Modification of Multimetallic Naphtha-Reforming Catalysts by Indium Addition

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Pt−Re−Ge/Al$_2$O$_3$ and Pt−Re−Sn/Al$_2$O$_3$ trimetallic naphtha-reforming catalysts were modified by the addition of indium. This additive negatively modified both the acid and metal functions of the catalysts. It produced a decrease in the activity in acid-catalyzed reactions such as the isomerization of *n*-pentane. Metal catalytic properties were inhibited, and the capacity for CO chemisorption also decreased.

Introduction

Catalytic reforming is one of the most important processes of the modern petroleum refining industry, either for the production of aromatic hydrocarbons (benzene, toluene, xylenes) or for the supply of high octane naphtha for the gasoline pool. Catalytic reforming catalysts are bifunctional. They have a metal function supplied by Pt particles deposited on the support. These particles are not fully adequate if used without modification and usually contain modifiers, commonly called "second metals" such as Re, Sn, Ir, and Ge. The catalysts also have an acidic function in charge of skeletal modifications of the reformed molecules. It is supplied by the support itself, usually chlorine-promoted γ-alumina. The first bifunctional reforming catalyst was Pt/γ-Al$_2$O$_3$, introduced in 1949 by UOP.[1] The first patent concerning Pt−Re/Al$_2$O$_3$ appeared in 1968,[2] and it was issued by UOP, a company that in the late 1960s started studies on catalytic reforming for producing high-octane gasoline and high purity hydrogen.[3] Later research revealed that these two objectives were best met with a low pressure process with continuous catalyst regeneration, for which standard Pt−Re catalysts were not adequate and hence new formulations were developed.[4−7] A continuous improvement of the naphtha-reforming process and catalyst is still underway today. Overall objectives are a greater efficiency of the process, a better use of the available feedstocks, and the processing of alternative raw materials. Regarding the process itself, the emphasis is put on getting higher liquid yields at lower hydrogen pressures with a smaller gas recycle. The current trend is to have catalysts that can withstand long operation cycles. This means that the net activity is sometimes disregarded in favor of a lower coking rate. Many patents propose the use of trimetallic catalysts to have catalysts with mild coking rates.[8−12]

A special issue is that of the isoparaffins/aromatics ratio. During reforming, not all normal alkanes are dehydrocyclized but some are only branched to form isoparaffins. Branched isoparaffins have a higher octane number than the original paraffins. Their octane number is, however, lower than that of the aromatics of equal carbon number. This disadvantage is considered to be compensated by the lower environmental impact of isoparaffins. Bearing this in mind, both the catalyst formulation and the process operation parameters can be fine-tuned to adjust the isoparaffins/aromatics ratio, as found in the patent literature.[8,9]

The activity, selectivity, and stability of naphtha-reforming catalysts depend on the kind of metals in the metal function, their oxidation state, their mutual interaction, and their dispersion over the support. These properties are strongly linked to the method of preparation and the conditions of activation of the catalysts.

Some patents have lately proposed new improved formulations of naphtha-reforming catalysts containing indium as a promoter. Wilhelm[13] pointed out that In addition markedly improves the activity, selectivity, and stability, increases the C$_5^+$ and hydrogen yields, and allows operation of the reformer at less severe conditions. Antos[14−17] proposed the use of catalysts containing In for getting reformate streams high in aromatics. Both authors reported that In improved the stability by decreasing the coking rate. In their patents, Bogdan[11,18] and Imai[9,19] reported that In addition improved the aromatization/cracking ratio and therefore the liquid yield. Recently, Le Peltier et al.[20] proposed the use of different catalysts, each of them containing Pt and other promoters (Re, In, Sn, W).

Despite the evidence disclosed in patents, there are only a few reports on the effect of In on naphtha-reforming catalysts in the open scientific literature. This work studies the influence of In addition on the catalytic properties of naphtha-reforming Pt−Re−Ge/Al$_2$O$_3$ and Pt−Re−Sn/Al$_2$O$_3$ catalysts.

Experimental Section

Catalyst Preparation. The support used was a commercial high-purity γ-alumina (Cyanamid Ketjen CK 300). Main impurities were Na (5 ppm), Fe (150 ppm), and S (50 ppm). The extruded alumina pellets were ground and sieved, and the 35−80 mesh fraction was separated and calcined in air (3 h at 650 °C). The specific surface area of this support was 180 m^2 g^{-1}, the pore volume was 0.49 cm^3 g^{-1}, and the average pore radius was 5.4 nm. These properties were not affected by the addition of the metal salts of Pt, Re, Ge, Sn, or In.

Monometallic Catalysts. Five-gram Al$_2$O$_3$ samples were immersed in a 0.2 N HCl solution (1.5 mL g^{-1}), and then solution containing the metal salt was added. After the solution was stirred for 1 h, the solution was made to evaporate by heating at 70 °C while being stirred gently. The catalyst was then dried at 120 °C overnight, calcined in an air flow (60 mL min^{-1}) for 4 h at 450 °C, and reduced in hydrogen (4 h, 500 °C).

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Trimetallic Catalysts. These were prepared by the coimpregnation method. In all cases, the impregnation volume was adjusted to yield the appropriate final concentration of each metal in the catalysts. The salts used were $H_2PtCl_6 \cdot 6H_2O$ (3.345 mg of Pt mL^{-1}), $SnCl_2 \cdot 2H_2O$ (25 mg of Sn mL^{-1}), $GeCl_4$ (3.11 mg of Ge mL^{-1}), and NH_4ReO_4 (20.18 mg of Re mL^{-1}). The solution of the Sn precursor was unstable and was prepared just before its use. $SnCl_2$ was first dissolved in deionized water and heated for 30 min at 70 °C. Then, aliquots of 37% HCl were added until the solution became transparent and was ready to be used. A HCl 0.2 M solution was added to the support (1.5 cm^3 g^{-1}) before impregnating the metal salts to add chloride as a competing ion and to ensure their homogeneous distribution. The solution containing the catalyst was first left unstirred for 1 h and then was gently heated at 70 °C to evaporate the excess liquid. The catalysts were finally dried at 120 °C overnight, calcined in air (4 h, 450 °C) and reduced in hydrogen (4 h, 500 °C). The impregnation volume was adjusted to obtain 0.3 wt % of each metal in the final catalyst (0.3% Pt−0.3% Re−0.3% Ge and 0.3% Pt−0.3% Re−0.3% Sn).

Tetrametallic Catalysts. Pt−Re−Ge/Al$_2$O$_3$ and Pt−Re−Sn/Al$_2$O$_3$ were impregnated with a solution of InNO$_3$. The impregnation volume was adjusted to get 0.1, 0.3, and 0.6% In on the final catalyst. After impregnation, the trimetallic catalysts were calcined at 450 °C in air for 4 h.

Catalyst Characterization. CO Chemisorption. The experiments were performed in a chemisorption equipment designed ad-hoc. First, the catalyst was placed in a quartz reactor and reduced in H$_2$ (500 °C, 2 h, 60 cm^3 min^{-1}). Then the carrier was switched to N$_2$, and the adsorbed hydrogen was desorbed (500 °C, 60 cm^3 min^{-1}) during 1 h. Then the cell was cooled to room temperature. Pulses (0.25 cm^3) of diluted CO (3.5% CO in N$_2$) were then succesively fed to the reactor. Non-chemisorbed CO was quantitatively transformed into CH$_4$ over a Ni/Kieselgur catalyst and detected in a flame ionization detector connected online.

Temperature-Programmed Desorption of Pyridine and Trimethylpyridine. The amount and strength of the acid sites of the catalysts were assessed by means of temperature-programmed desorption of pyridine (Py). In this way, both Brønsted and Lewis acid sites were probed. To distinguish between them, additional tests of thermodesorption of 2−4−6 trimethylpyridine (TMPy) were performed. This molecular probe was adsorbed selectively on Brønsted sites because of steric hindrance. Both reagents were supplied by Merck (99.9%). The procedure was the same for Py and TMPy. Two hundred milligrams of the catalyst to be tested was first immersed in a closed vial containing the base for 4 h. Then the vial was open, and the 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 of nitrogen (40 mL min^{-1}) was made to flow over the sample all throughout the experiment. A first step of desorption of weakly adsorbed base 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 millivolts) was sampled at 1 Hz and recorded in a computer device.

The total amount of adsorbed pyridine and trimethylpyridine 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.

Temperature-Programmed Reduction. These tests were performed in an Ohkura TP2002 equipment with a thermal conductivity detector. At the beginning of each temperature-programmed reduction (TPR) test, the catalyst samples were pretreated in situ by heating in air at 250 °C for 1 h. Then they were heated from room temperature to 700 °C at 10 °C min^{-1} in a gas stream of 5.0% hydrogen in argon.

Cyclohexane Dehydrogenation. The reaction was performed in a glass reactor with the following conditions: catalyst mass = 50 mg, temperature = 350 °C, H$_2$ = 36 cm^3 min^{-1}, cyclohexane = 0.727 cm^3 h^{-1}. Before the reaction started, the catalysts were treated in H$_2$ (36 cm^3 h^{-1}, 500 °C, 1 h).

Cyclopentane Hydrogenolysis. Before the reaction, the catalysts were reduced for 1 h at 500 °C in H$_2$ (60 cm^3 min^{-1}). Then they were cooled in H$_2$ to the reaction temperature (350 °C). The other conditions were catalyst mass = 150 mg, pressure = 0.1 MPa, H$_2$ flow rate = 40 cm^3 min^{-1}, cyclopentane flow rate = 0.483 cm^3 h^{-1}. The reaction products were analyzed in a gas chromatograph connected online.

n-Pentane Isomerization. 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 H$_2$/n-C$_5$ = 6. n-C$_5$ was supplied by Merck (99.9%). At these reaction conditions, there were no internal or external mass transfer limitations in the catalyst particles, as confirmed by the calculus of the Weisz−Prater modulus ($\Phi \ll 0.01$) and the Damköhler number ($Da \approx 0$), respectively. For the calculus, 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. 1/8 in., 3-m length) maintained at 40 °C was used for the chromatographic separation of the products. The conversion of n-C$_5$ was defined as:

$$n\text{-}C_5 \text{ conv} = \frac{n\text{-}C_5^i - n\text{-}C_5^0}{n\text{-}C_5^i} \qquad (1)$$

n-C$_5^i$ is the number of n-C$_5$ molecules at the reactor inlet, and n-C$_5^0$ is the number at the reactor outlet. The selectivity to each product i was defined as:

$$S_i = \frac{\text{yield of } i}{n\text{-}C_5 \text{ conv}} = \frac{A_i f_i n_i}{M_i \left(\Sigma \frac{A_i f_i n_i}{M_i} \right) \cdot n\text{-}C_5 \text{ conv}} 100 \qquad (2)$$

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.

n-Heptane Reforming. The reactions were performed in a fixed bed tubular reactor with the following reaction conditions: 0.1 MPa, 500 °C, H$_2$/n-C$_7$ = 6, and WHSV = 4 h^{-1}. The catalysts were first reduced in H$_2$ (12 cm^3 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.

Temperature-Programmed Oxidation. The carbon deposits on the surface of the catalysts were studied by means of temperature-programmed oxidation (TPO). The coked catalyst (40−60 mg) was first charged to a quartz reactor. Then the carbon was burned in an oxidizing stream (60 cm^3 min^{-1} of diluted oxygen, 5% O$_2$ in N$_2$ vol/vol). The temperature of the cell was increased from 30 to 650 °C with a heating rate of 10 °C min^{-1}. The outlet gases were fed to a methanation reactor
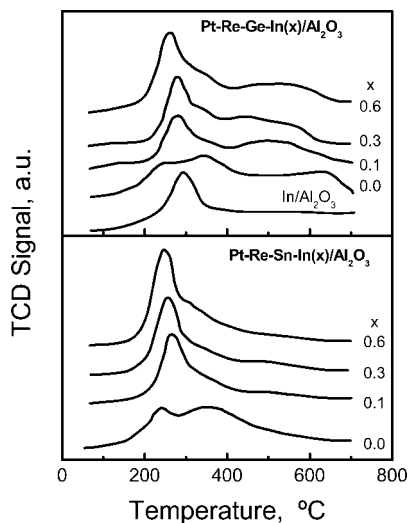
Figure 1. TPR results. Monometallic 0.3% In/Al_2O_3, $Pt-Re-Ge/Al_2O_3$, and $Pt-Re-Sn/Al_2O_3$ catalysts with different In contents.

Figure 2. Pyridine TPD traces. Monometallic 0.3% In/Al_2O_3, $Pt-Re-Ge-In/Al_2O_3$ and $Pt-Re-Sn-In/Al_2O_3$ catalysts.

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 flame ionization detector, 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 with known carbon content.

Results and Discussion

Figure 1 shows the TPR traces of the In/Al_2O_3, $Pt-Re-Ge-In(x)/Al_2O_3$, and $Pt-Re-Sn-In(x)/Al_2O_3$ catalysts. Previous reports[21,22] indicated that Pt has a great reduction peak at 240−260 °C and a smaller one at 300 °C corresponding to the reduction of oxychlorinated species that are in strong interaction with alumina. Supported Re has a wider reduction temperature range centered around 590 °C, with a small shoulder at low temperatures due to the interaction of oxychlorinated species with the support. The pattern of Ge reduction is similar to that of Re. It has a peak of reduction that reaches temperatures as high as 600 °C. Figure 1 shows that the $Pt-Re-Ge$ trimetallic catalysts have reduction peaks at 600, 360, and 240 °C. The low temperature peak corresponds to the reduction of Pt, and the peak at 360 °C can be attributed to the reduction of Re and Ge oxides in interaction with Pt.[23] Pt catalyzes the reduction of the Ge and Re oxides.[24] Finally, the peak at 600 °C can be attributed to segregated Ge and Re. Monometallic indium has a wide reduction peak with a maximun at 295 °C (Figure 1). It can be attributed to the reduction of species with different dispersions. The different reduction patterns reported for supported In oxides are generally attributed to the different reducibility of particles of different size. Smaller particles are reduced at lower temperatures.[25,26] When In is added to the trimetallic $Pt-Re-Ge$ catalysts, the TPR trace shows a new peak at about 300 °C that could be due to alloyed $Pt-In$. The shoulder at 340 °C could be due to Ge and Re oxychlorinated species in interaction with Pt. The broad peak at about 550 °C would correspond to segregated Re and Ge species. It can be seen that as the amount of In is increased the peak at 300 °C and the shoulder at 340 °C are also increased.

The Sn/Al_2O_3 TPR trace has been previously reported[27] and is therefore not included. The reduction trace of the monometallic Sn oxide is broad, beginning at 150 °C and ending at 550
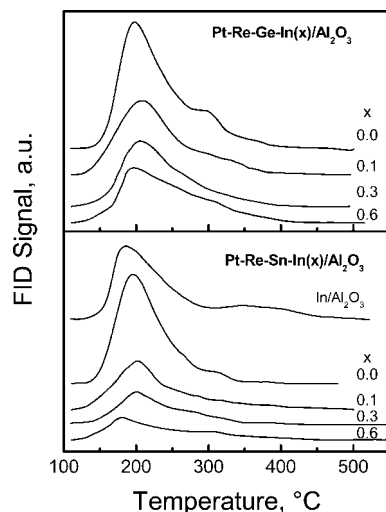
°C, with two reduction zones at 200−300 and 380−520 °C. This is an indication of an interaction between Sn oxide and alumina, probably producing Sn aluminates. According to the literature,[28] Sn(IV) is reduced to Sn(II) that cannot be reduced to Sn(0) because of the great interaction with the support. It can also be seen in Figure 1 that $Pt-Re-Sn$ catalysts have a peak at about 250 °C that is due to the reduction of Pt oxide and a little fraction of Sn and Re oxides in interaction with Pt. A second peak between 300 and 600 °C can be deconvoluted into two smaller ones at 300−450 °C, attributed to the reduction of Re and Sn oxides, and at 450−600 °C attributed to the reduction of segregated Re oxides and small amounts of Sn oxide. In the In-doped catalysts, a peak at 300 °C may correspond to the interaction of $Pt-In$ species. The shoulder at 350 °C and the broad peak between 450 and 600 °C can be attributed to segregated Re and Sn species. Again, it can be seen that as the In amount is increased the reduction peak at 300 °C also increases. For both the $Pt-Re-Ge$ and $Pt-Re-Sn$ catalysts, the reduction trace is modified by the addition of In. This indicates that In interacts with the metal phase.

The CO adsorption results confirm that In is in strong interaction with Pt as revealed by the TPR experiments. In addition markedly decreases the CO adsorption capacity of the metal function. PtReGe and PtReSn catalysts containing as low as 0.1% In do not exhibit measurable CO adsorption values.

The amount of pyridine desorbed as a function of the heating temperature gives information on the total amount of acid sites and their strength distribution.[29−31] This information is disclosed in Figure 2. It can be seen that there exists a decrease of the total acidity when In is added in the case of both the $Pt-Re-Ge$ and the $Pt-Re-Sn$ catalysts. These results are in agreement with literature reports[25] that indicate that, although In is amphoteric, it can be considered slightly basic. Therefore, when In is deposited over the catalysts the acid sites are blocked and the total acidity is decreased. From the TPD data, it can be seen that In addition eliminates almost all the strong acid sites (sites desorbing pyridine in the 300−400 °C range) in both catalyst series (Figure 2).

As detailed in Table 1, the addition of small amounts of In (0.1%) greatly affects the total acidity of $Pt-Re-Ge$ and $Pt-Re-Sn$ catalysts. The total acidity is decreased by 35 and 50%, respectively. At higher In amounts (0.6%), the percentage of decrease of the acidity is lower. This could be because In tends to crystallize at high surface concentrations. Table 1 also

Table 1. Total Acidity (Brønsted + Lewis) and Brønsted Acidity As Determined by Temperature-Programmed Desorption of Pyridine (Py) and 2,4,6-Trimethylpyridine (TMPy)

catalyst	total acidity, μmol Py g^{-1}	Brønsted acidity, μmol TMPy g^{-1}
In(0.3)	280	142
Pt−Re−Ge−In(0.0)	450	220
Pt−Re−Ge−In(0.1)	302	161
Pt−Re−Ge−In(0.3)	252	145
Pt−Re−Ge−In(0.6)	243	127
Pt−Re−Sn−In(0.0)	330	152
Pt−Re−Sn−In(0.1)	165	100
Pt−Re−Sn−In(0.3)	106	90
Pt−Re−Sn−In(0.6)	89	74

contains the results of the TPD experiments with TMPy. These results indicate that Brønsted sites are also depleted when In is added to the Pt−Re−Ge or the Pt−Re−Sn catalysts but they are less affected than the Lewis sites. One column of Table 1 also contains the values of the area of the pyridine TPD trace of the In(0.3)/Al$_2$O$_3$ catalyst reference. If a comparison is made, it can be seen that the total acidity of the monometallic is 40% of the acidity of the trimetallic PtReGe/Al$_2$O$_3$ catalyst without In.

The properties of the metal function were evaluated by means of the test reactions of hydrogenolysis of cyclopentane (HCP) and dehydrogenation of cyclohexane (DCH). The results of HCP are plotted in Figure 3. The hydrogenolytic activity is greatly decreased by a small In addition (0.1%). This passivating effect on the Pt activity can be explained by considering that the hydrogenolysis mechanism starts with the adsorption of two adjacent carbon atoms over neighboring metal sites, first producing the rupture of the C−H bonds. The carbons continue to dehydrogenate and the C−C bond becomes weaker while the C−metal bond is strengthened. The amount and strength of adjacent C−metal bonds establish the rate of the reaction. For the onset of the reaction surface, metal atom pairs or greater surface metal atom ensembles are needed (i.e., a determined size of Pt particles is needed). In the case of the trimetallic catalysts, the ensembles have already been reduced in their effective size in comparison to monometallic supported Pt catalysts, because of the dilution effect of Ge and/or Sn.[32] This effect is enhanced by In addition. Catalysts with higher In contents do not have a meaningful cyclopentane hydrogenolysis activity level.
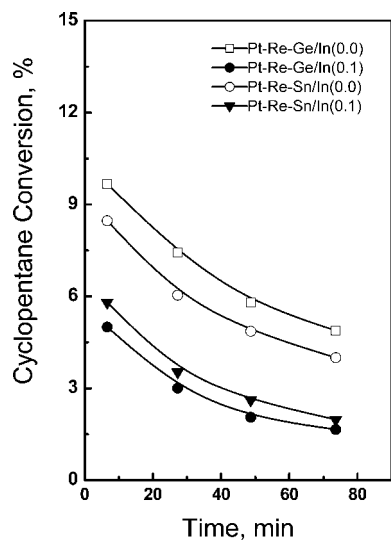
Figure 3. Results of hydrogenolysis of cyclopentane. Conversion as a function of time-on-stream. Pt−Re−Ge−In and Pt−Re−Sn−In catalysts.
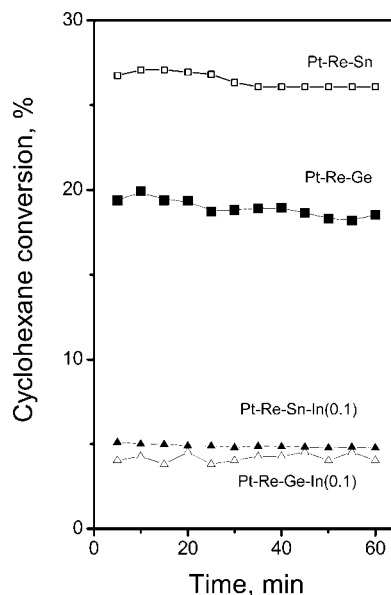
Figure 4. Results of cyclohexane dehydrogenation. Conversion as a function of time-on-stream. Pt−Re−Ge−In and Pt−Re−Sn−In catalysts.

Table 2. n-Pentane Reaction Test[a]

catalyst	X%	S_{i-C5}, %	S_{C3}, %	coke, %
Pt−Re−Ge−In(0.0)	39.8	78.9	7.8	0.55
Pt−Re−Ge−In(0.1)	29.7	82.7	6.1	0.35
Pt−Re−Ge−In(0.3)	10.7	58.9	5.4	0.30
Pt−Re−Ge−In(0.6)	9.9	15.9	3.4	0.27
Pt−Re−Sn−In(0.0)	38.1	40.7	5.9	0.43
Pt−Re−Sn−In(0.1)	35.7	82.7	5.5	0.32
Pt−Re−Sn−In(0.3)	20.9	59.3	4.7	0.20
Pt−Re−Sn−In(0.6)	12.9	56.3	3.6	0.19

[a] Conversion values, selectivity to branched isoparaffins, and catalyst coke content. 240 min time-on-stream.

Figure 4 shows the results of the cyclohexane dehydrogenation test. The metal activity is very much affected by the addition of In to the trimetallic catalysts. Mazzieri et al.[32] showed that Pt/Al$_2$O$_3$ is the most active catalyst in the DCH test. Addition of Re, Ge, or Sn decreases the activity mainly because of a blocking effect. These atoms are deposited on top of Pt particles and preclude the adsorption and formation of adsorbate−metal bonds (geometric effect). Another explanation invoked is usually the modification of the electronic properties of the Pt atoms (electronic effect). When a fourth metal is added, the effect on the electronic density of Pt is higher than in the case of the trimetallic catalyst. As in the case of hydrogenolysis, the catalytic activity is negligible at high In contents.

Table 2 contains conversion values of the n-C$_5$ reaction test and selectivity values to branched C$_5$ isomers and propane. It is accepted that the isomerization of n-paraffins occurs by a bifunctional metal−acid mechanism.[33] The reaction begins on the metal sites with the dehydrogenation of the paraffin to an olefin. Then the linear olefin is converted to a branched one over the acid site. This branched alkene is finally hydrogenated over a metal site. This bifunctional mechanism is controlled by the acid-catalyzed step;[33] therefore, the yield of isopentane can be taken as an indirect measure of the activity of the acid function. The results in Table 2 indicate that for both Pt−Re−Ge and Pt−Re−Sn catalysts the addition of In produces a decrease of conversion. The conversion decrease upon In addition correlates with the parallel decrease of acidity. For both catalyst series, In addition decreases the C$_3$ yield. This is a product produced by a bifunctional mechanism controlled by the acid

Table 3. *n*-Heptane Reaction Test[a]

catalyst	conversion, %	selectivity, %				coke, %
		C_1	C_1–C_4	toluene	i-C_7	
Pt−Re−Ge−In(0.0)	22.8	0.77	2.8	5.3	24.1	0.62
Pt−Re−Ge−In (0.1)	16.9	0.76	1.5	45.1	15.3	0.41
Pt−Re−Ge−In(0.3)	10.2	0.57	0.3	51.1	11.1	0.37
Pt−Re−Ge−In(0.6)	2.6	0.45	0.2	61.6	8.5	0.31
Pt−Re−Sn−In(0.0)	38.7	0.69	1.7	16.2	19.9	0.54
Pt−Re−Sn−In(0.1)	31.7	0.41	1.1	44.4	14.2	0.40
Pt−Re−Sn−In(0.3)	15.2	0.38	0.9	49.8	10.1	0.36
Pt−Re−Sn−In(0.6)	10.4	0.25	0.2	59.3	8.3	0.30

[a] Conversion, selectivity to toluene, methane, and gases, and catalyst coke content. 240 min time-on-stream.

sites.[33] Remarkably, the catalysts with 0.1% In have more selectivity to i-C_5 than the catalyst without In. This effect can be explained by a decrease in the amount of strong acid sites. On the weaker acid sites, the olefins would become isomerized rather than cracked.

Table 2 also shows the amount of carbon on the catalysts at the end of the *n*-pentane reaction. The amount of carbon decreases as the load of In is increased. This confirms that In addition reduces both the dehydrogenating and polymerizing activity. The metal function is responsible for the formation and accumulation of coke because it produces great amounts of dehydrogenated compounds that are coke precursors, which polymerize over the acid sites. The tetrametallic metal function would be resistant to coking because the reactions leading to carbon deposition on the metal are structure-sensitive and need a minimum size of Pt ensembles to proceed with a high rate.[34−37]

Table 3 contains results of conversion and selectivity to toluene and gases as obtained in the *n*-C_7 reforming reaction at 240 min time-on-stream. Coke contents at the end of the runs, as determined by TPO, are also included in this table. As the In content is increased, the *n*-C_7 conversion is decreased. This is related to the loss of acid sites by neutralization with basic In species and to the decrease of the metal activity by In addition. On the other hand, the selectivity to toluene increases upon In addition while the selectivity to light gases (C_1–C_4) and the selectivity to i-C_7 isomers decreases. This is because toluene production depends on the dehydrocyclization activity. This reaction proceeds by a bifunctional mechanism in which the metal produces unsaturated intermediates while the acid sites catalyze the isomerization and ring closure steps. The controlling steps are the acid-catalyzed ones.[38] The unsaturated intermediates can be cracked on the acid sites producing C_1–C_4 light gases. When In is added, toluene dealkylation producing methane is inhibited. The acid cracking of the olefinic intermediates is also decreased (Table 3). Both effects contribute to increase the toluene yield. Isomerization reactions are also inhibited. This result is unexpected because isomerization reactions are bifunctional and the global reaction rate is controlled by the acid function.

Finally, Table 3 indicates that the hydrogenolytic activity decreases with In addition in agreement with the results of cyclopentane hydrogenolysis. Again, the carbon deposits at the end of the experiment decrease at higher In contents.

Conclusions

The addition of indium to Pt−Re−Ge and Pt−Re−Sn naphtha-reforming catalysts has effects on both the acid and metal functions.

The TPR results reveal the formation of Pt−In alloys and other species in interaction such as Re−In, Ge−In, and Sn−In.

With the reaction conditions employed in this work, trimetallic Pt−Re−Ge/Al_2O_3 and Pt−Re−Sn/Al_2O_3 catalysts promoted with In do not chemisorb CO.

The hydrogenation and hydrogenolysis activities decreased upon In addition. The total acidity also decreased. As a result, the activities in the reactions of *n*-pentane and *n*-heptane decreased while the selectivities to i-C_5 and toluene increased.

Acknowledgment

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