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Preparation, characterization and catalytic behavior in methanol decomposition of nanosized iron oxide particles within large pore ordered mesoporous silicas

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Abstract

Nanosized iron oxide particles within various ordered mesoporous silicas (SBA-15, SBA-16, Fm3m, Ia3d) have been prepared from the corresponding nitrate and acetylacetonate precursors. N_2 physisorption, X-ray diffraction and Moessbauer spectroscopy are used for their characterization. The reductive properties of the modified materials were investigated by temperature-programmed reduction with hydrogen. Methanol decomposition to H_2, CO and methane was used as a test reaction. Some differences in the iron state, its phase transformations in reductive medium and also some variations in its catalytic behavior were observed and discussed in view of the iron oxide particle size dispersion and its dependency on the pore geometries of the silica supports.

Keywords: Nanosized iron oxide; Large pore mesoporous silicas; TPR; Moessbauer spectroscopy; Methanol decomposition

1. Introduction

Ordered mesoporous silicas have gained a considerable interest due to their promising application prospects in high-tech applications in such diverse fields as electronics, catalysis, separation and sensing, to name a few [1–21]. The reasons for this are obvious, these materials can be synthesized with different pore sizes and pore geometries, they exhibit high specific surface areas and pore volumes, can easily be surface modified and are normally thermally stable [11–21]. A very flexible means of synthesizing large pore silicas with different pore geometries and pore sizes is the use of triblock copolymers as structure directing agents under acidic conditions [15,22–26]. Much efforts have been made to characterize the potential mesopore interconnectivity in mesoporous silica, and a number of methods have been used for the purpose, such as high-resolution transmission electron microscopy, Pt and carbon replication, selective pore blocking chemical modification, monitoring of pore accessibility after modification of the pore surface with various ligands, adsorption of molecules with different sizes and analysis of adsorption and desorption branch of the corresponding isotherms [27–33]. There are now solid proofs for the existence of a bimodal (micro and meso) porosity in the triblock copolymer templated silicas with micro and/or mesopores located within the silica walls. A number of different mesostructures have been synthesized, including SBA-15 with two-dimensional (2D) hexagonal arrangement of uniform cylindrical mesopores [34–38], the cubic large mesopore silica structure Ia3d exhibiting two independent interpenetrating networks of pores [22,23], SBA-16, belonging to the Im3m space group with a body centered cubic arrangement of spherical pores

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connected through smaller pore aperture [15,24,25], and Fm3m, with a similar, but face-centred cubic arrangement of pores [26].

Among the various applications, it was also reported that mesopore silicas are perspective supports for the formation and stabilization of nanosized metal/metal oxide particles and number of reports aim at their preparation and characterization [39–45]. It was shown that these composite materials of nanometer scale are of considerable interest for the development of advanced quantum confined electronic and optical devices, and also as catalysts [10]. In principle, the properties of the loaded species are often discussed in view of their strong interaction with the support. This effect depends on various factors such as the size of metal/metal oxide particles, their distribution within the support and the nature and textural characteristics of the porous structure as well. The catalysts behavior is rather complicated due to the fact that their final, usually stable state forms not only during the preparation procedure, but also in the course of the catalytic reaction caused by the interaction with the reaction medium. It was shown, that nanometer sized iron particles, supported on mesoporous silicas exhibit high catalytic activity and stability in various catalytic reactions [39,46–48]. In our previous investigation we demonstrated that the selectivity of methanol decomposition of iron modified mesoporous materials (M41S, SBA-*n*, CMK-*n*) depends strongly on the iron nanoparticle dispersion, the latter being regulated by the pore size of the support [49–53]. Under the reductive catalytic medium, phase transformations to magnetite combined with a high selectivity to methane were found for the finely dispersed hematite particles, while formation of metallic iron and/or iron carbide were observed for the samples containing larger particles, leading to a high selectivity to CO and hydrogen. It was therefore suggested that methanol conversion to H_2, CO and/or methane could be used as a test reaction for the elucidation of the loaded iron particles dispersion, and could also give very useful information about the silica pore architecture [49–53]. Furthermore, there is considerable interest in methanol decomposition to various products such as H_2, CO, methane, etc. due to the potential application as an alternative source for effective and ecological fuel or for the synthesis of valuable products for the chemical industry [54–57].

In the present study we discuss the state of iron oxide species obtained by different iron precursors from an aqueous or organic medium within the pore system of various ordered mesoporous silicas with cage- (SBA-16, Fm3m) or channel-like (SBA-15, Ia3d) structures. The aim is to give further support for the usefulness of using methanol decomposition for probing the state of the iron oxide particles and to gain information about the influence of iron oxide precursor and support architecture on the overall iron oxide state. Furthermore, special attention is paid to phase transformations occurring under reductive medium.

2. Experimental

2.1. Material

Parent mesoporous silicas of SBA-15 (SB15), SBA-16 (SB16), Fm3m (Fm) and Ia3d (Ia) type were synthesized as in Refs. [15,22,26]. The template free materials were impregnated with either:

(i) an aqueous solution of 0.025 M $Fe(NO_3)_3$ and dried in a rotary evaporator at 313 K; or (ii) a chloroform solution of 0.025 M Fe(III)-acetylacetonate and dried in a rotary evaporator at room temperature.

The metal content of all modified samples was about 6 wt.% iron modified analogues obtained on the base of mesoporous silicas MCM-41 and MCM-48 (standard procedure of synthesis [42], BET surface area of 1000–1300 m^2/g, pore volume of 0.8–0.9 $\times 10^{-6}$ m^3/g), were used as reference samples. Their preparation, physicochemical characterization and catalytic properties in methanol decomposition to H_2, CO and methane were widely discussed in [49,50,58]. In order to elucidate the effect of pore architecture more precisely, here reference samples with similar iron particle sizes distribution were studied (see Section 3.4). Before the characterization all samples were pretreated in a flow of air (60 ml/min) at 773 K for 2 h and they were denoted as initial samples.

The samples will be referred as Fe/S(N) or Fe/S(A), where S is the symbol of the corresponding silica support and the capital letter in the brackets represents the precursor used (nitrate—N or acetylacetonate—A, respectively).

2.2. Methods of investigation

Small-angle X-ray scattering (SAXS) and powder X-ray diffraction (XRD) measurements were performed on a Kratky compact small-angle system with CuKα radiation (wavelength $\lambda = 1.542$ Å). The N_2 physisorption was determined at 77 K using a Micromeritics ASAP 2010 sorptometer. The samples were outgassed at 423 K for 12 h before measurements. NLDFT calculations were performed using Autosorb 1 for Windows 1.25 software (Quantachrome Instruments) [59].

The TPR-TGA (temperature-programmed reduction-thermogravimetric analysis) investigations were performed in a Setaram TG92 instrument. Typically, 40 mg of the sample were placed in a microbalance crucible and heated in a flow of 50 vol% H_2 in Ar (100 cm^3/min) up to 873 K at 5 K/min and a final hold-up of 1 h. Prior to the TPR experiments the samples were treated in situ in a flow of air up to 773 K at a rate of 10 K/min followed by a hold-up of 1 h.

The Moessbauer spectra were obtained in air at room temperature with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A $^{57}Co/Cr$ (activity ≅ 10 mCi) source and an α-Fe standard were used. The experimentally obtained spectra were fitted by the least