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RESEARCH NOTE

Nanocatalysis: Selective Conversion of Ethanol to Acetaldehyde Using Mono-atomically Dispersed Copper on Silica Nanospheres

James L. Gole* and Mark G. White†

School of Physics and †School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

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Silica nanospheres, $d \sim 30$ nm, are prepared at elevated temperature from an Si/SiO$_2$ mixture. Under ambient conditions, the high population of surface hydroxyl on these nanospheres, confirmed by FTIR spectroscopy, is probed by decorating the surfaces of the spheres with the metal complex copper (II) acetylacetonate: Cu(acac)$_2$. This metal complex, known to be anchored by the surface SiOH species, is converted into the active catalyst by thermolysis of the ligands. The resulting monatomic copper distribution forms a selective catalyst whose conversion efficiency appears to be at least comparable to if not better than CuO/fumed silica. In contrast to the fumed silica, the preparation of this catalyst support is environmentally benign. © 2001 Academic Press

INTRODUCTION

It has been suggested that nanometer-size particles, properly treated, can be used to form high-surface-area catalysts whose efficiencies improve on existing catalytic function (1). We have synthesized dispersed silica (SiO$_2$) nanospheres in gram quantities using a novel technique that does not require solvents and produces no byproducts to compromise the environment. The synthesis technique (2) relies on a mixture of silicon and silicon dioxide, heated under a flow of UHP argon to elevated temperature for a specified duration. The synthesis method produces silica nanospheres, having a nearly monodisperse particle size of about 30 nm (Fig. 1). These spheres, as demonstrated by high-resolution transmission electron microscopy and X-ray diffraction, are amorphous, as samples display several of the same physical properties as the fumed silica produced from the flame hydrolysis of silicon tetrachloride (e.g., the product Cab-O-Sil) (3). In this paper, we examine the silica nanosphere surface properties and demonstrate the presence of surface silanol groups (–SiOH) which can be used to sequester active Cu sites for the selective conversion of ethanol to acetaldehyde.

Infrared spectroscopy as it reveals the presence of certain functional groups on the surface of solids (4) is effective in evaluating the presence of silanols (–SiOH) (5) on the silica surface. We have used this technique to describe the effectiveness of a reactive base to remove silanol groups from silica–alumina (6). In this paper we include the results of an IR analysis of the surface of the silica nanospheres.

A surface population of –SiOH groups on silica can influence the bonding of metal complexes to the surface (7). The loading of the metal complexes and the resulting morphology of the supported metal ions is influenced by the –SiOH groups on the surface. In this paper we probe the surface chemistry by contacting a silica sample, a portion of which is displayed in the TEM micrograph of Fig. 1, with Cu(acac)$_2$ in acetonitrile in sufficient concentration to produce a silica that contains ∼3 wt% Cu. This same procedure has been used to make monatomic dispersions of Cu ions on fumed amorphous silica produced by the Cabot Corporation (Cab-O-Sil) (8). The purpose of the present experiment is to determine (i) whether the surface environments of the two silicas display a similar affinity for anchoring Cu ions to the surface as isolated ions, and (ii) the relative selectivity and efficiency of the Cu decorated silica nanospheres.

The products of the ethanol dehydrogenation reaction ($C_2H_5OH \rightarrow H_2 +$ products) depend upon the ensemble size of supported Cu ions (8). Isolated copper ions catalyze only the dehydrogenation to acetaldehyde, whereas multiple Cu ensembles show high yields of ethyl acetate in addition to acetaldehyde. Thus, the ethanol/acetaldehyde probe reaction can be used to define the presence of monatomic dispersions of Cu ion from an examination of the product distribution (8).

EXPERIMENTAL

Figure 1 corresponds to a TEM micrograph of the nearly monodisperse SiO$_2$ nanospheres of diameter ∼30 nm, which can be generated in gram quantities on the cold plate of an elevated high-temperature synthesis device which we have described elsewhere (2). By adjusting flow parameters and temperature, it is possible to generate

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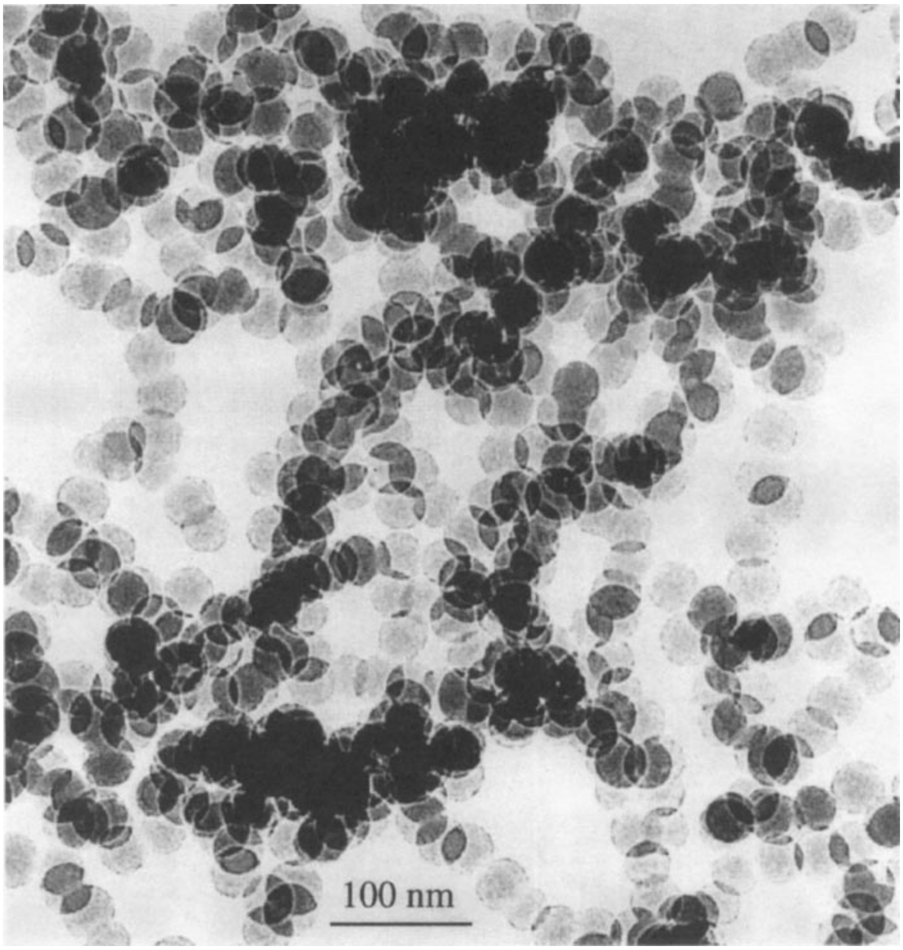

FIG. 1. TEM of virtually "monodisperse" SiO_2 nanospheres 30 nm in diameter.

nanospheres ranging in diameter to at least 10 nm in virtually monodisperse distributions. It is possible to generate these nanospheres not only from Si/SiO_2 mixtures but also from SiO powders albeit at somewhat higher temperatures!

We have examined the surface properties of the produced silica nanospheres directly by Fourier transform infrared spectroscopy (FTIR) and indirectly by measuring their activity and selectivity for the ethanol dehydrogenation reaction to acetaldehyde. The details of the FTIR apparatus used in this study have been described elsewhere (9). Here, we repeat these protocols to examine the novel silica nanospheres ($d \sim 30$ nm). For these studies, powders of the silica were placed in a sample chamber, which could be evacuated to 1 mTorr and which could be heated to 300°C.

The Cu/silica catalysts were prepared through batch impregnation of 1 g of the silica with sufficient $Cu(acac)_2$ metal complex to produce a sample having 3 wt% Cu. The complex was added to 25 mL of acetonitrile solvent and allowed to reflux with stirring for 24 h. The solid was separated by filtration and dried at room temperature for 18 h. This solid was dried at 100°C for 1 h and then placed in a microreactor tube.

The ethanol dehydrogenation reaction was completed in a microcatalytic reactor, the details of which have been described earlier (7c). Prior to the reaction, the catalyst was heated to 350°C for 1 h in flowing helium, then cooled to the reaction temperature. The reaction conditions were 330°C, 20 mL per minute of He carrier gas flow over a 100-mg bed of catalyst having a Cu loading of 3 wt%. Five- to 10-μL pulses of ethanol were vaporized into the He carrier gas stream to create the reactant feed. Pulses of unreacted ethanol and the products of reaction were partitioned on a GC column and detected by a thermal conductivity detector inside a GOW-MAC GC.

RESULTS AND DISCUSSION

The characterization of the silica nanospheres by FTIR spectroscopy is outlined in Fig. 2. The nanospheres were scanned just after their introduction into the sample chamber at 25°C and 1 atm. Subsequently, the samples were

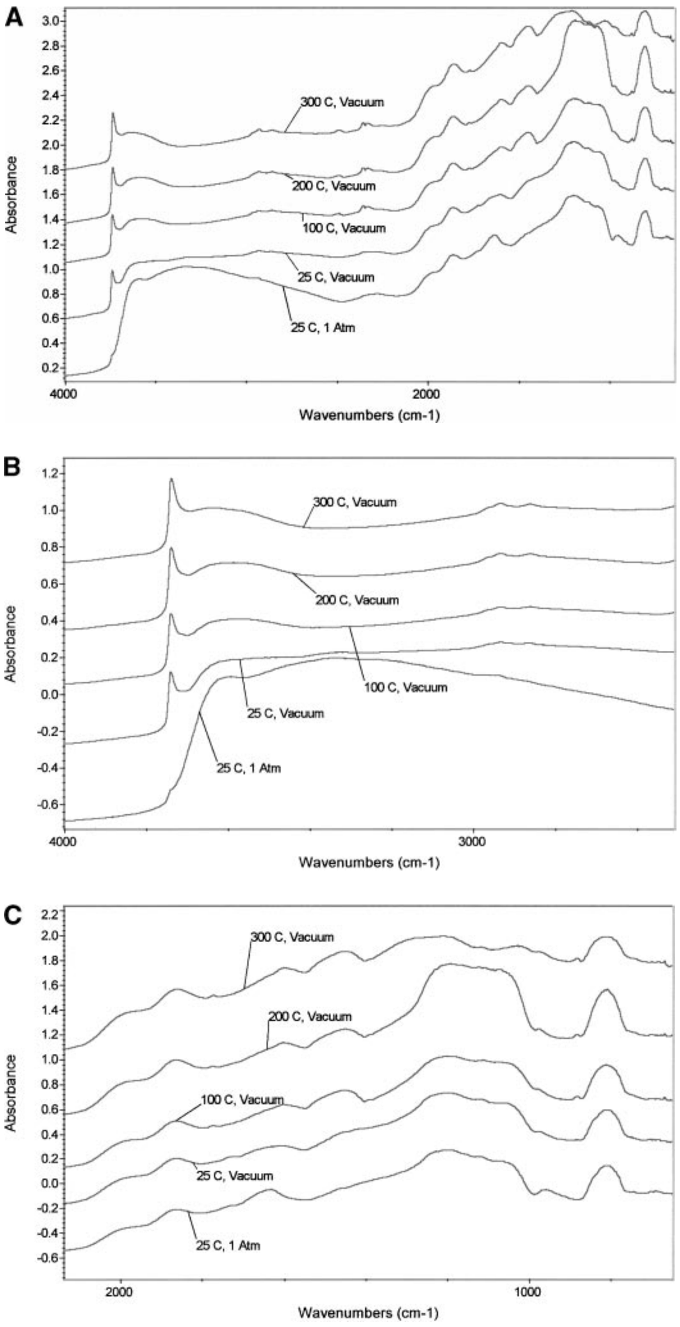

FIG. 2. FTIR of SiO_2 nanospheres. (A) Scan of full spectrum, 4000–600 cm^{-1}. (B) Scan of OH region, 4000–3000 cm^{-1}. (C) Scan of fingerprint region, 2000–600 cm^{-1}.

evacuated to <1 mTorr at 25°C and their spectrum was recorded. The nanospheres were then heated to 100, 200, and 300°C *in vacuo* and their spectra were recorded under these conditions.

In Fig. 2, we depict scans of the entire spectrum from 4000 to 600 cm^{-1} (Fig. 2A), the OH region (Fig. 2B, 4000–3000 cm^{-1}), and the fingerprint region (Fig. 2C, 2000–600 cm^{-1}) at each of the above-described conditions. Under 1 atm pressure at room temperature, the sample shows a large, broad peak (Figs. 2A and 2B) between 3000 and 4000 cm^{-1} that is characteristic of adsorbed, molecular water. This feature decreases to a negligible level immediately upon evacuation at room temperature. This result suggests that most of the water is only weakly adsorbed to the silica nanospheres. Additional peaks (Fig. 2C) are present at 1800, 1600, 1200, and 800 cm^{-1}. *In vacuo* at 25°C, we observe a sharp peak at $\sim$3700 cm^{-1} and a broad peak near 3400 cm^{-1} (Fig. 2B). When the sample is heated to 300°C under vacuum, the peak at $\sim$3700 cm^{-1} grows even sharper and the adjacent peak at 3400 cm^{-1} grows smaller (Fig. 2B), demonstrating further water removal. With increased heating above 200°C, the peaks at 1200 and 800 cm^{-1} at first increase and then broaden and (Fig. 2C) decrease in intensity as a shift of intensity to higher frequency features is apparent.

We compare the results, which we obtain for the nanospheres with the literature data for Cab-O-Sil (3, 5). Flame-hydrolyzed, amorphous silica shows a signature for the SiO–H vibration near 3743 cm^{-1} and a broad peak near 3400 cm^{-1} that corresponds to adsorbed water. Additionally, Si–O vibrations are evident at 1800 and 1600 cm^{-1}. It appears that the surface functional groups found on the silica nanospheres are similar to those found to be present on Cab-O-Sil.

The effect of the Cu/silica nanocatalyst on the ethanol dehydrogenation reaction is presented in Table 1. Acetaldehyde was the only product observed. Forty-five percent of the ethanol was converted over about 3 mg of Cu in the 100-mg sample of Cu/silica using the nano-silica sample. The conversion per mg of Cu in this sample is 45%/3 mg or 15% conversion/mg Cu. Compare this to the results reported by Kenvin and White (8) for a Cu/silica prepared from Cab-O-Sil and operated under similar conditions (300°C, 5.1 mg Cu ion + 143 mg of silica, 15.5 mL/min of He carrier, 1–2 L of ethanol in liquid pulses). These authors observed 25% conversion over 5.1 mg Cu for a 5.1% conversion/mg Cu. No other products were observed.

These results demonstrate that the conversion efficiency for the catalyst formed from the copper loaded silica nanospheres is at least comparable to if not better than that formed from the fumed silica (within the accuracy of the microcatalytic technique for determining catalyst activity).

TABLE 1

Summary of Results

Species	This work (mol %)	Kenvin (Cu/Cab–O–Sil)[8] (mol %)
EtOH	55	75
Acetaldehyde	45	25
Other products	0	0

Moreover, the selectivity to form acetaldehyde is the same for the two catalysts. Each solid catalyzes the single reaction to form the simple dehydrogenation product without the side reaction corresponding to ethyl acetate coupling. The absence of the ethyl acetate-forming reaction shows that no large ensembles of Cu are present in either sample.

We conclude that the new source of silica may represent an improved catalyst support for well-dispersed Cu. In fact, the results obtained using the nanospheres clearly demonstrate only the products of monoatomically dispersed Cu (only acetaldehyde is observed) with an apparently improved efficiency. The process for forming this new catalyst suggests an additional advantage in that it might replace the present technique for making fumed amorphous silica by a process that is environmentally benign. The currently applied process for making fumed silica burns silicon tetrachloride to make silica and HCl. The present process, which relies on an elevated temperature synthesis involving only an Si/SiO_2 mixture, eliminates the need to handle silicon tetrachloride and it does not produce the acid gas.

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