

Synthesis and characterization of nanoparticles of iron oxide supported on aluminium and silicon oxide by polymeric precursor method.

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Abstract – Iron oxide dispersed on Al or Si oxides were prepared via a polymeric precursor derived from the Pechini method. The catalysts were characterized by DRX and MS. The presence of nanoparticles of iron oxide, aluminum and silicon oxide was observed by X-ray diffraction. The presence of hematite and maghemite superparamagnetic were confirmed by Mössbauer spectra.

The materials were synthesized by the polymeric precursor method [1]. This method is based on the chelation of cations (metals) by citric acid in a water solution. Aluminum nitrate nonahydrate, iron nitrate nonahydrate, tetraethylorthosilicate (TEOS), citric acid (CA) monohydrate, and ethylene glycol (EG) were used as starting chemicals. A CA/metal ratio of 1.5:1 (mol) was used for all the samples. The metal amount is the sum of Fe, Al and/or Si. The mass ratio of CA/EG was kept at 2:3. Samples with different Fe to Al and Fe to Si molar ratios were prepared and labeled FeAl-X and FeSi-X, where X denotes the Al:Fe and Si:Fe molar ratio.

The results of X-ray diffraction analysis (DRX) are presented in Figure 1. The FeAl-14 catalyst presented the profile of an amorphous solid, whereas the FeAl-4 sample showed broader peaks, which can be assigned to a small crystal size. The 2- θ degree value of the broader peaks and the relative intensities, suggests Al₂O₃ phase formation for the FeAl-4 sample. On the other hand, the FeSi-12 and FeSi-3 catalysts showed the pattern of hematite (α -Fe₂O₃, JCPDS 86-2368). Additionally, the FeSi-3 sample profile point to the maghemite phase (γ -Fe₂O₃, JCPDS 39-1346) formation.

This apparent aluminum influence in the hematite crystallization can be assigned to the ionic radii. The radii of Al³⁺ (0.53 Å) species is closer to the radii of Fe³⁺ (0.67 Å) species, if compared to Si⁴⁺ (0.39 Å). The similar ionic radii enable the insertion of Al³⁺ into the lattice in place of Fe³⁺, which makes the hematite crystallization difficult. Nevertheless, if the hematite phase is formed in the FeAl-14 and FeAl-4 samples, its crystal size is very small. The average crystallite diameter of the different phases estimated with the Scherrer's formula, showed the phases with a particle size between 4.0 and 13.0 nm for the different samples.

The local environment of iron atoms in the iron-containing samples was investigated by Mössbauer spectroscopy. The room temperature spectra obtained for samples FeAl-4 and FeSi-3 (Figure 2) show similar features with a central doublet suggesting that iron is in a superparamagnetic state. For the sample FeSi-3, on the other hand, two six line-subspectra are observed. One of them, with isomer shift relative to α -Fe $\delta = 0.25$ mm s⁻¹, quadrupole shift $\epsilon = -0.20$ mm s⁻¹, and magnetic hyperfine field $B_{hf} = 51.1$ tesla is assignable to maghemite, while the other sextet is due to hematite phase.

The synthesis method used in this enable the preparation of materials containing nanoparticles of iron oxide which present a superparamagnetic phenomenon.

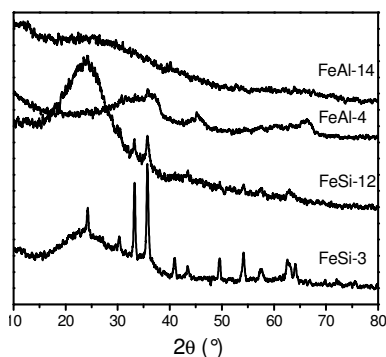


Figure 1: X- ray diffraction profile after calcinations.

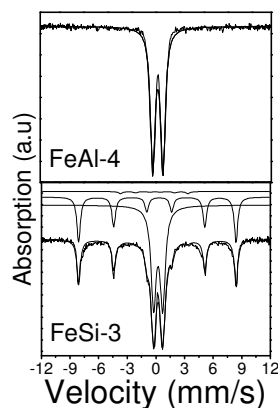


Figure 2: ⁵⁷Fe Mössbauer spectra at room temperature.