



Acid site density effects in zeolite-catalyzed 1-butene skeletal isomerization



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ABSTRACT

We have investigated the effect of acid site density on the catalytic performance of high-silica ($50 \leq \text{Si}/\text{Al} \leq 380$) H-HPM-1 zeolite in the 1-butene skeletal isomerization. Changes (≤ 0.5) in the number of framework Al atoms, and thus of Brønsted acid sites, per unit cell (60 tetrahedral atoms) led to striking variations in both 1-butene conversion and isobutene selectivity. Combining isobutene yield with catalyst durability, H-HPM-1 with a framework Si/Al ratio of 350 was found to perform better than any of the catalysts studied for this reaction thus far.

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1. Introduction

1-Butene skeletal isomerization to isobutene has received steady attention in both industry and academia, not only because of the importance of its product in need of making various commodity chemicals such as methyl *tert*-butyl ether, a gasoline additive, but also because of the low initial isobutene selectivity (e.g., ca. 35% over H-ferrierite with Si/Al = 8.9 at 400 °C and 7.5 h⁻¹ weight hourly space velocity (WHSV)) of the proton form of zeolite ferrierite (framework type FER), the most extensively studied catalyst for this reaction [1–7]. A selectivity higher than 60%, together with a fairly good stability, is observed only for the aged catalyst with coke deposits present [6]. Despite considerable efforts, however, no attempts to elucidate whether the intriguing catalytic behavior of H-ferrierite is due to a change in the prevailing reaction mechanism (i.e., from an unselective bimolecular pathway to a selective monomolecular one) have been successful until very recently [2–7].

In our preliminary communication [8], we have used ¹³C-enriched 1-butene as a reactant in 1-butene skeletal isomerization over H-ferrierite with Si/Al = 8.9 under dynamic conditions (continuous flow reaction) and ascertained that the formation of isobutene and pentenes proceeds mainly by monomolecular and bimolecular mechanisms, respectively, regardless of the catalyst deactivation by coke formation. Therefore, it is now clear that its simultaneous decrease in conversion and increase in isobutene

selectivity with increasing time on stream (TOS) have no connection with mechanistic changes, although the contribution of the unselective bimolecular pathway to the overall isobutene formation decreases rapidly.

We have also reported that H-HPM-1 (STW) with Si/Al = 110, a new medium-pore zeolite with a three-dimensional chiral framework consisting of helical 10-ring pores (5.8 × 5.4 Å) intersected by straight 8-ring pores (4.5 × 3.2 Å) [9,10], is much better in selectively producing isobutene than not only H-ferrierite, which has a much lower Si/Al ratio (8.9), but also the same zeolite with a similar Si/Al ratio (85) [8]. Here we show that not only the 1-butene conversion and isobutene selectivity of this high-silica zeolite but also its durability is markedly altered, when changes in the number of framework Al atoms (Brønsted acid sites) per HPM-1 unit cell, i.e., 60 tetrahedral atoms (T-atoms), are 0.5 or smaller. Given both isobutene yield and catalyst durability, H-HPM-1 with a framework Si/Al ratio of 350 turned out to be more efficient than any of the earlier catalysts tested, revealing the importance of Brønsted acid site (framework Al) density as a key factor governing the isomerization activities of zeolites. To date, there are few studies focusing on the catalytic properties of very high-silica (Si/Al > 200) zeolites in this reaction, especially of those quite selective for isobutene formation [11].

2. Experimental

Four HPM-1 zeolites with bulk Si/Al ratios ranging from 50 to 380 were synthesized by heating under rotation (60 rpm) at 160 °C for 18 days an aluminosilicate gel with the composition

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10SiO₂·xAl₂O₃·5.0ROH·4.9HF·40H₂O, where *x* is varied between 0.0125 ≤ *x* ≤ 0.10 and *R* is 2-ethyl-1,3,4-trimethylimidazolium. When necessary, seed crystals (4 wt% of the silica in the gel), the proton form of HPM-1 with Si/Al = 110 previously prepared, were added. We refer to these four samples as HPM-1(*n*), where *n* is the bulk Si/Al ratio in each zeolite. As-made zeolites were converted into their proton form by calcination in air at 550 °C for 8 h. For comparison, the mixed NaK form of ferrierite with Si/Al = 8.9 was obtained from Tosoh and converted into its proton form by refluxing twice in 1.0 M NH₄NO₃ solutions for 6 h followed by calcination at 550 °C for 2 h. The physicochemical properties of zeolites synthesized here were characterized by using various analytical tools, as described in our recent report [8].

1-Butene skeletal isomerization was conducted under atmospheric pressure in a continuous-flow microreactor. Each catalyst was activated under flowing N₂ (50 mL min⁻¹) at 550 °C for 2 h and then kept at 400 °C. Then, 1-butene (99%, RIGAS) was fed into the microreactor at the same temperature and 7.5 or 24.0 h⁻¹ WHSV. The reaction products were analyzed online in a Varian CP-3800 gas chromatograph equipped with a CP-PoraPLOT Q capillary column (25 m × 0.25 mm) and a flame ionization detector, with the first analysis carried out after 5 min on stream. The coke species formed in zeolite catalysts during skeletal isomerization were characterized by gas chromatography–mass spectroscopy [12] followed by comparing with the NIST database [13].

3. Results and discussion

The representative products from fluoride-mediated syntheses using 2-ethyl-1,3,4-trimethylimidazolium as an organic structure-directing agent (OSDA) and aluminosilicate gels, where the Si/Al ratio is varied from 10 to 400 while fixing the H₂O/SiO₂ ratio to 4.0, can be found in Table S1. We were not able to crystallize pure HPM-1 even in the presence of seed crystals, when Si/Al ratio in the synthesis mixture is smaller than 50. This may probably be due to the large concentration of double-4-ring (D4R) units with quite acute T–O–T angles in its framework. For high silica zeolites, in fact, the D4R units tend to be too stressed to be directly synthesized except when fluoride is occluded inside [14]. Since the amount of positive charges introduced by Al substitution is limited to the amount (6 per unit cell with 60 T-atoms and 6 D4R units) of OSDAs, a competition between Al and F⁻ for incorporation into HPM-1 will be established with the F⁻ concentration that decreases as the Al content increases. If such is the case, the F⁻ concentration should then be too low to stabilize the zeolite framework at a Si/Al ratio lower than a certain value.

The powder X-ray diffraction patterns of four as-made HPM-1 zeolites with different Si/Al ratios synthesized in this work show that they are highly crystalline (Fig. S1), and no reflections other than those from the HPM-1 structure are observed [9,10]. Their high crystallinity can be further supported by the N₂ BET surface

area data in Table 1. While all HPM-1 materials appear as heavily interpenetrated crystallites, in addition, there are no noticeable differences in the crystallite size (Fig. S2). As shown in the ²⁷Al MAS NMR spectra of their proton form (Fig. S3), on the other hand, extra framework Al species, as well as framework tetrahedral Al ones, were always observed. Since the spectra (not shown) of four as-made HPM-1 zeolites exhibit no resonance corresponding to octahedral Al, we can conclude that a non-negligible portion of Al has been extracted from the framework during the calcination and exchange steps, which is particularly true for H-HPM-1(210). Elemental analysis reveals that the Si/Al ratio in each zeolite is essentially the same as the value in its synthesis mixture (Table 1). The ammonia temperature-programmed desorption results show that the total area of desorption is well correlated with the bulk Si/Al ratio of all four H-HPM-1 zeolites prepared here (Fig. S4). The numbers of their framework Al atoms per unit cell have been determined by combining the concentration ratios of Brønsted acid sites to Lewis ones derived from pyridine IR measurements (Fig. S5) and the bulk Si/Al ratios were calculated from elemental analysis. These values, which are also listed in Table 1, will allow us to interpret the observed differences in the catalytic properties of H-HPM-1 zeolites based mainly on the effect of Brønsted acid site density, since skeletal isomerization generally proceeds over Brønsted acid sites [5].

Fig. 1 shows 1-butene conversion and isobutene selectivity and yield as a function of TOS in the 1-butene skeletal isomerization over four H-HPM-1 zeolites with different bulk Si/Al ratios (50–380) at 400 °C and at mild (7.5 h⁻¹ WHSV) and severe (24.0 h⁻¹ WHSV) flow rates, respectively. When WHSV was fixed to 7.5 h⁻¹, 1-butene conversion decreases notably with increasing Si/Al ratio in the zeolite, but remains almost unchanged over the period (12 h) of TOS studied here. A similar trend is also observable for the selectivity to isobutene, as well as for the selectivities to propene and pentenes (Table S2), the two major by-products of this reaction, although selectivity differences between two zeolites with higher Si/Al ratios, i.e., H-HPM-1(210) and H-HPM-1(380), are not significant. Among the four catalysts, as a result, H-HPM-1(50) and H-HPM-1(110) with lower Si/Al ratios gave the highest 1-butene yield (42%) at 12 h on stream. In contrast, the 1-butene yields of H-HPM-1(210) and H-HPM-1(380) at the same TOS were characterized to be 37 and 27%, respectively. Therefore, it is clear that the catalytic performance of high-silica (Si/Al ≥ 50) H-HPM-1 zeolites is greatly influenced when changes in the number of framework Al atoms (Brønsted acid sites) per unit cell are 0.5 or smaller (Table 1).

At a higher WHSV of 24.0 h⁻¹, essentially the same results can also be obtained in the beginning of the reaction. Unlike the case of a low WHSV (7.5 h⁻¹), however, the extent of changes in both 1-butene conversion and isobutene selectivity, and thus of those in isobutene yield, with TOS was found to significantly vary with the Si/Al ratio in zeolite catalysts. For example, H-HPM-1(50) gives

Table 1
Physicochemical properties of H-HPM-1 zeolites synthesized in this study.

Zeolite	Si/Al ratio ^a	Framework Al per unit cell	BET surface area ^b (m ² g ⁻¹)			Acidity ^c (μmol pyridine g ⁻¹)		
			Total	Microporous	External	Brønsted	Lewis	Total
H-HPM-1(50)	50 (50) [65]	0.91	630	540	90	99	30	129
H-HPM-1(110)	110 (110) [150]	0.40	550	480	70	37	15	52
H-HPM-1(210)	210 (200) [350]	0.17	610	510	100	17	12	29
H-HPM-1(380)	380 (400) [500]	0.12	530	450	80	10	3	13

^a Determined by elemental analysis. The values in parentheses and square brackets are Si/Al ratio in the synthesis mixture and framework Si/Al ratio in each zeolite calculated from the concentration ratio of Brønsted acid sites to Lewis ones obtained from pyridine IR measurements, respectively.

^b Calculated from N₂ adsorption data.

^c Determined from the intensities of the IR bands of retained pyridine at 1545 and 1455 cm⁻¹ after desorption at 200 °C after 2 h, respectively, by using the methods described elsewhere [12].

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