FT-IR STUDIES OF INTERNAL, EXTERNAL AND EXTRAFRAMEWORK PROTONIC AND CATIONIC SITES OF H- AND Co-EXCHANGED FER, MFI AND MOR TYPE ZEOLITE MATERIALS

Maria Bevilacqua[1], Tania Montanari[1], Carlo Resini[1], Aida Gutiérrez-Alejandre[2], Jorge Ramírez[2] and Guido Busca[1]
[1] DICheP, Università di Genova, P.le J.F.Kennedy, I-16149, Genova, Italy.
[2] UNICAT, Depto. de Ingeniería Química, Facultad de Química, UNAM, Cd. Universitaria 04510 México D.F. (Mexico).

Introduction

Protonic zeolites such as H-FER, H-ZSM5 and H-MOR find industrial application as acid catalysts in several reactions such as butene skeletal isomerization, xylene isomerization and toluene disproportionation. The activity of these materials is associated to the presence of the bridging Si-(OH)-Al protonic sites supposed to be located in the internal cavity of the zeolites. Additionally, shape selectivity effects are due to molecular sieving due to the cavities.
Co-exchanged zeolites have been found to be active in deNOx technology, particularly in CH_4-SCR and in hydrocarbons total and partial oxidation.
The molecular sieving effect typical of zeolite materials is at the base of their use as selective adsorbants and shape-selective catalysts. The main factor allowing molecular sieving and, consequently, shape selectivity is generally considered to be exclusively steric, i.e. only the molecules having a critical diameter lower than the channel diameter are allowed to enter the cavity. However, active sites also exist at the external surface of zeolite crystals. These sites are sometimes considered to be responsible for unwanted non-selective catalysis. Additionally, extraframework sites are frequently present and can also have a role either as active site or as material hindering the molecular diffusion into the cavities.
In this communication we will summarize recent data obtained, through FT-IR spectroscpy, on the characterization and the distinction of internal, external and extraframework protonic and cationic sites in H- and Co-exchanged MFI [1, 2, 3, 4, 5], FER [6, 7] and MOR type zeolite structures. The study involves in situ adsorption of differently hindered nitriles (acetonitrile, propionitrile isobutyrronitrile pivalonitrile and 2,2-diphenylpropionitrile).

Results and Discussion

FT-IR spectra were recorded with a Nicolet Nexus instrument with a resolution of 4 cm^{-1} using pressed disks of pure zeolite powders, activated by outgassing at 773 K into the IR cell. A conventional gas manipulation / outgassing ramp connected to the IR cell was used. The adsorption procedure involves contact of the activated sample disk with gases and vapors at increasing pressures and outgassing in steps at r.t. or increasing temperatures.
The data show that the strong Brønsted sites of H-FER and H-MFI are located only into the cavities. Lewis sites are observed on H-MFI, both on the inner and on the

outer surface, and on H-FER on the outer surface only. Both molecular sieving and chemical phenomena govern the access to the cavities. In particular, while most *tert*-butyl group containing molecule is not allowed to enter the cavities in our experimental conditions. Extraframework material in H-MFI seems to be in part dispersed in the internal cavity surface and in part blocks the channels.
In H-MOR sample the adsorption of more and more hindered nitriles allows to evidence the different distribution of the protonic sites between the main channels, the side pokets and the smaller channels, and those allocated on the external surface.
The adsorption of the nitriles probe molecules on Co-exchanged samples enables us to identify the presence of cationic sites both on internal and external zeolitic surfaces and to evaluate their accessibility.

References

1. M. Trombetta and G. Busca, *J. Catal*., 187 (1999) 521.
2. M. Trombetta, T.Armaroli, A.Gutiérrez-Alejandre, J.Ramírez and G.Busca, *Appl. Catal. A General*, 192 (2000) 125.
3. M. Trombetta, A. Gutiérrez-Alejandre, J. Ramírez and G. Busca, *Appl. Catal. A General*, 198 (2000) 81.
4. T. Armaroli, M. Trombetta, A. Gutiérrez Alejandre, J. Ramirez Solis and G. Busca, *Phys. Chem. Chem. Phys*., 2 (2000) 3341.
5. T. Armaroli, M. Bevilacqua, M. Trombetta, F. Milella, A. Gutièrrez Alejandre, J. Ramirez, B. Notari, R.J. Willey and G. Busca, *Appl. Catal. A General*, 216, (2001) 59.
6. M. Trombetta, G. Busca, M.Lenarda, L. Storaro and M. Pavan, *Appl. Catal. A General*, 182 (1999) 225.
7. M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani and R. J. Willey, *J.Catal*., 179 (1998) 581.