

Comparative Evaluation of Mn Substitution in a Framework Site in MnAPSO-34 and Mn-impregnated SAPO-34 Molecular Sieves Studied by Electron Spin Resonance and Electron Spin-Echo Modulation Spectroscopy

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Abstracts: MnAPSO-34 and Mn-impregnated SAPO-34 (Mn-SAPO-34) sample were prepared with various manganese contents and studied by electron spin resonance (ESR) and electron spin-echo modulation (ESEM). Electron spin-echo modulation analysis of 0.07 mol % Mn (relative to p) in MnAPSO-34 with adsorbed D₂O shows two deuteriums at 0.25 nm and two at 0.36 nm from Mn. This suggests that two waters hydrate an MnO₄ configuration with a D-O bond orientation for the waters as expect for a negatively charged site at low manganese content (0.07 mol%), the ESR spectra of MnAPSO-34 and MnH-SAPO-34 exhibit the same parameters ($g \approx 2.02$ and $A \approx 87$ G), but the spectra obtained from MnAPSO-34 samples are better resolved. TGA of as-synthesized MnAPSO-34 shows that the decomposition temperature in the range 200-600 °C of the morpholine is 12 oC higher than that in as-synthesized MnH-SAPO-34. Infrared spectra shows that the position of a band at about 15 cm⁻¹ toward higher energy in MnAPSO-34 versus MnH-SAPO-34. The modulation depth of the two-pulse ESE of MnAPSO-34 with adsorbed D₂O is deeper than that of MnH-SAPO-34 with adsorbed D₂O. Three-pulse ESEM of MnAPSO-34 and MnH-SAPO-34 with adsorbed deuterium oxide shows that the local environments of manganese in the hydrated samples are different, suggesting that Mn(II) is framework substituted in MnAPSO-34 since it obviously occupies an extra-framework position in MnH-SAPO-34

Referance

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