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BOOK OF FULL ABSTRACTS

Jointly Meeting of the
Italian Zeolite Association (AIZ)
Czech-Italian-Spanish (CIS) Conference
Italian Interdivisional Catalysis Group (GIC)

XVI National Congress of Zeolites Science and Technology

8th Czech-Italian Spanish Conference on Molecular Sieves and Catalysis

XXI National Congress of Catalysis

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ENTRAPPING OF IBUPROFEN AND ATENOLOL WITHIN Y ZEOLITE: A NEUTRON POWDER CHARACTERIZATION AFTER DRUGS ADSORPTION

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Pharmaceuticals and personal care products are considered to be among the most common organic wastewater contaminants. Due to the widespread use and their slow natural degradation, the complete removal of these compounds from water is still a challenging task. Studies on conventional biological drinking-water treatment processes, such as biofiltration, have shown their largely ineffectiveness in pharmaceuticals removing.[1] Instead, due to their high selectivity, rapid kinetics, reduced interference from salt and humic substances,[2] as well as the excellent resistance to chemical, biological, mechanical and thermal stress, zeolites have proved their effectiveness when used as sorbent materials. Furthermore, synthetic zeolites can be regenerated through thermal treatment without loss of performances, thus giving more than a few advantages in terms of economy and environmental friendliness.[3-4] In this work, the removal of two different pharmaceutical products (*i.e.*, ibuprofen and atenolol) from aqueous solution by organophilic zeolite Y (*i.e.*, Si/Al ratio=200) was investigated. Ibuprofen (*ibu*, $C_{13}H_{18}O_2$) is a nonsteroidal anti-inflammatory drug with anti-inflammatory, analgesic, and antipyretic effects; atenolol (*atn*, $C_{14}H_{22}N_2O_3$) is a cardioselective beta-blocker that is widely used in the treatment of hypertension and angina pectoris. Both compounds are considered ubiquitous contaminants of waters and due to their chemical structure and molecular dimensions, the removal through conventional methods is not ensured. Zeolite Y is characterized by a pore structure that allows to very large molecules, like pharmaceuticals, the access within the so-called *supercage*. Based on this, it has been decided to study the Y zeolite sorption capacity toward ibuprofen and atenolol drugs by using neutron powder diffraction. Specifically, the aim was to determine 1) amount and position of adsorbed-drugs, 2) host-guest interactions of drugs molecules within the zeolite framework. Both drug-loaded zeolites were obtained ion exchanging the as-synthesized form with deuterated ibuprofen and atenolol in aqueous solution for 140 h at room temperature and then washing with D_2O. Diffraction data were collected at the D2B beamline (ILL; Grenoble) at low temperature (4 K). Rietveld refinements were performed using the GSAS software,[5] in the *Fd*-3 space group. The extra-framework sites were firstly located by difference Fourier maps and then optimized using EXPO2014(ref. 6) in order to obtain reasonable bond lengths and angles and calculate the H atoms position. Results obtained from cell parameters analysis confirmed the presence of ibuprofen and atenolol within the *supercage* in both drug-zeolite systems. Indeed, compared to the bare zeolite lattice, the cell volume determined after drug adsorption is strongly increased (*i.e.*, bare-Y= 24.291(1), *ibu*-Y=24.323(1), *atn*-Y=24.337(1)). The Difference Fourier maps analysis allowed to

locate both molecules within the supercage and, in both cases, it was observed that drugs can statistically assume six different orientations. No co-adsorbed water molecules were detected. The refinement of extraframework occupancies revealed that Y zeolite was able to adsorb about 11.55 % of ibuprofen and 33.68 % of atenolol. In both cases, direct bond interaction between extraframework molecules and framework oxygen atoms were highlighted. Specifically, ibuprofen is directly bound to the O4 and O1 framework oxygens, whereas the atenolol only interacts with the O1. Finally, the analysis of structural parameters allowed to calculate ellipticity (ε) and Crystallographic Free Area (CFA) for both systems. The CFA calculated after molecules adsorption is higher than the unloaded zeolite (i.*e.*, bare-Y=46.26, *ibu*-Y=56.58, *atn*-Y=48.16), while the ellipticity remains unchanged in the *ibu*-Y systems and increases in the *atn*-Y one. These structural results confirm the high flexibility of Y zeolite framework, which adapts its pores geometry and shape to host guest molecules without undergoing to non-reversible structural distortions. All the results gained prove the high efficiency of the organophilic Y zeolite in the adsorption of pharmaceutical compounds characterized by high molecular dimensions, thus suggesting a possible use as sorbent material in water remediation processes.

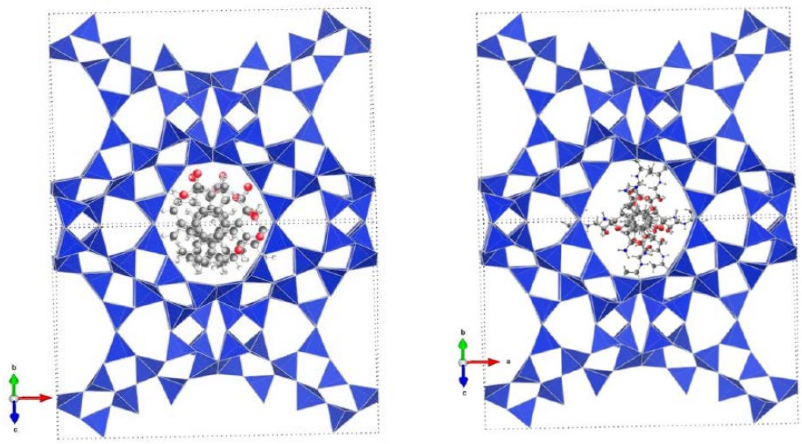

Figure 1. Molecules of ibuprofen (left) and atenolol (right) localized within the Y zeolite *supercage.*

References:

[1]Ternes, T.A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H.J.; Haist-Gulde, B.; Preuss, G.; Wilme, U.; Zulei-Seibert, N. Environ. Sci. Technol. **2002**, 36, 3855.

[2]Braschi, I.; Martucci, A.; Blasioli, S.; Mzini, L.L.; Ciavatta, C.; Cossi, M. Chem. **2016**,155, 444.

[3]Rodeghero, E.; Martucci, A.; Cruciani, G.; Bagatin, R.; Sarti, E.; Bosi, V.; Pasti, L. Catal. Today. **2016**, 227, 118.

[4]Martucci, A.; Rodeghero, E.; Pasti, L.; Bosi, V.; Cruciani, G. Micro. Meso. Mater. **2015**, 215, 175.

[5]Larson, A.C.; Von Dreele, R.B. Los Alamos National Laboratory Report, 86.

[6]Altomare, A.; Cuocci, G.; Giacovazzo C.; Moliterni, A.; Rizzi, R.; Corriero N.; Falcicchio, A. J. Appl. Crystallogr. **2013**, 46, 1231.