in the PtIn/Al₂O₃ catalyst, the Pt oxides are reduced at 150 °C due to a decreased Pt-support interaction induced by indium [22].

The TPR of fresh trimetallic catalysts were previously reported [22]. It was found that the addition of indium to Pt–Re increases the size of the peak centered about 390 °C. For this reason, this peak could be due to the reduction of In and Re species in close interaction with Pt while the reduction shoulder found at 590 °C corresponds to segregated Re species.

The PtReIn(0.1) catalyst treated at 550 °C shows a big peak centered at about 320 °C attributed to the simultaneous reduction of Pt and Re oxides, as well as a small fraction of oxides of In. There is a small reduction peak at 200 °C due to the reduction of Pt oxides segregated from Re and In. The third peak at temperatures higher than 550 °C is attributed to the reduction of segregated Re oxides. Comparing with the fresh catalyst, it is possible to conclude that the treatment at 550 °C produces a segregation of In because Pt and Re are reduced at a lower temperature (big reduction peak centered about 350 °C), i.e., the reduction start at a lower temperature since In does not impede the Pt oxides reduction. The catalyst treated at 650 °C has a big reduction peak at high temperature (570 °C) highlighting an important amount of Re segregates from Pt particles. The reduction peak (320 °C) attributed to a simultaneous reduction of Pt, Re and In is also decreased. A similar reduction pattern is found for the

Table 4 Metal content of the catalysts before and after high temperature treatment as determined by ICP-OES

Catalyst	Pt (wt%)	Re (wt%)	In (wt%)
PtReIn(0.1) fresh	0.22	0.28	0.086
PtReIn(0.1) sint. 550 °C	0.22	0.27	0.089
PtReIn(0.1) sint. 650 °C	0.22	0.21	0.087
PtReIn(0.3) fresh	0.22	0.29	0.29
PtReIn(0.3) sint. 550 °C	0.21	0.27	0.26
PtReIn(0.3) sint. 650 °C	0.21	0.29	0.28

Table 5 Dispersion, metal particle size and values of conversion (%) and TOF numbers during cyclopentane hydrogenolysis and cyclohexane dehydrogenation over the studied PtReIn catalysts

Catalyst	D (%)	dp (nm)	DH (%)	CH, TOF	HC (%)	CP, TOF	TPD area
PtRe fresh	62	nd	47.6	2.07	42.0	0.261	2.15
PtRe sintered at 550 °C	48	nd	37.6	2.11	36.2	0.225	nd
PtRe sintered at 650 °C	28	nd	22.6	2.18	20.5	0.128	nd
PtReIn(0.1) fresh	58	2.1	37.7	1.75	8.9	0.055	1.00
PtReIn(0.1) sintered at 550 °C	62	2.1	40.7	1.77	12.2	0.076	0.40
PtReIn(0.1) sintered at 650 °C	38	2.2	30.8	2.18	2.0	0.012	0.16
PtReIn(0.3) fresh	53	2.5	34.1	1.73	4.5	0.028	0.49
PtReIn(0.3) sintered at 550 °C	53	2.2	29.4	1.49	3.0	0.019	0.24
PtReIn(0.3) sintered at 650 °C	43	2.0	27.4	1.72	1.9	0.012	0.08

D metallic dispersion, dp particle size obtained from TEM, TPD area are referred to PtReIn(0.1) fresh catalyst, TOF molecules of CH or CP converted by Pt superficial atoms and by second, nd no data

PtReIn(0.3) catalyst, i.e., at low temperature treatment, there is a big reduction peak at 320 °C due to a simultaneous reduction of Pt, Re and In but with a lower amount of In due to the lower reduction temperature compared with the PtReIn(0.3) fresh catalyst. At high temperature treatment, the big reduction peak centered at 570 °C shows an important fraction of Re species segregated from Pt.

In sum, by TPR it can be deduced that a lower temperature treatment (550 °C) leads to the segregation of Re and In from Pt species. The peak due to a simultaneous reduction of the three metals is produced at a lower temperature. At high temperature treatment (650 °C), the peak attributed to the co-reduction of Pt, Re and In is decreased while the peak due to segregated Re (570 °C) is increased.

Table 5 shows the dispersion values obtained by CO chemisorptions, the mean particle size diameter obtained by TEM, the area of the pyridine TPD trace and the conversion and turnover frequency values of cyclopentane hydrogenolysis and cyclohexane dehydrogenation. The bimetallic PtRe catalyst suffers a stronger decrease of the metal dispersion and also the dehydrogenation and hydrogenolysis activity decreases with the temperature treatment. However, the TOF number of cyclohexane dehydrogenation is slightly increased while the TOF on cyclopentane hydrogenolysis is decreased. In the case of trimetallic catalysts, it can be seen that the particle size practically does not change with the thermal treatment. For the PtReIn(0.3) catalyst the size is even decreased. These results are very surprising because it is known that at high temperatures in an air atmosphere, Pt and Re are sintered forming larger crystal particles [51]. Thus, indium prevents the sintering of Pt and Re, this influence being stronger at higher contents. On the other hand, the dispersion decreases at high temperatures (650 °C) for both catalysts while at 550 °C there is an increase in the case of PtReIn(0.1) and no variation in the case of PtReIn(0.3). The conversion values of cyclohexane

dehydrogenation follow the dispersion trend but the turnover number of the PtReIn(0.1) catalyst increases with the temperature treatment while on the PtReIn(0.3) catalyst the TOF does not change between the fresh and the catalyst treated at 650 °C. Hydrogenolysis has a different behavior. Only the PtReIn(0.1) catalyst treated at 550 °C shows higher hydrogenolytic conversion and TOF than the corresponding fresh catalyst. The turnover frequency on cyclopentane hydrogenolysis of the PtReIn(0.3) catalyst shows a constant decrease with the increases of the temperature treatment.

In order to explain these results, it is necessary to take into account, as previously mentioned, that dehydrogenation is not a demanding reaction whereas hydrogenolysis requires ensembles of atoms of adequate size. In the case of the bimetallic PtRe catalyst, the treatment at 550 and 650 °C produces a sintering and a segregation of Re particles. For this reason, the TOF dehydrogenation reaction is increased due to lower electronic modification or blockage of Pt by Re. In the trimetallic catalysts, the treatment at a moderate temperature (550 °C) produces a segregation of the indium atoms from the metal active phase (Pt and Pt–Re). As a consequence, dehydrogenation and hydrogenolysis are recovered in the PtReIn(0.1) catalyst. In the case of the PtReIn(0.3) catalyst, the segregation of indium also occurs but the higher amount of In ensures that some remaining In stays in interaction with the active phase. The values of TOF on the cyclohexane dehydrogenation show that there is a segregation of In on the PtReIn(0.1) catalyst due to the increases of TOF with the temperature treatment. On the PtReIn(0.3) catalyst, the TOF on the cyclohexane reaction shows a little decrease at 550 °C and a recovery of the fresh catalyst at 650 °C. This phenomenon could be due to the high In content which not allowed liberate the active metal phase at 550 °C.

Hydrogenolysis is a demanding reaction [52]. It needs large ensembles of Pt metal atoms. Ensembles with both Pt

and Re have higher hydrogenolytic activity than ensembles of each metals independently [53] and the hydrogenolysis of CP can be used as an indirect measure of the Pt–Re interaction [53, 54]. This interaction was studied by Augustine and Sachtler [52, 54] using Pt, Re and Pt–Re catalysts supported on Al_2O_3 and SiO_2 . They measured the hydrogenolysis of CP and the isotope exchange and reported that PtRe is 40 times more active for methane formation by hydrogenolysis than the separate metals. According to these authors, the reason of this synergistic effect can be ascribed to the fact that the heat of adsorption on the metal surface is decisive in the formation of the substrate-metal complex that will undergo C–C bond breaking. An ensemble containing only Pt atoms would have a lower heat of adsorption than pure Re, while an intermediate value would be observed in the case of bimetallic particles containing Pt and Re. As a conclusion, on the PtRe catalyst the treatment at 550 and 650 °C produces a segregation of Re due to the lower TOF on cyclopentane hydrogenolysis, i.e., lower amounts of active Pt–Re ensembles. Moreover, the higher temperature treatment, the higher Re segregation from Pt. It is important to point out that the CP TOF of PtRe fresh catalyst is tenfold that of the PtReIn(0.3) fresh catalyst and five times that of the PtReIn(0.1) fresh catalyst, thus making evident the demanding character of cyclopentane hydrogenolysis. On PtReIn(0.1) catalysts, the treatment at 550 °C produces a segregation of In and Re but the segregation of In is more important (TOF is increased), thus producing a catalyst with high dehydrogenation and hydrogenolysis activity. The treatment at 650 °C produces more segregation of Re and In. As a consequence, the hydrogenolysis activity decreases and the dehydrogenation activity is increased (see TOF numbers). In the case of PtReIn(0.3), the same phenomenon occurs but the influence of In is higher (destroys Pt–Re ensembles) because of the higher In content. TOF on cyclopentane hydrogenolysis of the PtReIn(0.3) catalyst continuously decreases as the temperature treatment increases since the segregation of In of the active phase (Pt–Re) is accompanied by the destruction of Pt–Re ensembles by Re segregation.

The pyridine thermodesorption technique provides valuable information about the support acidity and acid strength distribution. The area under the desorption trace is proportional to the total acidity. Relative total acidity values, taking as reference the PtReIn(0.1) fresh catalyst, are shown in Table 5. The total acidity decreases upon thermal treatment, mainly at higher temperatures, probably by loss of chlorine. Centeno and coworkers [55] found desorption of chlorine during the TPR of Pt and Pd alumina supported catalysts evidencing the elimination of chlorine by heat treatment. The elimination of chlorine must be similar in the case of the regeneration of coked catalysts.

Thus, the recovery of the acid function is not achieved during regeneration and, as a consequence, regenerated catalysts have a poor catalytic performance for *n*-C₇ reforming.

4 Conclusions

Cyclohexane dehydrogenation and cyclopentane hydrogenolysis reaction tests show that the regeneration treatment with oxygen diluted in nitrogen can fully recover the activity of the metal function despite some observed segregation of Re and In. In the case of the reaction of *n*-heptane reforming, it was found that the regenerated catalysts have lower activity and stability than the fresh ones. The selectivity to C₇ isomers and aromatics of the regenerated catalysts was lower than that of the fresh catalysts. This behavior was attributed to chlorine losses during regeneration.

The experiments at high temperature in air showed that In prevents the sintering of Pt and Re but at high temperatures (650 °C), a segregation of Re from the Pt–Re phase occurs that decreases the hydrogenolytic activity.

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