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LETTER TO THE EDITOR

On the Accessibility of Acid Sites in Ferrierite for Pyridine[1]

Ferrierite (FER) in its proton exchanged form is of commercial interest as a catalyst for the skeletal isomerization of alkenes (1, 2). Although the aspects of the catalytic properties of FER are well documented, the mechanistic aspects of the conversions and the importance of the concentration, strength, and accessibility of acid sites are still debated. In this context the question whether pyridine is a suitable probe molecule for quantitative analysis of acidity of FER was recently addressed in two publications (3, 4). In both of them, the accessibility of pyridine was reported to be geometrically constrained. Approximately 60% of the Brønsted acid sites were observed to be accessible to pyridine at 400 K, while increasing the temperature to 570 K improved the accessibility to 80% (3). Trombetta *et al.* (4) report, in contrast, that pyridine adsorbs mainly on the external SiOH groups of H-FER and leaves the bridging OH groups unaffected. This would suggest that pyridine is not able to enter the FER pores. While acknowledging that small differences in the crystallinity of FER may induce large changes in diffusivity, the complete inaccessibility for pyridine would require such a poor quality of sample (requiring that all pore entrances are blocked) that it is hardly conceivable.

Revisiting the problem of accessibility of pyridine in FER, adsorption of pyridine on H-FER (ammonia sorption studies using gravimetry for this sample indicated concentration of acid sites to be 1.95 mmol/g) at various partial pressures and temperatures was studied. The experiments were carried out using a vacuum infrared cell placed in a BRUKER IFS88 IR spectrometer. NH_4-FER (TOSOH, LOT NO. 1277, Si/Al 9, Na $< 0.01\%$) was pressed into self-supporting wafers of approximately 5 mg and activated *in situ* at 673 K. Detailed information on the experimental procedures can be found in Ref. (5). For sorption measurements, the partial pressure of pyridine was increased stepwise from 10^{-2} to 10^{-1} mbar. The integrated intensities of the bands at 3741 cm^{-1} (SiOH groups), 3607 cm^{-1} (SiOHAl groups), 1541 cm^{-1} (pyridinium ions), and 1452 cm^{-1} (pyridine coordinated to Al^{3+}) were used to monitor the quantitative changes of hydroxy groups and the sorbate. Upon admission of pyridine at 298 K and a constant partial pressure of 10^{-2} mbar, the intensity of the band at 3607 cm^{-1} decreased and bands of pyridinium ions increased. Additionally, also the intensity of the band at 3741 cm^{-1} decreased slightly in parallel to the increase of bands of hydrogen bonded pyridine (3300–2800 cm^{-1}). Note that it was not possible to reach a constant coverage at 10^{-2} mbar pyridine pressure despite the extended equilibration time (21 h). Neither the integrated intensities of the free bridging OH groups nor the band at 1541 cm^{-1} (characteristic for pyridinium ions) reached constant values within this period. The integral intensity of the band at 3607 cm^{-1} decreased by 45%, indicating the fraction of Brønsted acid sites interacting. With respect to the controversial results of Ref. (4), it is speculated that the time permitted for equilibration was not sufficient to allow a substantial fraction of pyridine to enter the FER pores. At 573 K and a partial pressure of 10^{-2} mbar equilibrium was not readily reached (see Figs. 1 and 2). After 42 h 78% of the Brønsted acid sites interacted with pyridine as compared with the 45% observed at room temperature. In order to probe whether or not the limited coverage is related to constraints in the accessibility of the Brønsted acid hydroxy groups or to the slow transport of pyridine in FER, the partial pressure was increased to 10^{-1} mbar pyridine at 573 K. Only then did the band of the SiOHAl groups at 3607 cm^{-1} disappear completely (Fig. 2). Figure 3 shows the correlation between the decrease of the OH band and the intensity of the band at 1541 cm^{-1}. At low coverages the 1 : 1 stoichiometry is not reached which is attributed to a small deviation from linearity of the absorption coefficients. Wichterlová *et al.* (3) report 80% coverage at this temperature. It should be noted that the intensity of the bridging hydroxy groups reached a steady level while the band of pyridinium ions continuously increased.

The results indicate that all Brønsted acid sites of FER are accessible for pyridine and, thus, pyridine is unsuitable for probing the acid sites on the exterior of FER crystals. Larger bases, such as di- and trimethylpyridines, are needed for that task (7).

The uptake rates deduced from the slopes of the integral intensities in Fig. 2 show an interesting trend giving indirect evidence for the distribution of acid sites in FER. At 10^{-2} mbar approximately 70% of the Brønsted acid sites were covered within the first 800 min (approximately 46%

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[1] Comments on “FT-IR Studies on Light Olefin Skeletal Isomerization Catalysis. III. Surface Acidity and Activity of Armorphous and Crystalline Catalysts Belonging to the SiO_2–Al_2O_3 System” by M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani, and R. J. Willey, *J. Catal.* **179**, 581 (1998).

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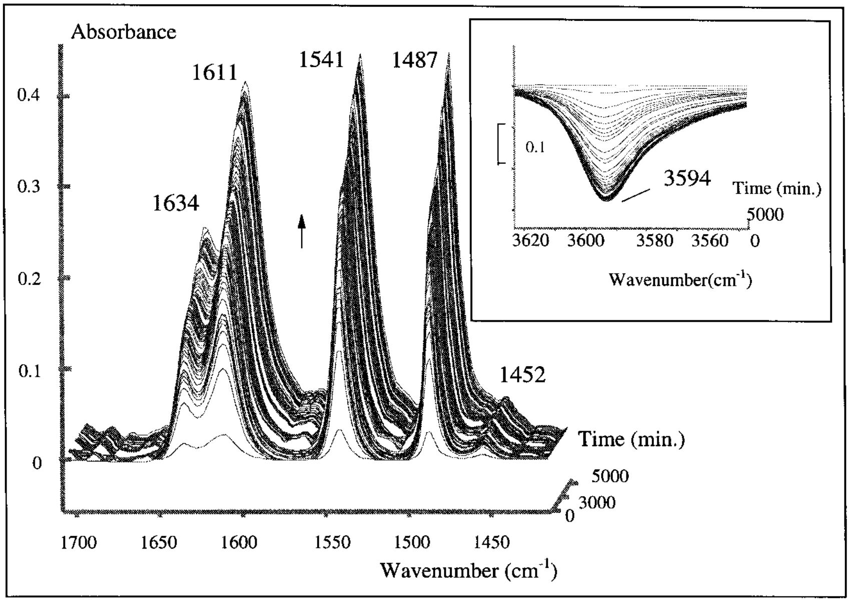

FIG. 1. IR spectra of pyridine on FER at 573 K and 10^{-2} and 10^{-1} mbar. Inset shows the consumption of the bridging hydroxy groups.

in the first 60 min), while it took about 1550 additional min to reach a coverage of 78%. For the remaining 22% of the Brønsted acid sites, approximately 2300 min were required (at 10^{-1} mbar pyridine partial pressure). This suggests in accordance with the results of Wichterlová *et al.* (3) a significantly higher resistance to cover 20% of the Brønsted acid sites. Based on MAS NMR measurements and alkali ion exchange the authors concluded that this fraction of Brønsted acid sites is primarily accessible *via* the 8-membered ring channels (8). Conceptually, it is straightforward to see that the transport in these is much slower than in the 10-membered ring channels. However, the experiments presented for 10^{-1} mbar pyridine at 573 K show clearly that pyridine is able to reach all of Brønsted acid sites. Results from molecular modeling are in line with this, indicating that pyridine can access the space in the channels confined by the 8-membered windows, but that a substantial barrier exists for pyridine to pass this window. This suggests that the combination of high temperature (increased lattice flexibility and kinetic energy of the sorbate) and pyridine partial pressure are indispensable to avoid excessive periods to reach full equilibration.

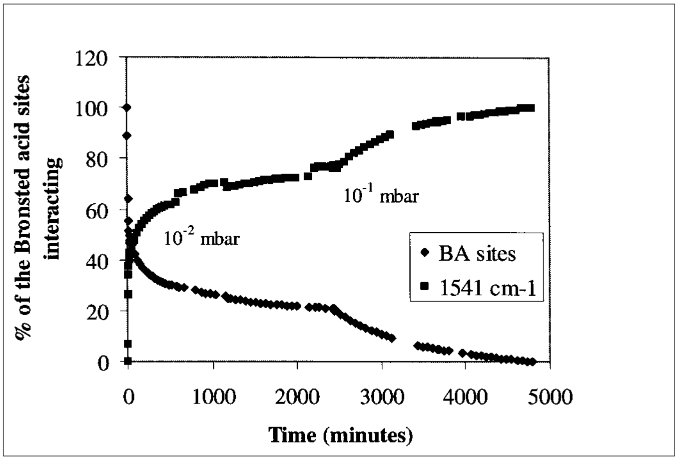

FIG. 2. Uptake profiles for pyridine on FER at 573 K and 10^{-2} and 10^{-1} mbar.

While this establishes that the dimensions of pyridine are small enough to access the interconnected channel system, it does not imply that Brønsted acid sites in the smaller pores contribute to the catalytic activity for sterically demanding reactions such as hydrocarbon skeletal isomerization. This is in line with reports that H-FER behaves

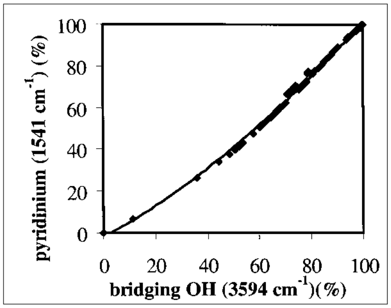

FIG. 3. Increase of normalized intensity for pyridinium ion (1541 cm^{-1}) versus decrease of bridging hydroxy groups (3594 cm^{-1}), 573 K, 10^{-2} and 10^{-1} mbar.

for these reactions (e.g., *n*-butene skeletal isomerization) like a molecular sieve with monodimensional pore structure (9).

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REFERENCES

1. Mooiweer, H. H., de Jong, K. P., Kraushaar-Czarnetzki, B., Stork, W. H. J., and Krutzen, B. C. H., *Stud. Surf. Sci. Catal.* **84**, 2327 (1996).
2. Houzvicka, J., and Ponec, V., *Catal. Rev.-Sci. Eng.* **39**, 319 (1997).
3. Wichterlová, B., Tvaruzkova, Z., Sobalik, Z., and Sarv, P., *Zeolites* **24**, 223 (1998).
4. Trombetta, M., Busca, G., Rossini, S., Piccoli, V., Cornaro, U., Guercio, A., Catani, R., and Willey, R. J., *J. Catal.* **179**, 581 (1998).
5. Eder, F., and Lercher, J. A., *J. Phys. Chem. B* **101**, 1273 (1997).
6. Lercher, J. A., and Rumplmayer, G., *Z. Phys. Chem.* N.F. **146**, 113 (1985).
7. Pieterse, J. A. Z., Veefkind-Reyes, S., Seshan, K., and Lercher, J. A., submitted for publication.
8. Sarv, P., Wichterlová, B., and Cejka, J., *J. Phys. Chem. B* **102**, 1372 (1998).
9. Byggningsbacka, R., Kumar, N., and Lindfors, L. E., *J. Catal.* **178**, 611 (1998).

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