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Catalytic Properties of Pt–Re/Al₂O₃ Naphtha-Reforming Catalysts Modified by Germanium Introduced by Redox Reaction at Different pH Values

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Ge was deposited by catalytic reduction on Pt–Re/Al₂O₃–Cl base catalysts prepared by coimpregnation. The nominal amounts of Ge incorporated from various impregnation media (H₂O, HCl, or NH₃) were 0.1, 0.3, 1.0, and 2.0 wt %. The catalysts were characterized by means of the test reactions of cyclohexane dehydrogenation and cyclopentane hydrogenolysis. The catalysts were further characterized by FTIR spectroscopy of adsorbed CO and adsorbed pyridine and by temperature-programmed desorption of pyridine. Blank treatments performed on the Pt–Re/Al₂O₃ base catalyst in the different media (without Ge addition) showed that the catalytic reduction method modified the properties of the parent catalyst depending on the pH of the solution. The Brønsted acidity decreased as the impregnation pH was increased, whereas the Lewis acidity of the catalyst was not substantially modified by any of the impregnation media. Catalysts with higher Pt–Re interactions were obtained after treatment in a solution of high pH (NH₃ medium). The interaction between Ge and the active metal phase increased with increasing Ge content. This interaction resulted in a decrease of the metal activity in cyclohexane dehydrogenation and cyclopentane hydrogenolysis. Catalyst performances were evaluated in *n*-heptane (*n*-C₇) reforming under pressure. The *n*-C₇ tests showed that trimetallic catalysts obtained by impregnation of small quantities of Ge (≤0.3 wt %) using a neutral aqueous solution are the most active and toluene-selective, especially compared to those prepared using HCl or NH₃ solution. Nevertheless, the use of ammonia in the impregnation medium allows one to decrease the amount of cracking products. Thus, the catalytic properties might be improved by using a slightly basic medium for the impregnation of Ge.

Introduction

In a catalytic reformer, reactions take place on acid and metal sites. Catalysts providing such functions are called bifunctional catalysts.^{1,2} The metal component has activity for hydrogenation and dehydrogenation reactions, whereas the support provides the activity for acid-catalyzed reactions, such as isomerization. The combined and synergic actions of the two types of active sites promote other reactions, such as dehydrocyclization. Undesirable reactions also take place. These reactions (hydrocracking and hydrogenolysis) decrease the yield of the process and deactivate the catalyst through coke formation on the active sites.³ The acid function is typically provided by chlorinated alumina (Al₂O₃–Cl). The metal function is typically supplied by supported Pt. Pt is rarely used in the pure state but is more often used in modern catalysts in an atomic-level mixture with other so-called “promoters”. Rhenium was the first promoter to be widely used in the manufacture of bimetallic catalysts. The first patents on Pt–Re catalysts were filed in the late 1960s and early 1970s.⁴ Bimetallic catalysts are more selective and stable than pure Pt and enable the reformer to be operated under less severe conditions (lower pressure, lower hydrogen-to-hydrocarbon ratio).

The deposition and progressive accumulation of coke is one of the main reasons for the deactivation of naphtha-reforming catalysts.^{3,5–7} New formulations of trimetallic catalysts have been tried to solve these problems. These materials exhibit lower

rates of deactivation by coke than their bimetallic counterparts.^{8,9} Many patents state the advantages of trimetallic catalysts;^{10–16} some also state that the catalyst performance in the catalytic reformer is improved by running the process continuously.^{10,11,15}

The dispersion and degree of interaction between the components of the metal function have a great influence on the coking rate of naphtha-reforming catalysts. For this reason, many preparation methods have been tried. Among these methods, the so-called catalytic reduction method has been developed and successfully used for the synthesis of Pt–Re,^{17,18} Pt–Sn,¹⁹ and Pt–Ir–Sn catalysts.¹⁹ In the catalytic reduction method cationic species of the promoter (Ge in the present case) are put into solution and reduced in situ over Pt metal sites by means of surface hydrogen chemisorbed over Pt atoms. Details of the preparation procedure can be found elsewhere.^{17,20}

In a recent work, we initiated a study on the influence of the pH of the Ge impregnation medium.²¹ In this report, we continue with the study of Pt–Re–Ge/Al₂O₃–Cl naphtha-reforming catalysts impregnated in different media (alkaline, acidic, neutral) by the catalytic reduction method. The catalysts were characterized by additional test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), and quasi-industrial conditions were used in an additional test of *n*-heptane reforming (pressure = 0.5 MPa, temperature = 500 °C, weight hourly space velocity = 2 h^{–1}).

Experimental Section

Preparation of Base Catalyst Pt–Re/γ-Al₂O₃, γ-Al₂O₃ (Cyanamid Ketjen CK-300, pore volume = 0.5 cm³ g^{–1}, specific surface area = 180 m² g^{–1}) was used as the support and was

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calcined at 500 °C for 4 h in air to eliminate organic impurities. HCl (0.2 M) was added ($1.5 \text{ cm}^3 \text{ g}^{-1}$), and the slurry was allowed to rest for 1 h. Then, H_2PtCl_6 and NH_4ReO_4 were added, and the slurry was gently stirred for 1 h at room temperature. It was slowly dried at 70 °C until a dry powder was obtained, which was further dried overnight at 120 °C. Finally, the powder was calcined in air ($60 \text{ cm}^3 \text{ min}^{-1}$, 300 °C) and reduced with H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$, 500 °C). The final contents of Pt and Re on the catalyst were 0.3 and 0.3 wt %, respectively. This catalyst is denoted as the base catalyst or the Pt–Re base catalyst.

Preparation of Trimetallic Catalysts. The reactor for catalyst preparation had a means for degassing the impregnating solution in order to eliminate dissolved oxygen. For the preparation of the trimetallic catalysts, the Pt–Re base catalyst was first prerduced with H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$) for 1 h at 300 °C; then it was cooled to room temperature under hydrogen. A solution of GeCl_4 was then added in amounts sufficient to obtain Ge theoretical mass percentages of 0.1, 0.3, 1.0, and 2.0 wt %. This Ge solution was further diluted by adding suitable solutions and to a final volume of 25 cm^3 . These solutions were chosen to produce different pH values in the impregnation medium: (i) pure water, (ii) aqueous NH_4OH , and (iii) aqueous HCl (0.2 M). After the degassing step, the solution was left in contact with the catalyst for 1 h, and hydrogen was bubbled at a rate of $300 \text{ cm}^3 \text{ min}^{-1}$. Then, the solution was removed, and the catalyst was rinsed with distilled water. The catalyst was then dried in a hydrogen stream ($60 \text{ cm}^3 \text{ min}^{-1}$, 100 °C) for 12 h. Finally, it was reduced in a hydrogen stream ($60 \text{ cm}^3 \text{ min}^{-1}$) at 500 °C. These prepared catalysts are denoted as Pt–Re–Ge(x , y) (x = Ge content, y = impregnating medium). The Ge content represents the weight percentage of Ge actually deposited. x = 0.0 corresponds to the blank experiment, i.e., the preparation procedure performed in the absence of GeCl_4 .

Measurement of Pt, Re, Ge, and Cl Contents. The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after digestion in an acid solution and dilution (experiments performed by the CNRS at the Service Central d'Analyse, Vernaison, France). The chlorine contents of the catalysts in their final state, i.e., after activation, were determined by means of potentiometry.

Fourier Transform Infrared (FTIR) Absorption Spectroscopy of Chemisorbed CO. The Fourier transform infrared spectra of adsorbed CO were obtained to study the effect of Ge deposition on the Pt–Re metallic phase. FTIR spectra of chemisorbed CO for the prepared catalysts were recorded within the wavenumber range of $4000\text{--}1000 \text{ cm}^{-1}$. A Shimadzu Prestige-21 spectrometer with a spectral resolution of 4 cm^{-1} was used, and spectra were recorded at room temperature. Self-supported wafers with a diameter of 16 mm and a weight of 20–25 mg were used. The experimental procedure was as follows: Catalyst samples were reduced under hydrogen flow at 400 °C (reached at a $10 \text{ }^\circ\text{C min}^{-1}$ heating rate) for 30 min. Samples were then degassed at $2.7 \times 10^{-3} \text{ Pa}$ and 400 °C for 30 min. After an initial (I) spectrum had been recorded, the samples were exposed to a $4 \times 10^3 \text{ Pa}$ CO atmosphere for 5 min, and then a second (II) FTIR spectrum was recorded. The chemisorbed CO absorbance for each sample was obtained by subtracting spectrum I from spectrum II.

Temperature-Programmed Desorption (TPD) of Pyridine. This test was used for measuring the amount and strength of the acid sites. Samples of 200 mg were impregnated with an excess of pyridine. Once the excess had been removed, physisorbed pyridine was eliminated by heating the sample in

a nitrogen stream at 110 °C for 1 h. Then, the temperature was raised at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to a final value of 450 °C. To measure the amount of desorbed pyridine, the reactor exhaust was connected to a flame ionization detector.

Fourier Transform Infrared (FTIR) Spectroscopy of Adsorbed Pyridine. Fourier transform infrared spectroscopy of adsorbed pyridine was used to determine the number of Lewis acid sites on the catalysts. Self-supported wafers with a diameter of 16 mm and a weight of 20–25 mg were used. Each wafer was pretreated in H_2 at 500 °C (heating ramp of $2 \text{ }^\circ\text{C min}^{-1}$) for 12 h and then in a vacuum at 400 °C for 1 h in a quartz cell with KBr windows. The cell containing the wafer was then cooled to 150 °C, and pyridine was injected into the system (250 Pa, 10 s). The nonadsorbed excess was eliminated by application of a vacuum ($2 \times 10^{-3} \text{ Pa}$, 60 s). The IR absorption spectrum was measured in a Nicolet 750 Magna IRTM instrument with Fourier transform (2 cm^{-1} resolution). The total amount of Lewis acid sites was calculated with the expression

$$Q (\mu\text{mol g}^{-1}) = \frac{1000AS}{\epsilon m} \quad (1)$$

where A is the integrated area of the infrared bands at 1451 and 1455 cm^{-1} , in absorbance units (cm^{-1}); ϵ is the molar extinction coefficient ($1.28 \text{ cm } \mu\text{mol}^{-1}$ for the pyridine Lewis band²²); S is the surface area of the wafer (cm^2), and m is the wafer mass (mg).

Cyclohexane (CH) Dehydrogenation. The cyclohexane (CH) dehydrogenation reaction was performed in a glass reactor under the following conditions: catalyst mass = 50 mg, temperature = 300 °C, pressure = 0.1 MPa, H_2 flow rate = $36 \text{ cm}^3 \text{ min}^{-1}$, cyclohexane flow rate = $0.727 \text{ cm}^3 \text{ h}^{-1}$. Before the reaction was started, the catalysts were treated in H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$, 500 °C, 1 h). The reaction products were analyzed in a gas chromatograph connected online. The cyclohexane dehydrogenation rate was determined from the conversion value according to the equation

$$\text{rate } (\mu\text{mol g}^{-1} \text{ s}^{-1}) = \frac{\text{conversion} \times n}{m_{\text{cat}}} \quad (2)$$

where n is the molar quantity of cyclohexane injected per second and m_{cat} is the catalyst mass, grams.

Cyclopentane (CP) Hydrogenolysis. The cyclopentane (CP) hydrogenolysis reaction was performed in a glass reactor under the following conditions: catalyst mass = 150 mg, temperature = 350 °C, pressure = 0.1 MPa, H_2 flow rate = $40 \text{ cm}^3 \text{ min}^{-1}$, cyclopentane flow rate = $0.483 \text{ cm}^3 \text{ h}^{-1}$. Before the reaction was started, the catalysts were treated in H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$, 500 °C, 1 h). The reaction products were analyzed in a gas chromatograph connected online. The cyclopentane hydrogenolysis rate was determined from the conversion value according to eq 2.

Sulfidation. Fresh unsulfided Pt–Re catalysts have a great activity for hydrogenolysis. Temperature excursions or heat fronts are attributable to the hyperactivity of the catalyst, which causes excessive hydrocracking, sometimes referred to as runaway hydrocracking. These temperature excursions are undesirable because the temperatures obtained often result in damage to the catalyst or production of excessive coke laydown on the catalyst with consequent catalyst deactivation. If uncontrolled, temperature excursions might even lead to damage to the reactor and its internals. For these reasons, in industrial practice, the hyperactivity of Pt–Re/ Al_2O_3 catalysts is suppressed by sulfidation.^{23–25} A simple sulfidation procedure was

employed in our case. Before the *n*-C₇ reforming reaction test, bimetallic Pt–Re blank catalysts were treated under a 5% H₂S/H₂ mixture for 1 h at 500 °C and were then treated under H₂ for 8 h at the same temperature. Catalysts with Ge were not sulfided because, in this case, Ge addition is supposed to produce an inhibition of the hydrocracking hyperactivity, rendering the sulfiding step unnecessary. Moreover, one objective of this work was to investigate whether Ge-doped catalysts can be used without any kind of sulfidation pretreatment.

***n*-Heptane Reforming Reaction.** This reaction was performed in a continuous flow reactor under the following conditions: catalyst mass = 1 g, temperature = 500 °C, pressure = 0.5 MPa, H₂ flow rate = 60 cm³ min⁻¹, *n*-C₇ flow rate = 3 cm³ h⁻¹ (i.e., H₂/*n*-C₇ gas mixture = 7.5:1 molar ratio). Effluent products were analyzed by an online chromatograph (Varian 3400) equipped with a flame ionization detector and a CP-Sil 5 capillary column. Product yields were obtained from the chromatographic data. The yield of product *i* is the percentage of *n*-heptane converted into this product and is calculated as

$$C_i (\text{yield}) = \frac{100C_i X}{\sum C_i} \quad (3)$$

where *X* is the total conversion and *C_i* is the molar quantity of *n*-heptane transformed into compound *i*.

Results and Discussion

1. Influence of the Impregnation Medium on the Properties of Pt–Re/Al₂O₃. To investigate the influence of the preparation method itself, some blank catalysts were prepared. Pt–Re base catalysts were subjected to the different steps of the catalytic reduction method, but no Ge was added to the solution. In this way, the effects on the Pt–Re catalyst by the combined influence of hydrogen bubbling, mild heating, and immersion in different media (ammonia, hydrochloric acid, and neutral aqueous solutions) could be assessed without the disturbing effect of Ge blocking. These control samples, depending on the type of solution used, are denoted as the NH₃, HCl, and H₂O blank catalysts.

In a previous work, we reported some results of temperature-programmed reduction (TPR) experiments.²¹ It was found that some rhenium interacts with the platinum, but some is segregated on the support. The interaction of the Pt–Re phase with the support is modified by the impregnation medium and decreases in the order HCl > H₂O > NH₃.

The total area under the pyridine TPD trace is proportional to the amount of acid sites on the catalyst. Area values and chlorine contents are plotted in Figure 1. As noted in a previous contribution,²¹ the total acidity of the Pt–Re base catalyst is modified by the catalytic reduction treatment. If impregnation is performed in an alkaline medium, the catalyst acidity is decreased. If impregnation is performed in an acidic medium, the catalyst acidity is increased. Treatment with an aqueous solution has no effect on the acidity. Figure 1 further reveals that the catalyst acidity is directly related to the chlorine content. This is a minimum after impregnation in NH₃ and a maximum after impregnation in HCl.

The acidity of the supported Pt–Re catalysts (base and blank) was also studied by means of FTIR spectroscopy of adsorbed pyridine (Py) (results not shown). Bands at 1451 and 1455 cm⁻¹ were found, corresponding to pyridine adsorbed over Lewis acid sites,²⁶ whereas no band due to pyridinium ion (PyH⁺) at 1540 cm⁻¹, attributable to Brønsted acid sites, was observed. This means that the Brønsted acid sites were not strong enough to

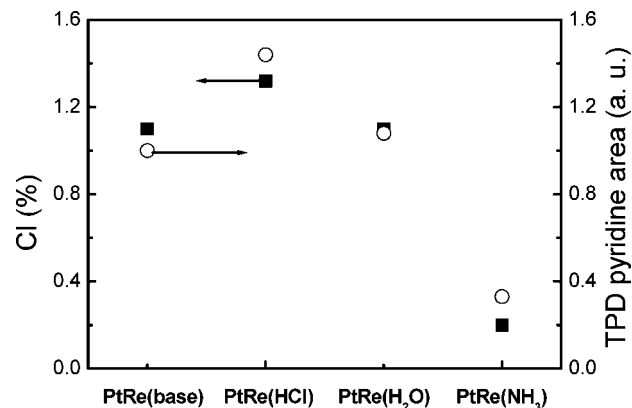


Figure 1. Percentage of chlorine and relative value of the total area of the pyridine TPD traces of the base and blank catalysts (no Ge added): (■) chlorine content, (○) total area of the pyridine TPD.

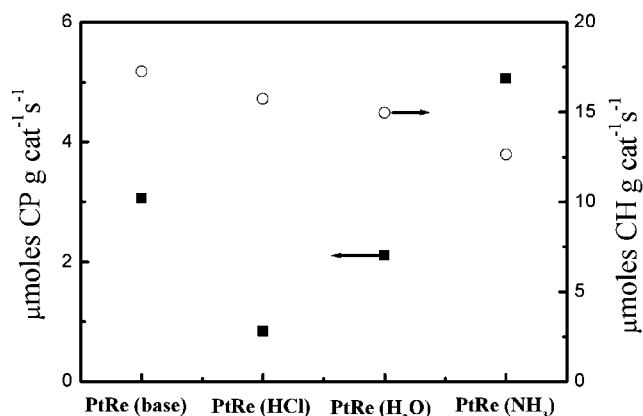


Figure 2. Specific activities for the hydrogenolysis of cyclopentane (CP) and dehydrogenation of cyclohexane (CH) for base and blank catalysts: (■) cyclopentane, (○) cyclohexane.

produce pyridinium ion, but it does not mean that there are no Brønsted acid sites. Bands at 1612–1630 cm⁻¹ were observed corresponding to adsorbed aromatic compounds.²⁷ Based on measurements performed at different temperatures, it is clear that the Lewis acid sites at 1455 cm⁻¹ were strong acid sites because they retained pyridine at temperatures higher than 250 °C. It was determined that the Lewis acidity of the supported catalysts was not affected significantly by the impregnation medium. The total amount of Lewis acid sites (*Q*) at 150 °C varied very little (between 235 and 250 μmol g⁻¹). As the Lewis acidity was not modified by the impregnation medium, the acidity variations as measured by the pyridine TPD tests must be attributable to changes in the concentration of Brønsted acid sites.

Figure 2 shows the activity values for the cyclohexane and cyclopentane reactions. Cyclohexane dehydrogenation is a reaction that is catalyzed by the metal function and is structure-insensitive.²⁸ The reaction rate is proportional to the total number of active metal atoms. For the experimental conditions used, the reaction is 100% selective to benzene. In turn, cyclopentane hydrogenolysis is a demanding reaction.^{29–31} In the case of Pt and Re, a synergistic effect exists for the hydrogenolysis reactions. The adsorption heat of the hydrogenolysis precursors adsorbed on the Pt ensembles is fundamental for the formation of the activated complex leading to the scission of the C–C bond. An ensemble of Pt atoms has a low adsorption heat, and pure Re has a high adsorption heat. Pt–Re ensembles have an intermediate value. For this reason, an ensemble of Pt and Re

Table 1. Percentages of Ge and Cl in the Pt–Re–Ge Catalysts Prepared in HCl, H₂O, and NH₃ Media as Determined by ICP-OES and Potentiometry

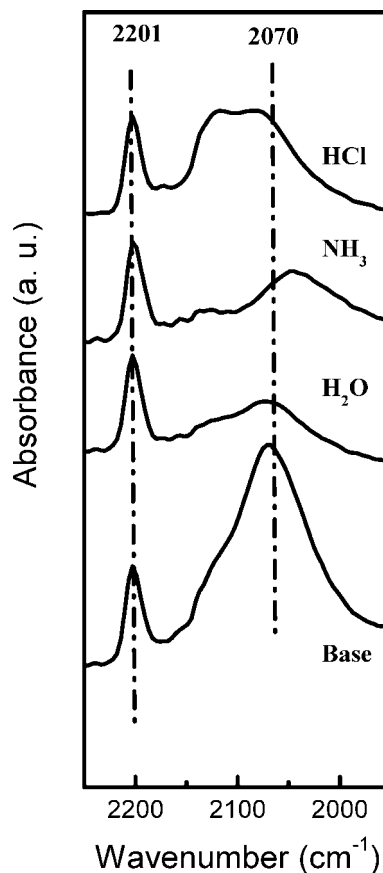
theoretical Ge (%)	Ge (%)			Cl (%)		
	HCl	H ₂ O	NH ₃	HCl	H ₂ O	NH ₃
0.1	0.10	0.10	0.10	1.32	1.10	0.20
0.3	0.30	0.30	0.30	1.34	1.06	0.20
1.0	0.60	0.80	1.00	1.35	1.22	0.23
2.0	0.90	1.40	1.90	1.35	1.31	0.45

atoms can have a higher activity than the single atoms depending on the nominal composition, with the optimum being obtained for a PtRe₂ composition for catalysts prepared by catalytic reduction.^{20,32} This reaction produces mainly *n*-C₅ but also C₁, C₂, C₃, and C₄ as products of deep hydrogenolysis. It can be seen in Figure 2 that the treatments modified the activity of the Pt–Re base catalyst. The activity in cyclohexane dehydrogenation decreased slightly when the pH of the impregnation solution was increased, whereas the opposite trend was seen in the case of the hydrogenolysis reaction. These results can be explained in terms of the modification of the Pt–Re interaction during the treatments involved in the catalytic reduction method. It has been widely reported that the higher the Pt–Re interaction, the lower the dehydrogenation activity.¹⁸ Therefore, the cyclohexane dehydrogenation results show that the Pt–Re(NH₃) catalysts have the highest Pt–Re interactions. In the same mode, the higher the Pt–Re interaction, the higher the hydrogenolytic activity.

To explain the difference in the degree of interaction between Pt and Re species depending on the treatment, it is important to recall that, in the base catalyst, part of the Re is reduced in interactions with Pt, and the other part is present as isolated species on the support.²¹ Therefore, when the prereduced base catalyst is put into contact with the impregnation medium (HCl, H₂O, or NH₃), the medium can modify both bimetallic particles and isolated species. Chlorine forms oxychlorinated species that have a strong interaction with the support and a very much reduced mobility during the final activation treatment.³³ As a consequence, the degree of interaction between Pt and Re depends on the Cl content of the catalyst. When an ammonia solution is used, chlorine is removed from the support, and the final concentration of oxychlorinated species is lower. TPR experiments performed on the Pt–Re(NH₃) catalyst²¹ have shown that it has a weak metal–support interaction, and hence, Pt and Re migrate freely over the support and are co-reduced. Because Re has a lower dehydrogenating activity than Pt, if Re blocks the active sites of Pt, the average activity is decreased. The higher Pt–Re interaction of the catalyst treated in ammonia solution produces a higher hydrogenolysis activity.

As a conclusion of this first part, the catalytic reduction method modifies the properties of the Pt–Re/Al₂O₃–Cl base catalyst in agreement with the results of a preliminary study.²¹ The modifications depend on the pH of the impregnating solution. At high pH values, the catalysts retain less chlorine, and the metals are reduced at a lower temperature because of the low metal–support interaction. The opposite effect is obtained when HCl is used in the impregnation medium. The Brønsted acidity decreases as the impregnation pH is increased, whereas the Lewis acidity of the catalyst is not substantially modified by either impregnation medium. Catalysts with higher Pt–Re interactions are obtained at high pH values of the impregnation solution.

2. Influence of the Deposition of Ge by Catalytic Reduction. Table 1 lists the percentages of Ge and Cl deposited from different media (H₂O, HCl, and NH₃) as a function of the

**Figure 3.** FTIR spectroscopy of adsorbed CO on the base and trimetallic catalysts with 0.3% Ge.

theoretical Ge content (maximum amount to be deposited). It can be seen that the amount of Ge deposited increased as the Ge concentration in the solution increased. The pH values of the impregnating solutions were 3.8–4.3 for H₂O, 2.0–2.2 for HCl, and 9.5 for NH₃. Higher pH values improved the deposition of Ge on the catalyst surface, and at higher Ge concentrations, the Cl content increased. These results could be related to the incorporation of Cl from the GeCl₄ precursor salt. The final amount of Cl on the catalysts prepared using H₂O and HCl was 1.1–1.3 wt %. When the NH₃ solution was used, this value decreased to 0.2–0.4 wt %. The low final concentration of chlorine in the catalysts impregnated in ammonia is assumed to be due to the formation of NH₄Cl in solution that is eliminated during the washing step.

TPR of Pt–Re–Ge trimetallic catalysts was also reported elsewhere.²¹ In the trimetallic catalysts, it was found that part of the Ge is isolated on the support and the amount of Ge in interaction with the bimetallic Pt–Re species follows the order according to the impregnation medium: HCl > H₂O > NH₃.

The interaction between the metals was also studied by FTIR spectroscopy of CO. CO is chemisorbed on metallic Pt but not on metallic Re or Ge.^{21,34} On the other hand, CO can be adsorbed on Pt particles in linear and bridged forms. In Figure 3, only the wavenumber region corresponding to linear CO is shown, because the band due to CO adsorbed in the bridged form, Pt₂CO, was too small to be studied.

As can be seen in Figure 3, all of the catalysts have an absorption band at 2201 cm^{−1}, which might be due to CO–Al₂O₃ interactions.³⁵ It is known that acid sites on the alumina surface are Al³⁺ ions that are tetrahedrally or octahedrally coordinated. Some authors have suggested that absorption bands located around 2200 cm^{−1}, shifted by ~20–25 cm^{−1} from

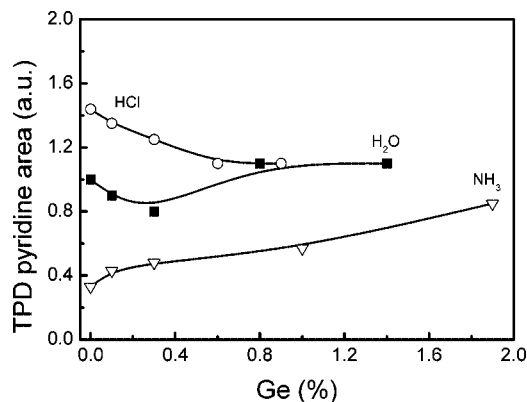


Figure 4. Areas of pyridine TPD traces for catalysts impregnated in different media and with different Ge contents.

this value, correspond to tetrahedral sites.^{36–39} This hypothesis was indirectly confirmed by Zecchina et al.³⁷ They did not find this band in α - Al_2O_3 , which has no tetrahedral acid sites.

The base catalyst has a main absorption peak located at 2070 cm^{-1} , which can definitely be attributed to CO chemisorbed on Pt. It is shifted to lower frequencies when the electron density of Pt increases or to higher frequencies when the electron density diminishes.⁴⁰ It must be pointed out that a small shift to higher frequencies was observed for catalysts prepared in H_2O or HCl and that the size of this peak was notably reduced for these catalysts. Such differences could be due to a Ge–Pt interaction, which would hinder the chemisorption of CO on Pt. Part of the Ge remains in the unreduced state after the hydrogen pretreatment at $400\text{ }^\circ\text{C}$ before CO chemisorption determinations.⁴⁰ Del Angel et al.⁴¹ found a shift of the Pt^0 absorption band to higher frequencies and linked this effect to an interaction between Pt and SnO_x or La_2O_3 species, which would stabilize the oxidized Pt^{2+} form. For the Pt–Re–Ge(0.3, NH_3) catalyst, it can be safely assumed that the influence of metallic or oxidized Ge on CO chemisorption is rather low, as TPR experiments demonstrated that those species were in a segregated state. On the other hand, because of the low catalyst acidity, Re atoms can migrate toward Pt, leading to the formation of Pt–Re ensembles. The corresponding increase in the electronic density of Pt (which is more electronegative than Re) would explain the observed peak shift to 2045 cm^{-1} on the Pt–Re–Ge(NH_3) samples.

A clearly defined band at 2120 cm^{-1} was observed for the trimetallic catalyst prepared in HCl . This band was small for the H_2O -prepared catalyst and much smaller when NH_3 was used in the catalyst preparation. For the base catalyst, the 2120 cm^{-1} band appeared as a shoulder on the main 2070 cm^{-1} band. The 2120 cm^{-1} band has been attributed⁴¹ to the influence of chloride ions.

All of these FTIR results for CO show that the trimetallic catalysts prepared with H_2O or HCl have a good interaction between Ge and the catalytically active species (Pt–Re). This interaction exists to a smaller extent for the catalysts prepared with NH_3 (Ge is mainly in a segregated state).

Figure 4 shows the pyridine TPD areas of the various trimetallic catalysts. It can be seen that, in the case of the catalysts prepared in HCl , an increase of the Ge content decreased the total acidity. The opposite occurred in the case of the NH_3 -prepared catalysts. In the case of the catalysts prepared in H_2O , the total acidity had an intermediate behavior with respect to the Ge content. The final acidity is a result of the action of the support, the metal oxides, and the chlorine atoms. Additional FTIR spectroscopic analyses of adsorbed pyridine (Py) were performed to distinguish between Lewis and

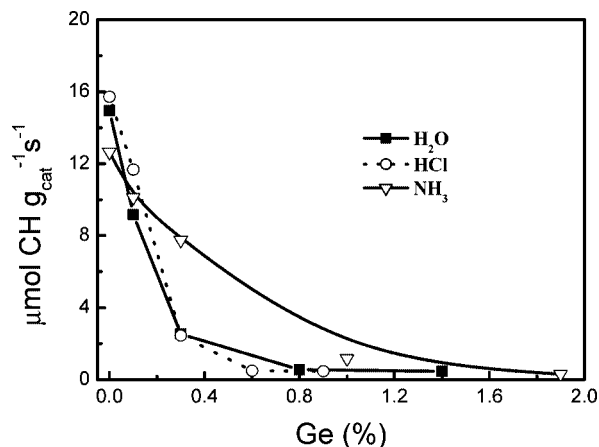


Figure 5. Activities in the dehydrogenation of cyclohexane (CH).

Brønsted acid sites. As in the case of the blank Pt–Re catalysts, the total amount of Lewis acid sites (Q) at $150\text{ }^\circ\text{C}$ was $235\text{--}250\text{ }\mu\text{mol g}^{-1}$ for all of the catalysts, irrespective of the impregnation medium or the Ge content, and the amount of Brønsted acid sites was too weak to produce adsorbed pyridinium ions. Table 1 shows that the Cl content increased with increasing Ge loading in the case of the NH_3 -prepared catalysts, whereas in the case of the H_2O - and HCl -prepared catalysts, the Cl content was essentially unchanged. Moreover, previous studies have shown that some of the Ge is deposited on the support by the catalytic reduction method.^{21,42} For these reasons, it can be thought that, in the H_2O - and HCl -prepared catalysts, Cl ions are displaced by Ge species and relocated in other support places, where they do not generate Brønsted acid sites. According to previous results, Ge addition induces a modification of the acid strength distribution, i.e., mainly a partial disappearance of strong acid sites.^{21,43}

Cyclohexane dehydrogenation results for the trimetallic catalysts are shown in Figure 5. Re has a very low activity, and Ge is completely inactive for this reaction. Therefore, the activity can be solely attributed to Pt. The dehydrogenating activity is decreased as the Ge content is increased whatever the catalyst series. This is easily rationalized in terms of the blocking of active Pt atoms by Ge. Re atoms can also be blocked by Ge, but as the dehydrogenation activity of Re is negligible, this effect can be disregarded. The H_2O - and HCl -prepared catalysts have a higher Ge–(metal function) interaction than the NH_3 -prepared ones as reflected by their lower dehydrogenating activities. This is in accordance with the TPR experiments presented elsewhere for the NH_3 -prepared trimetallic catalysts,²¹ showing a large amount of hydrogen consumed at high temperature corresponding to a large part of Ge isolated on the support.

Figure 6 shows the conversions of cyclopentane for the trimetallic catalysts relative to the blank catalyst of each series. A dramatic decrease of the hydrogenolytic activity can be seen for all of the catalysts at higher Ge contents. At low Ge contents ($\leq 0.3\text{ wt } \%$), the hydrogenolytic activity is only slightly affected in the case of the NH_3 -prepared catalysts, indicating a lower interaction compared to the two other series and confirming the lower Ge–(metal function) interaction in this case. It is interesting to compare the evolution of the activities in cyclohexane dehydrogenation and cyclopentane hydrogenolysis as a function of the Ge content. At low Ge contents ($< 0.3\text{ wt } \%$), it can be seen that the decrease in the hydrogenolytic activity is higher than the decrease in the dehydrogenating activity for the H_2O - and HCl -prepared series. This can be explained by

recalling that hydrogenolysis is a demanding reaction whereas dehydrogenation is not. Hydrogenolysis needs a minimum size of Pt ensembles to proceed. Ge loaded in small amounts would destroy these ensembles. In contrast, dehydrogenation depends on the action of single exposed Pt atoms and, hence, is less affected by Ge deposition. At high Ge contents (>0.3 wt %), both reactions suffer extensive deactivation because of the blocking of active sites. Comparing the conversion patterns of the two reactions in the case of the H₂O- and HCl-prepared catalysts, it can be concluded that they have similar interactions between Ge and the Pt–Re active phase.

3. *n*-C₇ Reforming Reaction. The three series of trimetallic catalysts were tested in *n*-C₇ reforming under pressure (at 6 and 20 h of time-on-stream). As seen previously in ref 42 for the H₂O-prepared series, at high Ge content (>0.3 wt %), the conversion is strongly affected; the same results were obtained for the HCl- and NH₃-prepared series. Consequently, Table 2 shows only the values of conversion and product yields obtained in the *n*-C₇ reforming test for the trimetallic catalysts with 0.1 and 0.3 wt % Ge. For comparison, the results obtained for the blank bimetallic catalysts are also given after sulfidation in order to decrease the excessive hydrogenolytic activity of these systems.

The H₂O-prepared blank bimetallic catalyst presents the highest conversion compared to the other blanks, with the lowest deactivation between 6 and 20 h of reaction. For petrochemical applications, toluene issued from dehydrocyclization is the most interesting product. Dehydrocyclization and *n*-C₇ isomerization are bifunctional reactions, and the limiting step occurs on the acid sites of the support.⁴⁴ The highest toluene yield was obtained with the HCl-prepared blank at 6 h of time-on-stream, but it strongly decreased after 20 h of reaction to finally reach a lower value compared to the two other blank catalysts. Concerning the C₁–C₄ yield, the highest values were observed for the H₂O-prepared blank catalyst. This result is explained by the highest C₁ and C₃ yields characteristic of the hydrogenolytic activity of the metal function and the cracking activity of the acid function, respectively. The NH₃-prepared blank sample presented the lowest C₁–C₄ yield mainly because of a low C₃ yield, resulting from the low acidity of this catalyst (Figure 1). Moreover, this sample shows the highest yield of C₇ isomers, which can be valuable products. Therefore, the treatment in NH₃ did not destroy all of the acidic sites even though a large amount of chlorine was removed. In NH₃, mainly the strong acid sites were inhibited, which led to a decrease of nonvaluable gases.

For the H₂O-prepared series, the addition of small amounts of Ge led to conversions similar to that of the blank presulfided catalyst and to higher toluene yields. On the other hand, for the HCl- and NH₃-prepared series, Ge addition induced a decrease of the conversion and toluene yield, all the more important when the Ge content was high. Regardless of the impregnation medium, Ge addition allowed for the production of C₁–C₄ light gases to be decreased compared to the respective presulfided blank catalyst. In the case of the NH₃-prepared trimetallic series, the obtained yields were the lowest, but unfortunately in this medium, the obtained trimetallic Pt–Re–Ge/Al₂O₃ catalysts presented rather poor catalytic performances in *n*-C₇ reforming.

Conclusions

In this work, we studied the catalytic properties of Pt–Re/Al₂O₃–Cl naphtha-reforming catalysts modified by Ge introduced by redox reaction at different pH values. For that purpose, the Ge precursor salt was introduced into solutions at pH values of around 2.1 (HCl), 4.0 (H₂O), and 9.5 (NH₃).

Blank catalysts prepared by the same method but with no Ge addition presented various Brønsted acid functions depending on the Cl content, but similar Lewis acidities. The activities in cyclohexane dehydrogenation and cyclopentane hydrogenolysis showed that the pH of the impregnation solution induced modifications of the Pt–Re interaction. The Pt–Re interaction increased according to the sequence HCl < H₂O < NH₃.

Regardless of the impregnation medium, Ge addition occurred on both the metal function and the support. The HCl- and H₂O-prepared series presented comparable characteristics, whereas in the case of the NH₃-prepared samples, the Pt–Re function was less poisoned by Ge addition. In this last medium, a significant portion of the Ge was deposited on the support.

The *n*-C₇ reforming reaction performed under pressure on the three blank catalysts showed that Pt–Re bimetallic catalysts treated in H₂O presented the highest conversion and

isomer yield, this result shows that the treatment in NH_3 did not destroy all of the acidic sites even though a large amount of chlorine was removed. In NH_3 , mainly the strong acid sites were inhibited, which led to a decrease of nonvaluable gases.

Unfortunately, for the trimetallic Pt–Re–Ge catalysts, only the H_2O -prepared series presented conversions, stabilities, and toluene yields that were comparable to, and even higher than (for 0.3 wt % Ge), those obtained with the presulfided bimetallic system. However, the amount of light hydrocarbons produced by the acid function remained significant on the H_2O -prepared series. This might be improved by slightly modifying the impregnation medium by adding small amounts of ammonia to obtain various pH values between 4.0 and 9.5 (H_2O - and NH_3 -prepared series, respectively, in the present work).

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