

# Gas-phase oxidation of alcohols over silver: The extension of catalytic cycles of oxidation of alcohols in liquid-phase

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## Abstract

Oxidation of alcohols (including C<sub>2</sub>–C<sub>6</sub> alkyl alcohols, cyclohexanol, benzyl alcohol, 1-octanol and allyl alcohol) to corresponding aldehydes or ketones has been performed over silver catalyst; the silver catalyst is highly active and selective to the reaction. The mechanism of oxidations of alcohols is inclined to oxidative dehydrogenation at low temperature region (<550 K). The facets of silver are ideal versatile facets to activate molecular oxygen and generate oxidative, strong basic oxygen species (O<sup>δ-</sup>), and weak acidic sites (Ag<sup>δ+</sup>) which can stabilize the organic intermediates, quickly. The facets of silver containing oxygen integrate several active catalytic sites existing in liquid-phase catalytic oxidation of alcohols and make catalytic reaction more effective.

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**Keywords:** Silver; Alcohols; Oxy-dehydrogenation; Multi-functional oxygen species

## 1. Introduction

Oxidation of primary and secondary alcohols to the corresponding aldehydes or ketones plays a fundamental role in organic synthesis owing to the versatility of the carbonyl group as a building block [1,2]. Traditionally, the oxidation of alcohols is mainly performed by using stoichiometric quantities of oxidants containing chromium [3], whereas those oxidants are fairly expensive and the systems using chromium-containing oxidants also generate large volumes of waste water containing heavy-metal. Furthermore, from economic and environmental aspect there is a growing demand for atom efficient catalytic methods that use clean oxidants such as H<sub>2</sub>O<sub>2</sub> and even O<sub>2</sub>. In practice, the oxidation of alcohols with air can be performed in the liquid phase or in the gas phase, depending mainly on the thermal stability and volatility of reactants and products. While many recent papers deal with studies on the oxidation of alcohols in solutions [4–11], little attention has been paid to the gas phase reaction and

attempts at industrial application failed owing to selectivity problems [12].

Although there are some disadvantages of gas-phase dehydrogenation, especially the high reaction temperature, the convenient separation of catalysts from catalytic reaction and almost additives-free processes encourage the studies of gas-phase dehydrogenation of alcohols. The gas-phase dehydrogenations of alcohols are focused on the platinum group elements [13,14], IB and IIB group elements [15–20] and base-dehydrogenation catalysts [21–24]. However, the dehydration of primary and secondary alcohols to alkenes or ethers can be a side reaction with the participation of active acidic sites in gas-phase dehydrogenation systems at high temperature. Moreover, oxidative degradation of the carbon chain to lower aldehydes or carboxylic acids, and/or total oxidation to carbon dioxide are also the main side reactions in oxidative dehydrogenation systems [16].

Silver is applied industrially in the manufacturing of formaldehyde and ethylene oxide [25]. In the past 27 years, some catalytic processes over silver-based catalysts have been understood at molecular level due to the developments of characterization technologies, and the studies of dehy-

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drogenation of alcohols over silver were mainly focused on methanol [26–42]. The oxidation of methanol to formaldehyde over silver was considered to be the first successful example of the impact of surface science studies upon heterogeneous catalysis [26]. However, there are few records of other alcohols [19,43–45].

Herein, we report silver-catalyzed oxidations of ethanol to acetaldehyde, 2-propanol to acetone, 2-butanol to 2-butanone, and cyclohexanol to cyclohexanone, which are performed in industrial scale mainly over ZnO, Cu, and Zn–Cu systems [16]. In order to investigate the interactions of  $\beta$ -carbon–carbon double bond and  $\beta$ -aromatic ring with silver, the catalytic reactions of allyl alcohol to acrolein and benzyl alcohol to benzaldehyde were performed over silver. With the aim to estimate the size effect on the catalytic processes over silver, catalytic reaction of 1-octanol was also conducted. In order to investigate the mechanism of the oxidation of alcohols, oxidative dehydrogenation or pure dehydrogenation, the oxidations of ethanol were also carried out on the  $O\alpha$ -saturated and  $O\gamma$ -saturated samples, respectively.

## 2. Experimental

Silver catalyst was prepared through the reduction of silver nitrate by sodium borohydride. 2.63 g sodium borohydride (analysis grade, Beijing chemical factory) was dissolved into 50 g distilled water, and 7.86 g silver nitrate (analysis grade, Beijing chemical factory) was dissolved into 100 g distilled water. Sodium borohydride solution was added dropwise into vigorously stirred silver nitrate solution at room temperature. The product was filtered and ultrasonic-assisting washed thoroughly with hot water for five times, then dried at 373 K in air overnight. A dim silvery white powder was obtained. The silver powder for test was 60–80 mesh. Commercial copper powder (the second smelting factory of Shanghai,  $\geq 99.5\%$ ) is 60–80 mesh.

$O\alpha$ -saturated and  $O\gamma$ -saturated silver catalysts were prepared in situ by the methods of van Veen et al. [30], and the experimental detail also can be found in our previous work [46]. In general, the condition of high temperature (923 K) and pure oxygen favors the generation of  $O\gamma$ -saturated silver catalyst, the low temperature (473 K) treatment of oxygen-free silver in pure oxygen can generate  $O\alpha$ -saturated one.

Catalytic experiments were conducted under atmospheric pressure in a vertical fixed-bed quartz tubular reactor with an internal diameter of 5.5 mm, and the sample bed was 5 mm high in general. Samples (60–80 mesh) were held in place with quartz-wool plugs. All samples were pre-treated in a flow of air (10 ml/min) at 573 K for 180 min and cooled to 353 K, if there is no specific statement. A thermocouple (type K) was attached to the outer wall of the quartz tube directly adjacent to the sample and used as the sensor of the temperature controller (Eurotherm model 808) to control a tubular furnace (ID 20 mm). *Note*: The oxidations of alcohols to aldehydes or ketones are highly exothermic

reactions, for example,  $\text{CH}_3\text{OH}_{(g)} + \text{O}_{(a)} = \text{CH}_2\text{O}_{(g)} + \text{H}_2\text{O}_{(g)}$   $\Delta H = -159$  kJ/mol, thus, maybe there exist temperature gradients in these reaction systems. In order to check the above problem, another thermocouple (coated with glass layer,  $\Phi \sim 1.5$  mm) should be placed in the catalyst bed. Because the silver catalyst is very active to the oxidation of benzyl alcohol to benzaldehyde, we had checked the reactor temperature gradient of the oxidation of benzyl alcohol. When the conversion of benzyl alcohol was less than 30%, there was no difference between the two thermocouples. With the conversion rising, the inner temperature got higher than the outer one; and the difference was about 12 K at the maximum conversion.

A gas chromatograph equipped with TCD detector was used, GDX-502 (the second chemical reagent factory of Tianjin, a commercial microporous microspherical copolymer of divinylbenzene–acrylonitrile, BET 170 m<sup>2</sup>/g, similar to Chromosorb<sup>TM</sup> 104) packed column for the analysis of carbon dioxide, and PEG-20M coated packed column for the analysis of organic compounds. In the cases of C1–C5 alcohols, on-line sampling method was used, and the temperature of furnace raised linearly at 1 K/min. In the cases of  $\geq C6$  alcohol, each reaction temperature was kept steady for about 10 min, and then the products were collected in a liquid nitrogen trap. External standard method was used for the analysis of products, and the conversions and the selectivity were calculated. In our analytic system, the direct detection of CO was not available, but the formation of CO could be estimated by the supply of O<sub>2</sub> and the yields of aldehyde or ketone, and CO<sub>2</sub>. In our experiments, the organic products of degradation of the carbon chain and dehydrations of alcohol, such as ethers and alkenes, were trace, and the yield of CO<sub>2</sub>, which was a main by-product, could meet with the yield of aldehyde or ketone and the supply of O<sub>2</sub>, thus, the formation of CO can be neglected.

Air was used as the oxidant at a flow rate of 20 ml (STP)/min. Alcohol was fed at 0.0214 mol/h by HPLC pump (Shimadzu LC-5A). The ratio<sub>mol</sub> of alcohol to O<sub>2</sub> was 2.0.

## 3. Results and discussion

Fig. 1 shows the temperature dependence of the conversions of alcohols and selectivities to aldehydes or ketones over metal silver catalyst in a small fixed-bed reactor at alcohol/O<sub>2</sub> ratio of 2.0. With temperature rising, the conversions of alcohols rise. Among these alcohols, benzyl alcohol is the most active one with almost 100% selectivity. The conversion of benzyl alcohol is about 40% at 453 K, which is below the boiling point of benzyl alcohol. Although the boiling point of benzyl alcohol is 478 K under 1 atm., the vapor pressure of benzyl alcohol is 48.88 kPa at 453 K [47]. In our reaction condition, when benzyl alcohol was gasified completely, the  $P_{\text{benzyl alcohol}}$  was 28.9 kPa. It was certain that benzyl alcohol was totally in gas-phase. Conversions of allyl alcohol and cyclohexanol are less than 10% even at 550 K.

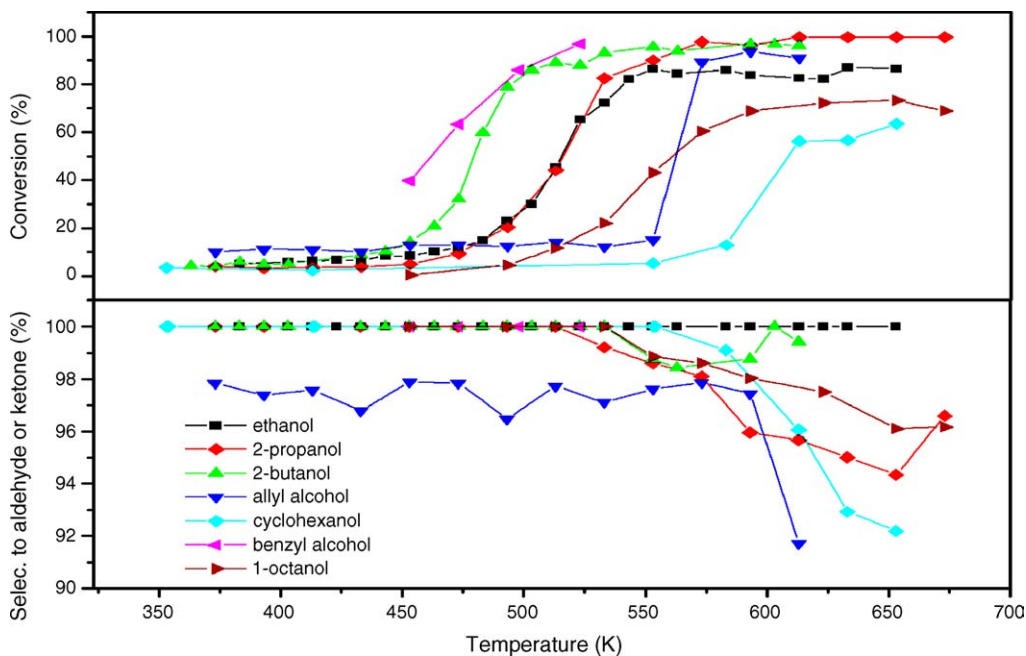


Fig. 1. Temperature dependence of the conversions of alcohols and selectivities to aldehydes or ketones over metal silver catalyst. Alcohol: 0.0214 mol/h; air: 20 ml/min, the ratio<sub>molar</sub> of alcohol/O<sub>2</sub> = 2.0.

In the case of benzyl alcohol, there is no H atom connecting with  $\beta$ -carbon and the conjugated  $\pi$  orbital structure composing of aromatic ring and carbonyl group is very stable. Thus, the oxidation of benzyl alcohol is very easy and the selectivity to benzaldehyde is very high. In fact, the oxidation of benzyl alcohol to benzaldehyde is a very popular model reaction for the study of catalytic oxidation of alcohols. Conversion of cyclohexanol is the most difficult. It can be explained that the hydrogen connected to alpha-carbon is difficult to be dehydrogenated because of the steric hindrance by cyclohexyl group. 1-octanol is also difficult to be oxidized because the long alkyl chain blocks other 1-octanol molecule to be adsorbed near the adsorbed 1-octanoxy group and the effective reaction area of catalyst is reduced.

Selectivity of oxidations of allyl alcohol, 2-propanol, cyclohexanol and 1-octanol to corresponding aldehydes or ketones is less than 98%. In the case of alcohol with large alkyl group, such as cyclohexanol and 1-octanol, the large alkyl group of adsorbed alcohol molecule blocks other alcohol molecule to be adsorbed near it, thus, the ratio of alcohol/O near the surface is reduced, and the selectivity to aldehyde decreases. In the case of cyclohexanol, when cyclohexanol is transformed into cyclohexanone, the tensile force of C<sub>6</sub>-ring rises with the change of hybrid manner of  $\alpha$ -carbon, which makes the stability of C<sub>6</sub>-ring decreasing. The local superfluous O $\delta^-$  species near the adsorbed cyclohexanone can also attack the positive carbonyl carbon atom and make the C–C bond of C<sub>6</sub>-ring broken, thus, the selectivity to total oxidation rises. The catalytic oxidations of 1-propanol, 1-butanol, 1-pentanol, 2-pentanol, 1-hexanol over silver were also performed. The results are shown in Fig. 2. Around 600 K, the

conversions reach the maximum values, and the selectivities begin to decrease with temperature rising.

In the above experiments, CO<sub>2</sub> is the main by-products, while the others, such as ethers, alkenes, carboxylic acids, are trace. It should also be noted that direct dehydrogenation of alcohols can occur at high temperature. Therefore, the conversions of alcohols are not stoichiometric with the amount of oxygen added, especially in the cases of long chain alcohols.

Copper and silver belong to the Copper Group in the periodic table. Copper is usually used in the processes of dehydrogenation of alcohols [16]. The catalytic behaviors of oxygen species on them are very similar because they are in the same group, yet there still exist some differences caused by the detailed electronic structures of each metal element. In order to obtain more mechanism information, catalytic reactions of methanol and ethanol were performed over metal copper and silver. In Fig. 3, it is clearly shown that catalytic performance of silver is better than that of copper. These results are similar to Madix's work [48]. In the case of ethanol, even 100% selectivity at 90% conversion can be obtained over silver catalyst at 550 K, at which the conversion is less than 30% over copper catalyst. The highest conversion of ethanol is about 80% with 99% selectivity at 630 K, and ~0.5% selectivity to formaldehyde (carbon chain degradation) and ~0.5% selectivity to ethylene (dehydration) are obtained.

The mechanism of gas-phase oxy-dehydrogenation of alcohols over silver is well known [16,26,27,44,48]. Under ultra high vacuum (UHV) condition, oxygen-free silver surface is inert to alcohols, while the oxygen pre-adsorbed silver surface is very active to cause alcohol adsorbed as alkoxy [27]. In real condition, there are some different mecha-

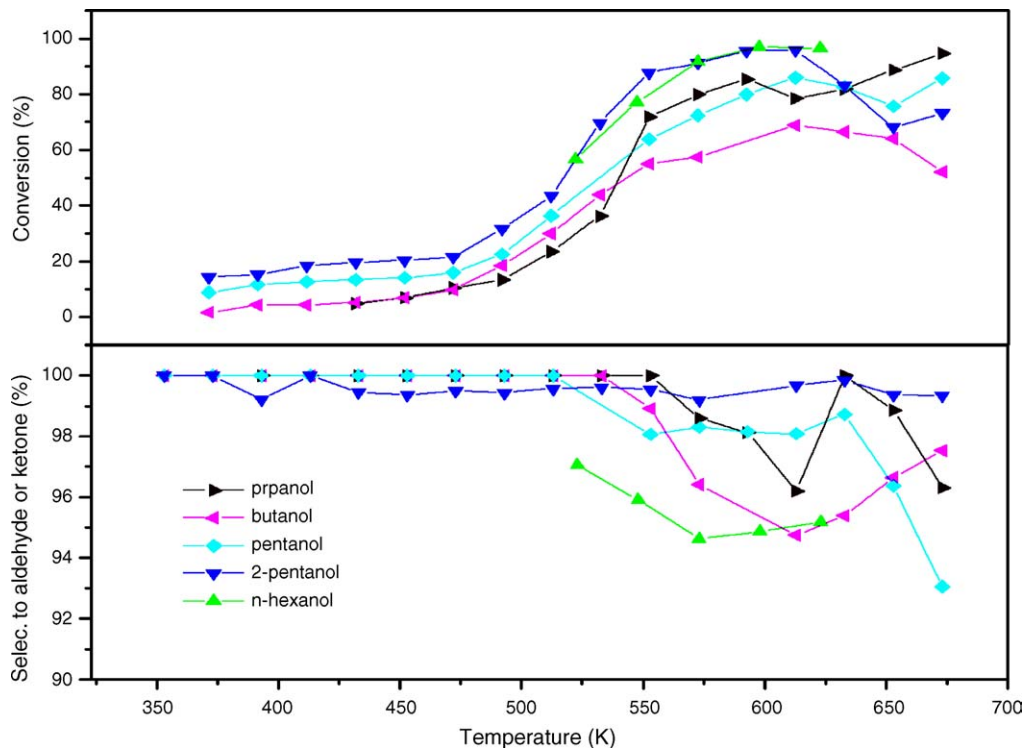


Fig. 2. Temperature dependence of the conversions of alcohols and selectivities to aldehydes or ketones over metal silver catalyst. Alcohol: 0.0214 mol/h; air: 20 ml/min, the  $\text{ratio}_{\text{mol}}$  of alcohol/ $\text{O}_2 = 2.0$ .

nisms (oxidative dehydrogenation or pure dehydrogenation, parallel or consecutive reaction scheme) claimed for dehydrogenation of alcohols, especially in the case of methanol. In order to investigate the mechanism occurred in our exper-

iments, we carried out the dehydrogenation of ethanol over  $\text{O}\alpha$ -saturated and  $\text{O}\gamma$ -saturated silver respectively. The reason for the choice of ethanol as a probe molecule is that the selectivity to acetaldehyde is almost 100% below 600 K. In

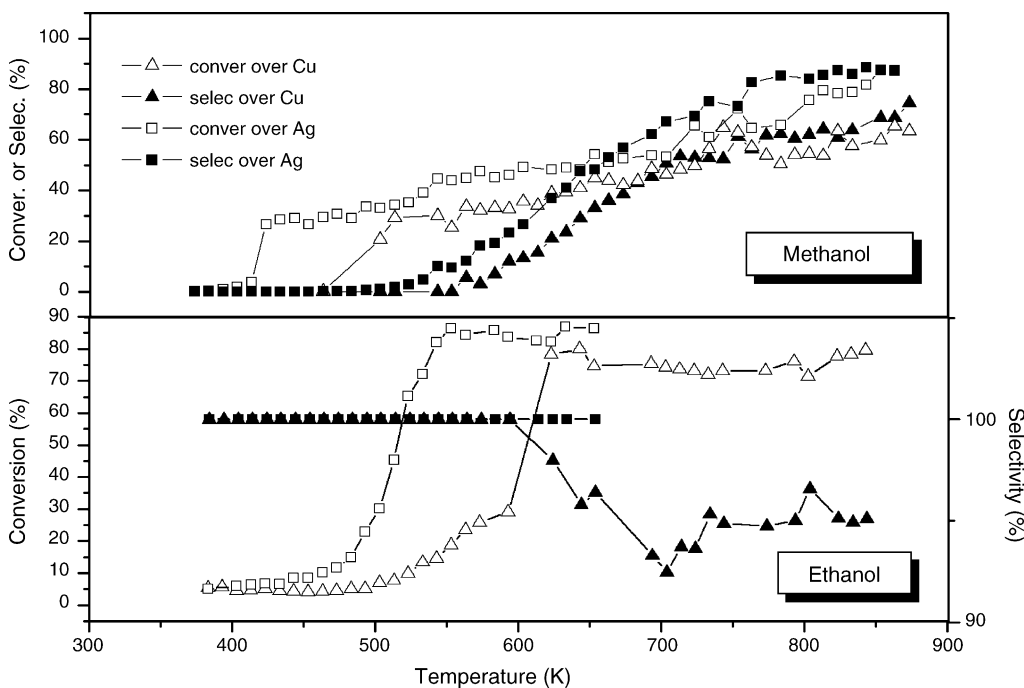


Fig. 3. Comparing the catalytic performance between silver and copper. Alcohol: 0.0214 mol/h; air: 20 ml/min, the  $\text{ratio}_{\text{mol}}$  of alcohol/ $\text{O}_2 = 2.0$ .

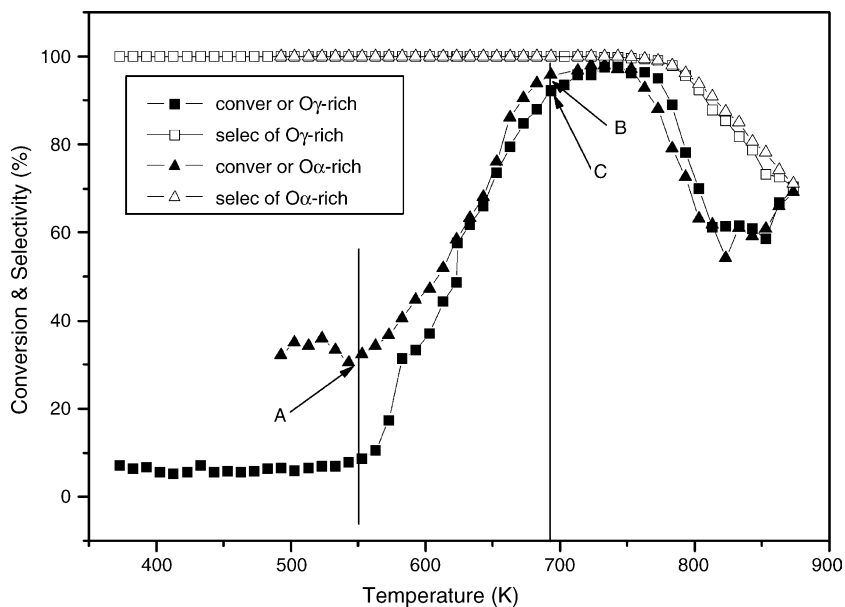


Fig. 4. Comparing the catalytic performance between  $O_{\alpha}$ -saturated or  $O_{\gamma}$ -saturated silver. Catalyst bed:  $\Phi 5.5 \text{ mm} \times 10 \text{ mm}$ ,  $1.2 \text{ mol}\% \text{ O}_2\text{-Ar}$ :  $4.0 + 0.1 \text{ ml (STP)/min}$ , the  $\text{ratio}_{\text{mol}}$  of  $\text{EtOH}/\text{O}_2 \sim 6.5$ , the oven temperature rising linearly at the rate of  $2 \text{ K/min}$ .

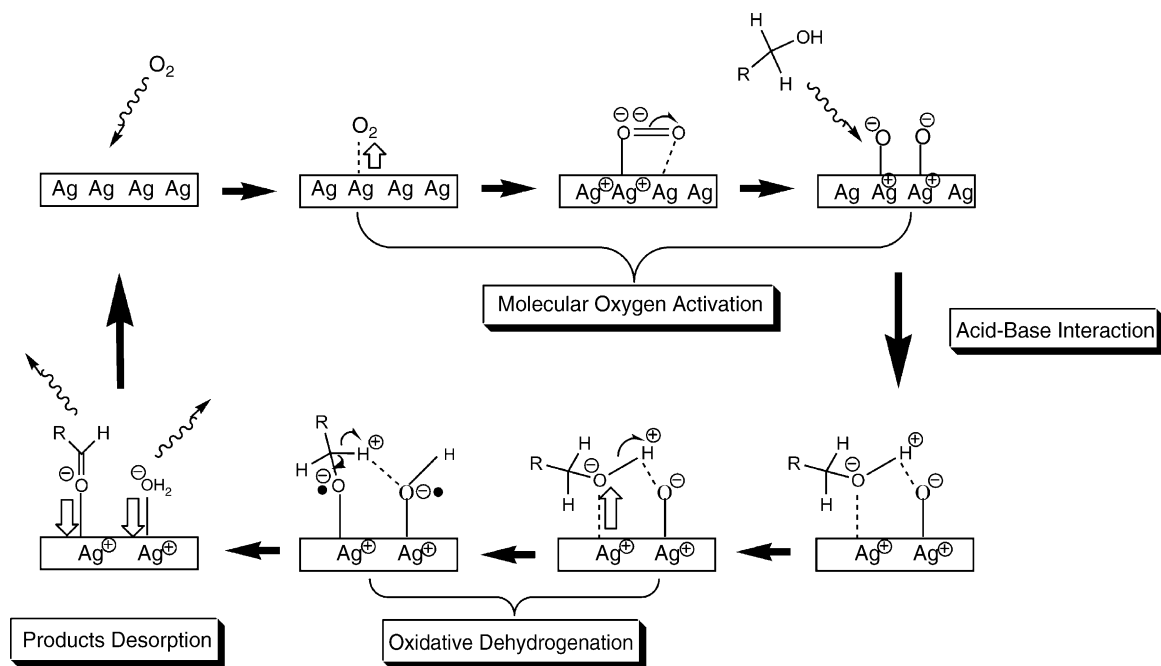
other cases, the formation of  $\text{CO}_2$  makes the analysis inconvenient.

In general, two kinds of oxygen species exist on silver surface,  $O_{\alpha}$  species, which are only stable at low temperature and are considered to cause the non-selective oxidation of methanol;  $O_{\gamma}$  species, which are stable even at high temperature and are considered to cause the selective oxidation of methanol. In Fig. 4, the differences between  $O_{\alpha}$  species and  $O_{\gamma}$  species are shown by the oxidation of ethanol to acetaldehyde. It is clearly shown that  $O_{\alpha}$ -saturated silver is more active than the  $O_{\gamma}$ -saturated one when temperature is lower than  $550 \text{ K}$ . According to the supply of oxygen, the gas-phase oxygen was used up stoichiometrically in the case of  $O_{\alpha}$ -saturated silver when temperature was lower than  $550 \text{ K}$ . With temperature rising, the conversions of ethanol over the two different silver catalysts raise gradually. When the temperature is higher than  $620 \text{ K}$ , the catalytic performances of them get alike. When the conversion of ethanol is more than  $\sim 35\%$ , the amount of oxygen for the reaction ( $\text{C}_2\text{H}_5\text{OH} + 0.5\text{O}_2 = \text{CH}_3\text{CHO} + \text{H}_2\text{O}$ ) is not stoichiometric. It is possible that the oxygen, which is dissolved in bulk phase of silver catalysts during the processes of catalysts treatment, participates the reaction. In order to check the hypothesis, we had compared the water peak of the gas-chromatogram of the three points (A, B and C) in Fig. 4. It was found that the areas of water peak were almost equal. Thus, the pure dehydrogenation of ethanol can occur at high temperature.

It is noticeable that the different oxygen species saturated silvers have different catalytic performance at lower temperature region ( $< 550 \text{ K}$ ). The  $O_{\alpha}$ -saturated silver has higher reactivity than the  $O_{\gamma}$ -saturated one. The catalytic performances depend on the kind of oxygen species greatly, therefore, it is reasonable to deduce that oxygen species directly

take part in the dehydrogenation of ethanol at lower temperature region ( $< 550 \text{ K}$ ). As shown in Figs. 1 and 2, most alcohols can get their maximum conversions when temperature is lower than  $550 \text{ K}$ . Thus, the oxidative dehydrogenation process should be the predominant process under our experimental conditions.

Recently, Voronova et al. [49] have investigated the effect of surface acidity of silver catalysts on the conversion of ethylene glycol into glyoxal, and they found that the surface acidity of silver catalysts can affect the activity of the catalysts. They proposed that the Lewis acid-base pair  $\text{Ag}^{\delta+} \cdots \text{Ag} - \text{O}^{\delta-}$  occurring on the oxidized surface of silver can react with alcohol molecule to generate an adsorbed long-lived alkoxy intermediate and  $\text{OH}_{\text{ads}}$ . In their work, they focused on the roles of acid sites of catalysts in alcohol oxidation. It is well known that  $O_{\alpha}$  species has more negative charge than that of  $O_{\gamma}$  species, thus,  $O_{\alpha}$  species is a stronger Lewis base than  $O_{\gamma}$  species. The results of oxidation of ethanol on different oxygen species saturated silver catalysts clearly show that the  $O_{\alpha}$ -saturated silver is greatly more active than  $O_{\gamma}$ -saturated silver below  $550 \text{ K}$ . It seems that the base sites also can affect the oxidation of alcohols. Scheme 1 illustrates the oxidative dehydrogenation process occurring on silver surface, and the oxidations of alcohol to corresponding organic acids and  $\text{CO}_x$  are omitted. It is well known that molecular oxygen can be adsorbed on silver surface and obtains electron from silver to form  $\text{O}_2^-$ . According to the molecular orbital theory, the bond order of  $\text{O}_2$  is 2.0. When  $\text{O}_2$  gets one electron to form  $\text{O}_2^-$ , an electron is filled into  $\pi_{2p}^*$  orbital and the bond order of  $\text{O}_2^-$  is 1.5. Thus,  $\text{O}_2$  is activated by silver and the  $\text{O}_2$  is cleaved into two active atomic oxygens. Alcohol is chemically adsorbed on the surface as alkoxy group while alpha-hydrogen is being



Scheme 1. Catalytic cycle of gas-phase oxidative dehydrogenation of alcohols over metal silver. The hollow arrows represent the directions of negative charge stream. The number of charge symbols (such as  $\oplus$ ) only qualitatively represents the charge.

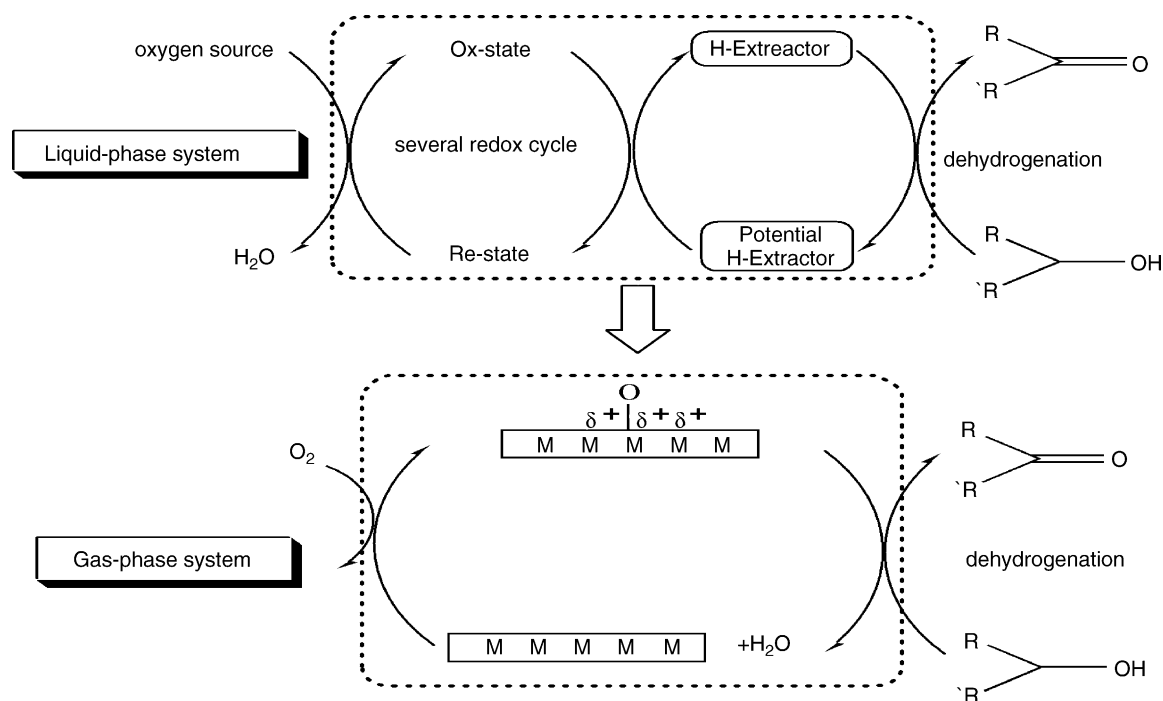
extracted by the pre-adsorbed oxygen species, then, the beta-H elimination of alkoxy occurs. During the processes, the surface oxygen species act as Lewis bases to induce the positive charged hydrogen atoms (the hydrogen of hydroxyl group is the most positive one in a usual alcohol molecular) to approach themselves, then extract hydrogen atoms from the alcohol and the consequent intermediates, and the surface metal atoms with positive charge act as Lewis acids to stabilize the adsorbed negative charged intermediates [50]. Finally, the adsorbed products are desorbed from the surface of catalyst. During the processes, the adsorbed oxygen species play an important role. At the beginning of the catalytic cycle, they carry a partial negative charge and seem like *basic species* due to electron transfer from silver. The strongest electrostatic interaction occurs between the basic species and the hydroxyl hydrogen (the most positive one in a usual alcohol molecule) of alcohol, thus, the reactive sites are locked and the selectivity rises greatly. Because their electronic structure is electron-lacking, they prefer to act as *oxidative reagent* to extract hydrogen atoms from alcohols with H–X (X = O or C) bond broken.

In the most transition-metal-containing systems of alcohol oxidation in liquid-phase, the metal complexes containing basic ligands are *indispensable* in the catalytic cycles. In general, the basic ligands are hydroxyl group [4,5], 2,2,6,6-tetramethylpiperidinyl-1-oxy group [9], alkoxy [6], peroxide group [6], which are potential hydrogen extractors. Therefore, it seems that the basic group of the active center may be an important factor in catalytic reaction. And the regeneration of active sites should often be coupled by several redox cycles. As shown in Scheme 2, the active sites in

the oxygen-containing silver surface integrate the cycles of hydrogen extraction and the cycles of oxygen source incorporation, which are necessary to the regeneration of the cycles of hydrogen extraction. The active oxygen species over silver can *directly* generate from molecular oxygen without any other catalytic cycles and act as both basic sites to induce the dehydrogenation and hydrogen extractor to accept hydrogen from alcohols.

From above discussion, we know that the basic species is an important factor in both liquid-phase system and gas-phase system. Then the basic strength of the active sites should be a key factor. Sanderson's work [51] shows that the oxygen of  $\text{Ag}_2\text{O}$  has the most negative effective charge,  $-0.46e$ , among the transition metal oxides, and that of  $\text{Cu}_2\text{O}$  is  $-0.44$ . The XPS study of Schoen shows that the  $\text{O}_{1s}$  binding energies of  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  [52],  $\text{Ag}_2\text{O}$ ,  $\text{AgO}$  [53] are 530.2, 529.8, 529.2, 528.6, respectively. XPS  $\text{O}_{1s}$  core-level binding energies can provide information about the charge on chemisorbed oxygen species and oxide ions. To a simple approximation, the higher the charge on oxygen is, the lower the  $\text{O}_{1s}$  binding energy is (note: final state relaxation effects can have a strong influence on  $\text{O}_{1s}$  binding energies, and are not considered here) [29]. Hence the oxygen species of silver oxides are the strongest basic species among them. Because the adsorptions of oxygen on silver and copper are very similar, it is reasonable to deduce that the oxygen species over silver have more negative charge.

It is also well known that acidic sites often promote alcohol dehydration and basic sites favor alcohol dehydrogenation [15,54,55]. Because the electronegativity differences between silver and oxygen, the Lewis acid-base pair  $\text{Ag}^{\delta+} \cdots \text{Ag} - \text{O}^{\delta-}$  occurs on the oxidized surface of silver.



Scheme 2. Comparison of catalytic cycles between liquid-phase system and gas-phase system.

According to Misono's classification of acid [56], the hardness of  $\text{Cu}^+$  and  $\text{Ag}^+$  are 3.45, 3.99, respectively.  $\text{Cu}^+$  is a boundary acid and  $\text{Ag}^+$  is a soft acid. It is well known that alkoxy is a hard base. Thus, the interaction between  $\text{Ag}^+$  and alkoxy is weaker than that between  $\text{Cu}^+$  and alkoxy, and the side reactions of alcohols caused by acidic sites should be reduced. Pestryakov's [57] and Madix's work [48] show that the active order for ethanol oxidation is  $\text{Ag} > \text{Cu}$ , and the order of selectivity to acetaldehyde is  $\text{Ag} > \text{Cu}$ .

Although the bulk  $\text{Ag}_2\text{O}$  decomposes at 503 K, the XPS study [58] shows that oxygen atoms are chemically adsorbed on silver even at 763 K. Wachs' work [59] also indicated that the "TOF (turnover frequency) of redox of methanol" [59] over  $\text{Ag}_2\text{O}$  is almost the highest among the metal oxides except  $\text{PtO}$ , and is about 60 times than the one over copper oxide. These indicate that the concentration of surface oxygen over silver is relatively low, and the catalytic cycle over silver is faster than that over copper. Hence, the catalytic performance of silver is very well.

#### 4. Conclusion

Based on the above discussions, the facets of silver should be regarded as ideal multi-functional facets to regenerate oxidative, strong basic oxygen species and weak acidic sites quickly for the catalytic cycles, such as molecular oxygen activation, alcohol chemical adsorption and the subsequent dehydrogenation. The higher TOF of redox of alcohols over silver and weaker acidic sites make the high selectivity to carbonyl compounds at high conversion over silver catalyst possible. During the processes, the oxygen species over sil-

ver are pivotal factors and play versatile roles: (a) acting as active basic sites to lock the reactive sites; (b) acting as active oxidative sites to extract hydrogen atoms from alcohol. Comparing with the liquid-phase oxidation systems, the advantages of the presenting system are basic-additives-free and heavy-metal-solution-free. The differences of catalytic performances between copper and silver can also be explained that the stronger basic oxygen species and weaker acidic sites over silver make the catalyst more active and selective. Therefore, silver is excellent and green for *oxy-dehydrogenation* of alcohols.

#### Acknowledgements

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2005.06.051](https://doi.org/10.1016/j.molcata.2005.06.051).

#### References

- [1] M. Hudlicky, *Oxidation in Organic Chemistry*, American Chemical Society, Washington, DC, 1990.

- [2] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [3] J. McMurry, *Fundamentals of Organic Chemistry*, fourth ed. (photocopy edition), China Machine Press, Beijing, 2002.
- [4] I.E. Marko, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, *Science* 274 (1996) 2044.
- [5] G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636.
- [6] R.A. Sheldon, I.W.C.E. Arends, A. Dijkstra, *Catal. Today* 57 (2000) 157.
- [7] W. Adam, C.R. Saha-Moller, P.A. Ganeshpure, *Chem. Rev.* 101 (2001) 3499.
- [8] T. Mallat, A. Baiker, *Chem. Rev.* 104 (2004) 3037.
- [9] R.A. Sheldon, I.W.C.E. Arends, G.-J. ten Brink, A. Dijkstra, *Acc. Chem. Res.* 35 (2002) 774.
- [10] B.Z. Zhan, A. Thompson, *Tetrahedron* 60 (2004) 2917.
- [11] J. Muzart, *Tetrahedron* 59 (2003) 5789.
- [12] K. Weissermel, H.J. Arpe, *Industrial Organic Chemistry*, VCH, New York, 1997.
- [13] A.H. Ali, F. Zaera, *J. Mol. Catal. A: Chem.* 177 (2002) 215.
- [14] H. Wieland, *Ber.* 54 (1921) 2353.
- [15] M. Muhler, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, vol. 5, VCH, Weinheim, 1997, p. 2274.
- [16] M. Kraus, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, vol. 5, VCH, Weinheim, 1997, p. 2159.
- [17] I.-D. Huang, L.M. Polinski, K.K. Rao, U.S. Patent 4,154,762.
- [18] V.Z. Fridman, A.A. Davydov, K. Titievsky, *J. Catal.* 222 (2004) 545.
- [19] W. Aquila, H. Fuchs, O. Worz, W. Ruppel, K. Halbritter, U.S. Patent 6,013,843.
- [20] S. Biella, M. Rossi, *Chem. Comm.* (2003) 378.
- [21] A. Philippou, J. Rocha, M.W. Anderson, *Catal. Lett.* 57 (1999) 151.
- [22] A. Valente, Z. Lin, P. Brandao, I. Portugal, M. Anderson, J. Rocha, *J. Catal.* 200 (2001) 99.
- [23] H. Idriss, E.G. Seebauer, *J. Mol. Catal. A: Chem.* 152 (2000) 201.
- [24] J.A. Wang, X. Bokhimi, O. Novaro, T. Lopez, R. Gomez, *J. Mol. Catal. A: Chem.* 145 (1999) 291.
- [25] B. Kempf, *Ullman's Encyclopedia of Industrial Chemistry*, electronic sixth ed., WILEY-VCH, Weinheim, 2002.
- [26] I.E. Wachs, *Surf. Sci.* 544 (2003) 1.
- [27] I.E. Wachs, R.J. Madix, *Surf. Sci.* 76 (1978) 531.
- [28] G.I.N. Waterhouse, G.A. Bowmaker, J.B. Metson, *Appl. Surf. Sci.* 214 (2003) 36.
- [29] G.I.N. Waterhouse, G.A. Bowmaker, J.B. Metson, *Appl. Catal. A: Gen.* 265 (2004) 85.
- [30] A.C. van Veen, O. Hinrichsen, M. Muhler, *J. Catal.* 210 (2002) 53.
- [31] H. Schubert, U. Tegtmeier, D. Herein, X. Bao, M. Muhler, R. Schlogl, *Catal. Lett.* 33 (1995) 305.
- [32] H. Schubert, U. Tegtmeier, R. Schlogl, *Catal. Lett.* 28 (1994) 383.
- [33] M. Qian, M.A. Liauw, G. Emig, *Appl. Catal. A: Gen.* 238 (2003) 211.
- [34] A.J. Nagy, G. Mestl, R. Schlogl, *J. Catal.* 188 (1999) 58.
- [35] A.J. Nagy, G. Mestl, D. Herein, G. Weinberg, E. Kitzelmann, R. Schlogl, *J. Catal.* 182 (1999) 417.
- [36] A. Nagy, G. Mestl, T. Ruhle, G. Weinberg, R. Schlogl, *J. Catal.* 179 (1998) 548.
- [37] A. Nagy, G. Mestl, *Appl. Catal. A: Gen.* 188 (1999) 337.
- [38] G.J. Millar, M.L. Nelson, P.J.R. Uwins, *J. Catal.* 169 (1997) 143.
- [39] G.J. Millar, J.B. Metson, G.A. Bowmaker, R.P. Cooney, *J. Catal.* 147 (1994) 404.
- [40] G.J. Millar, J.B. Metson, G.A. Bowmaker, R.P. Cooney, *J. Chem. Soc. Chem. Commun.* (1994) 1717.
- [41] R.B. Grant, R.M. Lambert, *J. Catal.* 92 (1985) 364.
- [42] A. Andreasen, H. Lynggaard, C. Stegelmann, P. Stoltze, *Surf. Sci.* 544 (2003) 5.
- [43] P. Gallezot, L. Ceroni, A. Perrard, *J. Mol. Catal. A: Chem.* 129 (1998) L127.
- [44] P.B. Merrill, R.J. Madix, *Langmuir* 7 (1991) 3034.
- [45] M. Imachi, N.W. Cant, R.L. Kuczkowski, *J. Catal.* 75 (1982) 404.
- [46] Z. Yang, J. Li, X.G. Yang, Y. Wu, *Catal. Lett.* 100 (2005) 205.
- [47] F. Bruhne, E. Wright, *Ullman's Encyclopedia of Industrial Chemistry*, electronic sixth ed., WILEY-VCH, Weinheim, 2002.
- [48] I.E. Wachs, R.J. Madix, *Appl. Surf. Sci.* 1 (1978) 303.
- [49] G.A. Voronova, O.V. Vodyankina, V.N. Belousova, E.V. Bezrukov, L.N. Kurina, *Kinet. Catal.* 44 (2003) 652.
- [50] M.A. Barteau, M. Bowker, R.J. Madix, *Surf. Sci.* 94 (1980) 303.
- [51] R.T. Sanderson, *Chemical Periodicity*, Reinhold, New York, 1960.
- [52] G. Schoen, *Surf. Sci.* 35 (1973) 96.
- [53] G. Schoen, *Acta Chem. Scand.* 27 (1973) 2623.
- [54] A. Cimino, F.S. Stone, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, vol. 5, VCH, Weinheim, 1997, p. 845.
- [55] M. Furukawa, Y. Nishikawa, S. Nishiyama, S. Tsuruya, *J. Mol. Catal. A: Chem.* 211 (2004) 219.
- [56] M. Misono, E. Ochiai, Y. Saito, Y.J. Yoneda, *Inorg. Nucl. Chem.* 29 (1967) 2685.
- [57] A.N. Pestryakov, V.V. Lunin, *J. Mol. Catal. A: Chem.* 158 (2000) 325.
- [58] J.F. Weaver, G.B. Hoflund, *Chem. Mater.* 6 (1994) 1693.
- [59] M. Badlani, I.E. Wachs, *Catal. Lett.* 75 (2001) 137.