Materials Research Bulletin 78 (2016) 72–82

Contents lists available at ScienceDirect

Materials Research Bulletin

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

SBA-15 loaded with iron by various methods as catalyst for DeNOx process

Daniel Macina[a], Zofia Piwowarska[a], Kinga Góra-Marek[a], Karolina Tarach[a], Małgorzata Rutkowska[a], Vladimir Girman[b], Artur Błachowski[c], Lucjan Chmielarz[a,*]

[a] Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland
[b] Pavol Jozef Šafárik University, Department of Condensed Matter Physics, Park Angelinum 9, Košice, Slovakia
[c] Pedagogical University, Institute of Physics, Podchorążych 2, 30-084 Kraków, Poland

ARTICLE INFO

Article history:
Received 20 November 2015
Accepted 15 February 2016
Available online 17 February 2016

Keywords:
Amorphous materials
Chemical synthesis
Catalytic properties

ABSTRACT

SBA-15 modified with iron by various methods was tested as catalyst of the DeNOx process. Two methods were used for deposition of iron: (i) molecular designed dispersion method to introduce Fe in the form of monomeric cations and (ii) ion-exchange of iron acetate oligocations, $[Fe_3O(OAc)_6 \cdot AcOH \cdot 2H_2O]^+$, for SBA-15 modified with propylsulfonic groups to introduce aggregated iron oxide species. The obtained samples were characterized with respect to: textural parameters (low-temperature N_2 adsorption), structure (XRD, TEM), efficiency of surface species anchoring (DRIFT, FTIR-PAS, TG-DTG and elemental analysis), form and aggregation of deposited iron species (Mössbauer spectroscopy, UV-vis-DRS, H_2-TPR, CO-FTIR), distribution of iron oxide species in the samples (TEM-EDX). SBA-15 modified with iron was found to be effective catalysts of selective reduction of NO with ammonia. It was suggested that iron deposited in the form of aggregated FeO_x species presents higher catalytic activity in the studied process comparing to monomeric Fe^{3+} cations.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Development of mesoporous silica materials was undoubtedly one of the most spectacular achievements in the field of materials chemistry [1]. Such materials, characterized by the uniform porous structure, high surface area and porosity, can be synthetized by surfactant directed methods [1]. The size and arrangement of pores can be adjusted by using various types of surfactants and also by controlling of the other synthesis parameters [2]. Therefore, since 1992, when the first successful synthesis of this type of materials was reported [1], many various types of mesoporous silicas have been developed and methods of their synthesis were described in scientific literature [e.g. 2–4]. Mesoporous SBA-15 silica is very important for possible catalytic applications due to relatively thick silica walls, what results in its increased mechanical, thermal and hydrothermal stability [5]. Moreover, SBA-15 is characterized by a relatively large pore diameter, what is important in case of deposition of bulky catalytically active species inside pores of this material. Pure silica mesoporous materials do not exhibit ion-exchange properties, what limits a spectrum of the methods for deposition of catalytically active components ensuring their uniform distribution in pore system. Impregnation methods typically result in a simultaneous deposition of active component in different forms (e.g. monomeric cations and metal oxide aggregates of various sizes) and may cause partial clogging of the pore system. An alternative method is synthesis of mesoporous silica containing guest cations (e.g. Al^{3+}) incorporated to the silica framework [6,7] and therefore, generating ion-exchange properties. Another way to generate ion-exchange properties in mesoporous silica is based on the post-synthesis introduction of anionic surface species able to accommodate cationic species [e.g. 8–10]. Various methods for controlled deposition of monomeric cations were reported in literature [11–13], however the number of reports presenting controlled deposition of strictly defined aggregated species is limited [e.g. 14,15]. Therefore the aim of the studies was deposition, in controlled way, iron in the form of small aggregated species. For comparison, as a reference sample SBA-15 loaded with mononuclear Fe^{3+} ions was obtained by grafting (molecular designed dispersion—MDD) method [16]. Catalytic activity of various types of iron species deposited on SBA-15 was compared in the DeNOx process.

---

* Corresponding author.
E-mail address: chmielar@chemia.uj.edu.pl (L. Chmielarz).

http://dx.doi.org/10.1016/j.materresbull.2016.02.026
0025-5408/© 2016 Elsevier Ltd. All rights reserved.

2. Experimental

2.1. Samples preparation

SBA-15 was prepared using 4 g of Pluronic P123 triblock copolymer surfactant (EO20–PO70–EO20, Sigma-Aldrich) dissolved in a water solution of HCl (37%, Sigma–Aldrich). Subsequently, a suitable amount of tetraethyl orthosilicate (TEOS, Sigma–Aldrich) was added. The mixture was stirred at 45 °C for 8 h and then aged at 80 °C for 15 h. The solid product was separated by filtration, washed with distillated water and dried at room temperature. Finally, the sample was calcined in air atmosphere at 550 °C for 6 h. Detailed description of SBA-15 synthesis as well as its characterization was presented in our previous papers [11,16].

SBA-15 was catalytically activated by deposition of iron species. Two various methods, resulting in deposition of iron in the form of monomeric (molecular designed dispersion method—MDD) and oligomeric metal oxides species (ion-exchange of iron oligocations—IE) were applied.

2.2. Molecular designed dispersion method (MDD)

SBA-15 was modified by grafting of iron acetylacetonate complex, $Fe(acac)_3$, on the silica surface, followed by its thermal decomposition to stable, highly dispersed, surface species according to the procedure presented in our previous paper [16]. 40 mmol of $Fe(acac)_3$ was dissolved in 100 cm^3 of zeolite (ZSM-5) dried toluene (POCH). Prior to the deposition process, SBA-15 was dried at 200 °C for 2 h. Subsequently, 1 g of SBA-15 was dispersed in a solution of $Fe(acac)_3$ and stirred for 1 h. Then, the modified SBA-15 sample was separated by filtration and washed with toluene. All these operations were performed in a glovebox flushed with dried air. Finally, the samples were vacuum dried at room temperature for 12 h and then calcined in air atmosphere at 600 °C for 16 h. The obtained sample is denoted as SBA-15-Fe(MDD).

2.3. Ion-exchange of iron oligocations (IE)

In the first step the surface of SBA-15 was modified with organic cationic species to generate ion-exchange properties using the procedure described previously by Trejda et al. [8] with some modifications. SBA-15 was thermally treated at 200 °C for 2 h to remove water adsorbed on its surface. Then, 2 g of mesoporous silica was dispersed in 50 cm^3 of zeolite (ZSM-5) dried toluene (POCH). The obtained slurry was heated to 110 °C and intensively stirred for 30 min. Then, 1.96 g of 3-(mercaptopropyl) trimethoxysilane (MPTMS, Sigma–Aldrich) was added and the obtained mixture was intensively stirred at 110 °C for next 20 h. After filtration modified SBA-15 was successively washed with toluene, methanol and distillated water and finally dried at room temperature (RT). The obtained sample, denoted as SBA-15-SH, was treated with a solution of H_2O_2 (POCH) to convert —SH groups to —SO_3H. SBA-15-SH was dispersed in 30% aqueous solution of H_2O_2 and stirred at RT for 24 h. Then, the sample was separated by filtration, washed with distillated water and ethanol and finally dried at RT. The obtained sample is denoted as SBA-15-SO_3H.

Parallel, iron acetate oligocations, $[Fe_3O(OAc)_6{\cdot}AcOH{\cdot}2H_2O]^+$, were synthetized according to the procedure described by Maes and Vansant [17]. $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in anhydrous ethyl alcohol (POCH) and then acetic anhydride (POCH) was added to the obtained solution. After heat evolution, the mixture was cooled in an ice bath under vigorous stirring. The resulting precipitate was separated by filtration and dried at RT in desiccator.

Iron acetate oligocations were introduced into SBA-15-SO_3H by ion-exchange method. A 1% solution of iron acetate oligocations was slowly added into a slurry containing SBA-15-SO_3H dispersed in distillated water. Another sample was obtained using 10% solution of iron acetate oligocations. The mixture was vigorously stirred at RT for 4 h. Subsequently, the solid product was washed and separated by filtration, then re-dispersed in distillated water, washed and again filtered. This procedure was performed until a pH of 7–8 was achieved (at least three times). In the next step, the obtained products were dried at 120 °C for 12 h. Finally, SBA-15, modified in this way, was calcined at 600 °C for 6 h. The obtained samples are denoted as SBA-15-Fe1(IE) and SBA-15-Fe10(IE), for exchanges performed with 1% or 10% solutions of iron acetate oligocations, respectively.

2.4. Characterization methods

Textural parameters of mesoporous supports and their calcined modifications with deposited iron species were determined by N_2 adsorption at −196 °C using a 3Flex (Micromeritics) automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 350 °C for 12 h. The specific surface area was determined using the BET equation, while pore size was enumerated using the BJH model. The total pore volume was determined by means of the total amount of adsorbed nitrogen at $P/P_0 = 0.98$.

The X-ray diffraction patterns of the mesoporous support and their modifications with iron were obtained with a Bruker D2 Phaser diffractometer. The measurements settings were 10 mA and 10 kV (Cu-Kα radiation; $\lambda = 1.54056$ Å), 2θ step scans of 0.02° and a counting time of 1 s per step.

The efficiency of surface functional groups anchoring was studied using FT-IR, thermogravimety and elemental analysis. FT-IR measurements, for the samples with grafted MPTMS (before and after oxidation with H_2O_2), were performed using a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) equipped with DRIFT (diffuse reflectance infrared Fourier transform) accessory and MCT detector. The outgassed samples were grounded with dried potassium bromide powder (4 wt.%). The measurements were carried out in the wavenumber range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}.

Thermogravimetric measurements were performed using a TGA/SDTA851^e Mettler Toledo instrument coupled on-line with a mass spectrometer (Thermostar, Balzers). The samples were heated in a flow of air (80 mL/min) with the ramping of 10 °C/min, in the temperature range of 30–1000 °C.

The content of carbon and sulfur in mesoporous supports modified with surface functional groups was determined using a CHNS Vario MICRO Cube microanalyzer.

The efficiency of $Fe(acac)_3$ anchoring was studied by analysis of the as prepared (non-calcined) samples using photoacoustic infrared spectroscopy (FTIR-PAS). The spectrum of the modified SBA-15 sample was measured on a Nicolet 20 SX spectrometer equipped with a McClelland photoacoustic cell. The spectrum (2000 scans) was collected in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. The FTIR-PAS spectrometer was placed in an isolated bench, which was purged with nitrogen to ensure that the sample was completely dried.

The STEM images for the SBA-15-Fe1(IE) sample were obtained with the use of a Tecnai Osiris 200 kV TEM/STEM system equipped with HAADF detector and Super-EDX windowless detector. The STEM images for the SBA-15-Fe(MDD) sample were obtained using a JEOL 2100F working at 200 KV, with Field Emission Gun (FEG). In both cases STEM micrographs were coupled with EDX data for the presentation of the chosen elements distribution.

The UV–vis–DR and Mössbauer spectroscopies as well as temperature programmed reduction (H_2-TPR) method were used for determination of iron species coordination and aggregation on the mesoporous supports.

Download English Version:

https://daneshyari.com/en/article/1487120

Download Persian Version:

https://daneshyari.com/article/1487120

Daneshyari.com