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A new synthetic route to produce metal zeolites with subnanometric magnetic clusters†

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By using a Co layered silicate as a source of Co and SiO_2, Co-Beta and Co-ZSM-5 zeolites with tetrahedrically coordinated cobalt were synthesized. Subnanometric clusters of Co can be produced and a magnetic material with superparamagnetic–paramagnetic phase transition is obtained.

Since ENI succeed in synthesizing Ti-silicalite,[1] this metal as well as others have been claimed to be part of some crystalline and amorphous metallosilicates.[2–9] Metal substituted zeolites and ALPO's have shown interesting properties as catalysts for performing selective oxidation reactions using peroxides or even oxygen as oxidants.[10–12] In addition, thermal treatments of this type of metallosilicates could also be useful to prepare 3D macroscopic distributions of stable very small clusters of the corresponding metals occluded and stabilized in the zeolite cavities. These clusters, besides their potential catalytic properties,[13] may present size dependent behavior, as superparamagnetism (SP), that can be interesting for both fundamental studies and their broad technological applications.

Here, we present a series of Co-zeolites which have been synthesized, starting from a layered silicate, with Co located in the framework. When the final zeolites are calcined they present a "unique" magnetic reversible phase transition by varying the temperature, without any structure modification.

The possibility of using layered silicates for the synthesis of pure silica zeolites and mesoporous materials was proposed by Hogan and Martin,[14a] Pal.Borbély *et al.*,[14b] Zones *et al.*,[14c] and by Yanagisawa *et al.*[15] Furthermore, Ko *et al.*[8a] were able to prepare Mn-silicalite starting with Mn ion exchanged magadiite. In this case, samples with Si/Mn = 17 were obtained where the Mn was in tetrahedral coordination atomically dispersed.

Cobalt-zeolites can be interesting materials not only as catalysts, but also because of their magnetic properties. Unfortunately, the synthesis of cobalt zeolites is difficult because the transition metals precipitate as insoluble hydroxides at the high pH of the synthesis. In order to avoid this, one might start with a source of Co that allows dosing the metal during the synthesis. Exchanged layered silicates as shown by Ko *et al.*[8b] for metals appeared to be an interesting alternative. However, even if one starts from cobalt exchanged layered silicates there is no guarantee that ion exchange between cobalt and the cationic organic structure director agent will not occur, and that the leached cobalt precipitate as hydroxide. In order to avoid this, we have applied here a synthetic strategy that involves the synthesis of the cobalt Beta and ZSM-5 zeolites starting with cobalt magadiite as a source of Si and Co where the cobalt is not ion exchanged but occupies framework positions. For doing so, we developed first a method for preparing metal magadiite.[16] Then, Co-ZSM-5 and Co-Beta zeolites were synthesized using as the source of silica and cobalt a Co-magadiite with a Si/Co atomic ratio of 50. This Co-magadiite was obtained by preparing a synthesis gel with the following molar ratio: SiO_2 : 0.2 NaOH : 0.5 trans-4-aminocyclohexanol : 15 H_2O : 0.02 $Co(CH_3COO)_2$. After stirring the gel was transferred to a Teflon-lined autoclave and heated at 423 K during 3 days. For Beta zeolite, 0.088 g of NaCl and 0.215 g of KCl were dissolved in a solution of 15.4 g of tetraethylammonium hydroxide in 8.58 g of water. 4.402 g of Co-magadiite were added under stirring. Then, 0.275 g of sodium aluminate and 0.056 g of NaOH and 2.92 g of water were added. In the case of Co-ZSM-5, a gel was prepared with 15.19 g of Co-magadiite, 151.19 g of water, 1.68 g of $Al_2(SO_4)_3$ $18H_2O$, 1.519 g of NaOH and 20.112 g of tetrapropylammonium bromide. The synthesis mixtures were loaded in Teflon-lined stainless steal autoclaves and heated at 448 K and 413 K under rotation during 15 and 6 days respectively. The solids obtained were washed with distilled water and dried at 373 K overnight.

Chemical analysis of the as synthesized sample gave 5 Co wt% in Beta and 2.9 Co wt% in ZSM-5. The XRD pattern (X'pert diffractometer, CuK_α radiation) of the as synthesized samples showed the characteristic peaks of zeolite Beta and ZSM-5 (Fig. 1a–b) and no diffraction peaks of magadiite or crystalline cobalt phases were observed even after calcination at 823 K indicating that if Co comes out from the framework the particles formed should be smaller than 2 nm. UV-Visible diffuse reflectance spectra given in Fig. 1a′–b′ show a band at ~ 210 nm which corresponds to metal–oxygen electron charge transfer and is characteristic of a tetrahedrally coordinated metal in a zeolite framework.[17]

Samples were examined by transmission electron microscopy (TEM) in an Hitachi M-800 microscope operated at an accelerating voltage of 200 kV. The samples were ground to a fine powder and diluted in acetone to give a 1:3 volume ratio. A drop of the slurry was allowed to dry onto a carbon coated Cu grid covered by a watch glass. TEM shows prismatic and shapeless grains of ZSM-5 with sizes between ~ 30 to 300 nm. At high resolution the porous nature of the zeolite was revealed (Fig. 2). No high electron density spots are observed and there is no diffracted contrast in the dark field images (not shown) indicating the absence of metallic particles within the microscope resolution, which is in agreement with the XRD results. Calcined Co-Beta sample presents the same features as calcined Co-ZSM-5 but the grains are smaller and featureless, as is common for Beta zeolite.

Regarding the magnetic properties, a similar behavior is observed with the two zeolites, with a larger magnetic susceptibility and a larger magnetic moment for the Co-Beta according to its

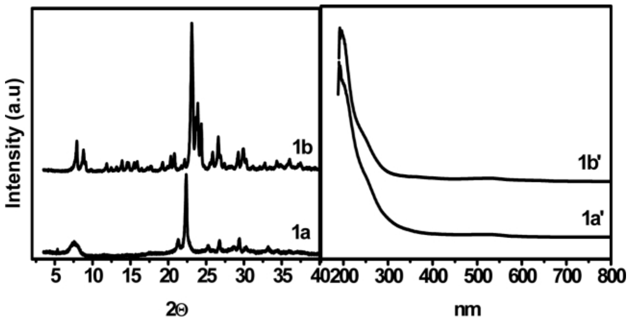

Fig. 1 X-ray diffraction patterns of cobalt Beta (a) and ZSM-5 (b) and UV diffuse reflectance spectra of Co-Beta (a′) and Co-ZSM-5 (b′).

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† Electronic supplementary information (ESI) available: X-ray diffraction patterns of Beta, ZSM-5 and magadiite; magnetization *versus* applied field divided by temperature. See http://www.rsc.org/suppdata/cc/b4/b407225a/

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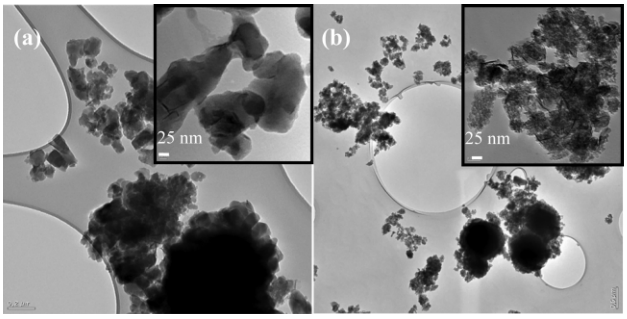

Fig. 2 Low and high resolution (inset) bright-field TEM Images of (a) ZSM-5-Co and (b) Beta-Co.

larger Co content. The most remarkable properties of these materials is a change in the magnetic behavior without structural modification when varying the temperature (Fig. 3). Indeed, while at 10 K the samples behave as typical SP nanoparticles,[18] this behavior is lost at 300 K and the samples behave as a pure paramagnetic material, with a linear susceptibility a hundred times smaller corresponding to a distribution of atomic Co.

This can be easily seen when plotting M *vs.* H/T (see ESI†): if particles were SP at all T, both curves (10 K and 300 K) should collapse.[18] The absence of hysteresis at low T indicates the absence of large particles and suggest highly monodisperse clusters. This observation of the change in behavior when varying the temperature is uncommon, while it has been described in theoretical work as the convolution of the thermal agitation of the magnetic dipole and phonon mediated spin de-coupling with T.[19] This property may open the possibility for using these materials as temperature magnetic switches.

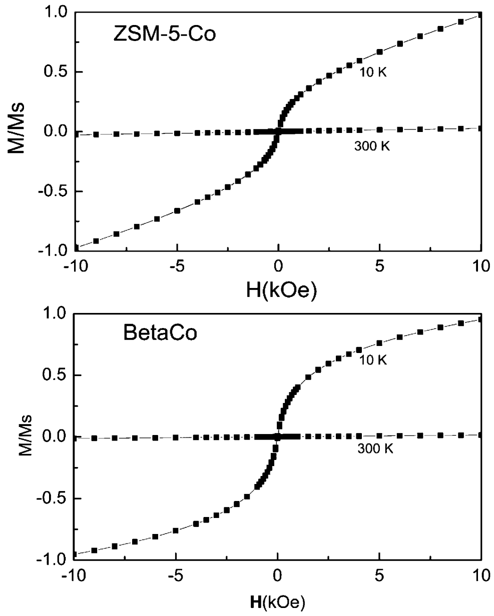

Fig. 3 Hysteresis loop at 10 K and 300 K for (top) ZSM-5-Co and (bottom) Beta-Co.

In conclusion, we have shown that by using a Co layered silicate (Co-magadiite) it is possible to synthesize Co-Beta and Co-ZSM-5 zeolites in which Co was incorporated in the framework. After calcination, clusters are formed with a size small enough to be undetectable by XRD or by high resolution electron microscopy. This facts together with the magnetization measurements suggest a narrow cluster size distribution which will be preserved until a certain cluster size where diffusion and growth lead to a log-normal distribution of sizes.

Owing to small size, monodispersity, chemical stability and the large amount of the clusters a superparamagnetic–paramagnetic phase transition below RT is easily observed in these samples when varying the temperature.

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