Isomerization of *n*-butane over ultrastable H-Y zeolites with different Si/Al atomic ratio

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Ultrastable H-Y zeolites with different Si/Al atomic ratios ($3 < \mathrm{Si/Al} < 11$) are active and selective catalysts for the *n*-butane isomerization. The initial activity of these catalysts is lower than that measured on tungsta supported on zirconia catalysts (WO_x/ZrO_2) and acidic mordenite catalysts; however, the Brønsted acid sites of the ultrastable H-Y zeolites are stable and selective towards isobutane. No deactivation of the catalysts was observed after 5 h of time on stream. In contrast, WO_x/ZrO_2 and acidic mordenite catalysts under the same experimental conditions are largely deactivated in less than 1 h of time on stream. The stability of the ultrastable H-Y zeolite in comparison to H-mordenite catalysts may be due to the three-dimensional structure of H-Y made of large supercages interconnected by apertures of 12 oxygen atoms. This structure may favour the diffusion of reactant and product decreasing the residence time and the ensuing degradation to coke. Acidic molecular sieves with monodimensional structure may favour the formation of the precursors of the coke responsible of the catalyst deactivation.

KEY WORDS: butane isomerization; ultrastable H-Y catalysts; catalysts deactivation; XPS characterization

1. Introduction

The isomerization of *n*-butane has a specific interest because isobutane can be alkylated with butenes to produce high octane number isooctanes and is a starting material for producing isobutene *via* dehydrogenation. Isobutene can be reacted with methanol or ethanol to produce methyl-*tert*-butyl ether (MTBE) or ethyl-*tert*-butyl ether (ETBE), which are employed as additives of gasoline, to increase the antiknock power and improve the combustion [1,2].

The use of halogen-containing catalysts, to reach the acid strength necessary for skeletal isomerization, is becoming problematic for environmental reasons. Hence, the search for strongly acidic catalysts which avoid the use of halogens is an important goal of the refining industry.

Zirconia-based catalysts, especially sulfated zirconia ([3,4] and references therein) and tungsta supported on zirconia ([5] and references therein), have high activity and selectivity for *n*-butane isomerization. On the sulfated zirconia catalysts the catalytic activity was correlated with the number of Brønsted acid sites and the strongest sites, which are able to retain pyridine against evacuation at 150 °C, were suggested to be the active sites for *n*-butane isomerization [3,4]. The main problem with these catalysts is their fast deactivation due to coke deposition. On sulfated zirconia catalysts less than 0.1 wt% of carbonaceous deposits was sufficient to reduce 90% of the initial activity in less than 1 h of time on stream [4].

Acidic molecular sieves like H-mordenites were also tested as an interesting alternative to conventional isomerization catalysts, although also for these catalysts the main limitation was found in their fast deactivation due to coke deposition [2]. The initial activity and selectivity to isobutane were similar to that found on sulfated and tungstated zirconia catalysts at 250 °C; however at higher temperature the selectivity decreases due to the formation of propane and pentane [2].

Ultrastable H-Y zeolites are much investigated as catalysts for hydrocarbon cracking activity [6]. In this paper ultrastable H-Y zeolites with different Si/Al atomic ratios, obtained by leaching with diluted HCl solutions, are investigate as specific catalysts for *n*-butane isomerization in comparison to H-mordenite and WO_x/ZrO_2 catalysts.

2. Experimental

The commercial ultrastable H-Y zeolite with $\mathrm{Si/Al} = 3.15$ was obtained from Tosoh (US HSZ-330 HUA). H-mordenite catalyst with $\mathrm{Si/Al} = 25$ was obtained from Süd Chemie. The preparation of the WO_x/ZrO_2 ($W = 17$ wt%) catalyst was reported previously [5].

Dealuminated ultrastable H-Y samples were prepared according to the procedure reported by Scherzer [7]. Dilute HCl solutions (0.1 M) were added to four H-Y portions (2 g in 250 ml of distilled water, starting each time with a different portion of the same commercial batch) until pH = 1.5. Each sample was kept 0.5 h at a set temperature (15, 30, 60 and 90 °C) under stirring. After separation, the solid was washed (Cl^- negative test in the solution), dried at 110 °C for 24 h and calcined at 550 °C in air for 5 h.

The Si/Al atomic ratios were obtained by energy dispersive X-ray spectrometry (Philips SEM515-EDAX 9900).

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The residual Na^+ content on all the H-Y samples was determined by atomic absorption (Varian SpectrAA-30) and found less than 0.2 wt%.

The powder diffraction patterns (XRD) were obtained with a Philips automated PW 1729 diffractometer using Cu Kα radiation (Ni-filtered).

X-ray photoelectron and X-ray excited Auger spectra were obtained using a Mg Kα radiation (1253.6 eV) with a Leybold–Heraeus LHS-10 spectrometer operating at constant transmission energy ($E_0 = 50$ eV). The X-ray source was operated at 12 kV and 20 mA. The surface composition was obtained from the peak areas of the Si(2p) and Al(2p) emission using the sensitivity factor method [8]. The Fermi level of the samples were determined using adventitious carbon with the binding energy of C(1s) fixed at 284.8 eV [9].

Textural characterization (BET specific surface area, external surface area and micropore volume by t-test using the Harkins and Jura isotherm equation [10]) was performed by N_2 adsorption–desorption at $-196\,°C$ using a Micromeritics ASAP 2010 analyzer. Before adsorption, the solids were preheated under vacuum in three steps: 1 h at 150 °C, 1 h at 250 °C, and finally 4 h at 350 °C.

Catalytic isomerization of n-butane was carried out in a flow apparatus, including: (i) a feeding section equipped with independent mass controllers; (ii) a down flow silica reactor, containing *ca.* 1 g of catalyst supported on a fritted disk, and vertically positioned in an electrical heater thermoregulated to within $\pm 1\,°C$ (the K-type thermocouple was in contact with the reactor wall in correspondence with the middle of the catalyst bed); (iii) a gas chromatograph equipped with a flame ionization detector connected to an integrator for peak area evaluation. Before each catalytic run the catalyst was heated in flowing oxygen at 500 °C for 0.5 h. The reaction was run with pure n-butane at atmospheric pressure, the WHSV was $0.8\ h^{-1}$ and the reaction temperature 300 °C. The mass balance with respect to carbon was 95–102%. Due to the uncertainty of the mass balance we were not able to estimate the amount of coke deposited from kinetic data. Details can be found elsewhere [5].

3. Results and discussion

The main features of the ultrastable H-Y zeolites are listed in table 1. All the ultrastable HY zeolites are active catalysts for the n-butane isomerization. It can be of interest to compare the isobutane yield values with those obtained previously in our laboratory for other isomerization catalytic systems, namely WO_x/ZrO_2 ($W = 17$ wt%, total surface area = external area = $50\ m^2\,g^{-1}$, due to the absence of micropores) [5] and with an H-mordenite (Si/Al = 25, total surface area = $430\ m^2\,g^{-1}$, external area = $104\ m^2\,g^{-1}$, micropore volume $0.14\ ml\,g^{-1}$) catalyst.

As shown in figure 1, HY catalysts have a much higher stability with time on stream in comparison to WO_x/ZrO_2 and H-mordenite catalysts. In fact, under our experimental conditions, the activity of WO_x/ZrO_2 and H-mordenite catalysts decreases after 3 h on stream by a factor 5 and 2, respectively.

When the selectivity to isobutane is considered (figure 2) one realizes that, at variance with the H-mordenite catalyst, only ultrastable the H-Y zeolites present interesting selectivity values although lower than those of tungsta/zirconia [5] and sulfated zirconia [4] catalysts. The low selectivity values found in H-mordenite and the high values found in H-Y may be related to their structure [11]. The crystalline architectures of the two zeolites indicate that in H-Y the reactants diffuse from a supercage to the next one in a three-dimensional system through apertures of 12 oxygen atoms, whereas in H-mordenite the reactants diffuse along monodimensional channels with apertures of 12 and 8 oxygen atoms [11]. Despite the high isobutane yield, H-mordenite shows only about 50–60% of selectivity to isobutane, the remaining being converted mainly to propane, pentanes and minor amounts of C_6 hydrocarbons. Considering our data (figures 1 and 2) we may tentatively suggest that, while the activity is mainly controlled by the acidity of the zeolite, the selectivity to isobutane is mostly internal diffusion controlled, the formation of isobutane *vs.* propane being favored in the wider and three-dimensional pore structure of H-Y zeolite.

Table 1
H-Y (US, Tosoh) before and after treatments with HCl 0.1 M at pH 1.5 for 0.5 h at different temperatures

Thermal treatment (°C)	Si/Al[a] (EDAX)	Si/Al[a] (XPS)	a (Å)	$(Si/Al)_F$[b]	Al_F[c]	Al_E[c]	SA ($m^2\,g^{-1}$)	V_μ ($ml\,g^{-1}$)	S_{ext} ($m^2\,g^{-1}$)
Untreated	3.44	1.78	24.37	13	13.9	29.3	730	0.27	43
15	6.30		24.34	17	10.7	15.6	985	0.37	55
30	10.2		24.34	17	10.7	6.4	833	0.30	48
60	4.85		24.34	17	10.7	22.1	1016	0.38	66
90	6.87	6.31	24.27	59	3.21	21.2	982	0.37	61

[a] Si/Al atomic ratios obtained by EDAX and XPS measurements, including framework and extra-framework Al species. The stated Si/Al atomic ratio for the untreated H-Y zeolite is 3.15.

[b] Si/Al atomic ratios including only the framework aluminum species calculated using the relationship between the a parameter and the Al content in the framework, Al_F, according to Sohn *et al.* [13].

[c] Number of framework (Al_F) and extra-framework (Al_E) aluminum species per unit cell of Y zeolite.

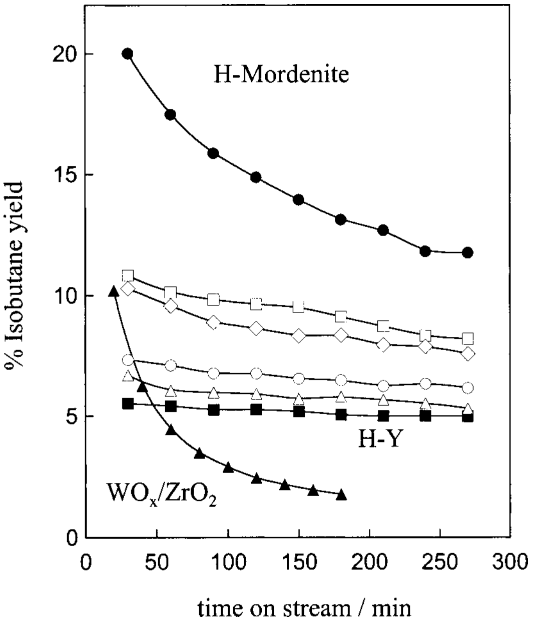

Figure 1. Isobutane yield on tungsta/zirconia, H-mordenite and ultrastable HY catalysts at 300 °C as a function of time on stream. (▲) Tungsta supported on zirconia catalyst ($W = 17$ wt%), (•) H-mordenite (Si/Al = 25), (■) H-Y (Si/Al = 3.44), (□) H-Y (Si/Al = 6.30), (◊) H-Y (Si/Al) = 10.2, (○) H-Y (Si/Al = 4.85), (△) H-Y (Si/Al = 6.87).

Our starting ultrastable H-Y zeolite (Si/Al = 3.15) has an isobutane yield of about 5% and a selectivity to isobutane of about 80%. The mild dealumination treatment at 15 °C substantially increased the activity with a moderate decrease in selectivity in comparison to the untreated material. The treatments at higher temperatures also increased the activity, but to a lower extent compared to the 15 °C treatment, with a selectivity decrease to 75% (figures 1 and 2).

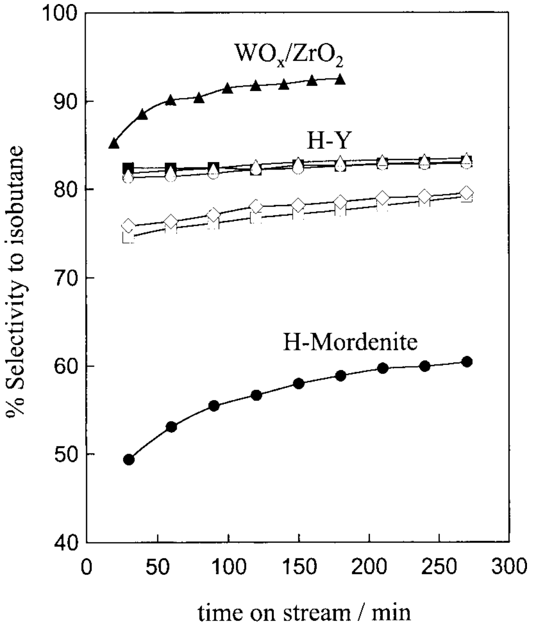

Figure 2. Isobutane selectivity on tungsta/zirconia, H-mordenite and ultrastable H-Y catalysts at 300 °C as a function of time of stream. (▲) Tungsta supported on zirconia catalyst ($W = 17$ wt%), (•) H-mordenite (Si/Al = 25), (■) H-Y (Si/Al = 3.44), (□) H-Y (Si/Al = 6.30), (◊) H-Y (Si/Al) = 10.2, (○) H-Y (Si/Al = 4.85), (△) H-Y (Si/Al = 6.87).

The *a* parameter of the cubic unit cell of Y zeolites (table 1) was determined by the XRD reflections in the 2θ range 45°–59° [12]. Using the *a* parameter the Si/Al ratio in the framework $(\mathrm{Si/Al})_\mathrm{F}$, was calculated according to Sohn *et al.* [13].

EDAX measurements gave the total Si/Al ratio, including both framework and extra-framework aluminum. From the total Si/Al, $\mathrm{Al_F}$ and $(\mathrm{Si/Al})_\mathrm{F}$ it is possible to calculate the number of extra-framework aluminum atoms per unit cell, $\mathrm{Al_E}$. All these data are collected in table 1. Information on the crystallinity of the HY samples, untreated and dealuminated, can be obtained from the XRD patterns in the 2θ range 15°–35° [12]. The treatment with dilute HCl solution at different temperatures does not affect the crystallinity of the samples.

The mild effect of the dealumination on the zeolite structure is also witnessed by the textural analysis. In fact, data in table 1 show that dealumination increased the micropore volume (V_μ) leading to a noticeable increase in the specific surface area, possibly related to the decrease in the extra-framework aluminum. No systematic dependence, however, was found between $\mathrm{Al_E}$ and the temperature of the treatment. On the other hand, no dramatic change of the mesoporous structure is evidenced by the external surface values, as reported for more severely treated Y zeolites [14].

From table 1 one can observe that the value of Si/Al = 3.15, stated by the manufacturer for the untreated material, is in fairly good agreement with the value found in this work by EDAX measurements (Si/Al = 3.44). The untreated sample contains a great amount of extra-framework aluminum (more than twice the framework aluminum). The framework aluminum decreases identically by treatments at 15, 30 and 60 °C with HCl at pH = 1.5, and very markedly by treatment at 90 °C. The extra-framework aluminum seems to change in a complex way, which may be the result of two processes: extraction of aluminum species from the framework and their transfer to the liquid phase.

The surface characterization of two representative H-Y samples (untreated and dealuminated at 90 °C) was obtained by XPS analysis. The XPS technique is important here because the HCl leaching first and foremost removes Al from the external surface of the H-Y crystals. Therefore, the XPS technique which is sensitive to the surface of the catalyst adds important information to understand the catalytic properties of the dealuminated catalysts.

In figure 3(a) we present an XPS wide scan of the region involving Si(2s), Si(2p), Al(2s) and Al(2p) photoemissions. The surface Si/Al atomic ratio of the untreated sample (1.78) is much lower than that of dealuminated sample treated at 90 °C (6.31), suggesting a noticeable decrease in surface aluminum concentration for the sample treated at 90 °C (table 1). The binding energy of the Al(2p) peak is at *ca.* 76 eV in the two samples (figure 3 (b) and (c)). Figure 3 (d) and (e) shows a complex feature of the Auger Al ($\mathrm{KL_{23}L_{23}}$) peak which can be curve fitted with three components at

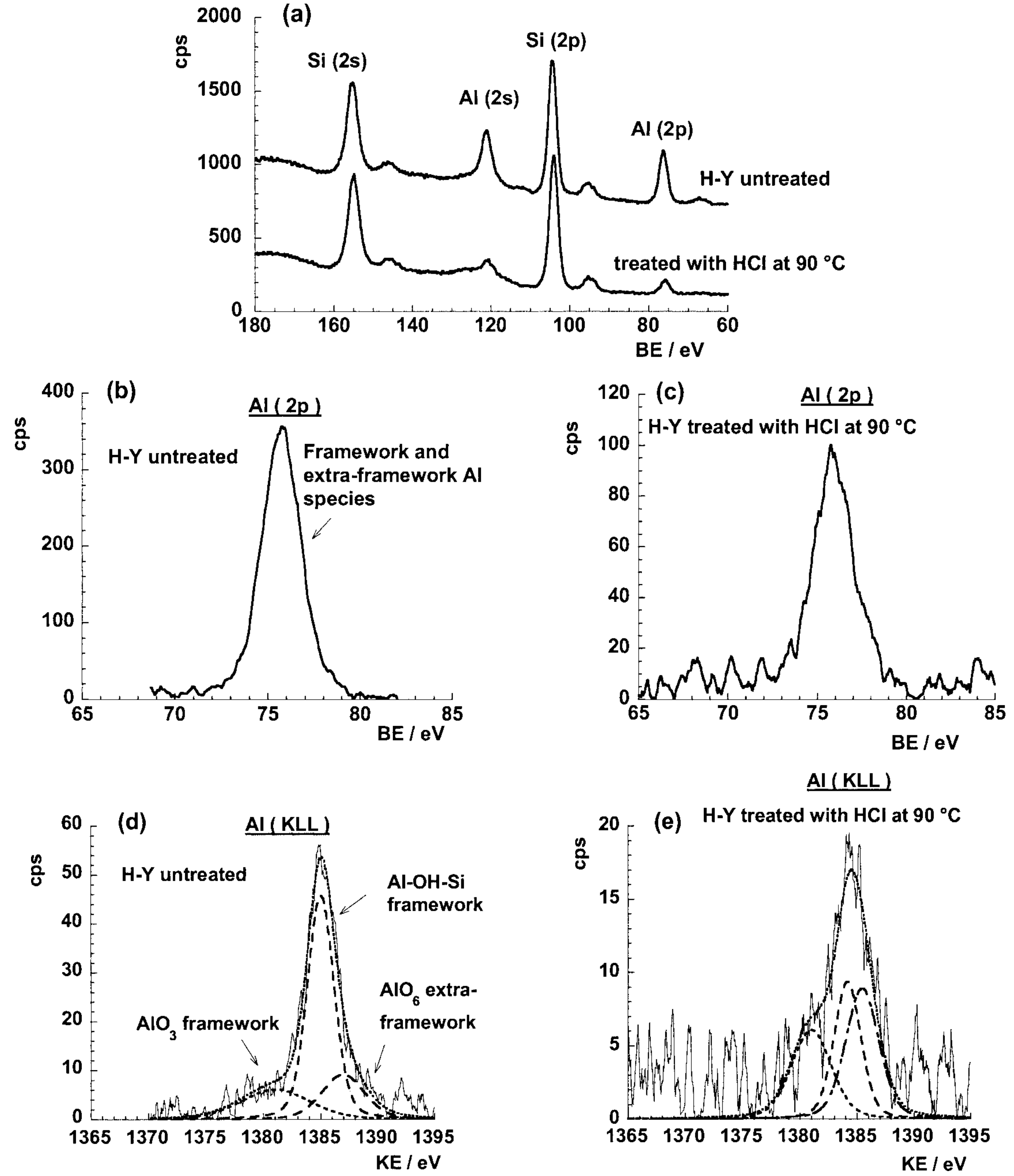

Figure 3. XPS results for untreated and dealuminated ultrastable H-Y catalysts (HCl, 90 °C, see text): (a) 2s and 2p core levels for Si and Al; (b) and (c) detail of the Al(2p) region; (d) and (e) Al (KLL) Auger spectra: the curve-fitting indicates the different aluminum species present at the surface of untreated and dealuminated H-Y catalysts.

ca. 1381, *ca.* 1385 and *ca.* 1386 eV. The Al Auger parameters, $\alpha'_{\mathrm{Al}} = E_{\mathrm{b}}(2\mathrm{p}) + E_{\mathrm{k}}(\mathrm{KL}_{23}\mathrm{L}_{23})$, have the following values: *ca.* 1457, *ca.* 1461 and *ca.* 1462 eV. According to literature data [15,16] these Auger parameter values can be taken as an indication of the presence of aluminum species with coordination number 3 (Lewis acid sites), 4 (Brønsted acid sites) and 6 (extra-framework species). The sample treated at 90 °C shows an increase of the relative concentration of the Lewis acid sites and of the extra-framework species with respect to the untreated one (figure 3 (d) and (e)).

The Brønsted acidity is the key property for isomerization activity. We see that for ultrastable H-Y zeolites the activity increases when passing from $(\mathrm{Si/Al})_{\mathrm{F}} = 13$ to $(\mathrm{Si/Al})_{\mathrm{F}} = 17$ and decreases at the higher $(\mathrm{Si/Al})_{\mathrm{F}}$ atomic ratios (figure 1 and table 1). It may be suggested that the activity increase is related to a decrease in the number of Al–OH–Si–OH–Al entities and to the increase in the number of isolated Al–OH–Si groups, which are considered stronger acid sites [17]. The increase in surface area with dealumination can also contribute to an easier access to the Brønsted acid sites. The activity decrease observed after the treatment at 90 °C may be related to a strong reduction in the number of Brønsted acid sites. However, the extra-framework aluminum should play a role in the activity, otherwise a sharper decrease in activity after the treatment at 90 °C should have been observed and the same activity value after the treatments at 15, 30 and 60 °C (same amount of framework aluminum, see table 1) should have been measured. A role of the extra-framework aluminum on the activity of dealuminated H-Y zeolites in heptane and decane isomerization was suggested by Remy *et al*. [15]. The importance of certain extra-framework Al species in the development of strong acidity in protonated zeolites was also discussed by Hall *et al.* [18] in the case of n-butane and n-pentane cracking at 400 °C, and by Beyerlein *et al.* [19] in the case of isobutene conversion at 500 °C.

Next we consider what could be the reason for the stability with time on stream of the H-Y catalysts in comparison to H-mordenite catalysts.

As suggested by Asuquo *et al.* [2], over H-mordenite catalysts n-butane is mainly converted to isobutene *via* a bimolecular mechanism at low temperature. In the first step, n-butane forms a butyl-carbenium ion by protonation at the strong Brønsted acid sites and subsequent dehydrogenation. A similar mechanism may be suggested in the case of H-Y catalysts.

During the present investigation we found that H-ferrierite is not active for n-butane isomerization probably because the Brønsted acid sites are not strong enough to form the butyl-carbenium ion from n-butane. On the other hand, the activity for the 1-butene isomerization on H-ferrierite is explained by Pazè *et al.* [20] with a bimolecular mechanism, which would favour the formation of coke over zeolitic structures with monodimensional channels and pore apertures of molecular dimensions (like H-ferrierite and H-mordenite).

We suggest that the stability with time on stream of our dealuminated H-Y zeolites, in comparison to H-mordenite, may be tentatively explained by the fact that the three-dimensional structure of the H-Y zeolite may favour the diffusion of reactant and product decreasing the residence time and the ensuing degradation to coke.

4. Conclusions

The main result reported in this study is the remarkable stability with time on stream of ultrastable H-Y zeolites in the isomerization of n-butane at 300 °C. The activity of these catalysts is lower than that reported for zirconia-based catalysts or for H-mordenite catalysts which, however, suffer a severe loss of activity with time on stream due to the poisoning of the acidic sites by coke. On the other hand, ultrastable H-Y zeolites present fairly high selectivity and stability with time on stream. In particular the selectivity is similar to that obtained on the most active catalysts (tungsta/zirconia and sulfated zirconia). We suggest that on ultrastable H-Y catalysts both the presence of strong Brønsted acid sites and the three-dimensional structure with supercages favour the diffusion of the isomerized products as they are formed and hinder the formation of coke.

Considering that in commercial practice high selectivity is usually more valuable than high activity, the relative comparison of H-Y and H-mordenite catalysts is strongly in favour of the ultrastable H-Y zeolites.

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