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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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TEMPLATE-REMOVAL-ASSOCIATED STRUCTURAL MODIFICATION OF ZSM-5 ZEOLITE WITH DIFFERENT Si/Al RATIO BY *IN SITU* SYNCHROTRON POWDER DIFFRACTION

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The study of the thermal behaviour of zeolites is of fundamental importance since their most relevant properties, such as catalytic activity, adsorption capacity, and molecular sieving can be exploited when zeolites are in their dehydrated/calcined form. Moreover, zeolites, and in particular the one in their acid form, are widely used in catalysis and these kind of processes, such as hydrocarbon cracking, require quite high temperatures. The zeolite thermal behaviour is influenced by several intrinsic chemical and structural factors (i.e. framework topology, Si/Al ratio, charge-compensating cations, coordination of bare cations, crystal size, heating rate, etc.).[1-3] The interplay of the factors listed above renders difficult the thermal stability prediction of any given zeolite. Ideally, the effect on the thermal stability of varying the framework Si/Al ratio is best evaluated in a series of isostructural zeolites having different Si/Al ratio. In particular template burning (or calcination) of the as-synthesized material is a key step in their activation for its application as a catalyst. Among them the ZSM-5 (MFI topology) is one of the most famous and largely used as solid acid because of its unique 3D framework structure with a dual-interconnecting channel system showing important catalysts application in the industrial and fine chemistry fields. Actually, its importance is growing also in different areas, such as biomedical, pharmaceutical fields and as sorbent material for the amino acid separation process. For this reason, the knowledge of its thermal behaviour, the kinetics of the water and template desorption process and consequent structural modifications is essential.

In this work, the step by step thermal dehydration process of four ZSM-5 zeolites with different Si/Al ratio, has been studied *in situ* by synchrotron radiation powder diffraction. Samples of ZSM-5 were prepared starting from the following reactants mixture: TPABr (98%, Fluka), NaOH (97%, Carlo Erba Reagenti), $Al(OH)_3$ (98%, Fluka), precipitated silica gel (100%, Merck) and distilled water.[4] In order to achieve different Si/Al ratio in the sample, the molar composition of the starting gel was changed by varying the amount of Al_2O_3 in the following starting mixture: $0.08Na_2O{-}0.08TPABr{-}xAl_2O_3{-}SiO_2{-}20H_2O$ where x ranges from 0.01 to 0.02 (i.e., the Si/Al [mol/mol] is equal to 11, 15, 26, 42, respectively).[4] The time-resolved experiment was performed at the MCX beamline at Elettra. For this study, powder samples of ZSM-5 were placed in a quartz-glass capillary using a gas blower to control the sample temperature. The evolution of the structural features was monitored through

36 structure refinements in the temperature range from 25 to 800 °C by full profile Rietveld analysis.
The time-resolved experiment, performed at the MCX beamline at Elettra allowed to monitor the evolution of the lattice parameters, the framework modification, together with the degradation of the TPA^+ and the release of water up to 800 °C through structure Rietveld refinements. In general, although the different chemistry of the framework, reflected in a slightly different template and water content, all the sample maintain a good crystallinity up to 800 °C and no amorphization or phase transitions are registered. So all the patterns were refined with the *Pnma* space group. Structural characterisation of samples having different Al content revealed no significant differences in the thermal stability. On the contrary, the beta angle variation was found to be affected by the Si/Al ratio. Specifically, the higher the Silicium content the greater the beta angle. In Figure 1 is reported the evolution of the unit cell volume increasing the temperature. In particular, up to 200 °C, a slight expansion of the volume is detected; then up to 800 °C, the structure undergoes to a continuous negative thermal expansion (NTE).

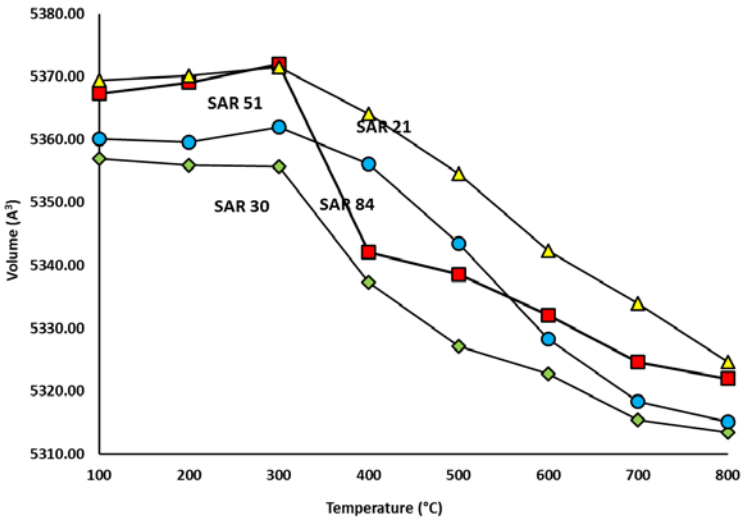

Figure 1. Evolution of the cell volume during the heating for all the ZSM-5 investigated.

Looking at the extraframework content, the structure refined reveals that the TPA^+ does not interact with the framework but only with the H_2O molecules through weak hydrogen bonds. In the 200-400 °C temperature range, the TPA^+ degrades and the framework shows the most important modification in particular the 10 MR became more circular and the CFA tends to decrease. These changes are reflected by the contraction of the cell volume due to a relaxation effect. The water molecules showed a linear decrease increasing the temperature. The zeolite at 400 °C resulted empty.

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