Synthesis and Catalytic Activity of Niobium-Containing Hexagonal Mesoporous Silica

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Niobium-containing hexagonal mesoporous silica has been synthesized using *n*-dodecylamine as a template; the novel material is very active as a catalyst in the epoxidation of propylene with hydrogen peroxide and alkyl peroxides as oxidants.

The synthesis of silica-based mesoporous materials has attracted great interest because it extends the range of molecular-sieve materials into the very large pore regime.[1] Incorporation of transition metal ions in these mesoporous structures is a very interesting and promising field of research. Hexagonal mesoporous silica (HMS) has several advantages among the mesoporous materials: 1) HMS can be easily formed by sol-gel reaction in the presence of primary alkylamine as template at room temperature;[2] 2) transition metal ions, such as Ti^{4+}, Al^{3+}, Zr^{4+}, V^{5+}, Cu^{2+}, Cr^{6+}, and Mn^{2+}, can be incorporated into the HMS framework uniformly with high contents;[2–7] 3) HMS possesses thicker framework walls, small crystallite size of primary particles, and complementary textural porosity,[8] which causes that transition metal-modified HMS usually shows high activity in the organic reactions.[2,9,10] Niobium compounds and materials have shown great promise in heterogeneous catalysis within the past decade.[11] Recently, Nb-MCM-41 has been recognized as a very attractive catalyst in the oxidation of organic compounds with hydrogen peroxide.[12,13]

Propylene oxide (PO) is one of the most important chemical feedstocks for producing resins such as polyurethane. It is produced commercially by etherification of chlorohydrin or organic hydroperoxide processes. The latter (Halcon process) has more ecological and economical benefits than the former and accounts for more than one million tons annual production of propylene oxide worldwide. Titanium silicate (TS-1) has been used to catalyze the epoxidation of propylene with hydrogen peroxide under mild conditions.[14] However, TS-1 cannot catalyze the epoxidation of propylene with alkyl hydroperoxide, such as *tert*-butyl hydroperoxide (TBHP), owing to the limited size of the silicalite pore.[15] In the present study, we report on the synthesis of niobium-containing mesoporous silica (Nb-HMS) at the first time. The novel material is very active as a catalyst in the epoxidation of propylene with both hydrogen peroxide and TBHP as oxidants.

Nb-HMS samples were synthesized at room temperature using *n*-dodecylamine as surfactant molecule. A solution which containing 0.1 mol of tetraethyl orthosilicate ($Si(OC_2H_5)_4$) and the required amount of niobium penta-ethoxide ($Nb(OC_2H_5)_5$) in 0.7 mol ethanol was added to a solution of *n*-dodecylamine (0.027 mol) and HCl (2 mmol) in water (3.63 mol). The resulting gel was stirred for 5 min and aged for 18 h at room temperature. The solid was recovered by filtration, washed abundantly with distilled water, air-dried at room temperature, and finally calcined in air at 923 K for 4 h. Ti-MCM-41, Ti-HMS, Nb-MCM-41, and TS-1 were prepared by the methods reported in the literatures.[1,4,13,14]

X-ray diffraction (XRD) patterns were recorded using a MAC Science MX-Labo diffractometer with Cu radiation operated at 40 kV and 50 mA. Infrared spectra were recorded on a JASCO FT/IR-680 spectrophotometer using a KBr pellet technique. Epoxidation of propylene was carried out in a 50-mL stainless-steel reactor. A portion of 0.2 g of catalyst, 6.5 mmol of 30% H_2O_2 or 70% TBHP, and 10 mL of methanol were added in the autoclave reactor, and then the reactor was charged with propylene at a constant pressure (0.8 MPa) at 298 K. After heating, the mixture reacted at 323 K under magnetic agitation for 4 h. The products were detected by gas chromatography and the residual H_2O_2 and TBHP were determined by iodometric titration.

The low-angle powder XRD patterns of the various samples are shown in Figure 1. Each sample exhibits an intense reflection corresponding to the (100) plane at 2–3 degrees and a broad shoulder near 5 degrees. These patterns are typical wormhole structures of HMS materials assembled from long alkyl chain neutral amines as surfactants.[10] The d_{100} spacings were 3.71 and 3.54 nm for HMS before and after calcination, and the d_{100} spacings were 3.86 and 3.69 nm for Nb-HMS before and after calcination. The d_{100} spacing shifted to lower diffraction angle by the Nb modification. Both HMS and Nb-HMS possess high surface areas above 1000 m^2g^{-1} measured by the N_2 ad-

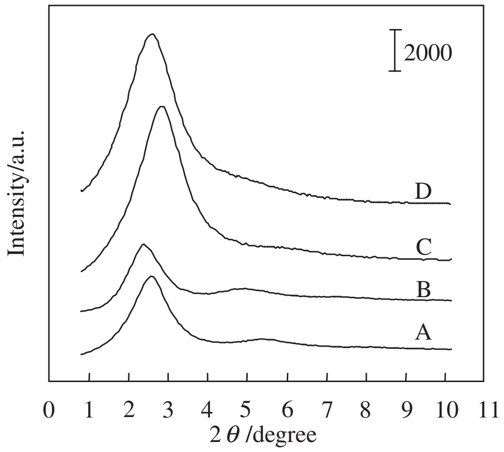

Figure 1. The XRD patterns of (A) HMS (before calcination), (B) Nb-HMS (before calcination, Nb/Si = 1:100 (molar ratio)), (C) HMS (after calcination), (D) Nb-HMS (after calcination, Nb/Si = 1:100 (molar ratio)).

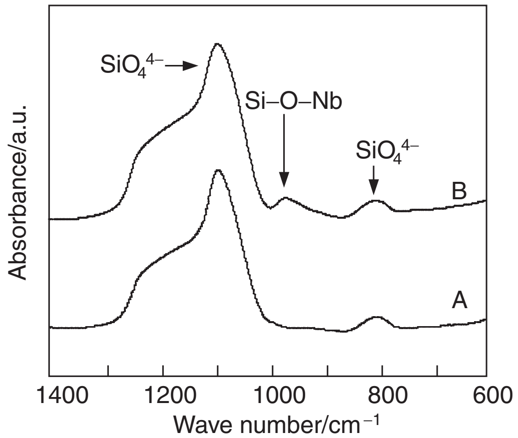

Figure 2. FT-IR spectra of calcined samples dispersed in KBr pellets. A: HMS, B: Nb-HMS (Nb/Si = 1:100 (molar ratio)).

sorption isotherms. Infrared spectra of HMS and Nb-HMS after calcination are shown in Figure 2. Both of the samples exhibit the symmetric stretching vibration bond at around 810 cm^{-1} and the anti-symmetric vibration band at around 1100 cm^{-1} of the tetrahedral SiO_4 structural units. HMS exhibits no band at around 960 cm^{-1},[6,9] but Nb-HMS exhibits an infrared band at around 960 cm^{-1} like in the infrared spectrum of Nb-MCM-41.[16] The band at around 960 cm^{-1} has been widely used to characterize the incorporation of metal ions in the silica framework as the stretching Si–O vibration mode perturbed by the neighboring metal ions.[16,17] The presence of an infrared band at around 960 cm^{-1} is the evidence for the isomorphous substitution of Si by Nb ions in Nb-HMS. The isomorphous substitution has been also proved by UV–vis spectroscopy. The UV–vis spectrum of Nb-HMS shows a single adsorption edge at 220 nm, where the formation of Nb–O–Si bonds is suggested.[18]

The catalytic activity and selectivity in the oxidation of propylene over various catalysts are shown in Table 1. The designed metal amounts of the samples were 1:100 for the M/Si molar ratio. The actual metal amounts in the products were measured by ICP analyses and the results were consistent with the designed metal amounts in the samples. Propylene was oxidized to produce propylene oxide as a main product, together with propylene glycol and methoxypropanol as by-products. The efficiencies of the oxidants (H_2O_2 and TBHP) were larger than 98% over all catalysts tested in this study (not shown in Table 1). Nb-HMS showed the highest activity and selectivity for PO in the oxidation of propylene with both H_2O_2 and TBHP as oxidants. Although Nb-MCM-41,Ti-HMS, and Ti-MCM-41 are also effective in the oxidation of propylene with H_2O_2 and TBHP, the activities and PO yields of them are lower than those of Nb-HMS. It seems that Nb is preferable to Ti and HMS is preferable to MCM-41 in the epoxidation of propylene. TS-1 showed high activity and PO yield in the oxidation of propylene with H_2O_2, but it reasonably showed the lowest activity with TBHP as the oxidant because the limited size of the silicalite pore (5.6 × 5.3 Å) seriously restricted TBHP to enter into the pores of TS-1. Nb-HMS is a highly active catalyst for the oxidation of propylene irrespective of the nature of the oxidants. Our synthetic approach therefore provides new opportunities for the design of mesoporous catalysts in the oxidation of organic compounds.

Table 1. Catalytic oxidation of propylene over various catalysts at 323 K[a]

Catalysts	Oxidation with H_2O_2		Oxidation with TBHP	
	Conv./%	Select./%	Conv./%	Select./%
Nb-HMS[b]	41.3	98.3	42.7	98.6
Nb-MCM-41[b]	32.5	96.7	34.6	97.3
Ti-HMS[c]	28.3	95.4	26.7	96.2
Ti-MCM-41[c]	26.2	96.3	24.8	95.9
TS-1[c]	40.5	98.1	13.2	90.4

[a]Autoclave: 50 mL; catalyst: 0.2 g; propylene: 0.8 MPa; 30% H_2O_2 or 70% TBHP: 6.5 mmol; methanol: 10 mL; reaction time: 4 h. [b]Nb/Si = 1:100 (molar ratio). [c]Ti/Si = 1:100 (molar ratio).

In conclusion, we have synthesized Nb-HMS using *n*-dodecylamine as surfactant molecule at room temperature. Infrared spectra and UV–vis spectra proved that Nb ions had been incorporated into the HMS framework uniformly in Nb-HMS. The resulting Nb-HMS material exhibited excellent catalytic activity and selectivity for PO in the epoxidation of propylene with hydrogen peroxide and alkyl peroxides as oxidants.

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