

Effect of Ge content on the metal and acid properties of Pt-Re-Ge/Al₂O₃-Cl catalysts for naphtha reforming

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ABSTRACT

The effect of the Ge content on the properties of the metal and acid functions of trimetallic naphtha reforming catalysts of platinum-rhenium-germanium supported on chloride alumina was studied. Pt, Re and Ge were loaded using the coimpregnation method. The elemental concentration of the catalysts used was: Pt = Re = 0.3%; Ge = 0.1%, 0.3%, 0.6% and 0.9% (weight basis). In order to make a comparison Pt/Al₂O₃ and Pt-Re/Al₂O₃ catalysts were prepared. The properties of the acid and metal functions were studied by physicochemical techniques and using test reactions. Reforming of n-heptane (450 °C, 0.1 MPa, H₂/nC₇ = 4, WHSV = 7.3) was used to evaluate the catalytic properties of the samples. It was found that the addition of small quantities of Ge (0.1%) decreased both the hydrogenolytic and dehydrogenation activities by breaking Pt-Re ensembles and modifying the electronic density of Pt. The latter was revealed by the decrease in the CO chemisorption capacity and the shift of the bands of linearly adsorbed CO. With respect to the acid function Ge addition produced a change in the acid strength distribution, increasing the amount of mild and weak acid sites and decreasing the amount of strong ones. This modification of the metal/acid balance had an effect over the distribution of products of n-heptane reforming. Both the isomerization activity and the stability of the catalyst were enhanced while the cracking and dehydrocyclization activities were decreased. The isoparaffins/aromatics ratio and the octane gain were improved and as a result the reformate product better adjusted to environmental regulations.

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1. Introduction

Naphtha reforming is the main supplier of gasoline and hydrogen in the refinery. The catalyst used in this process is metal–acid bifunctional. The metal function, supplied by finely divided Pt particles, promotes the de/hydrogenation reactions. The acid function, supplied by the chlorine promoted support, catalyses isomerization and cyclization reactions needed for producing high octane compounds such as aromatic hydrocarbons and branched isoparaffins.

Current naphtha reforming catalyst has greatly evolved from the first formulation that consisted of monometallic platinum supported over chloride alumina (Pt/Al₂O₃-Cl) and was introduced in 1949 by UOP [1]. Nowadays most commercial naphtha reforming catalysts are multimetallic (Pt-M-N/Al₂O₃-Cl) with a variety of components (M, N) like Re, Ir, Sn, Ge, etc., added to the base catalyst. The steps in the evolution have comprised screening of additives and variation of the preparation and activation conditions in order to improve the stability (rate of sintering of the

Pt particles and the rate coke formation) and selectivity of the catalyst.

Due to the progressive modification of the environmental restrictions on the composition of gasoline (e.g. US Clean Air Acts, 1990 onwards) [2] one key objective of these catalyst modifications has been the modulation of the catalytic selectivity in order to increase the yield of isoparaffins and to reduce the yield of aromatics.

The practice of adding a second metal to the base Pt-containing metal function was started in 1968 when Chevron patented the first bimetallic PtRe/Al₂O₃-Cl [3]. Re addition improved the stability of the catalyst and enabled a 50% reduction of the reactor pressure (comparing to the conditions needed in a reactor with a monometallic Pt catalyst) for a similar length of the operation cycle [4–6]. Other metallic promoters were later incorporated to Pt; Ge [7], Sn [8–10] and Ir [11,12] being the most important. PtRe/Al₂O₃ and PtIr/Al₂O₃ bimetallic catalysts had a high hydrogenolytic activity, producing methane and other light alkanes. This drawback was eliminated by presulfiding the catalysts, but these treatments make the activation process difficult. PtGe/Al₂O₃ and PtSn/Al₂O₃ catalysts have the advantage that they do not need sulfidation. This enables their use in processes with continuous catalyst regeneration.

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Bifunctional trimetallic catalysts belong to the latest generation of naphtha reforming catalysts used for the octane enhancement of refinery naphtha streams and many publications and patents propose their use, claiming milder coking rates [13–17]. In the last decade these catalysts have gradually replaced the previous industrial bimetallic catalysts because of their higher stability, adaptability to different feedstock and resistance to poisons [18,19].

Continuous improvement of the naphtha reforming process and catalyst are still underway. Main objectives are: (i) increasing the yield of multibranched isoparaffins in the reformato to prove a good octane number while reducing the content of aromatic hydrocarbons (increase of isoparaffins/aromatics ratio); (ii) obtaining stability of the component an enhanced resistance to deactivation thus allowing longer operation periods.

The selectivity of trimetallic naphtha reforming processes is adjusted by modification of both the metal and acid function. In the case of the metal function the addition of a second and a third component to the Pt promoted base catalyst produces many different effects: (i) it modifies the electronic state of the metal [20]; (ii) it changes the geometry of adjacent Pt atom clusters; (iii) it changes the final Pt particle size by inhibiting the sintering of supported Pt particles [21–24]. (i) and (ii) directly affect the de/hydrogenation reaction kinetics of the formation of olefins, cycloparaffins and coke. (i) and (iii) regulate the effective size of Pt clusters and hence the rate of hydrogenolysis. In the case of the acid function multicomponent addition affects both the strength and amount of support acid sites. Higher acid strengths increase the acid-catalyzed coking and cracking rates. Milder acid strengths benefit isomerization rates due to the inhibition of consecutive cracking and polymerization reactions [25,26].

The changes of the metal properties depend partly on the charge of the promoter and its relative electronegativity in relation to Pt while the modifications of the support acid function depend on the amount and acid/base properties of the supported promoter oxide. Despite the technical importance of trimetallic catalysts most information on their structure and catalytic properties is the property of process companies and is not available in the open literature.

The Sn and Ge components have been used as third element in PtRe/Al₂O₃ replacing the presulfiding treatment [15,25]. Also only a fraction of their oxides is reduced to the metallic state and these Sn⁰ and Ge⁰ elements interact or are alloyed to Pt or Re, dilute Pt atoms and reduce the hydrogenolytic activity of Re in the same way as Re-S.

We have studied the effect of Sn content as the third element in Pt-Re-Sn trimetallic catalysts [25] and more recently, the effect of Ge content as a second element in Pt-Ge bimetallic catalysts [26]. The effect of Ge content in Pt-Re-Ge trimetallic catalysts is studied in this work, complementing these series of works. This trimetallic catalyst has been less studied than the Pt-Re-Sn catalyst, which has a wider application in the industry. In this work the effect of the addition of varying amount of Ge to Pt-Re catalysts were studied by means of physical–chemical characterization techniques and test reactions for the metal and acid functions. The catalysts were further tested in the reaction of n-heptane reforming.

2. Experimental

2.1. Catalysts preparation

Three catalysts series were prepared: (I) monometallic, Pt, Re and Ge catalysts with a metal content of 0.3% and supported over chloride γ -alumina (Pt/Al, Re/Al and Ge/Al samples); (II) bimetallic, Pt-Re and Pt-Ge catalysts with 0.3% of both metals (PtRe/Al and PtGe/Al); (III) trimetallic Pt-Re-Ge catalysts with 0.3% of Pt and Re, and

0.1%, 0.3%, 0.6% and 0.9% of Ge (PtReGe(0.1)/Al; PtReGe(0.3)/Al; PtReGe(0.6)/Al and PtReGe(0.9)/Al). All catalysts were prepared using a commercial γ -alumina as support (Cyanamid Ketjen CK-300, pore volume = 0.5 cm³ g⁻¹, specific surface area = 180 m² g⁻¹, impurities: Na = 5 ppm, Fe = 150 ppm, S = 50 ppm). The alumina pellets were ground, sieved to 35–80 mesh and then calcined in air at 600 °C for 3 h. The metals were added using a standard method of coimpregnation of the precursor salts dissolved in aqueous solution. In all cases the impregnation volume was adjusted in order to yield the appropriate concentration of each metal in the final catalyst. The salts used were H₂PtCl₆·6H₂O (3.345 mg Pt cm⁻³), NH₄ReO₄ (20.18 mg Re cm⁻³) and GeCl₄ (3.23 mg Ge cm⁻³). The catalysts were prepared according to a technique described elsewhere [25]. An HCl 0.2 M solution was added to the support (1.5 cm³ g⁻¹) before impregnating the metal salts in order to introduce chloride as a competing ion and to assure a homogeneous distribution of them. The solution containing the catalysts was first left unstirred for 24 h and then it was gently heated (0.5 °C min⁻¹) at 70 °C in order to evaporate the excess liquid. The catalysts were dried at 110 °C overnight, calcined in air (60 ml min⁻¹, 4 h, 450 °C) and then, flushed with N₂ for 30 min and reduced in flowing H₂ (60 ml min⁻¹, 4 h, 500 °C). Finally the catalysts were cooled to room temperature in a hydrogen flow and flushed with nitrogen previous to their discharge.

2.2. Catalyst characterization

2.2.1. Catalyst elemental composition

The Pt, Re and Ge content of the solids was determined by atomic emission spectroscopy (ICP-AES) using an ARL model 3410 equipment. The solids were dissolved in a digestion pump with a mixture of 1 mL sulphuric acid, 3 mL chlorhidric acid and 1 mL nitric acid. The chlorine content of the catalysts was determined by the Volhard–Charpentier method.

2.2.2. 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 °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 switched to 5% H₂/Ar (50 ml min⁻¹) mixture. Then it was heated from room temperature to 850 °C at a heating rate of 10 °C min⁻¹. The effluent gas was passed through a cold trap before TCD in order to remove water from the exit stream.

2.2.3. 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 was immersed for 4 h in a closed vial containing pure pyridine (Merck, 99.9%). 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 cm³ min⁻¹). Weakly adsorbed pyridine was first desorbed in a first stage of stabilization by heating the sample at 110 °C for 2 h. The temperature of the oven was then raised to 600 °C at a heating rate of 10 °C min⁻¹. The reactor outlet was directly connected to a flame ionization detector to measure the desorption rate of pyridine.

2.2.4. CO chemisorption

the experiments were performed in a chemisorption equipment designed ad-hoc. The reduced catalyst was placed in a quartz reactor and first over reduced *in situ* in a hydrogen stream (500 °C,

1 h, $60 \text{ cm}^3 \text{ min}^{-1}$). Then the carrier was switched to N_2 and the adsorbed hydrogen was desorbed (500°C , $60 \text{ cm}^3 \text{ min}^{-1}$) for 1 h; then the cell was cooled down to room temperature. Then 0.25 cm^3 pulses of diluted CO (3.5% CO in N_2) were 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 on-line.

2.2.5. CO-FTIR spectroscopy

FTIR spectra of pre-reduced and evacuated samples were taken at room temperature in a Nicolet 5ZDX spectrometer in the $400\text{--}4800 \text{ cm}^{-1}$ range with a resolution of 4 cm^{-1} . Self supported wafers were successively reduced at 500°C under hydrogen flow for 30 min and outgassed at 10^{-6} Torr at the same temperature for 30 min. After recording the IR spectrum, the samples were contacted with 30 Torr of CO for 5 min and then a second spectrum was recorded. Then the sample was outgassed at 10^{-6} Torr at room temperature for 30 min and a new spectrum was obtained. The absorbance of chemisorbed CO outgassed at room temperature was obtained by subtracting the first and the last spectra.

2.2.6. Temperature programmed oxidation

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

2.2.7. Reaction test

The catalyst was charged in a glass tubular fixed-bed reactor of 8 mm internal diameter, forming a bed of 6 mm height, and was reduced *in situ* with hydrogen (60 ml min^{-1}) for 1 h at 500°C before each reaction test (to reduce surface Pt atoms oxidized in contact with room air). All reactions were performed at atmospheric pressure and in the presence of hydrogen (AGA, 99.99%). The analysis of reactants and reaction products was carried out using a Shimadzu GC-8A gas chromatograph connected on-line and equipped with a flame ionization detector and a capillary column of copper tube coated with squalene (ID 1/16" in, 100 m length) maintained at 110°C . From these compositional data the total conversion (X) and the yields to each reaction product (Y_i) were calculated on a carbon basis according to the formula in the following lines.

The conversion was defined as:

$$X = \frac{HC^i - HC^0}{HC^i} \quad (1)$$

where HC^i is the concentration of the fed hydrocarbon at the reactor inlet and HC^0 is the concentration of the non-reacted hydrocarbon at the reactor outlet.

The selectivity to each product i was defined as:

$$S_i = \frac{\text{yield of } i}{X} = \frac{A_i f_i n_i}{M_i (\sum A_i f_i n_i / M_i) X} \quad (2)$$

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

The RON of the products mixture was calculated using the method of Walsh and Mortimer [27]. The RON gain (ΔRON) in the reforming reactor was calculated as the difference between the RON of the products mixture and the RON of n-heptane (0).

2.2.8. Cyclohexane dehydrogenation

The dehydrogenation of cyclohexane (CH) to benzene is a reaction that is insensitive to the structure of the metallic active site and was used as one of the test reactions of the metal function. It was performed under the following conditions: catalyst mass = 0.1 g, 300°C , molar ratio $\text{H}_2/\text{CH} = 16$, WHSV = 12.6. Cyclohexane was supplied by Merck (spectroscopy grade, 99.9% pure). The specified sulphur upper limit was 0.001%.

2.2.9. Cyclopentane hydrogenolysis

In contrast to the previous reaction, hydrogenolysis of cyclopentane (CP) is a reaction that is sensitive to the structure of the Pt metal sites. CP was supplied by Merck (99.9%). Reaction conditions were: catalyst mass = 0.15 g, 350°C , hydrogen flow rate = $40 \text{ cm}^3 \text{ min}^{-1}$, CP flow rate = $0.48 \text{ cm}^3 \text{ h}^{-1}$.

2.2.10. n-Pentane isomerization

The isomerization of n-pentane was used as a test reaction for the acid function. $n\text{C}_5$ was supplied by Merck (99.9%). The reaction was carried out with 0.1 g of catalyst, for 4 h, at 500°C , WHSV = 4.5 and molar ratio $\text{H}_2:n\text{C}_5 = 6$.

2.2.11. n-Heptane dehydrocyclization

The reforming of n-heptane was used as a test reaction for both the metal and acid functions. This is a typical reaction for measuring the metal/acid balance of the catalyst functions. n-Heptane was Carlo Erba (RPE, 99% pure, GLC). 0.15 g of the catalyst were charged to a glass reactor and the reaction was carried out for 6 h at 450°C , molar ratio $\text{H}_2/n\text{C}_7 = 4$ and WHSV = 7.3.

For all reaction tests the experimental conditions ensured that the reactions proceeded under chemical control with no mass transfer problems, as revealed by the calculation of the Weisz-Prater modulus ($\Phi \ll 0.01$) and the Damköhler number ($\text{Da} \approx 0$). The mass transport coefficients were estimated from known correlations.

3. Results and discussion

Table 1 contains data related to the elemental composition of the catalysts. They had about 0.3% Pt and Re. The Ge content was in the expected range of 0.1–0.9%. All catalysts had about 0.9% Cl, a normal value for commercial naphtha reforming catalysts [3] and in accord with the chlorine equilibrium value at the calcination temperature (450°C) used in their pretreatment.

The TPR traces of the catalysts are included in Fig. 1. These traces are quite different depending on the composition of the catalysts. The results corresponding to the monometallic Pt/Al, Re/Al and Ge/Al catalysts and to the bimetallic PtRe/Al and PtGe/Al catalysts have already been described and discussed in our previous contribution dealing with this system [14,15,25,26]. These curves are repeated in Fig. 1(A) as a reference. The trace of the Pt/Al catalyst has a symmetric and well defined peak at 225°C corresponding to the reduction of PtOCl_2 species on the surface and a little shoulder at 360°C associated with the reduction of platinum species interacting strongly with the support [28,29]. The monometallic Re/Al and Ge/Al traces have a single reduction peak with a maximum at 580°C and 620°C , respectively, which can be

Table 1
Elemental composition of the catalysts.

Catalyst	Composition (wt%)			
	Pt	Re	Ge	Cl
Pt/Al	0.31	–	–	0.90
PtRe/Al	0.30	0.31	–	0.89
PtGe/Al	0.29	–	0.28	0.95
PtReGe(0.1)/Al	0.28	0.29	0.09	0.94
PtReGe(0.3)/Al	0.29	0.30	0.29	0.93
PtReGe(0.6)/Al	0.28	0.31	0.61	0.92
PtReGe(0.9)/Al	0.30	0.30	0.88	0.93

attributed to Re^{4+} [30] and Ge^{4+} reduction [29]. The PtRe/Al trace has a reduction peak at 230 °C, with a shoulder at 360 °C and another peak at 530 °C. The PtGe/Al trace has a peak at 240 °C with a shoulder at 380 °C and another peak at 550 °C. The comparison with the TPR trace of Pt/Al indicates that for PtGe/Al and PtRe/Al the main peak is related to the reduction of Pt and that the shoulders at 360–380 °C correspond either to the reduction of Re and Ge oxide species in the neighborhood of Pt particles or to the reduction of Pt alloyed with Re or Ge [31]. The shift of the Pt reduction peak to higher temperatures indicates that the promoter delays the reduction of Pt oxide. The reduction delay can be due to a blocking effect or an effect of electronic interaction. The peaks at 530–550 °C are due to the reduction of segregated Re or Ge in high interaction with the support [15].

In the TPR traces of the trimetallic catalysts (Fig. 1(B)) the peaks approximately coincide with those of the PtGe catalyst. The addition of different amounts of Ge modifies the relative sizes of the peaks. Increasing the Ge content increases the formation of segregated Ge and broadens the peak of reduction of the PtReGe alloy. In the preparation of the catalyst the reduction in hydrogen was performed at 500 °C and therefore the non-alloyed fraction of Ge probably remained in the form of a segregated oxide. It can also be seen that although the Ge concentration increases the position of the peak corresponding to the reduction of Ge oxide remains

Table 2
Area and position of the peaks of desorption of pyridine as a function of temperature. Trimetallic PtReGe/Al catalysts of varying Ge content and bimetallic PtRe/Al catalyst.

Catalyst	Area, (a.u.) ($^{\circ}\text{C} \times 10^{-4}$)	Peak at ($^{\circ}\text{C}$)
PtRe/Al	1.52	207
PtReGe(0.1)/Al	1.43	196
PtReGe(0.3)/Al	1.45	192
PtReGe(0.6)/Al	1.44	190
PtReGe(0.9)/Al	1.49	188

fairly constant at about 620 °C. In contrast the peaks of reduction of the Pt species, isolated or combined with Ge and Re, are shifted to lower temperatures (from 256 °C to 198 °C and from 347 °C to 304 °C). This shift confirms that there was a modification of the reducibility of the oxides when the amount of promoter was increased. This effect was attributed to the direct interaction of Ge with the active metal phase.

The results of the acidity measurements are summarized in Table 2. Pyridine desorption as a function of the temperature for the catalysts tested produced TPD traces with relatively symmetric peaks. The area and position of these peaks varied upon Ge addition. Ge addition produced a little decrease of the total area and a shift of the positions to lower temperatures. Table 2 contains this kind of data for trimetallic catalysts of varying Ge content and for the bimetallic catalyst PtRe/Al. The total amount of acid sites (proportional to the area under the TPD trace) was slightly affected by Ge addition. With respect to the position of the peak of the TPD trace (related to the acid strength of the sites) it can be seen that the strength of the acid sites was decreased upon Ge addition. Taking the peak of the PtRe/Al as a reference the addition of small Ge amounts shifted the position of the desorption peak to lower temperatures. In other words the population of strong acid sites was decreased and the population of weak and mild acid sites was increased. These results would coincide with those obtained by TPR indicating that the increase in the concentration of Ge produced an increase of the fraction of Ge present as an oxide. GeO_2

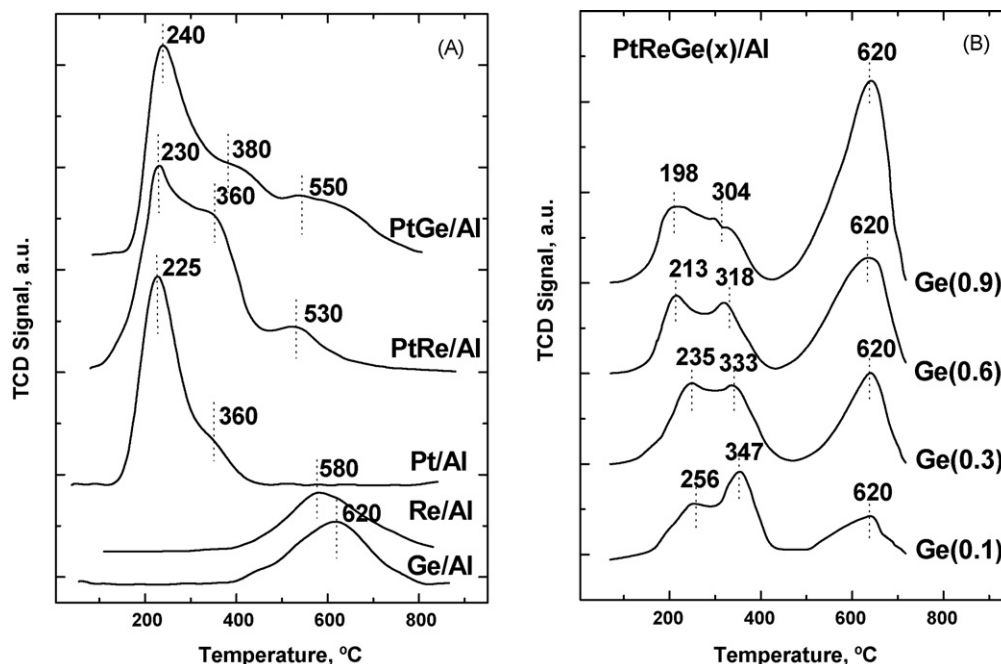


Fig. 1. (A) Temperature programmed reduction (TPR) traces of the monometallic, Pt/Al, Re/Al and Ge/Al and bimetallic catalysts, PtRe/Al and PtGe/Al. (B) TPR traces of the trimetallic catalysts: PtReGe(0.1)/Al, PtReGe(0.3)/Al, PtReGe(0.6)/Al and PtReGe(0.9)/Al.

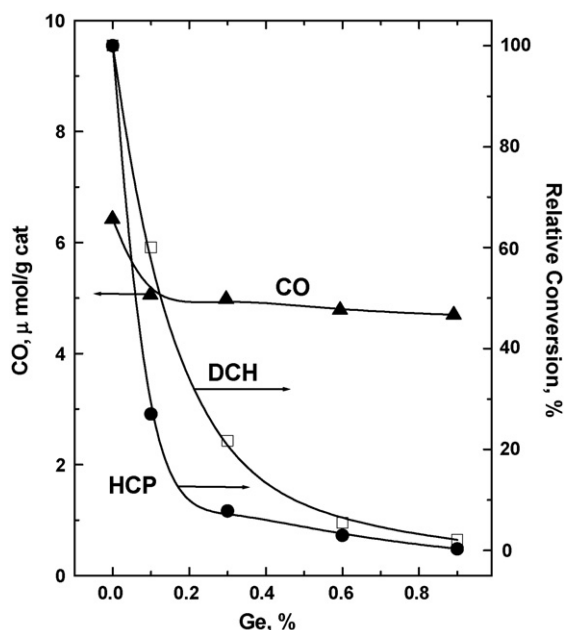


Fig. 2. Effect of Ge content on the metal function properties. CO chemisorption and relative conversion in the reactions of cyclohexane dehydrogenation (DCH) and cyclopentane hydrogenolysis (HCP). Values at 120 min time-on-stream.

is weakly acid and we can suppose that when it interacts with strong acid sites of the support it produces an average decrease of the acid strength of the site.

Fig. 2 shows the influence of the Ge content on the amount of CO chemisorbed, the hydrogenolytic activity and the dehydrogenating activity. In the conditions in which the experiment was performed, CO was selectively chemisorbed over Pt and no adsorption over Ge or Re was detected. We can see that there is an initial drop of 21% in the capacity for chemisorption of CO upon the addition of 0.1% Ge and that there are no meaningful additional changes upon further Ge addition. With respect to the evolution of the conversion of the studied reactions the addition of 0.1% Ge decreases the dehydrogenating activity by 40% and the hydrogenolytic activity by 73%. When the Ge content is 0.3% the hydrogenolysis, a structure-sensitive reaction, is practically completely suppressed. On the other side, the dehydrogenation of cyclohexane, a structure-insensitive reaction, is not suppressed but is continuously decreased. These results could be due to a decrease of the metal area produced by the coverage of the surface of Pt and Re particles by Ge atoms. It could also be related to a change in the electronic state of Pt due to the interaction of this metal with acidic GeO_x species, as pointed out in reference [20].

FTIR absorption experiments were used to study the nature of the metal surface sites. CO was adsorbed over the metal sites at room temperature and its IR spectra recorded in order to study the strength of the metal–CO bond. CO is adsorbed in linear or bridge form over the Pt surface particles. The zone of the IR spectrum corresponding to the absorption by the linear form of adsorbed CO shows an envelope of different signals and gives information on the electronic changes in the Pt surface. In contrast to the Pt catalysts, CO is not chemisorbed over monometallic Re/Al or Ge/Al catalysts. When Pt interacts weakly with the support surface CO adsorption in the linear form gives a well-defined band located at 2075 cm^{-1} [32]. When CO is adsorbed over bimetallic particles the band is displaced and new shoulders appear as a consequence of additional minor vibration modes due to the Pt–promoter direct interaction or the indirect interaction between promoter and the support or between Pt and the promoted support. It has been thus

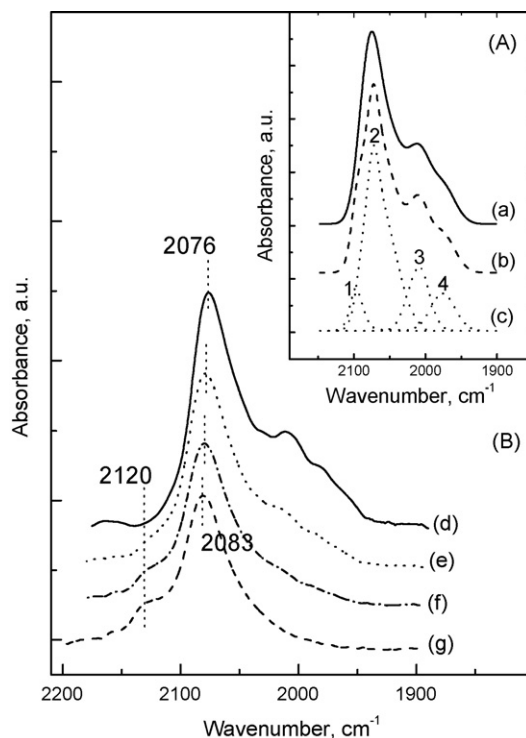


Fig. 3. FTIR spectrum of CO linearly adsorbed on the PtReGe/Al catalyst samples at 20°C . (A) PtReGe(0.22)/Al; (a) original spectrum; (b) sum of deconvoluted peaks; (c) peaks obtained after deconvolution (taken from Ref. [15]). (B) Original spectra of the rest of the samples; (d) PtReGe(0.1)/Al; (e) PtReGe(0.3)/Al; (f) PtReGe(0.6)/Al; (g) PtReGe(0.9)/Al.

reported that the incorporation of Re in PtRe/Al shifts the maximum of the band to 2070 cm^{-1} and generates a shoulder at 2011 cm^{-1} , related to the adsorption of CO over electron-rich Pt centers ($\text{CO-Pt}^{\delta-}$) [14]. Ge addition to Pt, as in PtGe/Al displaces the maximum of the band to 2080 cm^{-1} and generates shoulders at 2102 cm^{-1} and 2120 cm^{-1} , related to the adsorption of CO over electron-deficient centers ($\text{CO-Pt}^{\delta+}$) [26]. The shift and intensity of the bands depend on the concentration of the used promoter and the method of promoter addition. In the case of the PtGe/Al catalyst changes in the Pt/Ge ratio produce different interaction degrees and different concentrations of electron-deficient sites [26]. Fig. 3 shows the spectra of the PtReGe/Al catalysts in the linear adsorption region. Fig. 3A shows the deconvolution of the spectrum of Pt–Re–Ge/Al $_2\text{O}_3$ –Cl (0.29% Pt, 0.3% Re and 0.22% Ge, taken from our previously published work [15]). This spectrum is the sum of four signals located at 2079 cm^{-1} (2), 2102 cm^{-1} (1), 2011 cm^{-1} (3) and 1978 cm^{-1} (4). The band at 2079 cm^{-1} , corresponds to CO adsorbed over Pt^0 with low electronic interaction with Re or Ge. The shoulders at 2011 cm^{-1} and 2102 cm^{-1} correspond to CO adsorbed over Pt in independently interacting with Re or Ge atoms. The band at 1978 cm^{-1} is a new band that appears seemingly due to a combined interaction between Re and Ge [15]. In Fig. 3B we can see the changes in the spectrum of the studied trimetallic catalysts due to changes in the concentration of Ge on the support. These results confirm that the increase of the Ge content creates more centers of electro-deficient Pt by interaction of acid Ge oxides with the Pt particles. In parallel the increase of the Ge concentration decreases the effect of the combined Pt–Re–Fe interaction that is found in catalysts with similar concentrations of each promoter.

Fig. 4 shows results of total conversion, yield to methane, C_1 , propane, C_3 and C_5 isoparaffins as a function of Ge content,

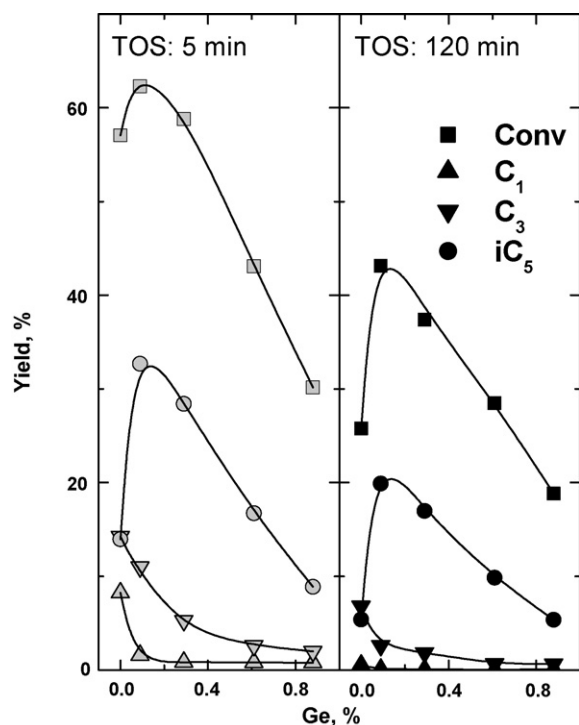


Fig. 4. n-Pentane reaction. PtReGe/Al catalysts. Total conversion, yield to methane, C_1 , propane, C_3 and iso-pentanes, iC_5 as a function of the Ge content at 5 min and 120 min time-on-stream.

obtained in the test of isomerization of n-pentane. The values were taken at 5 min and 120 min of time-on-stream, i.e. at the beginning and at the end of the experiment. The measurements at these two different reaction times enable to study the effect of Ge on coke-free fresh catalysts (5 min TOS) and the effect of coke on stabilized catalysts (120 min TOS). It can be seen that at 5 min TOS the addition of small Ge amounts (0.1%) increases the conversion of the catalyst and improves its selectivity to isomers. A great decrease of the hydrogenolysis (formation of C_1) and a moderated decrease of the cracking (formation of C_3) can also be seen. This beneficial effect is gradually lost at higher Ge concentrations. These results are in accordance with the decrease of the metal activity displayed in the hydrogenolysis of cyclopentane and the shift of the pyridine desorption peak of the TPD experiments. The decrease of the amount of strong acid sites is supposed to produce an inhibition of the cracking. At 120 min TOS the catalysts are covered with coke and it has reached a pseudo-stationary state. In these catalysts the effect of Ge on the selectivity is blurred by the effect of coke deactivation. Specifically the coke masks the effect of Ge over the hydrogenolysis activity (methane forming activity) and the cracking activity (propane formation). In spite of this a beneficial effect of Ge on the formation of branched isomers and the low coke formation can still be seen. The conversion drop of the reference catalyst (no Ge) is greater than that obtained with the catalyst doped with small Ge percentages.

Fig. 5 shows the results of total conversion and the yield to different products in the reaction of reforming of n-heptane as a function of the Ge content and the time-on-stream. At 5 min the surface of the catalyst is supposed to be free of coke. At 240 min a pseudo-stationary state is reached. The catalyst is covered with a coke layer that has an additional effect on the selectivity. The initial points of the graphs correspond to %Ge = 0, i.e. to the reference bimetallic catalyst PtRe/Al. It can be seen that the addition of small amounts of Ge (0.1%) increased the conversion of the catalyst, both

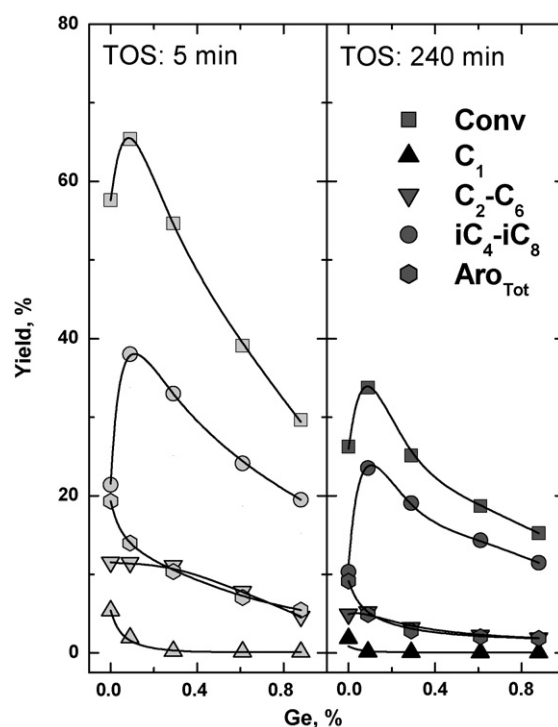


Fig. 5. n-Heptane reaction. PtReGe/Al catalysts. Total conversion and yield to different product as a function of the Ge content at 5 min and 240 min time-on-stream.

in the initial first minutes and in the final stable state. Ge contents higher than 0.1% produced a decrease of the initial and final activity in comparison to the reference bimetallic catalyst. If we focus on the difference between the values of conversion at 5 min and 240 min it can be seen that in the case of the trimetallic catalysts the pseudo-stationary state is achieved faster than in the case of the bimetallic catalyst. It can also be seen that the difference in conversion is lower in the case of the trimetallic catalysts, i.e. the stability is improved.

With respect to the relative activity of different reactions results such as the yields to C_1 , C_2 – C_6 n-paraffins (produced by cracking), C_4 – C_8 isoparaffins, total aromatics (benzene and toluene) and cycloparaffins give an insight on their relative importance. We can see that the relative proportions between yield values are similar irrespective of the time-on-stream analyzed (5 min or 240 min). The only difference found is the decrease of the conversion that is due to the deactivation by coking. Ge addition mainly affects the hydrogenolysis and therefore the production of methane. It also produces an increase of the production of isoparaffins and a small decrease of the yield to aromatics. For small amount of Ge added (0.1%) no modification can be seen of the yield to C_2 – C_6 paraffins. Higher Ge amounts produce a decrease. These results confirm that small Ge amounts modify the properties of the metal function, inhibiting hydrogenolysis and decreasing the dehydrocyclization activity. They also change the acid strength of the support, favoring the production of isomers. Once the catalysts get covered with a coke layer the effect of Ge on the hydrogenolytic activity and the formation of aromatics gets blurred by the distortion of deactivation. In spite of this effect the catalysts are still more selective to branched isomers and more stable. This is surely due to the lower concentration of acid sites of high strength.

Fig. 6 shows the influence of the Ge content on several merit parameters for the reaction of n-heptane reforming, at 5 min and

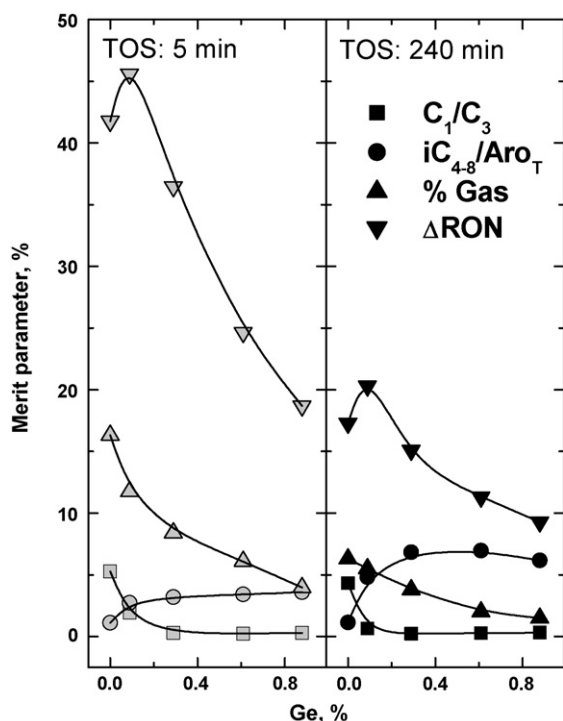


Fig. 6. n-Heptane reaction. PtReGe/Al catalysts. Merit parameter: methane/propane molar ratio (C_1/C_3), isomers/aromatics yield ratio (iC_{4-8}/Aro_T), octane gain (ΔRON) and weight percentage of gases (%G), as a function of the Ge content at 5 min and 240 min of time-on-stream.

240 min of time-on-stream. The values plotted correspond to; (i) the molar C_1/C_3 ratio (that reflects the metal/acid balance); (ii) the yield to light gases (that reflects the cracking activity and is inversely proportional to the liquid yield); (iii) the ratio between the values of the yield to isoparaffins and the yield to total aromatics, (iv) the RON gain. It can be seen that the addition of Ge produces an increase of the iC_{4-8}/Aro_T ratio (Aro_T = benzene, toluene and cycloparaffins) and the RON gain, thus favoring the quality of the product. Ge addition also produces a decrease of the yield of light gases thus increasing the liquid yield. The values of the merit parameters are practically constant from 0.3% Ge to higher values and the more active catalyst is always the one with 0.1% Ge.

Fig. 7 shows the results of the temperature programmed oxidation tests (TPO). The samples became coked during the reforming of n-heptane. The TPO trace of the reference catalyst PtRe/Al (Ge(0.0)) has two peaks of coke combustion, one centered at about 230 °C and another at 370 °C. Previous reports [33,34] indicate that the carbon burning at low temperatures corresponds to a highly hydrogenated coke, deposited on the metal function (metallic coke) while the carbon that burns at higher temperatures corresponds to a more polymerized coke, deposited on the acid sites (acid coke). TPO traces of the trimetallic PtReGe/Al catalysts with varying Ge content show a decrease of the metallic coke and the area of acid coke. Therefore it can be said that the addition of Ge to PtRe/Al produces a decrease both of the metallic and acid coke. The metallic coke practically disappears at Ge contents higher than 0.3%. This is because the metal phase of the trimetallic catalyst contains ensembles of atoms of three metals and thus the deposition of coke becomes difficult. Coke deposition on the metal demands big ensembles with a size similar to those needed for hydrogenolysis [35,36]. Thus these results are consistent with the ones shown in Fig. 2.

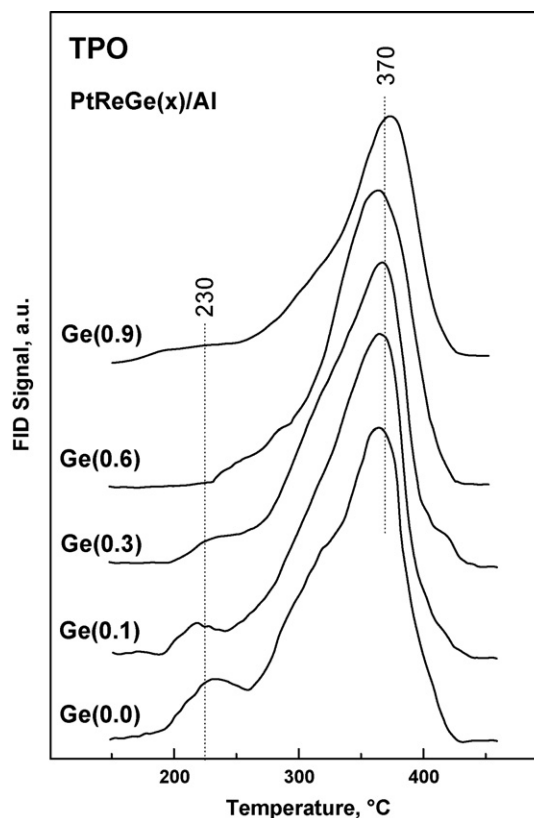


Fig. 7. n-Heptane reaction. Temperature programmed oxidation of coke deposited after a reaction span of 4 h. PtReGe(0.0)/Al, PtReGe(0.1)/Al, PtReGe(0.3)/Al, PtReGe(0.6)/Al and PtReGe(0.9)/Al.

The total coke content was calculated by integrating the area under the TPO trace and by calibration against standard tests with catalysts of known carbon content. This calculation yielded the following results: 0.23% C for the PtRe/Al catalysts, 0.21% C for PtReGe(0.1)/Al, 0.20% C for PtReGe(0.3)/Al, 0.19% C for PtReGe(0.6)/Al and 0.15% C for PtReGe(0.9)/Al. A clear trend of declining coke content as the Ge content grows can be seen. These results confirm that the addition of Ge decreases the coking rate over both functions.

The performance of the trimetallic catalysts under reaction conditions indicates that Ge in low amounts promotes the rupture of Pt ensembles. This affects the activity of the metal function and thus the reactions which are structure-sensitive (hydrogenolysis) are drastically inhibited. As the amount of Ge is increased isolated Ge particles appear on the support and are transformed into acidic oxide species during the calcination pretreatment. These oxide particles modify both functions. The effect on the acid function is the net decrease of sites of strong acidity. Most probably these sites are transformed into sites of medium acid strength by interaction with the Ge oxide species. Other medium strength and weak sites are formed by interaction between the Ge oxide species and amphoteric and weak acid sites of the support. When the oxide species get in close vicinity or on top of Pt particles an electronic induction effect also appears. Electrons from Pt are depleted by polarization from the electronegative Ge oxide species. Electrodeficient Pt domains are thus formed and the metal activity is modified. The capacity of Pt for the chemisorption of reactants and hydrogen is decreased and also the de/hydrogenation capacity is inhibited. When the oxide Ge species are reduced and Ge is alloyed to Pt a similar effect is produced and a modification of the metal function also occurs.

The increase of the population of acid sites of medium strength and the decrease of the amount of strong acids sites favors the formation of isomers and decreases the coking and cracking rates. The modification of the metal activity changes the activities for dehydrogenation and dehydrocyclization.

In summary, small amounts of Ge in trimetallic PtReGe/Al catalysts produce some improvements over the performance of standard bimetallic PtRe/Al catalysts. These improvements are related to the quality of the reformate product and the operation of the reactor. The reformate contains less aromatic hydrocarbons and more branched isoparaffins. The reformate thus complies better with current restrictions on the formulation of motor gasolines. The decreased coking and cracking rates improve both the liquid yield and the stability of the catalyst, which can be operated for longer times between regeneration shutdowns.

4. Conclusions

The trimetallic PtReGe/Al catalyst with a 0.1% Ge content was the most active in the reforming of n-heptane. It was also the most selective for the formation of isoparaffins and the most stable of the series.

Ge affects both functions of the catalyst simultaneously. It decreases the metal activity of Pt, it increases the population of acid sites of medium and weak acid strength and decreases the amount of strong acid sites. As a result and in comparison to the Ge-free PtRe/Al catalyst, the isoparaffins/aromatic molar ratio and the RON gain are enhanced, the contribution to hydrogenolysis is inhibited, cracking and coke formation are decreased and the stability of the catalyst is improved.

Ge contents between 0.1% and 0.6% improve the stability and the selectivity to isoparaffins but produce too high a decrease of the conversion in comparison to the parent PtRe bimetallic catalyst.

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