Dehydroisomerization of *n*-pentane to isopentene on molecular sieves impregnated with platinum

Gabriel Herrera P., Daniel Lardizábal G., V.H. Collins Martínez and A. Aguilar Elguézabal *

Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes 120, Chihuahua, Chih. CP 31110, Mexico
E-mail: fredae@mail.cimav.edu.mx

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The direct conversion of *n*-pentane to isopentene by dehydrogenation and isomerization in a single step was studied on Pt supported over SAPO-11, ferrierite (FER) and HZSM5 molecular sieves. The Pt/SAPO-11 presented the best selectivity to mono-branched pentenes. The characterization of acidic sites with isomers of propylamine revealed a better capacity for SAPO-11 to diffuse mono-branched amines and that is considered a consequence of its pore geometry, which could explain the obtained selectivity.

KEY WORDS: dehydroisomerization; *n*-pentane; platinum; molecular sieves

1. Introduction

During the last years, there has been an increasing interest in the study of the dehydroisomerization of *n*-alkanes, *n*-butane being the most studied molecule [1–4]. The interest in this reaction comes from the importance of isobutylene as intermediate for the petrochemical industry, the MTBE and synthetic gasoline production. Nevertheless, the use of MTBE, as well as butane content in gasoline is being severely questioned. In fact, the reduction of aromatics and butanes as well as the substitution of the MTBE are the main requirements for the future gasoline formulation. The increase of alkylated fraction in gasoline (produced from isoalkenes), and the use of TAME are the most promising alternatives. The problem associated to the use of MTBE is due to its high solubility in water, which has caused the contamination of groundwater due to the leaking of storage tanks and pipelines. On the other hand, TAME, besides its lower solubility in water has lower vapor pressure, which reduces the air pollution as compared with MTBE [5]. The TAME synthesis is made by the etherification of 2-methyl-1-butene and 2-methyl-2-butene isomers, and scarce work has been published on dehydroisomerization of *n*-pentane to produce these isomers.

Actually the process to produce TAME consists in the etherification of the C_5 fraction obtained from the depentanizer unit after FCC. The dehydroisomerization of *n*-pentane to increase the content of 2-methyl-1-butene and 2-methyl-2-butene in the C_5 fraction from the depentanizer unit is advantageous to obtain higher TAME yield.

In the hydroisomerization of *n*-paraffins the use of bifunctional catalysts with a good balance of acidity and metal content has shown high efficiency, like metal (Pt and Pd) doped zeolites [6]. According to Tromp *et al.* [7], an adequate zeolite for *n*-paraffin hydroisomerization must have low content of strong acid sites in order to avoid cracking of the hydrocarbon and thus, the formation of carbon on the surface of the zeolite. Besides the above mentioned, the size of the pentane molecule was taken in consideration and thus, for this study, the medium size molecular sieves SAPO-11, ferrierite and HZSM5 were selected as the active supports.

The main objective of this work was to determine the activity and selectivity in dehydroisomerization of *n*-pentane over Pt/SAPO-11, Pt/FER and Pt/HZSM5. The influence of pore geometry and acidity on the activity and selectivity was investigated.

2. Experimental

2.1. Molecular sieve synthesis

Aluminosilicates were synthesized by hydrothermal methods [8]. For HZSM5 with a SiO_2/Al_2O_3 ratio of 150, 20 g of silicic acid (Avocado, 98%), 0.5 g of sodium hydroxide (J.T. Baker, 98.7%), 10 g of tetrapropyl ammonium bromide ($C_4H_{28}NBr$, Fluka, 98%) were mixed on 5 ml of distilled water. After 2 h of stirring, 10 ml of dipropylamine ($C_6H_{15}N$, Fluka, 99%) were added and the stirring was maintained by 3 h more. Simultaneously 0.93 g of aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$, Monterrey, 98.7%) were dissolved in 5 ml of water by adding 0.2 ml of sulfuric acid (H_2SO_4, Monterrery, conc.) and stirring was maintained for 1 h. Both solutions were mixed under constant stirring and distilled water was added to complete 250 ml, the stirring was kept constant by 2 h. The obtained pH was 11.4. The produced gel was transferred to an autoclave and maintained at 160 °C during 64 h. The obtained solids were separated by centrifugation and washed repetitively with distilled water. Drying was done at 120 °C for 2 h, and the solids were cal-

* To whom correspondence should be addressed.

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cined at 550 °C for 6 h under air flow of 80 ml/min. The obtained sodium ZSM5 form is transformed to the acid form by ammonium sulfate exchange ($(NH_3)_2SO_4$, J.T. Baker, 99%) with a 1 M solution under ambient temperature and stirring for 1 h. The molecular sieve was washed repeatedly till water of washing was free of sulfate ions, dried at 120 °C for 2 h and calcined at 500 °C for 3 h under air flow to eliminate ammonium and thus obtain the acid form.

The FER was prepared from 10 g of sodium silicate solution (27% of SiO_2 and 14% of NaOH, Sigma) and 7.5 ml of distilled water. This solution was maintained under stirring by 0.5 h, meanwhile 0.4 g of tetramethyl ammonium hydroxide ($C_4H_{13}NO{\cdot}5H_2O$, Fluka, 98%) in 5 ml of distilled water was dropped slowly to the solution. Subsequently, the product was maintained under stirring by 2 h at ambient temperature. Another solution was prepared by mixing 2 g of aluminum sulfate and 7.5 ml of distilled water. These solutions were mixed and maintained under stirring for 2 h under ambient temperature. The pH of the obtained gel was 11.6. The gel was matured at ambient temperature during 24 h and afterwards the gel was transferred to a stainless steel autoclave and kept at 160 °C under self-generated pressure during 96 h. The obtained solids were separated from solution by centrifugation and washed repetitively with distilled water. Drying was done at 120 °C for 2 h and the calcination of molecular sieve was performed at 550 °C during 6 h. The obtained FER was in the sodium form, so the FER was treated as the NaZSM5 to obtain the acid form.

The SAPO-11 was prepared from a solution of 28.4 g of aluminum isopropoxide ($C_9H_{21}AlO_3$, Sigma) and 30 ml of distilled water, which was stirred for 1 h and maintained under ambient temperature during 24 h for the maturation step. Simultaneously, 1.5 ml of tetra-ethylorthosilicate ($(CH_3CH_2)_4SiO_4$, Sigma, 99%) were added to 7.8 ml of orthophosphoric acid (H_3PO_4, J.T. Baker, 85%) and 20 ml of distilled water. The matured gel obtained from aluminum isopropoxide was milled and incorporated to the ethylorthosilicate and orthophosphoric acid solution as well as 11.4 ml of dipropylamine ($C_6H_{15}N$, Fluka, 99%). The resulting gel was transferred to a stainless steel autoclave and kept at 210 °C under self-generated pressure during 24 h. The obtained solids were separated from solution by centrifugation and washed repetitively with distilled water. Drying was done at 120 °C for 2 h and the molecular sieve was calcined at 550 °C during 6 h under airflow.

Before metal impregnation, molecular sieves were pressed into disc form and subsequently crushed and sieved to obtain particles in the range of 40–60 mesh. Active metal was deposited on supports by incipient wetness using chloroplatinic acid ($H_2PtCl_2{\cdot}6H_2O$). The metal salt was dissolved in the appropriate water amount to obtain 0.5 wt% of metal on support. After the metal solution was added to the support, the mixture was maintained at ambient temperature during 4 h, and the obtained solid was dried at 120 °C for 2 h. The calcination was performed at 500 °C under airflow during 2 h.

2.2. Catalysts characterization

The study of the accessibility of the isomers of C_5 molecules to the internal pores of the molecular sieves was made by the adsorption–desorption of *n*-propylamine and isopropylamine on a thermogravimetric balance TGA 2950 Hi-Res Analyzer from TA Instruments. Before the adsorption [9], the molecular sieve was cleaned by heating to 350 °C under nitrogen flow (150 ml/min) and the sample was kept at this temperature during 30 min or until constant weight was obtained. Then the sample was cooled to 75 °C maintaining the nitrogen flow. At this temperature, nitrogen was saturated with the amine and the gas mixture was passed over the molecular sieve during 30 min or until constant weight was obtained. Condensed amine was removed at the adsorption temperature passing pure nitrogen during 1 h when constant weight is reached. For desorption of the amine the sample was heated at 10 °C/min from 75 to 850 °C.

The BET surface area was determined by nitrogen adsorption in a Quantachrome model Autosorb 1C. Identification of main crystalline phase for each sample was determined by XRD analysis on an X′Pert MPD diffractometer from Phillips, using Cu Kα radiation and graphite monochromator filter.

2.3. Activity test measurement

The catalytic activity measurements were conducted in a glass Pyrex fixed-bed continuous reactor with an on-line GC analytical system. The reaction conditions were $W/F = 0.3\ h^{-1}$, catalyst mass of 0.15 g, H_2/C_5 ratio of 2, atmospheric pressure and reaction temperatures ranging from 200 to 400 °C. The products were analysed by gas chromatography in an Autosystem XL from Perkin–Elmer, using FID as detector and a Petrocol DH capillary column 100 m × 0.25 mm × 0.5 μm from Supelco. Before reaction test, the metallic phase was reduced by a nitrogen/hydrogen flow of 30 ml/min (2 ratio) during 1 h at 550 °C.

3. Results and discussion

3.1. Characterization

As can be determined from figure 1, the XRD patterns of as-synthesized molecular sieves correspond with the phases of SAPO-11, FER and HZSM5, respectively [10,11]. Table 1 shows conditions of synthesis as well as the amount of isopropylamine and *n*-propylamine adsorbed during acidity characterization. The adsorbed amount of *n*-propylamine is higher for all the cases when compared with the adsorbed isopropylamine. The linear molecular geometry of *n*-propylamine presents less diffusion restriction [7] than the branched isopropylamine. Under equivalent conditions, only SAPO-11 presents almost the same amount of adsorbed species for "*n*" and "iso" structures. According to these results, the desorption of the isopentene from the active site

Table 1
Physicochemical properties of the molecular sieves.

Molecular sieve	Gel	S_{BET} (m^2/g)	SiO_2/Al_2O_3[a]	n-$C_3H_7NH_2$ (mmol/g)	i-$C_3H_7NH_2$ (mmol/g)
SAPO-11	$1.2n$-$(C_3H_7)_2NH_2 \cdot 0.2SiO_2 \cdot Al_2O_3 \cdot P_2O_5 \cdot 42H_2O$	200	0.2	0.5496	0.5044
FER	$0.62(CH_3)_4NOH \cdot 1.5Na_2O \cdot 15.2SiO_2 \cdot Al_2O_3 \cdot 300H_2O$	255	15.0	0.8441	0.4958
NaZSM-5	$4.5(C_3H_7)_4NBr \cdot 12Na_2O \cdot 90SiO_2 \cdot Al_2O_3 \cdot 2000H_2O$	318	150.0	0.8686	0.5042

[a] SiO_2/P_2O_5 mole ratio.

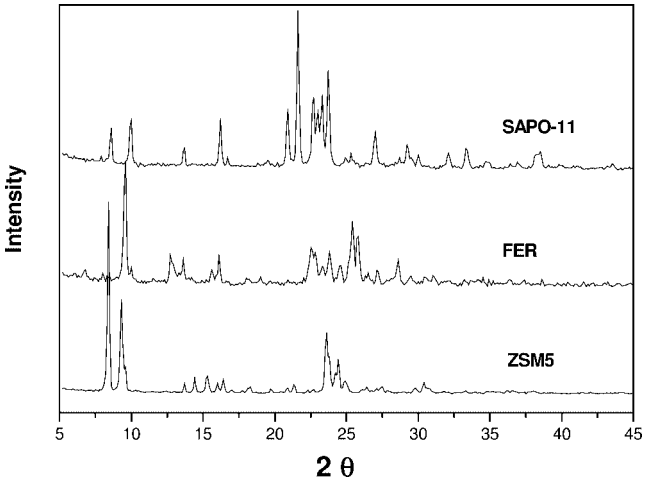

Figure 1. XRD patterns of as-synthesized molecular sieves.

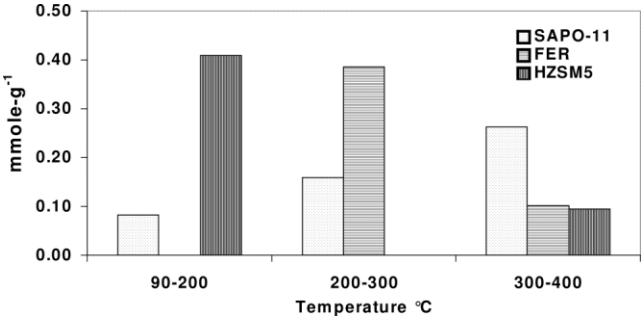

Figure 2. Thermodesorption of isopropylamine for the molecular sieves before Pt impregnation.

could be less restricted for the SAPO-11 structure, than for the case of FER and HZSM5.

If we consider the total amount of desorbed isopropylamine (which is almost the same for the three supports), an equivalent catalytic activity could be expected for the three catalysts. Nevertheless, different results on catalytic activity are be obtained as a result of the differences in the content and distribution of acid sites.

The strength of the acid sites is correlated with the temperature at which isopropylamine leaves the catalyst surface. From the results of isopropylamine thermoprogrammed desorption, three desorption temperature ranges (figure 2) were selected. For HZSM5 the observed acid strengths were only weak and strong (low and high desorption temperatures) and medium strength was almost negligible. For low strength maximum was obtained at 95 °C with a shoulder at 170 °C, and for the signal for high strength, the maximum was observed at 335 °C. For FER no desorption was observed at low temperature, but only at medium and high temperatures. Maxima of the two signals were obtained at 235 and 385 °C. For SAPO-11 three kinds of strength were observed through amine desorption temperature, presenting maxima at 95, 235 and 390 °C.

As can be seen in figure 2, the major population of acid sites was at low and medium strength for HSZM5 and FER, respectively, meanwhile SAPO-11 presented its major content of acid sites on high temperature range for isopropylamine desorption, *i.e.*, strong acid sites.

3.2. Catalytic activity measurements

According to the thermodynamic studies [12], the optimum reaction conditions to obtain maximum yield to isopentane must be between 200 and 400 °C, nevertheless in spite of the use of catalysts, to reach the equilibrium composition in that temperature range, a long residence time is required, far from the typical values of industrial processes. For this reason, studies on the development of catalysts for this reaction always involve reaction temperatures above 400 °C, where selectivity to isopentane is sacrificed to obtain higher yields at lower reaction time.

The dehydroisomerization reaction consists of two steps, dehydrogenation and isomerization. The first step is carried out over metal where the alkane is transformed to the corresponding alkene. Afterwards the alkene is isomerized over acidic sites, unless other reactions occur simultaneously such as cracking, cyclization, dienes formation and oligomerization.

To determine the contribution of homogeneous reaction during the catalytic tests, reaction measurements were made under the same conditions as for the activity tests, but without catalyst. The n-pentane cracking products were detected above 450 °C, conversion being 0.10% at this temperature and 0.13% at 500 °C. The activities of the studied catalysts were measured at $W/F = 0.30\ h^{-1}$, and H_2/n-C_5 ratio of 2 and under atmospheric pressure.

The impregnated metal was platinum, at 0.5 wt%, which is the best ratio of metal/support for alkane hydroisomerization according to Sinha [13]. The reaction of n-pentane was carried out below 500 °C, where homogeneous reactions were almost negligible.

Figure 3(A) shows the activity of the catalysts. As can be observed, the activity increases as Pt/SAPO-11 < Pt/FER <

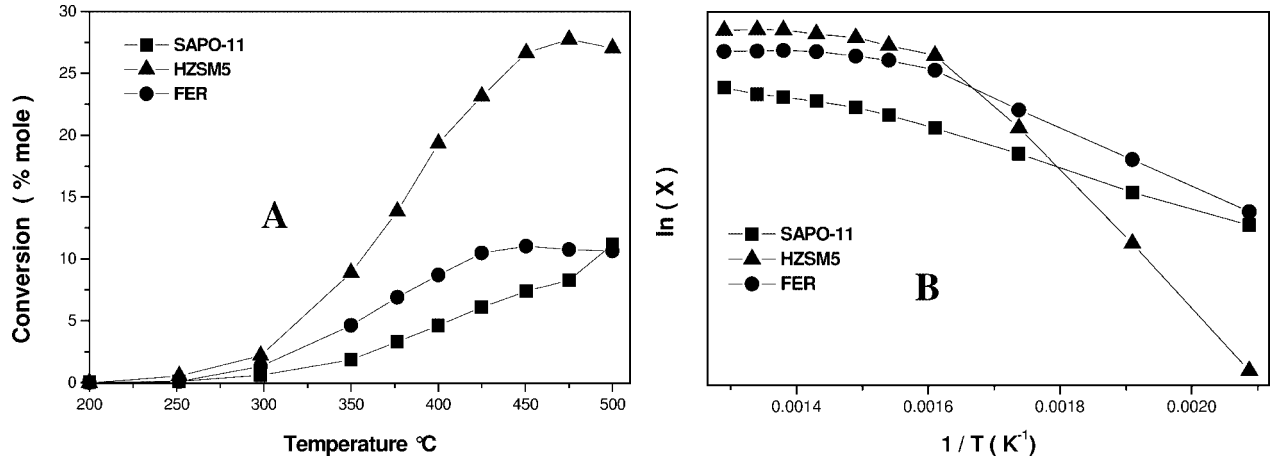

Figure 3. (A) Influence of temperature on conversion. (B) Arrhenius plots for the *n*-pentane dehydroconversion over the catalysts (Pt/molecular sieve).

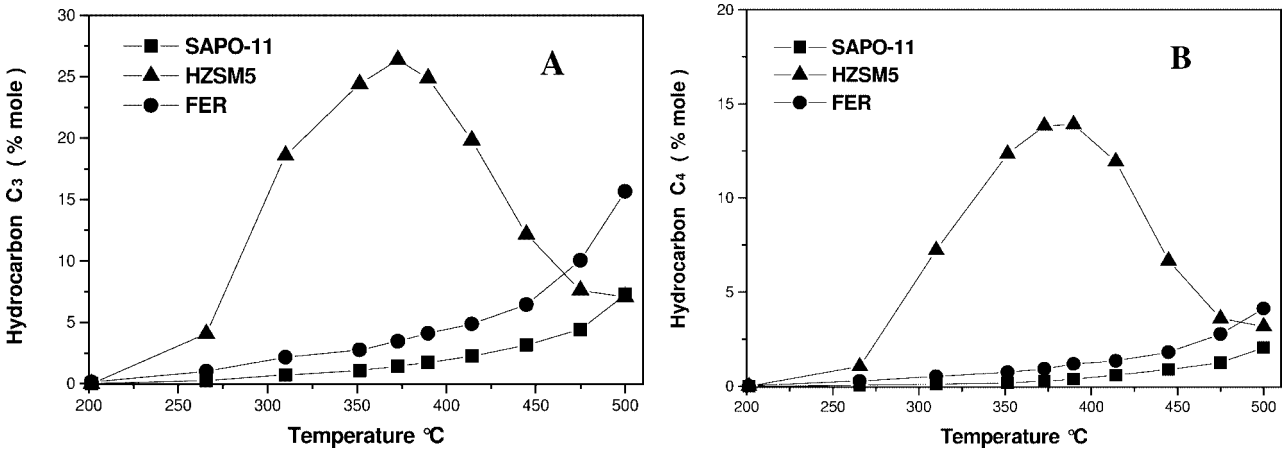

Figure 4. Selectivity to cracking of the *n*-pentane dehydroisomerization over the catalysts (Pt/molecular sieve): (A) produced hydrocarbon group C_3; (B) produced hydrocarbon group C_4.

Pt/HZSM5. For the calculation of the conversion (X), the total consumption of *n*-pentane is considered, *i.e.*, all reactions which transform *n*-pentane are taken into account, as cracking, cyclization and others. For this reason, the activity could be correlated with the total acidic sites as measured by *n*-propylamine, and in fact, there is a direct correspondence between activity and *n*-propylamine adsorption.

The Arrenhius plot is presented in figure 3(B) and as in the case of activity, the apparent activation energy was also related to total acidity. According to the slope obtained for the Arrenhius plot in the 250–375 °C range, the apparent activation energy ranges from 17 to 55 kcal/mol, indicating that the process is controlled by a chemical step. Above 375 °C, the apparent activation energy becomes lower than 5 kcal/mol for the three samples, which concerns a process controlled by a diffusion step. This behavior on the change of slope for the apparent activation energy was also reported for hydroisomerization of *n*-heptane [5].

After the activity test, the discharged catalysts presented a change in their original color, from white to gray or black, being more black in the following sequence: Pt/HZSM5 > Pt/FER > Pt/SAPO-11. The formation of carbon at the catalysts surface can be correlated with the change observed in the apparent activation energy. At lower temperatures, for the Pt/HZSM5 catalyst, the isomerization and cracking reactions may be carried out at the pore mouths, but as temperature increases, the carbon formation on accessible acidic sites forces the reactive molecules to diffuse to acidic sites located at the interior of particles, the diffusion step being so the controller one. This deactivation of accessible active sites also occurs on Pt/FER and Pt/SAPO-11 catalysts, but at lower extent.

For the Pt/HZSM5 catalyst a maximum of C_3 formation is observed at 375 °C, meanwhile for the Pt/FER and Pt/SAPO-11 catalysts, a continuous increase in yield for C_3 and C_4 is obtained (figure 4). As was mentioned above, besides cracking and dehydroisomerization, cyclic compounds, dienes and dimers are formed as temperature increases, in fact the lowering of cracking and dehydroisomerization yields is due to the production of those compounds.

As was mentioned before, TAME synthesis is carried out by isopentene and methanol reaction, but this etherification is selective for 2-methyl-1-butene and 2-methyl-2-butene isomers. As can be seen in figure 5, these two isomers

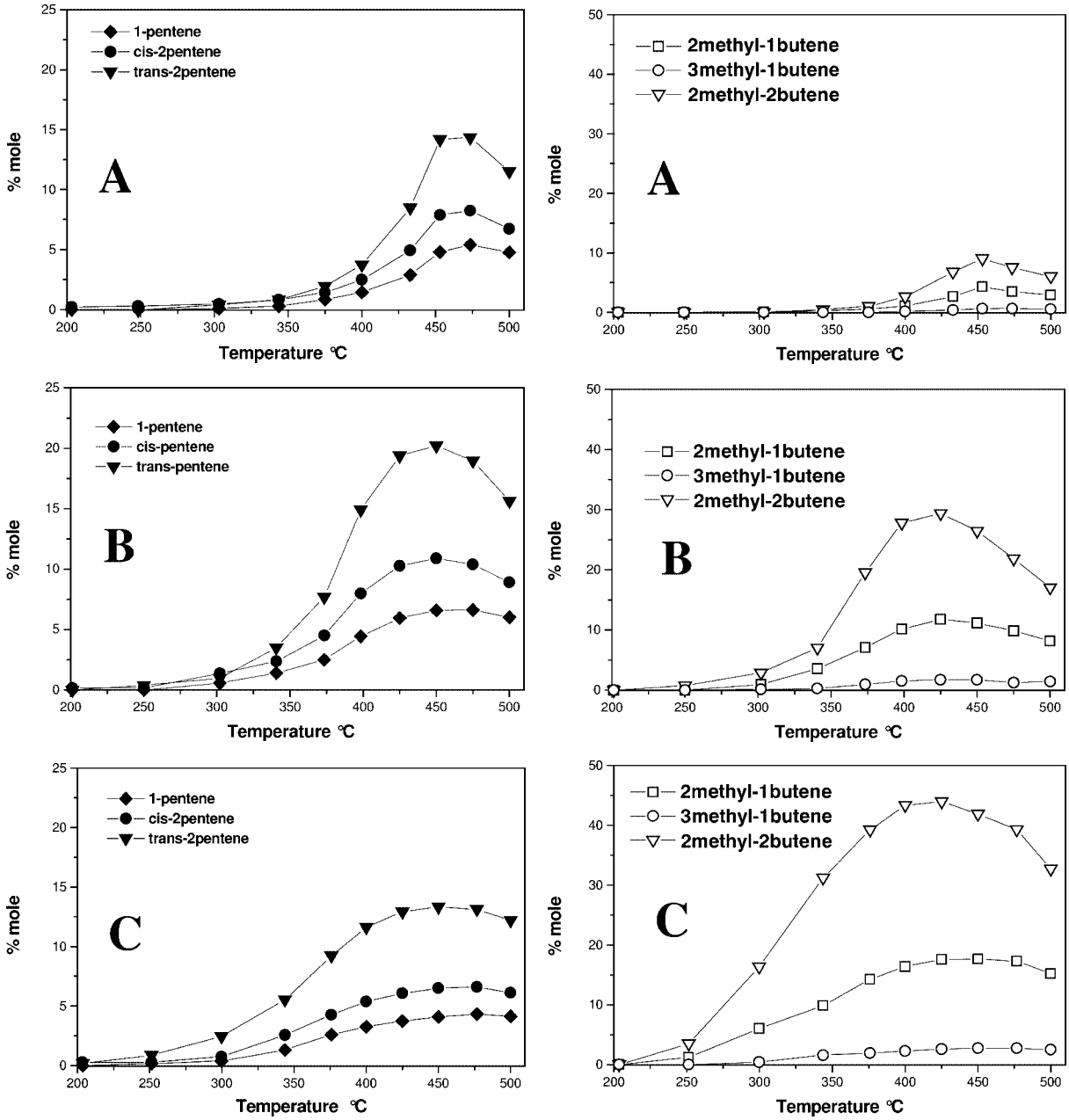

Figure 5. Products of the hydroisomerization of *n*-pentane dehydroconversion over the catalysts (Pt/molecular sieve). Selectivity to linear and mono-branched alkenes: (A) HZSM5, (B) FER and (C) SAPO-11.

appear as the main products for Pt/SAPO-11 and Pt/FER, but they are low for Pt/HZSM5.

According to Torsten and Bettina [12], at chemical equilibrium, the isopentenes are formed preferably than linear pentenes, but as temperature increases from 200 to 440 °C the linear structure becomes favored. The observed trend for the selectivity of products (figure 5) is that the change of positive to negative slope is presented 25 °C before for branched isomers than that of the linear ones.

The isomerization/cracking ratio (figure 6) keeps higher for Pt/SAPO-11 in the whole temperature range studied, which indicates that acidity and structure of the Pt/SAPO-11 catalyst directs reaction toward isomerization rather than cracking.

According to these results, a better yield to isopentenes was obtained for the Pt/SAPO-11. The porous geometry of this molecular sieve seems to favor the isomerization of pentenes. The frames of these three zeolites consist of ten member rings and HZSM5 has cylindrical channels of 5.6 × 5.3 Å [010] and 5.5 × 5.1 Å [100]; for FER, the channels are 5.4 × 4.2 Å [001] and 4.8 × 3.5 Å [010]; meanwhile the SAPO-11 has only one kind of channel, which is 6.3 × 3.9 Å [100]. The difference in kinetic diameter of *n*-pentane and isopentane is approximately 1 Å, being almost 6 Å for the iso structure and 5 Å for the linear one. As can be deduced, the pore geometry of SAPO-11 can favor the diffusion of the isopentene structure.

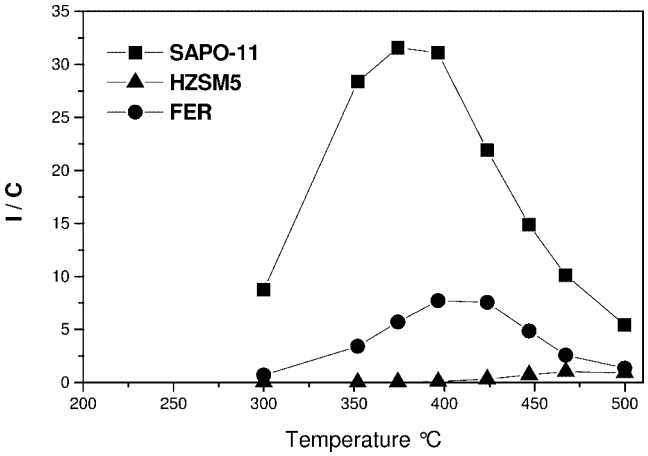

Figure 6. Influence of the temperature on isomerization/cracking (I/C ratio) over the catalysts (Pt/molecular sieve).

4. Conclusions

The results of the adsorption/desorption of iso and *n*-propylamine showed that the geometric structure of pores in HZSM5 and FER leads to a similar behavior, presenting a restriction for the isopropylamine adsorption. For the pore geometry of SAPO-11 that restriction was not observed. For this reason, it could be expected that under the same reaction conditions, for HZSM5 and FER based catalysts, some of the linear pentene could be isomerized to isopentene, but esteric restrictions lead to cracking of the molecule, thus lowering the yield to the isopentenes.

The Pt/SAPO-11 presented selectivity to the isopentenes 2-methyl-1-butene and 2-methyl-2-butene (active for TAME production) higher than 50% with conversions around 10%, these values being superior to those obtained with HZSM5 or FER based catalysts.

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