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Catalytic oxidation of methanol to methyl formate over silver – a new purpose of a traditional catalysis system

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Catalytic reaction was performed in the *unregarded* temperature region over silver catalysts with long catalytic lifetime for the conversion of methanol to methyl formate. O_α-saturated or O_γ-saturated silver catalysts were studied individually to identify the roles of O_α, O_γ in the oxidative esterification of methanol over an unsupported polycrystalline silver catalyst. A synergic process is proposed based on the coexistence of α-oxygen species and γ-oxygen species on the surface of polycrystalline silver at about 573 K.

KEY WORDS: formaldehyde; methanol; methyl formate; oxygen species; silver; synergic effect.

1. Introduction

Methyl formate is an intermediate in the manufacture of formic acid and formamide [1] and is considered as an important product in C_1 chemistry. It can also be used as a starting material in the production of high-purity carbon monoxide and undergoes a great variety of reactions leading to the formation of acetic acid, acetaldehyde, methyl acetate and acetic anhydride [2]. In recent years, it was also found that methyl formate is an effective gasoline additive instead of MTBE [3].

According to our knowledge, the studies on catalytic dehydrogenation of methanol to methyl formate were mainly focused on the systems, namely V_2O_5–TiO_2, SnO_2–$MoO_3$and Cu–SiO_2, and three types of mechanisms have been summarized by Louis *et al.* [4] for the catalytic conversion of methanol to methyl formate.

The copper-based catalysts have been applied in industrial scale for dehydrogenation of methanol to methyl formate by Mitsubishi Gas Chemical Co. [5] (Cu–Zr–Zn or Cu–Zr–Zn–Al system) with approximately 50% conversion of methanol, about 90% selectivity to methyl formate, and Air Products Co. [6] (copper–chromite system). Methanol can also be oxidative dehydrogenated to methyl formate by soluble chromium compound catalysts [7].

However, there are still some shortcomings for the copper-based catalysts. The catalytic activity and selectivity to methyl formate of these catalysts are strongly affected by the preparation and activation methods, as the formation of methyl formate is sensitive to the structure of active sites [8]. Hence, most copper-based catalysts are not stable enough because of the congregation of copper atoms, the polymerization of formaldehyde on active sites, and the coking on active sites. In addition, the direct dehydrogenation of methanol to methyl formate, $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$ ($\Delta H^0_R = 98.9$ kJ mol^{-1}), is a thermodynamic limited reaction and the decomposition of methyl formate becomes the main reaction at higher temperature, so it is unfavorable to obtain a high yield of methyl formate at higher temperature. Contrary, the oxy-dehydrogenation of methanol to methyl formate is a thermodynamic favorable reaction, $2CH_3OH + O_2 \rightarrow + HCOOCH_3 + 2H_2O$ ($\Delta H^0_R = 472.8$ kJ mol^{-1}).

It is well known that silver-based catalysts are the most important ones used in industrial scale, and the silver catalysts are commonly used in the manufacturing processes of formaldehyde and ethylene oxide [1]. The production of ethylene oxide is usually performed between 473 and 573 K over silver catalysts and the process of formaldehyde is commonly above 873 K [1]. Methyl formate is considered as a by-product during the manufacture of formaldehyde over silver catalyst [1,9]. So, it seems that the region between 473 and 873 K for methanol oxidation is *unregarded*. The work of Wachs *et al.* [10] showed that methyl formate is a main product in the process of methanol oxy-dehydrogenation over Ag (110) surface under ultra high vacuum (UHV) condition. Because of the popular attention aiming to the formaldehyde and ethylene oxide processes, only find a few records concerning methyl formate as a product over the catalysts based on silver can be found till now [9,11–13]. In this paper, we report that catalytic oxidative reaction of methanol to methyl formate in the *unregarded* temperature region over silver catalysts and the reaction is related to a synergic process concerning α-oxygen species and γ-oxygen species on the surface of silver.

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2. Experimental

Silver catalyst was prepared through the reduction of silver nitrate by sodium borohydride. 2.63 g sodium borohydride (analysis degree, Beijing chemical factory) was dissolved into 50 g distilled water, and 7.86 g silver nitrate (analysis degree, Beijing chemical factory) was dissolved into 100 g distilled water. Sodium borohydride solution was added dropwise into vigorously stiffed silver nitrate solution at room temperature. The product was filtered and washed thoroughly with hot water, then dried at 373 K in air overnight.

Oxygen (99.9%), argon (99.99%), and methanol (analysis degree) were used without further treatment except that the methanol (30 mL) used in the experiment shown in section 3.3 was treated to remove the soluble oxygen by bubbling argon (20 mL min^{-1}) accompanying with ultrasonic for about 20 min.

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 per-treated in a flow of air (10 mL min^{-1}) at 573 K for 180 min and cooled to 373 K *in situ*, 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 (Eurotherrn model 808) to control a tubular furnace (ID 20 mm). *Caution*: It should be reminded that the range of methanol explosive limits (ICSC No. 0057) is between 6 and 35.6 vol% in air and the operation of the experiment should be carefully under protection.

An on-line gas chromatograph equipped with GDX-502 (a kind of microporous microspherical copolymer of divinylbenzene–acrylonitrile) packed column and TCD detector was used for separation of $N_2/O_2/CO$, CO_2, formaldehyde, H_2O, methanol, and methyl formate within 4 min. Normalization method was used to calculate conversion of methanol and selectivity to products.

O_α-saturated and O_γ saturated silver catalysts were prepared in a home-made setup (illustrated in Scheme 1) *in situ* by the methods of Veen *et al.* [14]. A straight tubular reactor (I.D. 5.5 mm) was loaded with 0.23 mL (~2.4 g) fresh silver catalyst (60–80 mesh) and free space was reduced by filling with quartz chip (40–60 mesh). Although the efforts has been done to reduce the free space of the part between four-way valve and six-way valve, there still existed about 8–9 mL free space. Control experiment indicated that the GC results of the succeeding isothermal flow experiments within 12 min are not reliable at the total feed rate (STP) of 1.2 + 0.2 mL min^{-1} in the setup condition. The reasons are the adsorption of organic compounds by setup and quartz chip and the delay of mass transfer by free space.

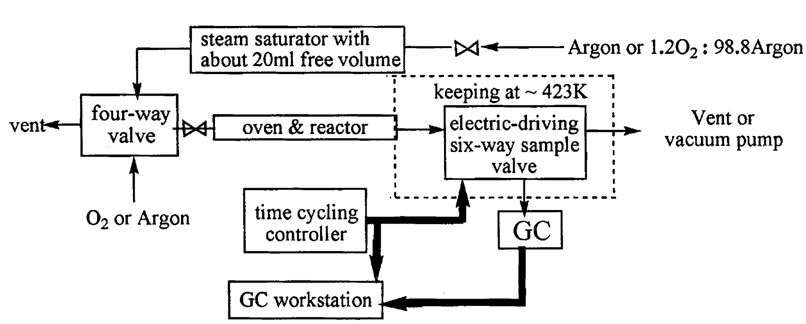
O_γ-saturated catalysts were prepared under severe conditions. The catalyst was treated in a vacuum at 373 K for 1 h, and then the reactor was heated with 10 K min^{-1} up to 923 K while 1bar pure oxygen was introduced approximately 1.0 mL min^{-1} (STP). After holding the sample at 923 K for about 8 h in oxygen, it was cooled to 723 K and kept in a vacuum or 1 h to remove adsorbed impurities. The sample saturated with dissolved O_β and O_γ species embedded in the topmost surface layer was obtained. A sample with a high coverage of O_α. was obtained by introducing 1bar pure oxygen on an oxygen-free catalyst at 473 K for more than 2 h.

Oxygen-free samples were prepared by temperature programmed reduction of O_γ-saturated catalysts in a 1:10 methanol-in-argon mixture. The sample was heated at 5 K min^{-1} from room temperature to 888 K in a continuous flow of about 1.0 mL min^{-1} (STP) streaming toward the vacuum applied at the reactor exit. After reduction of the sample for about 90 min at maximum temperature, the reactor was subsequently cooled to room temperature at 20 K min^{-1} in the reduction mixture.

3. Results and discussion

3.1. *Effect of temperature on the distribution of products*

It is well known that temperature can affect distribution of oxygen species on silver; therefore, it is necessary to investigate the temperature effect on the



Scheme 1. The setup for isothermal flow experiments thick arrow represent signal line, thin arrow represent gas line.

reaction. In order to associate with the industrial production process of formaldehyde, the ratio of methanol to oxygen and GHSV were similar to the "hard" condition, which has been used in industry scale [15]. The methanol conversion and yields of products via temperature are shown in Figure 1. In the range of reaction temperature from 400 to 500 K, carbon dioxide is the predominant product caused by α-oxygen species on the surface of silver [16]. And the yield of carbon dioxide almost keeps relatively constant over 500 K. Formaldehyde is the main product over 700 K, which is attributed to the action of γ-oxygen species embedded in the sub-surface of silver by many scientists. With the temperature rising, both the yield and selectivity of formaldehyde obviously rise in the experiment condition. It was found that methyl formate as one of the predominant products appears in the range of 450–700 K and the maximum yield appears around 573 K. This is a coexistence range of both α-oxygen species and γ-oxygen species on the surface of silver as Nagy *et al.* reported [17]. It was almost all α-oxygen species adsorbed on the topmost surface of silver at low temperature (< 500 K) in oxygen-rich condition, which resulted in the ~100% selectivity to CO_2. It was almost all the γ-oxygen species embedded in the topmost surface of silver at high temperature (~800 K), which resulted in the ~90% selectivity to formaldehyde. Nagy *et al.* [18] had theoretically calculated the equilibrium compositions of Ag, Ag_2O, and AgO as a function of temperature. Their work shows that phase transformation region of Ag_2O to Ag is between 503 and 600 K. Raman spectroscopic study of Waterhouse [19] also shows that the ratio of O_γ/O_β reaches the maximum at about 573 K. Theses implied that the formation of methyl formate might be attributed to a synergistic effect concerning γ-oxygen species and α-oxygen species on the surface of silver. For comparing, electrolytic silver was also tested in the same reaction condition and the similar results were obtained.

3.2. *Effect of the ratio of methanol to oxygen on the distribution of products*

As described above, the formation of methyl formate should be related to both γ-oxygen species and α-oxygen species on the surface of silver. XPS study of Waterhouse *et al.* [13] shows that the ratio of methanol to oxygen can alter the concentrations of oxygen species within the near-surface region of silver catalysts. As illustrated in Figure 2, the oxidation of methanol to methyl formate also performed under various oxygen concentration conditions at 573 K, at which a maximum yield of methyl formate is obtained in figure 1. Methyl formate is still predominant and the selectivity to methyl formate markedly increases with the decrease of oxygen concentration, while the selectivity to carbon dioxide decreases simultaneously. The selectivity to formaldehyde increases slightly with increasing of the concentration of methanol. It indicated that the formed formaldehyde is a strong adsorption species over silver at 573 K and the degree of its further oxidation depends on the coverage degree of oxygen over silver.

3.3. *The role of different oxygen species in the catalytic reaction*

In recent years, the oxygen species over silver have been classified as O_α, O_β, and O_γ by their electronic states and spatial locations [20–22], and many scientific groups have paid much attention on their role in the dehydrogenation of methanol, epoxidation of ethylene. In order to investigate the role of different oxygen species involved in esterification of methanol, O_α-saturated and O_γ-saturated silver catalysts were prepared in reference to Veen *et al.* [14]. In order to obtain information on synergetic effects between O_α and O_γ, flow experiments involving the codosing of methanol and oxygen were performed.

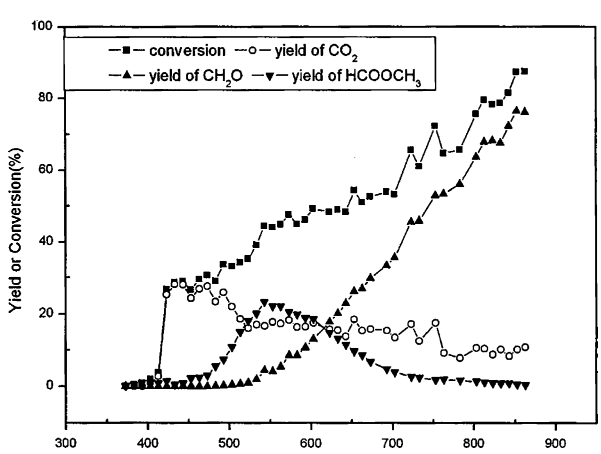


Figure 1. Conversion and yields via temperature air 1200 mL h^{-1}, methanol (liquid) 1.0 mL h^{-1}, catalyst 0.11 mL.

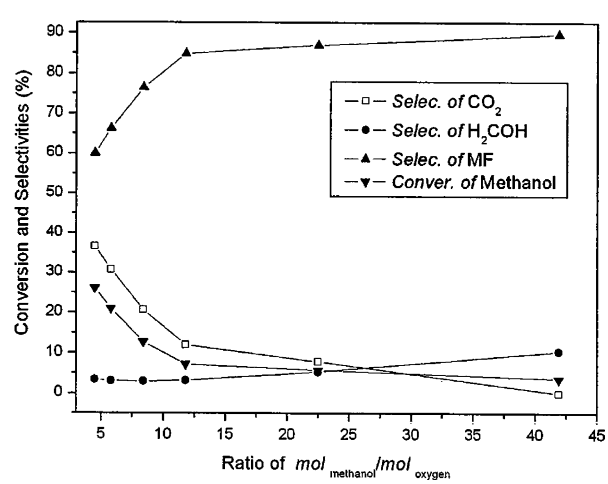


Figure 2. Effect of the ratio of $mol_{\mathrm{methanol}}/mol_{\mathrm{oxygen}}$ on the conversion and selectivity at 573 K, methanol (liquid) 1.0 mL h^{-1}, GHSV Jhonty = 1.04×10^4 h^{-1}, nitrogen as balance gas.

In the home-made setup as shown in Scheme 1, O_γ-saturated silver catalyst was cooled from 723 K to 573 K at 20 K min^{-1} in a continuous flow of argon approximately 20 mL min^{-1}. A methanol–O_2–Ar (8.2:1.1:90.7) mixture (O_2–Ar Mixture 1.2 + 0.2 mL min^{-1}) or a methanol–Ar (8.2:91.8) mixture (Ar 1.2 + 0.2 mL min^{-1}) was introduced to the reactor subsequently. The results are respectively shown in figure 3a and b. O_α-saturated silver catalyst was heated from room temperature to 573 K at 20 K min^{-1} in a continuous flow of pure oxygen approximately 20 mL min^{-1} and purged immediately by argon approximately 20 mL min^{-1} for 10 min. After purging, a methanol–O_2–Ar (8.2:1.1:90.7) mixture (O_2–Ar mixture 1.2 + 0.2 mL min^{-1}) or a methanol–Ar (8.2:91.8) mixture (Ar 1.2 + 0.2 mL min^{-1}) was also introduced to the reactor subsequently. The results are respectively shown in figure 3c and d.

The conversions of methanol and selectivities to fomaldehyde, carbon dioxide and methyl formate for isothermal flow experiments in different systems at 573 K are shown in figure 3. It should be pointed out that the results during the initial period of 12 min on stream are not reliable, and the reasons have been stated in experiment section. The succeeding statements focus on the results after the 12th min. In the systems without O_2 (figure 3b and c), the conversions almost keep 5–6% during the experimental period. In the systems with O_2 (figure 3a and d), the conversions decrease from ~30 to 14% during the succeeding experimental period.

In O_γ–O_2–methanol system (figure 3a), formaldehyde could hardly be detected by GC and the selectivity to methyl formate keeps at above 80%. And the selectivity to formaldehyde is 3–4 times as much as the one of methyl formate in O_γ–methanol system (figure 3b). Comparing O_γ–O_2–methanol system (figure 3a) with O_γ–methanol system (figure 3b), the yields of carbon dioxide are almost equal at ~1.5%.

Comparing figure 3a, with d, the conversions of methanol are almost equal, but the selectivities to all products are quite different respectively in the two systems. In O_α–O_2–methanol system (figure 3d), the selectivities to formaldehyde and carbon dioxide increase comparing with the O_γ–O_2–methanol (figure 3a) system. It should be emphasized, that the selectivity to methyl formate is several times as much as the selectivity to formaldehyde in the systems with O_2 (figure 3a and d) and the contrary results were obtained in the systems without O_2 (figure 3b and c).

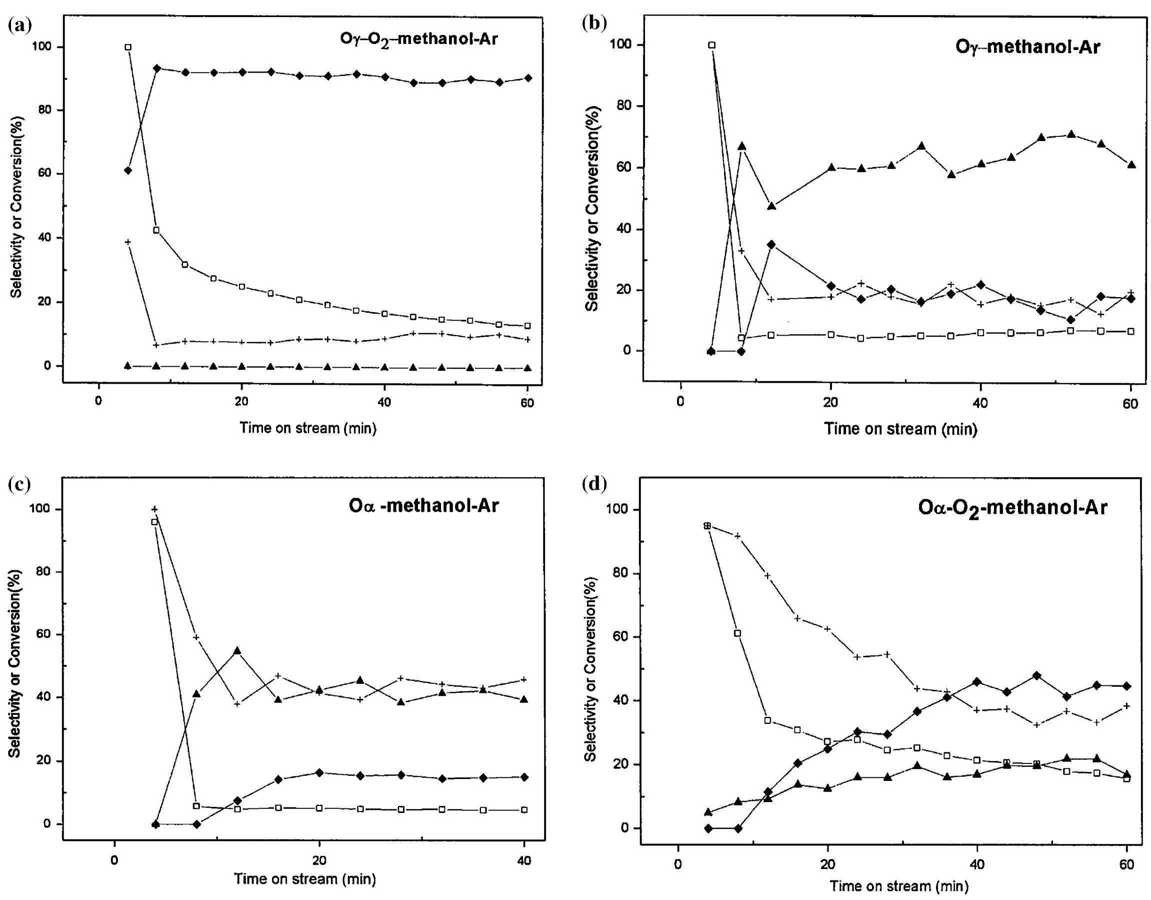


Figure 3. Conversion and selectivity via time on stream –□– conversion of methanol, –◆– selectivity to methyl formate, –▲– selectivity to formaldehyde, –+– selectivity to carbon dioxide.

In figure 3c and d, the selectivity of carbon dioxide is higher than the corresponding O_γ systems (figure 3b and a), which can be explained by the deep-oxidation ability of O_α species. In the case of O_α systems, the addition of oxygen gas also improved the selectivity to methyl format and inhibited the formation of formaldehyde apparently. But the effect of the addition of oxygen gas to O_α, system is not remarkable, comparing with that to O_γ system.

In order to estimate the influence of the direct dehydrogenation of methanol in the above four systems, methanol–Ar (8.2:91.8) mixture (Ar 1.2 + 0.2 mL min^{-1}) was also introduced to an oxygen-free silver catalyst at 573 K. After 20 h, a ~0.5% constant conversion of methanol with ~99% selectivity to formaldehyde was obtained. Hence, it can conclude that the direct dehydrogenation of methanol only takes a small part in above four systems.

3.4. Lifetime of silver catalyst

It has been introduced that the short lifetime is the usually shortcoming for the copper-based catalysts [8], so the lifetime test was also performed over the silver catalyst. The fresh silver catalyst was pretreated in air flow (10 mL min^{-1}) at 573 K for 180 min. In Figure 4, the yield of methyl formate decreased from ~24 to 20% within the initial 200 min and from ~20 to 18% in the rest of test period. The yield of formaldehyde almost kept at 1–2%. The conversion of methanol also kept constantly at ~28%. The yield of carbon dioxide raised from ~3 to 7% within the initial 200 min and slowly to ~10% in the rest of test period. These indicated that the surface state of catalyst should be altered while reaction going along and the change of surface state caused the selectivity to carbon dioxide.

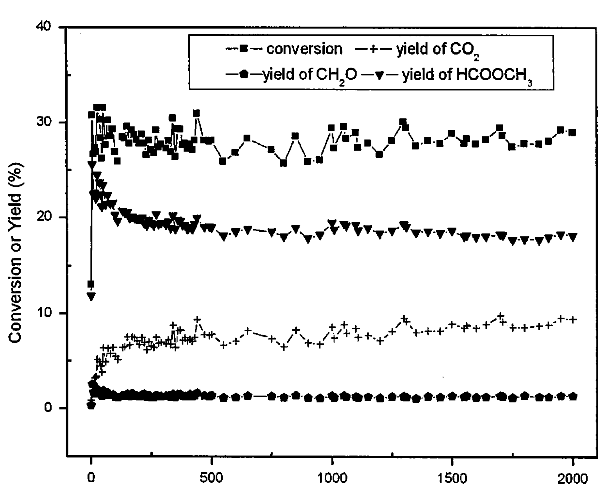


Figure 4. Lifetime test air 600 mL h^{-1}, methanol (liquid) 1.0 mL h^{-1}, temperature 573 K, catalyst 0.11 mL.

4. Discussions

The work of Wachs *et al.* [10] proposed that the catalytic conversion of methanol to methyl formate obeys Tischenko, mechanism via a surface hemiacetal intermediate. New insight into the reaction mechanism of conversion methanol to formaldehyde has appeared since 1980's from spectroscopic investigations, which demonstrate the influence of different atomic oxygen species on reaction pathway and selectivity [20–22]. The α-oxygen species over silver was considered to contribute to the oxidation of methanol to formaldehyde, formic acid, and carbon dioxide in sequence and the γ-oxygen species causes the selective oxidation to formaldehyde [17].

In figure 1, the result is similar to the recent work of Nagy *et al.* [17] and Waterhouse *et al.* [13]. The temperature at which a maximum yield of methyl formate appears is about 573 K, which is the boundary of desorption temperature regions of α-oxygen species and bulk oxygen species [17,19]. It can be explained that the concentration of weakly chemisorbed α-oxygen species which can be formed *directly* from gas phase oxygen decreases and the concentration of O_γ. increases with temperature rising. Above 500 K, bulk oxygen species begin to migrate to sub-surface and surface of silver to form γ-oxygen species, and α-oxygen [16], which will desorb into gas phase rapidly or participate in the chemiadsorption of methanol species correspondingly. And γ-oxygen species participate the catalytic reaction as catalysts while temperature rising [16,17]. Obviously, the heterogeneous catalytic process occurs over the catalyst surface, so the α-oxygen species and γ-oxygen species should be the essential species for the oxidation of methanol. At low temperature, almost 90% consumed methanol was oxidized to carbon dioxide, and the selectivity to carbon dioxide decreased because of the decrease of the coverage degree of α-oxygen species with temperature rising. This result is consistent with the O_2-TDS results of Nagy *et al.* [17,23] and Waterhouse *et al.* [19] in some degree. Above 500 K, the yield of methyl formate increases linearly with temperature rising until about 573 K, and the yield of formaldehyde increases while temperature rising. The work of Nagy *et al.* [18] shows that phase transformation region of Ag_2O to Ag is between 503 K and 600 K. Raman spectroscopic study of Waterhouse *et al.* [19] also shows that the ratio of $O_\gamma/O\beta$ reaches the maximum at about 573 K. With temperature rising, the stick time of α-oxygen species on catalysis decreases [24], so the ratio of $O_\alpha/O\gamma$ decreases. The maximum yield of methyl formate was obtained at certain ratio of O_α/O_γ. The *in situ* Raman studies of Waterhouse *et al.* [13] also showed that the υ(Ag–O) mode of γ-oxygen reached the maximum value at about 550 K and O_α, O_β, O_γ and OH incorporated in the silver subsurface/bulk) exist in methanol–C_2–silver system at 573 K. Veen *et al.* [14] suggested that γ-oxygen lowers the coverage of α-oxygen. And Lambert [25] suggested that subsurface oxygen species compete with the adsorbed surface oxygen for metal electron density, and thus cause the surface species to become more electrophilic and as known that nucleophilic oxygen species is easy to cause complete oxidation. In the catalytic process, the coverage of γ-oxygen as a function of temperature controls the coverage and electron density of α-oxygen, both of which affect the degree of oxidation of absorbed species. Perhaps, a synergic process is involved in the formation of methyl formate with the participating of $O_\alpha$and Oγ.

In figure 2, the selectivity to methyl formate decreased while the oxygen concentration increased, and contrarily the selectivity to CO_2 increased at 573 K. When the molecular ratio of methanol to oxygen is more than ~12, the slopes of the curves of selectivity to $C0_2$ and methyl formate are small. When the ratio is less than ~12, the total of the slopes of the curves of selectivities to CO_2 and methyl formate is almost zero. It indicates that the complete oxidation of methanol to CO_2 can be stopped by abundant methanol at the low coverage of α-oxygen. Therefore, it can be deduced that the methanol or methoxy instead of oxygen species attack the formic species, oxidized from adsorbed formaldehyde, which is the precursor of carbon dioxide, and the way to carbon dioxide is inhibited. The work of Veen *et al.* [14] also showed that α-oxygen also causes the selective formation of formaldehyde at low coverage. Millar *et al.* [26] suggested that α-oxygen could attack the chemiadsorbed methyl formate to form formic and methoxy species. According to the principle of microscopic reversibility, the reversible reaction can also occur. It is reasonable to propose that the adsorbed methoxy species can attack formic species to form methyl formate. At high ratio of methanol to oxygen, plenty of strongly adsorbed methoxy (from chemiadsorption between methanol and α-oxygen) can be expected near formed formic species and the selectivity to methyl formate is high.

In section 3.3, the study was carried on to confirm the existence of synergic effect of O_α and O_γ in the catalytic reaction. Comparing the systems (figure 3a and b) of O_γ-saturated silver catalysts, the addition of oxygen gas can improve the selectivity to methyl formate. It is surprising that formaldehyde is hardly detectable in O_γ–O_2–methanol (figure 3a) system with ~14% conversion of methanol, while the yield of formaldehyde is ~4% with ~6% conversion of methanol in figure 3b. It is well known that gas phase oxygen can chemical adsorb on silver to form O_α at low temperature. *In-situ* Raman studies of Wang *et al.* [27] and Waterhouse [13] show that O_α can exist over silver under real catalytic reaction condition in stead of UHV at 573 K. In O_γ–O_2–methanol (figure 3a) system and O_γ–methanol (figure 3b) system, methanol is dehydrogenated to form adsorbed formaldehyde by O_γ at first. In O_γ–O_2–methanol (figure 3a) system, methanol also chemisorbs with O_α, species to form $CH_3O_{(a)}$ and $OH_{(a)}$, and an $OH_{(a)}$ or O_α reacts with a neighbor adsorbed formaldehyde to form formic species, then another neighbor adsorbed methoxy as a strong base to attack the formic species to form adsorbed methyl formate. Perhaps, the dehydrogenation of formaldehyde and the attack of methoxy occur at the same time. The total result is that formaldehyde is captured to form methyl formate at high selectivity. Comparing figure 3a with d, the selectivities to carbon dioxide of the two systems are very different at similar conversion level, though methanol was over dosed very much in the two systems according to the stoichiometry of oxy-dehydrogenation. In O_α systems (figure 3c and 3d), the selectivities to carbon dioxide are similar at different conversions. Therefore, it can only be explained that surface regions in favor of the formation of O_α species are very small and separated by O_γ–Ag structure over the O_γ-saturated catalysts. The small number of O_α species in local area and the big energy barrier for mass transfer of O_α between different local areas cause the low selectivity to carbon dioxide. However, it should be emphasized that the coexistence of O_α, O_γ is very essential to the formation of methyl formate at a high selectivity.

In O_γ–methanol (figure 3b) system, the concentration of O_α formed from gas phase is small enough, so, the O_α-induced-chemiadsorption of methanol is almost inhibited. When a formaldehyde molecule is formed by O_γ, the probability of the reaction of the formaldehyde molecule with O_α formed from gas phase and methoxy is small in the system. So the synergic process hardly occurs and the selectivity to methyl formate reduces. At 573 K, the bulk oxygen can migrate to sub-surface and surface. O_γ–Ag structure with adsorbed formaldehyde may be the preferential structure for the migration of bulk oxygen. The probability of the reaction between the out-migrated oxygen and the near adsorbed formaldehyde is great by the reason of space-and-time priority and the probability of the reaction between methanol in gas phase and the out-migrated oxygen is less than the former. So the selectivity to carbon dioxide increases.

5. Conclusion

The catalytic oxy-dehydrogenation of methanol to methyl formate can be realized over silver catalysts. The temperature region between 500 and 650 K is the catalytic window for methyl formate. The low concentration of oxygen favors the formation of methyl formate. And the synergic effect with the participating of O_α and O_γ was discussed. The potential manufacture route for the methyl formate in the equipments for the production of formaldehyde can be expected.

Acknowledgments

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References

[1] Ullman's Encyclopedia of Industrial Chemistry, electronic version of the sixth edition (WILEY-VCH, Weinheim, 2002) and the references therein.
[2] E. Gerard, H. Gotz, S. Pellegrini, Y. Castanet and A. Mortreux, Appl. Catal. a-Gen 170 (1998) 297 and the references therein.
[3] J.S. Lee, J.C. Kim and Y.G. Kim, Appl. Catal. 57 (1990) 1and the references therein.
[4] C. Louis, J.M. Tatibouet and M. Che, J. Catal. 109 (1988) 354.
[5] M. Yoneoka and M.D. Osugi, 753,634, DE 2,753,634 (1978).
[6] J.V. Martinez de Pinillos, G.B. De La Mater and H. Ladenheim, EP 26,415 (1979).
[7] D.J. Drury and J. Pennington, EP 60,718 (1981).
[8] E.D. Guerreiro, O.F. Gorriz, G. Larsen and L.A. Arrua, Appl. Catal. a-Gen 204 (2000) 33 and the references therein.
[9] L. Lefferts, J.G. Van Ommen and J.R.H. Ross, Appl. Catal. 23 (1986) 385.
[10] I.E. Wachs and R.J. Madix, Surf. Sci. 76 (1978) 531.
[11] Vanderspurt and H. Thomas, U.S. 4,052,424 (Oct 4,1977).
[12] A.Y. Bulakh, Y.G. Medvedevskikh and S.K. Chuchmarov, Vestn. L'vov. Politekhn. In-ta 149 (1981) 167.
[13] G.I.N. Waterhouse, G.A. Bowmaker and J.B. Metson, Appl. Catal. a-Gen 265 (2004) 85.
[14] A.C. Veen, O. Hinrichsen and M. Muhler, J. Catal. 210 (2002) 53.
[15] A.N. Pestryakov, V.V. Lunin, N.E. Bogdanchikova, V.P. Petranovskii and A. Knop-Gericke, Catal. Commun. 4 (2003) 327 and the references therein.
[16] A.J. Nagy, G. Mestl and R. Schlogl, J. Catal. 188 (1999) 58.
[17] A. Nagy, G. Mestl, T. Ruble, G. Weinberg and R. Schlogl, J. Catal. 179 (1998) 548.
[18] A. Nagy and G. Mestl, Appl. Catal. a-Gen 188 (1999) 337.
[19] G.I.N. Waterhouse, G.A. Bowmaker and J.B. Metson, Appl. Surf. Sci. 214 (2003) 36.
[20] G.J. Millar, J.B. Metson, G.A. Bowmaker and R.P. Cooney, J. Chem. Soc. Faraday T 91 (1995) 4149.
[21] H. Schubert, U. Tegtmeyer and R. Schlogl, Catal. Lett. 28 (1994) 383.
[22] H. Schubert, U. Tegtmeyer, D. Herein, X. Bao, M. Muhler and R. Schlogl, Catal. Lett. 33 (1995) 305.
[23] A.J. Nagy, G. Mestl, D. Herein, G. Weinberg, E. Kitzelmann and R. Schlogl, J. Catal. 182 (1999) 417.
[24] A. Andreasen, H. Lynggaard, C. Stegelmann and P. Stoltze, Surf. Sci. 544 (2003) 5.
[25] R.B. Grant and R.M. Lambert, J. Catal. 92 (1985) 364.
[26] G.J. Millar, J.B. Metson, G.A. Bowmaker and R.P. Cooney, J Chem Soc Chem Comm (1994) 1717.
[27] J.H. Wang, X.H. Xu, J.F. Deng, Y.Y. Liao and B.F. Hong, Appl. Surf. Sci. 120 (1997) 99.