Promoting effects of Re, Cl and alkali metal on silver catalysts for ethylene epoxidation: A theoretical study

Mikhail A. Salaev,[a],* **O.V. Vodyankina**[a]
[a]*Tomsk State University, Tomsk, 634050, Russia*
**Corresponding author: +7 3822 20 04 19, mik.salaev@gmail.com*

Abstract: The effects of Re, Cl and alkali metal co-promotion of silver catalysts for ethylene epoxidation are studied computationally using density functional theory approach. The new insights on the nature of Re, Cl and alkali metal co-promotion are proposed. The synergistic action of the said promoters is considered. The reasons for different performance of alkali metal promoters are assumed.

Keywords: silver, ethylene epoxidation, promotion.

1. Introduction (11-point boldface)

Ethylene oxide is one of the most important building blocks in chemical industry. α-Alumina-supported Ag catalysts are used to manufacture ethylene oxide in industry by gas-phase epoxidation reaction. Various promoters are added to the catalysts to boost catalyst selectivity towards ethylene oxide and/or ethylene conversion, including alkali metals, rhenium, chlorine, etc. [1]. Since the amounts of promoters are extremely low, the known experimental techniques do not allow revealing the mechanism of their action. In the meantime, theoretical methods can be used to address this challenge. Thus, in [2] Cl was assumed to block the vacant oxygen sites, prevent the unfavorable surface restructuring and formation of OMC yielding acetaldehyde. A combination of Cs and Cl promoters was shown to result in $CsCl_xO_y$ surface species. Cs was assumed to create surface oxygen vacancies and reduce the catalyst selectivity. In our previous work [3] we have shown that the synergistic effect of Re and Cs co-promotion can be caused by formation of $CsReO_x$ species, with Cs stabilizing Re oxyanion to promote ethylene epoxidation over Ag catalysts. The role of Re is proposed to be connected with altering the distribution of electronic density, compensating oxygen vacancies, covering non-selective sites and providing "optimal" holdup time of initial compounds, products and oxametallacycles over the catalyst surface.

The present work is focused on new insights on the nature of Re, Cl and alkali metal co-promotion of silver catalysts for ethylene epoxidation. We attempt to show synergistic effects originating from co-promotion and explain why different alkali metals show different promoting performance.

2. Theoretical

Multiple systems containing neutral relaxed Ag clusters and/or ethylene and/or atomic oxygen species and/or promoter(s) (Re and/or Cl and/or alkali metal) were calculated using the Gaussian'09 program package installed at SKIF "Cyberia" supercomputer of Tomsk State University. Low O coverage was modeled by adding a single oxygen atom to each model developed. The results for Ag_{20} cluster were used as a reference for subsequent calculations and benchmarking with the known literature data. Formation of oxametallacycles yielding ethylene oxide precursor is mainly considered.

B3LYP/LANL2DZ level of theory was used. Geometries of all obtained structures were fully optimized. Predicted change in energy below -1.0D-08 was taken as a convergence criterion. In all cases, the nature of stationary point was checked by vibrational frequency calculations. The absence of imaginary vibrational frequencies confirmed the stationary character of the structures. When the structure had imaginary frequencies, IRC calculations were carried out to determine the transition state. The binding energies of gas phase molecules and intermediates were calculated as a difference between the total energy of the system comprising interaction of the molecule/intermediate with the cluster and total energy of the said molecule/intermediate.

3. Results and discussion

Figure 1 shows the principle model taken for calculations.

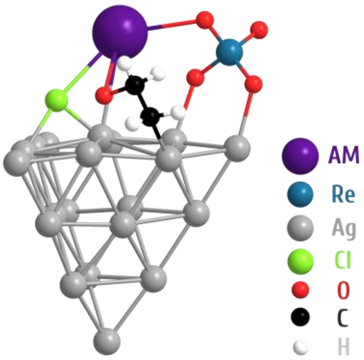

Figure 1. Principle model taken for calculations.

Periodic trends for changing of the geometries of the oxametallacycle intermediate and complexes of promoters have been found. In general, for Cl-less systems, an increase of M–Ag and M–C bonds as well as M–O distances towards 2-fold oxygen and the one in the ReO_4 moiety is observed in a row from Na to Cs. A slight decrease of Ag–O distances towards $O_{2\text{-fold}}$ and the one of ReO_4 moiety as well as Ag–C and C–O distances is observed in the same row. Transition from Li to Na results in opposite trend. When Cl atom is added, Li to Na transition follows the general trend. The M–C and C–O distances are higher for Cl-containing models, except those for Cl-containing Li-containing models. The M–Ag and Ag–C as well as M–C and C–O pairs show antibate trend for both types of models. Ag–O and C–O show simbate trends for models with and without Cl. M–$O_{2\text{-fold}}$ and M–O_{ReO4} distances are higher for Li- or Na-containing Cl-less models. For K-, Rb- and Cs-containing models, the opposite situation is observed.

The binding energies for interactions of oxametallacycle intermediate were estimated. The new insights on different performance of alkali promoters are discussed given their electronic structure. The mechanism of synergistic action of the promoters considered is assumed.

4. Conclusions

The co-promoting effects of Re, Cl and alkali metal have been studied. The synergistic action of the said promoters is considered. Periodic trends for Cl-less and Cl-containing models have been revealed. The results obtained correlate with known experimental and theoretical data.

References

1. (a) Patent US WO 2010123675 A1, 2009, Dow Technology Investment LLC, (b) Patent US 2671764, 1954, Jefferson Chemical Company, Inc.
2. M.O. Özbek, I. Önal, R.A. van Santen, ChemCatChem 5 (2013) 443.
3. M.A. Salaev, O.V. Vodyankina, Catal. Today, 2017, Under review.