Efficient selective oxidation of propylene by dioxygen on mesoporous-silica-nanoparticle-supported nanosized copper

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A B S T R A C T

A direct synthetic route was developed to prepare mesoporous-silica-nanoparticle-supported copper catalysts featuring ordered mesostructures with extensive intraparticle voids, a high degree of silica condensation, and a high dispersion of copper species. After hydrogen reduction, the catalysts containing nanosized metallic copper showed superior and stable catalytic activity for the selective oxidation of propylene by dioxygen, with high conversion of both reactants and high yield and formation rate of acrolein. The best catalyst outperformed the state-of-the-art silica-supported copper catalysts, representing one of the most active acrolein-production catalysts. Results of in situ X-ray absorption spectroscopy, in situ diffuse reflectance infrared Fourier transform spectroscopy, and other characterizations suggested that the metallic copper transformed and mainly stayed in the 1+ oxidation state under reaction conditions and that factors including the small size of copper and the presence of silanol groups on the silica support were crucial for the catalytic performance of the catalysts.

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1. Introduction

Supported nanocatalysts containing highly dispersed metals generally exhibit high activity in heterogeneous catalysis, mainly owing to their high surface area with an abundance of low-coordination surface sites [1–8]. The preparation of metal nanocatalysts on high-surface-area supports remains challenging because nanosized metals tend to agglomerate or sinter during catalyst preparation and/or under catalytic reactions [1,3,4,6,8]. This is especially true for the preparation of copper catalysts, which have been widely applied in important industrial processes [9,10] and are promising for selective oxidation [11–21], hydrogenation [22–25], photocatalysis [26–29], and other reactions. Methods including ammonia-induced deposition precipitation [6,30], fatty-acid-assisted assembly [31,32], solid state grinding [33,34], vacuum thermal preparation [15], and co-gelation [35] have been reported to deposit copper particles on high-surface-area silicas, but the dispersion of copper remains low for these materials.

Obviously, there is a strong need for new strategies to prepare high-surface-area silica-supported nanosized copper catalysts.

Among the reactions catalyzed by copper, the selective oxidation of propylene with dioxygen (O_2) to produce acrolein is of great interest [11,15,17,20,36,37] because it is a green reaction that produces the high-value-added acrolein for the manufacture of acrylic acid, methionine, and other important chemicals [11,38–40]. Supported copper catalysts have been shown to be active for this reaction, with the product selectivity mainly associated with the oxidation state of copper and the reaction temperature [1,11,17,19,20,41]. Supported CuO_x [11,15] and copper-incorporated zeolites [41,42] are reported to produce acrolein, with CO_2 and ethanal as main byproducts, and higher reaction temperatures result in higher propylene conversion accompanied by decreased acrolein selectivity. Making small Cu (or CuO_x) particles on high-surface-area supports has been suggested to be a way of achieving high propylene conversion and high acrolein selectivity simultaneously at relatively low temperature [1,6]. Recently, we reported a method of preparing highly dispersed copper nanoparticles on mesoporous SBA-15 silica [15]. The SBA-15-supported copper catalysts exhibited high conversion of propylene and high selectivity for acrolein and outperformed other silica-supported copper catalysts [43]. The study indicates that the small

size of copper is the most crucial factor in high catalytic activity for the reaction. In addition to the size effect, the surface properties of the support may also affect the catalytic performance of the supported catalysts. For example, Fukuoka et al. found a promotional effect of the surface silanol groups in the preferential oxidation of carbon monoxide catalyzed by platinum nanoparticles supported on mesoporous FSM-16 silica [44]. Nevertheless, for supported copper catalysts, the possible influence of the surface properties of the support on their catalytic performance has seldom been discovered and studied.

Here we report a direct synthesis of MCM-41-type mesoporous silica nanoparticle (MSN)-supported nanosized copper catalysts and catalytic studies on the selective oxidation of propylene with O_2. The synthesis was based on the "pH-jump" synthesis of mesoporous MCM-41 silica [45], with the ammonia complex of Cu(II) as the metal precursor. The addition of ethyl acetate (EA) caused a drastic drop in solution pH and simultaneously initiated the cooperative self-assembly of ordered mesophases and the condensation of silicates, as well as the deposition of copper oxide species. The copper oxide species in the resulting materials (abbreviated as CuMSN) were subsequently transformed to nanosized metallic copper by hydrogen reduction. We found that the reduced CuMSN exhibited superior catalytic activity and stability for the selective oxidation of propylene with O_2 to produce acrolein, and that the silanol groups on the silica surface of CuMSN facilitated the adsorption of propylene, thereby enhancing the conversion of the reactant. The acrolein yield for the best CuMSN was almost four times the value for the state-of-the-art SBA-15-supported copper catalyst under relatively mild reaction conditions [15]. Techniques including hydrogen temperature-programmed reduction, in situ X-ray absorption spectroscopy, and in situ diffuse reflectance infrared Fourier transform spectroscopy were employed to identify the promotional effect in the CuMSN-catalyzed oxidation of propylene by O_2.

2. Experimental

2.1. Materials preparation

The preparation of CuMSN was based on the "pH-jump" synthesis of pure silica MSNs [45]. The solution containing cetyltrimethylammonium bromide (1.14 g, Acros), sodium metasilicate (2.02 g, J.T. Baker), and water (675 mL) was mixed well with a calculated amount of the stock solution of the ammonia complex of Cu(II) (prepared by adding ammonia solution (50 mL, 3.0 M) into an aqueous solution (50 mL, 0.1 M) of copper nitrate (Showa)). EA (9.76 mL, Alfa) was then quickly added to the mixture, which was vigorously stirred for 30 s, then kept static at 35 °C for 24 h, and finally aged at 90 °C for 24 h. The surfactant molecules in the as-synthesized samples were removed by calcination at 540 °C or by repeated solvent extraction (with an ethanol solution of ammonium nitrate (0.025 M) at 50 °C for 15 min for three times). The calcined and solvent-extracted samples with varied copper-to-silicon (Cu/Si) ratios of x% are denoted as xCuMSN-C and xCuMSN-E, respectively.

A reference sample with Cu/Si of 3% was prepared by impregnation of the calcined pure silica material (i.e., 0CuMSN-C) with an aqueous solution of copper nitrate followed by calcination at 540 °C. The reference sample is denoted as 3CuMSN-IC.

2.2. Materials characterization

Dynamic light scattering (DLS) measurements were conducted on a particle size analyzer (Brookhaven Instruments Corporation, Holtsville, NY). Inductively coupled plasma–mass spectroscopy

(ICP-MS) data were obtained using a Perkin–Elmer SCIEX-ELAN 5000 device. Powder X-ray diffraction (PXRD) patterns were obtained on a Mac Science 18MPX diffractometer using CuKα radiation. N_2 physisorption isotherms were measured at 77 K using a Quantachrome Autosorb-1-MP instrument. The desorption branches were analyzed by the density functional theory (DFT) method to evaluate pore sizes, and the adsorption branches in the relative pressure range 0.05–0.30 were used to calculate surface areas by the Brunauer–Emmett–Teller (BET) method. Pore volumes were evaluated at a relative pressure of 0.95. Solid-state ^{29}Si MAS NMR spectra were measured on a Bruker AVANCE III spectrometer using a 4-mm MAS probe. SEM images were obtained with a field emission JEOL JSM-7000F microscope operating at 10 kV and equipped with an energy dispersion X-ray (EDX) spectrometer. The samples were coated with Pt before measurements were performed. TEM images were taken using a JEOL JEM-2010 microscope operated at 200 kV and equipped with an EDX spectrometer. Diffuse reflectance UV–visible absorption spectra were recorded on a JASCO V-650 spectrophotometer equipped with a diffuse reflectance accessory.

2.3. Hydrogen temperature-programmed reduction

Hydrogen temperature-programmed reduction (H_2 TPR) was performed at atmospheric pressure in a conventional flow system. A sample (40 mg) was placed in a tubular reactor and heated at a rate of 10 °C min^{-1} in a mixed gas stream (10% H_2 and 90% N_2) with a flow rate of 30 mL min^{-1}. The K- and P-values for the measurements were 55–140 s and 5–20 K, respectively [46,47]. A cold trap that contained a gel formed by the addition of liquid nitrogen to acetone in a Thermos flask was used to prevent water from entering the thermal conductivity detector.

2.4. Estimation of surface area and dispersion of metallic copper

The surface area and the dispersion of metallic copper in the reduced CuMSN catalysts were estimated by a method combining H_2 TPR and N_2O oxidation [15,30]. The freshly prepared catalyst was first analyzed by H_2 TPR to calculate the total number of copper atoms in that catalyst. After H_2 TPR, the reduced catalyst was cooled to 80 °C under N_2, and the atmosphere was then switched to 10% N_2O/N_2 for 30 s to oxidize the surface atoms of the metallic copper nanoparticles to Cu (I) according to the reaction $2Cu_{(s)} + N_2O_{(g)} \rightarrow Cu_2O_{(s)} + N_{2(g)}$. The thus-produced Cu_2O monolayer was quantified by H_2 TPR and the amount of H_2 consumed was used to calculate the surface area of copper by assuming an average surface density for the metal of 1.4×10^{19} atoms m^{-2} [15,30]. The dispersion of copper was calculated from the number of surface copper atoms and the total copper content of the catalyst. The data were also used to estimate the average particle size of copper nanoparticles in the reduced catalyst by assuming a spherical particle shape. The equations to calculate surface area (S_{Cu}), dispersion (D_{Cu}), and average particle size (d_{Cu}) of copper nanoparticles are

$$S_{Cu} \ (\text{in m}^2/\text{g}_{Cu}) = (2 \times Y \times N_{av})/(X \times M_{Cu} \times 1.47 \times 10^{19})$$
$$\approx 1353 \times Y/X,$$

$$D_{Cu} \ (\text{in } \%) = (2 \times Y/X) \times 100\%,$$

$$d_{Cu} \ (\text{in nm}) = 6/(S \times \rho_{Cu}),$$

where X is the H_2 consumption for complete reduction of the copper in the catalyst, Y is the H_2 consumption for the reduction of surface Cu(I) species (formed by N_2O oxidation), N_{av} is Avogadro's constant (6.02×10^{23} mol^{-1}), M_{Cu} is the relative atomic mass of copper