



STRUCTURAL DETERMINATION OF CATALYTICALLY-ACTIVE Ag^+ SITES IN AN Ag-Y ZEOLITE: A COMBINED ANOMALOUS XRPD AND EXAFS STUDY

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Catalytically-active centres within the complex structure of a silver-exchanged zeolite were located using a combination of X-ray techniques.

Zeolites [1] are nanoporous crystalline aluminosilicates formed by a framework of corner-sharing $[TO_4]$ tetrahedra, where T represents a silicon or an aluminum atom. The chemical composition can be described by the general formula: $X^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]^{x-}$. Formally, the introduction of trivalent Al(III) into $[TO_4]$ units (substituting tetravalent Si(IV) atoms) induces a net negative charge on the framework (x^-) which must be compensated by the presence of charge-balancing extra-framework cations ($X^{n+}_{x/n}$). Such cations act as Lewis acid centres, being electron acceptors.

Starting from the basic $[TO_4]$ constituent, the framework of any zeolite is constructed by progressively connecting two adjacent $[TO_4]$ units by sharing an oxygen atom, which becomes a bridge between the two T atoms (T-O-T). Using the $[TO_4]$ unit as the sole building block, the remarkable flexibility of the T-O-T angle (from $\approx 100^\circ$ up to 180°) allows the realisation of an impressive number of different zeolites, characterised by a regular system of intercrystalline voids and channels of well-defined size, (in the nanometre and sub-nm range), accessible through apertures of well-defined dimensions. The regularity in channel dimensions controls accessibility and makes zeolites much more selective in the adsorption of specific molecules as compared to amorphous carbon or silica gel, which have irregular pore systems. This is the reason for their widespread use as molecular sieves. The same characteristics explain the ever-increasing

role that zeolites and related zeotypes have in heterogeneous catalysis (e.g. for the petrochemical industry, pollution control and fine chemistry). Moreover, their ability to encapsulate organised molecules, crystalline nano-phases and supramolecular entities inside their channels and pores makes zeolites promising materials in the field of low-dimensional physics, where the quantum effects due to the spatial confinement become observable. Semiconductor quantum wires and quantum dots can thus potentially be obtained by hosting semiconductor crystalline nano-phases inside the channels or cages, so obtaining interesting applications in the fields of optoelectronic, non linear optics, photochemistry, and chemical sensors [2]. The same idea applies for metal and bimetallic dots: the incorporation of such nano-particles inside the pores or channels of zeotype materials opens a new frontier in the chemistry of metal-supported catalysts.

In this article we report on the structural determination of an Ag-Y zeolite ($Si/Al = 2.63$) obtained by a combined anomalous X-ray powder diffraction, (XRPD), and EXAFS study performed on beamlines BM16 and BM29, respectively. Silver-exchanged zeolites are used in several catalytic and photocatalytic processes, which take advantage of the presence of both isolated Ag^+ ions and aggregated Ag_n clusters. Examples include the photochemical dissociation of H_2O into H_2 and O_2 , the disproportionation of

ethylbenzene, the oxidation of ethanol to acetaldehyde, the aromatisation of alkanes and alkenes, the selective reduction of NO by ethylene, and the photocatalytic decomposition of NO [3].

The first step in the characterisation of a zeolite involves a thermal treatment to remove all the molecules coming from the ambient atmosphere already adsorbed on the catalytically-active centres. This activation process is essential to guarantee the study of a well-defined system [4]. Once this step has been achieved, measurements can be performed *in situ*, either on the activated sample (i.e. the zeolite under vacuum conditions) or after adsorption of a well-defined amount of high-purity gas onto the sample. The conditions of the activation process are critical for silver-exchanged zeolites because an increase in the activation temperature, suitable to remove the most strongly bonded molecules, has the disadvantage of promoting the aggregation of Ag^+ ions into Ag_n clusters [5]. Such clusters, needed for some catalytic application (*vide supra*), are undesired if the aim of the study is the location of isolated Ag^+ ions. Based on our previous study of the zeolite Ag-ZSM-5 [6,7], an activation temperature of 120° was adopted.

XRPD experiments were carried out on an Ag-Y zeolite activated in a borosilicate glass capillary at the Ag-K edge [$\lambda = 0.486093(2) \text{ \AA}$], just before [$\lambda = 0.486103(2) \text{ \AA}$] and far away [$\lambda = 0.491153(2) \text{ \AA}$], in order to single

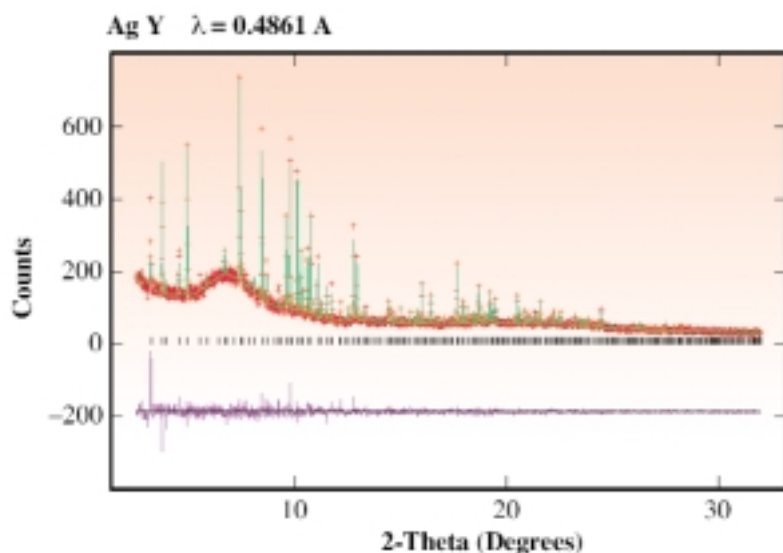


Fig. 1: Observed, calculated and difference profiles and reflection positions of the Ag^I-Y zeolite.

out, as much as possible, the contribution coming from the silver cations. Figure 1 shows the high resolution XRPD pattern collected at [$\lambda = 0.486103(2) \text{ \AA}$]. A Rietveld refinement was performed simultaneously on the three data sets. This made it possible to obtain the zeolite framework and to locate the near totality of the expected (on the basis of the Si/Al ratio) Ag⁺ counterions: 52.0(4) out of 52.9 per unit cell. The result is quite remarkable when compared with that obtained in the cases of Cu⁺-Y [8] and of Rb⁺-Na⁺-Y [9] (also BM16 data), systems where we were able to locate only 41.0(5) and 48(1) cations, respectively. This noticeable improvement is ascribed to the following factors: (i) the higher scattering power of Ag; (ii) the simultaneous use of three separate data sets; (iii) the extra information in the patterns arising from the anomalous-scattering effect.

Figure 2 illustrates the structure of zeolite Y, which is generated by connecting sodalite units with hexagonal prisms to give a framework containing large cavities (supercages) with a diameter of about 13 Å. Figure 2 also shows the position of the five different extraframework Ag⁺ sites obtained from the Rietveld refinement, labelled as sites I (8.2), I' (17.4), IIa (6.6), IIb (15.2) and I'_m (4.6) (the occupancy per unit cell is given in parenthesis). Four of the sites are positions typical of dehydrated cations. In contrast, I'_m is in the middle of the sodalite cage: implying that such ions



Fig. 2: Representation of the Y zeolite framework and cation location. In the fraction of the framework located in the upper right part of the figure O atoms are represented in red and the T atoms (Si or Al) in yellow. For clarity, in the remaining part of the framework, only yellow sticks have been adopted. Ag^I cations are represented as spheres and are labelled with I, I', IIa, IIb and I'_m. The supercage cavity, where guest molecules can be hosted, can be seen in the centre of the figure.

must be coordinated to residual water molecules. In anhydrous conditions, the positively-charged cations are actually in contact with the walls of the cavities, where they interact with the negatively-charged oxygen atoms of the framework. The fact that so few cations, less than 5 out of 52, are coordinated by water molecules indicates that the temperature for the activation procedure was appropriately selected.

We have used the output of the Rietveld refinement to simulate the EXAFS data (collected at BM29) and shown in Figure 3. In theory we have to simulate five EXAFS signals representing the contribution to the overall signal coming from the Ag absorbers located in the 5 different sites found by XRPD. The contribution coming from the hydrated I'_m site has been ignored because: (i) less than 10 % of the absorbers occupy this site and (ii) a rather high Ag-OH₂ Debye-Waller factor is expected. Moreover, since sites I' and IIb show a similar local environment, (three oxygen atoms at the close distance of 2.46 or 2.47 Å), the corresponding contributions were merged. As a result, 3 different contributions have been used to simulate the experimental EXAFS signal. For each contribution, the Ag-O distance was fixed at the crystallographic value (2.31 Å for IIa, 2.61 Å for I and 2.465 Å for I' and IIb), while the coordination number was obtained from the theoretical number of first-shell O neighbours multiplied by a weighting factor obtained from the Rietveld refinement. Ref. [8] describes the procedure for the Cu⁺-Y case in great detail. The two superimposed spectra at the bottom of Figure 3 represent the experimental EXAFS signal, filtered on the Ag-O peak, and the best fit obtained by adding the three contributions described above, where the refined parameters were one common ΔE and three different Debye-Waller factors. The quality of the EXAFS fit, obtained with only four independent variables on such a complex sample, represents a conclusive proof of the quality of the Rietveld refinement from the XRPD data.

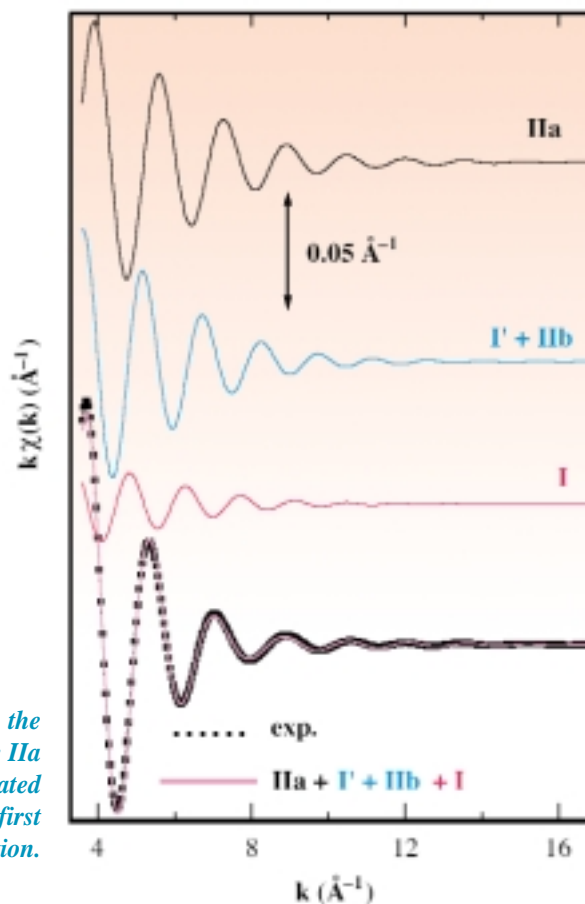
We conclude that the use of anomalous diffraction data collected at the high resolution powder diffraction beamline (BM16) has allowed us to locate nearly all extraframework Ag⁺ ions hosted in a Y zeolite, *i.e.* 52.0(4) out of 52.9. The XRPD data have been of fundamental help in the understanding of the complex Ag-K edge EXAFS signal generated by Ag⁺ ions probing different local environments (BM29 data). These studies enhance our understanding of the structure of cation-exchanged zeolites and in particular of the extraframework cations which are known to determine the catalytic properties of such zeolites. ■



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Best fit and simulated EXAFS spectra of the contribution to the overall signal of silver cations located in, from top to bottom: site IIa (I' and IIb merged) and I and sum of the three simulated contributions (full line) superimposed with the experimental first shell filtered $k\chi(k)$ function.



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