Synthesis and evaluation of Cu/SAPO-34 catalysts for NH$_3$-SCR 2: Solid-state ion exchange and one-pot synthesis

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ABSTRACT

Cu/SAPO-34 catalysts are synthesized using two methods: solid-state ion exchange (SSIE) and one-pot synthesis. SSIE is conducted by calcining SAPO-34/CuO mixtures at elevated temperatures. For the one-pot synthesis method, Cu-containing chemicals (CuO and CuSO$_4$) are added during gel preparation. A high-temperature calcination step is also needed for this latter method. Catalysts are characterized with surface area/pore volume measurements, temperature programmed reduction (TPR), electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectroscopies, and scanning electron microscopy (SEM). Catalytic properties are examined using standard ammonia selective catalytic reduction (NH$_3$-SCR) and ammonia oxidation reactions. For Cu/SAPO-34 samples prepared by SSIE, Cu presents both as isolated Cu^{2+} ions and unreacted CuO. The former are highly active and selective in NH$_3$-SCR, while the latter catalyzes a side reaction; notably, the non-selective oxidation of NH$_3$ above 350 °C. Using the one-pot method followed by a high-temperature aging treatment, it is possible to form Cu/SAPO-34 samples with predominately isolated Cu^{2+} ions at low Cu loadings. However at much higher Cu loadings, isolated Cu^{2+} ions that bind weakly with the CHA framework and CuO clusters also form. These Cu moieties are very active in catalyzing non-selective NH$_3$ oxidation above 350 °C. At very low reaction temperature temperatures (<155 °C), standard NH$_3$-SCR over Cu/SAPO-34 catalysts appears to be kinetically limited. However at higher temperatures, multiple rate limiting factors are possible.

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1. Introduction

Cu/SAPO-34 is one of the Cu/Chabazite catalysts that are currently commercialized as selective catalytic reduction (SCR) catalysts for diesel engine exhaust after-treatment. It has been known for some time, however, that Cu/SAPO-34 synthesis using a traditional aqueous solution ion exchange (IE) method is not straightforward [1–3]. This is due primarily to the fact that SAPO-34 undergoes facile irreversible hydrolysis during IE, leading to catalysts with low specific surface areas, micropore volumes and poor crystallinity. In our first paper of this series [4], Cu/SAPO-34 formation *via* aqueous solution IE was systematically studied using SAPO-34 samples synthesized with various structure-directing agents (SDAs). Interestingly, we found that the extent of irreversible hydrolysis depends strongly on two factors: Si–O–Al bond density within the SAPO framework, and zeolite framework stress. During

solution IE, a SAPO-34 sample with higher Si–O–Al bond density and framework stress decomposes much more readily than a sample with low Si content and relatively low crystallinity. Regardless of the SAPO-34 substrate used, a high-temperature (*e.g.*, 800 °C) aging treatment inevitably leads to substantial surface area and pore volume loss for Cu/SAPO-34 samples generated using this method [4]. It should be emphasized that Cu/SAPO-34 catalysts formed with solution IE are still highly active and selective in NH$_3$-SCR. *However, samples synthesized using this method cannot be considered very well-defined for fundamental and lab-to-lab comparative studies.*

To circumvent issues associated with solution IE, two alternative synthesis methods, one-pot synthesis and solid-state ion exchange (SSIE), are considered here. In one-pot synthesis, Cu-containing chemicals are introduced in the gel preparation step prior to hydrothermal synthesis. These could be Cu salts or CuO [5], or Cu-containing SDAs [6,7]. Following the synthesis and calcination steps, one obtains Cu/SAPO-34 directly. SSIE is a commonly used method to introduce charge compensating cations in zeolites [8]. Typically, zeolites and metal halides are thoroughly mixed together and the mixture is heated to elevated temperatures in flowing inert

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gas or vacuum to facilitate ion exchange. Alternatively, SSIE can be performed by passing metal halide vapors through a zeolite bed held at a certain elevated temperature. When zeolites are in hydrogen or ammonium forms, SSIE is particularly suitable since the hydrogen halides generated are readily removed. This allows high exchange levels that are generally difficult for solution IE. To our knowledge, Cu/SAPO-34 formation *via* SSIE first appeared in the open literature in 1992 [9]. In the present study we systematically investigated SSIE and one-pot methods in Cu/SAPO-34 formation with the aims of: (1) providing simple yet efficient methods that can be readily reproduced by other researchers; and (2) generating model catalysts (*e.g.*, samples with solely isolated Cu^{2+} ions) that are suitable for structure–function relationship type of studies. The model catalysts thus generated were further tested for NH_3-SCR to probe such relationships.

2. Experimental

2.1. Catalyst synthesis

As is well-known, SAPO-34 can be synthesized with various Si/Al/P precursors, gel compositions and SDAs. Minor structural differences in SAPO-34 samples, however, may have profound effects on their catalytic behavior [10,11]. Therefore, five different SAPO-34 substrates were used in the SSIE section. However, for the sake of simplicity, only two are discussed in detail below. One of these samples was purchased from ACS Material®, and is denoted here as SAPO-34-ACS. The other was prepared in-house, using morpholine (MOR) as SDA, 85% o-phosphoric acid as the P source, aluminum hydroxide as the Al source, and fumed silica as the Si source. Poly(ethylene glycol), PEG-400, was also used as a crystal growth inhibitor (CGI) to generate uniform and small particles [12]. All chemicals used in our syntheses were purchased from Sigma-Aldrich with purities of analytical grade or better. This sample is denoted as SAPO-34-MOR. More details for the preparation this sample and other in-house synthesized SAPO-34 samples have been published elsewhere [4]. Table 1 lists the initial gel composition prior to synthesis of SAPO-34-MOR, and BET surface areas and micropore volumes (from the *t*-plot method) of the two SAPO-34 samples measured with a Quantachrome Autosorb-6 analyzer and using liquid nitrogen. Note that surface areas and pore volumes of these two samples are almost identical. This was one of the main reasons that these two substrates were chosen for detailed comparison. We also used three other in-house samples for SSIE and these are detailed in Supplementary information (SI-1). SEM images for all of the SAPO-34 samples are also shown in SI-1.

SSIE was first tested by thoroughly mixing anhydrous $CuCl_2$ and SAPO-34, and then the mixture was slowly heated in a tube furnace under dry N_2. Unfortunately, SAPO-34 completely decomposed in this process. Presumably, an acidic environment, formed by the dissolution of the generated HCl into residual H_2O, led to SAPO-34 decomposition. Our control experiments show that SAPO-34 readily decomposes in hot acid solutions. Next, nanosized CuO (Sigma-Aldrich, average particle size ~50 nm, confirmed from our own XRD analysis using the Scherrer equation) was used as the Cu source. In this case, SAPO-34 and CuO powders were thoroughly mixed inside a mortar and the mixtures were calcined in air at various elevated temperatures for various periods. Cu/SAPO-34 catalysts were successfully synthesized *via* this method.

During one-pot synthesis, $CuSO_4$ and CuO were chosen as the Cu sources. $CuSO_4$ could be added directly at any stage of the gel preparation. However, CuO must first be dissolved in phosphoric acid. More details regarding gel preparation can be found elsewhere [5]. After hydrothermal synthesis at 200 °C for 30 h under continuous stirring, the solids were separated from the mother liquid *via*

centrifugation and washed with deionized water for 3 times. Finally, they were dried at 120 °C under flowing N_2 and calcined in air at 600 °C for 5 h. A portion of the samples were further calcined in air at 800 °C for 16 h.

2.2. Catalyst characterization

Cu contents of the Cu/SAPO-34 samples were determined with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) conducted at Galbraith Laboratories (Knoxville, TN, USA). Prior to measurements, the samples were partially dehydrated at 150 °C for 2 h in vacuum to remove adsorbed moisture. BET surface areas and t-plot method micropore volumes of the samples were measured with a Quantachrome Autosorb-6 analyzer. Prior to analysis, the samples were dehydrated under vacuum overnight at 250 °C. Temperature-programmed reduction (TPR) was performed on a Micromeritics AutoChem II 2920 analyzer. After purging the hydrated samples (*i.e.*, samples stored in air and, thus, saturated with moisture) with pure N_2 at 10 mL/min at room temperature for 30 min, TPR was carried out in 5% H_2/Ar at a flow rate of 30 mL/min. Temperature was ramped linearly from ambient to 800 °C at 10 °C/min and H_2 consumption was monitored with a TCD detector. 50 mg of catalyst was used for each H_2-TPR experiment. Powder X-ray diffraction (XRD) measurements were performed on a Philips PW3040/00 X'Pert powder X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å). Data were collected with 2θ ranging from 5° to 50° with a step size of 0.02°. Scanning Electron Microscopy (SEM) was conducted on a FEI Helios 600 FIB-SEM instrument. Samples were mounted on a carbon tape and 5 nm of carbon was deposited onto the samples for conductivity. Imaging was done at 5 keV. Electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) experimental details have been described elsewhere [4].

2.3. SCR and NH_3 oxidation reaction tests

NH_3-SCR reaction kinetics were measured using a plug-flow reaction system described elsewhere [4]. Powder samples were pressed, crushed and sieved (60–80 mesh) prior to use. For standard SCR, the feed gas contained 350 ppm NO, 350 ppm NH_3, 14% O_2, 2.5% H_2O and balance N_2. NH_3 oxidation reactions were conducted in the same manner without NO_x. Stoichiometries for these reactions are shown below:

Standard SCR reaction : $4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O$;

NH_3 oxidation reaction : $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.
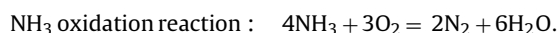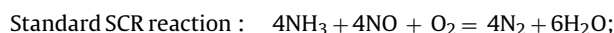
All of the gas lines were heated to over 100 °C to avoid water condensation. The total gas flow was 300 sccm, and the gas hourly space velocity (GHSV) was estimated to be ~400,000 h^{-1} for a catalyst amount of 30 mg. Concentrations of reactants and products were measured by an online Nicolet Magna 560 FTIR spectrometer with a 2 m gas cell maintained at 150 °C.

For temperature-dependent steady-state reaction measurements, the catalysts were first activated in 14% O_2/N_2 flow for 1 h at 550 °C. Following which, NO, NH_3 and H_2O were added to the feed to start the SCR reaction. At each target temperature, a minimum waiting time of ~45 min was applied to insure steady-state reaction. NO_x and NH_3 conversions were calculated based on the following equations:

$$NO_x \text{ Conversion\%} = \frac{(NO + NO_2)_{inlet} - (NO + NO_2 + N_2O)_{outlet}}{(NO + NO_2)_{inlet}}$$
$$\times 100$$