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Effect of Ge and CeO_2 on Pt–Ge/Al_2O_3–CeO_2 reforming catalysts

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ABSTRACT

The preparation, characterization and catalytic properties of Pt/Al_2O_3, PtGe/Al_2O_3, Pt/Al_2O_3–CeO and PtGe/Al_2O_3–CeO_2 catalysts are reported. Supports were prepared by impregnating commercial boehmite with cerium nitrate. The solids were calcined at 650 °C to obtain Al_2O_3–CeO_2 mixed oxide supports. The catalysts were characterized by means of H_2 and NH_3 thermodesorption (TPD) measurements, FITR-pyridine and FTIR-CO adsorption spectroscopy. Cyclohexane dehydrogenation and n-heptane reforming reactions were used to evaluate the catalytic activity. It was found that the role of Ge in the bimetallic PtGe catalysts was to dilute the platinum conglomerates, diminishing the number of Pt total surface atoms and inhibiting the Pt hydrogenolytic properties. On the other hand, cerium oxide significantly modified the acidity of the cerium-containing supports. The PtGe/Al_2O_3–CeO_2 catalyst showed a high selectivity towards isomerized olefins in the n-heptane reforming and a high resistance to self-deactivation. It is demonstrated that by inducing modifications to the alumina support, improved catalysts for n-heptane reforming can be obtained.

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1. Introduction

Bifunctional metal–acid catalysts have been widely used for the naphtha catalytic reforming process in which naphtenes and paraffins are transformed into isomeric and aromatic hydrocarbons [1,2]. In these catalysts, the metallic function provides the hydrogenation–dehydrogenation properties. The acidic function, which makes the cyclization and isomerization reactions possible, is given by the support. The Pt/Al_2O_3 catalyst is without any doubt the reference catalyst of the first generation of reforming catalysts used in the reforming units [3]. Platinum is a very active metal for the hydrogen–carbon bond formation and alumina is an oxide with important acid properties. However, extended carbon–carbon rupture (hydrogenolysis) is produced by the metal, and on the other hand, the alumina acidity is not enough to yield important amounts of isomerized products. In the second generation of reforming catalysts, bimetallic catalysts were obtained by adding a second metal like Re [3–5], Ge [6,7], Sn [8–10] or Ir [11] to the Pt/Al_2O_3-based catalysts. The dilution of the platinum conglomerates was produced and the hydrogenolytic properties of platinum were notably diminished. Trimetallic reforming catalysts have been proposed to improve the naphtha reforming process. Pt–Re–Ge/Al_2O_3 and Pt–Ir–Ge/Al_2O_3 catalysts [12] have been reported as examples of the aforementioned. In such catalysts, the activity of either the Pt–Re or Pt–Ir bimetallic system remains practically unmodified, but the addition of germanium modifies the acidity of the catalysts, since germanium oxide has been considered as a source of acid sites [13]. The impregnation with a third metallic precursor like germanium produces improved reforming catalysts by modifying the active metallic and acid phases in the trimetallic catalyst [14].

Advanced reforming catalysts have been obtained by varying the active elements on the alumina surface. However, as far as we know, modifications to reforming catalysts by altering the alumina support have been scarcely reported. In this way, Pt–Sn/Al_2O_3 bimetallic catalysts have been prepared by adding the tin precursor to the gelling aluminum alkoxide (sol–gel method). The catalysts prepared in such a way are solids that strongly inhibit the formation of benzene during the n-heptane reforming reaction [15,16]. The benzene formation suppression has been explained by the formation of electro-deficient Pt conglomerates that can be deposited on or close to SnO_x patches. On the other hand, Pt–Pb and Pt–Sn bimetallic catalysts supported over Al_2O_3–La_2O_3 have also been reported for the n-heptane reforming reaction in which improved selectivity to iso-olefins and the suppression of aromatic compounds has been observed [17,18].

The purpose of the present work is to study the effect of the preparation method on the catalytic properties of a Pt–Ge catalyst supported on alumina–ceria. The support was prepared by the incorporation of cerium nitrate to commercial boehmite (Catapal B). After the formation of the Al_2O_3–CeO_2 mixed oxide (650 °C), the metallic precursors were added by the incipient co-impregnation method. The catalysts were characterized by nitrogen adsorption, TPD-NH_3, TPD-H_2, FTIR-CO and FTIR-pyridine spectroscopy. The

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catalytic activity was evaluated in the cyclohexane dehydrogenation and n-heptane reforming reactions. Germanium was used since it modifies the platinum metallic properties as well as the support acidity, meanwhile cerium oxide was chosen because it has been reported as alumina additive in various patents [19,20], but its role in reforming reactions has not been reported in scientific literature.

2. Experimental

2.1. Preparation of catalysts

The γ-Al_2O_3 reference support was obtained by calcining the boehmite phase in air. The γ-Al_2O_3–CeO_2 support was prepared by impregnating commercial boehmite with an aqueous solution of Ce $(NO_3)_3 \cdot 6H_2O$ (Strem Chemicals, 99.99%) in the appropriate amount to obtain 5 wt% of Ce on the support. After calcining the supports in air flow at 650 °C for 6 h, the monometallic platinum and the bimetallic PtGe (Pt:Ge molar ratio of 1:1) catalysts were prepared by impregnating and co-impregnating the alumina and alumina modified supports with $H_2PtCl_6 \cdot 6H_2O$ (Strem Chemicals, 99.9%) and $GeCl_4$ (Aldrich 99.99%) HCl (0.1 M) solutions. The nominal weight percents for Pt and Ge were 0.5 and 0.185, respectively. After impregnation, the catalysts were dried at 100 °C and then calcined in air at 500 °C for 4 h and finally reduced in hydrogen flow at 500 °C for 4 h. The catalysts were labeled as Pt/Al and Pt/Al–Ce5 for the Pt monometallic catalysts supported on alumina and alumina–ceria with 5 wt% of Ce. The bimetallic catalysts were labeled as PtGe/Al and PtGe/Al-Ce5, the first one for the PtGe supported on alumina and the second one for PtGe supported on alumina–ceria with 5 wt% of Ce.

2.2. Temperature-programmed desorption (TPD-H_2, TPD-NH_3)

Hydrogen chemisorption was carried out in a Zeton Altamira AMI3 apparatus. The reduced sample was first reactivated "in situ" in hydrogen flow at 400 °C for 1 h. Afterwards, the temperature was diminished to room temperature and the hydrogen flow was replaced by a 20% H_2/He (Praxair-UHP) flow until saturation. The hydrogen in excess was displaced by flowing argon and then the hydrogen thermal desorption was carried out from room temperature to 500 °C with a heating rate of 10 °C min^{-1}. The hydrogen accessibility of the Pt catalysts was determined from the area of the TPD thermograms using a calibrated loop and assuming H/Pt = 1 as the stoichiometric ratio. Previous TPD-H_2 experiments have shown that Ge does not adsorb hydrogen under such conditions.

The TPD-NH_3 measurements to determine the total acidity of the catalysts were performed employing the same protocol mentioned above for the TPD-H_2, using in this case a 20% NH_3/He (UHP) ammonia gas mixture.

2.3. Infrared spectroscopy of CO adsorption (FTIR-CO)

FTIR-CO adsorption was carried out at room temperature using an FTIR NICOLET Magna 560 spectrometer. The samples pressed in thin wafers were placed in a Pyrex glass cell equipped with CaF_2 windows which allows heat treatments. The samples were reactivated "in situ" in hydrogen atmosphere at 400 °C for 1 h and then submitted to vacuum (10^{-6} Torr) at 400 °C for 30 min. After, the temperature was decreased to room temperature (25 °C) and the CO admission was carried out. The CO excess (Praxair-UHP) was evacuated under vacuum during 30 min and the absorption spectra were subsequently recorded.

2.4. FTIR of pyridine adsorption

The type of acid sites was determined by FTIR-pyridine adsorption with a Nicolet Nexus 479 spectrometer with a resolution of 3.8 cm^{-1} and 50 scans. The annealed material was passed into thin self-supported wafers. Then, they were placed in a glass Pyrex cell with CaF_2 windows. Hydrogen was admitted into the cell at 400 °C for 1 h and then the sample was evacuated (10^{-6} Torr) in situ at 400 °C for 30 min. The adsorption was carried out in the cell at 25 °C by introducing into it the pyridine contained in a glass bulb coupled to the cell. The pyridine excess was desorbed under vacuum at room temperature and the spectra were recorded from 100 to 400 °C with 100 °C steps.

2.5. Cyclohexane dehydrogenation reaction

The dehydrogenation reaction was carried out at 300 °C in a conventional flow reactor used in the differential mode at low conversion (<15%). Prior to the catalytic activity determination, the catalysts were reactivated "in situ" in hydrogen flow for 1 h at 400 °C. The catalyst mass was varied from 0.020 to 0.050 g when necessary to maintain the low conversion. The partial pressures of cyclohexane and hydrogen were 48.2 and 711.8 Torr, respectively. Hydrogen saturated with cyclohexane was flowed through the reactor. The products were analyzed by on line gas chromatography. A GS-Alumina column (30 m × 0.53 μm) was used.

2.6. n-Heptane conversion reaction

In catalysts previously reactivated "in situ" at 400 °C with hydrogen flow for 1 h, the n-heptane conversion was determined in a conventional flow reactor used in the differential mode at low conversion (<15%). The reactants were n-heptane by Merck and UHP hydrogen. The reaction conditions were set as follows: n-heptane and hydrogen partial pressures of 11 and 749 Torr, respectively, catalyst mass of 0.020–0.050 g and reaction temperature of 490 °C. Hydrogen saturated with n-heptane was flowed through the reactor. The products were analyzed by on line gas chromatography. A GS-Alumina column (30 m × 0.53 μm) was used. The products were identified with an HP-GC–MS 5973 gas chromatograph–mass spectrometer.

3. Results and discussion

3.1. Characterization of catalysts

Platinum, germanium and chlorine contents for the various catalysts were determined by inductively coupled plasma spectroscopy (ICP) and the values are reported in Table 1. For Pt, the

Table 1
Characterization of the PtGe/Al–Ce catalysts.

Catalyst	Pt (wt%)	Ge (wt%)	Cl (wt%)	H/Pt accessibility	TPD-NH_3 (μmol/g)	Rate[a] (10^6 mol s^{-1} g_{cat}^{-1})
Pt/Al	0.56	–	0.74	0.65	246	345
Pt–Ge/Al	0.56	0.15	0.73	0.35	73	274
Pt/Al–Ce5	0.38	–	0.95	–	89	243
PtGe/Al–Ce5	0.52	0.17	0.94	–	199	110

[a] Cyclohexane dehydrogenation.

nominal (0.5 wt%) and real contents are in good agreement (0.56–0.52 wt%) with the exception of the Pt/Al–Ce5 catalyst where a lower value was obtained (0.38 wt%). For Ge, the real content (0.15–0.17 wt% Ge) correlates well with the nominal ones (0.185 wt%). On the other hand, the chlorine content was determined in the catalysts. It was found that when cerium oxide is present in the support, the chlorine content increases around 25% (0.95 and 0.94 wt% for Pt/Al–Ce5 and PtGe/Al–Ce5, respectively) in comparison with the alumina supported catalyst without CeO_2, 0.74 wt% for Pt/Al and 0.73 wt% for PtGe/Al catalysts. The ability of cerium oxide to retain chlorine has been observed and reported by several authors [18,21] and the role of the chlorine content in metallic catalysts has been correlated to the formation of Pt–Cl species, where platinum has been identified as Pt^+ oxidized species.

3.2. Platinum dispersion

As it is well known, cerium oxide chemisorbs hydrogen; therefore the platinum dispersion on the catalysts in the present work was determined only on the samples free of ceria. A high hydrogen platinum accessibility was obtained on the Pt/Al catalyst (H/Pt = 0.65), meanwhile for the PtGe catalyst, an important diminution in the platinum dispersion was observed (H/Pt = 0.35), Table 1. The significant diminution in the platinum accessibility is due to the deposition of germanium atoms on the surface of the platinum particles. The dilution of the platinum conglomerates was then produced [6,13,22,23].

3.3. TPD-NH_3 measurements

The surface acidity of these catalysts was determined by means of TPD-NH_3 measurements and the results are reported in Table 1. An important variation in the desorbed NH_3 amount was observed on the various catalysts. However, a shift to lower temperatures of the NH_3 desorbed for the Pt/Al–Ce5 and PtGe/Al–Ce5 modified catalysts with respect to the Pt/Al and PtGe/Al samples must be noted (Fig. 1). If the temperature of the ammonia desorption peak is considered as an indirect determination of the strength of the acid sites, the cerium-containing catalysts showed acid sites that were weaker than those obtained on the Pt/Al and PtGe/Al catalysts. Thus, the PtGe/Al–Ce5 catalyst developed a high number of acid sites, but with low strength.

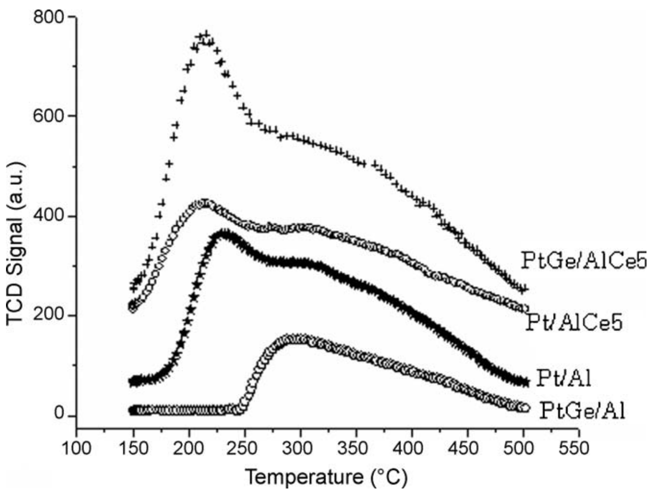

Fig. 1. Ammonia TPD for Pt and PtGe supported on alumina and alumina–ceria catalysts.

3.4. FTIR-pyridine adsorption

On the other hand, in Fig. 2, pyridine desorption as a function of temperature for selected samples is illustrated. In the FTIR-pyridine adsorption spectra only Lewis acid sites can be seen in all the catalysts. These results show that the nature of the acid sites is not modified either by the presence of germanium or by cerium oxide.

3.5. FTIR-CO adsorption study

The FTIR spectra of CO adsorbed on the different catalysts are shown in Fig. 3. A single peak was observed concerning the Pt/Al and PtGe/Al catalysts at 2065 and 2075 cm^{-1}. These peaks correspond to linear CO adsorbed on the Pt reduced catalysts [24] this means that no additional effects on the electronic properties are detected on platinum by the addition of Ge.

However, the presence of CeO_2 on the Pt/Al–Ce5 and PtGe/Al–Ce5 catalysts produced a modification in the nature of the Pt surface atoms. In these catalysts, an additional peak located at 2119 cm^{-1}, which has been associated with the oxidized Pt^{2+} species, can be seen [18,25]. Cerium oxide has redox properties that can modify the electronic properties of transition metals and then the formation of Pt oxidized species can be expected on the platinum–cerium catalysts [26].

3.6. Cyclohexane dehydrogenation

The cyclohexane dehydrogenation reaction is a reaction that is carried out on the metal function and it is considered as an insensitive reaction, which means that the activity is proportional to the surface metal active atoms. Therefore, the activity can give information about the number of active atoms on the surface. The activity values for the cyclohexane dehydrogenation reaction expressed as mol s^{-1} g_{cat}^{-1} are reported in Table 1. As it was expected, a diminution in the activity of the PtGe/Al catalyst due to a diminution of the accessible platinum atoms in the catalyst was observed.

Low activity was also observed in the cyclohexane dehydrogenation on the Pt/Al–Ce5 catalyst with respect to the Pt/Al parent catalyst. In this catalyst, the presence of the Pt^{2+} species, which is a less active oxidized species for the hydrogenation–dehydrogena-

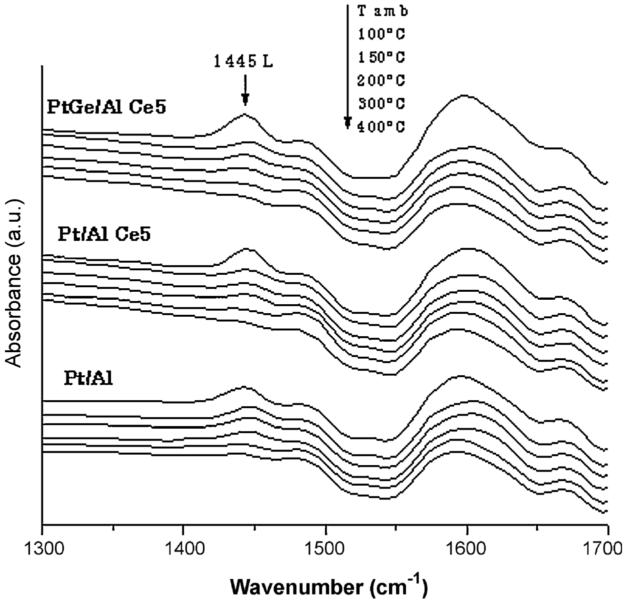

Fig. 2. Pyridine FTIR desorption spectra for selected Pt and PtGe catalysts supported on alumina and alumina–ceria catalysts.

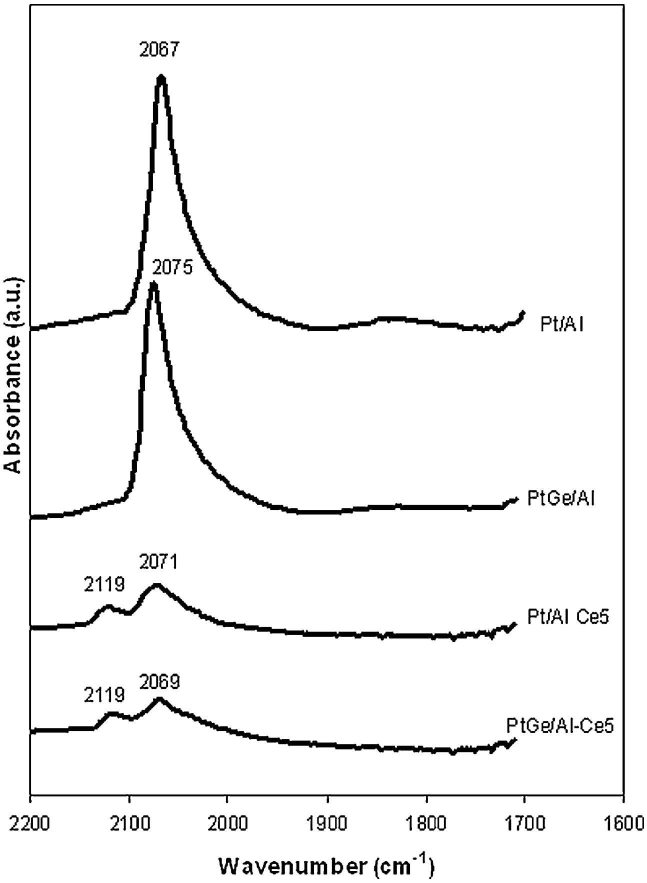

Fig. 3. FTIR-CO absorption spectra for Pt and PtGe on alumina and alumina–ceria supported catalysts.

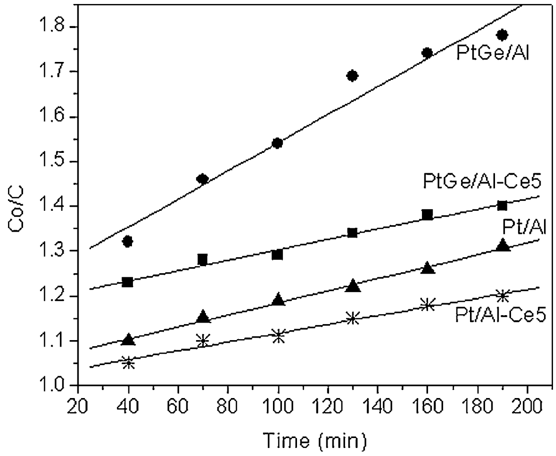

Fig. 4. Deactivation of catalysts as a function of time for Pt and PtGe supported on alumina–ceria catalysts.

tion reactions, was detected. This explains the diminution in the dehydrogenation activity of this catalyst. When Ge and CeO_2 are both present, as in the PtGe/Al–Ce5 catalyst, the activity is significantly diminished. In this catalyst, the deposition of Ge on the Pt surface atoms and the formation of Pt^{2+} species boost the low capacity of the catalyst for the cyclohexane dehydrogenation reaction.

3.7. n-Heptane dehydrocyclization

Germanium addition effect. The n-heptane reaction activity is expressed as initial rate $(\mathrm{mol\,s^{-1}\,g_{cat}^{-1}})$ at $t = 10$ min and the obtained values for the different catalysts are reported in Table 2. The activity showed by all the catalysts is very similar, no clear additive effects were observed. On the other hand, the selectivity pattern obtained for the Pt/A catalyst was modified by the presence of Ge and CeO_2 (Table 2). The presence of Ge on the PtGe/A catalysts produced the following effects: (i) a drastic decrease in the selectivity towards C_1–C_6 products and (ii) an improvement in the formation of toluene and iC_7 olefins and a total inhibition of benzene formation. The hydrogenolysis of C–C bonds is mainly favored on large surface platinum atoms; hence, the addition of Ge atoms produced the reduction of large ensembles of platinum atoms on the surface reducing the cleavage of C–C bonds and consequently the C_1–C_6 yield. The formation of benzene in the n-heptane dehydrocyclization has been reported as a product of the toluene dealkylation over the metallic surface [15,18] and then Pt diminishes its dealkylation capacity by the dilution effect produced by Ge. The diminution of the acidity on the PtGe/A catalyst (Table 1) due to the deposition of Ge on the acid sites of the support [13] leads to a reduction in the bifunctional process, rising the olefin ($iC_7{=}$) production.

Cerium oxide effect. With the addition of cerium oxide to the support in the Pt/A–Ce5 catalyst, both the catalytic properties of Pt and support were modified. Platinum in this catalyst shows Pt^{2+} species (PtO) and cerium oxide leads to a diminution of the support acidity. As a consequence, the bifunctionality of this catalyst is reduced and the formation of isomerized olefins is increased.

For the PtGe/Al–Ce5 catalyst, the dilution of Pt by Ge atoms and the diminution of the strong acidity of the support by the presence of cerium oxide produce a very interesting catalyst. The selectivity pattern for this catalyst shows high selectivity to isomerized olefins (Table 2). In this catalyst the olefin formation is highly favored instead of the dehydrocyclization reactions.

The deactivation constant of the catalysts was determined assuming a second order Levenspiel's deactivation equation used for self-deactivation on supported metal catalysts, $C_o/C = 1 + k_d t$ [27]. The deactivation of the catalysts was followed and the constant deactivation rate was calculated after the equilibrium was reached (40 min) and 190 min on stream by plotting C_o/C vs. time, where C_o is the initial concentration, C is the conversion at time t and k_d is the deactivation constant (Fig. 4). The deactivation constant (k_d) for the n-heptane reaction was calculated from the slope in Fig. 4 and the values are reported in Table 2. The values obtained for the different catalysts are similar, although it is clear that the PtGe/Al–Ce5 and Pt/Al–Ce5 catalysts show a constant trend toward lower deactivation rates than those obtained on the catalysts without cerium oxide. These results show that cerium

Table 2
Activity and selectivity for the n-heptane dehydrocyclization on PtGe/Al–Ce catalysts.

Catalyst	Rate $(10^6\,\mathrm{mol\,s^{-1}\,g_{cat}^{-1}})$	k_d[a] (10^4)	Selectivity (%)				
			C_1–C_6	iC_7	$iC_7{=}$	Benzene	Toluene
Pt/Al	28.2	14	28	9	31	2	30
PtGe/Al	40.0	26	1	8	52	0	39
Pt/Al–Ce5	25.7	10	13	5	56	3	23
PtGe/Al–Ce5	29.9	11	2	13	72	2	11

[a] Deactivation constant.

oxide catalysts are more resistant to self-deactivation in the n-heptane dehydrocyclization reaction.

The role of cerium oxide in the n-heptane reforming is then related to the formation of oxidized species (Pt^{2+}) as well as to a diminution of the acidity of the support. As a result, the hydrogenolytic properties of the metal as well as the bifunctionality, which resides on the support acidity, were strongly modified. Therefore, the Pt–Ge/Al_2O_3–Ce catalyst is highly selective, giving low aromatic yields and low deactivation rates. The results of the present work show that by modifying the support, alumina–ceria improved reforming catalysts can be prepared.

4. Conclusions

It was shown that by adding Ge and CeO_2, important modifications in the catalytic properties of Pt/Al_2O_3-type catalysts can be obtained. It was found that the role of germanium is principally related to the dilution of the platinum conglomerates, diminishing the platinum hydrogenolytic properties. As for cerium oxide catalysts, important modifications in the platinum oxidation state (Pt^{2+}) as well as in the support acidity were observed. It is shown that on the Pt–Ge/alumina–ceria catalyst, the hydrogenolysis, dehydrocyclization and deactivation reactions were strongly inhibited, meanwhile a high selectivity to iso-olefins was obtained.

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