Structural Study of two EUO-type zeolites by neutron diffraction

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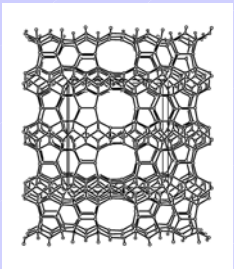
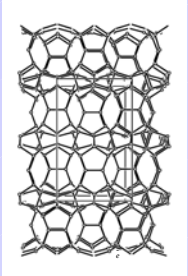
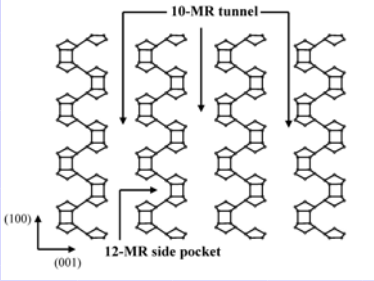
Abstract

Souverijns et al. [1] found different molecular selectivity properties in two EUO-types zeolites that are crystallized in presence of two organic templates: hexamethonium (HM) and dibenzylammonium ions (DBDMA). They suggested that this dissimilarity in the molecular shape selectivity is originated from a different distribution of the active sites over the side pockets and the main channels of the EUO zeolites. We have studied the structure of both zeolites by neutron diffraction to investigate their thesis. The structural comparison of the two EUO-type zeolites agrees with the model proposed by Souverijns et al. [1].





View of the EUO framework along the 10-MR channels and along the pockets sides (right and left figure respectively). The oxygen atoms have been omitted for clarity, the silicon atoms are represented as circles.

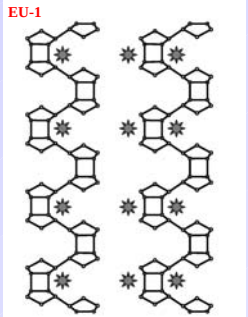


Section through the EUO framework structure perpendicular to the (010) direction showing the 10-MR tunnel system with 12-MR side pockets.

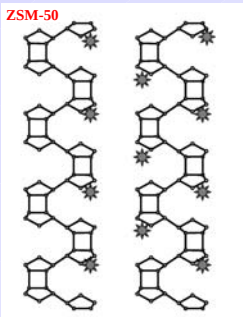
Acid sites distribution in the framework

Souverijns et al. [1] explain the disparity in shape selectivity by a different location of the framework aluminum atoms in the two materials. This hypothesis is supported by molecular packing arguments based on energy minimization of the SDA in the zeolite pores. They propose that for ZSM-50 the active-sites are located in the 12-MR side lobes (the associated aluminum T-sites are Si6 and Si7), whereas for EU-1, the active-sites are located in the 10-MR channels and at the bottom of the side pockets. Therefore, the proposed aluminum T-sites for EU-1 are Si1, that is located at the bottom of the side pockets, Si9 and Si10, that are associated to the 10-MR channel section that faces the center of the side pockets, and Si6, Si7 and Si8, that conform the 10-MRs (the atomic sites "*Sin*", where n=1,2, …10 are shown in the figure bellow).

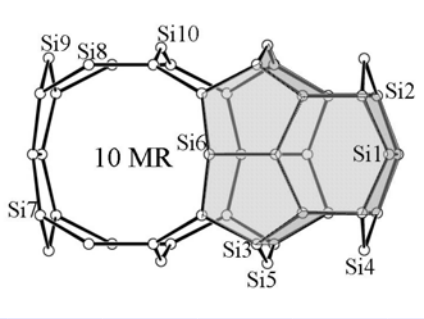
These two figures bellow are a representation of the models suggested by Souverijns et a. [1]



Location of the acid sites in EU-1 (Si1, Si9 and Si10 and Si6, Si7 and Si8).



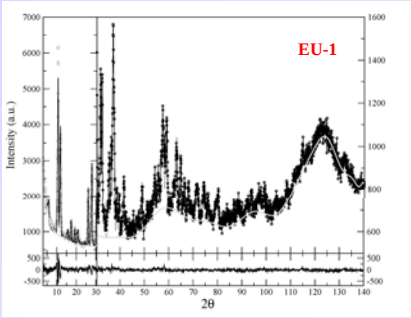
Location of the acid sites in ZSM50 (Si6 and SI7) .

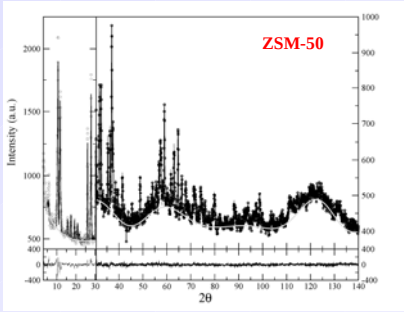


Section of the EUO framework structure perpendicular to the (001) direction showing one 10-MR pore system with a12-MR site pocket

Neutron diffraction Experiments

The refined structure for the all silica material describes very well the powder diffraction patterns of the EU-1 and ZSM-50 zeolites (see figures bellow).

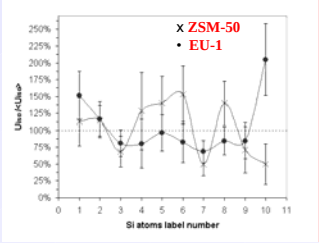




Calculated and observed diffraction patterns (solid line and open circles respectively)

Conclusions

- Upon refining a displacement parameter for *each* of the silicon atoms, the deviation of the displacement parameters from the average value (calculated over all the silicon atoms) has been interpreted as disorder originated by the presence of aluminum in the framework. The result of the study shows that the most probable sites for EU-1 belong to the sites proposed by Souverijns et al. [1], for ZSM-50 the results are not so unambiguous since the amount of information about the aluminum content in the data is three times smaller, however the study agrees for the most part, since we have found that the most probable site is described in the model.



Refined displacement parameters for each of the T-sites in EU-1 and ZSM-50.

$$U_{iso} \pm \sigma(U_{iso}) > \langle U_{iso} \rangle$$

ZSM-50	EU-1
Si6 and Si8	Si10 and Si1

- The study of the deformation of the EU-1 and ZSM-50 structures from the ideal all silica structure shows that, while the deformation along the **a** and **b** directions is of the same order and magnitude for the two zeolites, the deformation along the **c** direction is from two to three times bigger for the EU-1 sample.

	ZSM-50			EU-1		
	a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
Neutron refinement(RT)	13.6861(8)	22.1838(17)	20.0662(14)	13.709(23)	22.218(8)	20.133(5)
GULP [2]	13.7300	22.5200	20.0110	13.7300	22.5200	20.0110
Briscoe et al. [3]				13.6950	22.3260	20.1780
	Components of the deformation tensor					
	e_{11}	e_{22}	e_{33}	e_{11}	e_{22}	e_{33}
Neutron refinement(RT)	-0.003	-0.015	0.003	-0.002	-0.013	0.006
EU-1, Briscoe et al. [3]				-0.003	-0.009	0.008

- The comparison between the atomic positions of the refined structures supports the model for the arrangement of the aluminum sites in the framework of the EU-1 sample.

References

[1] W. Souverijns, L. Rombouts, J.A. Martens and P.A. Jacobs, *Microporous Materials*, 4 (1995) 123.
[2] GULP - a computer program for the symmetry adapted simulation of solids, J.D. Gale, *JCS Faraday Trans.*, 93 (1997) 629.
[3] N.A. Briscoe, D.W. Johnson, M.D. Shannon, G.T. Kokotailo and L.B. McCusker, *Zeolites*, 8 (1988) 74.

Acknowledgements

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