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POSTER PRESENTATION

410 TH

NMR SPECTROSCOPY OF INDOMETHACIN MOLECULES EMBEDDED WITHIN THE MESOPORES OF SILICATES AND METAL-ORGANIC FRAMEWORKS

Gregor Mali, Tomaž Čendak, Emanuela Žunkovič, Tina Ukmar Godec, Venčeslav Kaučič

National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia
EN-FIST Centre of Excellence, Dunajska 156, SI-1000 Ljubljana, Slovenia

Solid-state NMR spectroscopy provides a unique tool for studying the structural properties of the mesoscopically confined drug, and for studying the drug-drug and drug-matrix interactions. We demonstrated this in model drug-delivery systems prepared from non-functionalized and functionalized SBA-15 mesoporous silicate matrices [1,2], Cr-, Fe-, and Al-based MIL-101 metal organic frameworks, and Al-based MIL-53 metal organic frameworks, loaded with different amounts of indomethacin molecules. In the SBA-15-based drug-delivery systems ¹H MAS and ¹H-¹³C CPMAS NMR spectroscopy indicated that only when concentration of indomethacin within the mesopores becomes sufficiently high (when the mass fraction of indomethacin within the sample exceeds 0.15), hydrogen bonds between the drug molecules become abundant. Nitrogen sorption analysis and comparison of ¹H spin-lattice relaxation times in progressively loaded SBA-15 matrices suggested that at low loading concentrations indomethacin forms a layer on the silicate walls of the mesopores, and that at moderate or high loading concentrations rigid nanoparticles that extend throughout the entire mesopore cross-section are formed. ¹H-¹³C CPMAS NMR spectrum of indomethacin embedded within the mesopores of SBA-15 closely resembled the spectrum of the bulk amorphous indomethacin and did not allow to draw firm conclusions about the molecular conformation and the packing of the drug molecules within the pores. On the contrary, variable-temperature ¹H spin-lattice relaxation measurements showed that the mesoscopically confined indomethacin is significantly different from the bulk amorphous indomethacin. It does not become rubbery and it exhibits a solid-solid transition at 363 K that is similar to the phase transition of the crystalline indomethacin solvate with tetrahydrofuran. In MIL-101- and MIL-53-based drug-delivery systems, in addition to the structural and dynamical information about the incorporated indomethacin molecules, ¹H MAS and ¹H-¹³C CPMAS NMR experiments provided a very convenient way for the determination of the amount of the loaded drug.

[1] T. Ukmar, A. Godec, O. Planinšek, V. Kaučič, G. Mali, M. Gaberšček, *Phys. Chem. Chem. Phys.*, 2011, 13, 16046-16054.

[2] T. Ukmar, T. Čendak, M. Mazaj, V. Kaučič, G. Mali, *J. Phys. Chem. C*, 2012, 116, 2662-2671.

411 MO

FERROMAGNETISM IN ANNEALED Ce_{0.95}Co_{0.05}O₂ and Ce_{0.95}Ni_{0.05}O₂ NANOPARTICLES

S. K. Misra,^a S. I. Andronenko,^b J. D. Harris,^c A. Thurber,^d G. L. Beausoleil II^d and A. Punnoose^d

^aConcordia University, Montreal, QC H3G 1M8, Canada, ^bKazan Federal University, 420008, Kazan, Russia, ^cNorthwest Nazarene University, Nampa, Idaho 83686, USA, ^dBoise State University, Boise, Idaho 83725, USA

This paper reports an investigation on the role of transition-metal ions in producing ferromagnetism in CeO₂ nanoparticles by electron paramagnetic resonance (EPR). Several samples of CeO₂ nanoparticles annealed at 200, 300, 400, and 500° C, doped with 5% Ni and 5% Co ions, characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetry analysis (TGA) and mass spectroscopy (MS), investigated by X-band EPR at 4, 10 and 300 K, and by magnetometry at 300K. Magnetic properties and EPR/FMR (Ferromagnetic Resonance) spectra of these nanoparticle samples were found to depend strongly on the annealing temperature (T_a), oxygen stoichiometry, and dopant-ion species. Different behavior of saturation magnetization in the samples with the dopants, Co and Ni, is found to be due to different - inward and outward - surface diffusion of these impurity ions, respectively, during annealing. Most notable features of the present study are as follows. (i) A detailed simulation of EPR/FMR spectra of isolated Co and Ni ions carried out here provides in-depth details on the role of the doped ions and oxygen (O[•]) defects played in the observed magnetic properties. More details on the spins and the corresponding spin-Hamiltonian parameters for the transitions metal ions Ni and Co present in the samples are found. This, in turn, helps to understand the role of the doped ions and oxygen (O[•]) vacancies on the observed magnetic properties. (ii) The various mechanisms of occurrence of ferromagnetism in Co- and Ni-doped CeO₂, as well as coexistence of ferromagnetic and paramagnetic phases in these samples have been unraveled. (iii) A model for the formation of superparamagnetic state in the sample of CeO₂, doped with 5% Ni, has been proposed here. (iv) EPR and TGA-MS data provide evidence for increased formation of oxygen vacancies as the annealing temperature, T_a, increases. This plays a major role in the magnetic properties of the annealed samples. (v) Different behaviors of saturation magnetization in the samples doped with Co ions as compared to those with Ni ions, from 200 to 400 C, are interpreted to be due to different - toward and outward surface diffusions, respectively, of these impurity ions during annealing.