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The Use of ITQ-7 as a FCC Zeolitic Additive

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The new zeolite ITQ-7 (ISV structure) has been tested as an additive of USY zeolites for gasoil cracking. The dimensions of its tridirectional system of channels, with pores between 6.1 and 6.3 Å and with lower tortuosity than those of the Beta zeolite, favor β-scission versus protolytic cracking and limit the extension of hydrogen transfer reactions. In the catalytic cracking of gasoil, when comparing with Beta zeolite, ITQ-7 produces higher gasoline yield, with lower content of aromatics, more isoamylenes, and higher olefinicity in the LPG fraction.

Key Words: **ITQ-7 zeolite; Beta zeolite; FCC; FCC catalysts; cracking catalysts; fluid catalytic cracking; microactivity test; octane enhancement; isoamylenes.**

INTRODUCTION

Fluid catalytic cracking (FCC) is one of the most important processes in the oil refining industry and is responsible for about 30% of the gasoline produced (1). We have assisted in the past years in the evolution of FCC from a process mainly directed to the production of liquid fuels, especially gasoline, to a process in which the production of C_3 and C_4 olefins and C_4^+ isoolefins has become an important issue. The new demands from the FCC unit (FCCU) have been achieved by working in two ways: on one hand through the modifications carried out in the units which involve shorter contact times in the reactor and in the stripping zone (2, 3), and on the other hand by new and more efficient catalysts.

The actual complexity in the product demand from the FCCU requires the use of more complex catalysts that involve active matrices with a well defined porosity (4), highly stable Y zeolites with the adequate acidity and micro-mesoporosity, and finally, the introduction of zeolite additives. As potential zeolite additives, large-pore zeolites other than Y, as for instance L (5), Omega (6, 7), or Beta (8–15), as well as medium-pore molecular sieves such as ZSM-5 (16, 17) or MCM-22 (18, 19) have been explored. Among all the above, the most successful has been ZSM-5, which is generally used today in FCC to increase the production of propylene. In the family of large-pore zeolites, Beta appears to be the most adequate additive since it increases the production of propylene and isobutene without too much penalty in gasoline (8). Increasing the yield of isobutene can be of interest if one takes into account that the units dedicated to producing metilterbutylether can now be used to dimerize isobutylene producing high-octane trimethyl pentenes (TMPEs). These TMPEs are hydrogenated to give trimethyl pentanes as the final products through a more environmentally friendly process (20, 21) than the actual alkylation units using HF or H_2SO_4 catalyst. It can then be expected that Beta zeolite will be revisited in its use as an FCC additive, especially if the synthesis cost can be decreased.

It is then of interest for future FCC scenarios to explore the possibilities of any new large-pore tridirectional zeolite discovered as the main microporous component of the cracking catalyst or, what appears to be more realistic, as an FCC additive. However, it has to be taken into account that since 1967, when Beta zeolite was discovered, no other tridirectional large-pore zeolite was discovered despite the large efforts made by researchers in the field of zeolite synthesis. Very recently a new pure silica polymorph with a three-dimensional system of large-pore channels has been synthesized (22) and named as ITQ-7 (Instituto de Tecnología Química number 7). This structure has linear pores along two directions, while the third channel running along the *c* direction is sinusoidal but with large linear sections of around 21 Å. The pore diameters of ITQ-7 are (2) 6.2×6.1 Å and (1) 6.3×6.2, while those of Beta zeolite are (2) 7.2×6.2 and (1) 5.5×5.5. Å. It appears to us that a structure such as ITQ-7 may have possibilities as an FCC additive as well as for other catalytic applications. However, up to now, ITQ-7 was only prepared as a pure silica polymorph and consequently it was of no use as an acid catalyst (22).

We have succeed in preparing Al-ITQ-7 which is acidic and is able to act as a cracking catalysts. Thus, we have explored the possibilities of this zeolite as a gasoil cracking additive, and the results are compared with those obtained using a Beta zeolite with the same chemical composition.

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EXPERIMENTAL

Materials

Al-ITQ-7 was prepared by first synthesizing a B-ITQ-7 which was subsequently exchanged following a method described previously (23). The B-ITQ-7 was synthesized starting from the following molar gel composition: $SiO_2 : 0.01\ B_2O_3 : 0.50\ C_{14}H_{26}NOH : 0.50\ HF : 3H_2O$, where $C_{14}H_{26}NOH$ is 1,3,3-trimethyl-6-azonium-tri-cyclo [3.2.1.4^{6,6}]dodecane hydroxide. The preparation method consists in dissolving 0.08 g of H_3BO_3 in 31.98 g of a 0.99 M solution of 1,3,3-trimethyl-6-azonium-tri-cyclo [3.2.1.4^{6,6}]dodecane hydroxide. Then 13.46 g of tetraethylorthosilicate (TEOS) was hydrolyzed in that solution, and the formed ethanol was completely evaporated by gently stirring. Finally, 1.34 g of HF (48.1% in water) and 0.020 g of pure silica ITQ-7 crystals were added and the mixture was homogenized. After 7 days of crystallization at 473 K in PTFE-lined stainless steel autoclaves at 60 rpm rotation, a powder was obtained that after calcination at 853 K yields a material whose XRD pattern (Fig. 1) corresponds to that of ITQ-7. The B-ITQ-7 was calcined at 853 K during 3 h and the resultant sample was exchanged with Al^{3+}. This was repeatedly washed with H_2O and the final material has a Si/Al ratio of 90 as determined by chemical analysis. A second ITQ-7 sample with a Si/Al ratio of 50 was prepared following the same procedure and exchanging twice with Al^{3+}.

TABLE 1

Characteristics of Samples Used in This Work

Sample:	ITQ-7(90)	ITQ-7(50)	Beta	USY-2.432	USY-2.426
Area BET ($m^2\ g^{-1}$)	423	477	463	641	551
Crystal size (m)	1–2	1–2	0.2	0.5	0.5
Si/Al	90	50	93	19[a]	62[a]
Brønsted acidity (mol Py g^{-1})					
$T = 523$ K	3	27	11	77	14
$T = 623$ K	1	26	10	45	3
$T = 673$ K	1	16	2	28	1
Lewis acidity (mol Py g^{-1})					
$T = 523$ K	29	24	5	9	10
$T = 623$ K	6	22	5	8	7
$T = 673$ K	4	19	2	7	4

Note. Acidity and acid strength distribution determined by IR-pyridine measurements at different desorption temperatures.

[a] Framework Si/Al ratio from XRD, other zeolites from chemical analysis.

A Beta sample with practically the same Si/Al ratio was synthesized in fluoride medium from a gel of the following molar composition: $SiO_2 : 0.005\ Al_2O_3 : 0.55\ TEAOH : 7.5\ H_2O : 0.55\ HF$. The preparation procedure was the following: Tetraethylorthosilicate (TEOS, Merck) was hydrolyzed under stirring in an aqueous solution of tetraethylammonium hydroxide (TEAOH, Aldrich). Then a solution obtained by dissolving metallic aluminum in aqueous TEAOH was added and the mixture was kept under stirring until the ethanol formed in the hydrolysis of TEOS was evaporated. HF (48 wt%, Aldrich) was added to the clear solution obtained, and a thick paste was formed. Finally, nanocrystalline zeolite Beta was also added. The crystallization was carried out in Teflon-lined stainless steal autoclaves at 413 K under rotation (60 rpm) during 3 days.

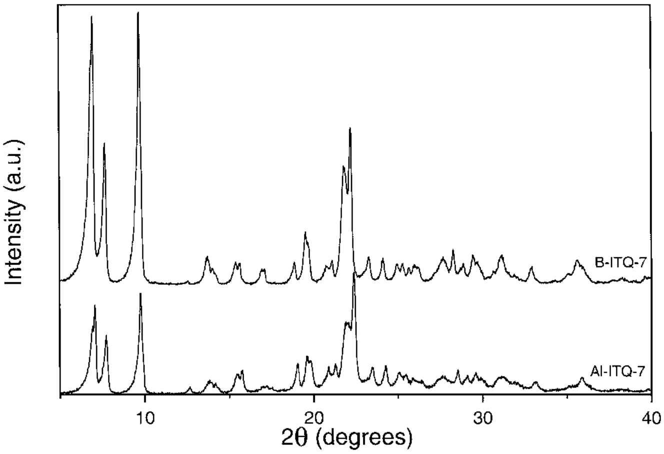

FIG. 1. XRD pattern of zeolite ITQ-7.

After this time the solids were recovered by filtration, washed with distilled water, and calcined at 853 K for 3 h. The Si/Al ratio of the zeolite, as determined by chemical analysis, was found to be 93. The average crystallite size measured by SEM was 0.2 μm.

The USY zeolites are commercial samples obtained from Zeolyst Intl. with the codes CBV720 and CBV760 corresponding to unit cells of 2.432 and 2.426 nm, respectively. The characteristics of the zeolites are given in Table 1.

IR experiments were performed using vacuum cells. Wafers of 10 mg cm^{-2} were degassed overnight under vacuum (10^{-3} Pa) at 673 K. The spectra were recorded and then pyridine (6×10^{-2} Pa) was admitted and after equilibration, the samples were outgassed for 1 h at increasing temperatures (523/623/673 K). After each desorption step, the spectrum was recorded at room temperature and the background subtracted. Quantitative determination of the amount of Brønsted and Lewis acid sites was derived from the intensities of the IR bands at ca. 1450 and 1550 cm^{-1}, respectively, by using the extinction coefficients given by Emeis (24).

Solid-state ^{27}Al and ^{11}B NMR spectra were recorded under magic angle spinning (MAS) at room temperature in a Varian Unity VXR-400WB spectrometer at 104.2 and 100.2 MHz, respectively.

TABLE 2

Vacuum Gasoil Properties

Density (15°C) g cc^{-1}	0.917
Aniline point (°C)	79.2
Sulfur (wt%)	1.65
Nitrogen (ppm)	1261
Na (ppm)	0.18
Cu (ppm)	<0.1
Fe (ppm)	0.30
Ni (ppm)	0.2
V (ppm)	0.40
ASTM D-1160 (°C)	
5%	319
10%	352
30%	414
50%	436
70%	459
90%	512
VABP (°C)	435
K (UOP)	11.82
Average molecular weight	407
Aromatic carbon (wt%)	22.96
Naphthenic carbon (wt%)	15.16
Paraffinic carbon (wt%)	61.88

Reaction Procedure

Zeolites ITQ-7 and Beta were tested directly for the cracking of a pure compound, *n*-decane, which can be representative of the gasoline fraction, and for the cracking of a vacuum gasoil (Table 2), as zeolite additives of a USY zeolite. The reaction experiments were performed in a MAT unit (18), which has been designed to accomplish the ASTM D-3907 standard. It works in an automatic regime with computerized control of a reactor, sample collecting, and analysis of gases and coke. Gases were analyzed by GC in a HP5890 with a two-column system in series and Ar as carrier gas. Hydrogen, nitrogen, and methane were separated in a 15-m, 0.53-mm-i.d. molecular sieve 5A column connected to a thermal-conductivity detector. C_2 to C_5 hydrocarbons were separated in a 50-m, 0.53-mm-i.d. alumina plot column and analyzed with a flame ionization detector. Liquids were analyzed, for *n*-decane cracking in a Varian 3400 with a 100-m, 0.25-mm-i.d. petrocol DH column, and in the case of gasoil as feed, by simulated distillation (SIMDIS) in a Varian 3800 equipped with a 10-m, 0.53-mm-i.d. MXT-2887 metal column supplied by Restek Corp., and the software STARD SD from Varian following the ASTM D-2887 standard. PIONA analysis was done in a Varian 3400 equipped with 100-m, 0.25-mm-i.d. petrocol DH and prefractionator columns, and the detailed composition of the gasoline was determined using the detailed hydrocarbon analysis (DHA) software supplied by Varian. Research octane number (RON) and Motor Octane Number (MON) were determined by means of the correlations published by Lugo *et al.* (25). Coke was measured by IR monitoring of the CO_2 formed during the catalyst regeneration. Complete combustion of CO is achieved by passing the combustion gases through a CuO/Cu_2O_3 catalytic bed at 623 K.

Experiments with *n*-decane as feed were done at 773 K, 60 s time on stream, and catalyst to oil ratio ranging from 0.3 to 0.7 (wt zeolite/wt oil). In all the experiments the amount of zeolite was constant and equal to 0.5 g. Zeolites were pelletized, crushed, sieved, and the 0.59- to 0.84-mm fraction was taken and diluted in 2.5 g of inert silica. In the case of gasoil cracking, the additive and the USY zeolite were placed in separated beds as described previously (18). The first bed at the top contains the USY zeolite (1.2 g of USY plus 0.3 g of silica) and the bed at the bottom contains the zeolitic additive diluted in 1.1 g of silica. The percentage of additive used in this work corresponds to weight of zeolitic additive per 100 g of USY zeolite. The cat/oil ratio was calculated by dividing the amount of USY zeolite by the amount of gasoil fed.

RESULTS AND DISCUSSION

Catalyst Characterization

The ^{11}B MAS NMR spectra of the uncalcined B-ITQ-7 sample showed (Fig. 2) the presence of tetrahedrally coordinated B. This was the starting material for obtaining the Al-ITQ-7 which should show stronger acidity and

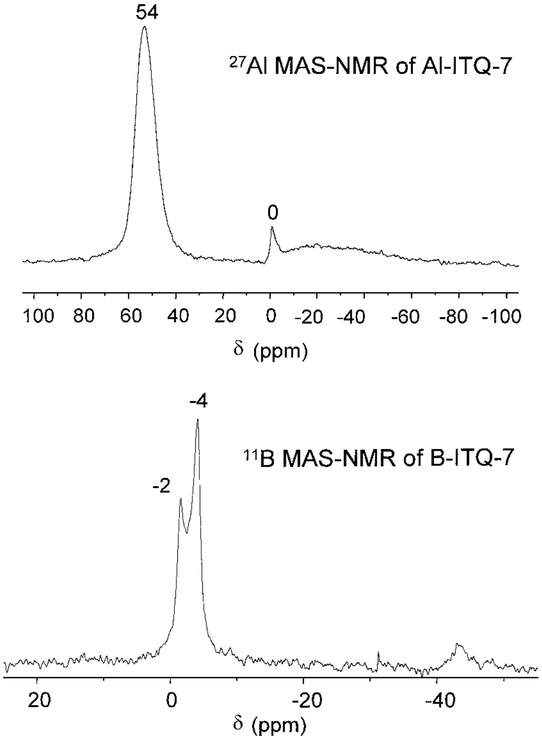

FIG. 2. ^{11}B MAS NMR spectra of uncalcined B-ITQ-7 and ^{27}Al MAS NMR spectra of Al-ITQ-7 after calcination and exchange of B-ITQ-7.

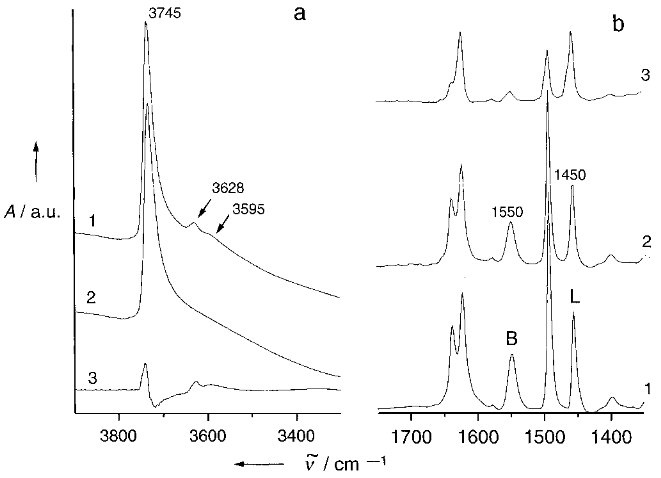

FIG. 3. IR spectra of Al-ITQ-7 in (a) the OH range: (1) after overnight pretreatment at 673 K, (2) after pyridine adsorption at 523 K, (3) difference spectra; and (b) pyridine vibration bands after desorption at (1) 523 K, (2) 623 K, and (3) 673 K.

consequently should be more appropriate than B-ITQ-7 as cracking catalyst. After calcining and exchanging the B-ITQ-7, an Al-ITQ-7 sample was obtained with a Si/Al ratio of 90 as determined by chemical analysis. ^{27}Al MAS NMR results (Fig. 2) clearly show that most of the Al is tetrahedrally coordinated (54 ppm) in framework positions. Following the same synthesis procedure another Al-ITQ-7 sample was synthesized with a Si/Al ratio of 50, and therefore with a potential larger number of acid sites. Both samples presented acidic bridging hydroxyl groups, which were indeed visualized by IR spectroscopy and quantified by pyridine adsorption–desorption followed by IR spectroscopy. More specifically, the IR spectrum of the Al-ITQ-7 sample in the OH region shows (Fig. 3) the presence of three bands at 3745, 3628, and 3595 cm^{-1}. The first band is assigned to silanol groups, while the other two bands should be attributed to fully accessible acid hydroxyls as they disappear after pyridine adsorption (Fig. 3). The IR bands associated to the interactions of pyridine with Brønsted (1550 cm^{-1}) and Lewis (1450 cm^{-1}) acids indicate that both types of sites are present in the Al-ITQ-7 sample (Fig. 3). Furthermore, by desorbing the pyridine at increasing desorption temperatures it was found that most of the acid sites in Al-ITQ-7 are of medium strength (those retaining pyridine after desorption at 523 K), while some are strongly acidic (those retaining pyridine at 623 K; see Table 1). A sample of Beta with a Si/Al ratio of 93 was prepared for comparison purposes, and it can be seen there that the Beta zeolite has a larger amount of Brønsted acid sites than ITQ-7 (Si/Al = 90), indicating that the effective Al framework concentration is larger in Beta. Moreover, it appears that the proportion of the stronger acid sites (pyridine desorption at 623 K), is higher in Beta zeolite, and this should certainly influence the catalytic activity.

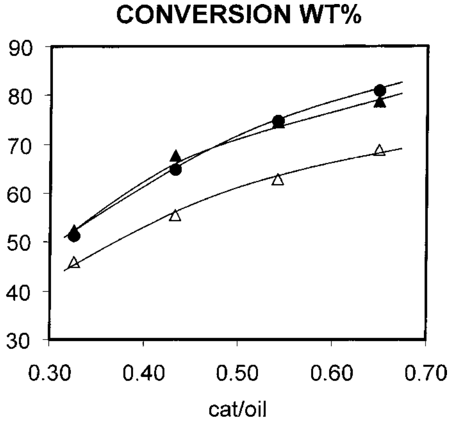

FIG. 4. Total conversion in the cracking of *n*-decane at 773 K and 60 s time on stream over (△) ITQ-7 Si/Al=90, (▲) Beta, (●) ITQ-7 Si/Al = 50.

The primary activity of ITQ-7 and Beta has been determined by measuring the *n*-decane cracking activity. The results given in Fig. 4 show that ITQ-7 is active for *n*-decane cracking and its activity is slightly lower than the activity of Beta, in good agreement with acidity measurements. In any case the good *n*-decane cracking activity of the Al-ITQ-7 sample indicates that it is worth studying the behavior of this material as a FCC zeolite cracking additive.

Cracking Activity

Influence of the pore topology. The gasoil cracking behavior of a base catalyst formed by USY (2.432 nm) zeolite dispersed in silica (top bed) and the ITQ-7 or Beta additive both with a nominal Si/Al ratio ~90 (bottom bed) and in amounts of 10 wt% with respect to the zeolite USY has been studied. The results from Fig. 5 indicate that the introduction of the additives does not change conversion but produces a change in the selectivities decreasing the yield of liquid fuels and increasing gases. These effects are more notorious in the case of Beta zeolite.

The fact that ITQ-7 has all pores with dimensions in the range of 6.1–6.3 Å while Beta zeolite has one of the pores with a diameter 5.5 × 5.5 Å should already have an impact on the conversion of the gasoil molecules occurring on the external surface at the pore mouth as well as an impact on gas formation. Moreover, even if ITQ-7 has a pore topology closely related to polymorphs A or B of the Beta zeolite (26), there is one important difference in the pore topology of ITQ-7 that can influence its cracking behavior. Indeed the Beta polymorphs A and B, as well as ITQ-7, have linear pores running along the [100] and [001] crystallographic directions, while the third pore along the [010] direction is sinusoidal in the Beta polymorphs. However, in the case of ITQ-7, the channel running along the [100] direction is sinusoidal but has larger linear sections of around 21 Å (22). In other words, the longer linear sections of this channel in ITQ-7 with respect to Beta, should give a lower channel

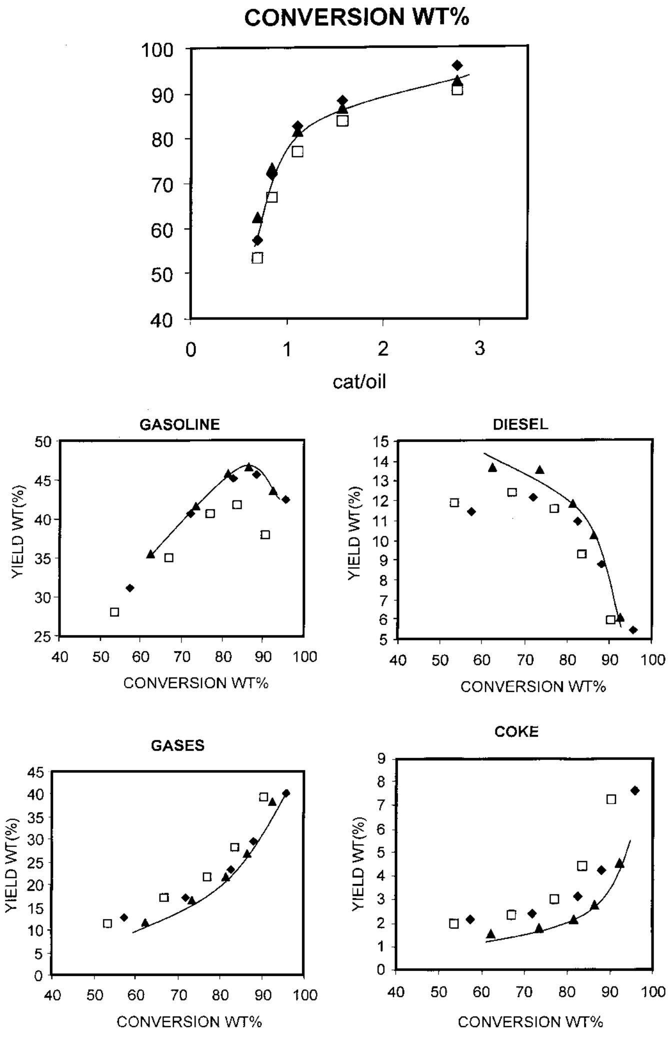

FIG. 5. Total conversion and selectivities in the cracking of gasoil at 793 K and 30 s time on stream over (▲, line) USY-2.432 nm as base catalyst and (☐) Beta and (◆) ITQ-7 Si/Al = 90 at 10 wt% of additive level.

tortuosity and a more homogeneous electric field gradient in ITQ-7 than in Beta. This, together with the presence of the narrower channel (5.5 × 5.5 Å) present in Beta, should be responsible for the higher recracking observed with Beta when compared with ITQ-7, which results in higher yields of gases and lower yields of liquid fuels with the former zeolite. Moreover, these differences in selectivity can also be partly due to the higher acidity of zeolite Beta.

The lower tortuosity of one of the channels and the lower heterogeneity of the electric field gradients in the pores of ITQ-7 should also be reflected in the C_3 to C_4 ratio observed in the products (27), and in the ratio of monomolecular (protolytic) to bimolecular (β-scission) cracking mechanism (28). In this case, since C_1 and C_2 are typical products from protolytic cracking, while iC_4 is a typical product of β-scission, it is possible to conclude that the higher the $C_1 + C_2$/isobutane ratio the higher will be the ratio of protolytic to β-scission mechanism. The results presented in Fig. 6, and in agreement with the differences in pore topology, clearly show that the C_3/C_4 and the $C_1 + C_2/iC_4$ ratios are lower when using Al-ITQ-7 than Beta zeolite as additive.

From an industrial point of view, it is highly desired to increase the amount of C_3 and C_4 olefins produced in the FCC. ZSM-5 has shown a very good ability to strongly increase the propylene produced when it is used as a zeolitic FCC additive (17, 29), while Beta zeolite was specially successful for increasing the C_4 and C_5 olefinic products and more specifically the yields of isobutylene and isopentene (9, 10). In our case, we can see (Fig. 6) that ITQ-7 gives higher ratios of propylene/propane, butenes/butanes and isobutene/isobutane than Beta. This indicates that a lower ratio of hydrogen transfer to cracking is taking place in the pores of Al-ITQ-7. In order to check this the gasoline produced when using ITQ-7 and Beta

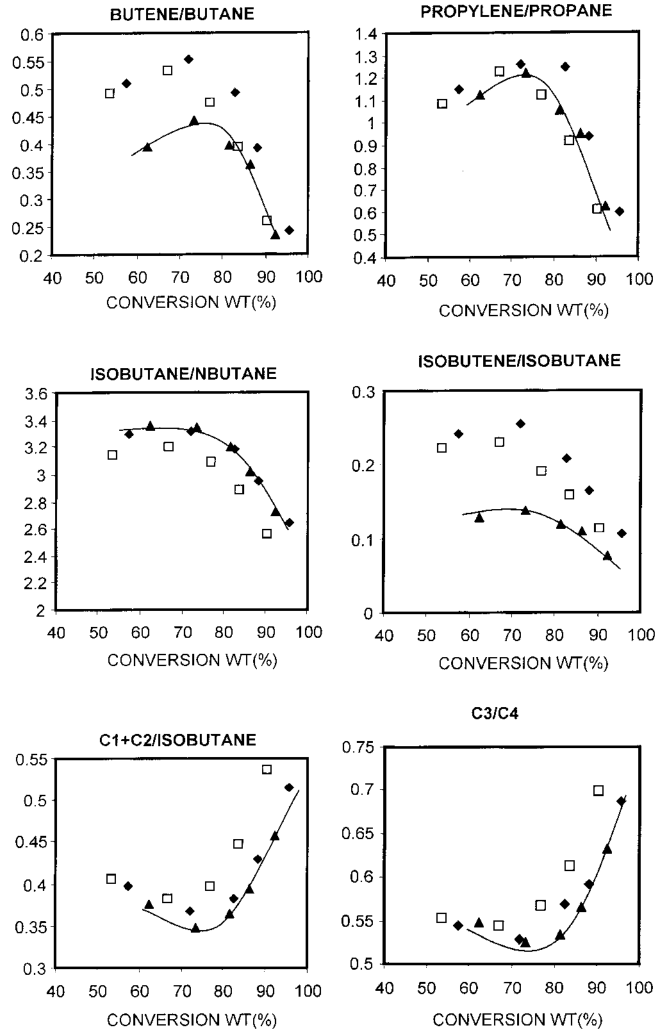

FIG. 6. Ratios of interest in the cracking of gasoil at 793 K and 30 s time on stream over (▲, line) USY-2.432 nm as base catalyst and (☐) Beta and (◆) ITQ-7 Si/Al = 90 at 10 wt% of additive level.

TABLE 3

PIONA Analysis and Detailed Composition of Gasoline Produced When Using Beta or ITQ-7 as Additives of a Zeolite USY (2.432 nm)

Catalyst:	Base catalyst (USY 2.432 nm)	USY-2.432+ 10% Beta	USY-2.432+ 10% ITQ-7(90)
Conversion wt%	72.0	72.0	72.0
n-Paraffins	3.7	5.1	5.0
i-Paraffins	26.6	23.0	25.3
Olefins	9.6	10.3	12.5
Naphthenes	12.4	12.7	11.8
Aromatics	47.7	48.9	45.4
RON	86.6	87.9	86.7
MON	82.2	82.9	82.3
Isoamylenes	0.69	1.04	1.33

has been analyzed in detail and the results are given in Table 3. The results obtained show that ITQ-7 produces less aromatics and more olefins with an important increase in isoamylenes, as compared to zeolite Beta. Our results indicate that the lower content in aromatics for ITQ-7 gasoline should produce a decrease of the research octane number (RON) of the gasoline produced; that is, however, compensated by the increase in isoparaffins and isoolefins obtained when using ITQ-7.

In conclusion, the pore topology of zeolite ITQ-7 appears to be very adequate for a cracking catalyst additive. The tridirectional pore network, with diameters in the 6.1- to 6.3-Å range and the lower tortuosity of one of the channels range favor β-scission with respect to protolytic cracking with the corresponding lower yield of gases and higher yields of liquids fuels. Meanwhile, the pore topology combined with high Si/Al ratios strongly decrease the rate of hydrogen transfer reactions, decreasing therefore the yield of aromatics in the gasoline, increasing the yield of isoamylenes, and producing higher olefin to paraffin ratios in LPG products.

Influence of additive activity. The impact of the zeolite additives can be increased by introducing more framework Al and consequently a higher number of acid sites as well as by introducing a larger amount of the additives.

In Figs. 7–9 the results obtained when introducing ITQ-7 (Si/Al = 90) as an additive in amounts of 10 and 20 wt% and when using the ITQ-7 with a Si/Al = 50 at 20 wt% are given. It can be seen there, that an increase of ITQ-7 content from 10 to 20 wt% decreases the liquid yields and increases the gases. However, the increase in the olefin/paraffin ratio is negligible, the iso$C_4^=$ to iso-C_4 being the most affected ratio. It appears then that most of the increase in butene selectivity is obtained at lower levels of additive and the incremental obtained after 10 wt% of ITQ-7 is small. A similar result was observed when using ZSM-5 as additive (30). However, ITQ-7 seems to have some activity for isomerizing 1-butene to isobutylene.

A higher effect on recracking and gas formation is seen when decreasing the Si/Al ratio of the ITQ-7 (Fig. 7), but the olefin to paraffin in the products remains practically unchanged (Fig. 8). However, the total yield of propylene, *n*-butenes, and isobutylene increases when increasing the framework Si/Al ratio (Fig. 9).

The C_3/C_4 and $C_1 + C_2/iC_4$ ratios also remain unchanged when increasing the Si/Al ratio (Fig. 8). Those ratios are mainly influenced by the structure, as shown in Fig. 6, and in a lower extension by the number and strength of the acid sites.

The detailed analysis of the gasoline produced when increasing the amount of ITQ-7 from 10 to 20 wt% is given in Table 4. More additive has little effect in the product distribution, except for isoamylenes, and consequently the effect on gasoline octane number is neglegible. The use of ITQ-7 of lower Si/Al ratio produces a gasoline (Table 4)

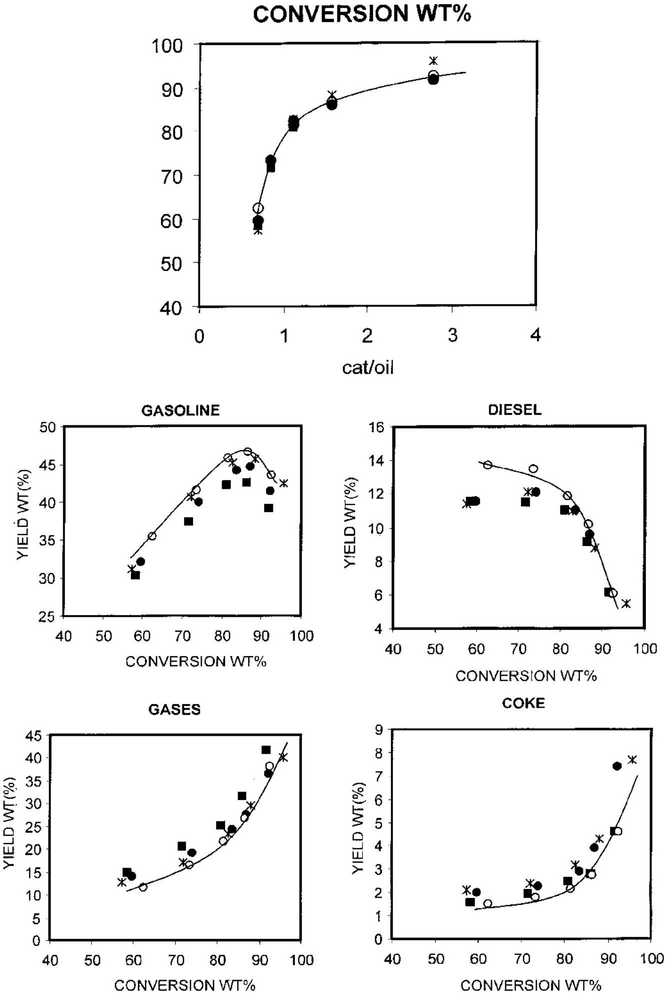

FIG. 7. Total conversion and selectivities in the cracking of gasoil at 793 K and 30 s time on stream over (○, line) USY-2.432 nm as base catalyst and (✱) ITQ-7 Si/Al = 90 at 10 wt% of additive level, (●) ITQ-7 Si/Al = 90 at 20 wt%, and (■) ITQ-7 Si/Al = 50 at 20 wt% of additive level.

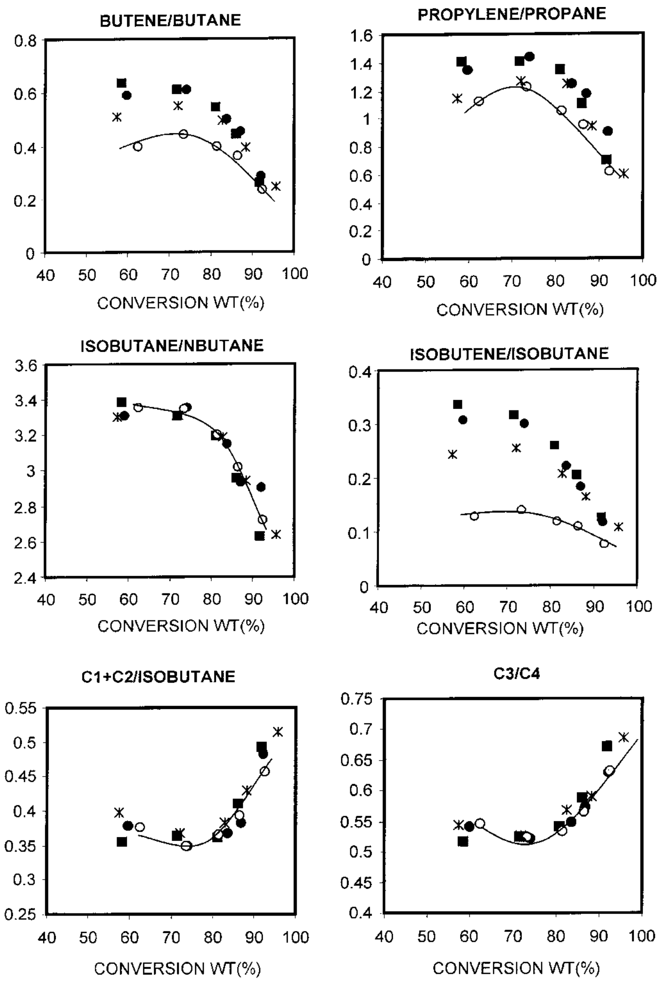

FIG. 8. Ratios of interest in the cracking of gasoil at 793 K and 30 s time on stream over (○, line) USY-2.432 nm as base catalyst and (⁎) ITQ-7 Si/Al = 90 at 10 wt% of additive level, (●) ITQ-7 Si/Al = 90 at 20 wt%, and (■) ITQ-7 Si/Al = 50 at 20 wt% of additive level.

with higher aromatic content and a decrease in isoparaffins with similar levels of olefins and naphthenes. RON and MON are also increased when using ITQ-7 with more framework aluminum. It seems that the benefit in the octane numbers comes mainly from the increase in the aromatic content. Thus high Si/Al ratios would be preferred to obtain gasoline with less aromatics and higher isoamylene yields.

Influence of the unit cell size of the base catalyst. Up to now the base catalyst used has been a USY zeolite with a unit cell of 2.432 nm. In order to see the effect of the additives when using different unit cell of the base USY zeolite, we have selected another sample of commercial USY with a unit cell of 2.426 nm (Table 1) and tested it with ITQ-7 (Si/Al = 90 and 50) as additive at 20 wt% (Figs. 10 and 11).

The results of the zeolite USY-2.426 as base catalyst show (Fig. 10) that this is less active than USY-2.432 as corresponds to its lower framework aluminum content, and the former produces less liquids and more gases and coke. The olefinicity of the C3–C4 fraction is also higher, showing a lower tendency to produce hydrogen transfer reactions.

TABLE 4

PIONA Analysis and Detailed Composition of Gasoline Produced When Using ITQ-7 at Different Percentage and Different Silica to Alumina Ratio as Additive of a Zeolite USY (2.432 nm)

Catalyst:	USY-2.432+ 10% ITQ-7(90)	USY-2.432+ 20% ITQ-7(90)	USY-.432+ 20% ITQ-7(50)
Conversion wt%	72.0	72.0	72.0
n-Paraffins wt%	5.0	5.0	4.4
i-Paraffins wt%	25.3	25.9	23.1
Olefins wt%	12.5	12.6	12.7
Naphthenes wt%	11.8	11.3	11.3
Aromatics wt%	45.4	45.2	48.4
RON	86.7	86.6	87.1
MON	82.3	82.0	82.5
Isoamylenes wt%	1.33	1.60	1.62

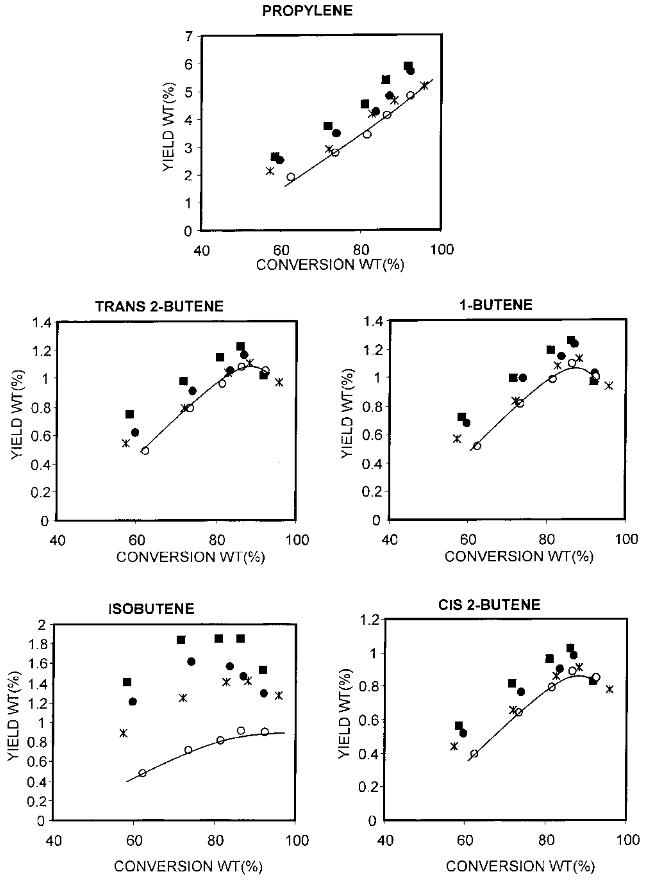

FIG. 9. C_3–C_4 olefin yields in the cracking of gasoil at 793 K and 30 s time on stream over (○, line) USY-2.432 nm as base catalyst and (⁎) ITQ-7 Si/Al = 90 at 10 wt% of additive level, (●) ITQ-7 Si/Al = 90 at 20 wt%, and (■) ITQ-7 Si/Al = 50 at 20 wt% of additive level.

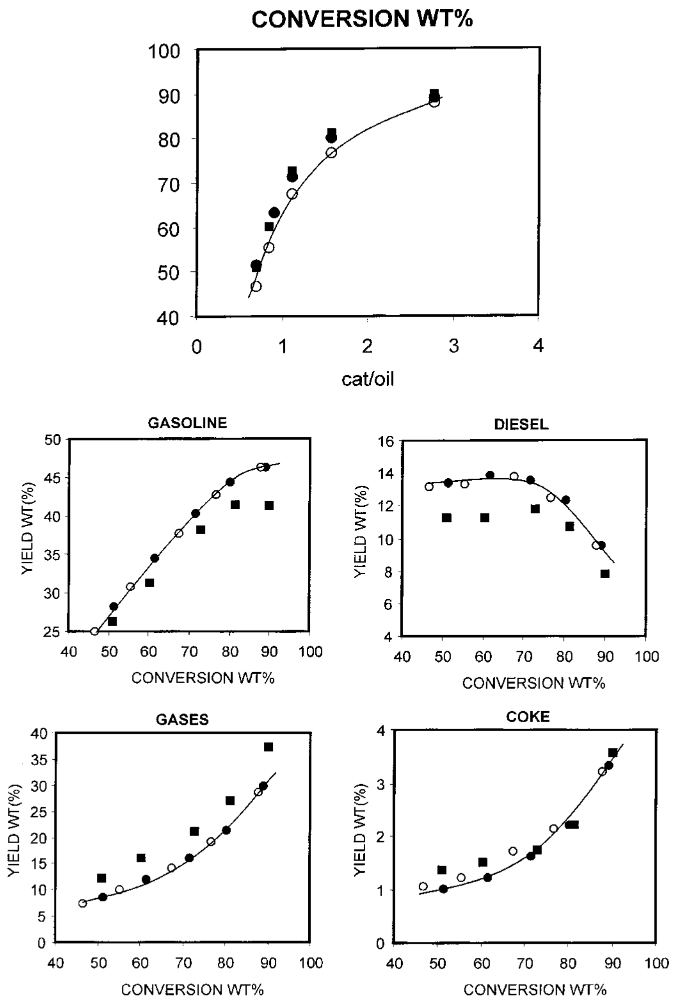

FIG. 10. Total conversion and selectivities in the cracking of gasoil at 793 K and 30 s time on stream over (○, line) USY-2.426 nm as base catalyst and (●) ITQ-7 Si/Al = 90 at 20 wt% and (■) ITQ-7 Si/Al = 50 at 20 wt% of additive level.

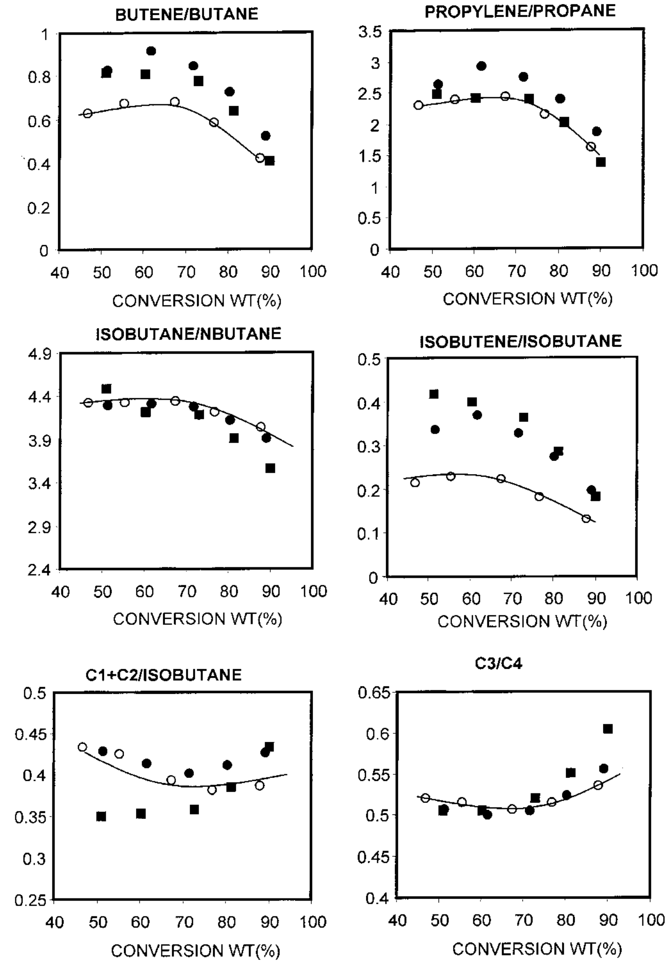

FIG. 11. Ratios of interest in the cracking of gasoil at 793 K and 30 s time on stream over (○, line) USY-2.426 nm as base catalyst and (●) ITQ-7 Si/Al = 90 at 20 wt% and (■) ITQ-7 Si/Al = 50 at 20 wt% of additive level.

When using ITQ-7 as an additive the effect is essentially the same as that found when working with the higher unit cell. Therefore the additive causes a decrease in gasoline and diesel and an increase in gases, which is more pronounced with the ITQ-7 sample with Si/Al = 50 (Fig. 10). The olefin to paraffin ratios in the C_3 and C_4 fraction, especially isobutene/isobutane increase, with little influence of the Si/Al ratio in the ITQ-7 (Fig. 11). This occurs despite the fact that the lower unit cell USY zeolite produces by itself high yields of olefins. The quality of the gasoline produced is shown in Table 5. When comparing the results of the catalyst with ITQ-7 (Si/Al = 90) as additive with those of the base catalyst USY-2.426 the differences are smaller than considering the base catalyst with higher unit cell. The main effect is again an increase in the olefin content including isoamylenes, while maintaining or even improving the octane numbers. When increasing the aluminum content of the additive (ITQ-7 Si/Al = 50) again an increase in aromatics and a decrease in isoparaffins are observed while maintaining octane numbers.

From the results presented, we can conclude that whatever the characteristics of the unit cell of the base catalyst

TABLE 5

PIONA Analysis and Detailed Composition of Gasoline Produced When Using ITQ-7 at Different Silica to Alumina Ratio as Additive of a Zeolite USY (2.426 nm)

Catalyst:	Base catalyst (USY 2.426 nm)	USY-2.426+ 20% ITQ-7(90)	USY-2.426+ 20% ITQ-7(50)
Conversion wt%	70.0	70.0	70.0
n-Paraffins wt%	5	4.2	4.4
i-Paraffins wt%	23.5	23.8	21.5
Olefins wt%	11.0	13.0	12.7
Naphthenes wt%	12.8	11.7	11.1
Aromatics wt%	47.7	48.3	50.3
RON	87.1	87.3	87.2
MON	82.7	82.9	82.7
Isoamylenes wt%	0.59	0.89	1.33

used, the addition of ITQ-7 increases the yields of isobutene and isoamylenes with high octane levels.

The full applicability of ITQ-7 is at present limited due to the high cost of production. Nevertheless, it cannot be discarded that future improvements in the technology of zeolite synthesis could drive to a more economic method of synthesis.

CONCLUSIONS

ITQ-7 zeolite has shown good properties as additive of USY zeolite for gasoil cracking. Its tridirectional pore structure with dimensions between 6.1 and 6.3 Å and the lower tortuosity with respect to Beta zeolite favor β-scission versus protolytic cracking and limits the extension of hydrogen transfer reactions. These properties are reflected in higher gasoline yield of high octane, lower aromatic and higher isobutene and isoamylene content, together with a higher propylene/propane and butenes/butanes ratios. The effect of ITQ-7 is optimum for high Si/Al ratios and moderate levels of addition. The positive effects of the addition of ITQ-7 are observed regardless the unit cell size of the Y zeolite used in the main catalyst.

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