Mean inner potential and skeletal density of zeolite MCM-41 using TEM

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Keywords: MCM-41, zeolite, TEM, tomography, holography

Abstract

Zeolites are aluminosilicates widely applied as support for catalysts in the chemical industry. We have used electron holography tomography (EHT) to characterise in three-dimensions inside and outside two MCM-41 zeolite nanoparticles (Figure 1A) the electrostatic potential and the charge density [1]. Moreover, we estimate the skeletal density of the zeolites from the three-dimensional electrostatic potential (Figure 1B). The composition of the sample, measured using energy-dispersive x-ray spectroscopy (EDX-TEM), is very close to silicon dioxide (SiO₂). Figure 1C is a high-magnification TEM image showing that the zeolite examined here is formed by a hexagonal ordered structure of amorphous SiO₂ and empty channels with a diameter of 1 nm. Insets in Figure 1C show a model and a magnified image of an unit cell of the channelled structure. Because SiO₂ is not a good electrical conductor during transmission electron microscopy observation the sample accumulated an electric charge. This effect implies that the electrostatic potential (shown in Figure 1B) has in first approximation two terms

\[ V(x, y, z) = V'_0(x, y, z) - |V_c(x, y, z)| \]

the first term \( V'_0(x, y, z) \) is called the mean inner potential (MIP), an average electrostatic potential that depends on the structure and composition of the unit cell of the sample. The second term \(|V_c|\) accounts for the contribution of the induced charge due to secondary emission during TEM observation (in typical TEM experiments its effect is to decrease the mean inner potential [2]. The density of electric charge induced in the sample is not homogeneous: It is small inside the particles (small \(|V_c|\)) and large close to the surfaces of the sample (large \(|V_c|\)) [2]. Correspondingly, the potential measured experimentally in Figure 1B reaches a maximum value of 14 Volts inside the particles and decreases towards their surfaces. The spatial resolution of EHT does not resolve the channelled structure of the zeolite, and the potential must be divided by 2 to get the real potential. Then, the potential inside the particle where the contribution of charging is minimum (therefore close to the real value of the MIP) is approximately 7 volts.

The curve in Figure 1D shows MIP values of MCM-41 for a realistic range of density values of SiO₂, calculated using a binding-approximation [4], and the unit cell sketched
in the inset of Figure 1C. Comparing the curve with the experimental value of MIP $\approx 7$ V we estimated the skeletal density of the MCM-41 zeolite nanoparticles to be approximately 2.1 gr/cm$^3$.

Figure 1. (A) Hologram of two MCM-41 zeolite nanoparticles acquired in a microscope FEGTEM Titan (B). Three-dimensional distribution of electrostatic potential (in Volts) inside and outside particles shown in (A) and measured using EHT. (C) Detail of the hexagonal structure of the zeolite with channels of 1 nm (B). (D) Theoretical values of the mean inner potential of the zeolites studied here using a binding approximation. The mean inner potential of the particles measured experimentally correspond approximately to an skeletal density of the zeolite of 2.1 gr/cm$^3$.

References

[5] We kindly acknowledge for funding to the EC project REGPOT AL-NANOFUNC.