JOURNAL OF CATALYSIS **171,** 329–332 (1997)
ARTICLE NO. CA971773

NOTE

Factors Affecting the Selective Isomerization of *n*–Butene into Isobutene over Ferrierite Catalysts

The selective isomerization of *n*–butene has been extensively investigated during the past few years (1–5) because of the need of isobutene for methyl-tertiobutyl ether synthesis.

Among the catalysts which are effective for this reaction, medium pore zeolites have been widely studied: it has been shown that after a few hours on stream, ferrierite (1, 2), ZSM-23 (MTT) (3), and ZSM-22 (TON) (4) are highly selective for isobutene formation.

In a recent note, O'Young *et al.* (5) have compared 10-member ring zeolite catalysts (FER, MTT, TON, MFI) and it has been concluded that "it is not very clear why FER is more selective than MTT even though FER has slightly larger intersecting channels." The authors compared the catalysts after several hours on stream where the solids acquired high selectivity to isobutene formation. The coke content and its location were considered to have a major effect on the selectivity. More recently, Pellet *et al.* (6) have investigated the influence of hydrothermal dealumination of FER and of subsequent acid washing treatment on the skeletal isomerization of *n*–butene. The authors concluded that the deactivation effect of unmodified FER "could be due to blocking of sites by carbon deposition or to spatial restrictions caused by carbon sterically limiting the nonselective reactions." They have shown that dealumination by steaming creates "two types of nonframework alumina." One type, located in the 8-MR channels, was relatively inert and resistant to extraction by acid treatment. The second type, located in mesoporous voids created by steam, was catalytically active but nonselective for isomerization. This type of alumina was easily removed by acid washing.

The aim of the present work was to investigate, on a ferrierite catalyst, the role of different factors which can affect the isobutene selectivity, these factors being:

—the presence of acid sites on the external surface of the zeolite crystal or in the mesoporosity of the solid,
—the density of the acid sites,
—the space available around the acid site.

To examine these factors, we have used a ferrierite (Si/Al = 10) which was synthesized without a template. Characterization of this material which exhibits high crystallinity will be reported elsewhere. This material has catalytic properties close to those of Tosoh ferrierite (1) from Tosoh Atlanta (U.S.A).

The synthesized material was washed with water and dried at 373 K overnight. This zeolite was then exchanged twice with ammonium nitrate (1 *M* solution) at 353 K overnight. After this treatment, the remaining content of K^+ and Na^+ is lower than 0.1% for both ions as indicated by elemental chemical analysis. This sample was then transformed in the protonic form by calcination under N_2 at 773 K overnight and will be labelled as the starting material.

Part of this batch was treated with a 1 *M* oxalic acid solution at 353 K for 4 h in order to remove the aluminum located on the external surface of the zeolite grain and in the mesoporosity of the zeolite crystal (7, 8).

Another part of the batch was exchanged with a $CsNO_3$ solution (1 *M* solution) at 363 K overnight. This exchange level was 90% as determined from the elemental analysis results. A third batch was prepared by exchanging the starting FER with a lithium nitrate solution (1 *M* solution for 4 h), and the exchange level was 95% as measured by elemental analysis.

Another part of the initial batch was heated for 3 h at 873 K in a flow of $N_2 + H_2O$ ($P_{H_2O} = 10$ kPa). Part of this hydrothermally dealuminated material was then treated in an oxalic acid solution (1 *M* solution) for 4 h at 363 K in order to remove the extraframework aluminum formed during the hydrothermal treatment and located on the external zeolite surface or in the mesoporosity.

All the catalysts were tested in the *n*–butene skeletal isomerization at 673 K. Reactants and products were analyzed by gas chromatography by using a PONA (Alletech France) capillary column. Infrared spectroscopy was used to estimate the number of acid sites (adsorbance of OH groups). For this purpose, samples were pressed into the form of small wafers with weights in the range of 20–25 mg; these wafers were mounted in an IR cell allowing *in situ* treatments. The samples were outgassed ($P = 10^{-3}$ Pa) overnight, at 673 K, before registration of the IR spectra.

The main characteristics of the different materials are summarized in Table 1. It appears from this table that the

0021-9517/97 $25.00

TABLE 1

Characteristics of the Different Solids under Study

Sample	H-FER[c]	A-H-FER[d]	H-Li-FER	H-Cs-FER	D-H-FER[e]	D-H-FER[f] + acid treatment
Si/Al[a]	10	13	10	10	10	Not measured
Number of acid sites[b]/mg (arbitrary units)	100	70	5	10	4	4

[a] As measured from chemical analysis.

[b] As measured by using IR spectroscopy. In arbitrary units, the adsorbance of the OH vibration at 3600 cm^{-1} was fixed to 100 for the starting material.

[c] Starting material after exchange with NH_4Cl and calcining at 773 K (see text).

[d] Sample treated with oxalic acid.

[e] Sample dealuminated through hydrothermal treatment.

[f] Hydrothermally dealuminated sample treated with oxalic acid.

starting material exhibited the highest number of acid sites (Bronsted acid sites as evidenced by IR OH vibration at 3600 cm^{-1}).

The oxalic-acid-treated sample, as expected (6), exhibited a lower number of acid sites, most of them being located inside the microporosity of the zeolite as we will report in an upcoming paper. The relative number of OH groups vibrating at 3600 cm^{-1} is in reasonable agreement with that calculated from the Al content determined by chemical analysis.

For Cs- or Li-exchanged samples, due to the high degree of exchange (see Table 1) the remaining number of OH groups is less than 10%: The OH concentration, as measured by IR spectroscopy, is in good agreement with the number of remaining protons as deduced from chemical analysis results (Li + Cs analysis).

For the hydrothermally dealuminated FER, the problem is more complex because part of the framework Al is extracted, causing a decrease in the corresponding number of acid sites ($\nu_{OH} = 3600$ cm^{-1}) but extra framework aluminum creates new hydroxyl groups ($\nu_{OH} = 3650$ cm^{-1}). Nevertheless, the number of acid OH groups was estimated by IR spectroscopy (Table 1). The Si/Al ratio of the starting material determined by ^{29}Si MAS–NMR is 10.2. The ^{27}Al MAS–NMR spectrum of this solid showed only a single line at +54 ppm assigned to tetra-coordinated Al, indicating that all Al-atoms are framework atoms. By contrast, the ^{27}Al MAS–NMR spectrum of the dealuminated FER showed a very small line at +54 ppm and two intense lines at ca. +30 ppm and 0 ppm attributed to penta- and hexa-coordinated Al respectively. It has not been possible to determine accurately the Si/Al ratio of the dealuminated sample because of the overlap of the signals of Si (1 Al, 3 Si) and Si (4 Si).

A treatment with oxalic acid does not change the number of OH groups vibrating at 3600 cm^{-1} but decreases the number of OH groups linked to extraframework Al.

These catalysts were used for *n*–butene isomerization at 673 K, $P_{C_4H_8} = 26$ kPa, supplemented to atmospheric pressure by nitrogen.

WHSV were adjusted to achieve low conversions. In order to avoid the coking of the solids with time on stream, the bracketing technique was used to measure the catalytic properties on fresh solids: the sample was reacted for 2 min with butene. After 2 min on stream, the reaction was interrupted and the reactor flushed with nitrogen (5 min), then with oxygen (30 min), and again with nitrogen (10 min) before the next experiment; in these experimental conditions (low conversion, short time on stream, bracketing technique) the results obtained by runing the last experimental point in experimental conditions identical to those used for the first experimental point indicated that the deactivation is minimized and results can be considered as being obtained on nondeactivated samples.

Table 2 lists the rates of isobutene formation. It appears that on H-Li-FER, H-Cs-FER, deal-H-FER, and acid leaching deal-H-FER, the rate of isobutene formation was low, as expected for these modified H-FER containing a small amount of the remaining protons. Figure 1 indicates

TABLE 2

Rate of Isobutene Formation on the Unmodified and Modified Ferrierite Catalysts, $T = 673$ K, $P_{C_4H_8} = 25$ kPa

Catalyst	H-FER	A-H-FER	H-Li-FER	H-Cs-FER	D-H-FER	D-H-FER + acid treatment
Isobutene rate formation (mol · h^{-1} g^{-1} catalyst)	1.1	0.49	0.05	0.04	0.08	0.07

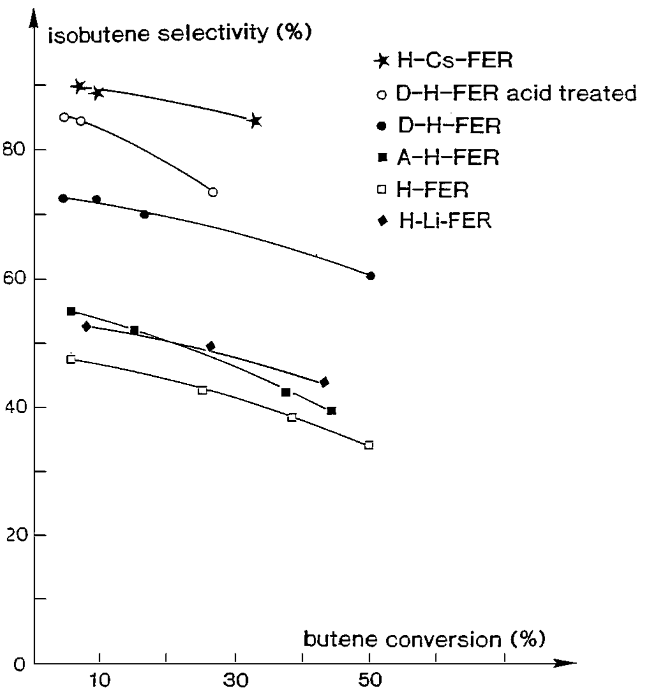

FIG. 1. Change in the isobutene selectivity as a function of the conversion for different solids. The reactant is 1-butene. Selectivity is on a carbon basis, with all linear butenes (1-butene, 2-*cis*, and 2-*trans* butene) being considered as reactants. Isobutene selectivity is given by the number of moles of isobutene formed/number of moles of 1-butene transformed into products different from 2-butenes. Conversion is defined as $(C_{\text{in}} - C_{\text{out}}/C_{\text{in}}) \times 100$, with C_{in} being the number of moles of 1-C_4H_8, $C_{\text{out}} = \Sigma 1\text{-}C_4H_8 + 2\text{-}cis\ C_4H_8 + 2\text{-}trans\ C_4H_8$).

that the fresh nontreated solid has a poor isobutene selectivity. Treatment with oxalic acid improved the isobutene selectivity, clearly indicating that the surface acid sites are not selective as reported earlier (1).

For the samples dealuminated via the hydrothermal treatment, the selectivity is improved, showing that the removal of some framework aluminum and the consecutive formation of extraframework aluminum either in the microporosity or in the mesoporosity is beneficial for the isobutene selectivity.

Indeed, it could be speculated that it is the density of protonic sites which is the major factor because the dealumination causes a decrease in the number of acid sites. In order to confirm (or to refute) this, we have exchanged a fresh H-FER with a lithium solution (1 *M* solution) at 353 K in order to have a H-Li-FER containing only 5% of the initial protons (see Table 1). This sample did indeed exhibit a reduced activity but the selectivity is not much improved (Fig. 1), clearly indicating that the density of acid sites is not governing the isobutene selectivity.

The hydrothermally dealuminated sample has been submitted to an additional oxalic acid treatment in order to remove, at least partially, surface aluminum. The isobutene selectivity was slightly improved, showing that the surface aluminum has a detrimental effect on the isobutene selectivity.

From these results, it is observed that the surface dealuminated sample exhibits a high isobutene selectivity compared to the fresh nontreated sample. These observations are in line with those reported recently by Xu *et al.* (2) who have attributed this effect to the removal of non-shape-selective acid sites.

A very large improvement in isobutene selectivity is observed on a hydrothermally dealuminated sample, either treated with oxalic acid or untreated. Again these results are in agreement with those of Xu *et al.* (2); these authors have attributed these improved performances to the fact that the "lowering of the number of acid sites decreases interactions between intermediates in adjacent acid sites."

In order to discriminate between the two effects of the dealumination treatment (reduction of the density of acid sites and reduction of the porosity of FER by extraframework aluminum), we have tested a H-Cs-FER material. The initial selectivity of this solid, containing nearly the same number of protonic sites as the H-Li-FER, is very high indicating that the major factor governing the selectivity is the space available around the active site. It is now likely, for hydrothermally dealuminated FER, that the improvement in isobutene selectivity is due to the presence of aluminum debris in the cavities and pores of the FER, decreasing the space available in the vicinity of the acid sites, thus rendering the FER shape selective for the *n*–butene skeletal isomerization. The ageing of the solid with time on stream is probably at the origin of the same phenomenon: coke deposits increasingly block the porosity, causing an increase of the isobutene selectivity with time on stream.

Coming back to the surprising result reported earlier indicating that FER zeolites are more selective than MTT (5), it has to be recalled that the results were certainly obtained on coked materials since the isobutene yields for FER were quite high. Very probably, the reverse order of classification would be obtained with uncoked zeolites. Work is in progress to confirm these interpretations.

ACKNOWLEDGMENT

This work has been funded by Total Raffinage et Distribution.

REFERENCES

1. Xu, W. Q., Yin, Y. G., Suib, S. L., Edwards, J. C., and O'Young, C. L., *J. Phys. Chem.* **99**, 9943 (1995).
2. Xu, W. Q., Yin, Y. G., Suib, S. L., Edwards, J. C., and O'Young, C. L., *J. Catal.* **163**, 232 (1996) [and references of the same authors included].

3. Xu, W. Q., Yin, Y. G., Suib, S. L., and O'Young, C. L., *J. Catal.* **150**, 34 (1994).
4. Simon, M. W., Suib, S. L., and O'Young, C. L., *J. Catal.* **147**, 484 (1994).
5. O'Young, C. L., Pellet, R. J., Casey, D. G., Ugolini, J. R., and Sawicki, R. A., *J. Catal.* 467 (1995).
6. Pellet, R. J., Casey, D. G., Huang, H. M., Kessler, R. V., Kuhlman, E. J., O'Young, C. L., Sawicki, R. A., and Ugolini, J. R., *J. Catal.* **157**, 423 (1995) [and references of Suib, S., and O'Young, C. L. included].
7. U.S. Patent to Mobil, PCT/U.S. 9303621.
8. Apelian, M. R., Fung, A. S., Gordon, J. K., and Thomas, F., "Preprints 14th North American Meeting of the Catalysis Society, Snowbird, UTah, June 11–16, 1995."

P. Mériaudeau*
Vu A. Tuan*
Le N. Hung*
C. Naccache*
G. Szabo†

**Institut de Recherches sur la Catalyse–CNRS*
2 Avenue Albert Einstein, 69626
Villeurbanne Cedex, France
†*Total Raffinage et Distribution*
BP 27, Harfleur 76700, France

Received January 15, 1997; revised June 2, 1997; accepted June 5, 1997