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Isomerization of C_5–C_7 *n*-alkanes on unidirectional large pore zeolites: activity, selectivity and adsorption features

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Abstract

The hydroisomerization–hydrocracking of nC_5–nC_7 is studied with a 12MR unidirectional zeolite (ITQ-4). Selectivity and kinetic parameters indicate that differences in pore topology are more important than acidity for determining isomerization selectivity. The adsorption of the paraffins is determined by van der Waals interactions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The actual lead phase out in gasoline together with future restrictions in the aromatic content, and also very probably in methylterbutylether (MTBE), will have a negative impact not only on the octane number of the gasoline pool, but also will reduce the total amount of gasoline produced. This is even worst if one considers that the limitation of the sulphur content may require to remove from the gasoline pool a part of the higher boiling gasoline produced in the FCC unit [1–4]. Taking into account the above scenario together with further limitations in the olefins content of the gasoline in order to decrease ozone problems, specially in large populated areas, it appears that branched paraffins are the preferred gasoline component. If this is so and taking into account the actual gasoline pool (Table 1) [5], it is evident that in future gasoline fuels would be highly desirable to increase the branched paraffin components which are produced by alkylation and isomerization units. It is then not surprising the large efforts made in recent years trying to overcome the main limitation of the gasoline alkylation process, i.e. the use of HF and H_2SO_4 as acid catalysts by developing more friendly solid alkylation catalysts [6,7]. In another direction, it will also be interesting to develop new paraffin isomerization catalysts that can selectively carry out the isomerization of C_5–C_7 *n*-paraffins. One type of C_5–C_7 paraffin isomerization catalyst is based on zeolites, and more specifically on Pt/mordenite [8]. This zeolite has strong acidity and is very suitable to isomerize the more difficult *n*-pentane. However, it is less selective when dealing with longer chain paraffins such as nC_6 and nC_7. It has been recently presented [9] that a large pore tridirectional zeolite such as beta, specially when synthesized with smaller crystal sizes, can be better than mordenite to isomerize nC_6 and specially nC_7 paraffins. Here, we have study the possibilities of a recently reported large pore unidirectional zeolite ITQ-4 [10] that can be synthesized with high Si/Al ratios. The results are compared with those obtained with mordenite, and through a kinetic study it has been possible to show that the

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Table 1
A gasoline pool composition

Fraction	Rate (vol.%)	Aromatic (vol.%)	Olefins (vol.%)	RON	MON
Reforming	29.6	66.2	0.7	98.6	88.6
LSR	4.0	3.9	1.0	74.4	80.9
Isomerization	4.0	0.9	0.4	85.4	82.9
FCC	41.4	29.3	19.4	92.2	80.8
Coker	0.7	4.5	35.2	28.0	74.5
Hydrocracking	2.7	2.7	0.2	82.6	79.2
Polymerization	0.3	0.5	94.6	94.4	81.9
Dimerization	0.2	0.1	98.1	95.3	81.2
Alkylation	13.3	0.4	0.5	93.2	91.1
Subtotal	96.3	33.4	13.7	93.1	84.9
Butanes	3.7			91–93[a]	
Total	100	32.1	13.2	93.2	85.0
RFG[b]		23.7	13.2	92.6	84.7

[a] Octane expressed by $(\mathrm{RON}+\mathrm{MON})/2$.

[b] Reformulated gasoline, CAA-1990.

heat of adsorption is the same on both zeolites, regardless the differences in acidity, and corresponds to the physical adsorption of the hydrocarbon. Owing to the different pore topology and acidity ITQ-4 is more selective than mordenite for isomerization of $n\mathrm{C}_7$.

2. Experimental

2.1. Material

A Pt/mordenite formulation suitable for light-straight-run (LSR) isomerization, and which contains 0.5% of Pt was supplied by CEPSA. The zeolite has a Si/Al of 20 and is highly crystalline. ITQ-4 was synthesized in our laboratories, following a reported procedure [10], with a Si/Al ratio of 20. Pt of 0.5% was incorporated into ITQ-4 by incipient wetness impregnation starting with an aqueous solution of hexachloroplatinic acid. The Pt containing samples were calcined in air at 500°C during 3 h and reduced “in situ” before the reaction. The BET surface areas of Pt mordenite and Pt/ITQ-4 are 314 and 446 $\mathrm{m}^2\,\mathrm{g}^{-1}$, respectively.

2.2. Catalytic experiment

The catalytic experiments were conducted in a fully automated stainless steel fixed bed continuous reactor with an on line analytical system (GC Varian 3400) equipped with a Petrocol DH50 column of 50 m. The reaction was carried out at different contact times (0.050–0.220 h) and different partial pressure of hydrocarbon (0.7–3.25 bar). The total pressure was 20 bar and reaction temperatures were varied between 270 and 320°C.

3. Results and discussion

In Fig. 1 the total conversion as well as the isomerization and cracking yields for *n*-pentane and *n*-hexane with ITQ-4 and mordenite catalysts are given. It can be seen there that mordenite is a more active catalyst than ITQ-4, being this specially visible when working at lower reaction temperatures. With respect to the isomerization yield this goes through a maximum with both reactants and catalysts when increasing reaction temperature or even better, when increasing the level of conversion [9]. This maximum in the isomerization yield is due to the coupling of the isomerization of *n*-paraffins and the cracking of the branched products formed. However, the results from Fig. 1 indicate that ITQ-4 is more selective towards paraffin isomerization than mordenite, and this is more clearly seen when working with *n*-hexane. In this case, the maximum isomerization yield is obtained at a similar temperature for both catalysts, but the ITQ-4 gives some 10% higher yield of branched C_6 products.

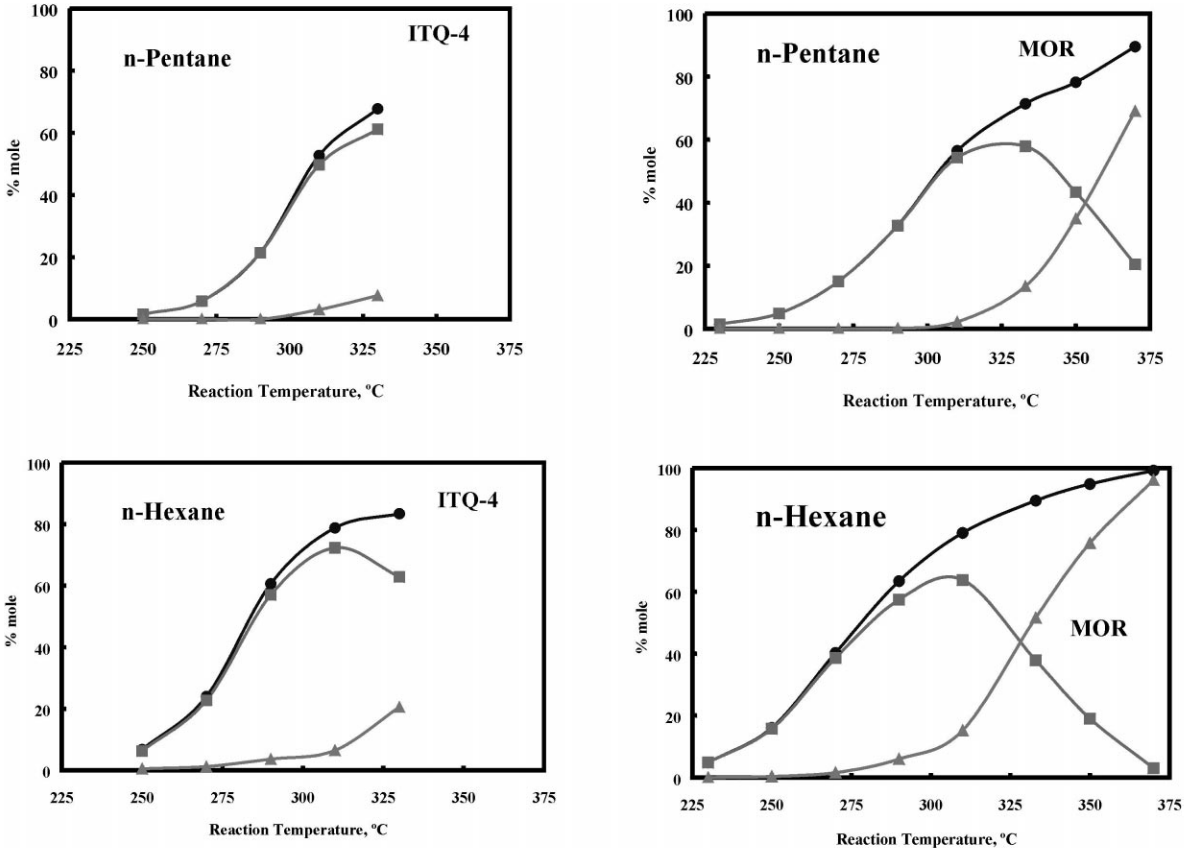

Fig. 1. Total conversion (●), isomerization (■) and cracking (▲) yields of *n*-pentane and *n*-hexane versus reaction temperature. Reaction conditions: 5.13 WHSV, 20 bar total pressure and H_2/hydrocarbon of 15 mol mol^{-1}.

Differences in isomerization–cracking selectivity in the two zeolites could be explained on the bases of differences in acidity and pore size within the two structures. In this way stronger acidity and narrower pore diameter would make, the average life time of the carbocations on the surface longer, and the diffusion of the branched products slower, respectively. Both factors will favour the cracking of the tertiary carbocations formed during isomerization before they desorb, and the readsorption and cracking of the branched paraffins before they leave the pores and come into the gas stream. The acidity results presented in Table 2 show that ITQ-4 has a higher amount of the strongest acid sites, i.e. those retaining pyridine at higher

Table 2
ITQ-4 and mordenite acidity measurement by adsorption of pyridine at different temperatures

Temperature °C	ITQ-4 (μmol pyridine/g cat.)		Mordenite (μmol pyridine/g cat.)	
	Brönsted	Lewis	Brönsted	Lewis
250	69	28	65	21
350	47	23	37	24
400	21	21	15	21

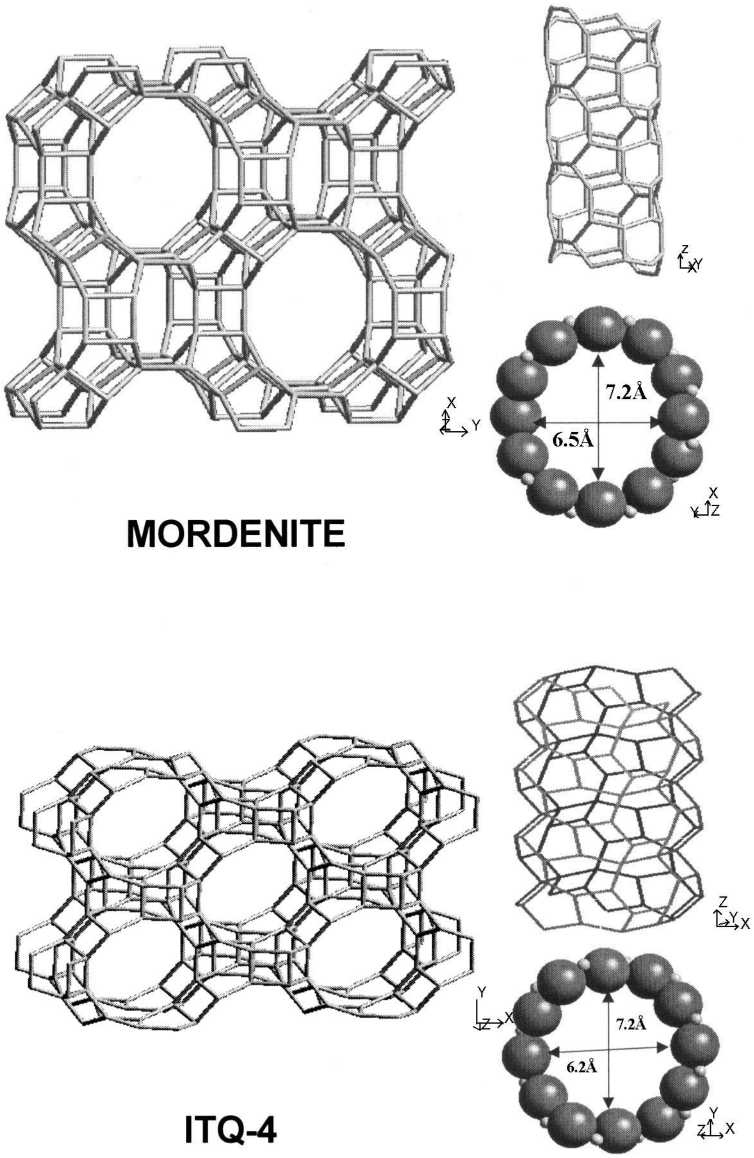

Fig. 2. Structure and pore size of ITQ-4 and mordenite zeolites.

desorption temperatures, even though the difference is small. Thus, from this point of view, the average life time of the carbocations on the surface should be higher in ITQ-4 than in mordenite, and consequently the cracking of adsorbed tertiary carbocations should be faster giving therefore with the former zeolite a lower selectivity to branched products. Since the opposite is observed experimentally we have to conclude that acidity is not the main factor controlling selectivity, but pore topology should play an important role here. If one looks into the crystallographic diameter of the pores they are 0.62×0.72 and $0.65 \times 0.72\,\text{nm}^2$ for ITQ-4 and mordenite, respectively (Fig. 2). Since the dimensions of the pores are very similar we cannot associate the differences in selectivity to pore diameter and consequently differences in pore geometry should be analysed in more detail. Looking at the pore topology of the two zeolites, it can be said that in mordenite there are side pockets that correspond to the crossing of the 12MR and 8MR channels, while in ITQ-4 there are lobs of much larger dimensions (1 nm wide [10,11]) than the side pockets in mordenite. We should then conclude that the differences in dimensions of the side pockets and lobs could be responsible for the differences observed. It may very well occur that the side pockets in mordenite with a highly constrained space are the preferred spots for the reaction to occur or even readsorption of the branched products could be highly favoured slowing down the diffusion of products. On the other hand, such restrictions will not take place in the very large lobs of the ITQ-4 but they may facilitate the diffusion of the products out, just as it occurs in very narrow-two direction roads in where only one car can pass, and "lobs" are build to "facilitate" the traffic. Following this, the differences in the instability of the branched products with both zeolite catalysts should be even more notorious when reacting *n*-heptane which has a higher probability of forming dibranched products than *n*-hexane. In this case pore size differences should be critical for the diffusion of dibranched products, with the corresponding differences in their cracking.

The results given in Fig. 3, clearly show that ITQ-4 is more selective for the isomerization of *n*-heptane than mordenite. When working with ITQ-4, ~40% yield of branched products are obtained for total conversion ~70% while with mordenite only 10% isomerization is observed at the same level of conversion. On the other hand, when a more detailed analysis of the products was carried out (Fig. 4), it was observed that monobranched isomers are by far the ones obtained in higher yields, while the dibranched and specially tribranched products are obtained in lower amount owing to the fast cracking occurring with any of the two zeolites. In any case it appears that the yields of dibranched isomers, even if they are present in lower amounts, are nevertheless higher with ITQ-4 than with mordenite.

3.1. Kinetics of isomerization of nC_5 and nC_6 on ITQ-4

For the kinetic study, experiments were carried out at different contact times, and in this way the conversion was varied in a large range from ~2 to ~25%, but in any case in a range where the cracking reaction is almost negligible.

Table 3
Values of apparent kinetic constants calculated at different reaction temperatures

n-Pentane		*n*-Hexane	
Temperature (°C)	k' ($atm^{-1}\,h^{-1}$)	Temperature (°C)	k' ($atm^{-1}\,h^{-1}$)
300	0.155	280	0.178
310	0.240	290	0.253
320	0.366	300	0.324

If one considers that the isomerization of nC_5 and nC_6 follows a Hougen–Watson type mechanism involving one molecule per active site [12], the kinetic rate equation can be written as

$$r = \frac{kK_p P_p [P_{H_2}]^a}{1 + K_p P_p + K_{ip} P_{ip}} \tag{1}$$

where r is the rate of the reaction, k the kinetic rate constant, K_p and K_{ip} the adsorption constants for *n*-paraffin and isoparaffin, respectively, a the order of reaction with respect to hydrogen and P_p, P_{ip} and P_{H_2} the partial pressures of *n*-paraffin, isoparaffin and hydrogen, respectively. If we assume that $K_p = K_{ip}$ then $1 + K_p P_p + K_{ip} P_{ip}$ should be a constant. Then, if P_{H_2} is constant, Eq. (1) can be simplified to

$$r = k' P_p \tag{2}$$

The fitting of the simplified model was adequated as can be seen in Fig. 5, and the apparent kinetic rate constants (k') obtained for both hydrocarbons are given in Table 3.

The results presented in Table 3, have been fitted to the Arrhenius equation and apparent activation energies of 28 and 19 $kcal\,mol^{-1}$ have been obtained for the isomerization of nC_5 and nC_6, respectively. It is surprising that *n*-hexane which isomerizes through the same mechanism than *n*-pentane and through the same type of protonated cyclopropane ring gives a significantly lower activation energy. This difference, however, can be easily explained taking into account that those values correspond to apparent activation energy and not to the true activation energies. Thus in order to calculate the true activation energies for the isomerization of the two hydrocarbons, the heats of adsorption

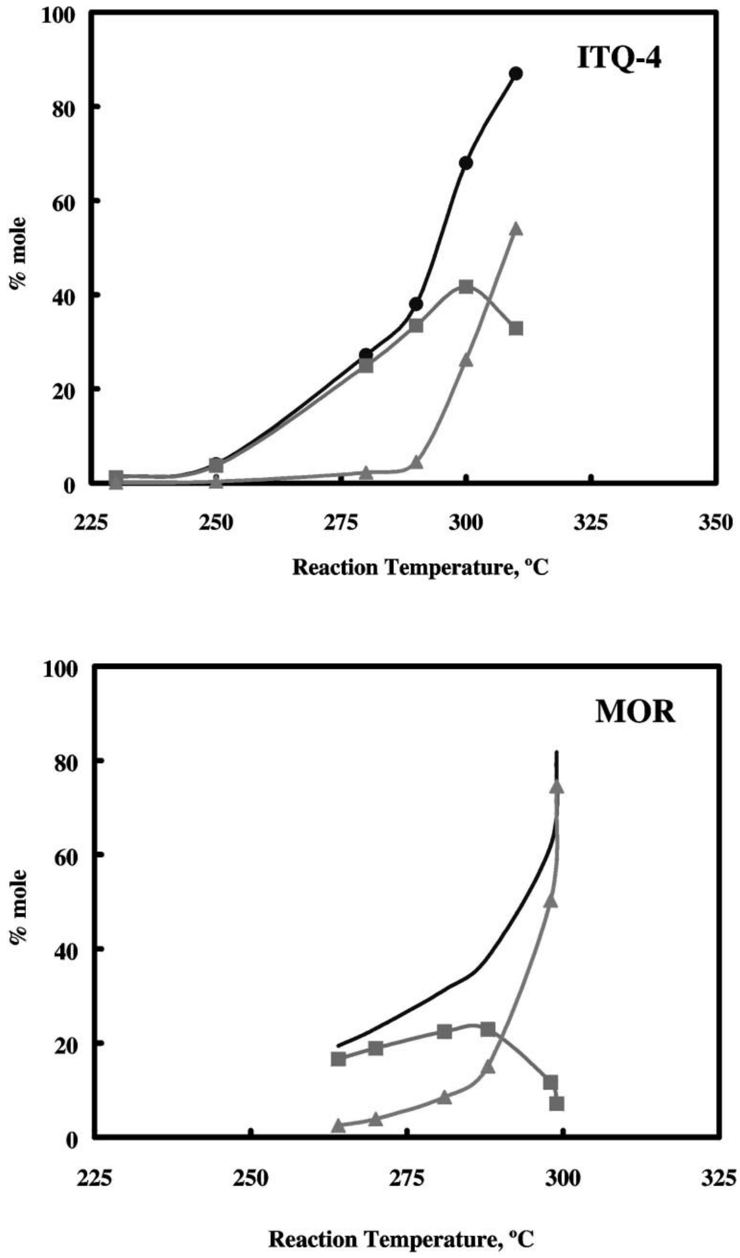

Fig. 3. Total conversion (●), isomerization (■) and cracking (▲) yields of *n*-heptane versus reaction temperature. Reaction conditions: 5.13 WHSV, 20 bar total pressure and H_2/hydrocarbon of 15 mol mol^{-1}.

have to be obtained. To do this, the initial rates for isomerization of *n*-pentane and *n*-hexane were measured at different hydrocarbon partial pressures and reaction temperatures (Table 4) and the results were fitted to the equation

$$r_0 = \frac{k'' K_\mathrm{p} P_{\mathrm{p}_0}}{1 + K_\mathrm{p} P_{\mathrm{p}_0}} \quad (3)$$

which includes the hydrocarbon adsorption constant and where k'' includes the hydrogen partial pressure.

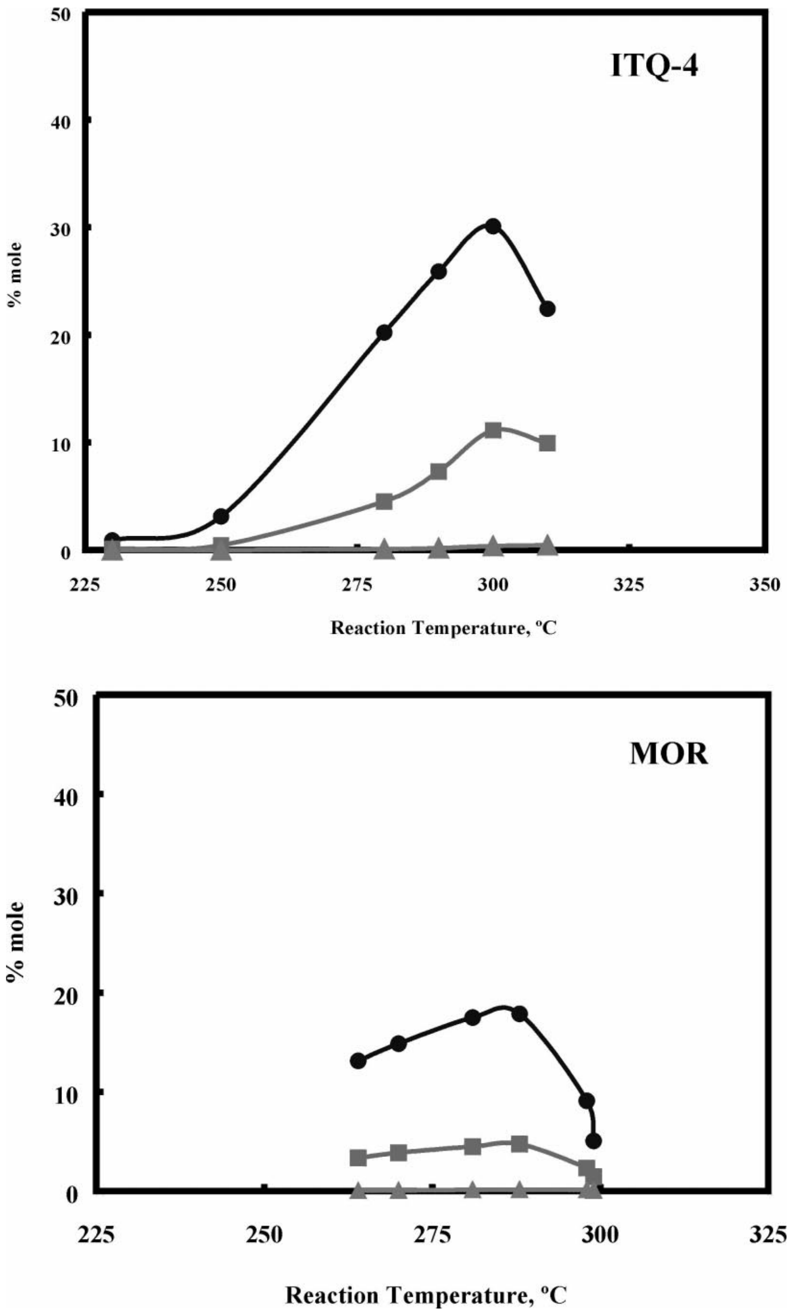

Fig. 4. Isomers distribution (monobranched (●), dibranched (■) and tribranched (▲)), versus reaction temperature during *n*-heptane isomerization. Reaction conditions: 5.13 WHSV, 20 bar total pressure and H_2/hydrocarbon of 15 mol mol^{-1}.

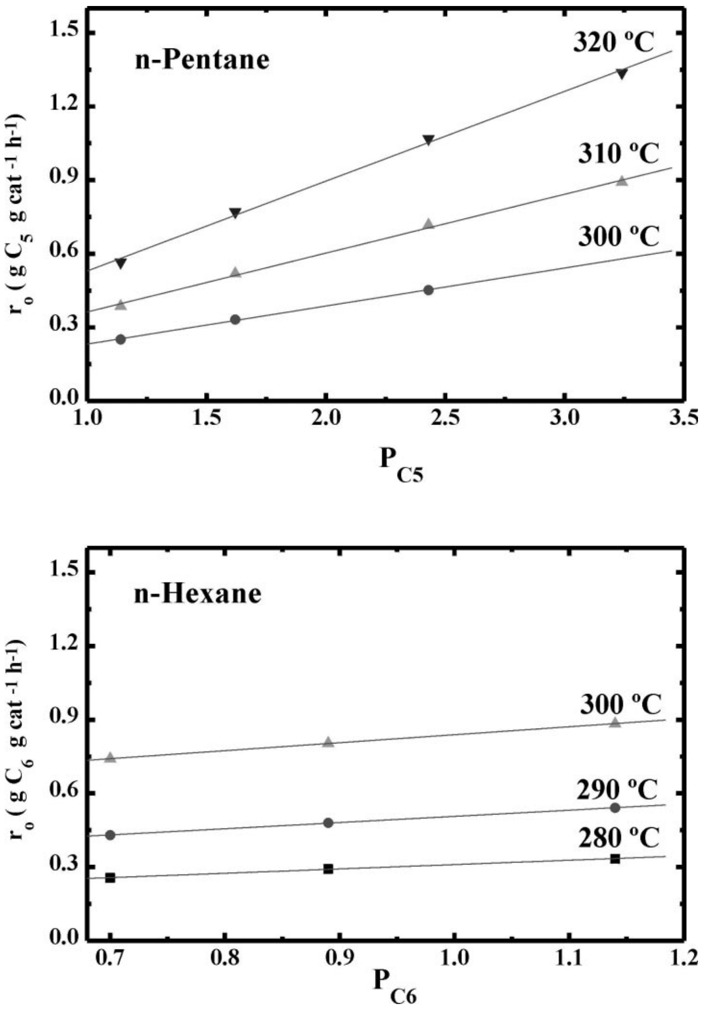

Fig. 5. Fitting of model simplified represented in Eq. (2).

The values of K_p were fitted to the Van't Hoff equation and the heat of adsorption for *n*-pentane and *n*-hexane were calculated to be -13 and $-23\,\mathrm{kcal\,mol^{-1}}$, respectively. The heats of adsorption obtained by Haag [13] during cracking of *n*-pentane and *n*-hexane were -17 and $-22\,\mathrm{kcal\,mol^{-1}}$, respectively, which are in good agreement with the results obtained here. Then, taking into account the heat of adsorption of *n*-pentane and *n*-hexane and the apparent activation energies given above, the true activation energies were calculated to be $41\,\mathrm{kcal\,mol^{-1}}$ for both *n*-pentane and *n*-hexane.

The $41\,\mathrm{kcal\,mol^{-1}}$ activation energy for the isomerization of *n*-pentane obtained experimentally can be compared with the value calculated when studying by means of molecular orbital calculations the reaction co-ordinate for the isomerization of the lineal carbenium ion to a branched C_5 carbenium ion which was $34\,\mathrm{kcal\,mol^{-1}}$ [14]. Those values are in a fair agreement if one takes into account the limitations involved when working with zeolite clusters.

It is remarkable that when we have carried out an analogous kinetic study but using mordenite as catalyst the heats of adsorption were -13 and $-24\,\mathrm{kcal\,mol^{-1}}$

Table 4
Conversion and initial rates values obtained in the *n*-pentane and *n*-hexane isomerization at different hydrocarbons partial pressures and different temperatures

τ[a]	P_{C_5} (bar)	Temperature (°C)							
		300		310		320			
		% Conv.	r_0[b]	% Conv.	r_0	% Conv.	r_0		
n-Pentane isomerization on ITQ-4									
0.054	3.24			4.9	0.891	7.3	1.337		
0.073	2.43	3.3	0.452	5.2	0.717	7.8	1.068		
0.109	1.62	3.6	0.332	5.7	0.519	8.4	0.770		
0.155	1.14	3.9	0.251	6.0	0.386	8.8	0.565		
τ	P_{C_6} (bar)	Temperature (°C)							
		280		290		300			
		% Conv.	r_0	% Conv.	r_0	% Conv.	r_0		
n-Hexane isomerization on ITQ-4									
0.135	1.14	4.5	0.344	7.3	0.541	11.9	0.884		
0.170	0.89	5.0	0.292	8.2	0.480	13.7	0.804		
0.213	0.70	5.5	0.256	9.2	0.430	15.8	0.741		
τ	P_{C_5} (bar)	Temperature (°C)							
		270		280		290		300	
		% Conv.	r_0	% Conv.	r_0	% Conv.	r_0	% Conv.	r_0
n-Pentane isomerization on MOR									
0.057	3.24	1.8	0.322	2.7	0.469	4.2	0.734	6.8	1.206
0.075	2.43	2.0	0.268	3.0	0.403	4.7	0.617	7.3	0.969
0.113	1.62	2.5	0.202	3.5	0.308	5.3	0.472	7.9	0.699
0.161	1.14	2.5	0.154	3.9	0.239	5.8	0.57	8.3	0.512
τ	P_{C_6} (bar)	Temperature (°C)							
		250		260		270		280	
		% Conv.	r_0	% Conv.	r_0	% Conv.	r_0	% Conv.	r_0
n-Hexane isomerization on MOR									
0.094	1.62					5.9	0.622	8.7	0.924
0.135	1.14	2.3	0.170	4.0	0.296	6.8	0.505	10.1	0.751
0.170	0.89	2.6	0.153	4.4	0.258	7.3	0.426	11.0	0.645
0.213	0.70	2.9	0.136	4.8	0.226				

[a] Contact time in hours.
[b] g hydrocarbon g cat.$^{-1}$ h^{-1}.

for *n*-pentane and *n*-hexane. As can be seen, no differences in the heat of adsorption of the paraffins were found with these two zeolites, regardless of differences in acidity. If this is so, then we have to conclude that the heat of adsorption calculated from the kinetic equation corresponds to the physical adsorption of the hydrocarbons. The physical adsorption for the hydrocarbons only involves van der Waals interactions, and therefore the acidity of the zeolite should have little influence on this step.

4. Conclusion

A recently synthesized large pore unidirectional zeolite ITQ-4 shows acceptable activity and selectivity towards the isomerization of C_5–C_7 normal paraffins. Its activity is lower than that of a mordenite catalysts, but the former is more selective towards isomerization. Differences in selectivity should be more notorious when using commercial feeds reaches in *n*-hexane and *n*-heptane. A kinetic study has been carried which shows that the true activation energy is the same for isomerizing *n*-pentane and *n*-hexane. The values obtained experimentally agree fairly well with those calculated in a previous work by studying the reaction coordinate during the isomerization of nC_5 on a zeolite cluster.

It has been found that the heats of adsorption determined kinetically correspond to the physical adsorption of *n*-pentane and *n*-hexane in the zeolite. The values obtained are the same for ITQ-4 and mordenite regardless of the differences in acidity, as should be if only van der Waals interactions intervene in the adsorption step.

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