Available online at www.sciencedirect.com

Catalysis Today 110 (2005) 323–329

www.elsevier.com/locate/cattod

Direct synthesis of copper faujasite

Beatriz O. Hincapie [a], Luis J. Garces [a], Sinue Gomez [b],
Ruma Ghosh [c], Steven L. Suib [b,c,*]

[a] Instituto de Quimica, Universidad de Antioquia, Apartado Aereo 1226, Medellin, Colombia
[b] Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA
[c] Unit 3060, Department of Chemistry, University of Connecticut, 55 N. Eagleville Rd., Storrs, CT 06269-3060, USA

Abstract

Copper containing faujasite has been successfully prepared for the first time using a direct synthesis method. Faujasite type zeolite can be prepared in the presence of copper species by tuning the synthesis conditions. Ammonium hydroxide was used to form a copper complex that was later mixed with the reacting gel. Sodium is required to obtain copper faujasite. The complete elimination of sodium ions from the starting gel produces amorphous material. Crystallization took place at 358 K for 11 days. Crystallization temperature of 373 K produces ANA type zeolite as an impurity. Increasing by two times the amount of copper complex added to the reacting gel increases the crystallization time of Cu-FAU from 11 to 20 days (the crystallization rate decreases). The copper containing faujasite obtained was characterized by XRD, FESEM, EDX, EPR, FT-IR, TPR, and BET. According to the XRD pattern only FAU type zeolite was obtained. According to TPR experiments, the reduction temperature for Cu^{2+} ions present in Cu-FAU prepared by direct synthesis was 70 K more than for Cu-FAU prepared by ion-exchange. This difference can be due to the different location of the copper ions in the supercages or in the sodalite cages of the faujasite.

Keywords: Cu-FAU; Zeolite Y; Direct synthesis; Copper tetraammonium nitrate

1. Introduction

Copper(II) exchanged Y zeolite has been used in different applications such as heterogeneous aziridination of styrene [1], to remove organo-sulfur species from commercial diesel fuel [2], as a heterogeneous catalyst for hydrogenations and cyclopropanation [3]. The development of zeolite based catalysts for reducing NO_x to N_2 by NH_3 have received a lot of attention for several reasons like (a) high NO_x conversion, (b) wide selective catalytic reduction window, (c) sulfur tolerance above 700 K, (d) less disposal problems for spent catalysts. The most efficient catalysts are based on transition metals ion-exchanged in zeolites. The reaction is regulated by the redox cycle of the transition metal ion (Cu^+/Cu^{2+}) [4]. Copper exchanged zeolites have also been used for CO hydrogenation and for N_2 storage [5]. Leaching of copper ions in the reacting media is one of the most common problems reported when copper exchanged zeolites are used as heterogeneous catalysts in liquid phase systems. Copper in solution generates undesirable reaction sub-products and limits the number of times than the catalyst can be reused [1].

New methods to synthesize copper containing zeolites are useful [2]. Direct synthesis of Cu-MFI has been previously reported. Copper species were present in the precursor gel and methylamine was used as a mineralizing agent to avoid precipitation of copper oxide. The reported advantages of the direct synthesis of Cu-MFI are the homogeneity of copper distribution in the sample and the reduction of copper leaching into solution [6]. In a different study, a copper(I) complex $[Cu(NH_3)_2]^+$ was formed in situ during the synthesis of the ferrierite framework [7]. Copper nitrate, ammonia, propylamine, silica, alumina, and hydrofluoric acid were used as raw materials [7].

Cu-zeolite Y (copper containing faujasite) has never been prepared in the presence of copper species by a direct synthesis method. We report the tuning of the synthesis conditions to prepare copper containing faujasite by a direct synthesis method. Ammonium hydroxide was used to form copper complexes and to avoid the precipitation of copper oxide in the alkaline media required to prepare the zeolite. Two different

---

* Corresponding author. Tel.: +1 860 486 2797; fax: +1 860 486 2981.
E-mail address: steven.suib@uconn.edu (S.L. Suib).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.09.030

molar ratios of Cu/Al_2O_3 were used to synthesize FAU type zeolite. The experiments to produce Cu-zeolite Y by direct synthesis method and the characterization of the product are reported here.

2. Experimental

2.1. Synthesis procedure

Two different procedures were tried to synthesize copper containing faujasite. In the first method (experiments 9–12), copper tetraammine complex was prepared in situ. In the second method (experiments F34-1–F37) crystals of copper tetraammine nitrate were prepared and mixed with the reacting gel.

Synthesis of copper(II) tetraammine nitrate: Deep blue crystals of copper(II) tetraammine nitrate are formed by addition of ethanol to a solution of copper nitrate in ammonia [8]. Copper nitrate (20 g) was completely dissolved under stirring with concentrated ammonium hydroxide. Ethanol was added to the previously prepared solution to precipitate the copper(II) tetrammine nitrate salt. The crystals were filtered and washed with ethanol.

Synthesis of copper faujasite:

(a) Experiments 9–12 (see Table 1 for batch and crystallization conditions): The materials obtained were synthesized by preparing the copper tetrammine nitrate in situ. Solution 1 was prepared by dissolving copper nitrate in ammonia. Solution 2 was prepared by dissolving sodium hydroxide and aluminate in double deionized water (DDW). Colloidal silica (Ludox LS-30) and solution 2 were added simultaneously to solution 1. The mixture obtained was stirred for 2 h and crystallized at the conditions shown in Table 1. The products were recovered by centrifugation, washed until the pH was less than 8, and dried overnight at 373 K. The procedure to synthesize copper faujasite was modified, since the products obtained were amorphous with copper oxide, gismondine, and faujasite as impurities. Cobalt, nickel, and zinc faujasite were prepared with batch composition shown in Table 1 and following the same procedure used to synthesize experiments 9–12.

(b) Experiments F34-1–F37: Copper(II) tetraammine nitrate was dissolved in water and combined with colloidal silica (Ludox LS-30). After 2 h of stirring, the gel was mixed with an aqueous solution of sodium aluminate and sodium hydroxide. The batch composition used is presented in Table 1. The gel obtained was aged for 24 h and then crystallized at 358 K for 11–20 days. The product was recovered by filtration under vacuum and washed with deionized water until $pH < 8$. The solid was dried overnight at 373 K.

Cu,Na-zeolite Y ion-exchanged was prepared by mixing 5 g of Na-zeolite Y (Aldrich) with 50 mL of a 0.5 M aqueous solution of copper nitrate and stirred for 5 min. The solid was filtered, washed, and dried.

2.2. Characterization

The XRD studies were carried out with a Scintag XDS-200 powder diffractometer on finely powdered samples using Cu Kα radiation and 45 kV and 40 mA. The step size was 0.02° (2θ) and a count time of 0.6 s with a scan rate of 2.0°/min. The XRD patterns were recorded for 2θ values between 5° and 40°.

Field emission scanning electron microscopy (FESEM) experiments for the determination of morphology were performed on a Zeiss DSM 982 Gemini field emission scanning electron microscope (FESEM) with a Schottky Emitter at an accelerating voltage of 2 kV with a beam current of about 1 μA. An ECON IV energy dispersive X-ray (EDX) analyzer Model 9800 was used to determine the silica to alumina ratio and the Cu/Al ratio of the prepared zeolites.

Fourier transform infrared spectra (FT-IR) experiments were done on a Nicolet Magna IR system 750 FT-IR spectrometer with a resolution of 4 cm^{-1}. Potassium bromide (KBr) pellets of the samples were analyzed in the range 4000–400 cm^{-1}.

The TEM measurements were performed on a JEOL 2010 FasTEM 200 kV instrument equipped with an EDAX energy dispersive spectrometer and a Gatan EELS/GIF system.

Table 1
Batch compositions and conditions used to prepare metal,Na-zeolite Y

Run #	NH_4OH/SiO_2	Na_2O/SiO_2	$Metal/Al_2O_3$ (metal)	Crystallization conditions		Product (XRD)
				Temperature (K)	Time (days)	
9	1.2	0.4	0.67 (Cu)	373	6	GIS + amorphous
10	1.2	0.2	0.67 (Cu)	373	6	CuO + amorphous
11	0.6	0.4	0.67 (Cu)	373	6	FAU + ANA + amorphous
12	0.6	0.2	0.67 (Cu)	373	6	Amorphous
F34-1	0.6	0.4	0.11 (Cu)	373	4	FAU + ANA
F37a	0.6	0.4	0.11 (Cu)	358	11	FAU
F37	0.6	0.4	0.22 (Cu)	358	20	FAU
Na-FAU	0	0.4	0	358	6	FAU
Co-FAU	0.6	0.4	0.3 (Co)	358	13	FAU
Ni-FAU	0.6	0.4	0.3 (Ni)	358	13	FAU
Zn-FAU	0.6	0.4	0.3 (Zn)	358	13	FAU

SiO_2/Al_2O_3: 10; H_2O/SiO_2: 12. F37 at 358 K, 11 days produces a mixture of FAU + amorphous.