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

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**A B S T R A C T**

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 (Na2SiO3·9H2O), sodium aluminate (NaAlO2), and sodium chloride at 423 K. The obtained samples were characterized by X-ray diffraction, the Brunauer–Emmet–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 m² 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.

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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 few very 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 m² 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 m² 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 (H₂O₂) 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 H₂O₂ 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 (NaAlO2) (Junsei Chemical) and water