Microporous and Mesoporous Materials 151 (2012) 180–187

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

The physico-chemical and catalytic properties of ferrite-containing MCM-41 and SBA-15 materials

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ARTICLE INFO

Article history:
Received 12 August 2011
Received in revised form 21 October 2011
Accepted 23 October 2011
Available online 29 October 2011

Keywords:
Ferrite
Cobalt oxide
MCM-41
SBA-15
VOC oxidation

ABSTRACT

Cobalt and iron modified MCM-41 and SBA-15 materials were prepared by incipient wetness impregnation technique and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 physisorption, temperature-programmed reduction (TPR-TGA), UV–Vis diffuse reflectance and Mössbauer spectroscopy. Formation of finely dispersed ferrite and cobalt-oxide species was observed on MCM-41 and SBA-15 supports. It was found that the surface properties of the mesoporous support and the temperature of precursor decomposition determine the type of formed metal oxides, their dispersion, reducibility and the catalytic activity in total oxidation of toluene.

1. Introduction

Mesoporous silica materials, with their uniform mesoporous channel structure and high specific surface area, are of particular interest as a catalyst support [1–11]. A wide variety of metal ions (Fe, Ti, V, Cr, Cu, Mn, etc.) has been introduced into the silica matrix to obtain materials with tunable catalytic properties [1–13]. It has been established, that the applied method of preparation, the type of salt precursors and supports used for modification strongly influences the state (localization, dispersion and oxidative state) of the loaded metal species.

The catalytic total oxidation has been considered as the most appropriate method for removal of volatile organic compounds (VOCs) [1–11]. This process is of great importance because of the strict regulations on the environmental standards which require reduction of their emission. The design of a catalytic system for complete oxidation of hydrocarbons is an important problem of the environmental catalysis. Supported noble metals and metal oxides have been investigated for the combustion of volatile organic compounds (VOCs) [2–6]. The high price of noble metals and their sensitivity to high temperature has driven scientists to search for a suitable catalyst. Supported metal oxides (Co, Fe, Ni, Mo, V, etc.) are an alternative to the noble metals as catalysts for complete oxidation. Among metal oxides, cobalt and iron containing catalysts are low cost, environmentally friendly, and relatively highly active for VOC elimination [7,9–11]. It is well known that the nature and dispersion of the metal oxide species are the key factors determining the activity and selectivity of the supported catalysts [5–11].

In this study, toluene has been chosen as VOC probe molecule because aromatics are regular constituents of industrial and automotive emissions and since toluene presents an important POCP (photochemical ozone creativity potential) [14]. Total oxidation of toluene has been studied over a large number of monometallic catalysts (Pt, Co, V, Cu, Cr, Fe, Mn and Mo on different types of supports (Al_2O_3, TiO_2 and active carbon)) [2,4,6–13,15–32]. Besides, the modification of a mesoporous material by two metals might create a new opportunity to obtain catalyst with higher activity and thermal stability than the single oxides as it has been recently published in our previous paper [11]. Our results show that pretreatment in air and hydrogen at 773 K of the CoFe/TiMCM-41 samples leads to the formation of finely dispersed cobalt ferrites particles having a positive effect on the catalytic performance in total toluene oxidation [11]. The appropriate ratio between two metals and their amount could facilitate the formation of ferrites and silica mesoporous support can stabilize them as finely dispersed particles.

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doi:10.1016/j.micromeso.2011.10.039

In the present study MCM-41 and SBA-15 materials were used as supports for cobalt ferrites nanoparticles formed by incipient wetness impregnation with iron and cobalt nitrates. The catalytic behavior of the modified samples was tested in the oxidation of toluene.

2. Experimental

2.1. Synthesis

The parent silica SBA-15 material was synthesized according to the well known procedure of Stucky and co-workers [33] with the following relative molar composition:

$$4\ \text{g}\ PEO_{20}PPO_{70}PEO_{20} : 0.24HCl : 0.04TEOS : 6.67H_2O.$$

The parent siliceous MCM-41 were synthesized by the sol–gel method of Grün et al. [34] with spherical morphology and 0.5–1 μm particle sizes. The composition of the synthesis mixture was:

$$1.0TEOS : 0.30C_{16}TMABr : 11NH_3 : 144H_2O : 58EtOH.$$

The silica source for both mesoporous supports was tetraethylortosilicate (TEOS) the templates were Pluronic [P123 triblock copolymer ($PEO_{20}PPO_{70}PEO_{20}$)] for SBA-15 and *N*-hexadecyltrimethylammonium bromide for MCM-41. Template was removed by calcinations in air at 723 for SBA-15 and at 823 K for MCM-41 with a heating rate of 1 K/min.

An incipient wetness impregnation technique with cobalt and iron nitrates was applied for loading of 15 and 23 wt.% metals, with Co:Fe = 1:2. The precursor salts were decomposed in air at 773 K and at 973 K for 2 h on MCM-41 and SBA-15 supports.

2.2. Characterization

X-ray patterns were recorded by Philips PW 1810/3710 diffractometer applying monochromatized CuK_α radiation (40 kV, 35 mA). Low angle patterns (1.5–10° 2θ for MCM-41 and 0.6–6° 2θ for SBA-15 materials) were also taken to check the ordering of the supporting silica materials. Metal oxide phases were determined based on ICDD database, the corresponding ICDD card numbers were: Co_3O_4 42–1467, $CoFe_2O_4$ 22–1086, and FeO 6–615. The patterns recorded at ambient were collected between 25° and 50° 2θ, by 0.02° steps for 10 s.

In situ XRD measurements were carried out in hydrogen flow (60 cm^3/min) in a high temperature HTK-1200 Anton–Paar chamber with temperature programming. They were recorded between 25° and 65° 2θ with 0.02° step size for 1 s. Crystallite sizes of the metal oxides were determined by the Scherrer equation evaluating the FWMH values with full profile fitting methods.

Nitrogen physisorption measurements were carried out at 77 K using Quantachrome NOVA Automated Gas Sorption Instrument. Samples were pretreated at 623 K in vacuum. The pore-size distributions were calculated from desorption isotherms by the BJH method.

TEM images were taken by using a MORGAGNI 268D TEM (100 kV; W filament; point-resolution = 0.5 nm). Samples were suspended in small amount of ethanol and a drop of suspension was deposited onto copper grid covered by carbon supporting film and dried at ambient.

The temperature-programmed reduction-thermogravimetric analysis (TPR-TGA) investigations were performed in a Setaram TG92 instrument. In a typical measurement 40 mg of sample was placed in a microbalance crucible and heated in a flow of 50 vol.% H_2 in Ar (100 cm^3/min) up to 773 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 an air flow (10 K/min) up to 773 K, followed by a hold-up of 1 h.

Diffuse reflectance spectra in the UV–Vis region were detected at ambient by a Jasco V-670 UV–Vis spectrophotometer equipped with NV-470 type integrating sphere using a $BaSO_4$ disk as reference. The data were collected between 900 and 200 nm wavelengths with 100 nm/min speed and with 2 nm bandwidth at 1 nm data pitch.

Mössbauer spectroscopic measurements (MS) were performed by a KFKI spectrometer, operating in constant acceleration mode with ^{57}Co/Rh source (0.5 GBq). The positional parameters are related to alpha-iron standard. The accuracy of these data is ca. ±0.03 mm/s. In situ spectra were recorded at ambient (300 K) and at liquid nitrogen (77 K) temperatures. Samples were first measured in their ambient, hydrated state. In the following step, the samples were treated in hydrogen at 653 K for 2 h and measurements were carried out in hydrogen atmosphere afterward. The following parameters of hyperfine interactions were extracted from the spectral components by computer fitting: isomer shift (IS), quadrupole splitting (QS), line widths (FW) and components' relative intensities (RI).

2.3. Catalytic activity measurements

Prior to the catalytic tests samples were pretreated for 1 h in air up to 623 K. Toluene oxidation was studied at atmospheric pressure using a fixed-bed flow reactor with air as carrier gas (30 ml/min). In the reaction 30 mg sample (particle size 0.2–0.8 mm) was tested, diluted with 60 mg glass beads of the same diameter, previously checked to be inactive. The reactor itself was a quartz tube of 15 mm inner diameter, with the catalyst bed at the middle. A thermocouple was positioned in the catalyst bed for accurate measurement of the catalyst temperature. All gas lines of the apparatus were heated continuously at 383 K in order to minimize VOC adsorption on the tube walls. The air stream passed through a saturator filled with toluene and equilibrated at 273 K (p_{toluene} = 0.9 kPa). The reactant was fed in the reactor with a flow rate of 30 ml/min and catalytic tests were carried out in the temperature range 600–723 K at WHSV of 1.2 h^{-1}. The reaction steady state was established after 30 min in each temperature. On-line analysis of the reaction products was performed using HP-GC with a 25 m PLOT Q capillary column. The turnover frequency (TOF) was calculated as the converted number of toluene molecules per metal atom per second.

3. Results and discussion

3.1. Physico-chemical properties

XRD data of the cobalt and iron modified silica materials in the low two theta region (not shown) confirm the preservation of the hexagonal structure after the impregnation process. In the higher two theta region, wide reflections with low intensity, typical of Co_3O_4 and $CoFe_2O_4$ on 23CoFe/MCM-41, whereas only reflections of $CoFe_2O_4$ can be observed on the SBA-15 support (15CoFe/SBA-15 and 23CoFe/SBA-15 samples), after calcination at 773 K (Fig. 1A). Thermal treatment at 973 K resulted exclusively in the formation of cobalt ferrite phase on both supports (Fig. 1B). Crystallite size of ferrite and cobalt oxide particles determined by the Scherrer method can be found in Table 1. Our data show that the particle size of ferrite phase on 773 K treated samples is similar (below 10 nm), but the amount of crystalline ferrite phase (crystallite size ⩾5 nm) is higher on the SBA-15 support. Salt decomposition at 973 K increased the particle size of ferrite phase on SBA-15 and decreased on MCM-41 sample. The latter can be explained by the stronger metal-support interaction, most of the metal ions form cobalt and iron silicates with the silanol groups of the silica matrix [35,36].