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The influence of preparation method on the structure and redox properties of mesoporous Mn-MCM-41 materials

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Abstract

Mesoporous silica materials modified by manganese have been prepared using surfactants containing different numbers of carbon atoms. Manganese has been introduced by the direct hydrothermal (HT), template ion-exchange (TIE) and impregnation methods. Structural properties have been investigated by the nitrogen adsorption–desorption, X-ray diffraction (XRD) and FT-IR studies. Redox properties have been investigated by the temperature-programmed reduction method (TPR) and transient CO oxidation reaction. It has been found that structural properties are strongly related to the type of surfactant used, the amounts and the way of Mn introduction. Large distortion effects are observed for samples prepared by the TIE method. Reducibility of the samples containing different pore dimensions and Mn loadings, prepared by TIE method, are very similar. Manganese oxide species in the catalysts of narrow pores and containing small amounts of manganese obtained by the HT and impregnation methods show low reducibility. During CO oxidation reaction some deactivation processes are observed for catalysts prepared by different methods and containing small amounts of Mn. A slight increase in activity for catalysts containing larger amounts of manganese is observed after high temperature treatment. Such changes are attributed to the interaction of manganese with silica and changes of oxidation state during thermal treatment.

Keywords: Manganese mesoporous silica materials; XRD; TPR; CO oxidation

1. Introduction

Since the discovery of the MCM-41 [1] and FSM-16 [2] in the early 1990s of the last century, great and fascinating progress has been made in the design, preparation, characterisation and application of mesoporous silica materials. Unique features of these materials are their regular structure, high surface area, extending 1000 m^2/g, and narrow pore size distribution in the range from 2 to 10 nm. Properties of these materials are easy to control using different preparation conditions, reagent ratios and thermal treatment conditions. In a typical synthesis of MCM-like materials silica skeleton is formed in a solution of suitable pH around self-assembled ionic or non-ionic surfactant micelles. Organic templates are removed by the calcination or extraction techniques [3,4]. It is well documented that pore diameter can be modelled using ionic surfactants with different numbers of carbon atoms in the hydrophobic alkyl chain [1,5], various oligomers or polymers as templates [6,7], suitable organic additives, such as 1,3,5-trimethylbenzene [8], as well as by the hydrothermal post-synthesis treatment [9,10].

Mesoporous silica materials have found wide application, e.g. in the adsorption processes and preparation of new nanostructured materials [11,12]. However, a real challenge is the application of these materials in the field of catalysis [13–17]. Attempts of improving the activity or thermal stability of pure silica materials have resulted in the preparation and successful application of a great number of new catalytic systems. The increase in thermal stability and changes of acid–base properties can be achieved by the incorporation of different ions, e.g. Al, Ti or Ga [18]. Modification of silica materials by addition of such ions as Cr, Fe, Co, V, Mo, Mn, Ru or Ce has yielded a new class of redox mesoporous catalysts [19–23]. In turn, the incorporation of small metal crystallites (e.g. Pt, Pd, Au, Ni or Cu) in the mesoporous silica materials has given interesting catalysts, utilised in the hydrogenation or oxidation reactions [24–27].

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A lot of attention has been paid to the preparation of hybrid inorganic–organic, very selective catalysts by introduction of various organic ligands. Different techniques have been developed for the preparation of modified silica mesoporous catalysts. In the direct hydrothermal method (HT), metal precursor is introduced directly into the synthesis mixture at the beginning of preparation process. In the template ion-exchange method (TIE), the metal ions are added into the as-synthesized silica material before template removal, and exchange the template cations. Finally the metal precursors can be introduced into the calcined silica materials (after complete removal of organic template) by simple impregnation techniques, chemical vapour deposition or more complex grafting methods.

The richness of the structures, oxygen mobility and often relatively low cost resulted in the wide applications and broad fundamental studies of the manganese catalysts [28,29]. Manganese is an active component of the redox catalytic systems, and can play either an oxidizing or reducing role ($Mn^{4+} \leftrightarrow Mn^{3+} \leftrightarrow Mn^{2+}$). The catalysts based on the bulk oxide systems, as well as supported catalysts, have been widely used in the deep and selective oxidation reactions of various organic compounds. These catalysts are utilised in the area of environmental chemistry, e.g. for abatement of volatile organic compounds or gaseous pollutants from combustion gases [30–32], and also in the field of organic synthesis, e.g. for selective oxidations of hydrocarbons or epoxidation of olefins [33,34]. Much attention has been focused on the preparation of complex catalytic systems containing manganese and noble metals such as Pd, Pt, Au or Ag [35–38].

After successful preparation of mesoporous pure silica materials several studies have been devoted to the introduction, characterisation and catalytic application of mesoporous manganese catalysts. Various techniques have been used for the preparation of such catalysts. In the DHT method manganese precursors such as chlorides [39,40], acetates [41–43] or nitrates [44] can be directly added to the synthesis mixture. Manganese has been also introduced by the TIE method developed by Iwamoto and co-workers [44–46]. Modification has also been performed using chemical vapour deposition method, e.g. by Caps and Tsang [47,48], or wet impregnation with different manganese salts [49]. A large number of papers have also been devoted to the incorporation of organic manganese complexes [50–56]. Mesoporous manganese catalysts have also been prepared using template assisted methods without silica, or using silica as the mesoporous template which is removed later by dissolution [57,58]. Such catalysts have been investigated in a broad range of catalytic oxidation processes, including epoxidation of styrene [44,51], olefins [53], oxidation of cyclohexane [41,55], ethylbenzene [42], styrene [56], sulfides [46], propene and CO [47], disproportionation of H_2O_2 [50]. In spite of extensive literature data, the influence of pore dimension on the redox properties of manganese oxide species in the mesoporous silica materials has not been widely studied. In the studies of Mn containing mesoporous silica catalysts the TPR technique is relatively rarely applied [48,59,60].

In the present paper, the structural and redox properties of the modified silica mesoporous materials containing different pore dimensions have been compared. Manganese has been introduced by three different ways. For characterisation of oxide species the TPR technique has been applied. This technique has been widely used in the studies of interactions between metal, oxygen and support in a large number of catalytic systems. As a simple catalytic test the CO oxidation reaction has been chosen. It is a well accepted opinion that the mechanism of carbon monoxide oxidation reaction is similar to that of hydrocarbon oxidation. It is often assumed that CO is chemisorbed on the surface of reducible oxide species, where it reacts with lattice oxygen, and then is desorbed as CO_2. The oxygen vacancy is filled up by adsorption of oxygen from the gas phase [47,61]. In our studies we have applied temperature-programmed technique with both temperature increase and decrease, which allowed us to observe some activation/deactivation processes.

2. Experimental

2.1. Catalyst preparation

Three series of materials characterised by different pore dimensions have been prepared. The silica MCM-41 materials have been synthesized using surfactant templates of different numbers of carbon atoms; dodecyltrimethylammonium bromide (MCM-41(12)), cetyl pyridinium chloride (MCM-41(16)), octadecyltrimethylammonium bromide (MCM-41(18)) and TEOS as silica source. In order to widen the pore diameters of MCM-41(18) materials 1,3,5-trimethylbenzene (TMB) was added to the reacting mixtures. The preparation procedure followed the method described in the literature [62]. In a typical synthesis of pure MCM-41 sorbent 6 g (MCM-41(12)), 7 g (MCM-41(16)) or 8 g (MCM-41(18)) of surfactant was dissolved in 360 cm^3 of distilled water. Ammonium hydroxide (25%) (30 cm^3) and weighed amount of TEOS (30 g) were added, and the mixture was stirred in thermostat for 1 h at 40 °C. The obtained product was filtered, washed with distilled water, dried at 80 °C for 2 h and calcined in air at 550 °C for 6 h.

The manganese ions were introduced to the catalyst by applying the direct hydrothermal synthesis, template ion-exchange [44,47] and wet impregnation techniques (Imp). In order to obtain materials with various metal contents different amounts of Mn precursor were added to the reacting mixtures. The obtained samples were coded A, B, C and D according to the increased loading. In the DHT method an aqueous solution of manganese(II) nitrate (1, 2 or 3 g of salt in 10 cm^3 of H_2O) as the metal ion precursor was added directly to the synthesis mixture before the hydrothermal process. Finally the product was filtered, washed, dried at 80 °C for 24 h and calcined in the same conditions as pure MCM-41 materials. In the TIE technique the template cations from the channels of the as-synthesized MCM-41 are exchanged with the metal ions in a solution. In the procedure to the as-synthesized MCM-41 sample an aqueous solution of manganese(II) nitrate was added