Catalysis Letters Vol. 98, No. 4, December 2004 (© 2004)

Shape selectivity of HFER zeolites as responsible for the positive effect of their Si/Al ratio on the selectivity to *n*-butene isomerization into isobutene

B. de Ménorval, P. Ayrault, N.S. Gnep, and M. Guisnet*

Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, UMR 6503, Faculté des Sciences, 40 avenue du recteur Pineau, 86022 Poitiers Cedex, France

Received 31 July 2004; accepted 19 August 2004

The selectivity and turnover frequency for isobutene production was shown to increase with the Si/Al ratio of fresh HFER. This can be explained by considering the zeolite pore system as a series of non-interconnected nanoreactors (the 10-MR channels) in which the molecules diffuse and react bimolecularly without any possibility of desorption before the exit.

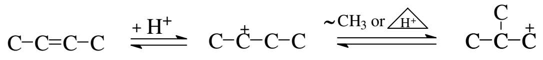
KEY WORDS: HFER, *n*-butene isomerization, mechanism:bimolecular, autocatalytic, shape selectivity.

1. Introduction

A large variety of catalysts based on alumina [1–5] or on medium pore size zeolites [6–12] have been found as active and selective for the skeletal isomerization of *n*-butene. However, the best catalyst seems to be the protonic form of ferrierite (HFER); indeed, this zeolite is capable of operating in the absence of water at relatively low temperature (623 K) with a high selectivity to isobutene and a high stability. Despite the very significant amount of research which has been carried out to determine the origin of the high selectivity of HFER to isobutene, the mechanism of *n*-butene isomerization remains much debated.

It has to be said that the catalytic behaviour of HFER catalysts is relatively complicated. In particular, the selectivity to isobutene of the fresh samples is generally poor and a high selectivity can be obtained only after a partial deactivation caused by the trapping of heavy products within the zeolite micropores. Over the fresh HFER sample, propene and pentenes are the main by-products, which is typical of a bimolecular mode of *n*-butene transformation, actually a mechanism involving successively *n*-butene dimerization, octene isomerization then cracking [6–15]. ^{13}C labelling experiments confirm the predominance of this bimolecular mechanism [16–18]. Whereas this mechanism of butene isomerization over the fresh HFER sample is now well admitted, it is the case neither for the origin of the selectivating effect of coke nor for the selective mode of isobutene production over the aged HFER samples.

The more simple explanation is that on the fresh samples, *n*-butene transforms simultaneously through the non-selective bimolecular mechanism and through the classical selective monomolecular mechanism; the increase in selectivity caused by aging would be due to the specific elimination of the acid sites responsible for the bimolecular *n*-butene transformation. The main objection against this simple proposal is that the monomolecular acid catalyzed formation of isobutene involves a highly unfavourable primary isobutyl carbenium ion:



$$C{-}C{=}C{-}C \overset{+H^+}{\rightleftharpoons} C{-}\overset{+}{C}{-}C{-}C \overset{\sim CH_3 \text{ or } \triangle H^+}{\rightleftharpoons} C{-}\overset{C}{\overset{|}{C}}{-}\overset{+}{C}$$

However, the positive effect that the HFER Si/Al ratio [10, 19, 20] and the decrease in *n*-butene pressure [10, 13, 21, 22] have on the selectivity to isobutene of fresh HFER is in favour of this proposal. Indeed, it could be expected that the rate of bimolecular reactions is more affected than that of monomolecular reactions by a decrease in acid site density or in *n*-butene pressure.

The improbability of a fast monomolecular *n*-butene isomerization led some authors to relate the selectivation of HFER to the development of a new reaction mechanism involving as active sites either carbenium ions resulting from the protonation of isobutene molecules which desorb slowly from the FER micropores [23] or of cyclopentenyl species [24] or of benzylic carbocations formed from the methyl polyaromatic molecules trapped in the FER micropores [25]. These reaction mechanisms which involve only facile steps are pseudo-monomolecular, i.e., only one molecule of the *n*-butene reactant is transformed per catalytic cycle. Therefore they can, like the monomolecular mechanism, explain that over-aged HFER *n*-butene isomerization is very selective and occurs without any change in the number of ^{13}C atoms. One argument in favour of the development of a new reaction mechanism is the

---

* To whom correspondence should be addressed.

1011-372X/04/1200–0211/0 © 2004 Plenum Publishing Corporation

increase in isobutene yield found at relatively short-time-stream with some zeolite samples and this even at low *n*-butene conversion [23]. However, no explanation of the high selectivity to isobutene of fresh HFER samples with high Si/Al ratios and low *n*-butene pressure could be proposed. It should, however, be remarked that if *n*-butene isomerization over the fresh HFER samples cannot occur through benzylic carbocations or cyclopentenyl species, it can proceed through the autocatalytic process, isobutene molecules being formed initially. Therefore, on the fresh HFER samples, the classical bimolecular mechanism and the autocatalytic reaction could coexist.

The aim of this paper is to provide an explanation of the increase in the selectivity to isobutene of fresh HFER zeolite based on the bimolecular and autocatalytic mechanisms only. For that, *n*-butene transformation was carried out at 350 °C and at different contact times over five HFER samples synthesized with different Si/Al ratios:6, 9.5, 10, 19 and 32, the acidity of which was characterized by NH_3 adsorption followed by IR spectroscopy. As it was previously shown [10, 19, 20], the selectivity to isobutene determined at similar values of conversion over the five samples was found to increase with their Si/Al ratio. A significant increase in the activity of the protonic sites for the production of isobutene (their turnover frequency) was also observed. To explain these observations, the HFER pore system was considered to be equivalent to a series of non-interconnected nanoreactors (the 10-membered ring channels); in these nanoreactors the reactant molecules have to diffuse without any possibility of desorption before their exit, undergoing a number of successive bimolecular reactions the more significant the higher the concentration of acidic sites.

2. Experimental

The HFER samples were supplied by Tosoh and Zeolyst. Their composition as well as their physicochemical characteristics are reported in Table 1. The porosity of the samples was characterized by nitrogen adsorption at −197 °C with a Micromeritics Tristar apparatus, the *t*-plot method being used for determining the micropore volume and the external surface area. The micropore volumes of the HFER 6, 9.5 and 10 samples are similar (≈ 0.15 cm^3 g^{-1}), those of HFER 19 and HFER 34 slightly greater. The external surface areas are close to 20 m^2 g^{-1} for HFER 6, 9.5 and 10 and approximate twice greater for the other samples. This suggests a smaller crystallite size for these latter samples.

The protonic acidity of the samples were estimated by NH_3 adsorption at 50 °C followed by FT-IR spectroscopy using the extinction coefficient corresponding to the NH_4^+ band at 1458 cm^{-1} as determined in a previous study [de Ménorval *et al.*, submited]. As could be expected, the higher the Si/Al ratio of the HFER sample, the lower the concentration of protonic sites (table 1).

The transformation of 1-butene was carried out in a fixed bed reactor under the following conditions:350 °C, atmospheric pressure, N_2/butene molar ratio of 9, weight hour space velocity (WHSV) of 13, 20, 60 and 120 h^{-1}, the HFER samples being previously pretreated *in situ* under nitrogen flow for 10 h at 500 °C. Whatever the contact time τ (taken as the reverse of WHSV) and the HFER sample, the distribution of linear butenes were always close to that at thermodynamic equilibrium. Therefore, the conversion into the various products were calculated by considering *n*-butene isomers as the reactant. Reaction products were analyzed on-line by FID gas chromatography using a 50 m fused silica Chrompack PLOT Al_2O_3/Na_2SO_4 capillary column. The analyses of the products were carried out at a very short of time stream (1 min), however, long enough to have a constant value of the GC peak area, hence a constant value of the reactant pressure in the reactor.

3. Results and discussion

3.1. *Influence of Si/Al on the selectivity to isobutene*

The *n*-butene transformation was carried out at four contact times $\tau = 1/\text{WHSV} = 0.0083, 0.0167, 0.05, 0.078$ h over the HFER 6, 10 and 19 samples and only at the highest τ value with the other samples. Table 2 shows that, despite the significant decrease in the protonic acidity with the increase in the Si/Al ratio (table 1), there is only a slight change in *n*-butene

Table 1
Origin, composition and physicochemical characteristics of the HFER samples

	Origin	Composition			Pore volumes (cm^3 g^{-1}			S_{ext} (m^2 g^{-1})	Acidity (mmol g^{-1})
		Si/Al	Na (ppm)	K (ppm)	Total	Micro	Meso		
HFER 6	Tosoh	6.1	500	400	0.223	0.148	0.075	18	1.33
HFER 9.5	Tosoh	9.3	nd	nd	0.198	0.148	0.05	21	nd
HFER 10	Zeolyst	10.2	280	nd	0.202	0.151	0.051	18	0.90
HFER 19	Zeolyst	18.8	60	nd	0.271	0.160	0.111	37	0.50
HFER 32	Zeolyst	31.6	150	nd	0.273	0.174	0.093	47	0.42

Table 2
Transformation of *n*-butene over the fresh samples (time-on-stream of 1 min)

	Conversion and yields (wt.%)			Rates (mmol h^{-1} g^{-1})			TOF (h^{-1})		
	X	$iC_4^=$ (S)	$C_3^= + C_5^=$	total	$iC_4^=$	$C_3^= + C_5^=$	total	$iC_4^=$	$C_3^= + C_5^=$
HFER 6	36.5	9.1 (25)	18.4	150	45	80	115	35	60
HFER 9.5	41.5	16.8 (40)	15.4		85*	60*			
HFER 10	44	18.2 (40)	15	180	95	60	200	105	66
HFER19	33	23.5 (71)	5.4	130	105	14	260	210	28
HFER 32	31	24.8 (80)	3.4		115*	9*		275*	22*

Conversion of *n*-butene X, yields in isobutene and propene + pentenes and selectivity to isobutene (S) for a contact time τ of 0.078 h; rates of *n*-butene transformation, of isobutene and of propene + pentenes formation and turnover frequencies values (TOF). Values within brackets denote selectivity to isobutene.* Estimated values (see in text).

conversion measured at $\tau = 0.078$ h on the fresh HFER samples:the highest conversion (44%) is found on HFER 10 which has an average value of acid site concentration, the lowest on HFER 32 which has the lowest concentration. The same can be observed for the other contact times. Thus for $\tau = 0.0083$ h, *n*-butene conversion was equal to 7, 8.5 and 6% on the fresh HFER 6, 10 and 19 samples respectively.

Whatever the catalyst and the value of τ (hence of conversion), isobutene, propene and pentenes are the main reaction products. *n*-butene, C6-C8 alkenes, ethylene and low amounts of ethane, propane, isobutane and pentanes are also formed. However, there is a large change in the product distribution with the Si/Al ratio of the catalyst:thus, for a contact time of 0.078 h and a *n*-butene conversion between 31 and 44%, the selectivity to isobutene increases significantly with the Si/Al ratio, passing from 25% with HFER 6 to 80% with HFER 32. The same trend can be observed at lower conversion; thus for $\tau = 0.0083$ h, the selectivity to isobutene is equal to 30, 55% and 80% for HFER 6, 10 and 19, respectively. These observations which are in good agreement with the data reported by several authors [10, 19, 20] confirm that a high selectivity to isobutene can be obtained over HFER samples which contain no (or only a very small amount of) carbonaceous deposits.

3.2. *Influence of Si/Al on the rates of production of isobutene and of propene + pentenes*

The rates of *n*-butene transformation and of isobutene and propene + pentenes production over fresh HFER 6, 10 and 19 were determined from the slopes of the tangents at $\tau = 0$ to the curves giving the conversion X or the yields as a function of τ (figure 1). The rate of isobutene production over HFER 9.5 was estimated from the rate r over HFER 10 by using the following equation derived from a reversible one order reaction

$$r_{9.5}/r_{10} = [\ln Xe/(Xe - X)]_{9.5}/[\ln Xe/(Xe - X)]_{10}$$

in which Xe and X are the values of *n*-butene conversion into isobutene at thermodynamic equilibrium and found on the fresh samples for $\tau = 0.078$ h, respectively. The same equation was used for determining the rate of isobutene production over HFER 32 by comparison with HFER 19. Furthermore, the rates of propene + pentenes production on HFER 9.5 and HFER 32 were estimated by considering the ratio between the rates over HFER 9.5 and 10 and over HFER 19 and 32, respectively as equal. As could be expected from the decrease in the acid site concentration with the increase in the Si/Al ratio, the higher the Si/Al ratio the lower the rate of propene + pentenes production. In contrast, there is an increase with the Si/Al ratio of the rate of *n*-butene isomerization (table 2). This quite unexpected observation seems difficult to be explained by the coexistence of bimolecular and mono or pseudo-monomolecular pathways over fresh HFER samples.

The turnover frequency (TOF) values were calculated from the rate values by considering all the acidic sites able to protonate NH_3 at 50 °C as active. Table 2 shows that for isobutene production TOF increases with Si/Al, whereas for propene + pentenes production, TOF values of 60–65 and 20–30 h^{-1} are found with HFER 6 and 10 and with HFER 19 and 32, respectively (table 2).

3.3. *A simple proposal for explaining the increase in selectivity and TOF in isobutene production with Si/Al*

The increase in isobutene selectivity with the Si/Al ratio hence with the decrease in acid site density can be explained by the coexistence of mono and bimolecular pathways over the fresh HFER samples:the bimolecular pathway (but not the monomolecular one) which comprises several steps would demand the participation of several protonic sites ($\geq$2), hence would be favoured on the HFER samples with low Si/Al ratios [10]. One other consequence of this demanding character of the bimolecular pathway would be an increase in the TOF value for the production of propene + pentenes with the density of acid sites, which is practically the case:indeed lower values of TOF were found for HFER samples with low Si/Al ratios. However, this effect of the acid site density is more limited than the one found for other bimolecular reactions [26, 27]. Moreover, the TOF value for the selective monomolecular isomerization of *n*-butene should be constant although a very significant increase with the Si/Al ratio of HFER can be observed (table 2).

The coexistence of classical bimolecular and autocatalytic pathways over the fresh samples does not provide any explanation of the increase with Si/Al of the selectivity and TOF for isobutene production.

The large differences between the FER samples could be due to differences in acidity or/and in porosity. Indeed, large differences in the acid site concentration and in the mesopore volume and external surface area (hence with crystallite size) were found between the zeolites. However, these two parameters, taken separately, do not seem capable to explain the difference in the catalytic properties. Furthermore, whereas an increase in acid strength with the Si/Al ratio could explain the increase in TOF, it could not explain the simultaneous decrease in the TOF value for propene + pentenes production. Moreover, an increase in acid strength should only occur at low Si/Al ratio (<10) i.e. up to the value at which the bridging OH groups can be considered as isolated [28, 29].

To explain the differences in the catalytic behaviour of the HFER samples, it seems therefore necessary to consider, together and not independently, their acid site concentration and their pore system. It is what is made here in a simplified model of the catalytic transformation of *n*-butene within the HFER micropores based on the following assumptions:

The *n*-butene transformation occurs essentially within the large 10-membered ring (MR) channels. Indeed only linear molecules *n*-butenes, propene etc. can diffuse through the 8-MR channels passing from one 10-MR channel to another [[30].

Only the classical bimolecular and autocatalytic isomerization pathways which are more facile than the monomolecular one can occur in these 10-MR channels.

In the 10-MR channels, reactant and product molecules can essentially diffuse in single file [31]. Counter diffusion is limited and molecules entering one channel have to diffuse along this channel without any probability of desorption before the exit, hence undergo various successive reaction steps. Therefore the 10-MR channels can be considered as nanoreactors operating in parallel. In each of these independent nanoreactors, the larger the concentration of protonic sites, the greater the number of successive reactions undergone by *n*-butene molecules. The products desorbing from each of the 10-MR channels would be completely different with the following limit cases:

i) In the channels with few protonic sites, *n*-butene molecules could undergo only a limited number of successive reactions steps. After a non-selective bimolecular process over protonic sites near the entrance of the 10-MR channels, *n*-butene molecules will isomerize selectively into isobutene through the autocatalytic pathway.

ii) In the channels with a large concentration of protonic sites, *n*-butene molecules will undergo a significant number of successive reactions, with consequent formation of a thermodynamically equilibrated mixture of all the products:butenes, propene, pentenes, etc. The composition of this mixture estimated by considering only *n*-butenes and the main products:isobutene, propene and pentenes was the following:*n*-butenes:22.3 wt.%, isobutene:25.2 wt.%, propene + pentenes:52.5 wt.%; the product mixture would thus contain 32.5 wt.% of isobutene for 67.5% of propene + pentenes [de Ménorval *et al.*, submitted].

The product mixture at the exit of the zeolite crystallite will be constituted by the sum of all the mixtures exiting from the channels, hence will have a composition intermediate between those obtained for cases (i) and (ii). Over a fresh zeolite having a high concentration of protonic sites, *n*-butene molecules entering the channels should be transformed into a quasi-thermodynamically equilibrated mixtures of butenes, propene and pentenes. This is practically what can be observed with HFER 6:at a conversion of 12%, the propene–pentenes–isobutene mixture is constituted by 30% of isobutene for 70% of propene + pentenes.

In contrast, with a fresh zeolite having a low concentration of protonic sites, *n*-butene will be selectively transformed within the 10-MR nanoreactors into isobutene through the autocatalytic process. This explains the high selectivity found on the fresh HFER 32 zeolite:80% at 31% conversion (table 2), a higher selectivity being expected at lower conversion.

It should be remarked that with this model, not only the concentration of protonic sites in the 10-MR channels but also their length (hence the size of zeolite crystallites) as well as the *n*-butene pressure should affect the selectivity to isobutene. Thus, the higher the *n*-butene pressure the greater the number of successive reactions undergone by *n*-butene molecules along a 10-MR channel hence, the lower the selectivity to isobutene as shown by several authors [10, 13, 21, 22]. Furthermore, the smaller the crystallite size hence the smaller the length of the 10-MR channels, the higher the selectivity to isobutene. This effect of the crystallite size is most likely responsible for a part of the very high selectivity to isobutene of the HFER 19 and 32 samples which present not only a low concentration of protonic sites but also a small crystallite size.

This simple model could also explain the increase in the activity of the protonic sites (TOF) for isobutene production (table 2). Indeed, the transformation of one *n*-butene molecule in a 10-MR channel requires more protonic sites on low Si/Al than on high Si/Al HFER zeolites. The decrease in the TOF for propene + pentenes production with Si/Al can be related to a decrease in the secondary transformation of isobutene in the 10-MR channels due to the decrease in both acid site concentration and crystallite size.

4. Conclusions

This comparison of the catalytic transformation of *n*-butene over fresh HFER samples with different Si/Al ratios, (hence with different acid sites concentration) confirms a significant increase with Si/Al in the selectivity to isobutene. In addition, it shows an increase in the activity of the protonic sites for isobutene production.

A simple model of the pore system of HFER was proposed to explain these observations. In this model, it is considered that *n*-butene transformation essentially occurs through bimolecular reactions within the 10-MR channels; *n*-butene molecules entering these channels have to diffuse along with them without any possibility of desorption before the exit, hence undergo various successive reactions. In each of these nanoreactors operating in parallel, the larger the concentration of protonic sites, the greater the number of successive reactions hence the greater the *n*-butene conversion and the lower the selectivity to isobutene. Therefore, the particular behaviour of HFER zeolite in *n*-butene transformation has the same origin than the shape selectivity of acidic MCM 41 samples for the bimolecular isomerization of *m*-xylene which was related to the presence of long non-interconnected channels and called Tunnel Shape Selectivity [32, 33].

References

[1] V.R. Choudhary and L.K. Doraiswamy, J. Catal. 23 (1971) 54.
[2] B. Juguin and J. Miguel, European Patent No. 664 85 (1982), Institut Français du Pétrole.
[3] J. Szabo, J. Perrotey, G. Szabo, J.C. Duchet and D. Corney, J. Mol. Catal. 67 (1991) 76.
[4] A.C. Butler and C.P. Nicolaides, Catal. Today 18 (1993) 443.
[5] Z.X. Cheng and V. Ponec, J. Catal. 148 (1994) 607.
[6] H.H. Mooiweer, K.P. de Jong, B. Kraushaar-Czarnetski, W.H.J. Storck and S.C.H. Krutzen in Zeolites and Related Microporous Materials:State of the Art, J. Weitkamp, H.G. Karge, H. Pfeifer and H. Holderich (eds.) *Stud. Surf. Sci. Catal.*, Vol. 84 (Elsevier, Amsterdam, 1994) p. 2327.
[7] C.L. O'Young, R.J. Pellet, D.G. Casey, J.R. Ugoli and R.A. Sawicki, J. Catal. 151 (1995) 467.
[8] M. Guisnet, P. Andy, N.S. Gnep, E. Benazzi and C. Travers, J. Catal. 158 (1996) 551.
[9] J. Houzvicka, S. Hansildaar and V. Ponec, J. Catal. 167 (1997) 273.
[10] M.A. Asensi, A. Corma and A. Martinez, J. Catal. 157 (1996) 561.
[11] P. Meriaudeau, V.A. Tuan, H. Le Ngoc and C. Naccache in Zeolite and Microporous Materials, H. Chon, S.K. Ihm and Y.S. Uh (eds.), *Stud. Surf. Sci. Catal.*, Vol. 105 (Elsevier, Amsterdam, 1997) p. 1373.
[12] M. Guisnet, P. Andy, N.S. Gnep, E. Benazzi and C. Travers, Oil Gas Sci. Technol.–Revue de l'IFP 54 (1999) 23.
[13] L. Domokos, L. Lefferts, K. Seshan and J.A. Lercher, J. Catal. 197 (2001) 68.
[14] M. Guisnet, P. Andy, N.S. Gnep, E. Benazzi and C. Travers, J. Catal. 158 (1996) 551.
[15] C. Pazè, B. Sazak, A. Zecchina and J. Dwyer, J. Phys. Chem. B 103 (1999) 9978.
[16] P. Meriaudeau, R. Bacaud, L. Ngoc Hung and V.A. Tuan, J. Mol. Catal. A 110 (1996) L177.
[17] K.P. de Jong, H.H. Mooiweer, J.G. Buglass and P. Maarsen, in Catalysts Deactivation, C.H. Bartholomew and G.A. Fuentes *Stud. Surf. Sci. Catal., Vol. 111* (Elsevier, Amstersdam, 1997) p. 127.
[18] J. Cjeka, B. Wichterlova and P. Sarv, Appl. Catal. A 179 (1999) 217.
[19] P. Meriaudeau, V.A. Tuan, Le N. Hung, C. Naccache and G. Szabo, J. Catal. 171 (1997) 329.
[20] D. Rutenbeck, H. Papp, H. Ernst and W. Schwieger, Appl. Catal. A 208 (2001) 153.
[21] J. Houzvicka and V. Ponec, Catal. Rev. Sci. Eng. 39 (4) (1997) 319.
[22] R.A. Comelli, Z.R. Finelli, N.S. Figoli and C.A. Querini.
[23] M. Guisnet, P. Andy, Y. Boucheffa, N.S. Gnep, C. Travers and E. Benazzi, Catal. Lett. 50 (1998) 159.
[24] A.G. Stepanov, M.V. Luzgin, S.S. Arzumanov, H. Ernst and D. Freude, J. Catal. 211 (2002) 165.
[25] P. Andy, N.S. Gnep, M. Guisnet, E. Benazzi and C. Travers, J. Catal. 173 (1998) 322.
[26] M. Guisnet, F. Avendano, C. Beary and F. Chevalier, Chem. Commun. (1985) 336.
[27] M. Guisnet, Acc. Chem. Res. 23 (1990) 392.
[28] J.A. Rabo and G.J. Gajda, in Guidelines for Mastering the properties of Molecular Sieves, D. Barthomeuf, E.G. Derouane and W. Hölderich (eds), *NATO ASI Series B; Physics, Vol. 221* (Plenum Press, New York, 1990) p. 273.
[29] D. Barthomeuf, Mat. Chem. Phys. 17 (1987) 49.
[30] F. Jousse, L. Leherte and D.P. Vercauteren, Mol. Simulat. 17 (1996) 175.
[31] L. Domokos, L. Lefferts, K. Seshan and J.A. Lercher, J. Catal. 203 (2001) 351.
[32] S. Morin, P. Ayrault, S. El Mouhid, N.S. Gnep and M. Guisnet, Appl. Catal. A 159 (1197) 317.
[33] M. Guisnet, S. Morin and N.S. Gnep in C. Song, J.M. Garcés and Y. Sugi (eds.), Shape-Selective Catalysis, Chemicals Synthesis and Hydrocarbon Processing, ACS Symposium Series 738, ACS, Washington, DC, 1999 p. 334.