

# Catalysis

# The Effects of Exposed Specific Facets and Sulfation on the Surface Acidity of Cu<sub>2</sub>O Solids

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Abstract: Cuprous oxide microcrystals with {111}, {111}/{100}, and {100} exposed facets were synthesized. <sup>31</sup>P MAS NMR using trimethylphosphine as the probe molecule was employed to study the acidic properties of samples. It was found that the total acidic density of samples increases evidently after sulfation compared with the pristine cuprous oxide microcrystals. During sulfation, new {100} facets are formed at the expense of {111} facets and lead to the generation of two Lewis acid sites due to the different binding states of  $SO_4^{2-}$  on {111} and {100} facets. Moreover, DFT calculation was used to illustrate the binding models of  $SO_4^{2-}$  on {111} and {100} facets. Also, a Pechmann condensation reaction was applied to study the acidic catalytic activity of these samples. It was found that the sulfated {111} facet has better activity due to its higher Lewis acid density compared with the sulfated {100} facet.

Design of catalysts with different morphologies is an important topic due to atomic arrangement on different facets leading to special surface and catalytic properties.<sup>[1]</sup> Cu<sub>2</sub>O is widely used in gas sensors, solar energy transformations, lithium-ion batteries and catalysis because of its small band gap (2.17 eV), simple synthetic method, nontoxicity, scalability, and abundance.<sup>[2]</sup> So, it is reasonable to realize that the synthesis of Cu<sub>2</sub>O with certain exposed facets has aroused extensive attention in the past years.<sup>[2c,3]</sup> Some morphologies of Cu<sub>2</sub>O reported include cubic exposed {100} facets, octahedra exposed {111} facets, rhombic dodecahedron exposed {110} facets, etc.<sup>[4]</sup> These pieces of research provide a number of desired samples to in-

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-	https://doi.org/10.1002/chem.201903231.

Chem. Eur. J. 2019, 25, 1-5

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vestigate surface properties of specific Cu<sub>2</sub>O facets.<sup>[5]</sup> For Cu<sub>2</sub>O, surface energies ( $\gamma_{(100)} < \gamma_{(111)} < \gamma_{(110)}$ ) and the amount of Cu dangling bonds ({100} < {111} < {110}) vary from different facets and these intrinsic features determine electronic properties of Cu<sub>2</sub>O surfaces. Therefore, many methods have been developed to modify the facets, such as etching, template, and deposition.<sup>[2c]</sup>

Sulfation of metal oxides is used to obtain solid acids.<sup>[6]</sup> Therefore, sulfated metal oxides have been widely studied, such as  $SO_4^{2-}/ZrO_2$ ,<sup>[7]</sup>  $SO_4^{2-}/TiO_2$ ,<sup>[8]</sup>  $SO_4^{2-}/SnO_2$ .<sup>[9]</sup> During the sulfation,  $SO_4^{2-}$  tends to bond with metal atoms on the surface of metal oxides. With the electron-withdrawing effect from S = O, the electrons on metal atoms prefer to move towards  $SO_4^{2-}$ , which leads to electron deficiency on metal atoms and the formation of stronger Lewis acid sites. Brønsted acid sites are formed if hydroxyl groups bond with these Lewis acid sites. However, it is rare to see the study on the acidic properties after sulfation of metal oxides with specific exposed facets. In the previous research we reported sulfated TiO<sub>2</sub> solid super-acids and found their acidic and catalytic properties are facet-dependent.<sup>[10]</sup>

In this work, three different Cu<sub>2</sub>O microcrystals with various morphologies were prepared including octahedra with dominant {111} facets, cuboctahedra with both {100} and {111} facets, and cubes with dominant {100} facets. These Cu<sub>2</sub>O samples were sulfated and <sup>31</sup>P MAS NMR was used to study their acid properties with trimethylphosphine (TMP) as the probe molecule. DFT calculations were applied to give the optimized models of SO<sub>4</sub><sup>2-</sup> bonded on {111} and {100} facets. Furthermore, the acid catalytic activity of all three solid acids was tested in Pechmann condensation of 5,7-dihydroxy-4-methyl coumarin.

Three types of Cu<sub>2</sub>O microcrystals with dominant {111} facets, both {100} and {111} facets and dominant {100} facets were prepared according to the published method<sup>[4b]</sup> and are denoted as C111, C100/111, and C100, respectively. In a typical process, 0.171 g of CuCl<sub>2</sub>·2H<sub>2</sub>O, a certain amount of PVP ( $M_w$ : 29000) (3.333 g for C111, 1.111 g for C100/111, and 0 g for C100) and 100 mL of deionized water were mixed in a 250 mL round-bottomed flask with stirring in a 55 °C water bath. Then, 10 mL of NaOH aqueous solution (2 mol L<sup>-1</sup>) was added dropwise. After 30 min, 10 mL of ascorbic acid aqueous solution (0.6 mol L<sup>-1</sup>) was added dropwise into the system. The mixture was aged for 3 hours. The resulting precipitate was collected with centrifuging and washed with water and absolute ethanol three times each. The obtained Cu<sub>2</sub>O microcrystals were dried

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at 60 °C in a vacuum oven over night. PVP was not observed on the surface of three Cu<sub>2</sub>O pristine samples (Figure S1 and S2, Supporting Information). In the sulfation process, 10 mL of  $(NH_4)_2SO_4$  aqueous solution (1 mol L<sup>-1</sup>) was added into a 50 mL three-necked round bottom flask. Then N<sub>2</sub> (80 mLmin<sup>-1</sup>) was purged continuously into the system to remove air in the flask. After 30 min, 0.25 g of Cu<sub>2</sub>O was added, followed by stirring for 8 hours with continuous N<sub>2</sub> flow. The resulting precipitate was centrifuged and washed with absolute ethanol, then dried in a vacuum oven at 60 °C over night. The product was calcined in N<sub>2</sub> at 250 °C for 2 hours and further at 300 °C for 1 h to remove residual (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The resulting sulfated Cu<sub>2</sub>O samples were denoted as SC111, SC100/111 and SC100 accordingly.

The powder XRD patterns of sulfated Cu<sub>2</sub>O are presented in Figure 1a. SC111, SC100/111, and SC100 are indexed to the crystal structure of Cu<sub>2</sub>O (JCPDS 05-0667, Figure S3). A trace amount of CuSO<sub>4</sub> (JCPDS 15-0775) is found in all sulfated samples, which is caused by oxidative corrosion on the surface of Cu<sub>2</sub>O in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. The SEM images of SC111, SC100/111, and SC100 are shown in Figure 1b–d. Compared to their pristine samples (Figure S4, Supporting Information), their morphologies remain unchanged after sulfation. To further confirm



**Figure 1.** (a) XRD patterns of SC111, SC100/111 and SC100. SEM images of (b) SC111, (c) SC100/111 and (d) SC100. (e) XPS spectra of C111, C100/111 and C100. (f) XPS spectra of SC111, SC100/111 and SC100.

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the surface component of sulfated samples, XPS was conducted and the results are shown in Figure 1e–f and Figure S5, Supporting Information. Before sulfation, there are only two peaks at 952.4 and 932.4 eV which are indexed to the characteristic peaks of Cu<sup>1</sup>  $2p_{1/2}$  and Cu<sup>1</sup>  $2p_{3/2}$ . After sulfation, the peaks of Cu<sup>1</sup> are still found. In addition, two weak peaks appear around 955.0 and 935.0 eV belonging to Cu<sup>II</sup>  $2p_{1/2}$  and Cu<sup>II</sup>  $2p_{3/2}$ . Meanwhile, the broad satellite peaks around 963.1 and 943.1 eV are observed, which are the characteristic peaks of Cu<sup>II</sup> with the d<sup>9</sup> configuration in the ground state.<sup>[11]</sup>

Solid-state NMR has been proven to be a powerful technique to study the surface properties of solid catalysts.<sup>[12]</sup> TMP is often used as a probe molecule to characterize detailed acidic properties, including acid-type, density, and strength. There are mainly three interaction modes of TMP adsorbed on the surface of solid acid sites. TMP molecules chemisorbed on Lewis acid sites span over a wide chemical shift range from -20 to -60 ppm. The protonation of TMP molecules on Brønsted acid sites results in the formation of TMPH<sup>+</sup> ionic complexes, giving rise to <sup>31</sup>P resonances in the range of 0 to -5 ppm. Also, the chemical shift at around -62 ppm indicates the physisorption of TMP molecules on the surface. Moreover, TMP molecules may be oxidized to TMPO by the surface of metal oxides.<sup>[13] 31</sup>P MAS NMR is applied here to study acid properties of sulfated Cu<sub>2</sub>O and the results are shown in Figure 2a. The peaks at -63.9 ppm are assigned to physisorption of TMP on sulfated Cu<sub>2</sub>O samples, and the peaks around 41.6 and 25.7 ppm are assigned to physisorped TMPO and P(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> formed from  $P(CH_3)_3$  and  $HP(CH_3)_3^+$ , respectively.

According to the 2nl+1 rule (*n* is the number of atoms connected with <sup>31</sup>P, *l* is the nuclear spin number of atoms connected with <sup>31</sup>P), coupling of a <sup>31</sup>P nucleus to a Cu nucleus with spin 3/2 will split the <sup>31</sup>P signal into a quartet in NMR spectra. Therefore, Lewis acid peaks in Figure 2a between -20 and -50 ppm are quartets. After deconvolution, two groups of



**Figure 2.** (a) <sup>31</sup>P MAS NMR spectra of TMP adsorbed on SC111, SC100/111 and SC100. (b,c and d) The spectral deconvolution results of Lewis acid areas of SC111, SC100/111 and SC100 with red lines indicating type 1 Lewis acid peaks and blue lines for type 2 Lewis acid peaks.

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quartets in these three samples can be observed (Figure 2bd). This indicates that all samples have two types of Lewis acid sites on the surface. In addition, the central chemical shift of a quartet represents acid intensity of corresponding Lewis acid sites. The Lewis acids with chemical shift around -39 and -33 ppm are denoted as type 1 and 2 Lewis acids, respectively, and type 2 Lewis acid sites have stronger interactions with TMP molecules and stronger acidity due to their downfield chemical shift. To illustrate both types of Lewis acids sites, the surface changes on {100} and {111} facets in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution (pH 4.3) need to be analyzed. Morphological evolution of Cu<sub>2</sub>O in acidic solution was discussed by Hua and co-workers.<sup>[5c]</sup> In acidic solution, {100} facets maintain, while {111} facets tend to be corroded from the edge along [110] to form {100} facets (Figure S6, Supporting Information). Combined with acid density results in Table 1, SC111 has the highest percentage of type 1 Lewis acid while SC100 has the highest percentage of type 2 Lewis acid among these three samples, it is reasonable to attribute type 1 Lewis acid sites to metal atoms on {111} facets, and type 2 Lewis acid sites to metal atoms on {100} facets. Brønsted acids are not found on all sulfated Cu<sub>2</sub>O samples. After sulfation, total acid density increases evidently compared to pristine Cu<sub>2</sub>O samples (Table S1, Supporting Information). The acid density is in the order of SC111 > SC100/111 >SC100. This may be owing to the sawtooth-like structures generated on {111} facets which results in more exposed binding sites seldom observed on {100} facets (Figure 3).<sup>[5c]</sup>

On {111} facets, the first layer contains 3-coordinated O atoms and the second layer is composed of coordinatively saturated Cu (Cu<sub>CSA</sub>) atoms and coordinatively unsaturated Cu (Cu<sub>CUS</sub>) atoms. On {100} facets, the first layer contains 2-coordinated O atoms, and the second layer is composed of Cu<sub>CSA</sub> atoms (Figure S7, Supporting Information). In (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solu-



**Figure 3.** HRTEM images of (a) SC111 and (b) SC100 in the corresponding crystal area (red circles in the insets).

tion, we believe that O atoms on the first layer of Cu<sub>2</sub>O are removed by oxidative corrosion, making Cu atoms in second layers exposed. Then CuSO<sub>4</sub> is generated if oxidative corrosion occurred, or SO<sub>4</sub><sup>2-</sup> binds with exposed Cu atoms to form Lewis acid sites. In order to find the most optimized binding models of SO<sub>4</sub><sup>2-</sup> on {111} and {100} planes, DFT calculations were applied (Figures S7–S8 and Table S2, Supporting Information). As shown in Figure 4, on {111} facets, two O (O<sub>s</sub>) atoms of SO<sub>4</sub><sup>2-</sup>



**Figure 4.** (a) Most optimized model of  $SO_4^{2-}$  bonded on  $Cu_2O$  {111}. (b) Most optimized model of  $SO_4^{2-}$  bonded on  $Cu_2O$  {100} with removal of one O atom on the surface.

are preferred to bind with two Cu<sub>CUS</sub> atoms. This mode does not need to remove O atoms on the first layer. On {100} facets, two O<sub>S</sub> atoms of SO<sub>4</sub><sup>2-</sup> are preferred to bind with two Cu<sub>CSA</sub> atoms which are linked with each other through an O atom before sulfation in the first layer. The bond length of Cu–O<sub>S</sub> is calculated to be 2.1 and 1.8 Å on {111} and {100} facets, respectively. Cu and O<sub>S</sub> are closer on {100} facets than on {111} facets, which means the electron-withdrawing effect of S=O to affect Cu atoms on {100} is stronger than that on {111} facets. Therefore, Lewis acid sites on {100} are expected to be stronger than those on {111} facets. In <sup>31</sup>P MAS NMR spectra, chemical shift of type 1 Lewis acid sites is around 38.5 ppm, while type 2 is around 32.5 ppm. Thus type 1 Lewis acid is assigned to Cu atoms on {111} facets, while type 2 is from {100} facets. This deduction is in good accordance with our analysis above.

Pechmann condensation of 5,7-dihydroxy-4-methyl coumarin was carried to study catalytic activity of Cu<sub>2</sub>O samples. After sulfation, the catalytic activity of Cu<sub>2</sub>O samples is improved compared with pristine Cu<sub>2</sub>O samples (Figure S9, Supporting Information). The changes of yield vs. reaction time of these three sulfated samples are presented in Figure 5. The yield of 5,7-dihydroxy-4-methyl coumarin is in the order of SC111 > SC100/111 > SC100, which indicates that sulfated {111} facets have higher catalytic activity than {100} facets. In Pechmann condensation, the reaction begins with electrophilic substitu-

Table 1. Acid properties of sulfated Cu₂O.									
Sample	Total acid density ( $\mu mol g^{-1}$ )	Type 1 Lewis acid $\delta ~[ppm]^{[a]}$ Acid density [µmol g <sup>-1</sup> ] [%]			Type 2 Lewis acid $\delta ~[ppm]^{[a]}$ Acid density [µmol g <sup>-1]</sup> [%]				
SC111 SC100/111 SC100	1018 632 450	-40.0 -39.0 -38.3	383 218 83.7	37.6 34.5 18.6	-32.5 -33.0 -32.5	635 414 366	62.4 65.5 81.4		
[a] For quartets, the central chemical shift of all four peaks represents acid intensity of the corresponding Lewis acid.									

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Figure 5. Yield of 5,7-dihydroxy-4-methyl coumarin over SC111, SC100/111, and SC100.

tion on the benzene ring, followed by transesterification and dehydration, and both Brønsted acid and Lewis acid can catalyze this process.<sup>[14]</sup> These three sulfated Cu<sub>2</sub>O samples have only Lewis acid sites with no obvious difference in acid strength, so the acid density of these three samples is the decisive factor for catalytic activity. From Table 1, it is found that total acid density, acid density of type 1 and type 2 Lewis acid are all in the order of SC111 > SC100/111 > SC100, which is in consistent with catalytic activity results. The result shows that {111} facets with higher Lewis acid density exhibit better catalytic activity than {100} facets.

In conclusion, sulfated Cu<sub>2</sub>O microcrystals are successfully obtained from pristine Cu<sub>2</sub>O with different ratio of {100}/{111} facets. Two types of Lewis acid sites are found on all three sulfated samples. It is evidenced by NMR and DFT calculation that type 1 and type 2 Lewis acid sites come from Cu atoms on {111} and {100} facets after binding with  $SO_4^{2-}$ , respectively. SC111 has the highest catalytic activity towards Pechmann condensation of 5,7-dihydroxy-4-methyl coumarin owing to its highest Lewis acid density. This work gives an example to study the surface structure of metal oxides using acidic results from <sup>31</sup>P MAS NMR, and may provide more inspiration on the exploration of relationship between crystal planes and catalytic properties.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (91645201, 21673046 and 21473036) and the Ministry of Science and Technology (2017YFB0602204).

# **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** acidity · cuprous oxide · facets · NMR spectroscopy · sulfation

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Manuscript received: July 16, 2019

Revised manuscript received: September 16, 2019 Accepted manuscript online: September 17, 2019 Version of record online:

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