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Magnetic properties of mesoporous cobalt–silica–alumina ternary mixed oxides

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ABSTRACT

Mesoporous cobalt–silica–alumina mixed oxides with variable cobalt content have been synthesized through slow evaporation method by using Pluronic F127 non-ionic surfactant as template. N_2 sorption analysis of the template-free mixed oxide samples revealed that these mesoporous materials have high BET surface areas together with large mesopores. Powder XRD, TEM, EDS, FT IR and EPR spectroscopic analysis have been employed to understand the nature of the mesophases, bonding and composition of the materials. Low temperature magnetic measurements of these mixed oxide materials show the presence of ferromagnetic correlation at elevated temperature though at low temperature paramagnetic to ferrimagnetic transition is observed.

1. Introduction

Aluminosilicate based materials have attracted wide-scale interest in different fields of research such as optical telecommunication [1,2], manufacturing of bioactive materials and heterogeneous catalysis for many decades [3,4]. In this context it is interesting to note that the porous materials containing heteroatoms like Mo, Mn, Co, Fe, Cu, Ti, Zn, Sn, etc. in their frameworks are able to improve the physical and chemical properties of the respective composite materials and the resulting material could be utilized in advanced applications like, catalytic transformations, biological activity, gas sensing, adsorption of heavy metals or molecules and so on [5–12]. In this context the magnetic properties of cobalt–silica–alumina mixed oxides are of particular interest from the view point of magnetic interactions between randomly distributed magnetic moments [5]. Various glassy materials containing transition metals like Mn, Fe, Co, Cu, etc. have been investigated for this purpose over the years [13–23]. These materials show remarkable similarity in the high temperature magnetic behavior, which follows Curie–Weiss law. The dominant magnetic interactions are of an antiferromagnetic or ferromagnetic in nature. In the low temperature region the Curie–Weiss law is deviated. At very low temperatures, the mixed oxide materials containing magnetic elements often manifest spin glass behavior [19–21] and superparamagnetic [18] features. The magnetic moments are sensitive to the metal ion concentration and also its local environment [14,24–26]. Hence, the magnetic and electron spin resonance measurements of mesoporous cobalt–silica–alumina ternary mixed oxides synthesized through the evaporation induced self-assembly (EISA) method would be a new addition in solid state chemistry research on ternary mixed oxide systems.

Here we report the magnetic studies of two cobalt–silica–alumina mixed oxide samples MCSA-121 and MCSA-141 with different cobalt loading, namely 21 mol% and 16 mol% of CoO in the aluminosilicate matrix. Based on the atomic ratios of the compositions Co:Al:Si: 1:2.22:2.64 and 1:1.74:4.38 as determined from the energy dispersive X-ray analysis, the cobalt content in MCSA-121 and MCSA-141 samples are 21 and 16 mol%, respectively. Accordingly the nominal composition of cobalt–silica–alumina ternary mixed oxides will be $(CoO)_{0.21}$–$(Al_2O_3)_{0.23}$–$(SiO_2)_{0.56}$ and $(CoO)_{0.16}$–$(Al_2O_3)_{0.14}$–$(SiO_2)_{0.70}$. Interestingly, we observed the existence of predominant ferromagnetic correlations at higher temperature, which is not common in mixed oxide systems. This observation is unique in these mesoporous cobalt–silica–alumina ternary mixed oxide materials. At lower temperatures there is a paramagnetic to ferromagnetic or canted antiferromagnetic transition. Based on our experimental observations, here we have suggested the formation of magnetic clusters in mesoporous cobalt–silica–alumina ternary mixed oxide pore walls, which freezes below 10 K.

2. Experimental

2.1. Material synthesis

The two mesoporous SiO_2–Al_2O_3–CoO samples MCSA-121 and MCSA-141 were prepared using Pluronic F127 template ($EO_{106}PO_{70}$

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EO_{106}, M_{av}=12,600) along with $Co(NO_3)_2$, tetraethyl orthosilicate (TEOS), $Al(O^iPr)_3$ (aluminum iospropoxide) as Co, Si, and Al sources, respectively. The detailed experimental procedure is reported in our previous report on mesoporous cobalt–silica–alumina mixed oxide material [12]. In a typical synthesis (for MCSA-121), 2.3 g of F127 (Sigma-Aldrich) surfactant was dissolved in 15 ml of absolute ethanol mixed with 20 mmol of glacial acetic acid (AcOH, E-Merck) and 12 mmol of 35% hydrochloric acid (HCl, E-Merck). After 1 h 2.5 mmol of cobalt salt (Loba Chemie, India) was added to this solution along with constant stirring. This was followed by the addition of 5.0 mmol TEOS (Sigma-Aldrich) with vigorous stirring for about 1 h. Finally, 2.5 mmol of $Al(O^iPr)_3$ (Loba Chemie, India) was added and the mixture was stirred for another 8 h at room temperature. Molar ratio of the mixture was Co:Si:Al=1:2:1. Then the resulting sol was allowed to evaporate at 313–323 K temperature under air for 7 days. The solid as-synthesized material was calcined at 673 K in air for 6 h to obtain the mesoporous MCSA-121 material. MCSA-141 material was synthesized in a similar procedure keeping Co:Si:Al atomic ratio 1:4:1 in the synthesis gel. Both cobalt–silica–alumina mixed oxide samples were heated at 1273 K to obtain crystalline spinel oxide phase.

2.2. Material characterizations

Crystallographic phases present in the samples were analyzed from the powder X-ray diffraction (XRD) patterns taken in a Bruker AXS D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample using Ni-filtered Cu$K\alpha$ (λ=0.15406 nm) radiation. A JEOL JEM 2010 transmission electron microscope was used to record transmission electron microscopy (TEM) images. BET surface area and nitrogen sorption isotherms were obtained using a Beckmann Coulter SA 3100 surface area analyzer at 77 K. Surface chemical compositions of two mesoporous cobalt–silica–alumina ternary mixed oxide samples were taken in an energy dispersive X-ray (EDS) spectrometer attached with a JEOL JEM 6700F field emission scanning electron microscope (FE SEM). Fourier transform infrared (FT IR) spectra of these samples were recorded on KBr pellets by using a Shimadzu FT IR 8300 spectrophotometer. X-Band electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectrum was recorded in a JEOL electron spin resonance spectrometer at room temperature and the corresponding EPR simulation was carried out by using the software provided with it. Magnetic measurements were carried out on powdered samples taking in parafilm capsule in the temperature range 2–300 K on a Quantum Design SQUID MPMS-XL magnetometer.

3. Results and discussions

3.1. Mesophase characterization

The physicochemical properties of both the cobalt–silica–alumina ternary mixed oxide materials are shown in Table 1. Small angle powder XRD patterns (not shown) suggested the existence of mesophases for the MCSA-121 and -141 samples [27]. On the other hand the N_2 adsorption–desorption analysis at 77 K revealed existence of mesopores of dimensions ca. 8.2 and 9.8 nm together with BET surface areas of 248 and 372 $m^2\,g^{-1}$ for samples MCSA-121 and -141, respectively. Details of adsorption isotherms and mesophase characterizations are given in our previous report [12].

3.2. Wide angle powder XRD analysis

In Fig. 1 wide angle powder diffraction patterns of the mesoporous cobalt–silica–alumina ternary mixed oxide materials are shown. The powder XRD data suggests that both MCSA-141 and MCSA-121 materials are crystalline in nature after high temperature heat treatment (1273 K). But these materials are amorphous after low temperature calcination (673 K, XRD pattern not shown). Identical crystalline phase is generated in both cases on high temperature heating (1273 K, spinel structure of $CoAl_2O_4$ (JCPDS no. 01-070-0753)) having face-centered cubic lattice (space group: $Fd3m$) with the unit cell parameter a=0.8095 nm. Possibly spinel $CoAl_2O_4$ structure is the most stable phase than the alumnosilicate phases with these chemical compositions. Since the MCSA-121 and -141 samples with silica concentrations of 1:2 yield same spinel structure $CoAl_2O_4$ on heating at 1273 K, this result suggested there is almost no effect of Si concentration on the crystalline phase that formed on high temperature calcinations of the mesoporous mixed oxide samples.

3.3. TEM image analysis

The TEM image of a representative MCSA-141 sample has been displayed in Fig. 2. From this TEM image it is evident that poorly ordered 2D-hexagonal mesophase with the pore channels run in one direction [28,29]. Estimated average dimension of pores is ca. 9.5 nm throughout the specimen and this result resembles well with the pore width obtained from N_2 sorption analysis.

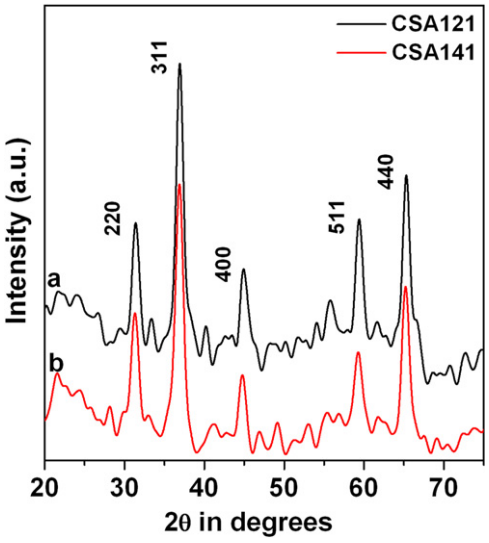

Fig. 1. Powder XRD patterns of MCSA-121 (a) and MCSA-141 (b) heated at 1273 K.

Table 1
Physicochemical data of all the mesoporous cobalt–silica–alumina ternary mixed oxides.

Sample name	*d* Spacing from XRD (nm)	BET surface area ($m^2\,g^{-1}$)	Pore volume (ccg^{-1})	Pore diameter (nm)	Wall thickness (nm)	Co:Si:Al synthesis gel	Co:Si:Al product (EDS)
MCSA-121	16.35	247.85	0.68	8.16	8.19	1:2:1	1:2.64:2.22
MCSA-141	14.01	372.63	0.66	9.80	4.21	1:4:1	1:4.38:1.71