Low-Temperature, Highly Selective, Gas-Phase Oxidation of Benzyl Alcohol over Mesoporous K-Cu-TiO₂ with Stable Copper(I) Oxidation State

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Selective oxidation of alcohols to aldehydes, in particular benzyl alcohol-to-benzaldehyde, is one of the most common organic transformations and is of fundamental importance for laboratory and commercial processes.1 Currently, benzaldehyde is produced through stoichiometric oxidation by manganese and chromium salts in the laboratory or by liquid-phase chlorination and oxidation of toluene in industrial processes.1 In the wake of increasing concern about the environment, the benzyl alcohol/benzaldehyde transformation should preferably be accomplished by using a highly selective and recyclable "green" catalyst that is able to use molecular oxygen as the oxidant.2

In practice, the oxidation of alcohols with molecular oxygen can be performed in the liquid or gas phase, depending mainly on the thermal stability and volatility of the reagents and products. The convenience of catalyst separation and solvent-free conditions make thermal stability and volatility of the reagents and products. The transformation should preferably be accomplished by using a highly selective and recyclable "green" catalyst that is able to use molecular oxygen as the oxidant.2

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The biggest disadvantage of gas-phase oxidation is the high reaction temperature, which tends to favor energy consumption, low selectivity, and deactivation of active sites. The reaction temperatures currently reported for gas-phase benzyl alcohol oxidation are generally above 300 °C, 100 °C higher than the boiling point (bp) of benzyl alcohol (203 °C), over various catalysts (e.g., Au/SiO₂, K/Ag/SiO₂, Cu/Na/ZSM-5, and Au-Cu/SiO₂), and no appreciable benzyl alcohol/benzaldehyde oxidation below 200 °C has been reported.

In this communication, we report a newly developed mesoporous ternary metal oxide (K-Cu-TiO₂) that is capable of activating the selective gas-phase oxidation of benzyl alcohol at a surprisingly low temperature, the bp of benzyl alcohol (203 °C). The low-temperature reaction conditions and the homogeneous integration of K and Cu(I) components into the TiO₂ matrix enable the stabilization of the active Cu(I) oxidation state and the resulting stable, excellent catalytic performance.

Mesoporous K-Cu-TiO₂ catalysts (3K-Cu-50TiO₂ and 3K-Cu-20TiO₂) were synthesized according to our previously reported ACHE method (Supporting Information (SI)).5 The catalysts possess a two-dimensional hexagonal mesoporous structure as confirmed by small-angle X-ray scattering and transmission electron microscopy (TEM) analysis (Figure 1). Mesoporous 3K-Cu-50TiO₂ and 3K-Cu-20TiO₂ have high surface areas, 150 and 144 m²·g⁻¹, respectively.

A detailed energy dispersive X-ray (EDX) element mapping measurement of mesoporous 3K-Cu-50TiO₂ at a resolution of ~10 nm shows uniform X-ray intensities of K, Cu, Ti, and O signals throughout the mesoporous particles, revealing the existence of a homogeneous distribution of multiple components (Figure 1b). Wide-angle X-ray diffraction (WAXD) analysis reveals only the anatase crystalline phase of 3K-Cu-50TiO₂ despite the copresence of Cu and K.

Figure 1. (a) TEM image of mesoporous 3K-Cu-50TiO₂ and (b) element mapping of a single mesoporous 3K-Cu-50TiO₂ particle.
TiO2 catalysts and their stable, excellent catalytic performance: (i) the stabilization of the Cu(I) oxidation state in mesoporous Cu-K-In our reaction system, two factors play very important roles in and a concurrent major modification of their catalytic properties. Continually exposing copper catalysts to oxidizing and reducing component in the proximity of Cu(I) integrated into the 3-D TiO2 reaction temperature (203 °C). For comparison, mesoporous Cu-ZrO2, Cu-SiO2, and Cu-Al2O3 were also synthesized and investigated as catalysts for gas-phase benzyl alcohol oxidation. They all show very poor activity (1%—7% conversion), implying that there is a synergistic effect between Cu and TiO2.

One of the biggest challenges in selective oxidation is the deactivation of catalysts during the course of a long-term reaction. Continually exposing copper catalysts to oxidizing and reducing environments generally leads to a change of their oxidation state and a concurrent major modification of their catalytic properties. In our reaction system, two factors play very important roles in the stabilization of the Cu(I) oxidation state in mesoporous Cu-K-TiO2 catalysts and their stable, excellent catalytic performance: (i) a low reaction temperature (203—223 °C). TPO studies reveal that the Cu(I)-to-Cu(II) conversion in mesoporous 3K-Cu-TiO2 starts at 222 °C. At a high reaction temperature (T = 230 °C, Tbed = 247 °C), complete Cu(I)-to-Cu(II) conversion leads to total oxidation of benzyl alcohol; (ii) homogeneous distribution of the K component in the proximity of Cu(I) integrated into the 3-D TiO2 host matrix. Making a mechanical mixture of KCl with Cu-TiO2 gives poor catalytic performance. After a 20-h reaction, more than 90% Cu(I) in Cu-20TiO2 is oxidized into Cu(II), together with an ~50% loss in benzaldehyde yield (Figure 2b,d). In contrast, after adding the K component, the Cu(I) % does not change (44% vs 45%) and the benzaldehyde yield only slightly decreases from 71.9% to 67.6%. The improved stability of Cu(I) of K-Cu-TiO2 against oxidation is also confirmed by the increased Cu(I)-to-Cu(II) conversion temperature (from 190 to 222 °C). After the homogeneous incorporation of the K species, the bonding energy of Ti2p1/2 and Cu2p1/2 of 3K-Cu-50TiO2 shifts down 0.6 and 0.4 eV due to increased electron density, which may be responsible for the improved stability of Cu(I) against oxidation. Homogeneous distribution of the K atoms is necessary to ensure the proximity of K ions to Cu and Ti species so that the electron transfer from Cu(I) is less favorable.

Clarification of the reaction mechanism is important for the future design of catalysts with enhanced performance. That the reaction occurs stoichiometrically without added oxygen supports the so-called classic dehydrogenation mechanism where the alcohol dehydrogenation and oxidant reduction steps are sequential, and not coupled (SI). The lower yield in the absence of O2 and formation of the surface hydride species as determined by EPR and spin trapping are both consistent with this mechanism (SI). In addition, benzaldehyde is readily oxidized by a free radical mechanism to benzoic acid, so that the very high benzaldehyde yield argues against a free radical mechanism dominating the chemistry here. For the catalyst performed with added O2, no surface hydride species are observed, suggesting that O2 acts as an efficient hydrogen acceptor and accelerates the reaction by creating the free active Cu(I) sites.

In summary, using a high surface area catalyst and the homogeneous distribution of multiple components integrated into a matrix, we have shown that the gas-phase oxidation of benzyl alcohol to benzaldehyde can be accomplished at low temperatures, with a high TOF (up to 108 h⁻¹). We believe that this strategy will be of general importance to other multicomponent heterogeneous catalytic reactions and has promise as an alternative to current alcohol oxidation processes.

Acknowledgment. We are grateful for financial support from the National Science Foundations of China (20873122 and J0830413) and the National Science Foundation (DMR 02-33728). We thank Dr. Peter Ford for helpful discussions.

Supporting Information Available: The synthesis of mesoporous materials, material characterization, and catalytic result analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References


JA9032499