

Effect of the method of addition of Ge on the catalytic properties of Pt–Re/Al₂O₃ and Pt–Ir/Al₂O₃ naphtha reforming catalysts

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Abstract

Pt–Re/Al₂O₃ and Pt–Ir/Al₂O₃ catalysts were modified by addition of an inactive metal, germanium, in order to suppress the strong hydrogenolytic activity of these types of catalysts. The influence of the addition method of germanium over Pt–Re and Pt–Ir catalysts was studied in order to find which one (catalytic reduction, successive impregnations and coimpregnation methods were used) produced the best trimetallic catalysts in terms of activity, selectivity and passivation of the hydrogenolytic activity of the metal function of the parent bimetallic catalyst. Ge addition produces a significant decrease of the activity of the metal function, affecting both non-demanding and demanding reactions and also the methane production during *n*-heptane reforming. It also produces an inhibition of the acid function but the resulting acid/metal activity ratio is higher than that of the bimetallic parent catalysts. Catalytic reduction was found to be the best method of Ge addition in the case of the Pt–Ir catalyst series, producing the most stable catalysts, with the lowest cracking and the highest toluene yield. The same was true for the Pt–Re catalysts prepared by coimpregnation.

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1. Introduction

During naphtha reforming a complex reaction network takes place which includes both desired and undesired reactions. The desired transformations are dehydrogenation of naphthenes, isomerization and dehydrocyclization of paraffins. Undesired reactions are the hydrogenolysis and the cracking of paraffins that produce light gases of negligible value and decrease the overall liquid C₅₊ yield. Coking is another secondary reaction which rate needs to be decreased in order to prevent the premature deactivation of the catalyst by the accumulation of carbon deposits on the active sites. It is widely accepted that the hydrogenation-dehydrogenation reactions occur over the catalyst metal sites while isomerization and dehydrocyclization proceed by a bifunctional metal–acid mechanism that is con-

trolled by the acid function. For this reason the naphtha reforming catalysts need to have two catalytic functions. The metal function is usually provided by Pt in the form of very small particles dispersed on the surface of the catalyst and its properties are fine-tuned by the addition of another element, the so-called metal function promoter that can be another noble metal, e.g. Ir, or another element with the desired properties (Sn, Ge). The acid function is provided by the support itself and in most applications is γ -Al₂O₃ treated with chlorine in order to increase its surface acidity. The first Pt/Al₂O₃–Cl catalyst was patented in 1949 [1]. The reaction on this catalyst had to be performed at high pressure (30 atm) in order to prevent deactivation and keep a stable activity level. In 1968, Chevron patented a Pt–Re/Al₂O₃–Cl catalyst [2] that enabled the whole process to be run at a lower pressure, with an increased C₅₊ yield, an enhanced selectivity to aromatics and a higher production of hydrogen. This bimetallic naphtha reforming catalyst produced a big leap forward in the

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technology of reforming catalysts and it was later followed by other bimetallic catalysts that tried to improve its properties, Pt–Ir/Al₂O₃–Cl, Pt–Sn/Al₂O₃–Cl and Pt–Ge/Al₂O₃–Cl being the most remarkable followers [3–5]. The Pt–Re and Pt–Ir catalysts had a strong hydrogenolytic capacity and sulfiding pretreatments had to be incorporated in the industrial practice to prevent the dangerous exothermal runaway produced by massive C–C bond cleavage of the feedstock in the early stages of the reaction.

The concept of modifying the properties of Pt by the addition of another element that can get in close interaction with it by means of chemical affinity has been further extended in the later years. Nowadays many patents propose the use of three or more components in the metal function [6–10] and the main focus of the innovations has been the increase of the selectivity to certain products or the improvement of the stability. These materials have been mainly developed at industrial laboratories and their composition is not accurately known or it has not been disclosed. The patents literature is too vague and of little use to elucidate their composition.

The objective of this work was to compare three different methods of addition of an inactive element, germanium, in order to improve the catalytic properties of Pt–Ir and Pt–Re naphtha reforming catalysts. Apart from the usual targets of high C₅₊ yield and stability the main focus of the work was to control the hydrogenolytic activity of the metal. The properties of the thus synthesized trimetallic catalysts were compared with those of presulfided bimetallic Pt–Ir and Pt–Re catalysts in order to see if a similar performance could be obtained. Indeed, the elimination of the sulfiding step in the industrial practice is considered to be of practical economical importance. A constant Ge content was used (0.3%) and three different methods of Ge addition were tried in order to determine the most convenient one. The methods tried were coimpregnation, successive impregnations and catalytic reduction. The metal and acid functions of the catalysts were characterized with a set of physicochemical techniques and test reactions. *n*-Heptane reforming under industrial conditions was used as a global performance test and the catalysts were compared in terms of conversion, toluene yield, hydrogenolytic activity and stability.

2. Experimental

2.1. Catalysts preparation

Pt–Ir–Ge/Al₂O₃ catalysts were prepared using a γ -alumina support supplied by AXENS (GOD, 210 m² g⁻¹, 0.60 cm³ g⁻¹). Pt–Re–Ge/Al₂O₃ catalysts were prepared using another alumina supplied by Ketjen (CK-300, 200 m² g⁻¹, 0.55 cm³ g⁻¹). The different supports used followed no purpose but reflect the different supply sources at the French and Argentine laboratories. The supports were crushed and sieved in order to keep the particles with sizes between 0.25 and 0.40 mm and then they were calcined in flowing air at 450 °C for 4 h. Pt–Re/Al₂O₃ catalysts were

prepared by coimpregnation of hexachloroplatinic acid (H₂PtCl₆) and ammonium perrhenate (NH₄ReO₄). The concentration of the impregnation solution was adjusted in order to get a final 0.3 wt% Pt and 0.3 wt% Re on the bimetallic catalyst. Pt–Ir/Al₂O₃ catalysts were prepared by coimpregnation of H₂PtCl₆ and H₂IrCl₆ and in this case the concentration of the noble metals in the final catalysts was 0.55 wt% Pt and 0.05 wt% Ir. The impregnation procedure was the same for both bimetallic catalysts. A certain amount of alumina was left in contact with hydrochloric acid for 1 h (1.5 cm³ HCl 0.2 mol L⁻¹ per gram of alumina). Then the solutions of precursor salts were added to the system and this was gently stirred for 1 h at room temperature. After drying in a water bath at 70 °C, the powders were put in a stove at 120 °C overnight. The catalysts were finally conditioned by heating in air at 300 °C for 4 h, flushing with nitrogen and then reducing in hydrogen (60 cm³ min⁻¹) at 500 °C for 4 h. Heating ramps were programmed at 10 °C min⁻¹.

For the sake of simplicity from now, the catalysts will be named with the only reference to the components of the metal function, e.g. Pt–Re stands for Pt–Re/Al₂O₃.

Trimetallic catalysts, Pt–Re–Ge and Pt–Ir–Ge, were prepared by three different methods: coimpregnation, successive impregnations and catalytic reduction. The impregnation solutions of GeCl₄ were regulated in order to get 0.3 wt% in the final catalysts (0.3Pt–0.3Re–0.3Ge and 0.55Pt–0.05Ir–0.3Ge).

For the coimpregnated catalysts, the technique used was the same as that described for the preparation of the bimetallic catalysts. For the successively impregnated catalysts, the 0.3Pt–0.3Re and 0.55Pt–0.05Ir bimetallic catalysts were acidified with HCl 0.2 mol L⁻¹ (1.5 cm³ per gram of alumina) and the slurry was gently stirred for 1 h. Then an appropriate amount of freshly prepared aqueous GeCl₄ solution was added and the slurry was gently stirred for another hour. Then the water was slowly evaporated by putting the containing vessel in a water bath at 70 °C. The solid was then dried at 120 °C overnight. The final catalysts were obtained by reducing at 500 °C in hydrogen (60 cm³ min⁻¹ H₂ for 4 h).

For the catalytic reduction, trimetallic catalysts were in this case prepared by making use of the catalytic action of the metal function of the bimetallic catalyst. A portion of the Pt–Re (or Pt–Ir) catalyst was placed in a fixed bed glass reactor. The reactant (GeCl₄ solution) was added dropwise from an ampoule placed above the reactor. Hydrogen or nitrogen was allowed to bubble through the catalyst bed or the ampoule from a three-way valve. The preparation procedure was the following: the bimetallic catalyst was first reduced at 500 °C for 1 h in hydrogen (60 cm³ min⁻¹) and then it was let to cool down to room temperature while keeping the flow of hydrogen. GeCl₄ solution (25 mL) with the appropriate concentration were placed in the ampoule and were degassed by bubbling nitrogen for 10 min. Then the solution was poured in the reactor and left in contact with the catalyst for 1 h under a constant hydrogen flow

(300 cm³ min⁻¹). After reaction, the solution was drained and the catalyst was dried by injecting hydrogen (60 cm³ min⁻¹), raising the bed temperature to 100 °C and keeping this temperature overnight. Finally the catalyst was activated by reduction in hydrogen (60 cm³ min⁻¹) at 500 °C for 2 h. All heating rates were set at 2 °C min⁻¹ to eliminate temperature gradients in the bed.

2.2. Catalysts characterization

The composition of the metal function was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after digestion in an acid solution and dilution. The chlorine content of the catalysts in their final state, i.e. after reduction in hydrogen at 500 °C for 2 h, was determined by means of potentiometry.

2.2.1. Temperature programmed reduction (TPR)

The experiments of temperature programmed reduction were performed in an Ohkura TP2002S apparatus equipped with a TCD detector, using 200 mg of samples. The samples used were those in the final state (after reduction at 500 °C). They were further reoxidized at 250 °C in situ by heating in a stream of 5%O₂/Ar for 1 h. After flushing the system with argon, the TPR test was started with a 10 °C min⁻¹ heating rate under a flow of a 5%H₂/Ar mixture. The final temperature was 700 °C.

2.2.2. Cyclopentane hydrogenolysis

Before the reaction the catalysts were reduced for 1 h at 500 °C in H₂ (60 cm³ min⁻¹). Then they were cooled in H₂ to the reaction temperature (350 °C). The other conditions are specified in Table 1. The reaction products were analyzed in a gas chromatograph connected on-line.

Table 1
Catalysts properties

Catalyst	Preparation method ^a	Ge (wt%) ^b	CH ^c	CP ^d
Pt–Re	CI	0.00	1.00	1.00
Pt–Re PreS	CI	0.00	0.60	0.15
Pt–Re–Ge	SI	0.29	0.64	0.13
Pt–Re–Ge	CI	0.30	0.70	0.38
Pt–Re–Ge	CR	0.26	0.59	0.22
Pt–Ir	CI	0.00	1.00	1.00
Pt–Ir PreS	CI	0.00	0.80	0.18
Pt–Ir–Ge	SI	0.29	0.22	0.11
Pt–Ir–Ge	CI	0.31	0.30	0.17
Pt–Ir–Ge	CR	0.29	0.40	0.17

Ge content as obtained by ICP-AES. Relative activity values, taking the bimetallic catalyst prepared by coimpregnation (CI) as a reference. Cyclohexane (CH) and cyclopentane (CP) reactions.

^a CI, coimpregnation; SI, successive impregnations; CR, catalytic reduction.

^b Pt–Re catalyst composition: Pt = 0.224%, Re = 0.23%. Pt–Ir catalyst composition: Pt = 0.55%, Ir = 0.05%.

^c Cyclohexane dehydrogenation, 350 °C, 0.1 MPa, catalyst mass = 10 mg, H₂ flow rate = 100 cm³ min⁻¹, CH flow rate = 2 cm³ h⁻¹.

^d Cyclopentane hydrogenolysis, 350 °C, 0.1 MPa, catalyst mass = 150 mg, pressure = 0.1 MPa, H₂ flow rate = 40 cm³ min⁻¹, CP flow rate = 0.483 cm³ h⁻¹.

2.2.3. Cyclohexane dehydrogenation

The reaction was performed in a glass reactor with the conditions described in Table 1. The reaction products were analyzed in a gas chromatograph with a flame ionization detector connected on-line. The only detected product was benzene.

2.2.4. Isomerization of 3,3-dimethyl-but-1-ene (33DMB1)

This reaction was used to selectively and quantitatively determine the concentration of the Brønsted sites of the catalyst. The conditions of the reaction are detailed in [11].

2.2.5. Temperature programmed desorption (TPD) of pyridine

The amount of the acid sites of the catalysts was assessed by means of temperature programmed desorption of pyridine. The conditions of the reaction are described in [12].

2.2.6. FTIR of adsorbed pyridine

The fourier transformed infra-red spectroscopy (FTIR) of adsorbed pyridine was used to determine the number of Lewis acid sites on the catalysts using a method described elsewhere [11].

2.3. *n*-Heptane conversion

The *n*-heptane conversion reaction was carried out with 1 g of catalyst in a continuous flow reactor at 5 bar and 500 °C. The reactant mixture consisted of a 3:1 H₂/*n*C₇ gas mixture, and the space velocity used was 2 h⁻¹. Effluent products were analyzed by an on-line chromatograph (Varian 3400) using a FID and equipped with a CP-Sil 5 capillary column.

3. Results and discussion

Table 1 displays a summary of the properties of the catalysts used, including their preparation method and the composition of the metal phase as obtained by ICP-AES. Table 1 also presents the activity values corresponding to the test of cyclohexane dehydrogenation and cyclopentane hydrogenolysis, written in relative terms with the sulfided bimetallic catalysts as point of reference. As expected sulfidation strongly suppresses the hydrogenolytic activity of Pt–Ir and Pt–Re catalysts and also reduces the activity in cyclohexane dehydrogenation to some extent. Cyclopentane hydrogenolysis activity was reduced to about one fifth its original value. Activity in cyclohexane dehydrogenation was less affected; there is a 20% reduction for the Pt–Ir catalyst and 40% for the Pt–Re one.

Ge addition inhibits also the dehydrogenation and hydrogenolysis activities but the effect is milder in the case of Pt–Re–Ge catalysts. This could be explained in terms of less interaction of Ge with the bimetallic Pt–Re particles and/or of different particle sizes depending on the preparation procedure. The activity drop is higher for cyclopentane hydrogenolysis than that found in the case of the

cyclohexane reaction, a fact that is easily explained by recalling that the cleavage of C–C bonds of cyclopentane is a demanding reaction and that the big ensembles of the original active phase are reduced in size by the dilution effect of interspersed Ge atoms. The catalysts prepared by successive impregnations (Ge added in the last place) displayed the lowest hydrogenolytic activity. This could indicate that this method was the most effective for producing Ge-(active phase) clusters in high interaction. Carvalho et al. [12] have indicated that during the successive impregnations of metal promoters the first elements (Pt and Re or Pt and Ir in our case) interact more strongly with the support while the element introduced in the last position (Ge in our case) encounters a more stabilized support surface in terms of adsorption and hence interacts more strongly with the metal function. Notably and contrary to previous reports [13–15], the catalytic reduction method does not seem to produce the catalysts with the highest interaction in their metal function. One explanation for the low interaction obtained is that a great proportion of Ge during the liquid phase catalytic reduction was not deposited over the metal but was anchored on other places of the support instead. If this was the case it must be concluded that the adsorption of Ge by electrostatic coulombic attraction on the support supersedes the affinity between Ge and the metal phase. Obviously, these Ge species did not migrate to the metal function during the reducing treatments.

TPR experiments were performed in order to compare the different trimetallic catalysts and to evidence the possible deposition of germanium on the support. Results corresponding to the TPR tests on Pt–Re–Ge and Pt–Ir–Ge are included in Fig. 1a and b. It has been demonstrated by Lieske et al. [16] and Lietz et al. [17] on Pt/Al₂O₃ that the TPR profiles depend strongly on the type and temperature of treatment undergone by the catalyst. However, as before the TPR all the trimetallic catalysts were submitted to the same pretreatment (reduction at 500 °C and reoxidation at 250 °C), the TPR profiles obtained for each series can be compared. Fig. 1a and b show that for a same composition (Pt–Re–Ge or Pt–Ir–Ge), the TPR profiles, and then the reducible species present in these samples, are different depending on the preparation method. The hydrogen uptake at temperatures higher than 500 °C, which is observed in all cases, could be attributed either to the reduction of isolated Re and/or Ge oxides in the Pt–Re series (Fig. 1a) or to the reduction of isolated Ge oxides spe-

Table 2

Assessment of the amount of Brønsted acid sites with the reaction of 3,3-dimethyl-but-1-ene and of the total amount of acid sites by means of thermally programmed desorption of pyridine

Catalyst	Preparation method ^a	wt% Cl ^b	Relative Brønsted acidity	Relative total acidity
Al ₂ O ₃ –Cl CK-30	–	1.39	2.12	1.35
Pt–Re	CI	1.35	1.00	1.00
Pt–Re–Ge	SI	1.39	0.89	0.94
Pt–Re–Ge	CI	1.43	0.79	0.84
Pt–Re–Ge	CR	1.18	0.70	0.67
Al ₂ O ₃ –Cl GFS	–	1.35	2.33	1.35
Pt–Ir	CI	1.37	1.00	1.00
Pt–Ir–Ge	SI	1.34	0.77	0.72
Pt–Ir–Ge	CI	1.29	0.65	0.64
Pt–Ir–Ge	CR	1.17	0.79	0.83

^a CI, coimpregnation; SI, successive impregnation; CR, catalytic reduction.

^b Determined by elemental analysis (ICP-AES), after the last step of reduction at 500 °C.

cies in the Pt–Ir series (Fig. 1b), the other species being reduced at lower temperature [18–21].

Table 2 contains values of the amount of the chlorine content, the Brønsted and the total acidities. The results were written in terms of relative acidity in order to make the results comparable since they come from different sources: pyridine TPD data in the case of the total acidity and 33DMBI isomerization for the Brønsted acidity. For all the catalysts, the chlorine content is in the same range, between around 1.2 and 1.4 wt%. From the comparison between chlorinated aluminas and the multimetallic catalysts, it can be seen that the presence of metal promoters decreases the Brønsted and the total acidities of the support. This effect is less significant with the bimetallic Pt–Re catalyst than with the Pt–Ir one. Trimetallic catalysts present lower Brønsted and total acidities than the corresponding bimetallic ones. The acidity decrease produced by Ge addition can be explained by the blocking of acid sites by Ge species. It can also be seen that the decrease in Brønsted acidity observed when Ge is added is accompanied by a proportional change of total acidity. In order to estimate the amount of Lewis sites in the conditions of reaction, FTIR measurements were performed on two catalysts, unsulfided Pt–Re and Pt–Re–Ge CR, pretreated in the same conditions of the catalytic test of *n*-heptane reforming (500 °C, H₂). The amount of acid sites was 206 μmol g⁻¹ for Pt–Re and 117 μmol g⁻¹ for Pt–Re–Ge CR. It can be seen that there is a decrease of the concentration of Lewis acid sites upon Ge addition. Then it can be concluded that Ge addition decreases the population of both kinds of acid sites simultaneously.

n-Heptane conversion values, yields in different products, *i*-butane/*n*-butane ratio values and coke contents for the Pt–Ir and Pt–Re catalysts can be found in Tables 3 and 4.

Toluene is an interesting product for petrochemicals industry whereas the formation of C₁ to C₄ cracking products should be avoided.

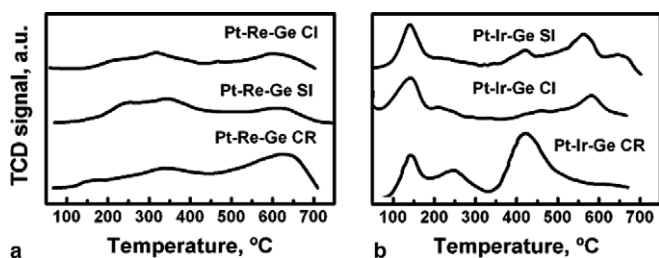


Fig. 1. Temperature programmed reduction results: (a) Pt–Re–Ge catalysts and (b) Pt–Ir–Ge catalysts.

Table 3
Conversion of *n*-heptane under industrial-type conditions (500 °C, 5 bar)

Catalyst	Preparation method	Time of reaction (h)	Conversion (%)	Toluene (%)	C ₁ –C ₄ (%)	Methane (%)	Propane (%)	(<i>i</i> -C ₄ / <i>n</i> -C ₄)	Coke (%)
Pt–Ir	CI	6	100	45.7	41.7	4.0	14.1	0.75	
		20	100	43.0	42.1	3.1	13.9	0.85	1.2
Pt–Ir–Ge	CI	6	98.1	40.9	35.7	1.9	12.0	1.07	
		20	97.3	42.0	32.4	1.6	10.8	1.16	2.2
	SI	6	99.1	46.1	34.8	1.6	11.2	1.24	
		20	98.1	41.9	33.4	1.4	10.7	1.25	2.9
	CR	6	99.3	45.8	35.6	1.4	11.5	1.27	
		20	98.5	45.2	33.5	1.3	10.8	1.28	2.8

Pt–Ir catalysts series.

Table 4
Conversion of *n*-heptane under industrial-type conditions (500 °C, 5 bar)

Catalyst	Preparation method	Time of reaction (h)	Conversion (%)	Toluene (%)	C ₁ –C ₄ (%)	Methane (%)	Propane (%)	(<i>i</i> -C ₄ / <i>n</i> -C ₄)	Coke (%)
Pt–Re	CI	6	95.4	26.4	47.4	1.9	15.9	0.61	
		20	92.1	22.3	47.6	1.5	16.3	0.78	2.4
Pt–Re–Ge	CI	6	98.0	42.6	36.4	1.3	12.0	1.16	
		20	96.4	40.9	34.5	1.3	11.3	1.18	2.0
	SI	6	98.0	42.8	35.4	1.9	11.1	0.94	
		20	94.1	32.9	35.8	1.9	11.3	0.84	3.2
	CR	6	96.4	37.1	38.8	1.3	13.0	1.05	
		20	94.8	36.9	37.1	1.3	12.5	1.15	1.0

Pt–Re catalysts series.

Concerning the Pt–Ir series (Table 3) it can be readily seen from the methane and propane yields that the hydrogenolytic and acidic activities are partly suppressed by the addition of Ge. Indeed, it is known that the methane is produced on the metal function whereas propane is favoured on the acid sites. The methane yield is 3–4% for bimetallic Pt–Ir whereas it is less than 2% in the case of the trimetallic catalysts. The lowest yield is displayed by the Pt–Ir–Ge CR catalyst. These results correlate with those of the toluene yield, which is also maximum for this catalyst. The results indicate that Ge effectively reduces the hydrogenolytic activity of the Pt particles. The decrease of the yield in propane by addition of germanium is less significant than the decrease of the yield in methane: the yield in propane is around 14% for the bimetallic catalyst whereas it is between 10.8% and 12% for the trimetallic ones. This decrease of the propane yield is in accordance with the results of acidity measurements presented in Table 2. The lower inhibiting effect on the acid function than on the metal one is confirmed by the values of the iso/normal butane molar ratio for the bimetallic and trimetallic catalysts. Indeed, this ratio is 1.1–1.3 for the trimetallic catalysts and 0.75–0.85 for the bimetallic one and it has been reported that this value, which is characteristic of the balance between the acid and the metal functions, should be in the range 0.80 ± 0.15 in a catalytic reformer unit [22]. In the case of the coke content results, the increased coking of the trimetallic catalysts compared to the bimetallic Pt–Ir catalysts could be explained by the decrease of the hydrogenolytic activity of the metal function leading to a lower rate of removal of coke precursors.

In the case of the Pt–Re series (Table 4) it is clear that Ge addition improves the catalytic properties of the unsulfided Ge-free catalyst. Conversion is upgraded but the best improvement concerns the toluene yield, which is increased almost twofold in the case of the Pt–Re–Ge coimpregnated catalyst. As it was the case for the Pt–Ir series, the *i*-butane/*n*-butane ratio is increased by the addition of Ge and the modification of the acid/metal balance is in favour of the acid function. However, this increase of the iso/normal ratio is not as high as in the case of the Pt–Ir–Ge catalysts. As expected Ge addition also suppresses the formation of gaseous products and thus increases the liquid yield.

A comparison of the performances of the presulfided bimetallic catalysts, the unsulfided bimetallic ones and the best trimetallic ones yields some important results (Table 5). In the case of the Pt–Re catalysts series, the upgrade of the performance of the unsulfided bimetallic catalyst by Ge addition or sulfidation is achieved in the same way in terms of the increase of the toluene yield and decrease of the hydrogenolysis activity. In the case of the Pt–Ir series, sulfidation produces a relative improvement of the catalytic performance that is better than that produced by Ge addition. In any case, the comparison between sulfidation and Ge addition must be looked upon with care because the results were obtained with catalysts aged no more than 20 h in the reactor and it is known in the industrial practice that sulfur loss in the catalytic reformer leads to some deactivation of the presulfided catalysts.

Table 5
Conversion of *n*-heptane under industrial-type conditions (500 °C, 5 bar)

Catalyst	Preparation method	Time of reaction (h)	Conversion (%)	Toluene (%)	C ₁ –C ₄ (%)	Methane (%)	Propane (%)	(<i>i</i> -C ₄ / <i>n</i> -C ₄)	Coke (%)
Pt–Ir	CI	6	100	45.7	41.7	4.0	14.1	0.75	
		20	100	43.0	42.1	3.1	13.9	0.85	1.2
Pt–Ir PreS	CI	6	97.7	55.5	23.1	2.3	7.2	0.85	
		20	97.1	52.6	23.7	2.4	7.3	0.87	3.0
Pt–Ir–Ge	CR	6	99.3	45.8	35.6	1.4	11.5	1.27	
		20	98.5	45.2	33.5	1.3	10.8	1.28	2.8
Pt–Re	CI	6	95.4	26.4	47.4	1.9	15.9	0.61	
		20	92.1	22.3	47.6	1.5	16.3	0.78	2.4
Pt–Re PreS	CI	6	99.5	49.8	33.4	1.4	11.0	1.21	
		20	99.4	49.6	33.6	1.3	11.1	1.27	1.5
Pt–Re–Ge	CI	6	98.0	42.6	36.4	1.3	12.0	1.16	
		20	96.4	40.9	34.5	1.3	11.3	1.18	2.0

Comparison between the fresh, presulfided and Ge-modified catalysts.

If the individual properties are inspected in detail it can be seen that the decrease of the hydrogenolytic activity, as reflected by the decrease of the methane yield, is more effectively obtained by Ge addition than by presulfidation, especially in the case of the Pt–Ir–Ge catalyst series. In the case of the toluene yield, the highest increase is obtained with sulfidation. Ge addition has a negligible effect on the yield in toluene for the Pt–Ir–Ge series whereas a similar upgrade is obtained for the Pt–Re–Ge series.

4. Conclusions

The addition of Ge to Pt–Re and Pt–Ir catalysts produces a marked decrease of the activity of the metal function. This inhibition affects both non-demanding reactions like cyclohexane dehydrogenation and demanding reactions, like cyclopentane hydrogenolysis, but the latter reaction is affected to a greater extent.

Ge addition provides a suitable way of suppressing the hydrogenolytic activity of bimetallic catalysts in the course of *n*-heptane reaction. Hydrogenolysis inhibition by Ge addition is in fact comparable or even stronger than that achieved by sulfidation. Ge addition leads also to a decrease of the amount of the total acid sites. From the *i*-butane/*n*-butane ratio, it can be deduced that the acid/metal balance is increased and higher than the ideal balance, which is only reached with the presulfided bimetallic Pt–Ir catalyst. As a result, the inhibition of the metal activity is more important than that of the acid activity.

The parameters of the preparation method (Ge content, pH, etc.) must be fine-tuned in order to optimize the global performances of the catalysts under industrial catalytic reforming conditions. Particularly, the acid/metal activity ratio should be modified to disfavour the formation of cracking products.

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