



Investigation of ruthenium–copper bimetallic catalysts for direct epoxidation of propylene: A DFT study

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ABSTRACT

Propylene epoxidation reactions are carried out on Ru–Cu(111) and Cu(111) surfaces with periodic density functional theory (DFT) calculations. Ru–Cu(111) surface is modeled as Cu(111) monolayer totally covering the Ru(0001) surface underneath, in accordance with the literature. It is shown that the Ru–Cu(111) surface is ineffective for propylene oxide formation since it has a lower energy barrier (0.48 eV) for the stripping of the allylic hydrogen of propylene and a higher energy barrier (0.92 eV) towards oxametallacycle formation compared to Cu(111) surface which has a barrier of 0.83 eV for hydrogen stripping and 0.75 eV for oxametallacycle formation. The reason behind this ineffectiveness is shown to be the higher basicity of the atomic oxygen adsorbed on Ru–Cu(111) compared to Cu(111), evaluated by the adsorption of sulfur dioxide onto the systems. The results are consistent both with recent publications about propylene epoxidation and previous studies performed about the structure of Ru–Cu catalysts.

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1. Introduction

Despite extensive research in academia and companies since decades, direct partial oxidation (epoxidation) of propylene with molecular oxygen still continues to be the “Holy Grail” of heterogeneous catalysis [1]. The industrial production of propylene oxide (PO) is essentially governed by two processes today, namely the chlorohydrin and the hydroperoxide processes. Both of these processes are unfavored because of environmental and economic reasons [2]. The chlorohydrin process produces the brine containing calcium chloride waste ~40 times larger than the amount of PO produced and thus causes serious environmental problems. On the other hand, the hydroperoxide process produces fixed amounts of styrene or t-butyl alcohol co-products ~3 times larger than the amount of PO produced, causing separation related problems and making the process economy dominated by the co-product market [3]. Thus, it is more than desirable to achieve a direct and selective process for the partial oxidation of propylene using oxygen.

There have been numerous experimental studies regarding the issue with different catalysts, supports and oxidants. Among the most promising of these is the use of gold nanoparticles supported on titania, discovered by Hayashi et al. [4]. In this process, molecular

oxygen is used and the PO selectivity is greater than 90%. However, the need for hydrogen co-feeding and low propylene conversion are major problems [5].

One other major discovery by Cowell et al. was that the Cu(111) surface was selective for the epoxidation of higher level alkenes, without the need of any doping or hydrogen addition [6]. It was also presented by the same group that using silica supported copper catalysts PO selectivities comparable to those stated by Hayashi et al. [4] could be obtained. Using XPS, AES and HREM, they concluded that the active form of copper was Cu⁰ species in highly dispersed, “atomic like” form [7].

Following these discoveries, there have been other studies using copper based catalysts with different dopants and oxidants [8–10]. There are examples of FeO [11], Au–Cu alloy [12] catalysts and also gas phase oxidation schemes [13]. However, although these studies are important steps in the solution of the problem, they are far from giving the desired performance in PO production. Moreover, the catalytically active state of the metal is under debate and there is little emphasis on the reaction mechanism.

Compared to the efforts in developing a better catalyst for PO production, there has been very little effort on understanding why the studied catalysts perform poor for the desired reaction [14,15]. However, in our opinion, in an issue such as propylene epoxidation in which experimental methods alone could not achieve success in solving the issue, theoretical studies on model catalysts would be invaluable since they could provide insight about the fundamentals of the reaction.

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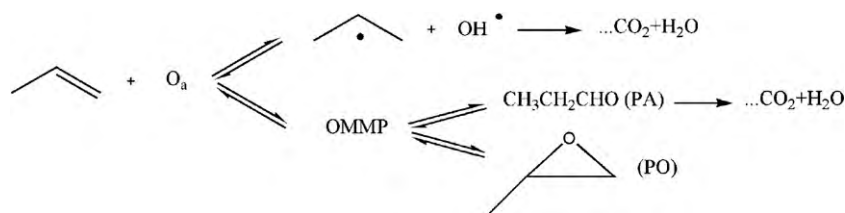


Fig. 1. Reaction mechanism for propylene epoxidation.

While the industrial production of the two-carbon analogue of PO, ethylene oxide (EO), can be achieved with direct oxidation using a supported silver catalyst, this is not true for PO [16]. The reason behind this fact is surmised to be the existence of allylic hydrogens in propylene molecule [17]. Later, through various experimental and theoretical studies, an oxametallacycle intermediate (referring to the Oxygen–Metal–Metal–Ethylene backbone, named as OMME) in ethylene epoxidation reaction is proposed to be the common intermediate for the formation of both EO and acetaldehyde, the latter being the precursor for combustion [18–21]. Following these discoveries there have been studies on particularly Ag–Cu [22] and various other Ag based [23,24] bimetallic catalysts used in ethylene epoxidation which also supported the formation of an oxametallacycle species. Finally, it was also proposed through a combination of TPRS, XPS, RAIRS analysis on Ag(1 1 1) surface that the oxametallacycle intermediate also exists for higher level alkenes [25].

In a recent theoretical publication, Torres et al. proposed that also for PO formation a common intermediate, OMMP (the analog of OMME) exists and the selectivity of the reaction towards PO formation is associated with the relative energy barriers of OMMP formation and allylic hydrogen stripping (AHS) reactions [14]. They also proposed that copper was superior to silver in PO selectivity because the adsorbed oxygen had a lower basicity than the one on silver. It was highlighted that the knowledge obtained from this model study could be regarded as a starting point for further studies. The reaction mechanism for propylene epoxidation as proposed in [14], which is also the mechanism investigated in our study, is illustrated in Fig. 1.

An interesting model system, after the famous discovery of Sinfelt, is the Ru–Cu bimetallic system [26]. This system received special interest in the previous decades due to specific reasons obtained from ethane hydrogenolysis reaction. First, although the two components are completely immiscible, i.e. no alloy formation, even at very high temperatures and after annealing [27], the Ru–Cu system showed unusual catalytic activity in the hydrogenolysis of ethane [26]. Second, it was also concluded by Sinfelt through an EXAFS investigation on “real” catalysts that copper would cover the surface of ruthenium completely in the form of a monolayer [28]. This study is also significant since it is one of the first studies to show the diagnostic power of EXAFS on catalyst characterization.

The results were also confirmed by other experimental and theoretical analyses [29–31]. It was further postulated that the Cu monolayer grows pseudomorphically to the Ru(000 1) surface underneath, forming a Cu(1 1 1) surface [29,31]. It was also shown by the group of Ertl that the model Cu monolayer on Ru(000 1) surface behaves similarly to Ru–Cu catalysts in experimental conditions [30]. They also stated through the interpretation of the results of AES, LEED, TPD and work function measurements, a charge transfer would occur from the Ru substrate to the upper Cu monolayer.

Because of these reasons and its precisely controllable surface structure, the Ru–Cu system represents a good model system to investigate how the electronic structure changes relate to catalytic activity. Thus, it would be valuable to link the information obtained about the Ru–Cu system with the hypothesis of Torres et

al. [14] about propylene epoxidation. Furthermore, to our knowledge, there are neither theoretical nor experimental studies on Ru–Cu catalysts as propylene epoxidation catalysts.

In this study, the catalytic activity of model Ru–Cu catalysts for propylene epoxidation are investigated in comparison to Cu catalysts. The observed inefficiency of Ru–Cu catalysts for PO formation will be discussed comparing the energetics of possible pathways on both Cu(1 1 1) and Ru–Cu(1 1 1) surfaces and the adsorption characteristics of the systems. The concept of oxygen basicity effect shown on elemental systems will be extended to bimetallic systems.

2. Computational methodology

Periodic, plane wave density functional theory (DFT) calculations within the supercell approach have been performed using Vienna ab initio simulation package (VASP). Cu(1 1 1) surface is modeled with a slab containing four atomic layers. Ru–Cu(1 1 1) bimetallic surface is modeled as one monolayer of copper atoms preferentially located over the threefold HCP sites of the Ru(000 1) surface (corresponding to $\theta = 1.0$), consistent with the experimental and theoretical literature [26,29,31]. The copper monolayer is optimized over an optimized Ru(000 1) slab consisting of four atomic layers.

Throughout the calculations, the bottom two layers of the slabs have been kept fixed to represent bulk structure while all other atoms in the systems have been relaxed in all degrees of freedom. A vacuum height of $\sim 10 \text{ \AA}$ is used over the slabs and the reactive species are optimized on only one side of the slab. A $p(3 \times 3)$ supercell is used for both systems corresponding to a coverage of $\theta = 0.11$ for all reactive species.

The reciprocal spaces of the supercells are described with a $4 \times 4 \times 1$ k-point Monkhorst-Pack mesh [32]. The exchange-correlation energy has been calculated within the generalized gradient approximation (GGA) using the PW91 functional [33,34]. The core electrons are described with the PAW method [35]. The energy cut-off is taken as 500 eV to ensure high precision. Total energies are calculated using a first-order Methfessel–Paxton smearing function with a width of 0.2 eV. Optimizations have been carried out until the net forces acting on atoms are smaller than 0.01 eV/Å. The dipole moment due to the usage of an asymmetric slab was removed with standard dipole correction [36]. The adsorption energies are calculated according to Eq. (1).

$$E_{\text{ads}}^X = E_{\text{system}}^X - E_{\text{vac}}^X - E_{\text{slab}} \quad (1)$$

where E_{system}^X is the total energy of X adsorbed on the metal slab, E_{vac}^X is the energy of X in vacuum and E_{slab} is the energy of the clean slab.

Saddle points in the minimum energy path are found with CI-NEB [37] method for each elementary step in the reaction mechanism after the initial and final states of the reaction have been optimized. CI-NEB calculations were performed by inserting eight images between the optimized initial and final states. The likely transition state (TS) structures produced by the CI-NEB method have been further refined. All TS structures have been characterized

by vibrational frequency analysis within the harmonic oscillator approximation. During the vibrational analysis, the relaxed atoms are displaced from their equilibrium positions twice (0.02 Å).

3. Results and discussion

3.1. Co-adsorption of atomic oxygen and propylene on Cu and Ru–Cu surfaces

Firstly, the Cu(111) monolayer was optimized over the Ru(0001) substrate. The copper atoms occupied the threefold hollow sites with a coverage of $\theta = 1.0$ as stated. The distance between the Cu monolayer and Ru substrate is calculated as 2.13 Å, in agreement with the 2.15 Å value of prior theoretical and experimental studies [27]. After the Ru–Cu(111) surface is optimized, atomic oxygen was adsorbed on the hcp sites of the Cu(111) and Ru–Cu(111) surfaces in accordance with the literature [14,15]. The Cu–O distance increased from 1.90 to 1.92 Å, and the adsorption energy increased from 4.65 to 4.88 eV, going from Cu(111) to Ru–Cu(111).

After atomic oxygen is adsorbed on the surface, the necessary step is propylene adsorption. The carbon of propylene having allylic hydrogens is named as C3, the neighboring carbon as C2 and the farthest carbon as C1. From various adsorption configurations on Ru–Cu(111), where propylene is located close enough to atomic oxygen, two stable configurations that can lead to OMMP formation (oxygen linked to C1) or AHS are investigated and the energetics are summarized in Table 1. The formation of another type of OMMP (oxygen linked to C2) was reported to be energetically unfeasible on various FCC metals including Cu(111) surface [14,15] and thus will not be the subject of our work.

From the investigation of Table 1, it can be concluded that propylene adsorbs more exothermically on Ru–Cu compared to Cu for both OMMP formation and AHS reactions. However, while for the Cu(111) surface, propylene is adsorbed a little more strongly in the precursor state for AHS, it is seen that for the Ru–Cu(111) surface the exothermicity is much higher for the adsorption of propylene in the OMMP precursor state.

3.2. OMMP formation and AHS reactions on Cu and Ru–Cu surfaces

After the adsorption of propylene, OMMP and adsorbed allyl radical structures are optimized. The detailed chemical explanations of the mentioned structures are given in a previous study [15]. The OMMP structure optimized over the Ru–Cu surface is illustrated in Fig. 2 in order to visually represent the bimetallic system under investigation.

From the minimum energy path connecting the initial and final states, the TS structures are also calculated. Optimized bond lengths of TS structures for OMMP formation and AHS reaction are given in Table 2.

It can be seen that in AHS reaction, the proton transferred from carbon to oxygen is located closer to oxygen on Cu than on Ru–Cu in the TS structure. For OMMP formation, O–C1 distance elongates and Cu–C2 distance shortens going from Cu to Ru–Cu.

Table 1
Energetics of propylene adsorption on metal surfaces (in eV).

For	Cu	Ru–Cu
OMMP	0.15	0.38
AHS	0.16	0.28

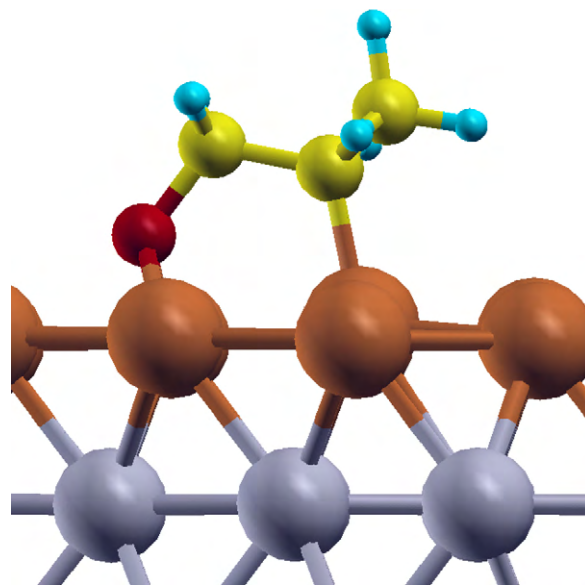


Fig. 2. Side view of OMMP structure over Ru–Cu surface.

3.3. PO and propionaldehyde (PA) formations on Cu and Ru–Cu surfaces

The OMMP intermediate formed can evolve either to PO or to PA, the latter thought as the precursor of combustion as illustrated in Fig. 1. The closure of the C–O bond and the ring formation results in PO formation. On the other hand, a proton transfer from the carbon bound to the oxygen atom to the unbound carbon results in aldehyde formation. Calculated bond lengths of TS structures for PO and PA formations are given in Table 3.

3.4. Energetics of the propylene epoxidation reactions

It is appropriate to divide the energetics of investigated mechanism into two parts, first part being the two competing reactions between OMMP and allyl radical formations and the second part being the two competing reactions between PO and PA formations after the OMMP intermediate has formed. We will follow the notation used in the previous theoretical studies [14,15] and refer to the first part as the primary chemistry and the second part as the secondary chemistry. The energetics obtained for the primary chemistry are given in Fig. 3 while the energetics for the secondary chemistry are given in Fig. 4.

Table 2
Relevant bond lengths of TS structures for OMMP formation and AHS reactions on Cu and Ru–Cu surfaces (in Å).

Bond lengths	Cu	Ru–Cu
O–H for AHS	1.23	1.26
C3–H for AHS	1.36	1.34
O–C1 for OMMP	1.96	1.99
Cu–C2 for OMMP	2.24	2.22

Table 3
Relevant bond lengths of TS structures for PO and PA formations on Cu and Ru–Cu surfaces (in Å).

Bond lengths	Cu(111)	Ru–Cu(111)
O–C1 for PO	1.47	1.47
O–C2 for PO	1.95	1.90
H–C1 for PA	1.23	1.22
H–C2 for PA	1.61	1.60

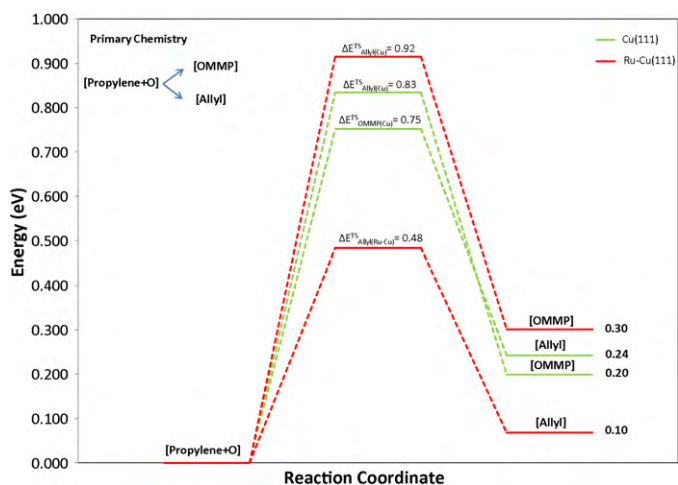


Fig. 3. Energy profile for primary chemistry of propylene epoxidation.

The results obtained on Cu(1 1 1) surface are consistent in trends with the prior study about propylene epoxidation on Cu(1 1 1) [14]. Furthermore, since the purpose of the study is not to obtain exact energies but to compare the relative barriers of steps on both Cu and Ru–Cu surfaces, the energetics can provide meaningful insight. These results are the evidence of a significant electronic effect of the Ru substrate on the Cu monolayer. An investigation of the primary chemistry reveals that while the formation of OMMP is favored on Cu(1 1 1) surface over the AHS reaction, the opposite is true (and to a great extent) over the Ru–Cu(1 1 1) surface. It is generally accepted that [14,15] the high PO selectivity is determined with a low barrier for OMMP formation compared to the barrier of hydrogen stripping. Thus, it can be concluded from the results that the Ru–Cu(1 1 1) surface would favor combustion instead of PO formation and would be ineffective as a selective PO epoxidation catalyst, based on the surface models and the reaction mechanism proposed. If we compare the secondary chemistry of the systems, it is seen that the barrier for PO formation has decreased slightly on Ru–Cu(1 1 1) surface compared to the Cu(1 1 1) surface, while the barrier for PA formation have increased. However, the slight decrease in the activation barrier of PO formation over Ru–Cu surface is incomparable with the decrease in the activation barrier of the AHS reaction and therefore would not effect the conclusion that Ru–Cu(1 1 1) surface would be less selective than Cu(1 1 1) surface.

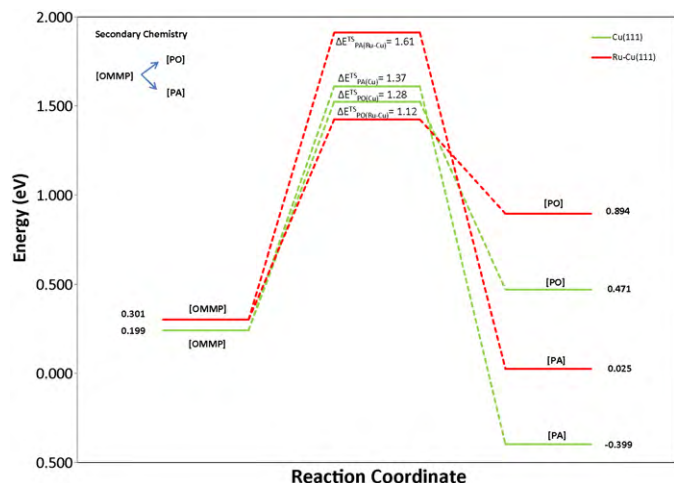


Fig. 4. Energy profile for secondary chemistry of propylene epoxidation.

Table 4

SO₂ binding energies (eV) and Bader charges on oxygenated Cu and Ru–Cu surfaces.

	Cu	Ru–Cu
SO ₂ binding energy	0.35	0.74
Bader charge on chemisorbed oxygen	6.98	7.01

Nonetheless, this conclusion about the propylene epoxidation effectiveness of the Ru–Cu(1 1 1) surface was not totally unexpected through the combination of information on the reason of metallic surface ability to epoxidize propylene [14] and the information about the electronic structure of the Ru–Cu catalyst surface [30]. In a previous publication of Christmann et al. [29], it was shown through work function measurements that a (slight) charge transfer would occur from Ru substrate to metallic Cu layer in Ru–Cu bimetallic catalysts. This would increase the electron density around the surface Cu atoms and consequently around the oxygen atom adsorbed on Cu(1 1 1) surface, making them more electronegative. Combining this with the hypothesis of Torres et al. [14], it can be expected that this phenomenon would increase the Lewis basicity of the oxygen adsorbed on Cu(1 1 1) and thus decrease the activation barrier of the allylic hydrogen stripping, since the highly basic oxygen atom would have an increased affinity to strip hydrogen atoms. Thus, it is of interest to evaluate the basicity of the oxygen atoms chemisorbed on the metal surfaces.

3.5. SO₂ adsorption on oxygen covered Cu and Ru–Cu surfaces

Recently, it was proposed that the amphoteric character of the oxygen adsorbed on the metallic surface was primarily responsible for the PO selectivity [14,15]. In essence, it was reported that the lower the basicity of the oxygen, the higher the PO selectivity. To validate this proposal, the adsorption of SO₂, a Lewis acid probe, was investigated on both Cu and Ru–Cu surfaces. SO₂ binding energy is known to scale with the basicity of the oxygen atom [14]. Bader charge analysis is also performed on these systems to compare the net charge on the chemisorbed oxygen atoms. The results obtained on both systems are given in Table 4.

It is immediately seen from the energetics that the Ru–Cu(1 1 1) surface has a higher binding energy, and thus a higher affinity to bind SO₂ and hence a higher basicity, compared with Cu(1 1 1) surface. Comparison of the bader charges of chemisorbed oxygens for two different systems also confirm that there is a slight increase in the net charge of oxygen on Ru–Cu(1 1 1) surface compared to Cu(1 1 1) surface, although this should be considered in its qualitative sense. Thus it is confirmed, through theoretical calculations that a charge transfer occurs from Ru substrate to Cu surface, in accordance with the previous studies on the electronic structure of Ru–Cu catalysts. Thus, the surface and the oxygen adsorbed become more basic. This phenomenon decreases the selectivity of the Cu(1 1 1) surface on Ru(0 0 1) towards OMMP, hence PO, formation compared to Cu(1 1 1) alone. So, the conclusion of previous studies on the effect of the basicity of the oxygen atom adsorbed are also confirmed in this study, linking the inefficiency of the Ru–Cu(1 1 1) system to the higher basicity of the oxygen atom adsorbed on it.

4. Conclusions

The epoxidation reactions of propylene on slab models of the metallic Cu(1 1 1) and bimetallic Ru–Cu(1 1 1) catalyst surfaces are investigated with periodic DFT calculations within the oxametallacycle reaction mechanism. Each elementary step is investigated through the calculation of TS structures and rigorous optimizations.

The results obtained on Cu(1 1 1) are consistent with the literature that Cu(1 1 1) favors oxametallacycle formation over AHS [14].

On the other hand, the results on Ru–Cu(1 1 1) indicate that the activation barrier for the stripping of the hydrogen atom is lowered, while the activation barrier for OMMP formation is increased on the Ru–Cu(1 1 1) surface compared to the Cu(1 1 1) surface. Thus, it can be concluded that the Ru–Cu(1 1 1) surface would be ineffective for PO formation and rather promote combustion.

In order to understand the reason behind this ineffectiveness of the Ru–Cu(1 1 1) surface compared to the Cu(1 1 1) surface, Bader charge analysis and chemisorptions of the probe SO₂ molecule on the oxygenated metal surfaces are performed. It is shown that the binding energy of SO₂ to surface oxygen increased for Ru–Cu(1 1 1) surface compared to the Cu(1 1 1) surface. The results extend the validity of the effect of the oxygen basicity on PO selectivity to bimetallic systems, making a reference point for further studies on potential bimetallic propylene epoxidation catalysts.

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