

# Nb-doped nano-hematites ( $\text{Fe}_{2-x}\text{Nb}_x\text{O}_3$ ): theoretical and empirical evidence of surface reactivity by *in situ* CO adsorption

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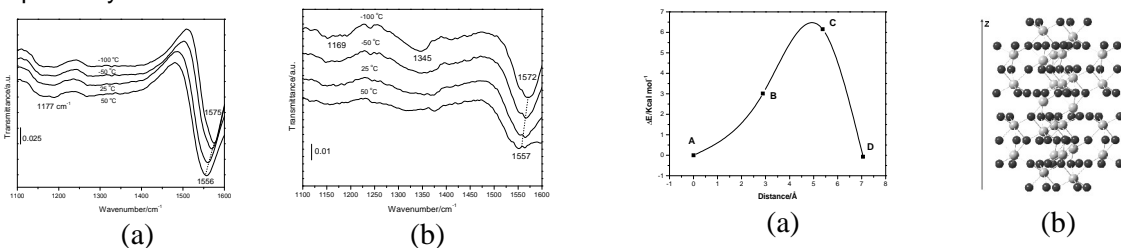
**Abstract:** A series of Nb-containing (nano)hematites,  $\text{Fe}_{2-x}\text{Nb}_x\text{O}_3$  (%Nb=0.00, 1.49, 5.00 and 9.24) was prepared using conventional co-precipitation method. Theoretical calculations and CO adsorption monitored by *in situ* infrared spectroscopy showed that the presence and the position of substituting niobium atoms in the structure of hematite modify its surface properties.

It has been observed that iron oxides such as magnetite, goethite and hematite are especially active for the oxidation reactions in aqueous medium. Traditionally, this activity was assigned to the formation of  $\text{Fe}^{2+}$  species in the magnetite structure, which can activate  $\text{H}_2\text{O}_2$ , by a Haber Weiss mechanism [1]. The activity of other iron oxide phases mainly hematite,  $\text{Fe}_2\text{O}_3$ , can be improved by the presence of different metals in the structure for decrease the particle size to nanometric dimension.

In this work, the introduction of niobium into the hematite structure was tested with the aim of producing a new active catalyst. The surface changes were studied by CO adsorption *in situ* and theoretical calculations.

For the CO adsorption tests, the catalyst powders were pressed into self-supporting 13 mm diameter discs weighing less than 20 mg. Those samples were placed inside a home-made quartz reactor and treated under vacuum at 400 °C for 2 h, after which the temperature was set to either -100, -50, 25 or 50 °C to carry out the adsorption experiments. 10 Torr of CO was introduced in the cell for 20 min, after which it was evacuated for 20 min and infrared spectra of the adsorbed CO were recorded with a resolution of 4  $\text{cm}^{-1}$  using a Bruker Tensor 27 FTIR spectrometer in transmittance mode and a DTGS detector [2]. Figure 4 shows a close up of IR spectra in the carbonate region for the pure and Nb-doped hematite (Hm-Nb10) recorded at different temperatures. It is interesting to observe that those signals are more intensive in pure hematite data suggesting that the introduction of  $\text{Nb}^{5+}$  in the structure of hematite modify the surface properties of the catalysts with preferential formation of carbonates on pure hematite during the CO adsorption.

Theoretical calculations were carried out by using the Gaussian 98 package using Molecular mechanics and the Oniom approach [3]. Each structure was fully optimized at a Molecular Mechanics (MM) level with a UFF force field. The influence of the Nb position on the ground state potential energy surface (PES) was studied using single-point energy calculations with the Oniom approach at both UFF force field and pbe1pbe/SDD levels, with cluster geometries from the optimization procedure. The nature of the stationary point was established after each optimization. This same computational procedure has already been used successfully for similar systems [4]. In order to obtain the potential energy curves for the position change of the doping element, an Nb atom was placed in each of the four different Fe positions within the hematite structure, that is, in each of the four layers seen in that structure as taken from the American Mineralogist Crystal Structure Database and shown in Figure 2b [5]. According to the results from those calculations, shown in Figure 2a, there is a stable state for Nb atoms at the topmost layer of the material (layer A). Interestingly, Figure 2a shows energy barriers of 3.01 and 6.15  $\text{kcal.mol}^{-1}$  for the Nb ion to travel inside the channel defined by Fe position within layers B and C, at 3.5 and 5.5 Å from the top layer, respectively.



**Figure 1:** FTIR spectra of pure (a) and Nb-doped hematite (Hm-Nb10) (b) in the carbonate region after addition of CO.

**Figure 2:** Potential Energy Curve obtained of hematite structure doped with Nb in the A, B, C and D (A) and structure of pure hematite, showing its four (A, B, C and D) layers. The gray and black balls correspond to iron and oxygen ions, respectively. Carvalho, M.S. Nazzarro, K. Sapag, Chem. Phys. Lett. 446 (2007) 133.

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