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Naphtha reforming Pt-Re-Ge/γ-Al_2O_3 catalysts prepared by catalytic reduction Influence of the pH of the Ge addition step

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Abstract

Pt-Re-Ge/γAl_2O_3 catalysts were prepared by the catalytic reduction method using different impregnation media (H_2O, HCl and NH_3) and different Ge contents (0.0, 0.1, 0.3, 1.0 and 2.0%). The influence of these preparation parameters on the activity for *n*-heptane conversion and the selectivity to toluene at atmospheric pressure was assessed. The catalysts were also characterized by ICP-AES, temperature programmed reduction, pyridine temperature programmed desorption and CO pulse chemisorption. The results show that as the pH is increased the Ge content increases and the catalysts present a lower hydrogenolytic activity and a lower toluene selectivity. Ge addition modifies both metal and acid functions. The catalyst with minimum Ge content prepared using water as impregnation medium has the best performance.

Keywords: Naphtha reforming; Trimetallic catalysts; Pt-Re-Ge; Catalytic reduction

1. Introduction

Catalytic reforming is one of the main processes of the petrochemical industry aiming to increase the octane number of virgin naphtha. Side reactions (hydrogenolysis and hydrocracking) produce light gases such as propane and butane. Catalytic reforming is also the main source of hydrogen in the refiner and is an important route to aromatic intermediate (benzene, toluene and xylenes).

During catalytic reforming long chain hydrocarbons are rearranged through isomerization, hydrogenation, dehydrocyclization and dehydrogenation reactions [1]. These reactions occur on acid and/or metal sites and they demand the use of bifunctional catalysts [2,3]. The acid function is typically provided by a solid support such as chlorinated alumina (Al_2O_3–Cl) and the metal function by a noble metal of the Group 8. The metal component is active for the hydrogenation and dehydrogenation reactions while the support has the acid strength necessary to promote the isomerization reactions. Synergetic action of both kinds of active sites promotes other reactions such as dehydrocyclization via a bifunctional reaction mechanism. Undesirable reactions such as hydrocracking and hydrogenolysis also occur lowering the yield of valuable products and deactivating the catalyst by the formation of coke on the active sites [4].

Reforming catalysts have been and continue to be studied and optimized. Current interests in this area of research are the influence of operating conditions on coke deposition (i.e. catalyst deactivation) and the influence of the formulation and preparation techniques on the activity and selectivity of the catalysts [5–7].

The advantage of the use of trimetallic catalysts over classic Pt-Re bimetallic catalysts is their lower coking rate and their higher resistance to deactivation [8,9]. These factors enable the process to be operated with smaller regeneration frequencies leading to a subsequent reduction of operating costs. For this

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reason many patents on trimetallic catalysts have been lately issued [10,11].

In this work, bimetallic Pt-Re/Al_2O_3 catalysts are modified by Ge addition introduced by catalytic reduction [12,13]. Particularly, the effect of the preparation conditions especially the pH value of the impregnation medium and the Ge amount on the catalytic performances are studied.

2. Experimental

2.1. Base catalyst Pt-Re/γ-Al_2O_3

γ-Al_2O_3 (Cyanamid Ketjen CK-300, pore volume = 0.5 $cm^3\ g^{-1}$, specific surface area = 180 $m^2\ g^{-1}$) was used as a support. It was previously calcined at 500 °C for 4 h in air in order to eliminate organic impurities. Then HCl (0.2 M) was added (1.5 $cm^3\ g^{-1}$) and after 1 h H_2PtCl_6 and NH_4ReO_4 were added. The slurry was gently stirred during 1 h at room temperature. Then it was slowly dried at 70 °C until a dry powder was obtained which was further dried overnight at 120 °C. Finally it was calcined in air (60 $cm^3\ min^{-1}$) at 300 °C and reduced with H_2 (60 $cm^3\ min^{-1}$) at 500 °C. The final content of Pt and Re were 0.3 and 0.3%, respectively. This catalyst is named as Pt-Re base catalyst.

2.2. Trimetallic catalysts

The apparatus used for the preparation had means for degassing the impregnating solution in order to remove dissolved oxygen. For the preparation of the trimetallic catalysts the base Pt-Re catalyst was first prereduced with H_2 (60 $cm^3\ min^{-1}$) for 1 h at 300 °C; then it was cooled down to room temperature under hydrogen atmosphere. The solution of $GeCl_4$ was then added and in amounts sufficient for obtaining Ge theoretical mass percentages of 0.1, 0.3, 1.0 and 2.0%. Such Ge solutions were previously diluted by adding suitable solutions to obtain a volume of 25 cm^3. These solutions were chosen in order to produce different pH in the impregnation medium: (i) pure water; (ii) aqueous NH_4OH; (iii) aqueous HCl (0.2 M). Before the degassing step the solution was let in contact with the catalyst for 1 h and hydrogen was bubbled at a rate of 300 $cm^3\ min^{-1}$. Then the solution was decanted and the catalyst was rinsed with distilled water. The catalyst was then dried in a hydrogen stream (60 $cm^3\ min^{-1}$, 100 °C) for 12 h. Finally it was reduced in this stream (60 $cm^3\ min^{-1}$) at 500 °C.

Prepared catalysts were named Pt-Re-Ge (x, y) (x = number, y = impregnating solution). The number gives the theoretical mass percentage of Ge deposited. $x = 0.0$ corresponds to the blank experiment, i.e. the preparation procedure was performed in the absence of $GeCl_4$.

2.3. Ge and Cl assessment

The composition of the metal function was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES). Chlorine on the support was determined by the Volhard–Charpentier method.

2.4. Temperature programmed reduction

This test allows one to assess the reducibility of the metal function and the degree of metal–metal and metal-support interactions. Reduction was performed up to 700 °C at a heating rate of 10 °C min^{-1}. Previously the samples were calcined at 400 °C (10 °C min^{-1}) for 1 h. An Ohkura TP2002S apparatus equipped with a thermal conductivity detector (TCD) was used.

2.5. Temperature programmed desorption of pyridine

This test was used for measuring the amount and strength of acid sites. Samples of 200 mg were impregnated with an excess of pyridine. Once the excess was removed, physisorbed pyridine was eliminated with a nitrogen stream at 110 °C for 1 h. Then the temperature was raised at 10 °C min^{-1} to a final value of 450 °C. In order to measure the amount of desorbed pyridine the reactor exhaust was connected to a flame ionization detector.

2.6. Dynamic chemisorption of CO

This technique was used to measure the dispersion of the Pt metal particles on the surface of the catalyst. Calibrated pulses of the adsorbate were injected in a stream of inert gas that flowed over the sample. These pulses were sent to the reactor until the sample was saturated. At the beginning of the experiment the sample (400 mg) was reduced at 500 °C (10 °C min^{-1}) for 1 h. Then nitrogen was made to flow over the sample for 1 h at 500 °C in order to eliminate adsorbed hydrogen. Then the sample was cooled down to room temperature in nitrogen and pulses of 0.6 μmole of CO were sent to the reactor.

2.7. n-Heptane test reaction

The reaction was performed in a fixed bed tubular reactor at 0.1 MPa, 500 °C, $H_2/n\text{-}C_7 = 6$ and WHSV = 4 h^{-1}. 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 by means of an on-line gas chromatography, using a ZB-1 capillary column and a flame ionization detector. The conversion of n-C_7 was defined as:

$$X = \frac{n\text{-}C_7^{i} - n\text{-}C_7^{o}}{n\text{-}C_7^{i}} \quad (1)$$

where n-C_7^{i} is the number of n-C_7 molecules at the reactor inlet and n-C_7^{o} is the number at the reactor outlet.

The selectivity to each product i was defined as:

$$S_i = \frac{\text{yield of } i}{X} = \frac{A_i f_i n_i}{M_i(\sum A_i f_i n_i / M_i)X} \times 100 \quad (2)$$

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

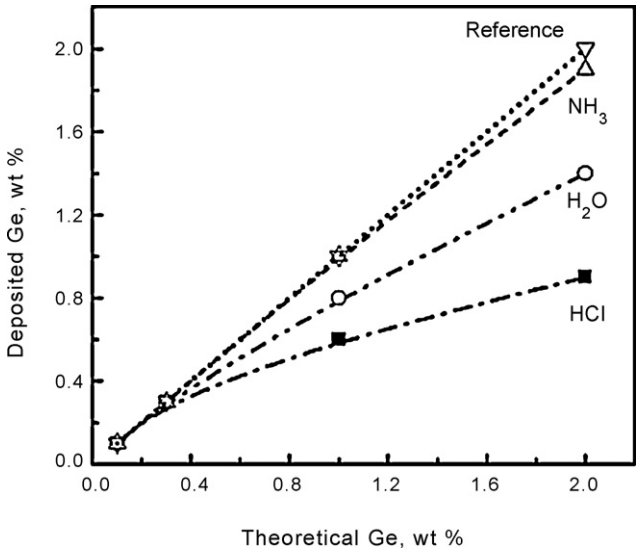

Fig. 1. Amount of deposited Ge on Pt-Re as a function of the theoretical Ge content for different media used.

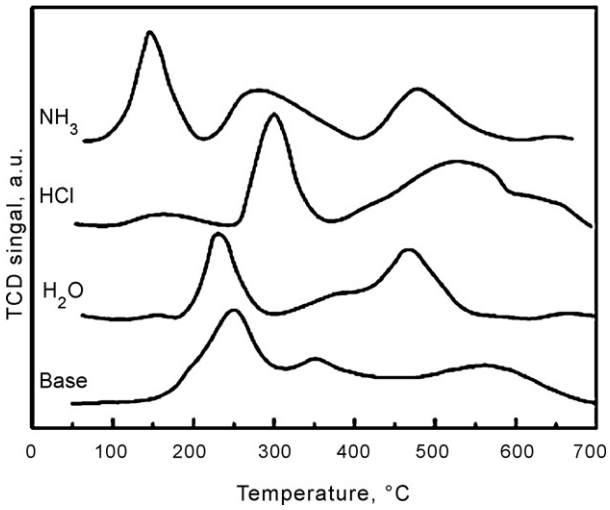

Fig. 3. TPR traces of Ge-free catalysts treated in different media Pt-Re-Ge (0.0, H_2O-HCl-NH_3) compared to the base catalyst.

3. Results and discussion

Fig. 1 shows the percentage of Ge deposited from different media (H_2O, HCl and NH_3) as a function of the theoretical (maximum) amount deposited. It can be seen that the amount deposited increases with the concentration in solution. The pH range values of the impregnating solutions were 3.8–4.3 for H_2O, 2.0–2.2 for HCl and 9.5 for NH_3. Higher pH values improve the deposition of Ge on the catalyst surface. Fig. 2 shows the variation of the Cl percentage of the catalysts as a function of the theoretical Ge amount. At higher Ge concentration values of the impregnating solutions the Cl content increases. These results could be related to the incorporation of Cl from $GeCl_4$.

The final amount of Cl on the catalysts prepared using H_2O and HCl in the impregnation was 1.1–1.3%. When the NH_3 solution was used this value decreased to 0.2–0.4%. The low final concentration of chlorine in the catalysts impregnated with a NH_3 solution is supposed to be due to the formation of NH_4Cl in solution that is eliminated during the washing step.

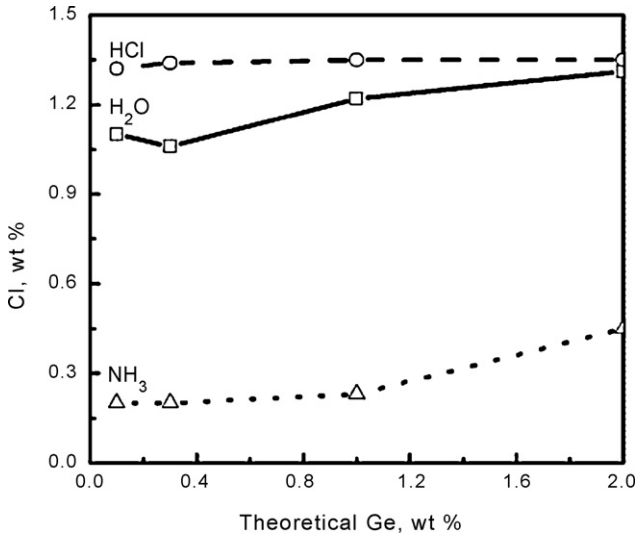

Fig. 2. Percentage of Cl on Pt-Re-Ge catalysts as a function of the theoretical Ge content for different media used.

In previous reports [14–16] it was found that subjecting the Pt-Re/Al_2O_3 to the conditions of the catalytic reduction method produces a modification of the metal function of the catalyst even if no promoter is impregnated. For this reason additional blank experiments with no Ge addition were performed. Fig. 3 shows the results of these blank experiments. TPR traces of the catalysts treated in H_2O, HCl and NH_3 (with no Ge addition) are compared to that of the untreated base Pt-Re catalyst. The base catalyst presents three reduction peaks. The first one located at 250 °C corresponds to the reduction of Pt and some Re in strong interaction with Pt. The second peak at 350 °C is attributed to the reduction of Re by the catalytic action of Pt. The third peak at 570 °C is due to the reduction of segregated Re. In the case of the catalysts treated with HCl a shift of the reduction peaks to higher temperatures can be seen. This was attributed to an increase of the chlorine concentration on the catalysts and therefore of the metal-support interaction. High values of the metal-support interaction would demand a higher reduction temperature. An opposite effect is seen in the catalysts treated with NH_3, i.e. the loss of chlorine produces a shift of the reduction peaks to lower temperatures.

Fig. 4 shows the TPR traces of the catalysts with a theoretical amount of 1% Ge impregnated in different media. In all cases the high temperature reduction peak (at about 500–600 °C) is bigger than that of the base catalyst (Fig. 3). This is due to the reduction of segregated Ge. The reduction zone at 240–480 °C in the TPR trace of the HCl impregnated catalyst indicates a strong Pt-Re-Ge interaction. The Pt-Re-Ge (1, NH_3) catalyst also has a smaller peak in the zone of intermediate reduction. This could be due to a lower interaction between the metals. A similar behavior was detected when analyzing the TPR traces of the other catalysts. It can be concluded that the degree of interaction between the

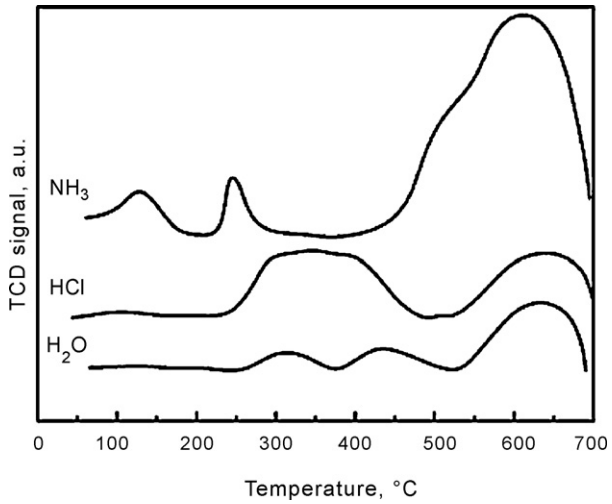

Fig. 4. TPR traces of Pt-Re-Ge (1, H_2O-HCl-NH_3) catalysts.

components of the metal phase follows the order: HCl > H_2O > NH_3. In order to study the influence of the addition of different Ge amounts the results obtained when using the HCl 0.2 M impregnating solution were analyzed. The corresponding TPR traces are plotted in Fig. 5. It can be seen that the peak of Pt reduction (located at 250 °C in the Pt-Re catalyst) is shifted to higher temperatures as the Ge content is increased. This shift is due to the interaction between Pt and Ge. The size of the reduction peak at 350–500 °C is also increased probably because of the reduction of Ge deposited in the neighborhood of Pt particles. Finally the growth of the peak of reduction at temperatures higher than 600 °C is remarkable. This effect is attributed to the reduction of segregated Ge. The decreased reducibility of Pt particles by Ge addition and the corresponding shift of the Pt reduction peak to higher temperatures has been reported by de Miguel et al. [17]. These results indicate that one part of Ge is deposited on the metal or in its neighborhood and another part on the support, far from Pt particles.

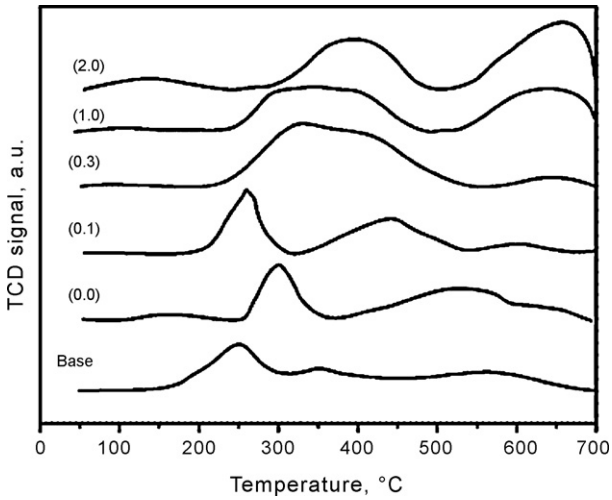

Fig. 5. TPR results corresponding to the base Pt-Re catalyst, the Pt-Re (0.0) blank catalyst and the Pt-Re-Ge (0.1-0.3-1-2, HCl) catalysts.

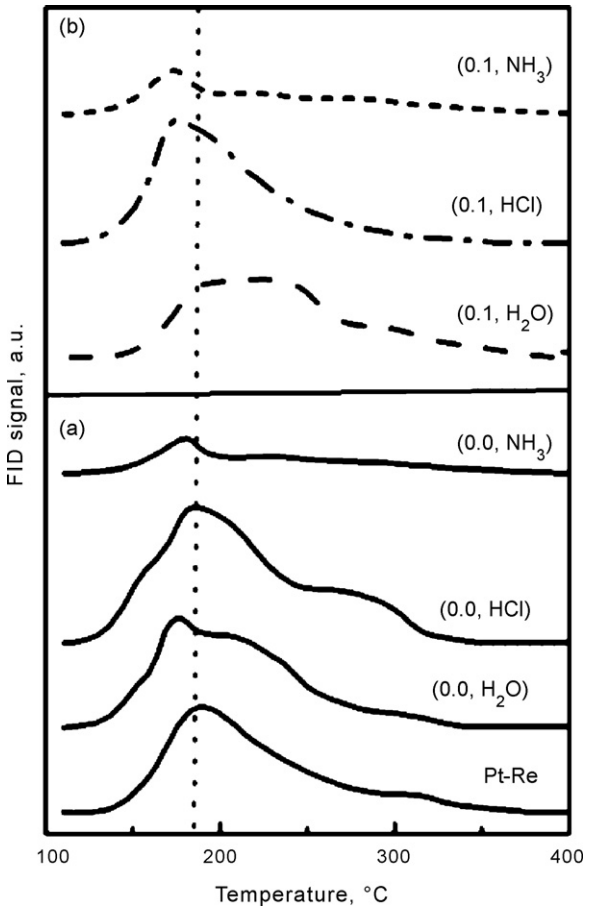

Fig. 6. TPD results. (a) Pt-Re and Pt-Re-Ge (0.0, H_2O-HCl-NH_3); (b) Pt-Re-Ge (0.1, H_2O-HCl-NH_3).

Pyridine is adsorbed on acid sites due to its basic character. Its desorption at low temperatures is related to the presence of weak acid sites while the desorption at high temperatures is related to the presence of strong acid sites. The total area under the TPD trace is representative of the total acidity of the catalyst.

Fig. 6a shows the pyridine TPD traces for the base Pt-Re catalyst and for the catalysts treated in different impregnation media and without Ge. It can be seen from the results of Fig. 6a that when a HCl solution is used as impregnation medium an increase of the acidity with respect to the base catalyst is produced. The increase of the acidity in the 220–320 °C zone is remarkable. When only water is used there is a small acidity increase. Conversely the addition of NH_3 during the preparation decreases the acidity of alumina and this effect seems to be related to the elimination of chlorine.

Fig. 6b shows the TPD results of the catalysts with 0.1% Ge (theoretical) prepared in different media. A similar trend as that seen in Fig. 6a is found with respect to the influence of the pH. It is also found that the addition of small amounts of Ge does not greatly modify the TPD traces in comparison with the TPD trace of the blank PtRe (0.0) catalyst treated by the catalytic reduction method.

Fig. 7 shows the results of the pyridine TPD test of the catalysts with a theoretical content of Ge of 0.1 and 2 wt.%

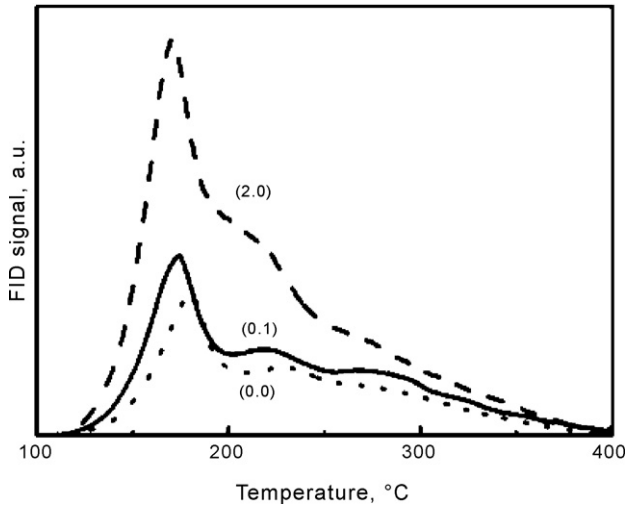

Fig. 7. Pyridine TPD traces of Pt-Re-Ge (0.0-0.1-2, NH_3) catalysts.

prepared in NH_3. Ge addition increases the acidity of the catalyst in accord with the results of Fig. 2 that showed an increase of the Cl content as the Ge theoretical amount was increased. However the amount of strong acid sites (desorbing at 300–400 °C) is not very much modified. Table 1 shows the relative values of the area below the pyridine TPD curves taking the value of the base catalyst as a reference. It can be seen that the addition of Ge in NH_3 produces a marked increase of the acidity of the catalyst while the addition of Ge in H_2O produces a minor effect. On the other hand, in the case of the catalysts prepared in HCl a decrease of the acidity upon Ge addition can be seen. This effect can be explained by the simultaneous action of Cl and Ge. In the case of the catalysts prepared in NH_3 the chlorine content varies from 0.2 to 0.4% when the Ge loading is increased to 2% (theoretical). The acidity is thus increased due to the combined action of Cl and the Ge oxides which are weak acids. In the case of the catalysts prepared in HCl, the Cl content remains practically constant at about 1.3% and therefore the acidity variation can only be attributed to the effect of the Ge oxides. The acidity decrease is a consequence of the weak acidity of the Ge oxide that probably blocks the strong acid sites of the support. In the case of the catalysts prepared in water the behavior is intermediate between those of the catalysts prepared in HCl and NH_3.

The results of CO chemisorption over selected catalysts are presented in Table 2. It is important to point out that previous reports have shown that both Ge and Re do not chemisorb CO at the conditions of the tests [18]. As Ge is added to the catalyst the amount of Pt atoms chemisorbing CO decreases indicating that the interaction between Ge and the active phase increases. This effect can be explained by existence of geometrical or electronic effects. In the first case Ge species are supposed to block the surface Pt atoms. In the second Ge would modify the electronic density of Pt and cause a decrease of its capacity for chemisorbing CO.

Table 1
Ratio between the pyridine TPD area of Pt-Re-Ge catalysts and the pyridine TPD area of the Pt-Re base catalyst

Catalyst	Impregnating solution		
	NH_3	H_2O	HCl
Pt-Re-Ge (0.0)	0.33	1.00	1.44
Pt-Re-Ge (0.1)	0.43	0.90	1.35
Pt-Re-Ge (0.3)	0.48	0.80	1.25
Pt-Re-Ge (1)	0.57	1.10	1.10
Pt-Re-Ge (2)	0.85	1.10	1.10

Table 2
CO/Pt atomic ratio values as obtained by CO chemisorption

Catalyst	CO/Pt
Pt-Re	0.47
Pt-Re-Ge (0.1, H_2O)	0.45
Pt-Re-Ge (2, H_2O)	0.31
Pt-Re-Ge (0.1,NH_3)	0.50
Pt-Re-Ge (2, NH_3)	0.39
Pt-Re-Ge (0.1, HCl)	0.44
Pt-Re-Ge (2, HCl)	0.26

Fig. 8 shows the values of n-C_7 conversion as a function of time for the catalysts prepared by catalytic reduction, Pt-Re-Ge (0.1, H_2O, HCl, NH_3). These results are compared with those corresponding to the base Pt-Re catalyst. It can be seen that the Pt-Re base catalyst had an initial conversion of 80%. Conversion decreased with time-on-stream. This was due to the formation of coke deposits on the metal and acid functions of the catalyst [19,20]. The same deactivation phenomenon occurred in the Ge doped catalysts. When Ge deposition was performed in water the catalytic activity was improved. The alkaline impregnation produced catalysts with low activity and the acid impregnation (in HCl) did not affect greatly the activity of the base catalyst. This could be due to three factors: (a) the different amount of Ge deposited; (b) the different distribution of Ge (over the metal and acid functions); (c) the different acidity. Table 3 shows the conversion values at 240 min time-on-stream for the different

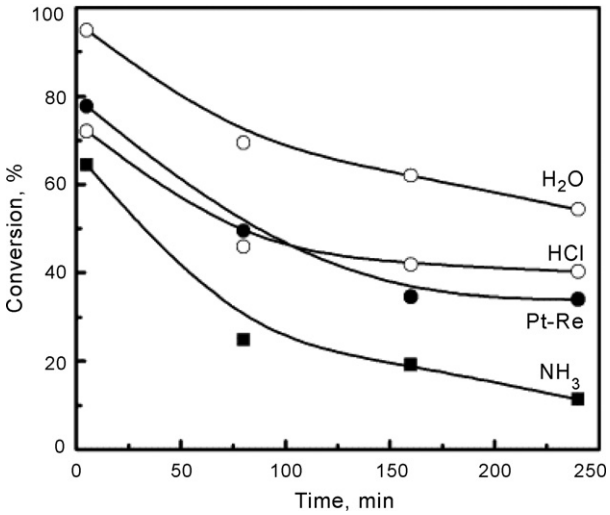

Fig. 8. Conversion of n-C_7 as a function of time-on-stream. Pt-Re and Pt-Re-Ge (0.1) catalysts.

Table 3
Conversion of n-C_7 at 240 min time-on-stream

Impregnating solution	Ge (%)			
	0.1	0.3	1.0	2.0
H_2O	54.6	38.1	23.4	19.2
HCl	40.7	32.1	15.8	12.1
NH_3	11.8	13.7	9.3	4.20

Table 4
Selectivity to toluene at 240 min time-on-stream

Impregnating solution	Ge (%)			
	0.1	0.3	1.0	2.0
H_2O	62.9	59.6	47.8	32.4
HCl	54.3	47.0	47.6	35.6
NH_3	53.9	47.0	42.3	38.4

catalysts as a function of the theoretical amount of Ge and the kind of impregnation media. When the amount of Ge in the impregnating solution increases the catalytic activity decreases due to a higher deposition of Ge that blocks the active sites of the catalysts. The most active catalysts were obtained when Ge impregnation was performed in water. The least active was the catalyst prepared in alkaline medium. Values of the selectivity to toluene are presented in Table 4. It is important to point out that the selectivity to toluene of the bimetallic Pt-Re catalyst was 51.1%. Therefore the addition of small Ge amounts (0.10%) increases the selectivity to toluene. Catalysts with higher Ge loading have lower selectivities. The values of Table 4 also indicate that the catalysts prepared in water have a greater selectivity to toluene. A low selectivity to toluene could be explained by a deposition of Ge on Pt-Re ensembles or in their neighborhood thus producing an unfavorable modification of the acid strength in the vicinity of the active metals responsible for producing olefins. These olefins are reaction intermediates that are converted into cyclic compounds over acid sites and further dehydrogenated afterwards to produce aromatic compounds. Dehydrocyclization is a bifunctional reaction controlled by the acid function [21,22].

The Pt-Re base catalyst has a selectivity to light gases (C_1–C_4) of 24.7. As it can be seen in Table 5 these selectivity values are decreased upon Ge addition. This decrease must be attributed to the effect of Ge species deposited partly on the metal and partly on the support. Indeed, Ge on the support produces a modification of the acid strength. As pointed out previously in the case of the catalysts prepared in NH_3, the Ge increases the total acidity but does not greatly modify the strong acid sites responsible for the cracking reactions. A similar phenomenon would explain the lower formation of light gases in the case of the catalysts prepared in H_2O and HCl. The total acidity is decreased in the case of the latter as the Ge content is increased. The best trimetallic catalyst seems to be the one prepared in water with a low Ge content (0.1 wt.%). This confirms that a good trimetallic should have a medium acidity and that a low content of an inactive modifier such as germanium produces an adequate balance between the acid and metal functions.

Table 5
Selectivity to light gases (C_1–C_4) at 240 min time-on-stream

Impregnating solution	Ge (%)			
	0.1	0.3	1.0	2.0
H_2O	17.3	11.8	9.8	6.8
HCl	24.2	15.3	10.2	6.5
NH_3	5.9	4.3	4.3	3.0

The decrease of the light gases yield is due to the inhibition of the cracking reactions that take place on the acid sites of the catalyst. Ge addition also decreases the effective size of the Pt-Re ensembles that produce methane by hydrogenolysis.

4. Conclusions

Catalytic reduction methods enable the deposition of variable amounts of Ge over the Pt-Re/Al_2O_3 catalyst. The magnitude of the deposition depends on the pH of the impregnating solution. The increase of the pH favors the deposition of Ge.

The TPR results indicate that the choice of the impregnation medium influences the final metal-support interaction. When diluted ammonia is used for impregnation the catalyst retains less chlorine and the metals are reduced at a lower temperature indicating that the metal-support interaction is weak. The opposite occurs when an HCl solution is used for impregnation. The behavior in the case of the impregnation with an aqueous neutral solution is intermediate. The degree of metal-support interaction follows the order: $HCl > H_2O > NH_3$.

With respect to the acidity of the Pt-Re-Ge/Al_2O_3 catalyst the main conclusions are the following:

- the total acidity of the catalyst decreases as the pH of the Ge deposition medium increases;
- when using the NH_3 solution, the higher the amount of Ge deposited the higher the total acidity of the catalyst. When HCl is used the opposite trend is seen though the medium and weak acidity increase. An intermediate behavior is observed in the case of the aqueous solution. It produces a catalyst of intermediate acidity that displays the best values of activity and selectivity to toluene. The catalysts with a low amount of Ge were more selective for the formation of toluene.

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