A DFT study on Cu doped Ag surfaces for propylene epoxidation

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Introduction

Although a great amount of effort has been put in ethylene oxidation catalysis during the last decade, this is not the case for propylene epoxidation. Theoretical studies in this subject have considered silver [1,2] and copper [2] surfaces. However, experiments have shown that using only silver and/or copper catalysts results in complete oxidation rather than epoxidation reaction. Recent experiments [3] revealed that copper doped silver catalysts supported on silica boost the selectivity and conversion of propylene epoxidation reaction.

In this work, considering the idea of the OMP/OMMP of the previous works [1,4] and the recent experiments, oxametallacycle structures of propylene are studied theoretically.

Materials and Methods

The calculations whose results are presented here are carried out using VASP [5] code, which uses periodic plane wave basis sets. The many-body systems are described with PAW [6,7], and GGA [8] for the exchange and the correlation energy proposed by Perdew and Wang (PW91) [9]. Except for the molecules and atoms in the gas phase, dipole corrections are included for the asymmetric slab calculations. The cut-off energies and k-points (Monkhorst Pack) used are; 341 eV and (4x4x1) for 4 layer p(3x3) slabs. The Cu doped slabs are prepared by replacing Ag atoms from the (111) surface with Cu atoms. The three slabs used are with 1 Cu atom (1/9 ML, ~2.1 wt%), 3 Cu atoms (3/9 ML, ~7.1 wt%) and 4 Cu atoms (4/9 ML, ~9.7 wt%).

Results and Discussion

We have studied the oxametallacycle of propylene on Cu doped Ag slabs. The early results have shown that adding Cu atoms to Ag (111) surface favored the OMP formation compared to pure Ag(111) and Cu(111) slabs. Furthermore, it has also been observed that increasing Cu content on the Ag slab increased the exothermicity of the OMP formation within low Cu loading range.

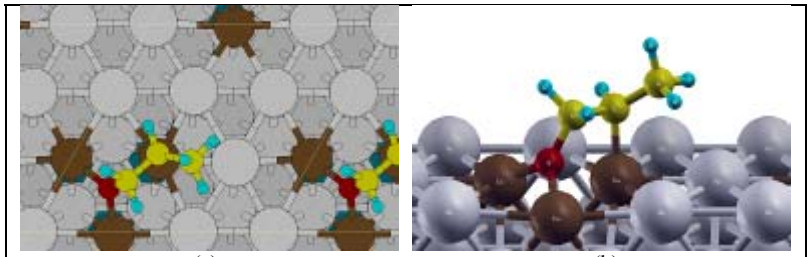

Figure 1. OMP structure on 3 Cu doped Ag slab; (a) top view; (b) side view.

Significance

The energetics of formation of propylene oxametallacycle was theoretically investigated by using Cu doped Ag slabs. Calculations obtained in this study showed that the formation of OMP on Cu doped Ag slabs is especially favored when compared to Cu only and Ag only slabs. Calculations of the formation of OMMP are being continued on all slabs.

References

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