Synthesis and magnetic properties of Co nanoparticles embedded in a zeolite matrix

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In the last decades nanoscale magnetism has drawn great scientific interest due to its potential applications [1]. When the size of magnetic particles is reduced to a few nanometers, they often exhibit a number of outstanding physical properties such as giant magnetoresistance, superparamagnetism, large coercivity, as compared to the corresponding bulk values. Due to these unique physical properties upon size reduction, magnetic nanoparticles contribute to revolutionary changes in a variety of applications from biomedicine to spintronics [2,3].

The structure of zeolites with pores or channels of well defined size are particularly suitable for the study of magnetic properties of magnetic cations introduced into the structure.6,14 In the case of zeolites of the type ZSM-5 (structure MFI: mirror framework inversion; Mobil five) the diameter of the channels is 0:51 – 0:56 nm [4].

Co-HZSM-5 zeolites were prepared by wet impregnation of NH_4-MFI with aqueous solution of cobalt salt to yield the desired wt % of the cation (2.8 Co wt% and 4.9 Co wt%,). The samples were dried at 110ºC and calcined at 500ºC under N_2 flow (10 ml/min) and then under an oxidizing atmosphere for 12 h. Finally, these powders were reduced from room temperature to 500ºC at 5ºC/min and holding at 500ºC for 5 h, in H_2 flow (5 ml/min). These samples were called reduced zeolites (CoxIR, x = 2.8, 4.9). The Co content was accurately determined by atomic absorption. Crystal structure was studied by means of X-ray diffraction in a powder diffractometer using CuKα radiation. Scanning electron micrographs (SEM) and energy dispersive spectra (EDS) were used to characterize the microstructure and elemental composition of the samples. Magnetic measurements were performed in a commercial SQUID, varying the temperature from 5 to 300 K, with applied fields ranging from 25 to 200 Oe, and at several constant temperatures with applied fields up to 5 T.

XRD patterns of the reduced samples reveal the presence of metallic Co in a cubic phase, as well as traces of hexagonal Co. However, the oxides were not completely reduced, as some peaks corresponding to CoO and Co_3O_4 are still present. EDS microanalyses show for both reduced samples bright spots on the surface of the zeolite matrix which would be Co metal, as there is not enough oxygen to account for any Co oxide on these spots. Moreover, the spectra on the matrix show some traces of Co. As this element is not part of the zeolitic framework, this indicates that some Co is below the surface, inside the channels of the zeolite (Fig. 1).

Curves of magnetization as a function of temperature are shown in Figure 2 for sample Co2.8IR. ZFC and FC curves diverge before 300 K. In the ZFC curve there is a sharp maximum at T = 7 K and two wider peaks around 160 and 285 K of much lower intensity (approximately 9% of the 7 K peak). The abrupt decrease of the first peak can not be fitted either with Brillouin nor Langevin functions but an exponential of the type $\exp(-T/T_1)$, with a decay constant T_1= 3.5 K. The most important contribution is a high background (ferromagnetic, and also observed at room temperature) to which the contribution of two different kinds of clusters is superimposed, with blocking temperatures of 160 and 285 K, corresponding to the broad maxima observed at these temperatures. For sample Co4.9IR, the

same behavior is observed, but with higher magnetization values, as expected for higher Co content.

Measurements of the low-temperature peak in the ZFC curves were performed in both reduced samples with different applied fields in order to study the blocking temperature dependence with the field. A decrease of the blocking temperature with increasing applied field is observed.

The M(T)-ZFC curves (see inset of Fig. 2) show a prominent feature —the appearance of a well-defined magnetization peak at low temperature followed by an exponential decay. We consider that two processes take place at low temperature, which give rise to this peak over the background produced by other contributions to the magnetization. For temperatures lower than a certain T_{crit} a tendency towards the equilibrium state with magnetization $M_{eq}(T,H)$ given by the Curie law. It is this process that produces a blocking temperature T_B. For temperatures above T_{crit} a fast evolution towards an equilibrium state with $M_{eq} = 0$, that produces an exponential variation of magnetization with temperature. This is consistent with a spins reorientation mechanism and the fact that the relaxation rate is constant allows us to propose that we are in presence of a mesoscopic quantum tunneling process.

References:

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Figures:

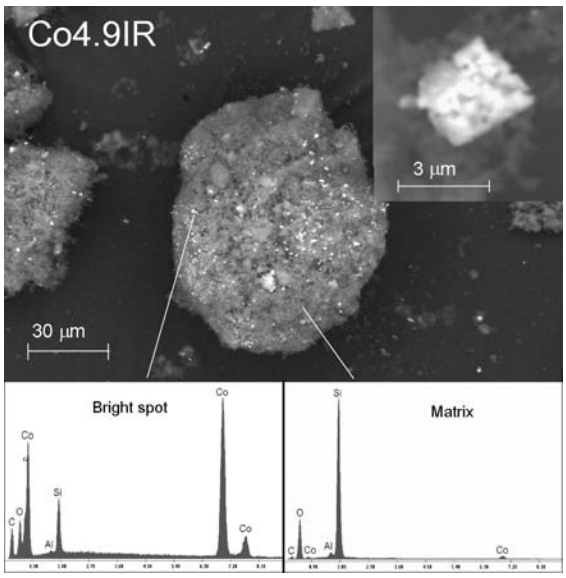

Figure 1. SEM micrograph of Co4.9IR (top) and EDS spectra taken to a bright spot on the particle (left bottom) and to the matrix (right bottom).

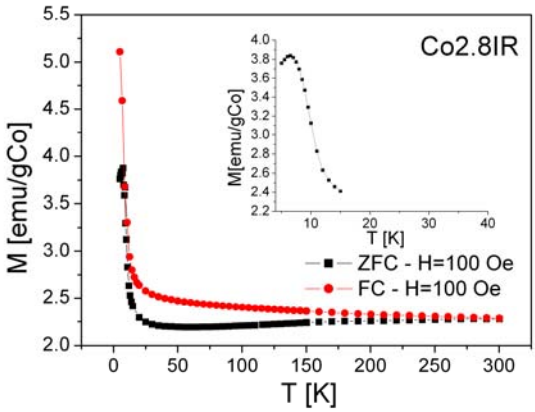

Figure 2. ZFC-FC magnetization curves for sample Co2.8IR. The inset shows in detail the low temperature peak.