



Magnetic behavior of Co clusters embedded in a zeolite matrix

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Abstract

A medium pore zeolitic material with MFI structure modified with Co cations was synthesized. The magnetization M and magnetic susceptibility χ were measured as a function of T after ZFC and as a function of the applied magnetic field for T between 4.2 and 30 K. No blocking temperature was detected and a pure superparamagnetic behavior was obtained. M vs. T and χ vs. T were adjusted by Brillouin and Langevin functions obtaining the same results in both cases. Curve fitting gave an effective moment of $\sim 90\mu_B$ for the cases under study. The results are analyzed in terms of the possible cluster structure that may appear.

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The catalytic properties of zeolites are strongly dependent on the presence of built-in cations. At the same time, these cations may show magnetic properties that depend on their aggregation state. 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. In this work, our aim is to study the magnetic properties of Co^{2+}

cations introduced into the zeolite structure by means of ion exchange followed by heat treatment.

Na-ZSM-5 zeolite ($\text{Si}/\text{Al} = 17$) with MFI structure was synthesized by hydrothermal crystallization [1]. H-ZSM-5 form was obtained by ion exchange with 1 M NH_4Cl at 80°C for 40 h, followed by calcinations for 16 h in N_2 and 10 h in air. Co-ZSM-5 was prepared by ion exchange of NH_4 -zeolite with 0.05 M CoCl_2 solution at 80°C for 10 h to yield a 3.8 wt% of Co. Afterwards, the sample was dried at 110°C and desorbed in N_2 flow at 500°C for 12 h. This was followed by calcination in air for 6 h: (1) at 500°C (yielding

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sample 3.8CoT1), (2) at 900 °C (yielding sample 3.8CoT2).

BET surface area determinations were carried out and X-ray powder diffraction patterns were collected using $\text{CuK}\alpha$ radiation. Also infrared analysis was performed and pyridine adsorption experiments were carried out in a thermostated cell with CaF_2 windows connected to a vacuum line, and a self-supporting wafer ($8\text{--}10\text{ mg cm}^{-2}$) was used. Pyridine (3 Torr) was adsorbed at room temperature for at least 10 h, and desorbed for 2 h at 250, 350 and 400 °C at 10^{-5} Torr. The strength of the sites was separated in three regions: weak, medium and strong acid sites as a function of pyridine retained between 250–350, 350–400 and above 400 °C, respectively.

The surface area of the Na-ZSM-5 and Co-ZSM-5 samples by BET method were 390 and $384\text{ m}^2\text{ g}^{-1}$, respectively, which are within the range of values expected for this kind of structures [2]. X-ray powder diffraction patterns of the Na and Co-zeolites confirm the high degree of purity and crystallinity of the samples, indicating that incorporation of cobalt ions into ZSM-5 does not affect its orthorhombic symmetry.

Fig. 1(a) shows the Fourier transformed infrared (FTIR) spectra of the H-ZSM-5 and Co-ZSM5 calcined at 500 and 900 °C, after desorption of pyridine at 400 °C. In all the samples, the presence

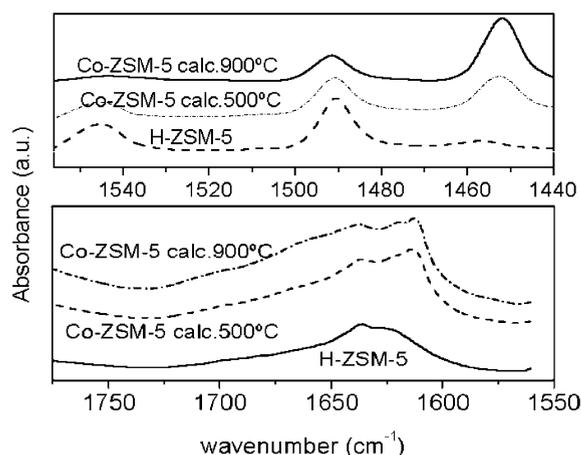


Fig. 1. FTIR bands of pyridine desorbed at (a) 400 °C in the $1400\text{--}1600\text{ cm}^{-1}$ region and (b) at 250 °C in the $1550\text{--}1800\text{ cm}^{-1}$ region.

of both Brönsted (1550 cm^{-1}) and Lewis (1450 cm^{-1}) acidic sites, can be observed. Co-ZSM-5 materials show the formation of a new electron–donor–acceptor Adduct (EDA) of pyridine to Lewis sites, compared with the H-ZSM-5, probably due to a Co unoccupied molecular orbital interaction with the probe molecule. Furthermore, new Lewis sites were very strong since they retain more pyridine than the parent H-ZSM-5 material after outgassing at 400 °C. The number of Lewis sites increased as Brönsted sites decreased upon introduction of Co. The new absorption band at 1612.6 cm^{-1} in Co-samples (Fig. 1(b)) indicates that a different Lewis site was generated which is not present in the H-ZSM-5 parent sample, in concordance with Ref. [1], from Zn-ZSM zeolite.

The measurements of magnetization M as function of temperature were made by the extraction method and the results for a field $H = 2\text{ T}$ are shown in Fig. 2 after zero field cooling (ZFC). The inset of this figure shows the loop M vs. H at room temperature.

The absence of a blocking temperature is noticeable. For both of the studied samples, the data can be fitted by either Brillouin or Langevin functions, giving the same results and a very good fitting to the experimental data, as shown in Fig. 2. This is an indication that we are in the classical limit of high magnetic moment. The fitting parameters confirm that Co^{2+} clusters are formed giving effective magnetic moments of $90 \pm 10\mu_B$

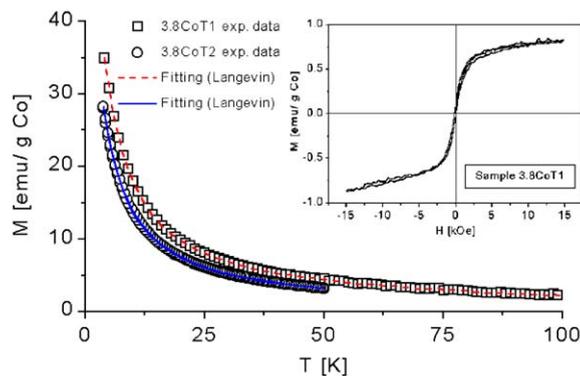


Fig. 2. Experimental data of $M(T)$ for $H = 2\text{ T}$ for both samples. The solid and dashed lines show the fitting made using a Langevin function. Inset: $M(H)$ at room temperature for sample 3.8CoT1.

per cluster for both samples. The calculated effective number of μ_B per ion is 4.7, almost the same as isolated Co^{2+} ions [3]. This means that there are 19 ions forming each cluster. No other contribution to the magnetization is found, either paramagnetic contributions of isolated ions or ferromagnetic behavior (this would be observed if metallic Co clusters were formed). However, there is evidence that some metallic Co may be present: in the inset of Fig. 2 the loop M vs. H at room temperature is shown for the sample 3.8CoT1 and a small ferromagnetic signal (of the order of the background in the $M(T)$ curves) is measured, with maximum magnetization of $0.8 \text{ emu g}^{-1} \text{ Co}$. This measurement was performed with a vibrating sample magnetometer (VSM), with larger sensitivity than the M vs. T curves, where M was measured by the extraction method.

The Co^{2+} clusters have a superparamagnetic behavior at all the measured temperatures. If we assume there is a maximum of three Co ions per zeolite unit associated with the Lewis sites in order to compensate the excess negative charge, this would mean that the ions are distributed in the channels of 6–7 cell units. ZSM-5 zeolites have a channel size of 0.56 nm [4] and we may estimate the volume V of clusters as the channel volume of seven adjacent unit cells, giving $V = 5.2 \times 10^{-27} \text{ m}^3$. With such a small volume even high-anisotropy materials become superparamagnetic at temperatures below 4.2 K. Due to the directionality of the channels in the zeolite structure the magnetic anisotropy could well be ascribed to shape anisotropy.

Measurements of M vs. H as functions of T were also performed at $T = 4.2, 10, 20$ and 30 K . All these curves, together with M vs. T curves fall into a single universal function $M = M(H/T)$ described by the aforementioned Brillouin or Langevin functions, as it can be seen in Fig. 3.

The AC initial susceptibility χ_{AC} was measured at 0.1, 1.0 and 10 kHz with an exciting AC field of 15 Oe. The results for the real and imaginary parts are shown in Fig. 4 for 1.0 kHz only, as no change with frequency was observed. Also here no blocking temperature was detected. The imaginary part of the susceptibility is almost zero, less than 1% of the real part, at all temperatures. This means that no relaxation is taking place in all the studied tempera-

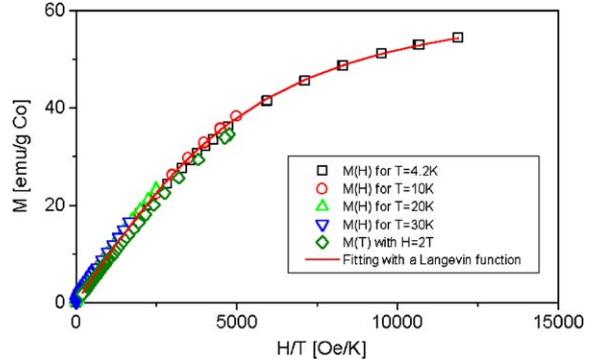


Fig. 3. Magnetization as a function of H/T from measurements made at constant H and constant T . The solid line corresponds to a fitting made with a Langevin function.

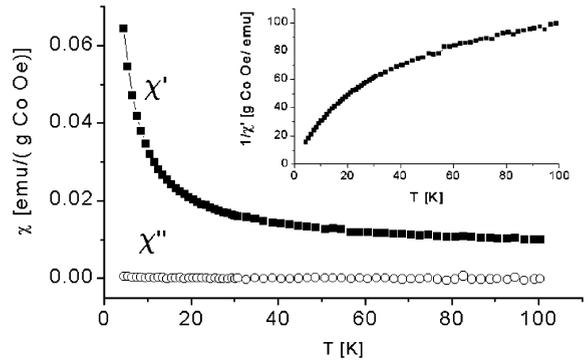


Fig. 4. For sample 3.8CoT1: Real (χ') and imaginary (χ'') parts of χ_{AC} and $1/\chi'$ (in the inset).

ture range. $1/\chi_{AC}$ is plotted as a function of T in the inset of Fig. 4. A nonlinear relationship can be seen in this figure and the magnetic behavior due to an ensemble of superparamagnetic clusters is evident.

The calculated Curie constants are 6.4×10^{-6} for sample 3.8CoT1 and 4.6×10^{-6} for sample 3.8CoT2, in units of $[\text{J K T}^{-2} (\text{g Co})^{-2}]$. There is a big difference in the Curie constant depending on the heat treatment. The heat treatment at 900°C reduces the overall magnetization with respect to the heat-treatment at 500°C , probably by oxidizing part of the Co ions to form CoO. Sample 3.8CoT1 has 39% of the magnetization of metallic Co and sample 3.8CoT2 has 30%. This behavior is similar to the one observed for Fe ions in ZSM-5 zeolite thermally treated at 580°C [5], where it was considered that Fe ions were expelled from the

zeolite framework to the cavities where they can form clusters. Also in Pt-Fe/KL zeolite this type of behavior was observed for calcinated samples [6].

In conclusion, magnetic measurements are suitable techniques to monitor the formation of clusters of ions in zeolite structures and may be related to the catalytic activity.

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