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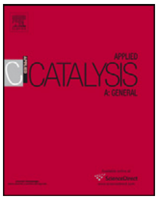

Nanocrystalline sodalite: Preparation and application to epoxidation of 2-cyclohexen-1-one with hydrogen peroxide

Norihito Hiyoshi *

Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan

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ABSTRACT

In this study, we have synthesized nanocrystalline sodalite and investigated its activity for the epoxidation of α,β-unsaturated ketone with hydrogen peroxide. Nanocrystalline sodalite was prepared by hydrothermal synthesis using sodium metasilicate ($Na_2SiO_3{\cdot}9H_2O$), sodium aluminate ($NaAlO_2$), and sodium chloride at 423 K. The obtained samples were characterized by X-ray diffraction, the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption isotherms, scanning electron microscopy (SEM), and energy dispersive X-ray analysis. The maximum BET surface area of the nanocrystalline sodalite prepared in this study was 73 $m^2\,g^{-1}$, and the average crystallite diameter of the sample was determined to be 47 nm by SEM. Nanocrystalline sodalite was found to promote the epoxidation of 2-cyclohexen-1-one with hydrogen peroxide. Epoxidation was observed to proceed mainly in the liquid phase and not on the surface of the nanocrystalline sodalite, and nanocrystalline sodalite was found to play a role in the pH adjustment of the liquid phase, which was required for the reaction to proceed. Further, nanocrystalline sodalite could be easily recovered by filtration after the epoxidation of 2-cyclohexen-1-one and used repeatedly for the reaction.

1. Introduction

Zeolites have widespread chemical industrial applications as catalysts, adsorbents, and ion exchangers. Most of the zeolites used in chemical processes have high surface areas due to micropores in zeolite structure. On the other hand, few studies have focused on zeolites with small pore openings that cannot be accessed by reactants or adsorbate molecules. Such zeolites consequently have small surface areas. For example, there have been very few attempts for the catalytic utilizations of ordinary microsized sodalite crystals because of their low surface area [1,2]. However, recent studies show that sodalite has potential as a catalytic material [1,3–7]. Mesoporous sodalite, with a surface area of around 190 $m^2\,g^{-1}$, has been synthesized and used as a catalyst for base-catalyzed reactions and a catalyst support of palladium metal particles for cross-coupling reactions [3,4]. High surface areas can also be obtained by nanosizing sodalite crystals [5,8–13]. Nanocrystalline sodalite with a surface area of up to 93 $m^2\,g^{-1}$ has been synthesized [9], and its catalytic activities for soot combustion have been reported [5]. The development and catalytic applications of sodalite with a high surface area are areas of considerable research interest.

The epoxidation of alkenes is extremely important in the chemical industry because various chemicals are derived from epoxides. Hydrogen peroxide (H_2O_2) is the preferred oxidant for epoxidation reactions in environmentally benign processes because only water is produced as the byproduct. Electron-deficient alkenes such as α,β-unsaturated ketone are commonly epoxidized with H_2O_2 under strongly alkaline conditions using bases such as hydroxides or carbonates of alkaline metals [14,15]. However, the use of strongly alkaline solutions causes undesirable side reactions, the production of vast amounts of wastes, and corrosion of apparatuses. Therefore, the use of solid base catalysts is highly desirable. Solid base catalysts such as hydrotalcite [16–19], calcium phosphate [20], and ion-exchange resins [21] have been studied for the epoxidation of α,β-unsaturated ketones.

In this study, we have prepared nanocrystalline sodalite and applied it to the epoxidation of a typical α,β-unsaturated ketone, 2-cyclohexen-1-one, in order to investigate the activity of nanocrystalline sodalite.

2. Experimental

2.1. Preparation

Three sodalite samples (S1, S2, and S3) were prepared using the same procedure, but different amounts of reagent were used (Table 1). Sodium aluminate ($NaAlO_2$) (Junsei Chemical) and water

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* Corresponding author. Fax: +81 22 237 5224.
E-mail address: n-hiyoshi@aist.go.jp

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Table 1
Synthesis condition of sodalite.

Sample	Temp., K	Time, h	Reagent used, g				Mol ratio SiO_2:Al_2O_3:Na_2O:H_2O:NaCl	Product recovered, g
			$Na_2SiO_3 \cdot 9H_2O$	$NaAlO_2$	NaCl	H_2O		
S1	423	42	12.6	3.65	60.0	3.88	2.0:1.0:3.0:28:46	4.81
S2	423	42	12.6	3.65	6.00	3.88	2.0:1.0:3.0:28:4.6	4.88
S3	423	42	12.6	3.65	30.0	20.0	2.0:1.0:3.0:68:23	4.11
			Na-A zeolite	NaOH	NaCl	H_2O		
S4	453	36	3.69	7.58	21.5	40.0	2.0:1.0:10:220:36	3.80

were mixed in a polyethylene vessel. Sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) (Wako Pure Chemical Ind.) was then added, followed by the addition of sodium chloride (NaCl) (Wako Pure Chemical Ind.) with vigorous mixing. The mixture was transferred to a Teflon-lined autoclave (98 cm^3) and heated at 423 K for 42 h. The resultant solid was dispersed in water (500 cm^3) and centrifuged, and it was then re-dispersed in 250 cm^3 of water and centrifuged twice. The final pH of the water was estimated to be 8–9 with indicator papers. The obtained solid was dried at room temperature, and ground with a mortar to form a powder. Another sodalite sample (S4) was prepared by mixing 3.69 g of Na-A zeolite (Wako Chemical), 7.58 g of sodium hydroxide (Wako Pure Chemical Ind.), 21.5 g of NaCl, and 40.0 g of water, following which it was subjected to hydrothermal treatment with the Teflon-lined autoclave (98 cm^3) at 453 K for 36 h.

2.2. Characterization

Powder X-ray diffraction (XRD) data were collected with a Cu-Kα source using a Rigaku RINT-2200VK/PC diffractometer operating at 40 mA and 30 kV. The surface areas of samples were determined by the Brunauer–Emmet–Teller (BET) method using nitrogen adsorption isotherms. After drying in vacuum at 523 K for 3 h, nitrogen adsorption isotherms at 77 K were measured using a Quantachrome AUTOSORB-1C instrument. Scanning electron microscope (SEM) images were collected on a Hitachi S-4800 field emission SEM operated at an acceleration voltage of 1 kV and work distance of 3 mm. Compositional analyses were performed using a Horiba EX-250 energy-dispersive X-ray analyzer attached to the microscope (SEM-EDX) for Al, Si, Na, and Cl, and an X-tec ED-05 energy-dispersive X-ray fluorescence (XRF) spectrometer for Al, Si, and Cl.

2.3. Epoxidation reaction

The epoxidation of 2-cyclohexen-1-one with H_2O_2 was performed in a test tube. 2-Cyclohexen-1-one (Wako Pure Chemical Ind.), the prepared powder, and in some cases water, were placed in the test tube with a rubber cap. An aqueous solution of H_2O_2 (30%, Wako Pure Chemical Ind.) was added, and the mixture was mixed with a magnetic stirrer at 298 K. A small portion of the reaction mixture was collected and analyzed with a GL-Science GC-4000 gas chromatograph equipped with an InertCap 1MS column (GL-Science) and a flame ionization detector. The pH of the reaction mixture was measured with a Horiba B-212 pH meter after filtration of the reaction mixture using a polytetrafluoroethylene (PTFE) membrane filter (0.45 μm). Recycling experiments were performed by repeating the following procedure. After the epoxidation of 2-cyclohexen-1-one, the solids in the reaction mixture were filtered from the reaction mixture using a PTFE membrane filter (0.45 μm) and washed with water. The solids thus recovered were calcined in air at 673 K and reused.

3. Results and discussion

3.1. Characterization of sodalite

The XRD measurements indicated that the products of the hydrothermal synthesis (S1, S2, S3, and S4) had a sodalite structure (Fig. 1A). All the diffraction peaks observed over 2θ ranging from 5 to 70° could be attributed to the sodalite structure [22]. The compositional analysis conducted with SEM-EDX demonstrated that the obtained sodalite samples comprised Na, Si, Al, Cl, and O. It is known that Cl^- anions can be incorporated into a sodalite structure with a ratio of one Cl^- anion per sodalite cage, and that an ideal unit cell of aluminosilicate sodalite containing Cl^- is $Na_8[AlSiO_4]_6Cl_2$ (Al:Si:Na:Cl = 1:1:1.33:0.33) [22]. The compositions of the obtained samples were close to this ideal formula (Table 2).

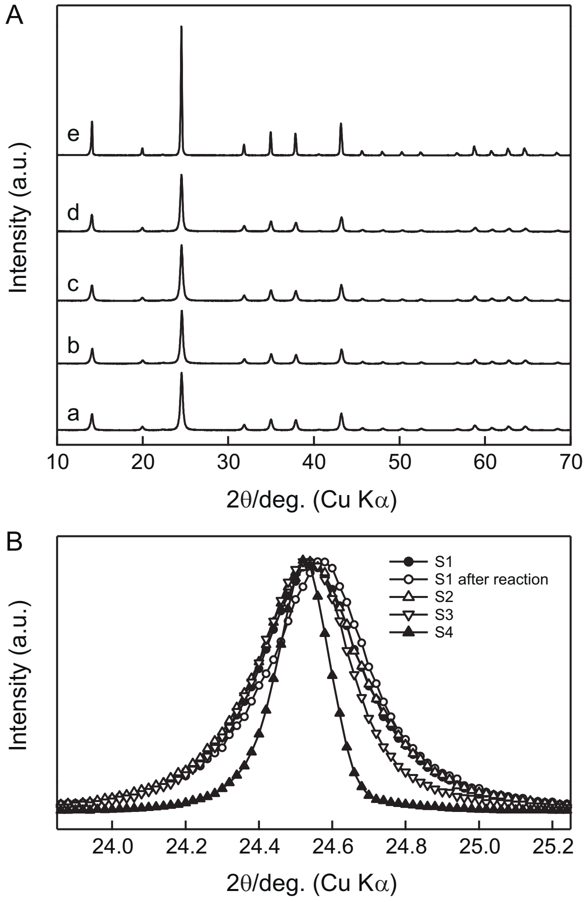

Fig. 1. (A) XRD patterns of sodalite samples. (a) S1, (b) S1 after four reaction–calcination cycles, (c) S2, (d) S3, and (e) S4. (B) Normalized 2 1 1 diffraction peaks of sodalite samples.