



Catalytic removal of organic template from TEA- β zeolite by copper ions



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ABSTRACT

The simultaneous decomposition of organic template and incorporation of copper ions into the zeolite were investigated during the heating mixture of copper chloride hydroxide and TEA- β zeolite under static air atmosphere. Detailed characterizations of the samples during calcination and subsequent copper removal treatment were performed with the aid of TG/MS, IR, XRD, pyridine-IR, XPS, ²⁷Al and ²⁹Si MAS-NMR. It was evidenced that the zeolite detemplation process facilitated the copper ions reduction and migration, inducing the solid ion exchange of copper species with TEA- β zeolite at lower temperature. These reduced copper ions migrated into the zeolite to occupy Brønsted acid sites, and acted as catalysts to accelerate the oxidative decomposition of organic molecules significantly. The result showed that the virtually complete removal of organic template and incorporation of copper ions were obtained in one step by calcination at 350 °C for 3 h, and these ingoing copper species could be easily removed by re-exchanging with ammonium solution. After detemplation and copper removal, the purified H- β zeolite could still retain a well-defined structure and Brønsted acid sites, showing a higher catalytic activity on the alkylation of benzene with ethylene compared with the conventionally prepared H- β zeolite.

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1. Introduction

Zeolite β is one of the widely used catalytic materials in chemical processing [1], which possessed high density of Brønsted acid sites and favorable pore structure, and can be synthesized with a wide range of silicon-to-aluminum ratios [2]. Tetraethylammonium (TEA) is commonly used as an organic template for a good control of β zeolite crystallization [2,3]. TEA has to be removed from the pores of the as-synthesised zeolite to obtain an accessible, active and stable hydrogen form or cationic type during post-synthesis [4]. Calcination over 550 °C in air was often used to decompose the TEA species efficiently [4,5]. However, the BEA structure was usually damaged to a certain degree during the high temperature calcination, especially for the relatively low SiO₂/Al₂O₃ ratio zeolite β . High temperature and steaming during calcination usually caused dealumination, agglomeration, and even collapse of the zeolite

structure [5,6]. Moreover, the acidity of zeolite β was also strongly dependent on its thermal activation temperature [7].

Although some new methods such as extraction [8], adding oxidant [9], micro-wave [10] and other combined techniques [11,12] were reported to remove the organic template successfully, they have poor efficiency and solvent problems, and were too costly for large scale industry application. Therefore, some catalytic methods were investigated and highlighted here. Krawiec et al. presented a new method to inject a Pt precursor into the inner core of the surfactant micelles of the template for the MCM-41 synthesis. Platinum were well dispersed as nanoparticles inside the pores of MCM-41, and this confined Pt particles acted as a catalysts for the oxidative removal of template at lower temperature (400 °C) [13]. The catalytic removal of template by platinum was also observed by Liu et al., who mixed the as-synthesized MnMgAlPO-5 with Pt/SiO₂ catalysts, and heated this mixture to 340 °C in a hydrogen flow. The result showed that the template was removed from the pores and the zeolite structure was preserved [14].

It is well-known that the supported copper exhibited a high activity in oxidative decomposition of chlorinated organics in air, acted like noble metals (Pt, Pd). Lago et al. proposed that the copper

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(II) and cuprous (I) chlorides acted as the active component in CuCl/KCl/SiO₂ catalyst for oxidative decomposition reaction. They further pointed out that the organics were chemisorbed to the copper surface, and the active oxygen in the oxychloride species would be assisting in breaking the C–H bond which was the rate limiting step in the whole organics decomposition process [15]. However, as the dimensions of hydrated copper complexes were often large in aqueous solution, they were hard to be introduced into the blocked channels of zeolite without detemplation.

Solid-state ion exchange (SSIE) is a promising method for the post-synthesis modification of zeolites. During thermal treatment in air, inert atmosphere or vacuum, the solid-state interaction can occur between the zeolite powder and the mixed metal halide or metal oxides (usually in high vacuum or inert atmosphere with high temperature). It allows the exchange of large multivalent cations into the cationic sites of zeolite, which is normally difficult in aqueous solution. Moreover, some new active sites can be created in SSIE during the redox atmosphere [16]. Kucherov et al. showed that the high temperature calcination of H-ZSM-5 or H-Mordenite with CuO, CuCl₂, CuF₂ in air, could result in migration of Cu (II) or Cu (I) ions from the outer surface into the cationic positions of zeolite. The number of introduced cations was related linearly to the Al³⁺ content (Brønsted acid sites) in the zeolite lattice [17]. Shwan et al. demonstrated that copper oxides could be reduced and become mobile during heating in NH₃ atmosphere, and these mobile copper species were easily introduced into zeolite through solid-state ion exchange reaction at lower temperature ($T \leq 250$ °C) than conventional one [18]. Neinska et al. also found that the reductive solid state ion exchange of indium(I) cations with TEA- β zeolite was achieved by thermal treatment of mixtures of TEA- β with In₂O₃ in non-oxidative atmosphere at 397 °C, and the decomposed products (e.g., ammonia, alkylamine, ethane) were acting as the reducing agents [19].

The present work described a new method to remove template from as-synthesized TEA- β zeolite at low temperature via incorporation of copper ions in one step. In this approach, the as-synthesized copper chloride hydroxide precursor and TEA- β zeolite powder were mixed together to form a uniform mixture, and then the mixture was heated at a low ramp rate in static air. When the SSIE reaction among the intimate mixture was taking place, the active copper ions incorporated into the zeolite matrix and TEA⁺ cations decomposed and were released from cationic positions of the zeolite. The residual TEA species were further catalytically decomposed and further removed from channels of the zeolite at low temperature. The active, ready to use Cu- β zeolite was obtained after the decomposition completed. Copper could be removed by ion-exchange using an ammonium solution.

2. Experimental section

2.1. Materials

The zeolite matrix was NH₄-TEA- β zeolite obtained by ammonium ion exchange from commercial Na- β zeolite, which was supplied by Sinopec Catalysts Co., Ltd, China. The chemical composition of NH₄-TEA- β zeolite was determined by XRF and found to be 7.3 wt% Al₂O₃, 92.5 wt% SiO₂, and trace of Na (<0.1 wt%) after calcination at 1000 °C.

The supported copper chloride hydroxide precursor in the present study was prepared by adding the ammonia hydroxide solution (28 wt%) into copper (II) chloride aqueous solution to form a gel (pH \approx 7). Then a specified amount of dried NH₄-TEA- β zeolite power was suspended in the gel slurry and mixed sufficiently by stirring. After filtering, washing with distilled water to remove the adsorbed chloride ions, the filter cake was dried overnight at 120 °C

to obtain an intimate mixture of copper chloride hydroxide and NH₄-TEA- β powder. Subsequently, the mixture was heated at the assigned temperature in muffle furnace and kept for 3 h under static air condition. Afterwards, the product was cooled down in atmosphere and exchanged with ammonium nitrate aqueous solution (5 wt%) to remove copper ions. Finally, the obtained powder was calcined at 300 °C for one hour, and a ready-to-use catalyst (20–40 meshes) was obtained after molding.

Hereinafter, the obtained samples were denoted as X_mCu β -Y, where a single Cu β was used to name the dry mixture of copper chloride hydroxide and NH₄-TEA- β powder. X represented the different stages of treatments, including the first calcination at assigned temperature (C), exchanging with ammonium cations after calcination (EC), and the final calcination treatment (CEC). The assigned calcination temperature “m” (in °C) marked as the subscript of X; and Y indicated the copper content corresponding to molar ratio of Cu to Al in the precursors. For comparison, NH₄-TEA- β zeolite (named as TEA- β) calcined at 350 °C and 550 °C were marked as samples C₃₅₀- β and C₅₅₀- β respectively. Sample Cu β _{free} was prepared by intimate mixing calcined TEA- β zeolite (800 °C in air.) and copper chloride hydroxide precursor. C₃₅₀Cu β _{free} was named after Cu β _{free} calcined at 350 °C for 3 h in static air.

2.2. Characterization

The element contents of all samples were measured by X-ray fluorescence spectroscopy (XRF, Rigaku ZSX Primus II) with an Rh target X-ray tube. Prior to measurements, all samples were dried at 120 °C for 2 h.

Thermogravimetric measurements (TG/DTG/DTA, TG/MS) were carried out on a TGA apparatus (Universal V3.9A from TA Instrument), equipped with a mass spectrometer Prisma QMS 200 (Balzers). Test was conducted under a dynamic air atmosphere (50 ml/min) with a heating rate of 10 °C/min from room temperature to 800 °C.

The specific surface area and pore volume were measured on a Micromeritics Tristar 3000 equipment. BET surface area was calculated using the BET equation, and the pore size distribution was obtained through desorption isotherm branch. The total pore volume (V_p) was derived from the adsorbed N₂ volume at a relative pressure of 0.99.

IR spectra of powder samples were determined by a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector. Spectra were recorded in the 4000 - 400 cm⁻¹ range with a resolution of 4 cm⁻¹ at room temperature.

X-ray powder diffraction (XRD) measurement was conducted on a Bruker D8 Advance X-ray diffractometer with a Ni-filtered Cu K α radiation source. The scanning 2 θ range was 10–80°, and the scanning speed was 2°/min [20].

A 300 MHz (7.05 T) magnet spectrometer (Varian INOVA-300) instrument with a standard bore CP MAS probehead in 6 mm zirconia rotors was used to record ²⁷Al and ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR). ²⁷Al spectra were recorded at the spinning frequency of 78.162 MHz with a MAS spinning rate of 5 kHz. 6000 scans were collected by using radio frequency pulses of 1.5 μ s with a recycle delay for 3 s. All ²⁷Al spectra took AlCl₃ (0 ppm) as the reference. ²⁹Si spectra were recorded at 59.621 MHz, with a MAS spinning rate of 3 KHz. A total of 3000 scans were acquired with a 4 μ s pulse width and a relaxation delay of 10 s. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS) at 0 ppm.

The total acidity of the detemplated samples were determined by a temperature-programmed desorption of ammonia (NH₃-TPD). Before adsorption of ammonia, the samples were treated under helium at 200 °C for 1 h and cooled at 100 °C in a He flow, then

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