Catalysis Letters 47 (1997) 143–154

Propane transformation over H-ZSM5 zeolite modified with germanium

Claudio Cesar Salguero[a], Yiu Lau Lam [b] and Martin Schmal [a,c,*]

[a] *NUCAT/COPPE/PEQ, Federal University of Rio de Janeiro, PO Box 68502, CEP 21945, Rio de Janeiro, Brazil*
E-mail: Nucat@peq.coppe.ufrj.br
[b] *CENPES-PETROBRAS, Rio de Janeiro, Brazil*
[c] *Escola de Química, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*

Received 21 March 1996; accepted 23 June 1997

The propane aromatization was studied over H-ZSM5 zeolite modified by Ge, Pt and Pt–Ge. The aromatization was performed in a micro-reactor at 773 K and at atmospheric pressure. The addition of germanium on H-ZSM5 increases the activity for propane transformation but decreases the selectivity toward aromatic compounds. The transformation of propane on Pt/H-ZSM5 indicates a significant increase in the activity and a decrease in the selectivity toward aromatics, while on the bimetallic Pt–Ge/H-ZSM5 catalyst both the activity and the selectivity toward aromatics increase. The dehydrogenation of propane over GeO_2/SiO_2 at 773 K and the *n*-heptane transformation over H-ZSM5 and Ge/H-ZSM5 at 673 K were performed. Results confirm the dehydrogenation capacity of GeO_2 and show similar activity and selectivity for *n*-heptane conversion on H-ZSM5 and Ge/H-ZSM5. The acidic properties of the catalysts were determined by TPD/NH_3 and IR/Py analyses. Results show that both the total and strong acidity decrease with the addition of germanium. Therefore, it seems that germanium affects the activity of propane conversion due to the dehydrogenation capacity of GeO_2, while the selectivity toward aromatics decreases due to the lower capacity of cyclization, by decreasing the acidity and the number of strong acid sites. In contrast, the Pt–Ge/H-ZSM5 catalyst presents the highest selectivity toward aromatics (53.4%) which is attributed to the decrease in hydrogenolysis capacity of platinum. The TPR results of the Pt–Ge/H-ZSM5 catalyst indicate interaction of Pt–Ge, and from the hydrogen consumption it was seen that Ge^{4+} is partially reduced to Ge^{2+}, which is attributed to the presence of metallic platinum.

Keywords: propane aromatization, germanium modified H-ZSM5, platinum–germanium modified H-ZSM5, acidity, activity

1. Introduction

The aromatization of light alkanes over metal-modified ZSM5 zeolite is very complex; it involves carbocation reactions and dehydrogenation reactions. The production of aromatic compounds, which are extensively used in the chemical industry as solvents or raw materials, is of great economical interest. Actually, two main industrial processes are in use: the M2-FORMING process [1], which transforms hydrocarbon fractions of 3 to 6 carbon atoms in gasoline, rich in aromatic compounds, and the CYCLAR process [2,3], which transforms LPG into aromatic compounds. Ono [4] presented recently an extensive review on aromatization of hydrocarbons.

The aromatization of light alkanes involves different steps: (a) activation of alkanes, (b) oligomerization, (c) cyclization and (d) aromatization [5]. Undesired cracking reactions may also occur on strong acid sites. On pure zeolite, the first step involves cracking of alkanes on acid sites [6–8], or dehydrogenation of alkanes by hydrogen transfer on strong acid sites. The oligomerization occurs preferentially forming compounds up to 6 or 9 carbon atoms but compounds up to 15 carbon atoms have been observed [9]. These oligomers can be cracked over acid sites to lower alkanes and alkenes or transformed by carbocation reactions of isomerization or cyclization. The oligomers may also be directly dehydrogenated in the presence of a metal by dehydrogenation, forming oligomers with one or more double bonds [10]. In these cases, the unsaturated oligomers may also be cyclized by thermal effects [10] after which they can be transformed to aromatics by hydrogen transfer with alkenes over the acid sites or by direct dehydrogenation of the ring on the metal.

Mériaudeau et al. [10] showed that the limiting step in the selectivity toward aromatics over H-ZSM5 is the hydrogen transfer from the cyclic compound to alkene, which results in a ratio of three alkane molecules to one aromatic molecule formed. The addition of a metal in ZSM5 affects the dehydrogenation activity and increases the selectivity toward aromatics. Metals, like Pt, Zn, Ga and Cu, as mono or bimetallic catalysts on H-ZSM5 were studied [10–13]. Platinum exhibits great dehydrogenation capacity, which favors both the activation and aromatization steps. However, the hydrogenolysis activity of Pt decreases the selectivity to aromatics due to the hydrogenolysis of oligomers and cyclic compounds [10]. Zinc metal and zinc oxide showed good dehydrogenation activity and promote the selectivity

---

[*] To whom correspondence should be addressed.

toward aromatics [11]. It is well known that ZnO suffers disproportionation to form metallic zinc and ZnO_2 under these reaction conditions [14]. The loss of the active phase is a consequence of the zinc vapor pressure at 773 K. Noteworthy was the presence of gallium on H-ZSM5, in the zeolitic framework, which presented the highest selectivity toward aromatics, as reported in the literature [7,8,12,15]. It does not have the inconvenience of hydrogenolysis activity or loss of the active phase.

Bittencourt et al. [13,16] studied the aromatization of propane and *n*-hexane with Cu/H-ZSM5 and Cu–Pt/H-ZSM5 catalysts and showed that the presence of copper increases the selectivity toward aromatics but decreases the total activity of the catalyst when compared to H-ZSM5 for the same reaction conditions.

In the present study we introduce Ge^{4+} as a modifier on H-ZSM5 zeolite for the aromatization of propane, exploring the isoelectronic properties of Ge^{4+} with Cu^{+}, Zn^{2+} and Ga^{3+}. Moreover, as has been shown for Pt–Ge on alumina based catalysts [17–20], the presence of Ge affects both the hydrogenolysis and the dehydrogenation activity of Pt.

2. Experimental

2.1. Catalysts preparation

The Na-ZSM5 zeolite was obtained by using *n*-butanol as template in the synthesis [21]. The resulting zeolite presented high crystallinity (measured by XRD) and a silica/alumina molar ratio of 39. The acid form was obtained after three sequential ion-exchanges at 353 K, for 2 h with 5 wt% NH_4Cl in solution (100 ml/g of zeolite). The NH_4-ZSM5 solid was dried at 383 K for 16 h and calcined at 823 K for 16 h under flowing air (1800 ml/h).

The metal-containing catalysts were prepared by incipient wetness impregnation at 353 K. A Ge^{4+} solution was obtained from hydrolysis of $GeCl_4$ (Aldrich) and dissolution in 0.05 N HCl at 353 K and then diluted to 5.5 g Ge/ℓ. A $Pt(NH_2C_2H_4NH_2)Cl_2$ solution with 2.39 g Pt/ℓ was used as a Pt source (Aldrich).

Similarly, two samples of GeO_2/SiO_2 were prepared containing 10 and 30 wt% of GeO_2, respectively, for the dehydrogenation activity test of germanium oxide. All catalysts were dried at 383 K for 16 h and calcined at 823 K for 16 h under flowing air of 1800 ml/h.

2.2. Reaction tests

The aromatization was performed in a fixed-bed micro-reactor at 773 K, varying the mass of catalyst from 30 mg to 1 g and the reactant flow rate from 10 to 100 ml/min. The reactant was a propane/nitrogen mixture (19.9–20.0% v/v of propane) (White Martins). The cracking reaction was performed at 673 K, using nitrogen saturated with *n*-heptane at 297 K. The propane dehydrogenation on GeO_2/SiO_2 was performed at 773 K, using 1 g of the catalyst and a flow rate of 10 ml/min.

The catalysts were pre-treated with a flow of N_2 at 30 ml/min at 773 K for 1 h. The Pt-based catalysts were previously reduced at 773 K, flowing 30 ml/min of H_2 for 1 h, followed by a N_2 flux of 30 ml/min for 30 min. The activity and selectivity of all samples were stabilized after 30 min of time on stream and no significant variations were observed after 1 h. Hence, all activities and selectivities values were compared after 40 min.

The products were analyzed by on-line gas chromatography, using a flame ionization detector and a capillary column PLOT-Al_2O_3/KCl with 50 m × 0.53 mm. The analysis was performed at 313 K for 3 min, followed by temperature rise at a heating rate of 8 K/min up to 443 K, and finally held constant until the formation of *o*-xylene. In a repeated test for observation of possible heavier products, the column was kept at a constant temperature for further 120 min, but no other products were detected. After injecting a standard mixture containing aromatic compounds, C_9 compounds were observed within 100 min of analysis.

2.3. Catalyst characterization

The metal contents, as shown in table 1, were obtained by plasma spectrometry on a Spectrometer-V Beckman. The micropore volume of the zeolite was determined applying the Dubinin–Radushkevich [22] method, described elsewhere by Maia [23]. Samples of 150 mg were first evacuated at 10^{-4} Torr, at 473 K, and then submitted to a N_2 flow of 130 ml/min, followed by evacuation at 10^{-4} Torr for 1 h. Then, the N_2 adsorption/desorption cycles were performed at 195 K. The results are presented in table 2.

The acid properties of the catalysts were determined by TPD of NH_3 and by infrared spectroscopy of pyridine (IR/Py).

200 mg of the sample were pre-treated under flowing N_2 at 25 ml/min, and 823 K for 1 h, followed by He at 30 ml/min and 423 K. Without further treatment, a mixture of NH_3/He (2.58% v/v) was introduced, at 30 ml/min and 423 K, followed by adsorption and desorption of reversible ammonia measurements. Then, TPD of the irreversible ammonia was performed raising the temperature from 423 K up to 823 K, at a heating rate of 10 K/min, passing He at 30 ml/min (figure 1). The

Table 1
Metallic composition of the zeolitic catalysts

Catalyst	Ge (wt%)	Pt (wt%)
Ge/H-ZSM5	0.31	–
Pt/H-ZSM5	–	0.18
Pt–Ge/H-ZSM5	0.25	0.20

Table 2
Micropore volume of the zeolitic catalysts

Catalyst	V_p (cm^3/g)
H-ZSM5	0.18
Ge/H-ZSM5	0.17
Pt/H-ZSM5	0.18
Pt–Ge/H-ZSM5	0.19

adsorption was obtained at 423 K in order to minimize the physical adsorption.

The IR/Py data were obtained by IR spectroscopy. The samples containing 20 to 25 mg were made into self-supported wafers and introduced in an IR cell and then evacuated at 10^{-4} Torr at 755 K for 8 h. After cooling to 423 K, pyridine vapor was introduced for 1 h and evacuated at 10^{-4} Torr. The IR spectra are presented in figure 2 and exhibit the Lewis and Brønsted acid sites at 1450 and 1545 cm^{-1}, respectively.

The TPR experiments were performed as described elsewhere [16]. Samples were introduced containing at least 6 mg of metal for the monometallic Ge/H-ZSM5 and Pt/H-ZSM5 and 12 mg for Pt–Ge/H-ZSM5 catalysts. They were pre-treated under Ar flux at 30 ml/min and 423 K for 1 h. After cooling to 298 K and switching to a H_2/Ar mixture, with 1.3% v/v H_2, at 30 ml/min, the temperature was raised at a heating rate of 10 K/min up to 1223 K for GeO_2 and Ge–Pt/H-ZSM5 and up to 923 K for Pt/H-ZSM5 samples. The TPR profiles are shown in figure 3.

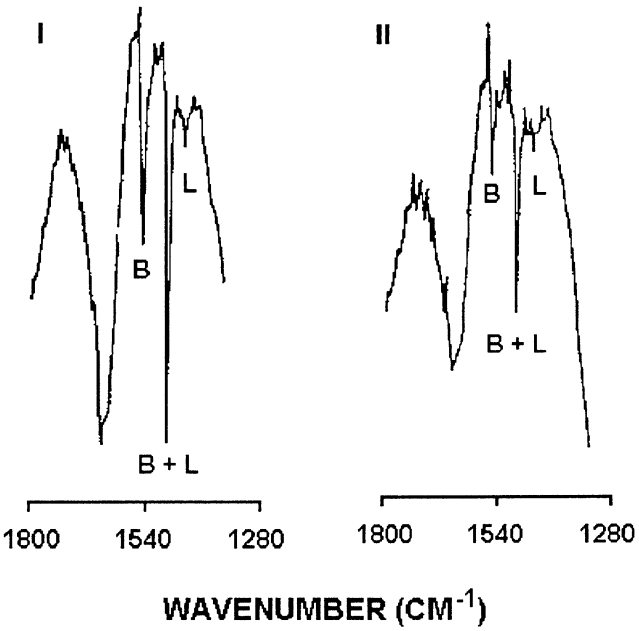


Figure 2. Acidity analysis by IR of adsorbed pyridine. (I) H-ZSM5, (II) Ge/H-ZSM5. (B) Brønsted sites and (L) Lewis sites.

3. Results and discussion

3.1. Catalysts

The hydrolysis of $GeCl_4$ in HCl solution was not complete between 6 and 9 mol/ℓ, forming complexes like $[Ge(OH)_nCl_{6-n}]^{2-}$. The chemistry of these complexes in aqueous solution is not very clear, but in dilute solution

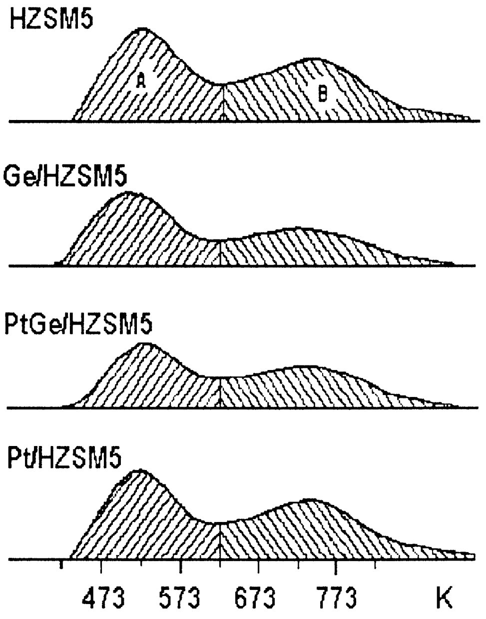


Figure 1. Total and strong acidity determination by TPD/NH_3. (A) Weak acid sites and (B) strong acid sites.

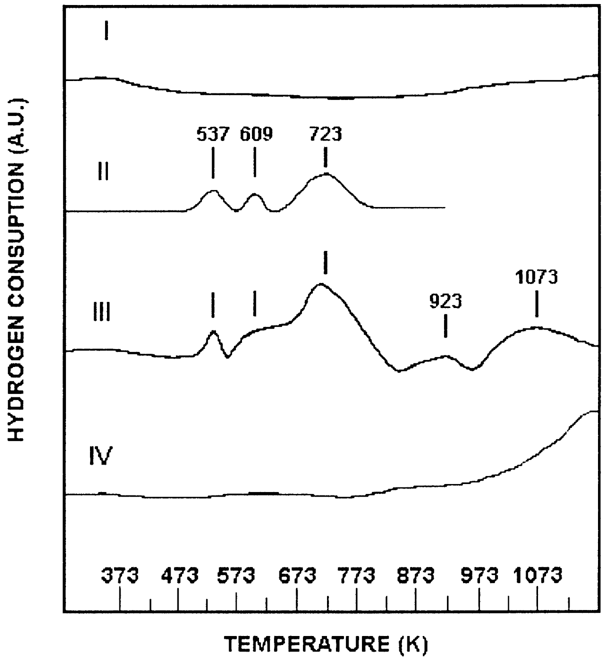


Figure 3. TPR/H_2 analysis of (I) Ge/H-ZSM5, (II) Pt/H-ZSM5, (III) Pt–Ge/H-ZSM5 and (IV) GeO_2.

Table 3
Total and strong acidity obtained by ammonium adsorption and TPD/NH_3 and the Brønsted/Lewis ratio for the zeolitic catalysts obtained by IR of adsorbed pyridine

Catalyst	Total acidity (mmol/g)	Strong acidity (mmol/g)	B/L ratio (IR)
H-ZSM5	0.66	0.32	4.7
Ge/H-ZSM5	0.45	0.18	3.5
Pt/H-ZSM5	0.62	0.30	3.0
Pt–Ge/H-ZSM5	0.42	0.19	2.6

Table 4
Apparent constant of activity for the zeolitic catalysts, in grams of reagent per grams of catalyst per hour, and its relative values

Catalyst	K_{app} (g/(gh))	$K_{\text{app}}/K_{\text{app(HZSM5)}}$
H-ZSM5	0.48	1
Ge/H-ZSM5	0.85	1.8
Pt/H-ZSM5	2.71	5.6
Pt–Ge/H-ZSM5	0.88	1.8

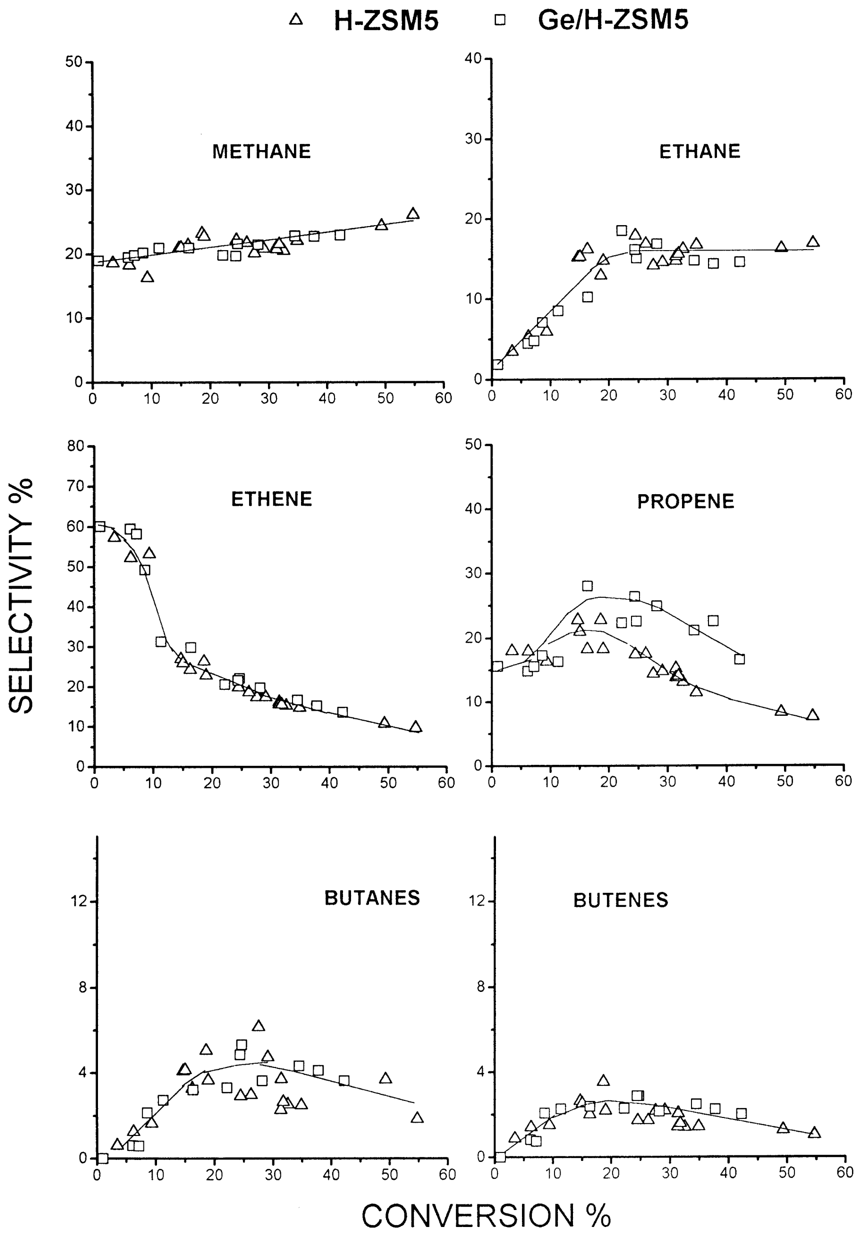


Figure 4. Selectivity as a function of the propane conversion for H-ZSM5 and Ge/H-ZSM5, at 773 K. (Continued on next page.)

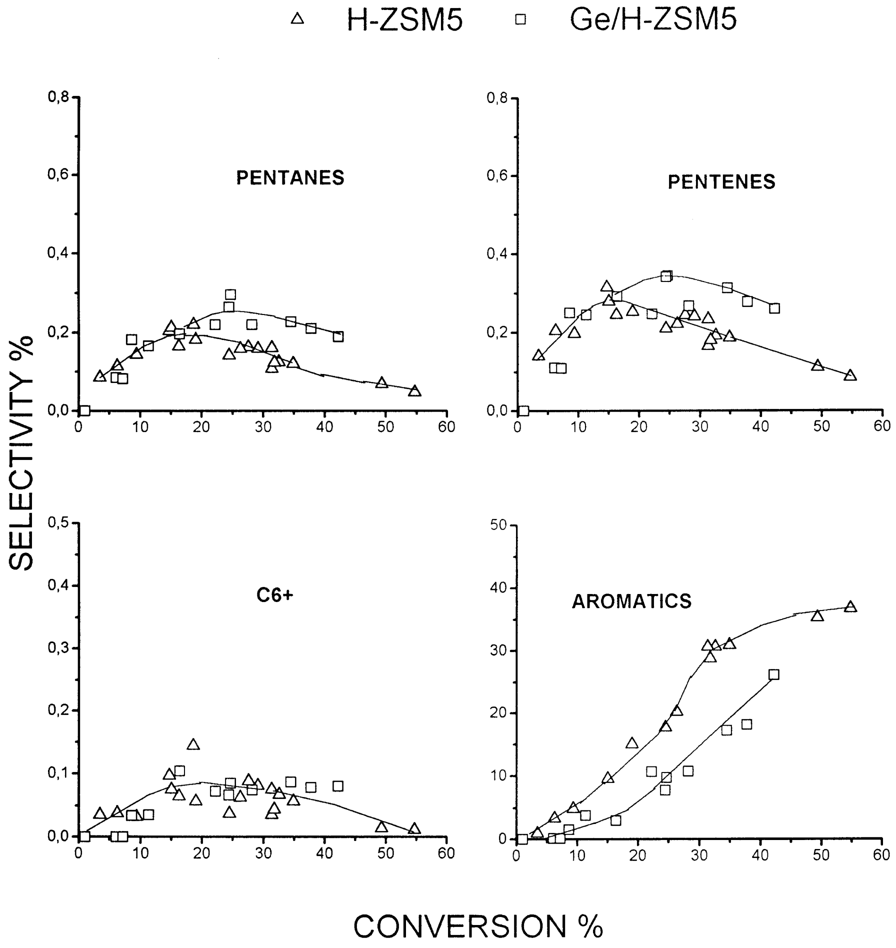


Figure 4. (Continued.)

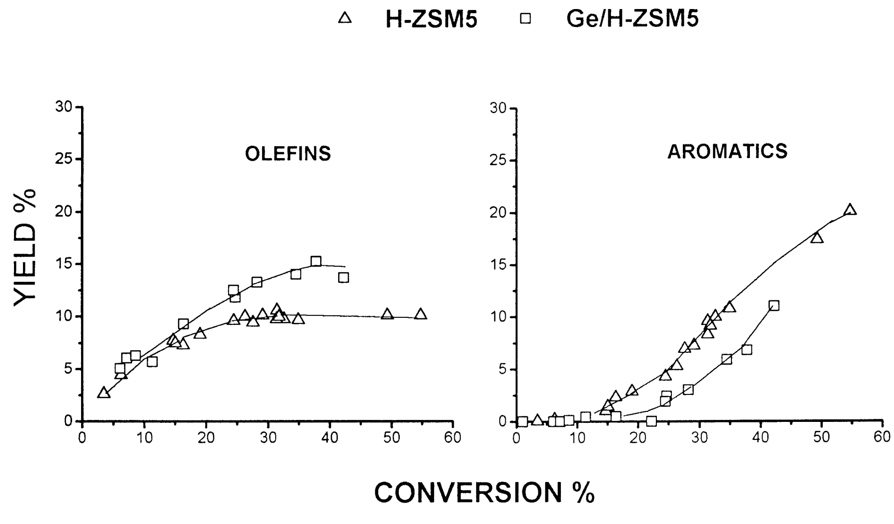


Figure 5. Yield of aromatic and olefin products as a function of the propane conversion for H-ZSM5 and Ge/H-ZSM5, at 773 K.

there are $[GeO(OH)_3]^-$, $[GeO(OH)_2]$ and $\{[Ge(OH)_4]_8(OH)_3\}^{3-}$ ions [24].

The results presented in table 2 show that the microporous volumes after impregnation of Ge were not significantly modified. All the catalysts exhibit adsorption/desorption isotherms of type I, and a small hysteresis, which is a characteristic of microporous materials [25].

The TPD/NH_3 and the acidity results are presented in figure 1 and table 3. Desorption peaks were observed at 523 and 723 K. These peaks indicate the desorption of weak and strong acid sites, respectively. Brønsted acid sites prevail in the latter case [26]. The introduction of Ge or Pt did not significantly change the temperature of the desorption peak. The amounts of weak and strong acid sites were determined by accounting the NH_3 desorbed below and above 623 K, respectively.

The IR/Py results of H-ZSM5 and Ge/H-ZSM5 catalysts are presented in figure 2, showing the characteristic spectra of the Lewis and Brønsted acid sites at 1450 and 1545 cm^{-1}, respectively. Table 3 presents the approximate Brønsted/Lewis acid sites ratio.

The total acidity and the number of strong acid sites decreased with the addition of germanium as well as the ratio of Brønsted/Lewis acid sites (table 3). This denotes a strong interaction of germanium oxide with the acid sites, specially with the Brønsted sites. Similar behavior was observed on Zn/H-ZSM5 by Yakerson et al. [27], who attributed this phenomenon to a solid-state reaction between ZnO and the Brønsted acid sites of the H-ZSM5 zeolite during the preparation and calcination. In contrast, the addition of platinum did not change the total acidity and the number of strong acid sites.

The TPR results indicate interaction of Pt–Ge in the bimetallic catalyst. The TPR of Ge/H-ZSM5 shows that H_2 was not consumed up to 1123 K, although GeO_2 can be reduced above 1023 K (figure 3). The TPR results of Pt/H-ZSM5 indicate that the H_2 consumption corresponds to 70% of reduction of Pt^{4+} to Pt^0 and 30% to Pt^{2+}, assuming that the reduction in the first step is Pt^{4+} to Pt^{2+} and then Pt^{2+} to Pt^0 in the second step, according to De Miguel [17]. The TPR profile of the Pt–Ge/H-ZSM5 catalyst displays two reduction zones. The first one below 853 K is similar to the Pt/H-ZSM5 catalyst, while above this temperature a partial reduction of Ge^{4+} to Ge^{2+} occurs. Thus, the H_2 uptake denotes a reduction of 46% of platinum oxide to Pt^0 and 54% to Pt^{2+}, while 87% of germanium remains as Ge^{4+} and only 13% was reduced to Ge^{2+}. This means that platinum promotes the partial reduction of germanium oxide, which denotes a Ge–Pt interaction [17].

3.2. Reaction tests

The reactions were performed varying the mass of the catalyst and the reactant flux which allows conversions between 0 and 60%. The reaction tests were reproduced twice at least for each conversion. Conversion (X), selectivity (S) and yield (Y) were calculated on carbon basis. The activity (K_{app}) was determined using the following equation [28]:

$$K_{app} = (F/W)\ \ln[1/(1-X)]\,, \qquad (1)$$

where F/W is the ratio of reactant flow rate and the mass of catalyst. Results are presented in table 4. The activity of the Ge/H-ZSM5 catalyst increases by a factor of 1.8 compared to H-ZSM5, but did not change by adding Pt on Ge/H-ZSM5. However, adding only platinum to H-ZSM5 increases the activity by a factor of 5.6, since

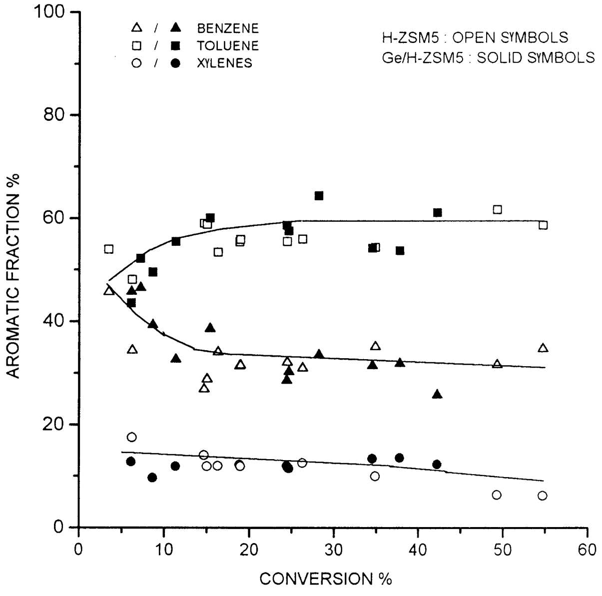


Figure 6. Fractions of benzene, toluene and xylenes over the total aromatics products obtained over H-ZSM5 and Ge/H-ZSM5, at 773 K.

dehydrogenation and hydrogenolysis occur on the metal, transforming in a large extent propane to propene, methane and ethene, in agreement with the mechanism proposed by Mériaudeau [10] and Gnep [29].

3.2.1. Propane and n-heptane conversion over H-ZSM5 and Ge/ H-ZSM5 catalysts

Figure 4 displays the selectivity of the main products as a function of conversion of propane at 773 K on H-ZSM5 and Ge/ H-ZSM5. The selectivities of C_1, C_2 and $C_{2=}$ were similar. This suggests that for low conversions (below 10%) the cracking of propane to C_1 and $C_{2=}$ prevails during the activation mechanism. Above 15% of conversion, propene increases due to the parallel mechanism of activation through direct dehydrogenation of propane to propene by hydrogen transfer on the acid sites. Similar results were obtained by Kitagawa [5] and Ono and Kanae [30], who proposed a different activation mechanism for higher conversions.

In opposite, Ge/ H-ZSM5 increases the formation of propene and of intermediate products of aromatization above 15% of conversion, but the selectivity toward aromatics decreases. Figure 5 shows the decrease of aromatics, followed by a higher formation of olefins.

The selectivity of aromatics over H-ZSM5 increased up to 35%, as observed by Guisnet [6]. However, the selectivity was only 16% on Ge/ H-ZSM5. The main aro-

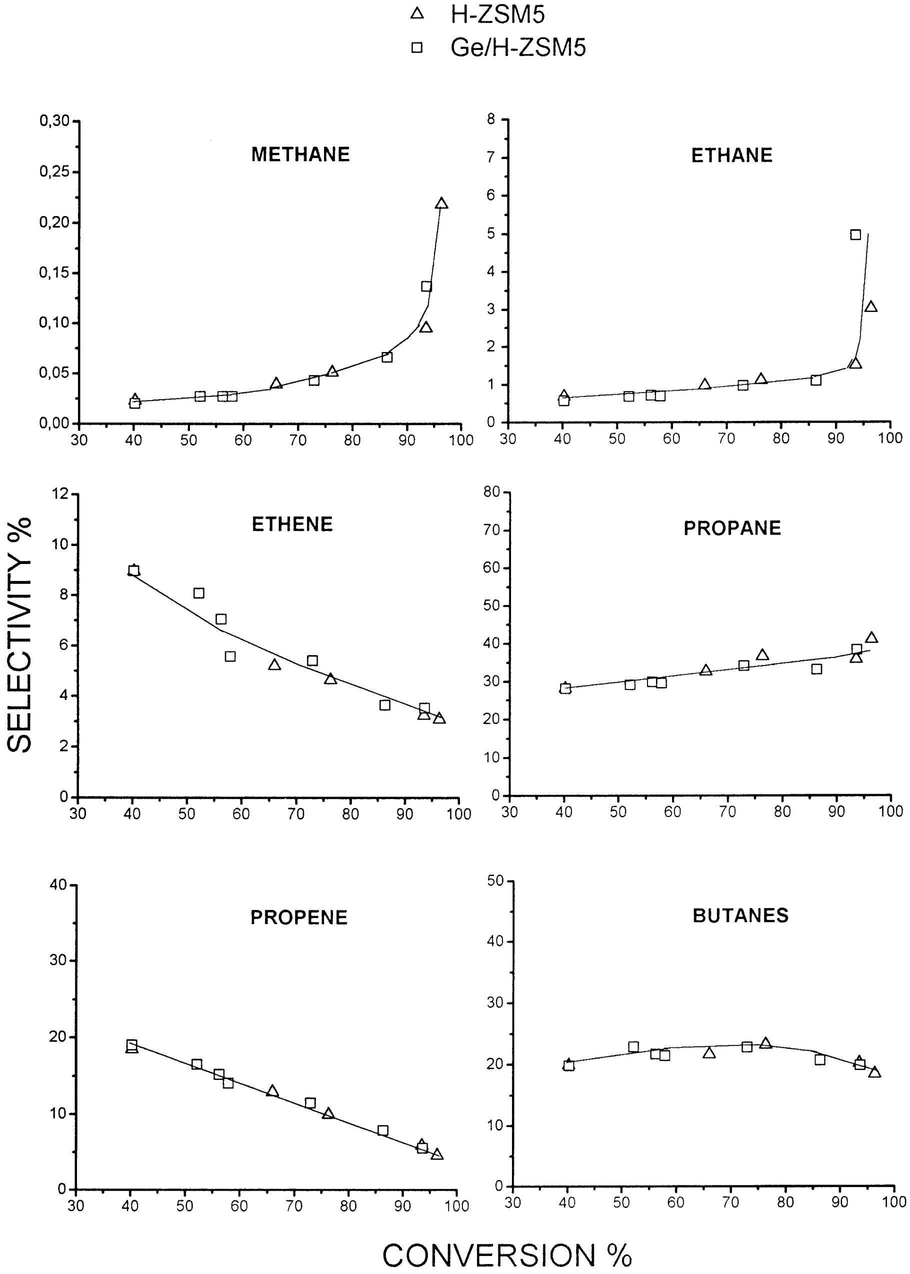


Figure 7. Selectivity as a function of the *n*-heptane conversion over H-ZSM5 and Ge/ H-ZSM5, at 673 K. (Continued on next page.)

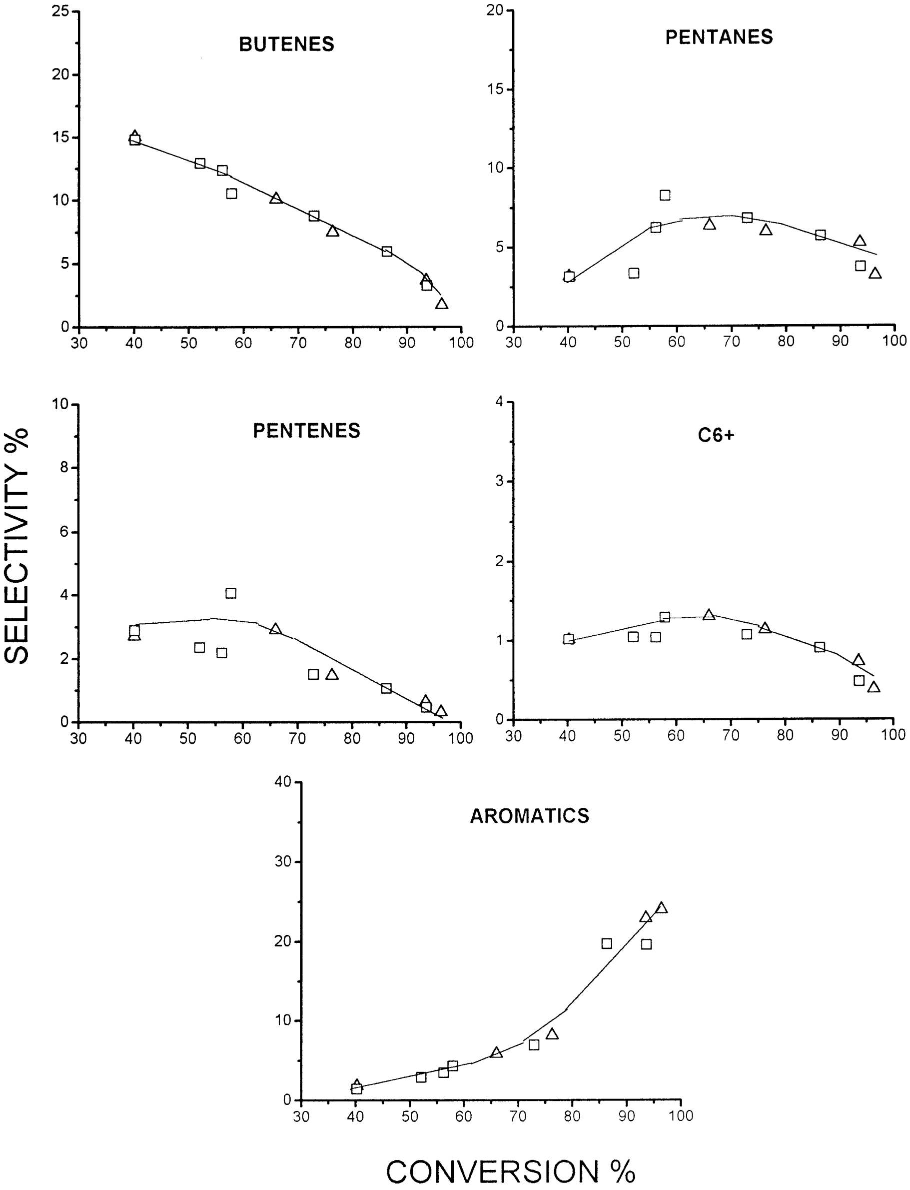


Figure 7. (Continued.)

matic products were benzene, toluene and xylenes (more than 98%) and only a small fraction of ethylbenzene. With increasing conversion the fraction of toluene increased in detriment of benzene and xylenes. Germanium did not modify the formation of the different aromatic fractions on the total aromatic product (figure 6), as already observed for Ga/H-ZSM5, according to Kitagawa [5].

To explain these results we did further experiments by performing cracking of *n*-heptane on Ge/H-ZSM5 and H-ZSM5, as well as propane dehydrogenation on GeO_2/SiO_2. The cracking reaction at 673 K shows that the activity and selectivity were not affected by adding germanium to H-ZSM5, as displayed in figure 7. The activities were quite similar (K_{app} = 3.3 g of propane/(g

Table 5

Conversion (Conv.) and selectivity values obtained over the GeO_2/SiO_2 catalyst, with 10 and 30% of germanium oxide content, and over pure Ga_2O_3 at 773 K by Gnep [15] and by Mériaudeau and Naccache at 803 K [31]

Catalyst	Conv. (%)	Selectivity (%)		
		methane	ethene	propene
10% GeO_2/SiO_2	0.1	5.3	13.2	81.5
30% GeO_2/SiO_2	0.4	0.5	1.3	98.2
Ga_2O_3 [31]	1.6	4.5	4.5	91.0
Ga_2O_3 [15]	10	10	20	70

of catalyst h)) on both catalysts. In summary, germanium did not affect the cracking activity of the zeolite. However, the dehydrogenation of propane on GeO_2/SiO_2 exhibits high selectivity toward propene, as shown in table 5. The activity was much lower than observed on Ga_2O_3 catalyst, as reported by Mériaudeau and Naccache [31] and Gnep [15]. Thus, germanium promotes the dehydrogenation reaction of propane, which increases the formation of olefins, mainly propene, and then the activity on Ge/H-ZSM5.

3.2.2. *Propane conversion over Pt/H-ZSM5 and Pt–Ge/H-ZSM5 catalysts*

The product selectivities on H-ZSM5, Pt/H-ZSM5 and Pt–Ge/H-ZSM5 are displayed in figure 8. The selectivities of methane and ethene on Pt/H-ZSM5 decrease with simultaneous increase of propene and ethane, which is attributed to the dehydrogenation activity of Pt, which increases the formation of propene by direct dehydrogenation, and the formation of a parallel activation favours the transformation of propane. The increase of ethane is attributed to the hydrogenolysis on Pt sites, according to Mériaudeau [10]. Therefore, propane dehydrogenation to propene prevails on the platinum sites and not cracking on the acid sites.

The Pt/H-ZSM5 catalyst exhibits also accumulation of the intermediate products, alkenes preferentially, as shown in figure 8. The greater formation of olefinic

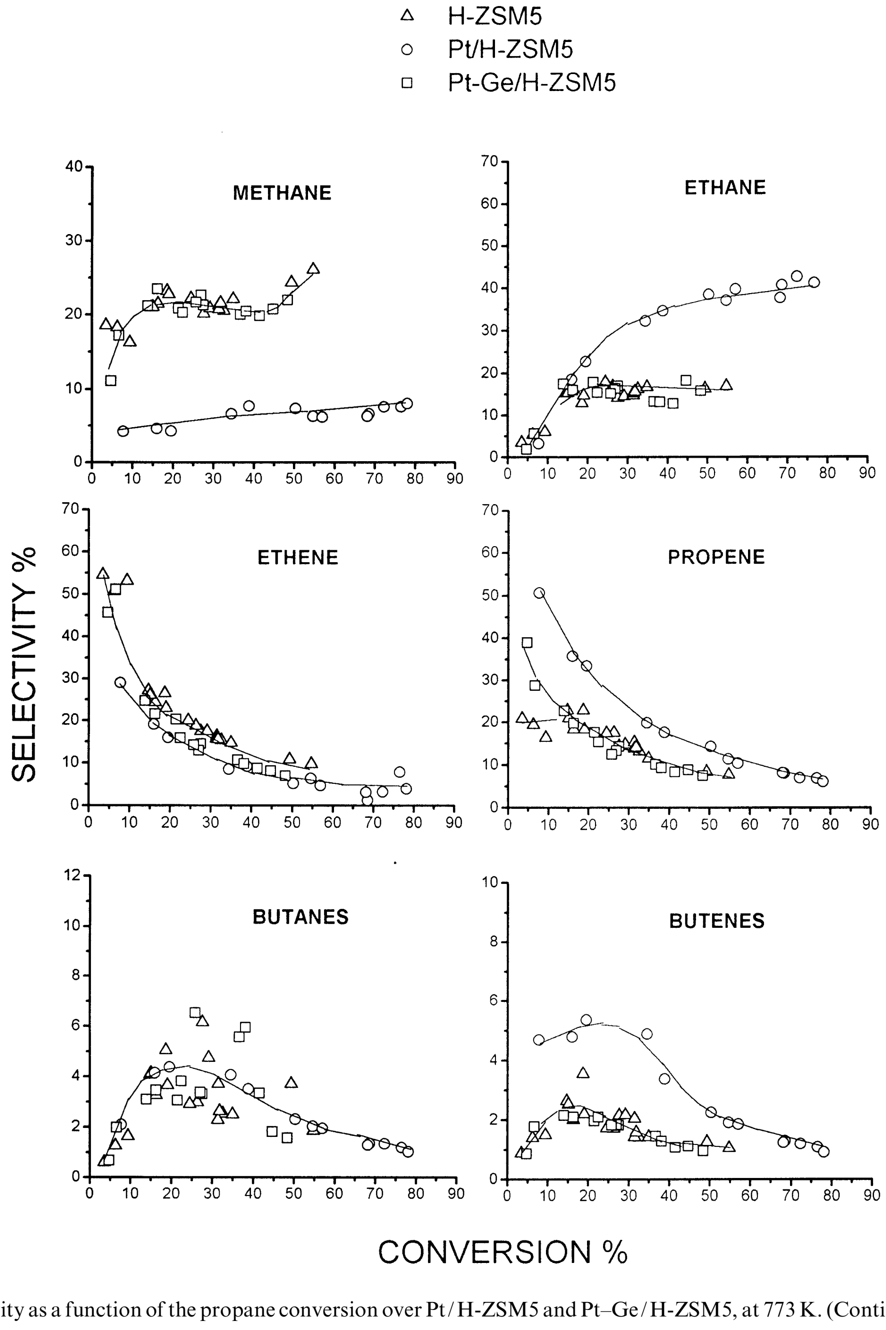


Figure 8. Selectivity as a function of the propane conversion over Pt/H-ZSM5 and Pt–Ge/H-ZSM5, at 773 K. (Continued on next page.)

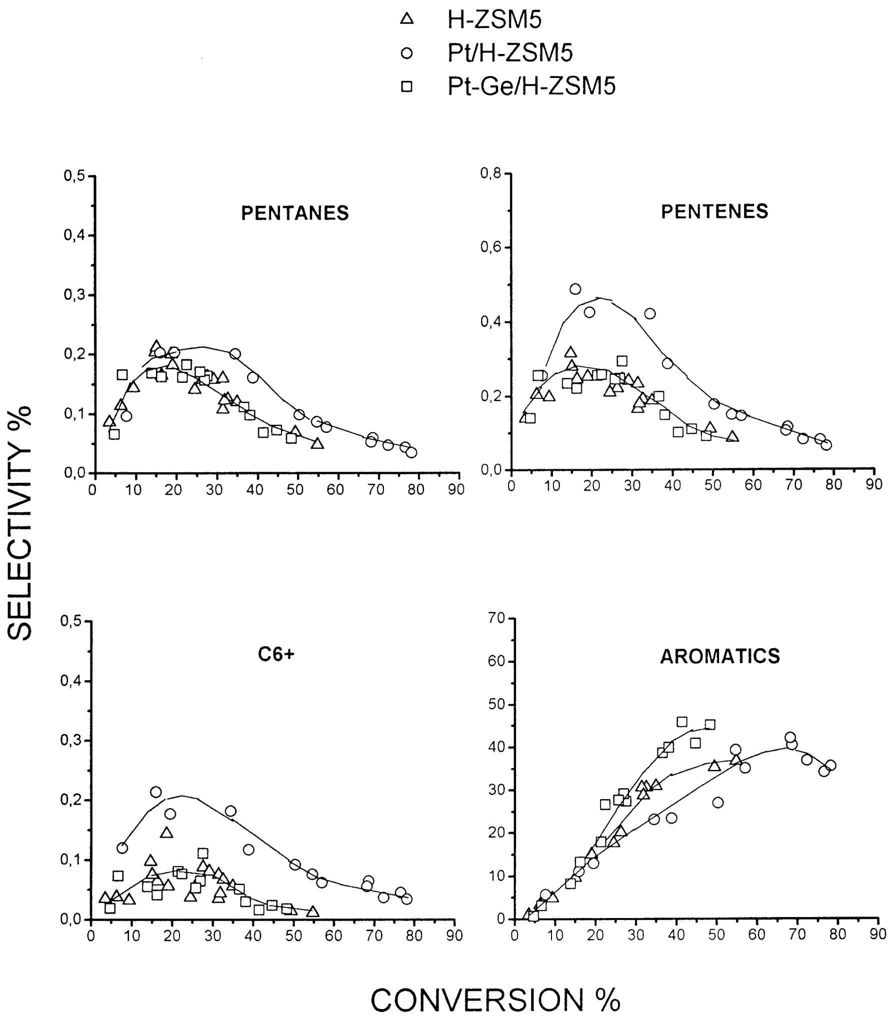


Figure 8. (Continued.)

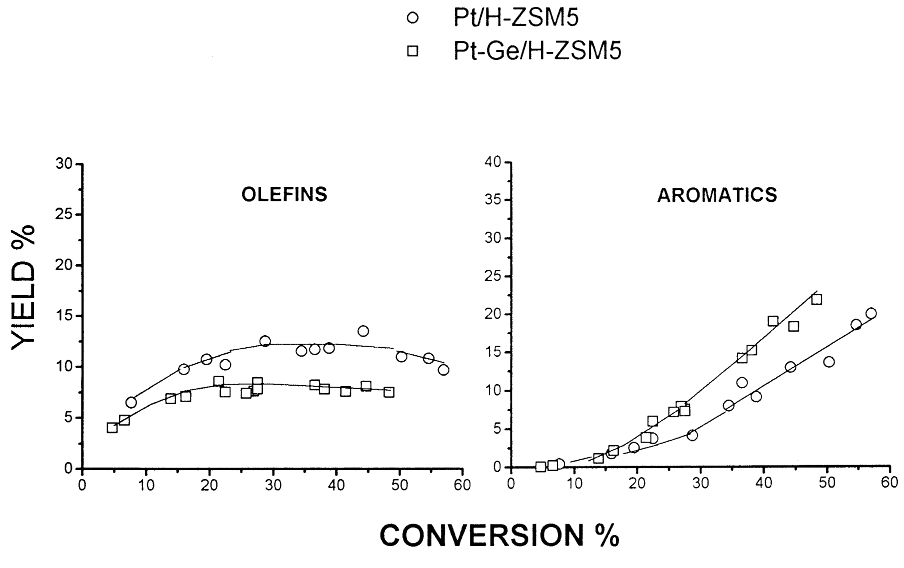
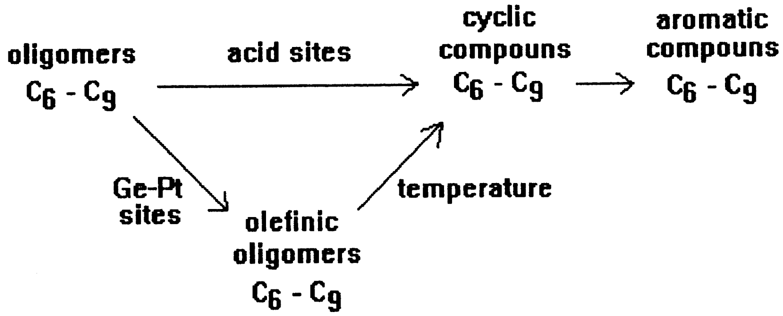


Figure 9. Yield of aromatic and olefin products as a function of the propane conversion for Pt / H-ZSM5 and Pt–Ge / H-ZSM5, at 773 K.



Scheme 1.

products and simultaneous accumulation of intermediate products results in a decrease of aromatics on Pt/H-ZSM5, as shown in figure 9. On the other hand, the Pt–Ge/H-ZSM5 catalyst exhibits higher selectivity toward aromatics and lower formation of olefinic compounds, while Pt–Ge/H-ZSM5 and H-ZSM5 catalysts presented similar selectivities for methane and ethane. Nevertheless, below 10% conversion the selectivity of propene on the bimetallic catalyst was greater than on H-ZSM5.

Dehydrogenation and hydrogenolysis prevail on the Pt/H-ZSM5 catalyst, increasing olefins and ethane, respectively. However, addition of germanium changes markedly the hydrogenolysis and dehydrogenation process on platinum, due to the Pt–Ge interaction, inhibiting the hydrogenolysis, in agreement with the literature [17–20]. Goldwasser [18] showed that the hydrogenation activity decreases five-fold on the Pt–Ge/Al_2O_3 catalyst, while hydrogenolysis disappears. DeMiguel [17] showed that germanium with Pt/Al_2O_3 catalyst decreases markedly hydrogenolysis, but also the dehydrogenation with less extent.

Similarly, Mériaudeau et al. [10] observed that on Cu–Pt/H-ZSM5 and Ga–Pt/H-ZSM5 catalysts the hydrogenolysis decreases and the selectivity toward aromatics increases. This was already observed by Shpiro [32] on Cr–Pt/H-ZSM5 and by Maggiore [33] on La, Re, Pb or Ir–Pt/H-ZSM5 catalysts.

In conclusion, germanium inhibits the hydrogenolysis on platinum sites but increases the dehydrogenation, since GeO_2/SiO_2 increases the dehydrogenation of propane (table 5). The acidity and the number of strong acid sites decreases by adding Ge on H-ZSM5, affecting the cyclization reaction and the formation of aromatic compounds. Dehydrogenation prevails on Pt–Ge sites, increasing the formation of olefinic oligomers, then transformed by thermal cyclization to cyclic compounds, which are more effective than the decreasing acidity in the presence of germanium (scheme 1).

4. Conclusion

The addition of germanium on H-ZSM5 changes the acid and active properties of the zeolite. The strong interaction between germanium oxide and the Brønsted acid sites of the zeolite change the acidic properties. Probably, this interaction is due to the occurrence of a solid-state reaction between germanium oxide and the Brønsted acid sites during the preparation and calcination step, similar to the ZnO/H-ZSM5 system, as observed by Yakerson [27]. The principal effects of germanium in the Ge/H-ZSM5 catalyst are: (a) the activity of propane increases, (b) the selectivity toward aromatics decreases and (c) formation and accumulation of intermediate products, preferentially alkenes.

The activity increases due to the dehydrogenation on germanium oxide, which prevents the expected decrease in activity due to the decrease of total and strong acid sites. The decrease of selectivity toward aromatics can be explained by the decrease of the number of strong acid sites, which reduces the cyclization capacity, and due to a greater formation of olefinic products, as a consequence of the dehydrogenation activity on germanium.

The selectivity of the Pt–Ge/H-ZSM5 catalyst was drastically affected, mainly due to changes in hydrogenolysis and dehydrogenation on Pt sites in the presence of Ge, and Pt–Ge interaction. Compared to the Pt/H-ZSM5: (a) the selectivity toward aromatic compounds increases, (b) the selectivity of ethane decreases and (c) lower accumulation of intermediate compounds.

The higher selectivity toward aromatics on Pt–Ge/H-ZSM5 was attributed to the decrease of the hydrogenolysis activity on platinum and the simultaneous increase in the cyclization capacity of unsaturated oligomers by thermal effects, increasing the aromatic formation.

References

[1] N.Y. Chen and T.Y. Yam, Ind. Eng. Proc. Dev. 25 (1986) 151.
[2] J.R. Mowry, R.F. Anderson and J.A. Johnson, Oil Gas J. (Dec. 1985) 128.
[3] P.C. Doolan and P.R. Pujado, Hydrocarbon Processing (Sept. 1989) 72.
[4] Y. Ono, Catal. Rev. Sci. Eng. 34 (1992) 179.
[5] H. Kitagawa, Y. Sendoda and Y. Ono, J. Catal. 101 (1986) 12.
[6] M. Guisnet, N.S. Gnep J.Y. Doyemet, A.M. Seco and F.R. Ribeiro, Appl. Catal. 43 (1988) 153.

[7] J. Bandiera, M. Dufaux and Y. Ben Taâarit, Appl. Catal. A 148 (1997) 283.

[8] B.W.L. Southward, R.J. Nash and C.T. O'Connor, Appl. Catal. A 135 (1996) 177.

[9] K.G. Wilsher, P. Smart, R. Western, T. Mote and T. Behring, Appl. Catal. 31 (1987) 339.

[10] P. Mériaudeau, G. Sapaly and C. Naccache, Stud. Surf. Sci. 49 (1989) 1423.

[11] T. Mole, J.R. Anderson and G. Creer, Appl. Catal. 17 (1985) 141.

[12] M. Guisnet, N.S. Gnep, J.Y. Doyemet, A.M. Seco and F.R. Ribeiro, Appl. Catal. 43 (1988) 153.

[13] R.C.P. Bittencourt, MSc thesis, COPPE/UFRJ, Brazil (1990).

[14] M.S. Scurrel, Catal. Today 3 (1988) 451.

[15] N.S. Gnep, J.Y. Doyemet and M. Guisnet, J. Mol. Catal. 45 (1988) 281.

[16] R.C.P. Bittencourt, M. Schmal and Y.L. Lam, Anais Ass. Bras. Quimica 40 (1991) 13.

[17] S.R. De Miguel, O.A. Scelza and A.A. Castro, Appl. Catal. 44 (1988) 23.

[18] J. Goldwasser, B. Arenas, C. Bolivar, C. Castro, A. Rodrigues, A. Fleitas and J. Giron, J. Catal. 100 (1986) 75.

[19] C. Bolivar, H. Charcosset, M. Primet, B. Arenas and R. Torrellas, in: *Annals 8th Iberoamerican Catalysis Congress*, Spain (1982) p. 162.

[20] M. Bowman and P. Biloen, J. Catal. 48 (1977) 209.

[21] Y.L. Lam, Brazil P.I. 8506248 (1985).

[22] M.M. Dubinin, J. Colloid Interf. Sci. 23 (1967) 487.

[23] A.S. Maia, DSc Qualify, COPPE/UFRJ, Brazil (1989).

[24] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed. (Wiley, New York) pp. 263–304.

[25] S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, 2nd Ed. (Academic Press, New York, 1982).

[26] E.G. Derouane and Z. Gabelica, J. Catal. 65 (1980) 486.

[27] V.I. Yakerson, T.V. Vasina, L.I. Lafer, V.P. Sytnyk, G.L. Dikh, A.V. Mokkov, O.V. Bragin and Kh.M. Minachev, Catal. Lett. 3 (1989) 339.

[28] W.G. Haag, Faraday Discussion Chem. Soc. 72 (1981) 317.

[29] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F. Ramoa Ribeiro and M. Guisnet, Appl. Catal. 35 (1987) 93.

[30] Y. Ono and K. Kanae, J. Chem. Soc. Faraday Trans. 87 (1991) 663.

[31] P. Mériaudeau and C. Naccache, J. Mol. Catal. 50 (1989) L7.

[32] E.S. Shpiro, G.J. Toluenova, V.I. Zaikovskii, O.P. Tkachenko, T.V. Vasina, O.V. Bragin and Kh.M. Minachev, Stud. Surf. Sci. 46 (1989) 143.

[33] R. Maggiore, S. Scirè, S. Galvagno, C. Crisafulli and G. Toscano, Appl. Catal. A 79 (1991) 24.