

Local environment of manganese incorporated in mesoporous MCM-41

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Abstract

Manganese containing MCM-41 was synthesised by the direct hydrothermal method (DHT) in the presence of cetyltrimethylammonium chloride (CTACl) as a template. The local environment of manganese incorporated in mesoporous silicate MCM-41 was investigated by XAS (X-ray Absorption Spectroscopy). XANES (X-ray Absorption Near Edge Structure) studies showed the coexistence of Mn²⁺ and Mn³⁺ cations in both, as-synthesised and template-free MnMCM-41 samples. The major part of manganese cations in the as-synthesised MnMCM-41 was Mn²⁺, while in the template-free MnMCM-41 the amount of Mn³⁺ was increased. EXAFS (X-ray Absorption Fine Structure) analyses revealed that major part of manganese cations in the as-synthesised MnMCM-41 were extra-framework with the Mn–O distance of 2.19 Å. Manganese cations in the template-free MnMCM-41 were incorporated into the framework and coordinated to three oxygens in the first coordination shell, with two of them at a shorter distance of 1.92 Å and one at a longer distance of 2.21 Å. Pulsed ESR (Electron Spin Resonance) and ESEEM (Electron Spin-Echo Envelope Modulation) investigations were in agreement with the XANES and EXAFS results.

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1. Introduction

Mesoporous silicates with pore openings from 2 to 10 nm are used as heterogeneous catalysts in oxidation reactions [1]. The incorporation of transition metals into their framework generates catalytically active acid sites. Catalytic properties of transition metal-functionalised

mesoporous silicates depend on the structure type, location and nature of the incorporated metal [1].

MCM-41 is a silicate material with unidimensional mesopores and pore openings of about 4 nm [2,3]. Functionalisation of MCM-41 by manganese leads to the effective heterogeneous catalyst for the epoxidation of styrene and stilbene with tert-butyl hydroperoxide (TBHP) [4]. Zhang et al. [4] characterised the local environment of MnMCM-41 synthesised by the direct hydrothermal (DHT) and template ion exchange (TIE) methods. The results suggested that Mn²⁺ and Mn³⁺ coexisted in the MnMCM-41 samples synthesised by

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both methods and a large part of manganese atoms could be incorporated into the framework of MCM-41 obtained by the DHT method. The coexistence of Mn^{2+} and Mn^{3+} cations was determined by X-ray Absorption Near Edge Structure (XANES) [4] and also by Electron Spin Resonance (ESR) [4,5]. Framework Mn^{2+} was detected in MnMCM-41 synthesised by the DHT method under mild alkaline conditions [5]. The authors suggested that the calcination in air might result in the oxidation of framework Mn^{2+} to framework Mn^{3+} besides the presence of extra-framework Mn^{2+} . Additionally, it was suggested that during reduction at high temperature, extra-framework Mn^{2+} ions might come closer to each other and migrate to framework ions, resulting in extra-framework-framework Mn^{2+} interactions [5]. Framework and extra-framework Mn^{2+} in MnMCM-41 was also determined by Electron Spin Echo Modulation (ESEEM) [6] and Electron-Nuclear Double Resonance (ENDOR) [7]. One Mn^{2+} framework and two Mn^{2+} extra-framework species were identified in MnMCM-41 synthesised by DHT under alkaline conditions [6]. Extra-framework hexa-coordinated Mn^{2+} and framework Mn^{2+} with distorted tetrahedral coordination were distinguished in MnMCM-41 synthesised by DHT under acidic conditions [7].

This paper reports for the first time on the local environment of Mn^{3+} present in MnMCM-41 synthesised by DHT method. XANES studies were used for the identification of the average oxidation number of manganese in as-synthesised and template-free MnMCM-41. EXAFS analysis was used for the determination of the first coordination sphere of manganese in as-synthesised and template-free MnMCM-41. Pulsed ESR and ESEEM studies of local environment of Mn^{2+} are also presented as a support to the XANES and EXAFS analyses [4].

2. Experimental

2.1. Synthesis

MnMCM-41 was synthesised hydrothermally from a gel with the following molar composition: 0.875 Na_2O :0.2 MnO :3.8 SiO_2 :7.2 CTACl (cetyltrimethylammonium chloride): 844 H_2O . The gel was prepared as follows: The 4.22 g of sodium silicate (Aldrich, SiO_2 : $\text{Na}_2\text{O} = 27\%:7\%$) was diluted in 5 g distilled water. 0.25 manganese acetate (Fluka, $(\text{CH}_3\text{COO})_2\text{Mn} \times 4\text{H}_2\text{O}$) was diluted in 22.5 g of distilled water. Manganese acetate was added dropwise to sodium silicate. The resulting mixture was blended using the magnetic stirrer for 10 min. 46.08 g CTACl (Aldrich, $[(\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3)]\text{Cl}$ 25%) was added to the solution. The pH was adjusted to 11 using 50% water solution of H_2SO_4 . Eleven grams of distilled water was added to the gel (pH = 11) and blended for 30 min. The resulting

gel was transferred to a 45-ml stainless-steel teflon-lined autoclave and heated under static conditions in an oven. After 1 day at 100 °C the crystallisation was completed and the MnMCM-41 product was washed three times with distilled water and dried at 70 °C. The as-synthesised MnMCM-41 was converted to a template-free material by heating at 540 °C in an oxygen flow for 5 h by using a heating rate of 1.5 °C/min. The light pink colour of the as-synthesised MnMCM-41 changed to light brown after the calcination.

2.2. Characterisation

X-ray powder diffraction (XRPD) patterns of as-synthesised and template-free products were collected on a Siemens D-5000 diffractometer using $\text{CuK}\alpha$ radiation at room temperature. The XRPD data were collected in the 2θ range from 1° to 10° in steps of 0.02° with 30 s per step.

The size and morphology of particles in the as-synthesised and template-free material were studied with a scanning electron microscope JEOL JSM 5800. The arrangement of channels in the mesoporous material was investigated by using high-resolution transmission electron microscopy (HRTEM) and the chemical composition of the samples was analysed using energy-dispersive spectroscopy (EDS). Specimens for TEM studies were prepared by ultrasonic dispersion of the material in distilled water and then mounted on a holey carbon grid. The specimens were additionally evaporated with carbon in order to prevent charging under the electron beam. TEM analyses were performed on a 200-kV field-emission gun (FEG) microscope (JEM 2010F UHR, JEOL), equipped with a Si(Li) detector for energy dispersive spectroscopy (EDS), fitted to an atmospheric thin window EDS spectrometer (Link ISIS 300, Oxford Instruments).

X-ray absorption spectra of as-synthesised MnMCM-41, template-free MnMCM-41 and reference compounds (Mn^{2+}O , $\text{K}_3[\text{Mn}^{3+}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, and Mn^{4+}O_2), were measured in the energy region of the Mn K-edge in transmission mode at the E4 beamline of the HASYLAB synchrotron facility at DESY in Hamburg, Germany. The beamline provided a focused beam from an Au-coated toroidal mirror and a Si(111) double crystal monochromator with about 1 eV resolution at the Mn K-edge. Harmonics were effectively eliminated by a plane Au-coated mirror, and by a slight detuning of the monochromator crystals, keeping the intensity at 60% of the rocking curve with the beam stabilisation feedback control. MnMCM-41 samples and reference compounds were prepared as self-supporting pellets with absorption thickness (μd) of about two above the Mn K-edge. The pellets were mounted on a sample holder in a high vacuum chamber of the beamline. The Mn K-edge jump in case of

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