Direct Epoxidation of Propylene over Stabilized Cu⁺ Surface Sites on Ti Modified Cu₂O

¹Xiaofang Yang, ¹Shyam Kattel, ²Xiong Ke, ¹Kumudu Mudiyansele, ¹Sanjaya D. Senanayake, ¹José A. Rodríguez, ¹Ping Liu, ¹Dario J. Stacchiola and ^{1,3}Jingguang G. Chen*

Abstract: Direct propylene epoxidation by O₂ is a challenging reaction because of the strong tendency for complete combustion. Results from the current study demonstrate the feasibility to tune the epoxidation selectivity by generating highly dispersed and stabilized Cu⁺ active sites in a TiCuO_x mixed oxide. The TiCuO_x surface anchors the key surface intermediate, oxametallacycle, leading to higher selectivity for epoxidation of propylene.

Propylene oxide (PO) is an important precursor largely produced for manufacturing numerous commodity chemicals (e.g. polyurethane and polyols). Current industrial production of propylene oxide is mainly through the chlorohydrin process and hydroperoxide mediated process, which are neither cost effective nor environmentally friendly because of generating chlorinated or peroxycarboxylic waste.^[1] Thus, identifying appropriate catalysts for direct and selective epoxidation of propylene with molecular oxygen (C₃H₆ + 1/2O₂ → C₃H₆O) has received considerable attention.^[2-9] For example, Au nanoparticles supported on TiO₂ or titanium silicalite zeolites exhibit high selectivity (> 90%) for PO.^[4] However, this approach requires co-feeding of large amount of H₂ and is limited by low conversion. In contrast to ethylene epoxidation utilizing Ag-based catalysts, at present no industrial-scale heterogeneous catalytic propylene epoxidation process with O₂ has been successfully developed.

The main challenge for direct propylene epoxidation with O₂ is that instead of partial oxidation, propylene is readily oxidized to generate CO₂ and H₂O. Some attempts have been made to improve the selectivity for PO, *i.e.*, reducing the Ag catalysts to an extremely small size (three atoms of silver),^[10] or illuminating copper oxide

catalysts with visible light to reduce Cu oxide during reaction.^[11] Even though those studies have provided interesting approaches to alter the selectivity for epoxidation, they may not yet be practical or effective enough to be applied in large scale production. More effort is still needed to search for novel oxidation catalysts that are stable, economic, and active with significantly enhanced selectivity to the desirable epoxidation product.

Identifying surface intermediates is a critical step to understand the reaction mechanism as the surface chemistry of intermediates governs the epoxidation reaction pathway. For instance, one of the most important intermediates for ethylene epoxidation has been identified as an ethylene oxametallacycle, which has an asymmetric ring structure with one carbon binding directly to the surface and the second carbon indirectly binding to the surface through an oxygen bridge.^[6, 12-13] Similarly, propylene oxametallacycle has been proposed as the reaction intermediate for propylene epoxidation.^[14] Even though these two oxametallacycle intermediates have a nearly identical structure, the surface chemistry of them is significantly different, resulting in different activity and selectivity. Specifically, the γ-hydrogen in the propylene oxametallacycle is very active and readily reacts with surface oxygen, leading to dehydrogenation and finally complete oxidation of the allyl species. The formation of the propylene oxametallacycle intermediate has been attributed to the higher selectivity for epoxidation on the copper surface.^[14] However, the activity of Cu catalysts is low with a conversion <4% at below 300 °C^[15] and deactivation occurs due to the full oxidation of copper to Cu²⁺.^[11] Thus, it is important to improve the activity by stabilizing Cu at low oxidation states under reaction conditions.

Mixed oxides such as spinels or perovskites are stable, highly ordered and are characterized by their unique electronic structure and physical/chemical properties.^[16] Thus, they have become the focus of numerous ongoing research efforts related to catalytic oxidation reactions.^[17] For instance, a mixed oxide made of TiCuO_x demonstrates high catalytic activity for CO oxidation with copper being stabilized as Cu⁺.^[18] The stabilization of Cu⁺ by TiO_x strongly suggests that TiCuO_x may show promising selectivity for propylene epoxidation. By stabilizing and controlling the density of the surface Cu⁺ sites, TiCuO_x may act as a potential candidate for catalyzing direct propylene epoxidation. To test this hypothesis, in this study a model Ti-Cu oxide catalyst grown on Cu(111) has been prepared by physical vapor deposition and its catalytic performance for direct propylene epoxidation is measured by temperature programmed desorption (TPD). The adsorption of propylene oxide and the formation of oxametallacycle have been also studied by soft X-ray photoemission spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS). This study shows that the model catalysts are active and selective for converting propylene to propylene oxide by direct partial oxidation, illustrating the importance of forming stable Cu⁺ sites in controlling the epoxidation activity and selectivity.

Dr. X. Yang, Dr. S. Kattel, Dr. K. Mudiyansele, Dr. S. D. Senanayake, Dr. J. A. Rodríguez, Dr. P. Liu, Dr. D. J. Stacchiola, and Prof. Dr. J.G. Chen
Chemistry Department
Brookhaven National Laboratory
2 Center St., Upton, NY 11973 (USA)

K. Xiong
Department of Chemical and Biomolecular Engineering,
University of Delaware
150 Academy St., Newark, DE 19716 (USA)

[*] Prof. Dr. J.G. Chen
Department of Chemical Engineering
Columbia University
500 W. 120th St., New York, NY 10027 (USA)
E-mail: jgchen@columbia.edu

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201xxxxx>. ((Please delete if not appropriate))

Acknowledgement: The work was sponsored under Contract No. DE-SC0012704 with the U.S. Department of Energy, Office of Science. The DFT calculations were performed using computational resources at the Center for Functional Nanomaterials, BNL, supported by US Department of Energy and the National Energy Research Scientific Computing Center (NERSC) supported by the Office of Science of the US Department of Energy under Contract No. DE-AC02-05CH11231.

Figure 1. Surface structures of TiCuO_x and CO adsorption. A. Atomically resolved STM images of TiCuO_x and corresponding DFT simulated surface structures (O: red, Ti: blue, and Cu: reddish-orange). Cu atoms in surface layers are enlarged. B. IRRR after CO adsorption on TiO_x modified surfaces. Peak assignments: 2098 cm^{-1} CO on Cu_2O , 2163 cm^{-1} CO on TiO_2 , 2129 cm^{-1} CO on TiCuO_x .

The TiCuO_x thin film was synthesized by depositing Ti oxide onto a Cu_2O surface and annealing under an O_2 environment. The Cu_2O surface was prepared by annealing a $\text{Cu}(111)$ in O_2 at 650 K.^[19] Deposition of TiO_x causes formation of both TiO_2 hexagonal islands and Ti modified row structures. Figure 1A shows the high resolution STM image of the surface structure with the Ti rich regions showing depressions. The detailed structure of this TiCuO_x thin film has been described in a previous paper^[18] and the STM images with large area are shown in the supporting information (Figure S1). The structural study by atomically resolved STM images, Near-Edge X-ray Absorption Fine Structure (NEXAFS) measurements, CO titration with Reflection-Absorption Infrared Spectroscopy (RAIRS) and Density Functional Theory (DFT) simulations confirmed the formation of mixed oxide, TiCuO_x . This surface demonstrated large enhancement for CO oxidation and superior chemical stability than Cu_2O because of the stabilization of Cu^+ by TiO_x .^[18] CO has been used as a probe molecule to further characterize the nature of the surface Cu sites and the results are shown in Figure 1B. New active sites for binding CO with the IR peak at 2129 cm^{-1} were created after submonolayer TiO_x modification, corresponding to the creation of the Cu^+ sites. The ability of the surface Cu^+ sites in oxidizing CO demonstrates a facile dissociation of O_2 , an ability that may extend to other oxidation reactions such as olefin epoxidation.

The formation of the propylene oxametallacycle intermediate has been proposed as the key step in the propylene epoxidation reaction.^[14] Thus, to examine if the mixed oxide surface of TiCuO_x exhibits catalytic activity for epoxidation, PO was adsorbed as a probe molecule on the surface and the resulting surface species were investigated by TPD, XPS and HREELS. Identification of the energy loss peaks in HREELS was assisted by DFT calculations. As a comparison, similar PO adsorption experiments on both $\text{Cu}(111)$ and Cu_2O surfaces were performed under two different adsorption temperatures, 110 K and 210 K. The full comparison and discussion of the TPD, XPS and HREELS results on all three surfaces are provided in the supporting information.

As shown in Figure 2, low temperature (110 K) adsorption on both $\text{Cu}(111)$ and Cu_2O results in all PO molecules desorbing at approximately 150 K, indicating weakly bound PO. A different TPD profile with a broad tail extending from 120 to 320 K is observed for the TiCuO_x surface. Most PO still weakly binds to the TiCuO_x surface after adsorption at low temperatures. However, the tail between 250 and 320 K suggests stronger bonding to the surfaces. This strong bonding

feature can be more readily observed after exposing PO on the TiCuO_x surface at 210 K. Large desorption peaks of PO appears at 200 ~ 330 K and the overall intensity is much larger than that desorbed from both $\text{Cu}(111)$ and Cu_2O surfaces in the same temperature range. The less amount PO desorption from both $\text{Cu}(111)$ and Cu_2O surfaces is due to the PO decomposition (Figure S2). Increasing the load of Ti on the Cu_2O surface causes the formation of large TiO_x islands.^[18] PO has less tendency to bind these TiO_x islands as shown in Figure 2D that less PO desorption is observed from a TiCuO_x surface with higher Ti coverages (0.9 ML).

The C1s XPS spectra have been found to be useful in identifying the oxametallacycle intermediate for ethylene epoxidation.^[6] In this study, C1s and O1s were recorded after PO was adsorbed at both 110 and 210 K on all three surfaces. Figure 3A shows the XPS spectra after adsorption of PO on TiCuO_x ; complete comparisons of the XPS spectra after PO adsorption are provided in the supporting information (Figure S3). The C1s spectra after PO adsorption on these surfaces at 110 K are essentially equivalent. After deconvolution, two peaks with the binding energy (BE) at 285.6 eV and 286.8 eV are displayed with an intensity ratio of approximate 1:2 (Figure 3A), which is the expected carbon ratio of the methyl group to the methylene group in the PO molecule. Thus, XPS results indicate that the epoxide ring remains intact at low temperatures and PO most likely weakly binds to the surface through the O atom.

Figure 2. Propylene oxide (PO) TPDs after the adsorption of PO on A. $\text{Cu}(111)$, B. $\text{Cu}_2\text{O}/\text{Cu}(111)$, and TiCuO_x surfaces with C. 0.5 ML and D. 0.9 ML TiO_x at 1). 110 K and 2). 210 K. $m/e=58$.

Different C1s features were obtained after PO adsorption on TiCuO_x at 210 K. As shown in Figure 3A, the C1s peak positions shift to slightly higher BE (0.2-0.4 eV). For such small chemical shifts in BE, the assignment of these two peaks is similar to that of the physisorbed PO. Specifically, the peak at 285.8 eV is due to the carbon not directly bound to oxygen (C-C) while the peak at 287.2 eV is due to the carbon directly bound to oxygen (C-O). However, the relative peak intensities at 285.8 and 287.2 eV are almost reversed with the larger peak at 287.2 eV, indicating that exposure to PO at 210 K results in a different adsorption geometry for PO on TiCuO_x . One possible surface species that formed at 210 K is an oxametallacycle.

To confirm the presence of the oxametallacycle intermediate, the surface species formed after PO adsorption has been further

studied by HREELS and DFT calculations (Figures 3B and 3C). As shown in the supporting information (Figure S4), low temperature

Figure 3. Identification of propylene oxametallacycle after PO adsorption on TiCuO_x . A. XPS of adsorbed PO at both 110 K and 210 K. B. HREELS of adsorbed PO at 110 K and 210 K, and DFT calculated vibrational frequencies of adsorbed PO and oxametallacycle. Vertical lines are DFT calculated vibrational frequencies. C. DFT Optimized PO and oxametallacycle adsorption configurations on TiCuO_x (O: red, Ti: blue, Cu: reddish-orange, C: grey and H: white).

(110 K) adsorption of PO produces very similar HREELS spectra for all the surfaces. The assignments of the peaks are summarized in supporting Table S1. The peak at 805 cm^{-1} is assigned to the C-C-O ring deformation and the presence of this peak indicates that PO is only weakly adsorbed without opening of the ring. Different HREELS spectra are obtained after the PO adsorption at 210 K. The peak at 805 cm^{-1} completely disappears on the Cu (111) and Cu_2O surfaces. More importantly, shifting of the peak from 805 to 899 cm^{-1} and the appearance of a new peak at 705 cm^{-1} are observed on the TiCuO_x surface. To gain further insights into the new peaks observed at higher temperatures, DFT calculations are performed to obtain the optimized geometries for PO and oxametallacycle adsorption on the Cu_2TiO_3 monolayer supported on Cu(111). As shown in Figure 3C, both PO and oxametallacycle prefers the Cu^+

sites in a η^1 and a η^2 conformation respectively. In both cases the Cu^+ is pulled outward the surface in interaction with the adsorbate, which enhances the adsorbate-surface binding. Furthermore, DFT calculated vibrational frequencies of the optimized PO and oxametallacycle on the TiCuO_x surface are compared to the experimental data. In general, the DFT calculated vibrational frequencies match very well with experimental HREELS measurements, strongly indicating the presence of the propylene oxametallacycle on the TiCuO_x surface. However, this intermediate is not present on either Cu(111) or Cu_2O surfaces after PO adsorption (Figure S4).

Overall, the combined results from TPD, XPS and HREELS provide strong evidence that PO is chemically adsorbed on the TiCuO_x surface to form the propylene oxametallacycle intermediate and then thermally desorbs as molecular PO by ring closing upon heating. Generating this di- σ -bonded oxametallacycle is critically important for catalyzing the direct propylene epoxidation. For example, improved selectivity to PO has been achieved on highly dispersed Ag catalysts because of its suitable electronic and geometric properties for anchoring this oxametallacycle intermediate.^[10, 20] Similarly, the presence of the oxametallacycle intermediate on TiCuO_x suggests the possibility of propylene epoxidation over this surface. To test this hypothesis, direct propylene epoxidation catalyzed by the TiCuO_x surface is explored next and compared to the Cu(111) and Cu_2O surfaces under low pressure conditions.

Figure 4. TPD of propylene epoxidation. A. Catalytic activity of TiCuO_x . B. Comparisons of Cu(111), Cu_2O and TiCuO_x in PO production ($m/e=31$). O_2 : 1.0×10^{-6} Torr, propylene: 1.0×10^{-6} Torr, 240 K for 60 minutes. Heating rate: 3 K/s.

Figure 4 shows the TPD results after co-exposing O_2 and propylene at 240 K. The possible products and their main m/e cracking patterns (in parentheses) from propylene oxidation are CO_2 (44), H_2O (18), acetone (58, 43), propanal (58, 57), propylene oxide (58, 43, 31), and acrolein (56). Propanal can be excluded as no ion

with $m/e=57$ was observed. The amounts of CO_2 and H_2O generated through complete combustion are also negligible (see Figure S5). Thus, the major desorption products are propylene oxide, acetone and acrolein. The quantification of each product is based on the analysis of the desorption peak areas of $m/e=58$, 56, 43, and 31, as described in the supporting information. As shown in Figure 4A, all the desorption peaks are centered at 300 K, which is higher than the desorption temperatures after PO chemisorption at 210 K and indicates that the desorption of these products is reaction-limited. Figure 4B compares the production of propylene oxide ($m/e=31$) among the four surfaces: Cu(111), Cu_2O , and TiCuO_x surfaces with 0.6 ML and 0.9 ML TiO_x . The TiCuO_x surfaces exhibit higher activity than Cu(111) or Cu_2O , with the highest activity (corresponding to 0.037 ML PO) from the 0.6 ML TiO_x surface. The calculated selectivity for PO is 69% for this surface, indicating that the TiCuO_x surface is active and selective for propylene epoxidation.

Surface oxygen basicity or nucleophilicity is considered as an important factor to determine the selectivity in both ethylene propylene epoxidation.^[14, 21] It has been proposed as a source for the different catalytic activity between copper and silver. For example, oxygen bonded to silver is more basic than oxygen bonded to copper. Consequently, silver favors allylic hydrogen stripping but copper favors stable metallacycle formation. Thus, to improve the selectivity for PO, the basicity (nucleophilicity) of the surface oxygen in the oxide should be reduced.^[21] Largely different from the facile reduction of Cu_2O by low pressure CO ,^[19, 22] the TiCuO_x surface cannot be reduced by CO under the same conditions, suggesting the lower basicity of the mixed oxide than seen for the Cu_2O .^[18] Modification of Cu_2O by TiO_2 appears to be an effective way in both stabilizing the Cu^+ and reducing the basicity of oxide, making TiCuO_x a promising catalyst for propylene epoxidation.

In summary, a model mixed oxide thin film formed by adding TiO_x to a Cu_2O surface has been explored for the direct epoxidation of propylene. Compared to Cu(111) and Cu_2O surfaces, the TiCuO_x surface is more active and selective for PO production. The TiCuO_x oxide can effectively stabilize surface Cu^+ and is ideal for anchoring the key surface intermediate, oxametallacycle, leading to higher selectivity for the epoxidation of propylene. The strategy of forming stable mixed oxide could lead to a simple method in catalyst preparation and flexibility in controlling the selectivity. Results from the current study demonstrates the potential to synthesize mixed metal oxides with stabilized Cu^+ sites, which could impact the future in producing PO by direct propylene oxidation.

Experimental Section

Samples were prepared and characterized in a UHV-system equipped with STM at BNL. HREELS was obtained at Columbia University. An Omicron STM was used to obtain room temperature images of mixed oxides, TiCuO_x . XPS was performed at beamline U12a in NSLS at incident energy of ~400 eV at an energy resolution of 0.3 eV. IRRAS studies were carried out with a Nicolet Nexus 670 Fourier-transform infrared (FTIR) at BNL. Further details of the methods are provided in the supporting information.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

- [1] T. A. Nijhuis, M. Makkee, J. A. Moulijn, B. M. Weckhuysen, *Ind. Eng. Chem. Res.* **2006**, *45*, 3447-3459.
- [2] Y. Pang, X. Chen, C. Xu, Y. Lei, K. Wei, *ChemCatChem* **2014**, *6*, 876-884.
- [3] X. Zuwei, Z. Ning, S. Yu, L. Kunlan, *Science* **2001**, *292*, 1139-1141.
- [4] T. Hayashi, K. Tanaka, M. Haruta, *J. Catal.* **1998**, *178*, 566-575.
- [5] S. Lee, L. M. Molina, M. J. López, J. A. Alonso, B. Hammer, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, M. J. Pellin, S. Vajda, *Angew. Chem. Internat. Ed* **2009**, *48*, 1467-1471.
- [6] S. Linic, H. Piao, K. Adib, M. A. Barteau, *Angew. Chem. Internat. Ed* **2004**, *43*, 2918-2921.
- [7] M. Ojeda, E. Iglesia, *Chem. Commun.* **2009**, 352-354.
- [8] B. Chowdhury, J. J. Bravo-Suárez, M. Daté, S. Tsubota, M. Haruta, *Angew. Chem.* **2006**, *118*, 426-429.
- [9] Q. Hua, T. Cao, X.-K. Gu, J. Lu, Z. Jiang, X. Pan, L. Luo, W.-X. Li, W. Huang, *Angew. Chem. Internat. Ed* **2014**, n/a-n/a.
- [10] Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. A. Curtiss, S. Vajda, *Science* **2010**, *328*, 224-228.
- [11] A. Marimuthu, J. Zhang, S. Linic, *Science* **2013**, *339*, 1590-1593.
- [12] J. W. Medlin, M. A. Barteau, *J. Phys. Chem. B* **2001**, *105*, 10054-10061.
- [13] J. W. Medlin, M. A. Barteau, J. M. Vohs, *J. Mol. Catal. A: Chem* **2000**, *163*, 129-145.
- [14] D. Torres, N. Lopez, F. Illas, R. M. Lambert, *Angew. Chem. Internat. Ed* **2007**, *46*, 2055-2058.
- [15] O. P. H. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov, R. M. Lambert, *J. Catal.* **2005**, *236*, 401-404.
- [16] M. A. Peña, J. L. G. Fierro, *Chem. Rev.* **2001**, *101*, 1981-2018.
- [17] I. E. Wachs, K. Routray, *ACS Catal.* **2012**, *2*, 1235-1246.
- [18] A. E. Baber, X. Yang, H. Y. Kim, K. Mudiyansele, M. Soldemo, J. Weissenrieder, S. D. Senanayake, A. Al-Mahboob, J. T. Sadowski, J. Evans, J. A. Rodriguez, P. Liu, F. M. Hoffmann, J. G. Chen, D. J. Stacchiola, *Angew. Chem. Internat. Ed* **2014**, *53*, 5336-5340.
- [19] F. Yang, Y. Choi, P. Liu, J. Hrbek, J. A. Rodriguez, *J. Phys. Chem. C* **2010**, *114*, 17042-17050.
- [20] A. Takahashi, N. Hamakawa, I. Nakamura, T. Fujitani, *Appl. Catal., A* **2005**, *294*, 34-39.
- [21] T. C. R. Rocha, M. Hävecker, A. Knop-Gericke, R. Schlögl, *J. Catal.* **2014**, *312*, 12-16.
- [22] A. E. Baber, F. Xu, F. Dvorak, K. Mudiyansele, M. Soldemo, J. Weissenrieder, S. D. Senanayake, J. T. Sadowski, J. A. Rodriguez, V. Matolín, M. G. White, D. J. Stacchiola, *J. Am. Chem. Soc.* **2013**, *135*, 16781-16784.

Layout 1:

Epoxidation Catalysis

Xiaofang Yang¹, Shyam Kattel¹, Xiong Ke², Kumudu Mudiyansele¹, Sanjaya D. Senanayake¹, Jose A. Rodriguez¹, Ping Liu¹, Dario J. Stacchiola¹ and Jingguang G. Chen^{*1,3}

Tuning selectivity towards epoxidation by forming mixed oxide:

Stabilization Cu^+ by TiO_x reduces the basicity of the surface oxygen which subsequently inhibits combustion and promotes the formation of oxametallacycle, leading to higher selectivity for epoxidation.

Page – Page

Direct Propylene Epoxidation of
Propylene over Stabilized Cu^+ Surface
Sites on Ti Modified Cu_2O