Complete CO Oxidation over Cu$_2$O Nanoparticles Supported on Silica Gel

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ABSTRACT

We find that nearly monodisperse copper oxide nanoparticles prepared via the thermal decomposition of a Cu(I) precursor exhibit exceptional activity toward CO oxidation in CO/O$_2$/N$_2$ mixtures. Greater than 99.5% conversion of CO to CO$_2$ could be achieved at temperatures less than 250 °C for over 12 h. In addition, the phase diagram and pathway for CO oxidation on Cu$_2$O (100) is computed by ab initio methods and found to be in qualitative agreement with the experimental findings.

Nanoparticles offer a larger surface-to-volume ratio and a higher concentration of partially coordinated surface sites than the corresponding bulk materials. The unique properties of nanoparticles are due to a strong interplay between elastic, geometric, and electronic parameters, as well as the effects of interactions with the support. The result of these features is often improved physical and chemical properties compared to the bulk material. It is for these reasons that heterogeneous catalysis at nanoparticle surfaces is currently under intense investigation in the catalysis community at large.[1,2] Conventional supported catalysts are generally produced by impregnation of a support medium with the desired metal ions followed by thermal treatments that result in small and dispersed active catalytic sites.[3,4] Many traditional catalysts based on the impregnation method[5,6] rely on the noble metals, in particular platinum, as the source for high activity. Such metals are recognized as a scarce resource as well as a limiting step in the development of viable energy alternatives to petroleum. Automotive exhaust catalysts (the three way catalyst) and fuel cells are examples of this tenet.[5,6] Any new system that overcomes these limitations will be invaluable.

There are several important processes in heterogeneous catalysis where removal of carbon monoxide is either desired or absolutely necessary, such as in the postprocessing of Syngas[7] to produce hydrogen as an energy source for use in fuel cells.[8,9] A byproduct of this reaction is CO; however, trace amounts of CO (>10 ppm) can poison a fuel cell electrode, drastically reducing its efficiency.[10−12] The Cu−Cu$_2$O−CuO system has been known to facilitate oxidation reactions in the bulk, suggesting it has potential as a cost-effective substitute for noble metals in various catalytic systems.[13−15] Here we describe a cheap, effective method of using copper oxide nanoparticles loaded onto silica gel as an exceptional catalyst toward CO oxidation at relatively low temperatures. Over sustained periods of time, conversions of 99.5% of CO to CO$_2$ are routinely observed and the catalyst structure is retained during the reaction. For example, during a 50 h period with the same ∼10 mg sample of copper oxide nanoparticles, over 30 L of CO is converted to CO$_2$ with an average conversion of 98 ± 1%.

With recent developments in nanoparticle synthesis leading to the ability to control size, reproducibility, and structural complexity, it becomes urgent to define specific target structures for the nanoparticles based on an understanding of the mechanism of the reactions occurring at their surfaces. Application of the most sophisticated computational techniques to examine all aspects of chemical behavior on nanoparticles is challenging due to the limitation of computational resources. However, as the facets of the nanoparticles have a well-defined surface geometry, insights from theory and modeling can be obtained from parallel calculations carried out on single-crystal surfaces. In addition to our experimental findings we describe the results of calculations of the phase diagram and pathway for CO oxidation on Cu$_2$O (100), which are in qualitative agreement.

Our synthetic methods enable us to generate nanoparticles of various copper oxide compositions and sizes in a predetermined fashion.[16] The procedure relies on the introduction of chemically reactive molecular precursors into inert, hot (250 to 350 °C) solvents (such as trioctylamine), in which they combine—in the presence of ligands—to form the desired nanocrystalline product through pyrolysis, decomposition, or other chemical reactions.[16,17] Careful consideration of the concentrations, stoichiometry, and nature
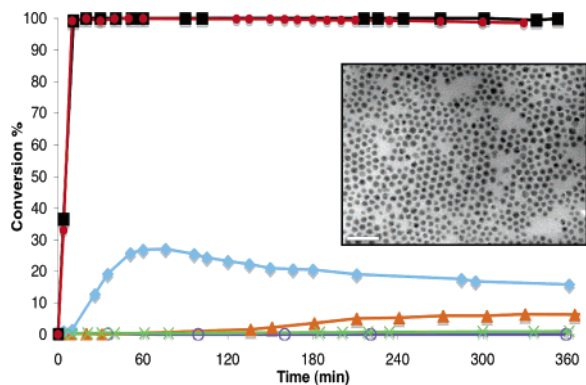
Figure 1. Conversion rates of CO to CO_2 for various types of copper and copper oxides run at 240 °C in 93% N_2, 3% O_2, and 4% CO. 13 mg of each powder and 75 mg of silica gel were used in each experiment: (□) 24 nm Cu_2O nanoparticles, 10 mg; (●) 11 nm Cu_2O nanoparticles, 10 mg; (◆) copper powder; (▲) Cu_2O powder; (×) CuO powder; (○) silica gel. Inset: TEM image of as prepared 6 nm Cu_2O nanoparticles. Scale bar = 50 nm.

Figure 2. X-ray powder diffraction patterns of the catalyst system at various stages: (A) as prepared Cu_2O nanoparticles 24 nm diameter, crystalline Cu_2O; (B) 10 mg of Cu_2O nanoparticles mixed with 75 mg of silica gel and heated under N_2 for 1 h at 240 °C, crystalline Cu_2O and Cu; (C) same as (B) with CO/O_2 (4%/3%) introduced for 1.5 h, final CO_2 conversion of 98%, crystalline Cu_2O; (D) same as (C), but run for 4.5 h, final CO_2 conversion of 99.8%, mixed crystalline Cu_2O/CuO; (E) same as (C), but run for 144 h, final CO_2 conversion of 85.1%, mixed crystalline Cu_2O/CuO.

of the addition is required to obtain nanocrystal nucleation that leads to the formation of a narrow size distribution (<5−10% root mean square diameter). The nanocrystal size can be controlled by the temperature, time allowed for growth, and the subsequent addition of ligands. The advantage of this procedure is that it can produce nanoparticles identical in crystal structure and almost identical in size, which can be dispersed in solvents and transferred to other media very easily without agglomeration on surfaces, as seen in the transmission electron micrograph (Figure 1 inset).

In previous studies of thin films and bulk powders the proposed mechanism of conversion of CO to CO_2 on a CuO surface is a redox cycle involving the reduction of Cu^{2+} to Cu^+ by CO. Oxygen is then supplied from the surface of the copper oxide and reacts with the CO to form CO_2.[4,13,14,18] Aside from the oxidation state of copper, the oxygen concentration is an important factor in the oxidation process. It has been reported[3,19] that much of the CO oxidation work with copper uses an inert gas, such as N_2, 1−2% CO, and 19% O_2, which readily oxidizes the copper to CuO. Concentrations of O_2 which result in a CO−O_2 ratio lower than 2:1 will reduce the copper to Cu^0.[14]

To obtain an optimized catalytic system, nanoparticle dispersions in hexanes were mixed with silica gel (SA ~ 500−600 m^2/g), stirred at room temperature, and transferred to the reactor. The nanoparticle ligand, oleic acid, both stabilizes the nanoparticles and prevents aggregation in solutions and in films, which is critical to the catalyst preparation prior to its use. A wide range of nanoparticle loadings were tested on silica gel. It is hypothesized that silica gel separates the nanoparticles thus preventing sintering and therefore maximizing the surface area available for oxidation.

Catalyst loading was a very important factor in the activity of our nanoparticle system, and therefore accurate values of the concentration of nanoparticle dispersions were needed. Gravimetric analysis was used to determine the concentration of particles (metal and ligand) in a given sample, and transmission electron microscopy (TEM) was used to
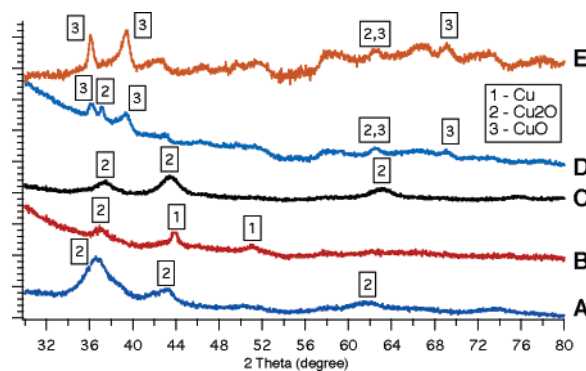
determine the average particle size in the sample. Because of the uniformity in size, accurate percent weight concentrations can be estimated and easily replicated using spectrophotometric calculations of concentration based on the absorption coefficient of the dispersion (see Supplementary Information).

To gain better insight into the Cu_2O nanoparticle based catalyst, thermogravimetric analysis (TGA) and X-ray powder diffraction (XRD) experiments were used to determine the composition and oxidation state, respectively, of the as-synthesized and postreaction materials. The thermogram (See Supplementary Information Figure 2) of Cu_2O nanoparticles shows they are coated with oleic acid after synthesis. TGA indicates that the oleic acid capping group is completely removed at 240 °C, suggesting that the Cu_2O nanoparticles are completely bare at the end of the pretreatment, prior to CO oxidation. The Cu_2O nanoparticles (Figure 2a) on silica are pretreated at 240 °C for 1 h under N_2, during which the exposed surface is partially reduced to Cu^0, as confirmed by XRD (Figure 2b). Upon introduction of CO and O_2 into the system there is low conversion for approximately 20 min, during which the nanoparticles revert to the Cu^+ state (Figure 2c). Oxidizing the sample in O_2 for 20 min prior to adding the CO reduces the induction period to less than 4 min.

In a typical experiment 1 mL of 0.03 M dispersion of Cu_2O nanoparticles in hexanes were mixed with 75 mg of silica gel and placed on a medium porosity glass frit. When loaded on to a continuous flow reactor and exposed to 4% CO, 3% O_2, and 93% N_2 at standard pressure and flow of 260 mL/min at 240 °C, it was found that conversion remains above 99.5% for over 12 h, after which it begins to gradually decline. The catalyst was tested for extended periods under continuous CO/O_2 flow, and over 144 h the conversion dropped from 99.9% to 85% (Supplementary Information, Figure 4). We also find that the conversion is independent of O_2 concentration; 2:1 ratios of CO−O_2 as well as 1:5 ratios of CO−O_2 result in a high percent of CO oxidation (See Supplementary Information). With such high catalytic activ-

ity, a deeper look into the mechanism was warranted. Studies of the mechanism of CO oxidation on copper oxides in the bulk have been complicated by many subtleties.[14] It is generally assumed that oxygen atoms are supplied to the carbon monoxide molecules adsorbed on the surface by the copper oxide lattice, and oxygen lost from the lattice is replenished through the adsorption and dissociation of gas phase oxygen. Presumably a similar process occurs for the nanoparticles but with an unexpected level of efficiency. In our reaction, the used catalyst shows evidence of CuO as well as Cu_2O (Figure 2d,e), suggesting a mixed state of Cu^+ and Cu^{2+}; however surface Cu^{2+} is an unlikely candidate for oxidation or O_2 dissociation. Consistent with previous reports for the bulk,[13] we believe the active catalyst state to be Cu^+ (in a Cu_2O lattice) which is either present from the onset or formed by reduction of Cu^{2+} by adsorbed CO. It is then thought that the CO combines with a surface oxygen to form CO_2.[14]

Theoretical calculations suggest that the lattice oxygen, not gas-phase oxygen, plays a critical role in the CO oxidation process, further verifying the Langmuir−Hinshelwood mechanism. To gain insight into the mechanism of catalytic CO oxidation on Cu_2O, the energetics and pathways for CO adsorption, diffusion and reaction on Cu_2O (100) were calculated, using density functional theory (DFT) with the generalized-gradient approximation for the exchange-correlation functional[20] using the plane wave pseudopotential method.[21] To meet the translation symmetry requirement, a supercell was built containing a Cu_2O (100) slab and approximately 14 Å of vacuum. The CO behavior was modeled for the O-terminated Cu_2O (100), as it was found to be more stable than Cu-terminated surface. The slab was comprised of alternate O and Cu layers (seven of O and six of Cu), with four atoms in the O layer and eight atoms in the Cu layer. One CO molecule on the surface of the Cu_2O corresponds to a (2×2) unit cell. Ultrasoft pseudopotentials[22] were used for all atoms under consideration. The cutoff energy for the plane-wave expansion was 400 eV, and the Brillouin zone was sampled with a $(7 \times 7 \times 1)$ k-point mesh. Two reaction pathways were considered for a CO molecule landing on the surface: one where it lands on a surface oxygen atom and another on a surface Cu atom. For both cases the CO trajectories were perpendicular to the surface. The results of calculations are illustrated in Figure 3.

To land on surface oxygen, CO has to overcome an activation barrier of about 0.4 eV. As CO overcomes the barrier and approaches the surface, the energy of the system decreases drastically by ∼2 eV. The CO molecule is found to react with the surface oxygen forming CO_2, which departs spontaneously from the surface (barrierless) creating an oxygen vacancy. On the other hand, if CO lands on a Cu atom, it approaches the surface without any barrier (see Figure 3), diffuses spontaneously to the neighboring surface oxygen, and produces CO_2 as in the earlier step. These calculations attest to the high propensity of CO to oxidize on Cu_2O (100) spontaneously by consuming a surface oxygen. This explains the high catalytic activity of Cu_2O observed even at low temperatures.
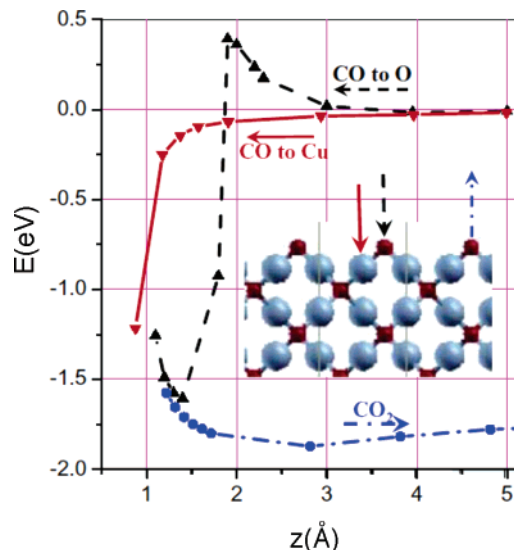

Figure 3. Calculated energetics for CO landing on a surface oxygen atom (dashed line) and on a Cu atom (solid line) and for CO_2 departure from the surface (dash−dot line). The pathways are schematically shown in the inset, in which O and Cu atoms are represented by the small and large balls, respectively. The z value indicates the separation between C atom and the initial position of the surface oxygen atom.

The oxygen vacancies created in the course of the CO oxidation will tend to reduce the catalytic activity of the surface. However, the surface oxygen may be restored by dissociative adsorption of gaseous O_2 present in the reaction environment. The O_2 concentration should be high enough to enable restoration of the surface oxygen. At the same time, the concentration of adsorbed oxygen should not exceed the amount at which it starts blocking the active surface sites. The healing of the reduced Cu_2O surface thus becomes an important issue and is the subject of continuing studies in our group.

In summary, we have developed a new catalyst system comprised of Cu_2O nanoparticles supported on silica gel that carries out very efficient oxidation of CO to CO_2. The active catalyst structure is thought to be a mix of crystalline Cu^{2+} and Cu^+. The presence of the silica gel extended the lifetime of the nanoparticles, presumably by preventing sintering, which decreases the effective surface area. The Cu_2O nanoparticles oxidized CO to CO_2 for over 144 h with no dependence on O_2 concentration before decreasing reactivity. Our system is a cost-effective, highly efficient alternative to current CO oxidation systems, thus opening the doorway to a variety of applications requiring cheap one-time use or short time frame catalysts for oxidizing CO to CO_2.

Supporting Information Available: Detailed experimental procedure, controls, thermograms, a long run time plot, and T_{50} data. This material is available free of charge via the Internet at http://pubs.acs.org.

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