Oral presentation

The interplay of temperature and extraframework cations content on CHA-zeolites flexibility: implications on gas separation processes

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Zeolites with **CHA** framework-type are of interest because of their applications in a variety of technological and industrial processes . The versatility of the framework, and the fact that it is a small-pores zeolite, makes it one of the most exploited porous material in the field of gas separation and selective catalytic reduction of NOx [1-3]. Particular attention has been devoted to the Na- and Cu-form of **CHA** [2-4]. The gas admission in the porous framework of **CHA** is a function of the extra-framework (EF) cation content, Si/Al ratio of the framework, and applied temperature. Being all zeolitic materials subjected to a thermal treatment prior to their use in gas separation/sorption processes, knowledge about the temperature-induced transformations is of great interest. Several authors investigated the **CHA** behaviour upon heating, applying different experimental conditions. A pioneer study [5] conducted on Na-CHA demonstrated that the dehydrated form at 320°C experiences a severe contraction of the unit-cell volume, accompanied by a rotation and squeezing of the double-six membered rings (D6mr) units. The same structural changes were not reported for a mixed cationic form (CaNaK-CHA) investigated by Zema et al. [6]. Similarly, the dehydrated forms of a Na-CHA evacuated in air at 250°C for 18-24 hours prior to CO_2 loading [4] did not show the same contraction and rotation of the D6mr units as reported by Mortier et al. [5]. At present, it remains enigmatic whether the structural modifications experienced by Na-CHA are relatively moderate up to 250°C (similarly to [4,6]), and the structure contracts only at temperatures higher than 300°C; or if other parameters such as the chemical composition (Si/Al ratio, EF cation content), heating rate, etc. affect the response to the heating stimuli. In order to answer this question, we performed an *in situ* temperature-dependent study of a Na-CHA from 25 to 350°C. In addition, by applying the same experimental conditions, we tracked the dehydration process of a Cu-CHA with the same Si/Al ratio of Na-CHA.

Our results showed that the Na-form releases most of the H_2O at 100°C, when a pronounced drop of the unit-cell volume (-12%) and symmetry lowering from $R\text{-}3m$ to $I2/m$ is observed. This structural modification, which is very similar to that reported by Mortier et al.[5], is maintained up to 350°C. In contrast, a different path is observed for Cu-CHA (Fig. 1a). The unit-cell volume contraction is less pronounced (-6%) and the framework maintains the configuration of the RT structure, although the diffraction pattern clearly showed a loss of crystallinity already at 200°C (Fig. 1b). The rehydration capacity of the two cationic forms is also very different. Finally, the implications on the gas separation capacity of Na-CHA after activation at high temperatures are discussed.

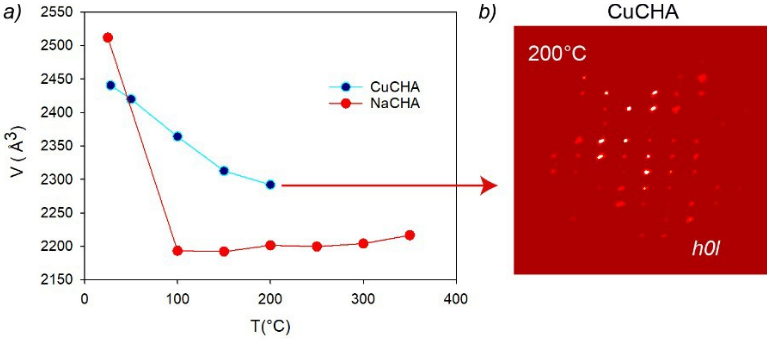

Figure 1. Unit-cell volume trend of Na- and Cu-CHA as a function of temperature (a). Reconstructed precession image of the *h0l* layer of Cu-CHA at 200°C (b).

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