



Short communication

Effects of Cl^- on Cu_2O nanocubes for direct epoxidation of propylene by molecular oxygen

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ABSTRACT

Promoters have been widely used in industrial catalysis but understanding the mechanism behind their function is still a challenging subject. As ideal model catalysts, nanocrystal catalysts with well-defined exposing facets and relatively large specific surface have attracted intense attention. We explored the effect of Cl^- loading on Cu_2O nanocubes enclosed by (100) facets for the direct epoxidation of propylene by molecular oxygen. Interestingly, a volcano-type curve was obtained when the selectivity and conversion are plotted as a function of the loading amount of Cl^- , indicating that optimal surface O/Cl^- ratio is critical for desirable catalytic performance.

1. Introduction

Propylene oxide (PO) is one of the bulk chemicals with about ten million tons annual production [1,2]. As compared to the industrialized chlorohydrin and Halcon method, direct epoxidation of propylene (DEP) with molecular oxygen appears an ideal alternative [3,4]. The DEP reaction has been studied mainly on Cu-, Ag- and Au-based catalysts [3–11]. Among them, Cu-based catalysts are claimed to be promising because the oxygen atoms thereon were suggested to be more electrophilic, thus more selective for DEP [4,10,12,13]. However, despite the much effort made, including crystal facet regulation [14] and particle size control [8,15], the unmodified Cu-based catalysts are still unsatisfactory for the reaction. The high PO selectivity (40% ~ 50%) could only be achieved at very low propylene conversion levels (usually < 1%); while when the conversion is increased, the PO selectivity dramatically decreases.

The mechanism(s) of DEP reaction appear(s) very complicated. One widely accepted mechanism involves the oxametallacycle (OMP) as the key intermediate to generate PO, which usually takes place on electrophilic oxygen species [5,13,16–18]. On the other hand, allylic C–H bond activation occurring on the nucleophilic oxygen species would be a competitive route, which leads to the formation of acrolein (ACR). Experimentally, the most common strategy to enhance the DEP reaction is to introduce chemical promoters to tune the chemical behavior of surface oxygen, and Cl^- and alkali metal ions have been frequently employed [5–7,19–21]. For example, Wang et al. [6] suggested that

alkali metal addition could reduce Lewis acidity of $\text{CuO}_x/\text{SBA}-15$ and thus increase the PO selectivity. In addition, Zhang et al. [7] proposed that the introduction of Cl^- effectively regulated the electrophilicity of Ag/BaCO_3 catalysts and suppressed deep oxidation of propylene. However, it is very difficult to decouple the roles of chlorine anions and metal cations when metal chlorides are used as promoters.

In this contribution, we systematically investigated the effect of Cl^- for DEP over Cu_2O model catalysts. In particular, Cu_2O nanocubes (Cu_2O -NCs) enclosed by (100) facets were synthesized via a surfactant-free wet chemical method. To rule out the influence of metal cations, the as synthesized Cu_2O -NCs were impregnated with the NH_4Cl solution with different concentrations. Through advanced characterizations, we found that the optimal ratio of O/Cl^- on the surface is the key to achieve the desirable catalytic performance. And the Cu_2O -NCs loaded with 0.33 wt% NH_4Cl at 150 °C displayed the best performance with 57% PO selectivity and a TOF of $3.4 \times 10^{-4} \text{ s}^{-1}$. Our work provides a signpost for exploring promoter effects by using well-defined nanocrystals.

2. Experimental

2.1. Chemicals and catalysts preparation

Chemicals: Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.0%), sodium hydroxide (NaOH, 96.0%) and D-(+)-glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

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Ammonium chloride (NH_4Cl , 99.5%) was purchased from Guangdong Guanghua Sci – Tech Co., Ltd., and all chemicals were used as received without further purification.

Cu_2O –NCs: Cu_2O –NCs were prepared via a surfactant–free wet chemical method with a revised protocol based on previous report [14]. In a typical synthesis, 20 mL of 0.1 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution was prepared in a 50 mL glass vial and placed in a water bath at 60 °C. Then, 6 mL of 1 M NaOH aqueous solution was added by one–shot under stirring and kept the reaction for 10 min. Finally, 6 mL of 1 M glucose aqueous solution was injected in one–shot and kept for 1 h. The color of the solution gradually changed from blue to brick red. After reaction, the as prepared products were collected by centrifugation and washed several times with ethanol and deionized water, then dried in oven at 60 °C and stored in vacuum for further use.

Cu_2O –NCs with Cl^- loaded: Desired amount of NH_4Cl was dissolved in a mixed solution of 1:4 (v/v) for water and ethanol. Then, 200 mg of the as prepared Cu_2O –NCs was immersed in the NH_4Cl solution and quickly dried under vacuum at room temperature. High percentage of ethanol in the solution was used to prevent serious chemical etching towards Cu_2O –NCs from NH_4Cl aqueous solution, which may destruct the surface structure of Cu_2O –NCs.

2.2. Catalytic reaction

The propylene epoxidation reaction was carried out on a fixed–bed reactor under atmospheric pressure. The catalyst sample in powder form ($W = 0.2$ g; $d_p < 0.64$ mm) was placed in a quartz reactor and first pretreated in He flow (50 mL min^{-1}) at room temperature for 30 min. The reactant gas mixture consisting of He, C_3H_6 and O_2 with a flow rate of 40 mL min^{-1} , 6.67 mL min^{-1} and 3.33 mL min^{-1} respectively ($\text{GHSV} \sim 15,000$ h^{-1}), was introduced into the reactor to start the reaction. The catalyst sample (0.2 g) was used in the temperature range of 125–250 °C, where at each temperature the reaction was left for 30 min before analysis of the effluent gas stream from the reactor.

Two on–line gas chromatographs were employed to analyze the reaction products composition, making use of three columns (FFAP capillary, Porapak Q and Molecular Sieve 5A columns) and flame ionization and thermal conductivity detectors in order to separate and detect C_3H_6 , O_2 , CO_2 and PO. To prevent condensation of organic products, all the lines and valves between the reactor and the gas chromatographs were heated to 120 °C.

2.3. Catalysts characterization

The phase composition of catalysts was acquired using a Rigaku Ultima IV X–ray diffractometer (Cu– $\text{K}\alpha$, operating at 35 kV and 15 mA). Scanning electron microscopy (SEM) (S4800 instrument,

Hitachi, Japan) was used to identify the size and morphology of the catalysts. Transmission electron microscopy (TEM) images and selective electron area diffraction (SEAD) pattern were taken by JEM–2100 high–resolution TEM (JEOL, Japan) with an acceleration voltage of 200 kV. Micromeritics TriStar 3020 and porosimetry analyzer (N_2 adsorption/desorption isotherms at 77 K) was employed to characterize the surface texture of catalysts (BET model) after pretreatment at 200 °C in vacuum for 3 h.

Quasi in situ X–ray photoelectron spectroscopy (XPS) was carried out by a PHI Quantum–2000 photoelectron spectrometer equipped with an Omicron Sphera II hemispherical electron energy analyzer (Monochromatic Al $\text{K}\alpha$ with 1486.6 eV operating at 15 kV and 300 W). The quasi in situ catalytic test was carried out in an independent sample chamber, where the catalyst sample was then vacuumed and transferred to the ultra–high chamber for analysis. All XPS data was adjusted based on the $\text{Cl}1s$ peak (binding energy at 284.6 eV).

High–sensitivity low–energy ion scattering spectroscopy (HS–LEIS) measurements were carried out on an Ion–TOF Qtac100 low energy ion scattering analyzer. He and Ne ions with a kinetic energy of 3 KeV and 5 KeV, respectively, were applied at a low ion flux of 1600 pA cm^{-2} as ion sources for etching. Temperature–programmed desorption mass spectrometer (TPD–MS) experiments were conducted on an automatic chemical adsorption instrument (Auto Chem II 2920, Micromeritics) coupled with a mass spectrometer (ThermoStar GSD 301 T2, Pfeiffer Vacuum) from 50 to 600 °C (0.2 mg Cu_2O catalyst was used). The desorption peaks of NH_3 , HCl and NH_4Cl were recorded based on the m/z value of 16, 36 and 53, respectively.

3. Results and discussion

3.1. Characterization of Cu_2O –NCs with and without Cl^- and their catalytic performance

The as prepared Cu_2O –NCs were highly uniformed with edge length in the range of 200–400 nm as shown in Fig. S1(a–c). The TEM and SAED images confirmed that the Cu_2O –NCs are enclosed by (100) facets. Fig. S1(d) and (e) illustrate that some small NH_4Cl particles appear on the surface of Cu_2O –NCs after NH_4Cl loading, and no significant corrosion of surface is observed. Powder XRD measurements illustrated that both unmodified Cu_2O –NCs and 1 wt% NH_4Cl – Cu_2O –NCs have nearly produced very similar diffraction patterns, both in good agreement with that of a standard Cu_2O phase (JCPDF No. 65–3288) as shown in Fig. S1(f). This indicates that NH_4Cl impregnation could only alter the structure of near surface layers.

Fig. 1 and Fig. S2(a) show the catalytic performance of Cu_2O –NCs with and without NH_4Cl , respectively. Cu_2O –NCs display preferential selectivity for CO_2 varying in the range of 40–80% in the temperature range of 150–250 °C. However, the maximal PO selectivity achieved is

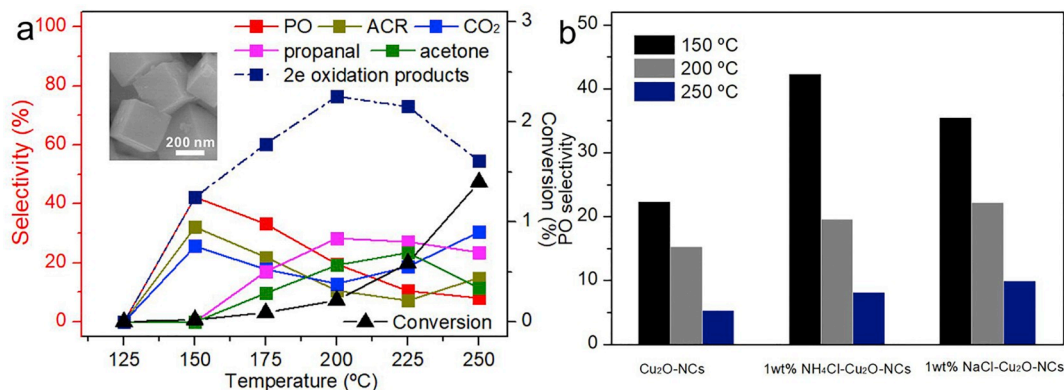


Fig. 1. (a) Catalytic performance and SEM image (insert) of 1 wt% NH_4Cl – Cu_2O –NCs. (b) Comparison of the PO selectivity of three Cu_2O –NCs–based catalysts at 150, 200 and 250 °C. The 2e oxidation products consisted of PO, propanal and acetone.

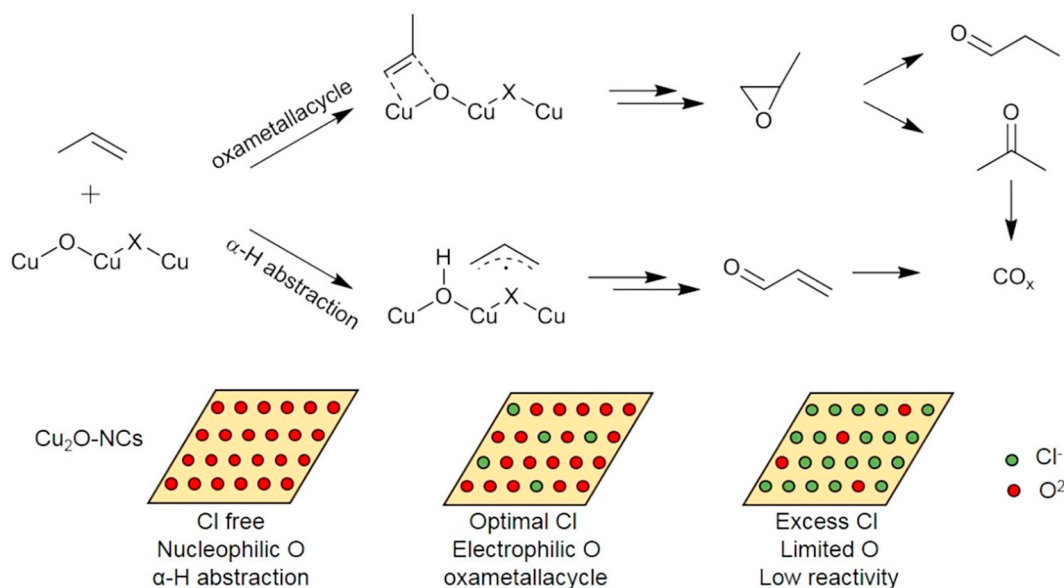


Fig. 2. Schematic illustration of the possible catalytic reaction network for the DEP reaction over $\text{Cu}_2\text{O}-\text{NCs}$ with and without Cl^- .

22.4% at 150 °C, and the maximum ACR selectivity is 39.5% at 200 °C. In contrast, when 1 wt% NH_4Cl is loaded, high PO selectivity of 42.3% and high ACR selectivity of 32.1% were achieved at 150 °C as shown in Fig. 1a.

In the case of 1 wt% $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$, the selectivity towards acetone and propanal sharply increases in the temperature range of 150–225 °C, while the CO_2 selectivity does not change very much (13.0–25.6%). These findings indicate that the presence of Cl^- suppressed the production of ACR and complete oxidation. To further verify the promoting effect of Cl^- , 1 wt% $\text{NaCl}-\text{Cu}_2\text{O}-\text{NCs}$ was prepared following the same impregnation method. Compared with the NH_4Cl -modified case, $\text{NaCl}-\text{Cu}_2\text{O}-\text{NCs}$ has relatively low PO selectivity value, as shown in Fig. S2(b), suggesting that the presence of Na^+ ions play a negative role for DEP. It should be noted that these catalysts demonstrate that the PO selectivity decreases to a certain extent when the reaction temperature exceeds 150 °C, as shown in Fig. 1b. In the temperature range of 150–200 °C, the decay of PO selectivity is relatively small for $\text{Cu}_2\text{O}-\text{NCs}$, ca. from 22.4% to 15.3%; while for 1 wt% $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$, the PO selectivity is largely decreased, ca. from 42.3% to 19.6%. This indicates that Cl^- modified catalysts suffer from a severe decay at relatively high temperatures.

To identify the possible catalytically active structure, the structure and composition of $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$ have been systematically studied. The morphology of 1 wt% $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$ after reaction in the 125–250 °C range showed no obvious change. Meanwhile, the relative XRD patterns shown in Fig. S3 show a Cu_2O phase except when the reaction temperature is higher than 200 °C, where Cu_2O appeared. In addition, quasi in situ XPS was used under the reaction atmosphere. As shown in Fig. S4, the XPS peaks of Cu 2p are slightly shifted to higher binding energies and the intensity of shake up peaks ~ 940–950 eV become stronger when the temperature is higher than 200 °C. The latter result further confirms the formation of CuO . However, Cu_2O is relatively stable between 125 and 200 °C based on the powder XRD and XPS analyses. In addition, the concentration of surface Cl^- based on the XPS measurements is plotted as shown in Fig. S5. It is clear that Cl^- concentration is kept decreasing during the catalytic process, and a decrease to 90% at 150 °C and 66% at 200 °C, respectively, was observed. In fact, Cl^- depletion from the catalyst surface was reported to be responsible for the serious deactivation of catalytic performance in alkene epoxidation [22,23], in harmony with the present results. Thus, the decay of the catalytic performance from 150 to 200 °C could be ascribed to Cl^- depletion from the catalyst surface rather than to the

oxidation of Cu(I) to Cu(II). Also, with Cl^- depletion of the catalyst surface results in the poor catalytic performance seen in the 200–250 °C range.

Fig. 2 illustrates the possible catalytic reaction network for DEP reaction over $\text{Cu}_2\text{O}-\text{NCs}$ with and without Cl^- . It is widely accepted that there exist two kinds of oxygen species over Cu_2O surfaces during DEP, namely nucleophilic and electrophilic oxygen species. The former prefers to attack the $\alpha\text{-H}$ of propylene, resulting in the formation of ACR and CO_x , while the latter tends to react with the $\text{C}=\text{C}$ double bond to yield the 2e oxidation products, such as PO, acetone and propanal. It is clear that with Cl^- deposition on the catalyst surface, 2e oxidation products are significantly increased, even up to 76%, while without the presence of Cl^- , the ACR selectivity was increased and the 2e oxidation products become < 30%.

3.2. Catalytic performance of $\text{Cu}_2\text{O}-\text{NCs}$ with different amounts of Cl^- loading

The well-defined surface structure of $\text{Cu}_2\text{O}-\text{NCs}$ allows us to count the density of Cu sites. In the present case, the BET surface area of $\text{Cu}_2\text{O}-\text{NCs}$ was found to be $2.4 \text{ m}^2 \text{ g}^{-1}$ such that the density of copper atoms on the outermost sublayer of $\text{Cu}_2\text{O}-\text{NCs}$ is $2.7 \times 10^{19} \text{ g}^{-1} \cdot \text{m}^{-2}$. As a result of this, 0.68 mg NH_4Cl should be loaded if the number of Cl^- is equal to the copper atoms, whose weight percentage of NH_4Cl is 0.33 wt%.

To investigate the influence of surface O/Cl^- ratio, $\text{Cu}_2\text{O}-\text{NCs}$ with 0, 0.03, 0.33, 1 and 10 wt% NH_4Cl loaded were prepared. Fig. 3 presents results of the catalytic performance of $\text{Cu}_2\text{O}-\text{NCs}$ with different NH_4Cl loadings. Clearly, there exists a volcano-type relationship between Cl^- loading and PO selectivity, where the 0.33 wt% $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$ is the best choice, exhibiting 57.2% and 48.7% PO selectivity at 125 °C and 150 °C, respectively. Interestingly, propylene conversion also illustrated a volcano-type relationship with NH_4Cl , whereas 0.03 wt% loaded sample had the highest conversion. Taking selectivity and conversion together, 0.33 wt% $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$ stands out from all Cu_2O catalysts, whose TOF value of PO is $3.4 \times 10^{-4} \text{ s}^{-1}$ at 150 °C, as shown in Fig. S6. In contrast, the TOF of $\text{Cu}_2\text{O}-\text{NCs}$ and 1 wt% $\text{NH}_4\text{Cl}-\text{Cu}_2\text{O}-\text{NCs}$ are only $1.36 \times 10^{-4} \text{ s}^{-1}$ and $0.44 \times 10^{-4} \text{ s}^{-1}$, respectively.

The composition of outermost surface of $\text{Cu}_2\text{O}-\text{NCs}$ loading with 0.03, 0.33 and 1.0 wt% NH_4Cl was further characterized by the ion etching technique and HS-LEIS, and results are shown in Fig. S7 and

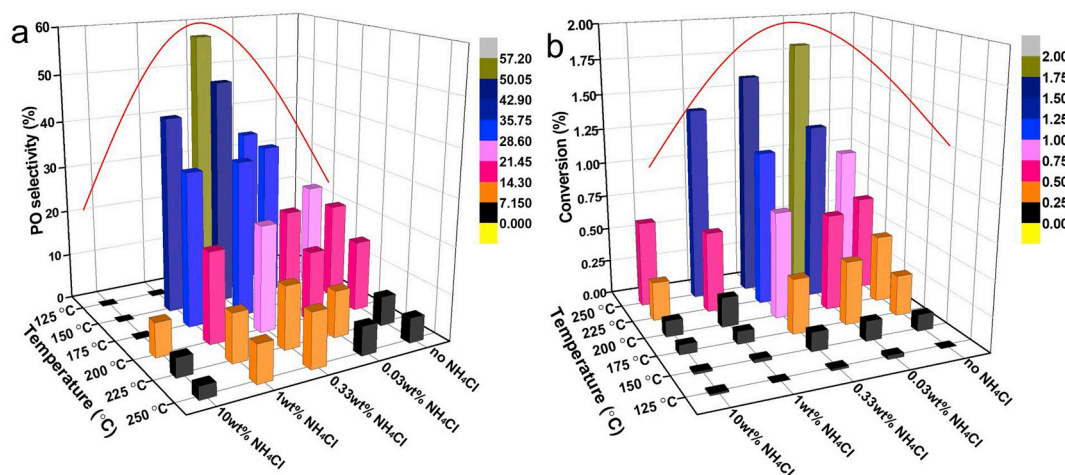


Fig. 3. (a, b) Catalytic performance in terms of propylene conversion and PO selectivity over the Cu_2O -NCs with different loadings of NH_4Cl .

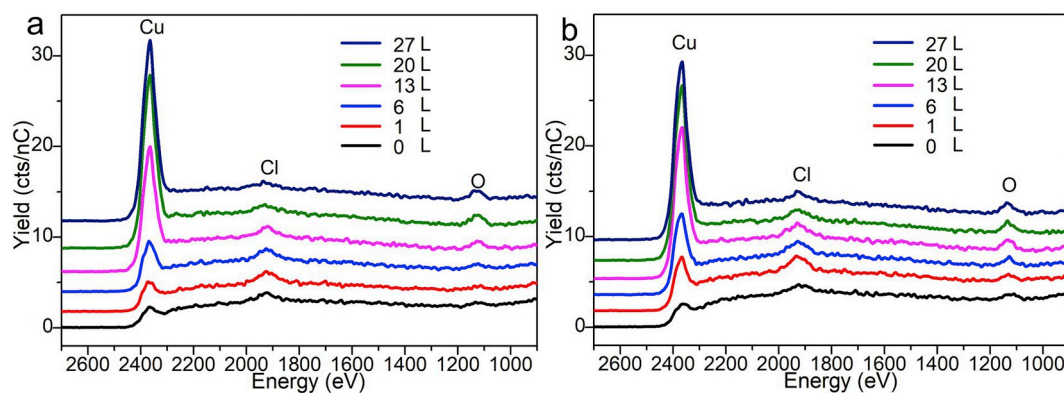


Fig. 4. HS - LEIS of (a) 0.33 wt% NH_4Cl - Cu_2O -NCs and (b) 1 wt% NH_4Cl - Cu_2O -NCs solids using Ne^+ as etching ion source.

Fig. 4, respectively. The number of removed $\text{Cu}_2\text{O}(100)$ layers is estimated from the etching depth (0.1 nm/layer). With the etching depth increasing, the intensity of peaks corresponding to Cu and O increases, while that of Cl peak decreases as the depth of Cl^- penetration is limited, which is in line with the fact that the shape of Cu_2O -NCs remains unchanged. In addition, the signal of Cl is much enhanced when more NH_4Cl is loaded.

To further reveal the specific interface between NH_4Cl and Cu_2O , 1 wt% NH_4Cl - Cu_2O -NCs was prewashed with deionized water to remove NH_4Cl particles from the surface and measured by TPD-MS. Surprisingly, the appearance of NH_3 desorption peaks and the absence of NH_4Cl or HCl desorption peak (see Fig. S8) on the washed sample indicate that partial amount of Cl^- might have been embedded into the Cu_2O lattice. All these come to the conclusion that excess Cl^- on the surface may block active sites and generate the inert CuCl phase [24]. Thus, the volcano-type relationship between the amount of Cl^- loading and PO selectivity (or conversion) can be understood by considering the compromise between more electrophilic oxygen species and denser active oxygen sites.

4. Conclusions

To summarize, the promotion effect of Cl^- in the DEP reaction was systematically demonstrated by using Cu_2O -NCs with (100) exposing facets as model catalyst. We disclosed that optimal surface O/ Cl^- ratio was critical for obtaining high selectivity values of PO. Cu_2O -NCs with 0.33 wt% NH_4Cl loading displayed the best catalytic performance with 57% PO selectivity and a TOF of $3.4 \times 10^{-4} \text{ s}^{-1}$. Our work provides a very powerful method to investigate the structure - catalytic property

relationship of model catalysts with small amounts of chemical promoters.

Declarations of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2019.105897>.

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