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Synthesis of ordered mesoporous silica membranes containing iron oxide nanocrystallites

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Abstract

This paper reports the first effort in synthesis of iron-containing ordered mesoporous silica membrane on porous α-alumina support by a dip-coating process. A pure silica sol and a series of iron-containing silica sol with Fe/Si molar ratio of 0.1, 0.2 and 0.3 were prepared using Pluronic P123 as template, tetraethylorthosilicate as silica source and hydrated iron nitrite as precursor under acid condition. The unsupported membranes were characterized by Fourier transform infra-red (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM) and nitrogen isothermal adsorption measurement. Characterization revealed that iron species present as highly dispersed γ-Fe_2O_3 nanocrystals in hexagonal walls for higher iron-containing samples (Fe/Si = 0.2, 0.3). All unsupported membranes maintain ordered mesoporous structure similar to SBA-15 and possess high surface area, large pore volume and uniform pore size. Introduction of iron to silica matrix can decrease pore diameter and increase the wall thickness of mesopores. Scanning electron microscopy (SEM) studies show that the prepared supported membrane is defect-free and energy-dispersive spectroscopy (EDS) analysis further confirm the formation of continuous mesoporous layer on α-alumina porous support. The gas permeance results indicate the supported membranes exhibit Knudsen diffusion behavior confirming the good quality of the membrane.

Keywords: Ordered mesoporous membranes; Iron oxide; Silica; Membrane synthesis; Gas permeation

1. Introduction

Ordered mesoporous silica has received much attention as promising membrane materials for the catalysis and separation applications [1,2]. In the last few years a considerable amount of work on the synthesis of ordered mesoporous silica layers as membranes was reported. The reported studies included synthesis of ordered mesoporous silica layers on coarse-pore disk or tubular porous ceramic supports using hydrothermal reaction [3–5], dip-coating [5–8], casting [9,10], aerosol-assisted deposition [11], solution growth [12], counter diffusion self-assembly [13], and interfacial growth [14,15]. Such supported mesoporous membranes offer potential applications in ultrafiltration process [16], membrane reactors [17] and controlled drug delivery [18].

All the mesoporous layers on porous supports reported in these studies were of pure silica, such as MCM-48 [3,4], MCM-41 [8,9], and MSU-X [14,15]. Compared to pure silica materials, metal-containing ordered mesoporous silica is more attractive, especially for use in catalysis. Among these materials, iron-containing mesoporous silica is of particular interest because of its unique catalytic properties for various reactions, e.g., Friedel-Crafts alkylation [19], partial oxidation of methane to formaldehyde [20], decomposition of methanol [21] and phenol [22], and the conversion of sulfur dioxide to sulfur trioxide in sulfur rich gases [23,24]. Enhanced catalytic performance for these reactions was observed with nanosized iron oxide on support of large surface area and pore volume, such as ordered mesoporous silica.

Several approaches were reported for synthesis of nanosized γ-Fe_2O_3 in mesoporous silica. The most common method is the wet impregnation of the porous material, such as MCM-41 [25], MCM-48 [26], SBA-15 [21], with an inorganic precursor like $Fe(NO_3)_3$, followed by conversion to iron oxide by calcination. This method is time consuming and the iron oxide particles may clog the pore entrance or be formed outside the mesopores. Nanosized γ-Fe_2O_3 can be also coated on ordered mesoporous

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silica matrix by the sol–gel method. Garcia et al. [27] reported a sol–gel method to overcome the difference in the hydrolysis and condensation rate between iron and silica precursors. Yang et al. [28] developed a comprehensive one-step route for synthesis of highly ordered mesoporous silica monoliths with various metal oxide nanocrystals, including Cr_2O_3, MnO, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, CdO, SnO_2, and In_2O_3. More recently, Supplit et al. [29] reported modification of surfactant method to synthesize iron-containing ordered mesoporous silica film on silicon wafer substrates. These pioneering works demonstrated the successful synthesis of composite materials of mesoporous silica containing nanosized γ-Fe_2O_3 via sol–gel process. However, to our best knowledge, there is no report on the synthesis of iron-containing mesoporous silica membrane on porous substrate. The objective of this paper is to report synthesis and characteristics of iron-containing mesoporous silica membranes on porous α-alumina support by a one step sol–gel dip-coating process. The obtained unsupported membranes were characterized by techniques such as, Fourier transform infra-red (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), SAED, and gas permeation.

2. Experimental

2.1. Support preparation and modification

Macroporous α-alumina disks of 20 mm in diameter and 2 mm in thickness were prepared by pressing calcined alumina powder (coded as A16 powder, Alcoa, TX). The A16 powder was thoroughly mixed with 11 wt.% deionized water prior to pressing. 2.1 g of the mixture was put in a mold and pressed at 6.9 MPa for 2 min and then at 26.2 MPa for 10 min. The supports were dried in oven at 40 °C to remove the water binder, and then sintered at 1150 °C for 30 h [13]. After sintering, the supports were polished with 500 and 800 grit polishing paper, washed with deionized water and then dried for 2 days at 40 °C.

The α-alumina supports were subsequently modified by silylation with octadecyltrichlorosilane (ODS) and methyltrichlorosilane in order to obtain hydrophobic surface as to prevent the hydrophilic silica sol from penetrating into the support during the dip-coating process. To do this, a support preheated at 200 °C for 48 h was immersed and quenched in 5% (v/v) ODS in toluene and dried after aging at 110 °C for 8 h. The ODS-modified macroporous support was then treated at room temperature for 2 h in 1% (v/v) methyltrichlorosilane in toluene and rinsed with dry toluene. Then the modified supports were dried at 110 °C for 8 h to remove residual toluene.

2.2. Synthesis of iron-containing silica sol and membranes

Pure and iron-containing silica sol with different Fe/Si molar ratios were synthesized based on the work of Yang et al. [28] with modification. The typical synthesis procedure is as follows: 1.4 g Pluronic P123 (P123, $EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$, BASF) was added to 2.8 g tetraethylorthosilicate (TEOS, Aldrich). It was stirred at 60 °C for 10 min till the P123 was dissolved absolutely. A calculated amount of hydrated iron nitrite ($Fe(NO_3)_3{\cdot}9H_2O$, Aldrich) corresponding to Fe/Si molar ratio equal to 0.1, 0.2 and 0.3 was dissolved in ethanol (18.0 g). The obtained solution or 18.0 g ethanol (for pure silica sol) was subsequently added to the mixture of P123 and TEOS and stirred for 10 min at 60 °C. Then it was cooled to room temperature, and 1.0 mL aqueous HCl ($0.05\,\mathrm{mol\,L^{-1}}$) was added to the solution and stirred for 2.0 h. After 24 h aging at room temperature, a clear sol with much lower viscosity was obtained. The final molar ratio of TEOS:$Fe(NO_3)_3{\cdot}9H_2O$:P123:HCl:H_2O:EtOH is 1:n:0.018:0.004:4.137:29.115, where n is the molar ratio of iron to silicon.

The unsupported membranes were prepared by pouring the pure or iron-containing silica sol into Petri dish. Supported membranes were obtained by dip-coating the modified α-alumina support disk with the iron-containing silica sol in which the Fe/Si molar ratio is 0.2. Both supported and unsupported membranes were dried in air at 25 °C and relative humidity of 80% for 48 h in a humidity controlled oven. The dried membranes were then calcined at 400 °C for 4 h (heating and cooling rate of $0.5\,^\circ\mathrm{C\,min^{-1}}$). The resultant unsupported membrane samples are denoted as S0, S0.1, S0.2, and S0.3, in which the arithmetic labels denote the molar ratio of iron to silicon. For the supported membranes the dip-coating, drying and calcination procedure were repeated five times in order to ensure complete coverage of the support.

2.3. Characterization

The unsupported membranes after calcination were ground into powders for characterization by XRD (Bruker D8 diffractometer using Cu Kα radiation with the step size of 0.02°/s at 40 kV and 40 mA). FTIR spectra of the unsupported membranes ($n = 0.2$) before and after calcination were collected in transmission mode on Nicolet 4700 FTIR spectrometer (Thermo Electron Corporation). Transmission electron microscopy study was performed on a JEOL JEM-2010 electronic microscope, operated at 200 kV. N_2 adsorption–desorption isotherms of unsupported iron-containing mesoporous silica membrane were measured on ground powder sample using Micromeritics ASAP-2020 at liquid nitrogen temperature (77 K). The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method. Scanning electronic microscopy (SEM micrographs) observation for supported iron-containing mesoporous silica membranes was performed on a FEI ESEM XL30 electronic microscope equipped with EDAX system. Membrane quality on α-alumina porous substrate and gas permeation properties were tested by the method of unsteady state permeation with helium, nitrogen, oxygen or argon.

3. Results and discussion

3.1. Structure of unsupported membranes

Fig. 1 shows the low-angle XRD patterns for unsupported membranes with different Fe/Si molar ratio after calcination at 400 °C for 4 h. For pure silica sample, S0, it exhibits a sharp diffraction peak at the 2θ of 1.11° and two weak peaks at 2θ of