Catalytic performance of various mesoporous silicas modified with copper or iron oxides introduced by different ways in the selective reduction of NO by ammonia

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Abstract

Mesoporous silicas (MCM-48, SBA-15, MCF), reflecting various porous structures, were modified with copper and iron oxides by two different methods. For a first series of the samples the molecular designed dispersion (MDD) method using acetylacetonate complexes of copper and iron was applied for the deposition of transition metal oxides on the silica supports. A second series of the catalysts was obtained by the incipient impregnation technique using aqueous solutions of the suitable metal nitrates. The modified materials were characterized with respect to the texture (BET), composition (electron microprobe analysis), coordination of the transition metals (UV–vis–DRS) and surface acidity (NH_3-TPD, FTIR). The mesoporous silica supports modified with transition metal oxides were tested as catalysts of the selective reduction of NO with ammonia. The catalytic performance of the studied samples depended on the method used for the deposition of transition metal oxide as well as the kind of mesoporous silica used as a catalytic support. In general, the Cu-containing mesoporous samples effectively operated at lower temperatures than silicas modified with iron. The samples obtained by the MDD method have been found to be more active and selective compared to the analogous samples prepared by the impregnation technique. An introduction of water vapor into the reaction mixture only slightly decreased the NO conversion and selectivity towards N_2 over the MCF mesoporous silica modified with copper or iron oxide.
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1. Introduction

The surface structure of the heterogeneous catalysts is a great importance for their catalytic performance. The impregnation methods do not ensure always uniform surface morphologies in the preparation of metal oxide catalysts. For the catalytic processes, which demand high selectivity and activity, it becomes important to produce uniform surfaces. Such a possibility offers the method of the molecular designed dispersion (MDD) [1–7]. The MDD technique consists of two steps [8,9]. In a first step, metalorganic complex reacts with the hydroxyl group of silica support, while in a second step, the adsorbed surface complex is decomposed in an oxygen-containing atmosphere at elevated temperatures, forming supported metal oxide catalysts. Acetylacetonate complexes of metals seem to be a very interesting group of compounds, which can be used for the deposition of an active phase on silica supports by the MDD method. Molecules of metal acetylacetonates are characterized by a relatively small size, what is important in the case of the deposition of metal oxide into microporous and mesoporous supports. The next important feature of acetylacetonate complexes of metals is their high reactivity towards silanol groups. The interaction of metal acetylacetonate molecules with the support surface may occur according to two different mechanisms. Firstly, π-electrons of the acetylacetonate ligand can be involved in hydrogen bonding with the surface hydroxyl group [8,9]. Secondly, surface hydroxyl group may react with $M^{n+}(acac)_n$ molecule, resulting in the formation of a covalent bond between metal and surface oxygen and loss of a ligand as pentanedione (Hacac). The mechanism of the $M^{n+}(acac)_n$ interaction with the surface depends also on the stability and geometry of the complex [8,9],

as well as on the properties of the support material [10,11]. Mesoporous silicas, characterized by well-ordered mesoporous channels and large surface areas are very promising supports for the deposition of transition metal oxides.

This paper presents the study of the mesoporous silicas modified with transition metal (Cu, Fe) oxides as catalysts of the selective reduction of NO with ammonia. Three silica mesoporous supports, characterized by different porous structure were investigated. MCM-48 exhibits a surface area exceeding 1000 m^2/g and a very narrow pore size distribution in the mesoporous range (typically 2–10 nm). Moreover, it has a unique three-dimensional structure, which makes the pore system more available for reactant molecules [12,13]. The SBA-15 and MCF silicas are characterized by hexagonal ordering of pores with diameter in the range 5–13 and 15–40 nm, respectively [14]. These silicas, which possess thicker walls and higher thermal stability as compared to the other mesoporous silicas [15], are promising catalyst support materials.

Copper- and iron-containing catalysts have been found to be active and selective in the process of NO_x reduction with ammonia. However, catalytic performance of these metals depends on different parameters e.g. loading, dispersion, method used for their deposition and kind of support [e.g. 16,17]. Various catalytic systems based on pure, supported and mixed copper and iron oxides [16–19], as well as cation exchange zeolites [20,21] and pillared clays [22,23] have been tested in this process. In general, the Cu-containing catalysts are active in the low temperature region, while the catalysts containing iron operate at higher temperatures. The aim of presented study is comparison of the catalytic performance of copper and iron oxides deposited by two different methods (impregnation and MDD) on various mesoporous silicas.

2. Experimental

Three different mesoporous silicas (MCM-48, SBA-15, MCF), reflecting a various porous structure, were used as supports for the deposition of transition metal (Cu, Fe) oxides.

The MCM-48 mesoporous silica was synthesized according to the procedure described by Collart et al. [24]. $C_{16–12–16}$ Gemini (2.89 g) and NaOH (0.35 g) were dissolved in 60.0 ml of distilled water. Then, 2 g of fumed silica (Aerosil 380) was added under vigorous stirring. The mixture was stirred for 30 min at room temperature (RT) and then the resulting gel was transferred into an autoclave and aged for 3 days at 130 °C. Subsequently, the solid was filtered and washed with distilled water. The solid product was resuspended in distilled water (30 ml) and aged in an autoclave at 130 °C for 24 h. This procedure step was carried out twice. The final product was separated by filtration, washed with distilled water and dried at RT.

Mesoporous silica SBA-15 was prepared according to the procedure given earlier by Van Bavel et al. [25]. Four grams of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(-ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$, Pluronic P123) was dissolved in 1.6 M HCl (150 ml) and then, 9.14 ml of tetraethyl orthosilicate (TEOS) was added. The obtained

suspension was stirred at 45 °C for 8 h and then aged at 80 °C for 15 h. The solid product was filtered, washed with distilled water and dried at RT.

The method of MCF synthesis was presented previously by Schmidt-Winkel et al. [26]. Pluronic P123 (4.0 g) was dissolved in 150 ml of aqueous HCl solution (1.6 M) at 35–40 °C. Then, NH_4F (46.7 mg) and 1,3,5-trimethylbenzene (mesitylene, 2.0 g) were added and vigorous stirred for 1 h. Subsequently, tetraethyl orthosilicate (TEOS, 9.14 ml) was added and the reaction mixture was stirred at 35–40 °C for 20 h. The resulting slurry was transferred to an autoclave and aged at 100 °C for 24 h. The obtained precipitate was filtered, washed with distilled water and dried at RT.

Two different methods were used for the deposition of transition metal oxides on the mesoporous silica.

2.1. The impregnation method

Transition metal (Cu, Fe) oxides were deposited in the mesoporous silica materials by a classical wet impregnation using aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$. The amount of metal nitrates used was calculated to obtain 3 wt.% of transition metal loading in the calcined catalyst. The samples were dried at RT for 3 days and then calcined in static air at 450 °C for 3 h. The catalysts obtained by the impregnation method are denoted Me(IMP)-support, where Me = Cu or Fe, support = MCM-48, SBA-15 or MCF.

2.2. The molecular designed dispersion (MDD) method

This method is based on reaction of surface silanol groups in the support with metalorganic complexes of transition metals. Acetylacetonate (acac) complexes of copper and iron were used as precursors of active phase. 1.2 mmol of $Cu(acac)_2$ or $Fe(acac)_3$ was dissolved in 100 cm^3 of zeolite dried toluene. Prior to the deposition process, the silica support was dried at 200 °C for 2 h. Subsequently, the mesoporous support (1.0 g) was added to the solution of acetylacetonate complex. Then, the suspension was stirred by 1 h. After reaction, the modified sample was separated by filtration, washed with toluene and vacuum dried at RT. All these operations were performed in an oxygen-free atmosphere. The samples modified with acetyla-cetonate complexes were calcined in an air atmosphere at 550 °C for 16 h. The catalysts obtained by the MDD method are denoted Me(MDD)-support, where Me = Cu or Fe, support = MCM-48, SBA-15 or MCF.

Transition metal loadings were determined by an electron microprobe analysis performed on a JEOL Superprobe 733 instrument.

Textural parameters of the samples were determined by N_2 sorption at −196 °C using an ASAP 2010 (Micromeritics) instrument after outgassing the materials under vacuum at 200 °C for 16 h. Surface areas were determined according to the BET method, while the pore size distributions were calculated from the adsorption isotherm using the BJH model.

Photoacoustic infrared spectra (FTIR-PAS) were recorded for the vacuum dried samples using a Nicolet 20 SX