Journal of Catalysis **187,** 521–523 (1999)
Article ID jcat.1999.2630, available online at http://www.idealibrary.com on IDEAL®

LETTER TO THE EDITOR

On the Characterization of the External Acid Sites of Ferrierite and Other Zeolites: A Reply to Pieterse *et al.*

In a recent paper (1) we addressed the characterization of the acidity of eight SiO_2–Al_2O_3 catalytic materials, some of which were amorphous, some crystalline, including the zeolites FER (ferrierite) and ZSM5 in their protonic forms. We used the IR spectra of adsorbed acetonitrile and pyridine, applied as basic probes, to compare them with their behavior in the conversion of 1-butene.

Incidentally, we found that under our experimental conditions (room temperature, 0.5 Torr and a few minutes of contact with the adsorbate vapor) pyridine did not appear to disturb the internal bridging OHs of FER. In contrast, under the same conditions, pyridine entered the ZSM5 cavities immediately and reacted with its Brønsted acidic internal bridging OHs. Figure 10 in Ref. (1) clearly shows that, while the OH stretching band of the internal OHs of FER at 3600 cm^{-1} was undisturbed, the bands of coordinated pyridine and of pyridinium ions were present. Under the same conditions, the sharp band at 3746 cm^{-1}, usually assigned to silanol groups located at the external surface of the protonic zeolites, strongly decreased in intensity. The subtraction spectrum, also reported in Fig. 10 of Ref. (1), showed clearly that, under those conditions, the only negative band was that at 3746 cm^{-1}. This was taken as evidence that some of the external terminal silanols of FER were able to protonate pyridine, thus providing evidence of significant Brønsted acidity. Therefore, the failure of pyridine to enter the FER cavities under those conditions is interesting, because it enabled us to characterize the external surface of this zeolite. Furthermore, we concluded that Lewis acid sites are also present at the external surface of FER.

Almost simultaneously, Wichterlová *et al.* (2) published a paper showing that, at 400 K, pyridine is still hindered considerably from entering the FER cavities.

Pieterse *et al.* (3) confirm these data. Their data show that, even at 573 K, the diffusion of pyridine into the FER pores is very slow. These authors confirm that, at room temperature, it takes a very long time before a partial decrease in the bands of the internal OHs of FER is observed. Thus, both Wichterlová *et al.* (2) and Pieterse *et al.* (3) showed that pyridine can indeed access the internal sites of FER but confirmed that at room temperature and short contact time access is substantially hindered. Pieterse *et al.* (3) show that the amount of pyridine entering the ferrierite pores increases with increasing contact time, temperature, and pyridine partial pressure, confirming the well-known effect of time and temperature on pore diffusion.

On the other hand, we disagree with the statement of Pieterse *et al.* (3) that “pyridine is unsuitable for probing the acid sites on the exterior of FER crystals.” The analysis of our and their data shows that it is because pyridine diffusion into the FER pores at room temperature is slow that a “time resolution” effect occurs that allows the perturbation of the external sites (immediately interacting with the adsorbates) well before the internal sites are detectably perturbed.

We were (and are) interested in continuing our investigation of the nature and behavior of the external sites of zeolite crystals rather than the diffusion of pyridine. More evidence was found recently that the external sites of zeolites can participate in acid catalysis, in agreement with the above conclusions obtained in our cited paper (1) as resulting from the pyridine adsorption experiments. These conclusions have been fully confirmed in more recent results, part of which already appeared in a paper (4), where pivalonitrile was used as a probe. Our experiments were conducted with several different FER samples. Figure 1a shows the spectrum of a sample (kindly provided by B. Wichterlová and probably the same described in (2)), whose Si/Al ratio is near 9. The spectrum in the OH region is typical of a good FER zeolite with a sharp OH stretching band at 3746 cm^{-1} (terminal silanols thought to be external) and a broader band at 3599 cm^{-1} (bridging hydroxy groups thought to be internal). Figure 1 presents the subtraction spectra, obtained after a few minutes contact with pivalonitrile and acetonitrile vapors, and their comparison. After contact with pivalonitrile (Fig. 1b), the band at 3746 cm^{-1} is strong and negative, showing that the terminal OHs are perturbed. Correspondingly a strong, broad, positive band is observed at 3440 cm^{-1}, due to the fact that the external OHs are H-bonded with adsorbed pivalonitrile molecules. In contrast, a very weak negative band is found in the region of 3600 cm^{-1} with an extremely weak maximum near 3610 cm^{-1}. This means that pivalonitrile, too, does not enter the pores of FER under our experimental conditions (room temperature, short contact time). The OH stretching of bridging OHs is shifted upward by a few cm^{-1}, due to a perturbation of the framework. This becomes clear when

0021-9517/99 $30.00

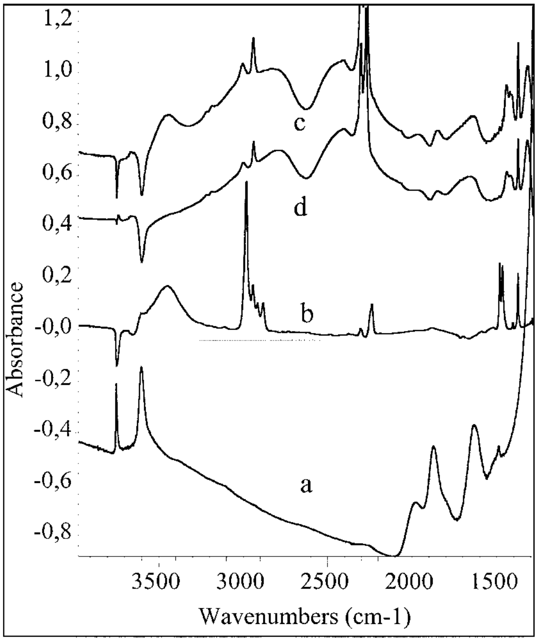


FIG. 1. FT-IR spectrum of FER activated by outgassing at 723 K (a), and subtraction FT-IR spectra relative to adsorption of pivalonitrile (b) and acetonitrile (c) on FER at room temperature (3 min contact, 0.5 Torr) and after outgassing at room temperature (d).

the unsubtracted spectrum is considered (see also below). A careful analysis of the subtraction spectrum shows that a broad component near 3000 cm^{-1} is probably present as well; it can be ascribed (as in the cases of amorphous (1) and mesoporous (4) silica–aluminas) to a fraction of the terminal silanols which are more strongly acidic. They are probably the ones that are able to protonate pyridine. The analysis of the CN stretching band shows a doublet, one component of which is observed near 2300 cm^{-1}, which corresponds to species bonded to Lewis sites. Thus, pivalonitrile adsorption also enabled us to test the external surface of FER and fully confirms the conclusions we proposed on the basis of pyridine adsorption experiments in (1).

The results of pivalonitrile adsorption on FER is reinforced by a comparison with the results of acetonitrile adsorption experiments. Acetonitrile immediately penetrates the FER pores and interacts with both internal and external sites. This is evident from the subtraction spectrum of Fig. 1c, where both bands at 3746 and 3599 cm^{-1} are clearly negative bands; they actually both totally disappeared in the unsubtracted spectrum. As has been reported for acetonitrile adsorption on ZSM5 (1, 5), the interaction of acetonitrile with the internal OHs of FER gives rise to the so-called ABC spectra, with strong components at 2800, 2450, and near 1600 cm^{-1}, due to a quasi-symmetrical and very strong H-bonding. The interaction of acetonitrile with the external silanols gives rise mainly to a band near 3400 cm^{-1} due to much weaker H-bonding. This is proven by what occurs upon outgassing (Fig. 1d): the negative band at 3746 cm^{-1} and the positive band at 3450 cm^{-1} disappear, while the negative band at 3599 cm^{-1} and the positive ABC bands are not affected. The features of acetonitrile adsorbed on the external surface are similar to those observed upon pivalonitrile adsorption; they cannot be analyzed in detail because they are superimposed on the spectrum of acetonitrile adsorbed on the internal OHs.

These data strongly support the evidence (already shown in our pyridine adsorption experiments but not emphasized in our discussion) that bridging sites (i.e., those characterized by the band at ca. 3600 cm^{-1}) are not detectable at the external surface of FER and are, consequently, present only in the internal surface. Conversely, the terminal silanols are almost exclusively located at the external surface. It is also confirmed that some of the external terminal silanols are significantly Brønsted acidic and that Lewis sites are also present at the external surface of FER.

Recently, we extended our studies to the external sites of other zeolites, such as ZSM5 and β. Under our experimental conditions (again short contact times and room temperature) pivalonitrile and orthoxylene did not enter the cavities of the ZSM5 sample (Si/Al ratio 23, from Engelhard) (6), thus enabling the characterization of the sites located at the external particle surface. Pivalonitrile adsorption did not perturb the internal bridging OHs of ZSM5 (3618 cm^{-1}) and caused only a very small upward shift, as for FER. Conversely, it caused the sharp band at 3745 cm^{-1} to disappear and produced a broader band near 3440 cm^{-1} (Fig. 2b). Interestingly, another component located near 3730 cm^{-1} was not perturbed either. This supports the assignment of this component to terminal silanols located at the internal surface of the zeolite in defect sites. The analysis of the CN stretchings suggests that two types of Lewis sites exist at the external surface of ZSM5 zeolite. Note, however, that our sample contains small amounts of extraframework alumina, and it seems likely that this material provides surface Lewis sites. Thus, under our conditions pivalonitrile does not enter the cavities of our commercial ZSM5 sample either. In contrast, it enters the cavities of β zeolite, whose bridging OHs give rise with pivalonitrile to the ABC type spectrum, thus providing evidence of a very strong H-bonding (7).

The data obtained using pivalonitrile and several other probes show that bridging OHs of ZSM5 (3618 cm^{-1}) are exclusively located at the internal surface, while most of the terminal silanols are located at the external surface. We also found that, on our ZSM5 zeolite sample, some of the external terminal silanols have a clearly enhanced Brønsted acidity with respect "normal" silanols of silica.

From these studies, we propose that bridging silanols are quite unstable structures that are formed only when a rigid structure (like that of the internal cavities of protonic small-pore zeolites) hinders their opening. On "elastic" or flat

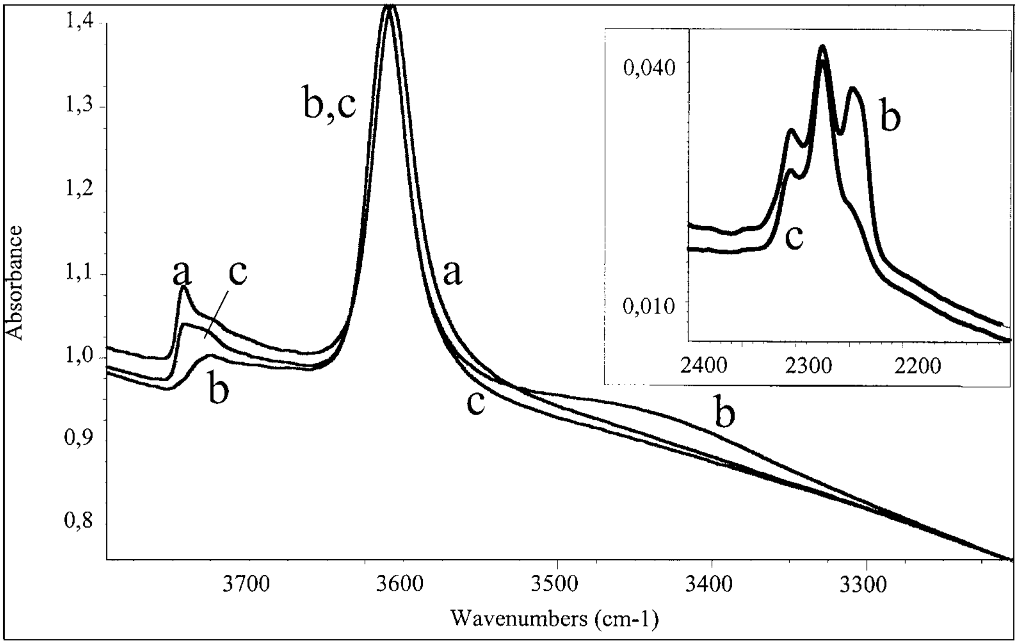
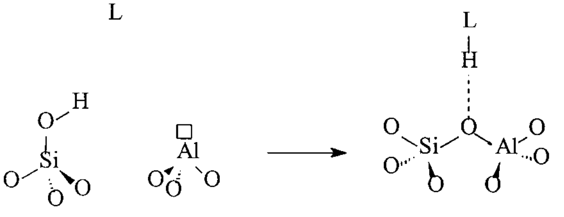


FIG. 2. FT-IR spectrum of ZSM5 activated by outgassing at 823 K (a) in contact with pivalonitrile vapor (3 min contact, 0.5 Torr) (b) and after outgassing at room temperature (c). In the insert: Subtraction spectra in the CN stretching region.

surfaces (like those of amorphous silica-aluminas (1, 4) or the external zeolite surfaces) they tend to open to terminal silanols. We propose that the location of a coordinatively unsaturated Al cation near these silanols allows the bridging of the oxygen atom only when the proton is transferred to a base (the oxygen becomes basic). This explains the enhanced acidity of these terminal silanols with respect to those of silicas, where the conjugated base of the silanol acid site cannot be stabilized by bridging (see Scheme 1).

In conclusion, we agree with Pieterse *et al.* (3) that the amount of pyridine (possibly also of pivalonitrile) accessing the FER cavities depends on contact time and temperature. On the other hand, we confirm that, by using short contact times and room temperature experiments, pyridine (and pivalonitrile) is a suitable probe for the external sites of FER, just as ortho-xylene and pivalonitrile are good probes for the characterization of the external sites of ZSM5. In this way, new data on the external surface of protonic zeolites can be obtained.



SCHEME 1. Proposed structure of the terminal Brønsted acidic OHs of amorphous and mesoporous silica-alumina and of the external surface of FER and HZSMS. (L is a base).

REFERENCES

1. Trombetta, M., Busca, G., Rossini, S., Piccoli, V., Cornaro, U., Guercio, A., Catani, R., and Willey, R. J., *J. Catal.* **179**, 581 (1998).
2. Wichterlová, B., Tvaruzkova, Z., Sobalik, Z., and Sarv, P., *Zeolites* **24**, 223 (1998).
3. Pieterse, J. A. Z., Veefkind-Reyes, S., Seshan, K., Domokos, L., and Lercher, J. A., *J. Catal.* **187**, 518–520 (1999).
4. Trombetta, M., Busca, G., Lenarda, M., Storaro, L., and Pavan, M., *Appl. Catal. A Gen.* **182**, 225 (1999).
5. Pelmenschikov, A. G., and van Santen, R. A., *J. Phys. Chem.* **97**, 10678 (1993); Pelmenschikov, A. G., van Wolput, G. H. M. C., Jänchen, J., and van Santen, R. A., *J. Phys. Chem.* **99**, 3612 (1995).
6. Trombetta, M., Armaroli, T., Gutierrez-Alejandre, A., Ramirez Solis, J., and Busca, G., in press.
7. Trombetta, M., Busca, G., Lenarda, M., and Storaro, L., manuscript in preparation.

Marcella Trombetta
Guido Busca

Dipartimento di Ingegneria Chimica e di Processo
"G.B. Bonino" Università
P. le Kennedy
I-16129 Genoa, Italy

Received June 28, 1999; revised July 14, 1999; accepted July 14, 1999