

Copper Nanocrystal Plane Effect on Stereoselectivity of Catalytic Deoxygenation of Aromatic Epoxides

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Supporting Information

ABSTRACT: Previous studies have shown that crystal planes of heterogeneous catalysts could display enhanced activity, such that higher turnover or chemoselectivity could be achieved. Here we report an example where the reaction stereoselectivity was significantly affected by the catalyst crystal planes. In copper-catalyzed deoxygenation reaction of aromatic epoxides, copper cubes, wires, and plates gave the olefin products with different *cis/trans* selectivities, whereas homogeneous copper catalysts showed poor selectivity. Scanning tunneling microscope and density functional theory studies revealed that the different adsorption mode and higher adsorption strength of epoxide oxygen on Cu{100} plane were responsible for the observed variation of selectivity. The copper-catalyzed deoxygenation reaction provided new practical access to *cis*-olefins from readily available aromatic epoxides. Our work also indicated that nanocrystal catalysts may provide useful stereochemical control in organic reactions.

The discovery of catalyst single crystal plane effects on solid surface-catalyzed reactions, marked by the observation that Fe{111} planes exhibit higher activity than Fe{100} and Fe{110} in catalytic ammonia synthesis,^{1,2} has greatly promoted the advance of surface science and catalysis. With aspiration to develop practical catalysts that could fully capitalize the advantage of such crystal plane effects, recent research on single-crystalline nanocrystal catalysts with large “effective” surface planes has witnessed remarkable advances.³ For instance, single-crystalline CeO₂ nanorods were shown to have a higher CO oxidation activity with CeO₂{100} and {110} than with CeO₂{111}.^{4,5} Somorjai et al. discovered that in the catalytic hydrogenation of benzene, the exposed {100} surface of Pt cubic nanoparticles was more active than the {100} and {111} mixture surfaces of Pt cuboctahedral nanoparticles.⁶ For the methane combustion, it was shown that the catalytic activity of Co₃O₄ nanocrystals followed the order of {112} > {011} ≫ {001}.⁷ The oxidation of CO was achieved at temperatures as low as -77 °C on Co₃O₄{110} planes that remained stable in a moist stream of normal feed gas.⁸ These examples illustrated the potential of

single-crystalline nanocrystals as highly active catalysts. The advantages manifested by the crystal plane effect, however, are confined to reactivity enhancement. As catalysis concerns both reactivity and selectivity,⁹ it remains a desirable goal to elicit crystal plane effect on reaction selectivity, especially stereoselectivity.¹⁰

Here we report a surprising finding of crystal plane-dependent stereoselectivity changes in a copper nanocrystal (wires, plates, and cubes) catalyzed deoxygenation reaction of aromatic epoxides. This reaction is not only a new catalytic transformation useful to organic synthesis but also provides an interesting example for the variation of reaction stereoselectivity with differently exposed catalyst crystal planes. Our finding suggested the potential of using well-defined nanocrystals as practical catalysts to catalyze organic reactions with both high activity and high stereoselectivity. Moreover, this reaction provides a new convenient and practical access to some synthetically interesting *cis*-olefins¹¹ from readily available epoxides.

Our study began with the finding of an unprecedented deoxygenation reaction of *trans*-stilbene oxide (**1a**) with a Si–B reagent¹² Me₂PhSi–Bpin ((dimethylphenylsilyl)boronic acid pinacol ester).¹³ The yields and the ratio of *cis/trans*-stilbene (**2a/3a**) were determined by ¹H NMR using 1,2,4,5-tetramethylbenzene as an internal standard. Without any catalyst, the reaction could take place at 60 °C in dioxane generating *cis*- and *trans*-stilbenes in a ratio of 1.0:2.1 (individual yield = 22% and 45%) after 1 h. The low yield and poor selectivity called for the finding of catalysts to improve the performance. Many homogeneous or heterogeneous catalysts (e.g., CuCl₂, CuO, CuI, Fe₂O₃, Au) failed to induce stereoselectivity to favor the production of *cis*-olefin. Nonetheless, copper in charcoal (3 wt %) as a commercially available catalyst (Aldrich 709107) was found to favor the formation of *cis*-stilbene, but the *cis/trans* selectivity varied from 4:1 to 1:1 among different experiments. Hypothesizing that the variation of stereoselectivity may arise from the heterogeneous nature of the exposed copper crystal planes in copper on charcoal, we conducted morphology-

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controlled synthesis of different nanocrystal copper catalysts and tested their activities.

Three general types of copper nanocrystals with well-defined shapes including cubes, wires, and plates were prepared by colloidal chemical synthesis.^{14,15} The nanocrystals structure and phase purity were determined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and electron diffraction. The obtained data established the exposed planes in the cubes, wires, and plates to be {100}, {100}/{111}, and {111} planes (Figure 1). The

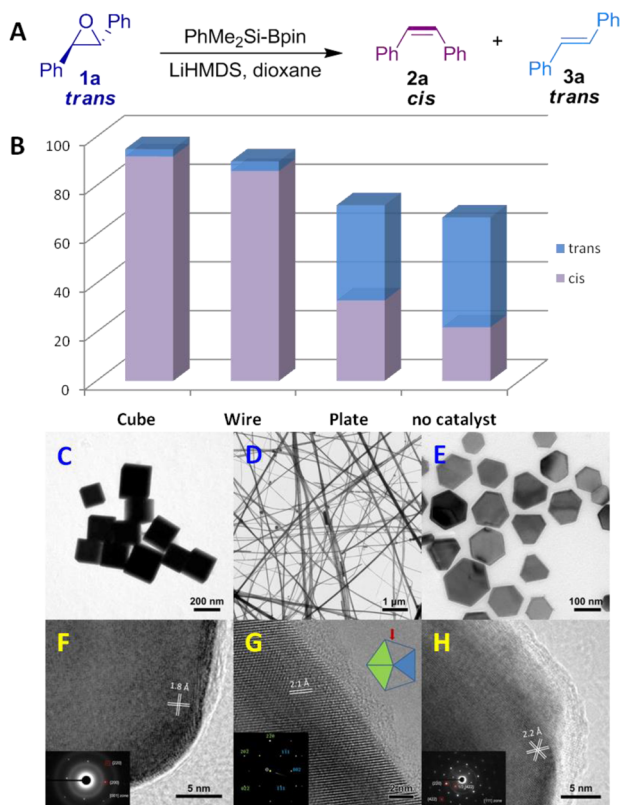


Figure 1. TEM and HRTEM images of Cu cubes (C,F), wires (D,G), and plates (E,H). Insets in (F–H) show the corresponding diffraction patterns.

three types of nanocrystals were then loaded on charcoal and used as the catalysts after the capping agent was removed by extensive washing (for detailed procedures, please see Supporting Information).

We observed remarkable change of *cis/trans* selectivities when the three catalysts were subjected to the reaction. When Cu cube was used as the catalyst under very low loading (0.01 mol %), the previously minor product (i.e., *cis*-stilbene) observed in the uncatalyzed reaction became the prevailing product in 95% yield and >20:1 *cis/trans* selectivity. A similar *cis/trans* selectivity (20:1) was observed when Cu wires were used, albeit in a slightly lower yield (90%). In contrast, both the yield of *cis*-stilbene (35%) and *cis/trans* selectivity (1:1) decreased drastically with Cu plates. The strikingly high stereoselectivity elicited by the Cu cubes and wires under a very low Cu catalyst loading (0.01 mol %), compared to those of Cu plates and the uncatalyzed reaction, was an interesting finding. As the Cu cubes and wires predominantly exposed the {100} crystal plane whereas the Cu plates mainly exposed the {111} surface, we concluded that the crystal plane effect caused the variation of stereochemistry.

To elucidate the origin of the crystal plane effect on stereoselectivity variation, we employed the scanning tunneling microscope (STM)¹⁶ to investigate the adsorption of *trans*-stilbene oxide on the Cu{100} crystal plane (Figure 2). Our data

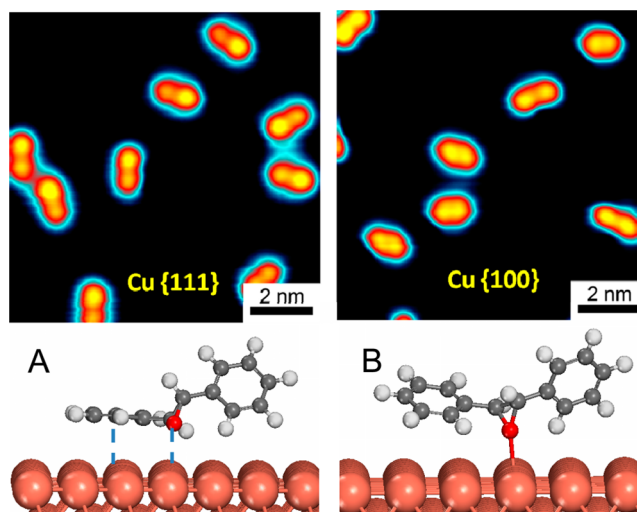


Figure 2. STM study of the adsorption (A) on Cu {111} surface and (B) on Cu {100} surface.

showed that the adsorption of *trans*-stilbene oxide on Cu{111} and Cu{100} generated distinct surface features. On the terraces of Cu{111} surface, *trans*-stilbene oxide exhibited a “cuneus” shape protrusion in topographic STM images, suggesting that one of the phenyl groups lies close (maybe flatly) on the surface. In contrast, the “dumbbell” shape image obtained on the Cu{100} surface substantiated an up-standing adsorption mode. In this case, the two lobes of each *trans*-stilbene-oxide molecule, as visualized by the STM images, appeared as two round protrusions with identical shape and height (each protrusion represents a phenyl ring), indicating that the molecules are anchored onto the surface without tilt.

To further compare the different adsorption strength of *trans*-stilbene oxide on Cu{111} and Cu{100} facets, we took the critical gap condition that was required to induce a lateral manipulation of a single *trans*-stilbene oxide molecule on either substrate by STM tip as a semiquantitative indicator. On Cu{111}, by approaching the tip over a single molecule and dragging it away, lateral movement of the target molecule could be successfully realized and repeated at the gap condition of 10 mV/14 nA, but it failed on Cu{100} under the same conditions. Employing stronger tip–molecule interaction, namely, further increasing the tunneling current to 20 nA or even 25 nA (more intense condition would lead to damage of the molecule), still could not overcome the energy barrier to move the molecule adsorbed on Cu{100}. Such a remarkable difference in our tip-induced manipulation experiment indirectly evidenced that the *trans*-stilbene-oxide bound much more firmly to Cu{100} than to Cu{111}.

Next we performed density functional theory (DFT) calculations to help in understanding the reaction. The molecular adsorption configuration of *trans*-stilbene oxide on Cu{111} and {100} surfaces is shown in Figure 2. The adsorption energies on Cu{111} and {100} surfaces were -0.17 and -0.28 eV, indicating a relatively weak chemo-adsorption between *trans*-stilbene oxide and Cu surfaces. We further considered the ring-opening dissociative adsorption configuration (Figure 3) where

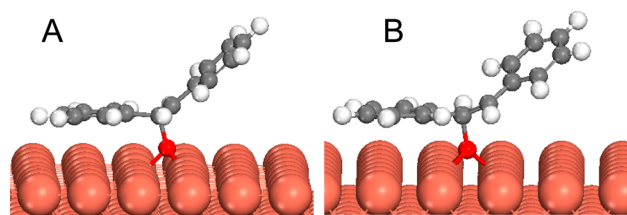


Figure 3. Dissociative adsorption based on DFT calculations (A) on Cu{111} surface, $E_{\text{ads}} = -0.10$ eV and (D) on Cu{100} surface, $E_{\text{ads}} = -0.60$ eV.

the epoxide ring is broken when oxygen is bonded to the Cu surface, which means that this intermediate tends to be captured by a silicon anion and lead to irreversible C–O bond cleavage in actual reaction solution (Figure 4). The calculated dissociative

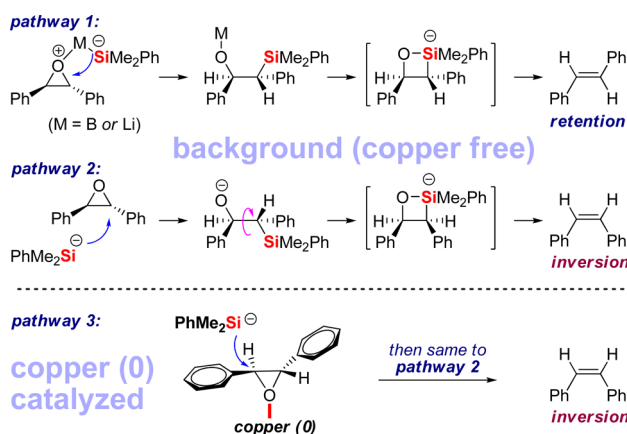


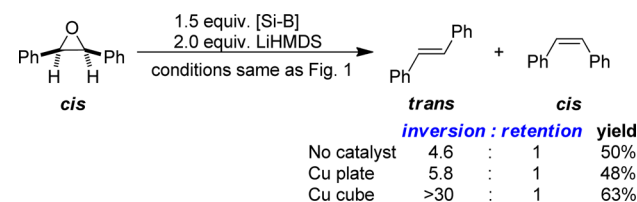
Figure 4. Proposed mechanism for *cis/trans*-stilbene formation.

adsorption energy on Cu{100} is 0.50 eV lower than on Cu{111} surface, indicating a significantly stronger adsorption of *trans*-stilbene oxide to Cu{100} surfaces than to Cu{111} surface. Overall, we conclude that the adsorbed *trans*-stilbene oxide can move easily on Cu{111} surface, while the chemisorbed *trans*-stilbene oxide is difficult to diffuse on Cu{100} surface, consistent with the STM results.

On the basis of the above experimental and theoretical results, we proposed that the copper-catalyzed deoxygenation reaction of stilbene oxides should proceed through a Peterson-type transformation (Figure 4). In this transformation the Si–B bond was activated to generate a silicon anion presumably through a base-promoted process as discussed in previous studies.¹² Two configurations of olefins were obtained (*cis/trans* selectivity = 1.0:2.1) under the uncatalyzed (e.g., copper free) conditions because there are two different modes for the attack of the silicon group to the epoxide (pathway 1 and pathway 2). However, once copper catalyst is added to the reaction, the strong chemo-adsorption between *trans*-stilbene oxide and Cu surfaces forces the attack of the silicon group to the epoxide from only one possible direction. It is remarkable that when Cu cube was used under very low catalyst loading (0.01 mol %), *cis*-stilbene is already obtained in 95% yield and >20:1 *cis/trans* selectivity. This observation suggests a very high catalytic effect due to the strong surface adsorption on Cu{100} surfaces. By comparison, when Cu{111} surface with much weaker adsorption is used, the copper plates afforded a much lower yield of *cis*-stilbene (35%) and *cis/trans* selectivity (1:1).

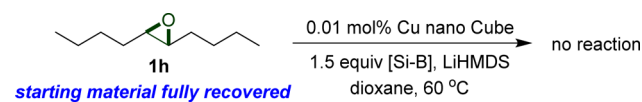
The above mechanism is consistent with the experiment on deoxygenation of *cis*-stilbene oxide (Scheme 1). In this system

Scheme 1. Deoxygenation of *cis*-Stilbene Oxide



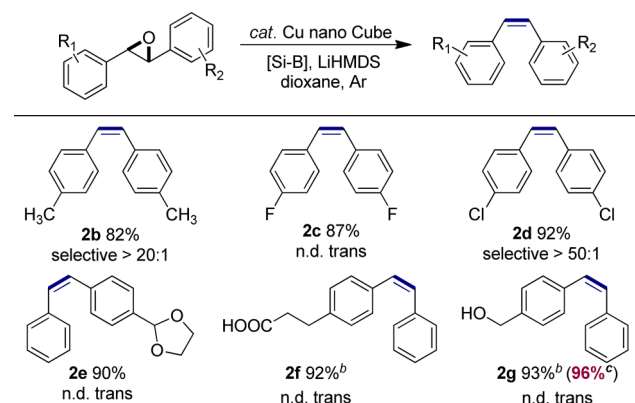
trans- and *cis*-stilbenes were produced in a selectivity of 4.6:1 under uncatalytic conditions. When Cu plate was used, the selectivity increased only slightly to 5.8:1. However, when Cu cube was used, the selectivity significantly improved to >30:1. Again, the inversion reaction mode was more effectively promoted by Cu{100} as compared to the Cu{111}. Furthermore, as both STM experiment and DFT calculation showed a close contact between the phenyl ring and the Cu surface, we were not surprised to find that an aliphatic epoxide was not a good substrate in the Cu-catalyzed deoxygenation reaction presumably to poor surface adsorption (Scheme 2).

Scheme 2. Use of Aliphatic Epoxide as the Substrate



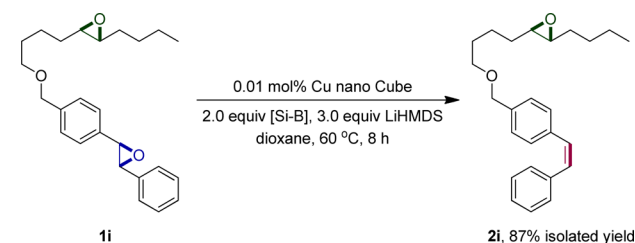
As *cis*-olefins are found in many bioactive molecules and synthetic intermediates, the present Cu nanocrystal-catalyzed epoxide deoxygenation reaction provides a new and interesting catalytic transformation in synthetic organic chemistry. The very low catalyst loading (0.01 mol %) also renders the reaction of practical utility. To demonstrate this we first examined the recyclability of the Cu{100} crystal plane catalyst (namely, 0.1 wt % of Cu nanocube loaded on charcoal). After filtration, washing and retreatment with the standard conditions in Figure 1A, a consistent yield (92–97% yield for each cycle) and selectivity (>20:1) could be obtained for over at least six cycles.

With a highly active yet robust Cu{100} catalyst in hand, we examined its utilization for a range of *trans*-stilbene oxides (Table 1). The scope of the substitution encompasses both electron-donating (i.e., Me, **2b**) and withdrawing ones (i.e., F, **2c**). Aryl chloride (**2d**) was tolerated in the reaction, making possible additional cross-coupling at the C–Cl bond. A number of synthetically relevant groups such as acetal (**2e**), unprotected acid (**2f**), and alcohol (**2e**) also survived the transformation. In a scaled-up reaction at gram quantity (**2g**, 5 mmol), the nanocrystal Cu{100} catalyst provided a high isolated yield (96%) of the *cis*-product. These results indicated that Cu{100} crystal constitutes a practical catalyst for the deoxygenation of *trans*-stilbene oxides to produce *cis*-stilbenes amenable to gram-scale operations. As olefins can be readily epoxidized with retention of stereochemistry, the Cu nanocrystal catalyzed reaction offers a new route for the production of *cis*-olefins with the advantage of late-stage synthesis from readily available *trans*-stilbenes. Furthermore, we took advantage of the fact that an aliphatic epoxide was not reactive to selectively deoxygenate an aryl epoxide moiety in **1i** (Scheme 3). Such a highly selective deoxygenation process has not been achieved in the past,

Table 1. Scope of Deoxygenation of *trans*-Stilbene Oxides^a

^aIsolated yield. Standard conditions: reactions were carried out on 0.2 mmol scale with 0.01 mol % of Cu nanocube@C, 1.5 equiv of [Si-B], 2.0 equiv of LiHMDS in 1 mL of dioxane under 60 °C for 8 h. The selectivity was determined by NMR analysis of the crude product. "n.d." means that trans product was not determined as it was undetectable after the reaction. ^bThree equivalents of LiHMDS was used. ^cGram-scale reaction (5 mmol).

Scheme 3. Selective Deoxygenation



demonstrating the unique usefulness of the present Cu catalyzed-reaction in organic synthesis.¹⁷ Taken together, we conclude that copper cube catalyzed deoxygenation of organic epoxides provides a new and practical reaction for the catalytic formation of usually challenging *cis*-olefins.

In summary, our experimental and theoretical studies have established the first example for crystal plane effects on stereoselectivity of Cu-catalyzed deoxygenation of organic epoxides. Nanocrystal catalysts with well-defined crystal planes represent a new paradigm to achieve stereochemical control in organic transformations. We envisage that the interdisciplinary corroboration between the increasingly sophisticated nanoscience and organic chemistry is poised to the discoveries of new organic reactions exemplified by this work.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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