

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 a gas-phase process more attractive for industrial applications. While many recent reports deal with the liquid phase aerobic oxidation with/without solvents,³ less attention has been paid to the gas-phase reaction, and attempts to develop a successful gas-phase industrial application have failed owing to selectivity and stability problems.⁴ 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,^{4a} K/Ag/SiO₂,^{4b} Cu/Na/ZSM-5,^{4c} and Au-Cu/SiO₂^{4d}), and no appreciable benzyl alcohol/benzaldehyde oxidation below 250 °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 mesophase 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

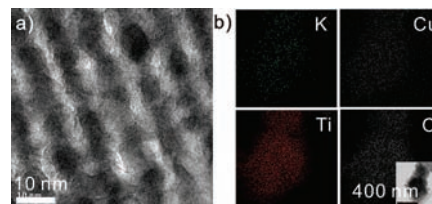


Figure 1. (a) TEM image of mesoporous 3K-Cu-50TiO₂ and (b) element mapping of a single mesoporous 3K-Cu-50TiO₂ particle.

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 (WXR) analysis reveals only the anatase crystalline phase of 3K-Cu-50TiO₂ despite the copresence of Cu and K.

The oxidation state of copper ions is a key factor that determines their catalytic property in selective oxidation reactions. X-ray photoelectron spectroscopy (XPS) was used to characterize the Cu oxidation state. The coexistence of Cu(I) and Cu(II) in fresh 3K-Cu-20TiO₂ catalyst is evidenced by a shoulder observed on the main peak at 931.6 eV (Figure 2a), which is assigned to Cu(I) species. The higher binding energy (BE) Cu 2p_{3/2} peak at 933.7 eV and its shakeup satellites are due to Cu(II). The Cu(I) percentage in fresh mesoporous 3K-Cu-20TiO₂ is estimated to be 44%.⁶ For mesoporous 3K-Cu-50TiO₂, only Cu(I) species are confirmed by XPS. These Cu(I) species can be completely oxidized to Cu(II) by oxygen at 250 °C as evidenced by temperature programmed oxidation (TPO) and XPS data. The electron paramagnetic resonance (EPR) spectrum of oxidized 3K-Cu-50TiO₂ exhibits a pronounced peak at $g_{\perp} = 2.132$ and a poorly resolved quadruplet at $g_{\parallel} = 2.383$, corresponding to isolated ions located in octahedral sites. It implies that the original Cu(I) also exists as isolated ions incorporated within the TiO₂ matrix.

Mesoporous K-Cu-TiO₂ is highly active in the selective oxidation of benzyl alcohol at a reaction temperature as low as 203 °C, the bp of benzyl alcohol. In our example, a high selectivity (>98%) to benzaldehyde with a conversion of ~72% is obtained between 203 and 223 °C over mesoporous 3K-Cu-20TiO₂ (Figure 2c), and the mesoporous 3K-Cu-50TiO₂ displays a stable yield of >99% for the benzyl alcohol-to-benzaldehyde transformation in this low temperature range (Figure 2d). Such a stable, excellent catalytic performance at this low temperature in gas-phase benzyl alcohol oxidation is very unusual.

The high surface area, integrated K, Cu(I), and TiO₂ matrix is responsible for the high activity of the K-Cu-TiO₂ catalyst at low temperatures, for the gas-phase benzyl alcohol oxidation. Pure TiO₂ shows very poor activity for this reaction (only 6.9% conversion).

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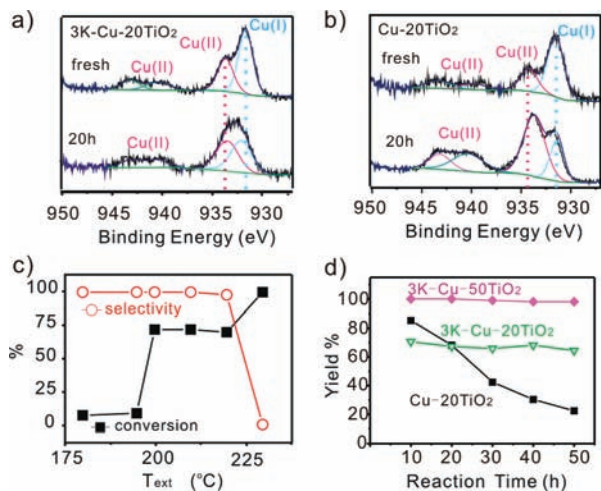


Figure 2. XPS spectra of mesoporous (a) 3K-Cu-20TiO₂ and (b) Cu-20TiO₂ before and after the reaction; (c) benzaldehyde selectivity and benzyl alcohol conversion as a function of the setup temperature (T_{ext}) over 3K-Cu-20TiO₂; and (d) benzaldehyde yields vs time on stream using Cu-TiO₂ (200 °C), 3K-Cu-20TiO₂ (210 °C), and 3K-Cu-50TiO₂ (210 °C) as the catalysts.

The incorporation of 0.2% Cu (Ti/Cu = 500) can significantly boost the benzyl alcohol-to-benzaldehyde conversion of TiO₂, from 6.9 to 46.1%. 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-20TiO₂ starts at 222 °C. At a high reaction temperature ($T_{\text{ext}} = 230$ °C, $T_{\text{bed}} = 247$ °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 Ti2p_{3/2} and Cu2p_{3/2} 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.⁷

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).² 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).⁸ 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.³

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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>.

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