

# Crystal-Plane-Controlled Selectivity of Cu<sub>2</sub>O Catalysts in Propylene Oxidation with Molecular Oxygen\*\*

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**Abstract:** The selective oxidation of propylene with O<sub>2</sub> to propylene oxide and acrolein is of great interest and importance. We report the crystal-plane-controlled selectivity of uniform capping-ligand-free Cu<sub>2</sub>O octahedra, cubes, and rhombic dodecahedra in catalyzing propylene oxidation with O<sub>2</sub>: Cu<sub>2</sub>O octahedra exposing {111} crystal planes are most selective for acrolein; Cu<sub>2</sub>O cubes exposing {100} crystal planes are most selective for CO<sub>2</sub>; Cu<sub>2</sub>O rhombic dodecahedra exposing {110} crystal planes are most selective for propylene oxide. One-coordinated Cu on Cu<sub>2</sub>O(111), three-coordinated O on Cu<sub>2</sub>O(110), and two-coordinated O on Cu<sub>2</sub>O(100) were identified as the catalytically active sites for the production of acrolein, propylene oxide, and CO<sub>2</sub>, respectively. These results reveal that crystal-plane engineering of oxide catalysts could be a useful strategy for developing selective catalysts and for gaining fundamental understanding of complex heterogeneous catalytic reactions at the molecular level.

**P**ropylene oxide (PO) and acrolein rank among the top industrial chemical intermediates produced annually and are currently manufactured by the partial oxidation of propylene. The selective catalytic partial oxidation of propylene with O<sub>2</sub> is the desirable green method for their industrial production. This method has been realized for the industrial production of acrolein with bismuth/molybdenum-based mixed-oxide catalysts; however, the current major methods for the industrial

production of propylene oxide are the environmentally unfriendly chlorohydrin process and equally environmentally unfriendly variations of the Halcon process.<sup>[1]</sup> Thus, great effort has been devoted to the development of efficient catalysts for propylene epoxidation with O<sub>2</sub>,<sup>[2–5]</sup> for which promising active components are limited to the IB elements (Cu, Ag, and Au). Copper is much more economical than gold and silver for use as an industrial catalyst. Copper-based catalysts have been examined for the partial oxidation of propylene with O<sub>2</sub>,<sup>[5]</sup> and cuprous oxide, instead of metallic Cu, has been proposed as the active structure.<sup>[6]</sup> The morphology of the oxide nanoparticle determines the exposed crystal planes and the surface composition/structure and thus significantly influences its catalytic performance.<sup>[7]</sup> Recently, uniform Cu<sub>2</sub>O nanocrystals with different morphologies were synthesized and demonstrated to exhibit morphology-dependent catalytic activity in CO oxidation with excess or stoichiometric O<sub>2</sub>,<sup>[8]</sup> the photocatalytic degradation of dyes,<sup>[9]</sup> and liquid-phase organic reactions.<sup>[10]</sup> Herein we report that the morphology and exposed crystal planes of capping-ligand-free Cu<sub>2</sub>O nanocrystals control the catalytic selectivity as well as the catalytic activity in propylene oxidation with O<sub>2</sub>; we also reveal the underlying structure–activity relationships of this complex heterogeneous catalytic reaction at the molecular level and identify the catalytically active sites (Scheme 1).

Uniform cubic, octahedral, and rhombic-dodecahedral Cu<sub>2</sub>O nanocrystals were synthesized according to well-established procedures, in which poly(*N*-vinyl-2-pyrrolidone) (PVP) and oleic acid (OA) capping ligands were employed to prepare octahedral and rhombic-dodecahedral Cu<sub>2</sub>O nanocrystals, respectively, whereas no capping ligand was used for cubic Cu<sub>2</sub>O nanocrystals.<sup>[11]</sup> As-synthesized cubic Cu<sub>2</sub>O nanocrystals (denoted as c-Cu<sub>2</sub>O) have sizes between 400 and

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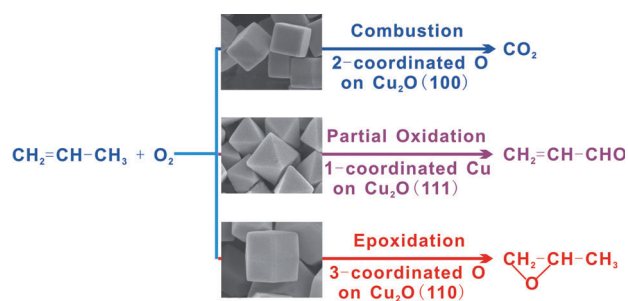
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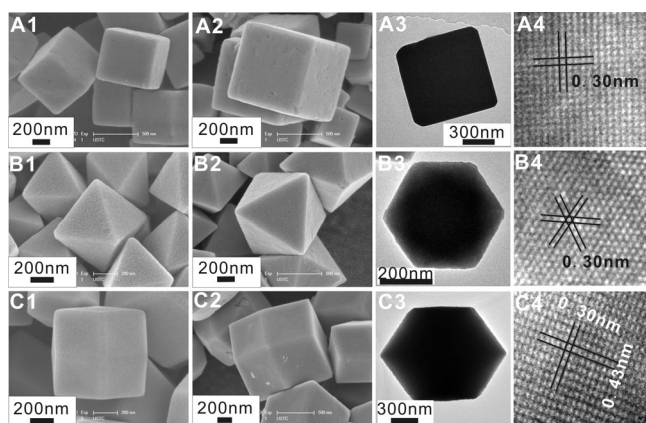
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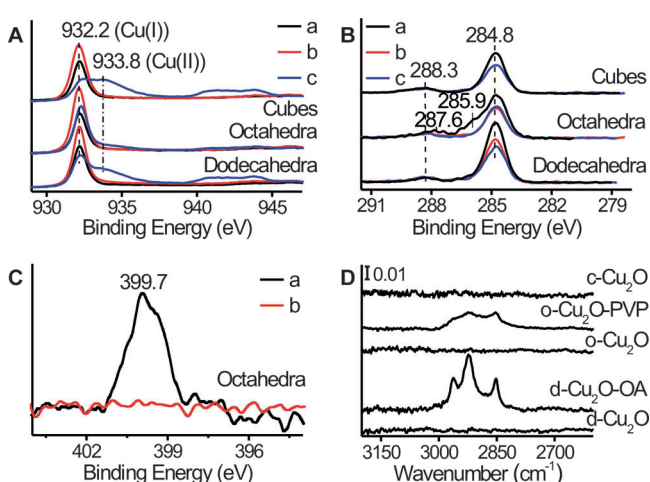


**Scheme 1.** Crystal-plane-controlled selectivity of Cu<sub>2</sub>O catalysts in the oxidation of propylene with molecular oxygen. The catalytically active sites on Cu<sub>2</sub>O are indicated for the different reaction pathways.



**Figure 1.** A1) SEM image of as-synthesized  $\text{Cu}_2\text{O}$  cubes; A2–A4) SEM, TEM, and HRTEM images of as-synthesized  $\text{Cu}_2\text{O}$  cubes subjected to controlled treatment at  $200^\circ\text{C}$  for 0.5 h; B1) SEM image of as-synthesized  $\text{Cu}_2\text{O}$  octahedra capped with PVP; B2–B4) SEM, TEM, and HRTEM images of capping-ligand-free  $\text{Cu}_2\text{O}$  octahedra; C1) SEM image of as-synthesized  $\text{Cu}_2\text{O}$  rhombic dodecahedra capped with OA; C2–C4) SEM, TEM, and HRTEM images of capping-ligand-free  $\text{Cu}_2\text{O}$  rhombic dodecahedra. The distances 0.43 and 0.30 nm correspond to the  $\{001\}$  and  $\{110\}$  planes of  $\text{Cu}_2\text{O}$ , respectively.

700 nm and selectively expose six  $\{100\}$  crystal planes (Figure 1 A1; see also Figure S1 A in the Supporting Information). As-synthesized octahedral  $\text{Cu}_2\text{O}$  nanocrystals (denoted as o- $\text{Cu}_2\text{O}$ -PVP) have sizes between 300 and 600 nm and selectively expose eight  $\{111\}$  crystal planes (Figure 1 B1; see also Figure S2 A). As-synthesized rhombic-dodecahedral  $\text{Cu}_2\text{O}$  nanocrystals (denoted as d- $\text{Cu}_2\text{O}$ -OA) have sizes between 600 and 900 nm and selectively expose 12  $\{110\}$  crystal planes (Figure 1 C1; see also Figure S3 A). XRD (see Figure S4) and Cu 2p XPS (Figure 2 A) confirmed that their crystal phases had the  $\text{Cu}_2\text{O}$  structure and their surfaces remained as  $\text{Cu}_2\text{O}$ . The specific BET surface areas of c- $\text{Cu}_2\text{O}$ , o- $\text{Cu}_2\text{O}$ -PVP, and d- $\text{Cu}_2\text{O}$ -OA were measured to be 1.49, 1.74, and  $0.774\text{ m}^2\text{ g}^{-1}$ , respectively (see Figure S5). Because of the synthetic proce-



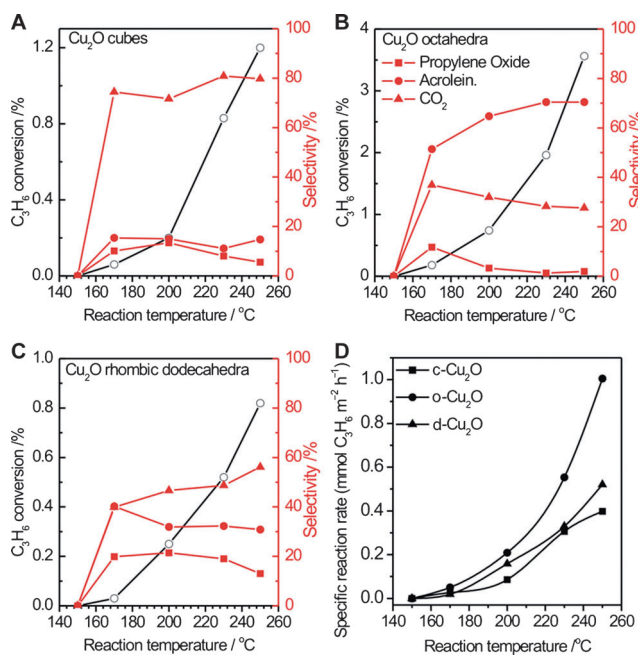
**Figure 2.** A) Cu  $2p_{3/2}$ , B) C 1s, and C) N 1s XPS spectra, and D) infrared spectra of a) as-synthesized  $\text{Cu}_2\text{O}$  nanocrystals, b) capping-ligand-free  $\text{Cu}_2\text{O}$  nanocrystals, and c) capping-ligand-free  $\text{Cu}_2\text{O}$  nanocrystals after evaluation of the catalytic performance up to  $250^\circ\text{C}$ .

dures used, o- $\text{Cu}_2\text{O}$ -PVP and d- $\text{Cu}_2\text{O}$ -OA are capped (with PVP and OA, respectively), but c- $\text{Cu}_2\text{O}$  is not. As shown in Figure 2 B–D, whereas o- $\text{Cu}_2\text{O}$ -PVP exhibits N 1s and C 1s XPS features and C–H stretching-vibration bands arising from capped PVP, and d- $\text{Cu}_2\text{O}$ -OA exhibits C 1s XPS features and C–H stretching-vibration bands arising from capped OA, c- $\text{Cu}_2\text{O}$  only exhibits C 1s features corresponding to adventitious carbon (284.8 eV) and carbonate species (288.3 eV)<sup>[12]</sup> but no C–H stretching-vibration bands.

The removal of capping ligands on nanocrystals without a change in their composition and structure remains challenging, but is essential for their use as catalysts.<sup>[13]</sup> We found that the controlled treatment of o- $\text{Cu}_2\text{O}$ -PVP and d- $\text{Cu}_2\text{O}$ -OA in a stream of a  $\text{C}_3\text{H}_6/\text{O}_2$  mixture balanced with  $\text{N}_2$  ( $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2$  2:1:22) enabled the selective removal of capping ligands without changing the composition and structure of the nanocrystals. Upon the controlled treatment of o- $\text{Cu}_2\text{O}$ -PVP in this way at  $200^\circ\text{C}$  for 0.5 h, the N 1s peak disappeared (Figure 2 C), the C 1s peaks at 285.9 and 287.6 eV also disappeared, and the C 1s peak at 284.8 eV was greatly attenuated (Figure 2 B); furthermore, the C–H vibration bands in the infrared spectrum disappeared (Figure 2 D). In the case of d- $\text{Cu}_2\text{O}$ -OA, the treatment temperature was increased to  $215^\circ\text{C}$  to remove the oleic acid surfactant, as evidenced by the disappearance of the C–H vibration bands in the infrared spectrum after treatment for 0.5 h (Figure 2 D) and the great attenuation of the C 1s peak at 284.8 eV (Figure 2 B). The morphology, bulk structure, and surface composition of o- $\text{Cu}_2\text{O}$ -PVP (Figure 1 B2–B4, Figure 2 A; see also Figure S4) and d- $\text{Cu}_2\text{O}$ -OA (Figure 1 C2–C4, Figure 2 A; see also Figure S4) did not change during this controlled treatment. Thus, we successfully acquired capping-ligand-free uniform octahedral (denoted as o- $\text{Cu}_2\text{O}$ ) and rhombic-dodecahedral (denoted as d- $\text{Cu}_2\text{O}$ )  $\text{Cu}_2\text{O}$  nanocrystals. Their synthesis was further supported by the experimental observations that CO was clearly chemisorbed on o- $\text{Cu}_2\text{O}$  and d- $\text{Cu}_2\text{O}$ , but not on o- $\text{Cu}_2\text{O}$ -PVP and d- $\text{Cu}_2\text{O}$ -OA (see Figure S6). C 1s XPS results (Figure 2 B) demonstrated that the surface carbon species on o- $\text{Cu}_2\text{O}$  and d- $\text{Cu}_2\text{O}$  as well as c- $\text{Cu}_2\text{O}$  were carbonate and adventitious carbon. Both are common on oxide-catalyst surfaces.

The novelty of our method to remove capping ligands on  $\text{Cu}_2\text{O}$  nanocrystals is the use of an atmosphere consisting of both oxidizing gas ( $\text{O}_2$ ) and reducing gas ( $\text{C}_3\text{H}_6$ ) with appropriate concentrations. On one hand, capping ligands on  $\text{Cu}_2\text{O}$  nanocrystals could be adequately oxidized by  $\text{O}_2$  and removed at relatively low temperatures to avoid a high-temperature-induced morphology change; on the other hand, the coexistence of  $\text{C}_3\text{H}_6$  and  $\text{O}_2$  in the atmosphere could cooperatively prevent  $\text{Cu}_2\text{O}$  nanocrystals from both oxidation and reduction. The latter hypothesis is further supported by the experimental results that the morphology, bulk structure, and surface composition of as-synthesized capping-ligand-free c- $\text{Cu}_2\text{O}$  remained unchanged after controlled oxidative treatment at  $200^\circ\text{C}$  for 0.5 h (Figure 1 A2–A4, Figure 2 A; see also Figure S4). Our method provides a promising general strategy for the selective removal of chemisorbed capping ligands on catalytic nanocrystals without changing their composition and structure.

The catalytic performance of the Cu<sub>2</sub>O nanocrystals in propylene oxidation with O<sub>2</sub> was evaluated. Propylene oxide, acrolein, and carbon dioxide were identified as the dominant reaction products. o-Cu<sub>2</sub>O and d-Cu<sub>2</sub>O were more catalytically active than the corresponding nanocrystals o-Cu<sub>2</sub>O-PVP and d-Cu<sub>2</sub>O-OA (see Figure S7), thus demonstrating that capping ligands on as-synthesized Cu<sub>2</sub>O nanocrystals suppress their catalytic activity. Capping-ligand-free Cu<sub>2</sub>O nanocrystals exhibited distinct morphology-dependent catalytic activity (Figure 3A–C). All Cu<sub>2</sub>O nanocrystals became active at



**Figure 3.** C<sub>3</sub>H<sub>6</sub> conversion and selectivity for propylene oxide, acrolein, and CO<sub>2</sub> of the C<sub>3</sub>H<sub>6</sub> oxidation with O<sub>2</sub> as catalyzed by capping-ligand-free A) Cu<sub>2</sub>O cubes, B) octahedra, and C) rhombic dodecahedra. D) Specific reaction rate of C<sub>3</sub>H<sub>6</sub> oxidation with molecular oxygen as catalyzed by capping-ligand-free Cu<sub>2</sub>O cubes (c-Cu<sub>2</sub>O), octahedra (o-Cu<sub>2</sub>O), and rhombic dodecahedra (d-Cu<sub>2</sub>O).

170 °C, and C<sub>3</sub>H<sub>6</sub> conversion increased with the reaction temperature. At the same temperature, C<sub>3</sub>H<sub>6</sub> conversion was catalyzed by the Cu<sub>2</sub>O nanocrystals with varying degrees of efficiency according to the order o-Cu<sub>2</sub>O > c-Cu<sub>2</sub>O > d-Cu<sub>2</sub>O. The specific propylene reaction rate normalized to the specific surface area of various Cu<sub>2</sub>O nanocrystals (Figure 3D) also followed the order o-Cu<sub>2</sub>O > d-Cu<sub>2</sub>O > c-Cu<sub>2</sub>O. Thus, Cu<sub>2</sub>O octahedra are more active in catalyzing C<sub>3</sub>H<sub>6</sub> oxidation with O<sub>2</sub> than Cu<sub>2</sub>O cubes and rhombic dodecahedra. This behavior exemplifies well the recently established concept of the morphology-controlled catalytic activity of oxide catalysts.<sup>[7]</sup>

Very interestingly, we observed that the catalytic selectivity of Cu<sub>2</sub>O nanocrystals in propylene oxidation with O<sub>2</sub> also depended sensitively on their morphology. c-Cu<sub>2</sub>O was very selective in catalyzing the propylene combustion reaction with a CO<sub>2</sub> selectivity of around 80% under the investigated reaction temperatures (Figure 3A), whereas o-Cu<sub>2</sub>O exhibited the highest selectivity for the partial oxida-

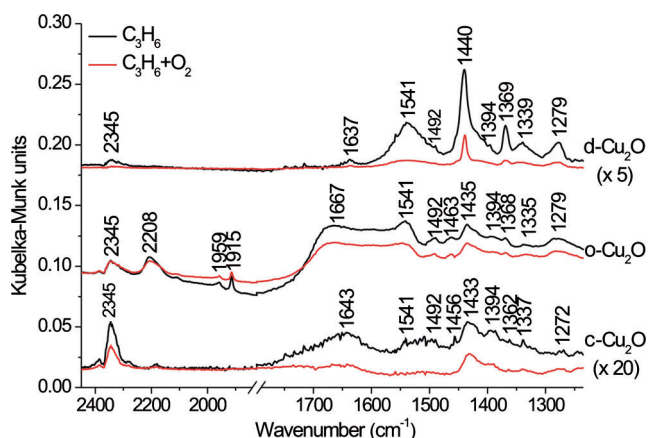
tion of propylene to acrolein (Figure 3B). At 170 °C, the selectivity for the formation of acrolein, propylene oxide, and CO<sub>2</sub> was 51, 12, and 37%, respectively. As the reaction temperature was increased, the selectivity for acrolein continued to increase at the expense of the selectivity for propylene oxide and CO<sub>2</sub>, and the selectivity for acrolein reached 71% at 250 °C. d-Cu<sub>2</sub>O exhibited comparable selectivity for the formation of propylene oxide (20%), acrolein (40%), and CO<sub>2</sub> (40%) at 170 °C (Figure 3C). When the reaction temperature was increased to 250 °C, the selectivity for propylene oxide did not change initially, but then decreased to 13% at 250 °C; the selectivity for acrolein gradually decreased; and the selectivity for CO<sub>2</sub> gradually increased. Therefore, in the catalysis of propylene oxidation with O<sub>2</sub>, c-Cu<sub>2</sub>O is the most selective of the three nanocrystal catalysts for the combustion of propylene to produce CO<sub>2</sub>, o-Cu<sub>2</sub>O is the most selective for the partial oxidation of propylene to produce acrolein, and d-Cu<sub>2</sub>O is the most selective for the epoxidation of propylene to produce propylene epoxide. These results for the first time demonstrate that the selectivity of oxide catalysts in reactions as complex as propylene oxidation with O<sub>2</sub> can be tuned by changing their morphology, thus offering a novel strategy to control the selectivity of oxide catalysts.

Propylene epoxidation with molecular O<sub>2</sub> is a highly desirable reaction but remains very challenging. We calculated the formation rate of propylene oxide and the turnover frequency (TOF) on the basis of surface Cu atoms for propylene oxidation with O<sub>2</sub> as catalyzed by d-Cu<sub>2</sub>O at 250 °C and compared both values with those found for the reaction catalyzed by previously reported representative supported copper-based catalysts (see Table S1 in the Supporting Information). Owing to the very small specific surface area of d-Cu<sub>2</sub>O, the formation rate of propylene oxide (0.057 mmol g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>) was quite low; however, the TOF value reached 1.46 × 10<sup>-3</sup> s<sup>-1</sup> and is comparable to that of the most active K<sup>+</sup>-promoted highly dispersed supported CuO<sub>x</sub> catalysts at 350 °C.<sup>[5b]</sup> For d-Cu<sub>2</sub>O nanocrystal catalysts, there is plenty of room to increase the propylene conversion rate by reducing their size and enlarging their specific surface area. Thus, Cu<sub>2</sub>O rhombic dodecahedra are a promising catalyst for propylene oxidation with O<sub>2</sub> to selectively produce propylene oxide together with acrolein.

Following the evaluation of the catalytic performance of the nanocatalysts up to 250 °C, SEM and TEM results showed that c-Cu<sub>2</sub>O, o-Cu<sub>2</sub>O, and d-Cu<sub>2</sub>O maintained their original morphologies and phase structure well (see Figures S1A3, S2A3, S3A3, and S4), but features arising from CuO appeared in the Cu 2p<sub>3/2</sub> XPS spectra (Figure 2A). This observation indicates the partial oxidation of Cu<sub>2</sub>O nanocrystals during the catalytic reaction; however, high-resolution TEM images (see Figure S1D3, S2D3, and S3D3) failed to show any lattice fringes arising from CuO. This result implies the likely formation of very thin CuO islands on the surface of Cu<sub>2</sub>O nanocrystals. No obvious accumulation of adventitious carbon and carbonate were observed by C 1s XPS (Figure 2B). We also investigated the stability of o-Cu<sub>2</sub>O at 240 °C (see Figure S8A) and d-Cu<sub>2</sub>O at 215 °C in the catalysis of propylene oxidation with O<sub>2</sub> (see Figure S8B). o-

Cu<sub>2</sub>O was very stable at 240°C and promoted approximately 2.5% C<sub>3</sub>H<sub>6</sub> conversion with around 80% selectivity for the formation of acrolein. d-Cu<sub>2</sub>O was not stable even at 215°C. During the reaction, C<sub>3</sub>H<sub>6</sub> conversion slowly decreased from 0.35 to 0.15%, the selectivity for propylene oxide slowly decreased from 18.4 to 12%, and the selectivity for acrolein slowly increased from 33.4 to 45.6%. After the stability test, the surface of o-Cu<sub>2</sub>O was slightly oxidized, but that of d-Cu<sub>2</sub>O was seriously oxidized (see Figure S9).

The above results clearly reveal that the morphology of oxide nanocrystals controls their catalytic selectivity as well as their catalytic activity. Figure 4 compares the DRIFTS spectra acquired for the chemisorption of C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> on

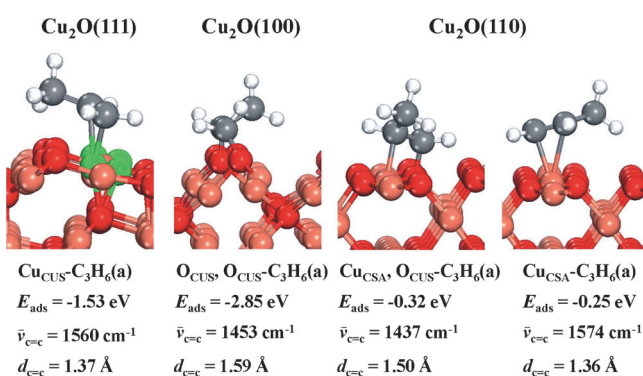


**Figure 4.** DRIFTS spectra of C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> chemisorption on capping-ligand-free Cu<sub>2</sub>O cubes (c-Cu<sub>2</sub>O), octahedra (o-Cu<sub>2</sub>O), and rhombic dodecahedra (d-Cu<sub>2</sub>O) at 230°C. DRIFTS = diffuse reflectance infrared Fourier transform spectroscopy.

different Cu<sub>2</sub>O nanocrystals at 230°C. The first observation is that on each type of Cu<sub>2</sub>O nanocrystal, the vibrational features of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> chemisorption are similar to those of C<sub>3</sub>H<sub>6</sub> chemisorption, except that their intensities are reduced. This observation infers that propylene oxidation with O<sub>2</sub> as catalyzed by Cu<sub>2</sub>O follows the Mars–van Krevelen (MvK) mechanism, and the lattice oxygen atoms of the Cu<sub>2</sub>O surface are the active oxygen species. The second observation is that o-Cu<sub>2</sub>O exhibits substantially stronger vibrational features than those of c-Cu<sub>2</sub>O and d-Cu<sub>2</sub>O. Thus, o-Cu<sub>2</sub>O is most active toward the chemisorption and surface reaction of C<sub>3</sub>H<sub>6</sub>, in agreement with the experimental result that o-Cu<sub>2</sub>O is much more catalytically active than c-Cu<sub>2</sub>O and d-Cu<sub>2</sub>O. The third observation is that the vibrational features vary on different Cu<sub>2</sub>O nanocrystals and indicates the morphology-dependent formation of surface adsorbates/intermediates upon C<sub>3</sub>H<sub>6</sub> oxidation on Cu<sub>2</sub>O nanocrystals. This behavior corresponds well to the morphology-dependent catalytic selectivity of the nanocrystals in propylene oxidation with O<sub>2</sub>.

To assist the assignment of the observed vibrational bands (see Table S2), we measured DRIFTS spectra for C<sub>3</sub>D<sub>6</sub> chemisorption (see Figure S10) and CO<sub>2</sub> chemisorption (see Figure S11) on different Cu<sub>2</sub>O nanocrystals. o-Cu<sub>2</sub>O, c-Cu<sub>2</sub>O, and d-Cu<sub>2</sub>O expose {111}, {100}, and {110} crystal planes, respectively, whose surface structures were optimized (see

Figure S12).<sup>[11]</sup> Coordinatively saturated Cu (Cu<sub>CSA</sub>) and O (O<sub>CSA</sub>) in the bulk cubic Cu<sub>2</sub>O are two-coordinated and four-coordinated, respectively. The Cu<sub>2</sub>O(111) surface is terminated with three-coordinated O<sub>CUS</sub> (CUS = coordinatively unsaturated) in the top layer and one-coordinated Cu (Cu<sub>CUS</sub>) and Cu<sub>CSA</sub> in the second layer in a 1:3 ratio. The Cu<sub>2</sub>O(100) surface is terminated with two-coordinated O atoms (O<sub>CUS</sub>) in the top layer and Cu<sub>CSA</sub> in the second layer. The Cu<sub>2</sub>O(110) surface is terminated with three-coordinated O<sub>CUS</sub> and Cu<sub>CSA</sub> in the top layer and Cu<sub>CSA</sub> in the second layer. Therefore, C<sub>3</sub>H<sub>6</sub> adsorption on Cu<sub>2</sub>O(111), (100), and (110) surfaces was also studied by DFT calculations, the results of which (Figure 5) support the experimental observations well. On Cu<sub>2</sub>O(111), C<sub>3</sub>H<sub>6</sub> is preferentially adsorbed at the Cu<sub>CUS</sub> site to form Cu<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) with an adsorption energy of -1.53 eV and a C=C stretching frequency of 1560 cm<sup>-1</sup>. Experimentally, on the o-Cu<sub>2</sub>O surface, chemisorbed C<sub>3</sub>H<sub>6</sub>



**Figure 5.** Optimized structures of the most stable C<sub>3</sub>H<sub>6</sub>(a) species on Cu<sub>2</sub>O(111), (100), and (110) surfaces with the adsorption energy, C=C stretching frequency, and C=C bond length. Red, gray, white, pink, and green balls represent O, C, H, coordinatively saturated Cu, and coordinatively unsaturated Cu, respectively.

species are only C<sub>3</sub>H<sub>6</sub>(a) with a C=C stretching frequency of 1541 cm<sup>-1</sup>. On Cu<sub>2</sub>O(100), C<sub>3</sub>H<sub>6</sub> preferentially bonds to two neighboring two-coordinated O<sub>CUS</sub> sites to form O<sub>CUS</sub>, O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) with an adsorption energy of -2.85 eV and a C=C stretching frequency of 1453 cm<sup>-1</sup>. Experimentally, on the c-Cu<sub>2</sub>O surface, the dominant chemisorbed C<sub>3</sub>H<sub>6</sub> species exhibits a C=C stretching frequency of 1428 cm<sup>-1</sup>. On Cu<sub>2</sub>O(110), bridge-adsorbed Cu<sub>CSA</sub>, O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) ( $\bar{\nu}_{\text{C=C}}$  = 1437 cm<sup>-1</sup>) and atop-adsorbed Cu<sub>CSA</sub>-C<sub>3</sub>H<sub>6</sub>(a) ( $\bar{\nu}_{\text{C=C}}$  = 1574 cm<sup>-1</sup>) have similar adsorption energies. Experimentally, on the d-Cu<sub>2</sub>O surface, C<sub>3</sub>H<sub>6</sub>(a) species with C=C stretching-vibration frequencies of 1541 and 1428 cm<sup>-1</sup> were both observed. The  $\bar{\nu}_{\text{C=C}}$  bands of O<sub>CUS</sub>, O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) and Cu<sub>CSA</sub>, O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) at 1428 cm<sup>-1</sup> are indistinguishable from the C–H bending-vibration bands (Figure 4), but their presence is evidenced in the case of C<sub>3</sub>D<sub>6</sub> chemisorption (see Figure S10), in which case the C–D bending-vibration bands are red-shifted away from the  $\bar{\nu}_{\text{C=C}}$  bands.

Besides the different chemisorbed C<sub>3</sub>H<sub>6</sub>(a) species, different surface intermediates form on various Cu<sub>2</sub>O nanocrystals. On the o-Cu<sub>2</sub>O surface, chemisorbed acrolein ( $\bar{\nu}_{\text{C=O}}$  at 1667 cm<sup>-1</sup>) is evident, and chemisorbed allyl ( $\bar{\nu}_{\text{C-C-C}}$  at 1428

and  $1406\text{ cm}^{-1}$ ; see Figure S10) and allene species ( $\bar{\nu}_{\text{C}=\text{C}}$  at  $1959$  and  $1915\text{ cm}^{-1}$ ), which are key intermediates for the partial oxidation of propylene to acrolein,<sup>[14]</sup> are also present. These observations agree with the high selectivity of *o*-Cu<sub>2</sub>O nanocrystals in catalyzing the partial oxidation of propylene to acrolein and indicate Cu<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) on Cu<sub>2</sub>O(111) as the active species. The C=C bond distance of Cu<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) was calculated to be  $1.37\text{ \AA}$ , whereas that of the gas-phase C<sub>3</sub>H<sub>6</sub> molecule is  $1.34\text{ \AA}$ . Thus, the C=C bond of Cu<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) is only marginally activated, and its entity can reasonably be preserved in the subsequent surface reactions, thus leading to the formation of acrolein.

On the *c*-Cu<sub>2</sub>O surface, CO<sub>2</sub>(a) ( $\bar{\nu}_{\text{as}}(\text{CO}_2)$  at  $2345\text{ cm}^{-1}$ ) and carbonate/carboxylate species (broad bands between  $1650$  and  $1350\text{ cm}^{-1}$ ) are dominant surface intermediates, in agreement with the high selectivity of *c*-Cu<sub>2</sub>O in catalyzing propylene combustion. The C=C bond distance of O<sub>CUS</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) on Cu<sub>2</sub>O(100) was calculated to be  $1.59\text{ \AA}$ ; thus, its C=C bond is significantly weakened and should undergo facile cleavage in the subsequent surface reactions. The epoxidation and combustion of propylene are the reaction pathways involving cleavage of the C=C bond. DFT calculation results (see Figure S13A) show that the activation energy for the epoxidation of O<sub>CUS</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) to give chemisorbed propylene oxide (C<sub>3</sub>H<sub>6</sub>O(a)) and the decomposition of O<sub>CUS</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) into adsorbed CH<sub>2</sub>(a) and CHCH<sub>3</sub>(a) is  $2.09$  and  $1.02\text{ eV}$ , respectively. This result indicates that O<sub>CUS</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) should preferentially undergo the combustion reaction, thus supporting the experimental results for *c*-Cu<sub>2</sub>O.

On the *d*-Cu<sub>2</sub>O surface, a chemisorbed allyl species is present (see Figure S10), and the presence of C<sub>3</sub>H<sub>6</sub>O(a) is indicated by the strong and narrow C-H bending-vibration band at  $1440\text{ cm}^{-1}$ . Such a feature does not appear in the case of C<sub>3</sub>H<sub>6</sub> chemisorption on *c*-Cu<sub>2</sub>O and *o*-Cu<sub>2</sub>O and can be reasonably assigned to  $\delta(\text{CH}_2)$  of C<sub>3</sub>H<sub>6</sub>O(a) by comparison with the infrared spectra of propylene, acrolein, and propylene oxide.<sup>[15]</sup> These observations agree with the production of both acrolein and propylene oxide through propylene oxidation with O<sub>2</sub> as catalyzed by *d*-Cu<sub>2</sub>O. The C=C bond distance of Cu<sub>CSA</sub>-C<sub>3</sub>H<sub>6</sub>(a) on Cu<sub>2</sub>O(110) was calculated to be  $1.36\text{ \AA}$ , and thus Cu<sub>CSA</sub>-C<sub>3</sub>H<sub>6</sub>(a) is reasonably considered to be the active species for the formation of acrolein; Cu<sub>CSA</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) on Cu<sub>2</sub>O(110) exhibits a significantly weakened C=C bond with a C=C bond distance of  $1.50\text{ \AA}$  and can reasonably be expected to undergo the surface reactions involving the breaking of the C=C bond. Interestingly, the results of DFT calculations (see Figure S13B) show that the activation energy for the epoxidation of Cu<sub>CSA</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) to give C<sub>3</sub>H<sub>6</sub>O(a) and the decomposition of Cu<sub>CSA</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) into adsorbed CH<sub>2</sub>(a) and CHCH<sub>3</sub>(a) is  $1.28$  and  $2.08\text{ eV}$ , respectively. These activation energies indicate that Cu<sub>CSA</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) should preferentially undergo the epoxidation reaction, thus supporting the experimental results for *d*-Cu<sub>2</sub>O. The different reactivities of O<sub>CUS</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) on Cu<sub>2</sub>O(100) and Cu<sub>CSA</sub>,O<sub>CUS</sub>-C<sub>3</sub>H<sub>6</sub>(a) on Cu<sub>2</sub>O(110) reflect the different reactivities of two-coordinated O<sub>CUS</sub> on Cu<sub>2</sub>O(100) and three-coordinated O<sub>CUS</sub> on Cu<sub>2</sub>O(110). Two-coordinated O<sub>CUS</sub> is more electrophilic than three-coordinated O<sub>CUS</sub> and

is thus more able to completely break the C=C bond of propylene to result in the combustion reaction. These results provide unprecedented comprehensive fundamental understanding of the structure–activity relationships and active sites of Cu<sub>2</sub>O catalysts in the catalysis of propylene oxidation with O<sub>2</sub> (Scheme 1).

In summary, we have successfully revealed the crystal-plane-controlled selectivity of Cu<sub>2</sub>O catalysts in the catalysis of propylene oxidation with O<sub>2</sub> and gained an understanding of their structure–activity relationships and catalytically active sites by the use of capping-ligand-free Cu<sub>2</sub>O octahedra, cubes, and rhombic dodecahedra as catalysts. Cu<sub>2</sub>O octahedra enclosed by {111} crystal planes are most selective for the formation of acrolein, and one-coordinated Cu<sup>I</sup> on Cu<sub>2</sub>O(111) is the active site; Cu<sub>2</sub>O cubes enclosed by {100} crystal planes are most selective for the formation of CO<sub>2</sub>, and two-coordinated O on Cu<sub>2</sub>O(100) is the active site; and Cu<sub>2</sub>O rhombic dodecahedra enclosed by {110} crystal planes are most selective for the formation of propylene oxide, and three-coordinated O on Cu<sub>2</sub>O(110) is the active site. These results reveal a strategy based on the morphology (crystal-plane) engineering of oxide catalysts as an effective approach for both the discovery of selective catalysts and the broadening of our fundamental understanding of heterogeneous catalysis. On one hand, 100% selectivity for the targeted product is the ultimate goal of heterogeneous catalysis. A catalyst nanoparticle enclosed by different crystal planes is intrinsically inappropriate as a means to reach this ultimate goal because different crystal planes will exhibit various selectivities. In this regard, catalyst nanocrystals that have a uniform morphology and selectively expose a single type of crystal plane are promising as highly selective catalysts. On the other hand, fundamental understanding of structure–activity relationships and active sites is a long-standing challenge for complex heterogeneous catalytic reactions. The traditional approach is to study single-crystal-based model catalysts under ultrahigh-vacuum conditions, but these systems often suffer from the so-called “pressure gap” and “materials gap”. Catalyst nanocrystals with uniform morphologies and well-defined structures are appropriate model catalysts for fundamental studies of practical heterogeneous catalytic reactions. The acquired fundamental understanding will be invaluable for the design of efficient catalysts. The success of this approach can be anticipated from our present results, which show that Cu<sub>2</sub>O octahedra are a promising catalyst for propylene oxidation with O<sub>2</sub> to produce acrolein, and that uniform Cu<sub>2</sub>O particles that selectively expose a high density of three-coordinated O sites are active in catalyzing propylene epoxidation with O<sub>2</sub> to produce propylene oxide: a highly desirable but very challenging catalytic reaction.

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