Journal of Catalysis 264 (2009) 88–92

Contents lists available at ScienceDirect

Journal of Catalysis

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

Research Note

Mesoporous sodalite: A novel, stable solid catalyst for base-catalyzed organic transformations

Ganapati V. Shanbhag, Minkee Choi, Jeongnam Kim, Ryong Ryoo *

Center for Functional Nanomaterials and Department of Chemistry, Graduate School of Nanoscience and Technology, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

ARTICLE INFO

Article history:
Received 26 February 2009
Revised 25 March 2009
Accepted 25 March 2009
Available online 26 April 2009

Keywords:
Mesoporous zeolite
Hierarchical
Sodalite
Basicity
Solid base
Knoevenagel
Claisen–Schmidt
Catalyst deactivation

ABSTRACT

Mesoporous sodalite with a mesoporous/microporous hierarchical structure was successfully synthesized using an organosilane surfactant. It showed about 10-fold high surface area and 4-fold large pore volume, as compared with sodalite with solely microporous structure. The basicity of MPSOD was higher than that of CsNaX or KAlMCM-41. The catalytic activities of this mesoporous zeolite were evaluated for various base catalyzed reactions involving bulky and small substrates, *viz.* Knoevenagel condensation, Claisen–Schmidt condensation in liquid phase, and acetonylacetone cyclization in vapor phase. The catalyst showed higher activity and longer lifetime than CsNaX and KAlMCM-41.

1. Introduction

The potential applications of heterogeneous base catalysts in specialty and fine chemical production have expanded significantly over the years [1–6]. Base-catalyzed condensation, addition, and isomerization reactions are some of the important steps for building large and complex molecules for the synthesis of many fine chemicals and pharmaceutical products. Basic solids such as Cs-ZSM-5 and MgO have been used as catalysts in industrial processes due to their activity, thermal stability, and reusability [7,8]. While metal ion-exchanged zeolites possess basic sites of relatively low strength, they can be easily regenerated from poisoning by air, as compared with strong solid bases, such as alkaline earth oxides [9]. Nevertheless, applications of basic zeolites are limited by slow diffusion of substrates into their micropores for bulky molecular reactions and rapid deactivation due to coke formation [10]. In principle, alkali metals can be ion exchanged onto MCM-41-like mesoporous aluminosilicate for application as a basic catalyst for bulky substrates. However, mesoporous materials built with amorphous frameworks have serious drawbacks due to weak basicity and low hydrothermal stability. Stronger basicity can be induced in materials like mesoporous aluminosilicates and metal-organic frameworks by modifications such as covalent grafting of amines and impregnation of basic metal oxides [11–16]. However, such modified catalysts also carry limitations such as low hydrothermal stability and leaching of active species, preventing them from finding practical applications.

Among the various strategies to synthesize mesoporous zeolites, very few were successful in obtaining high crystallinity with tunable mesoporosity. In one such work, Choi et al. reported a direct synthesis route to mesoporous zeolites with a tunable mesoporous structure using amphiphilic organosilane surfactants as a mesopore-directing agent [17]. The mesoporous MFI zeolite thus synthesized exhibited much higher catalytic activities for the conversion of bulky molecules than a conventional MFI zeolite, providing evidence that the catalytic conversion occurred at the mesopore walls [18]. In catalytic reactions involving small molecules, these two kinds of zeolites initially showed no significant difference, but the mesoporous zeolite exhibited remarkably improved catalytic lifetimes. However, the successful catalytic application has mostly been limited to high silica mesoporous MFI zeolites, which are useful for acid-catalyzed reactions. It is therefore of interest to develop a high aluminum-containing mesoporous zeolite with a basicity similar to the existing basic zeolites. Sodalite is a zeolite with high aluminum content (Si/Al = 1) and high stability in basic solution. However, it thus far has not found any significant catalytic applications due to its inaccessible cages with small pore openings (2.8 Å).

---

* Corresponding author. Fax: +82 42 350 8130.
E-mail address: rryoo@kaist.ac.kr (R. Ryoo).

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.03.014

In the previous works, we had successfully synthesized mesoporous zeolites and zeolite-type solids such as MFI, BEA, LTA, and AlPO via direct hydrothermal assembly methods [17–21]. In this study, we report a new basic solid catalyst, *viz.* mesoporous sodalite with high aluminum content and highly crystalline zeolitic walls. This basic mesoporous zeolite was synthesized using an amphiphilc organosilane surfactant, followed by ion exchange with K^+. The catalytic activity was compared with that of a basic alkali-exchanged NaX and NaAlMCM-41 (Si/Al = 1) for reactions involving bulky and small substrates. The K^+-exchanged mesoporous sodalite has been studied in detail, since K^+ salts are inexpensive and have better exchange ability than Cs^+ salts. The mesoporous sodalite was tested in C–C bond-forming reactions in liquid phase, which involved bulky substrates. Knoevenagel condensation is a key step in the preparation of several pharmaceutics including the antimalarial drug lumefantrine, whereas Claisen–Schmidt condensation products such as 2′-hydroxychalcone and flavanone derivatives are used in the synthesis of anti-inflammatory, anti-allergic, and anti-cancer drugs [22,23]. The catalyst has been further tested in vapor phase intramolecular aldol condensation of acetonylacetone to form a cyclopentenone derivative as the major product. Cyclopentenone derivatives are used as intermediates in the synthesis of perfumes and antibiotics [24].

2. Experimental

2.1. Synthesis of catalysts

A highly crystalline mesoporous sodalite was synthesized by mixing an organosilane $[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{16}H_{33}]Cl$ (51.5 wt% methanol solution) with sodium metasilicate ($Na_2SiO_3.9H_2O$), sodium aluminate (53% Al_2O_3, 43% Na_2O), NaOH, and H_2O to achieve a gel composition of 1.7 SiO_2/15 Na_2O/1 Al_2O_3/80 H_2O/0.3 organosilane in mole ratio. The gel was heated at 423 K for 6 h in a tumbling autoclave for precipitation of sodalite. The zeolite product was collected by filtration, and washed with hot distilled water until the pH of the filtrate was neutral. The product was then dried and calcined in air at 823 K. This sample is designated by MPSOD. Another sample of mesoporous sodalite was synthesized with a gel composition of 1.5 SiO_2/20 Na_2O/1 Al_2O_3/160 H_2O/0.5 organosilane, by following the same hydrothermal procedure as MPSOD except for 373 K. This sample was denoted as MPSOD-1. A third sample of sodalite was synthesized by the same procedure as for MPSOD, except that the organosilane surfactant was not used. This sample without mesoporosity is denoted as SOD. NaAlMCM-41 with Si/Al = 1 was synthesized according to the procedure reported elsewhere [25]. NaX zeolite was procured from Aldrich.

2.2. Cation exchange of catalysts

Cation exchange of Na-form of all the catalyst samples was performed with 0.5 M chloride solutions of K^+ or Cs^+. One gram of the powder was stirred with 10 ml of the solution at 353 K for 3 h. The resultant mixture was then cooled to RT, filtered, and washed repeatedly with distilled water until it was free from Cl^- and physisorbed metal ions. This procedure was performed three times in all to ensure maximum cation exchange. The resulting exchanged materials, i.e., K^+-exchanged MPSOD (hereafter KMPSOD), K^+-exchanged microporous sodalite (KSOD), KAlMCM-41, and CsNaX, were dried at 403 K for 12 h. They were subsequently calcined in static air at 773 K for 4 h except for KAlMCM-41 (containing template), which was calcined by a previously reported procedure [26]. Besides, as synthesized AlMCM-41 was used for cation exchange since the calcined sample was not stable under the applied experimental conditions.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded with a Rigaku Multiflex diffractometer equipped with Cu $K\alpha$ radiation (40 kV, 40 mA). The textural properties of the samples were measured by N_2 sorption at liquid nitrogen temperature with a Quantachrome AS-1MP volumetric adsorption analyzer. Samples were dried at 573 K in a dynamic vacuum for 2 h before the N_2 physisorption measurements. The specific surface area was determined using the standard BET method on the basis of adsorption data. The pore size distributions were calculated from both the adsorption and desorption branches of the isotherms using the BJH method and the Kelvin equation. Elemental analyses were performed by inductively coupled plasma spectroscopy (ICP) using an OPTIMA 4300 DV (Perkin–Elmer) instrument. Nitrogen content was measured by an elemental analyzer, EA-110 (Thermo Finnigan). Transmission electron micrograph (TEM) images were obtained with a Tecnai G2 F30 microscope at an operating voltage of 300 kV. Scanning electron microscopy (SEM) was conducted using a Hitachi S-4800 microscope operating at 2 kV without a metal coating. ^{27}Al MAS–NMR spectra were recorded on a Bruker AM-300 NMR spectrometer (see Supplementary information (hereafter SI) for details). Basicity measurements were carried out by TPD of adsorbed CO_2 using a Belcat-M instrument (see SI).

2.4. Catalytic activity measurements

Knoevenagel condensation of 4-isopropylbenzaldehyde (4-IPB) with ethylcyanoacetate (ECA) was carried out in a Pyrex reactor equipped with a reflux condenser (Eyela Chemistation) under a N_2 atmosphere to prevent the oxidation of aldehyde. No solvent was used in the reaction. In a typical reaction, 10 mmol of 4-IPB and 10 mmol of ECA were mixed with 0.05 g of catalyst and stirred at 353 K. The products were analyzed by an Acme 6100 gas chromatograph fitted with a flame ionization detector and a HP-1 capillary column.

Claisen–Schmidt condensation of 2′-hydroxyacetophenone (2-HAcPh) with benzaldehyde was carried out in a Pyrex reactor under N_2 atmosphere. Five millimole of 2-HAcPh and 10 mmol of benzaldehyde were heated at 423 K with 0.05 g of the catalyst. After the reaction, the reaction mixture was diluted with 2 ml of THF to confirm the dissolution of all the components, and was then analyzed as described above.

Vapor phase cyclization of acetonylacetone (AcAc) was conducted in a fixed bed, down flow reactor using 0.5 g of catalyst pellets (20–35 mesh). The catalyst was pre-activated in a flow of air at 773 K for 2 h, and then cooled down to the reaction temperature. High purity N_2 (30 ml min^{-1}) was used as a carrier gas. The feed (AcAc) was vaporized before passing into the reactor. The product was analyzed with an Acme 6100 gas chromatograph fitted with Supelco α-Dex225 capillary column. Products of all the above-mentioned reactions were identified with authentic samples and GC combined with mass spectroscopy.

3. Results and discussion

3.1. Catalyst characterization

The percentage compositions of different metal ions present in the catalyst are listed in Table 1. Nitrogen content was measured by elemental analysis, and the result indicated that the N-containing groups (from the organosilane) were completely removed by the work-up and calcination steps. Wide angle XRD patterns of MPSOD and MPSOD-1 consisted of peaks that were typical of microporous sodalite (Fig. 1B). The two prominent peaks at