Direct dehydrogenation of methanol to formaldehyde over pre-treated polycrystalline silver catalyst

Li-Ping Ren,[a] Wei-Lin Dai,[a],*, Xin-Li Yang,[a] Jian-Hua Xu,[b] Yong Cao,[a] Hexing Li[b] and Kangnian Fan[a],**

[a]*Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China*
[b]*Department of Chemistry, Shanghai Normal University, Shanghai 200234, P. R. China*

The polycrystalline silver after pre-treated with oxygen at high temperature was found to show excellent activity and selectivity in the process of direct dehydrogenation of methanol to anhydrous formaldehyde and the active oxygen species for this reaction was observed and proposed as the active centeres with *in situ* Raman scattering.

KEY WORDS: polycrystalline silver; *in situ* Raman spectroscopy; dehydrogenation of methanol; oxygen species; formaldehyde.

1. Introduction

Methanol, a widely used and commodity chemical, which can be named as one of the four stanchions in the chemical industry, whose annual output exceeds 30 million tons, has been paid more and more attentions for its comprehensive applications. One of the important downstream products of methanol is formaldehyde and polycrystalline silver catalyst remains one of the most commercially viable systems for the partial oxidation of methanol to formaldehyde as selectivity of 90% and almost 100% conversion, which had been applied in industry since 1888 [1,2]. However, the mechanism for this process remained a controversial issue for many years, virtually all discussion pivoting on the identity of the active sites of the reaction system [3–20].

It is well-known that oxygen species on silver were found to play a key role in the selective oxidation of methanol, and many studies working on the surface molecular, surface atomic, subsurface atomic and bulk atomic oxygen species have been reported in the literature [21–24]. However, although there is still about 36% molar ratio of H_2 produced in the above commercial process, no reports clearly illustrated the active sites of the catalyst concerning the production of H_2 [25]. Hence, finding out the active sites for the production of H_2 in this process is a very important step to understand the mechanism of the partial oxidation of methanol and may be very useful for the improvement of the industrial process.

For the first time, we designed a gimmicky experiment for the determination and confirmation of the active sites during the dehydrogenation process by using the specially pre-treated polycrystalline silver catalyst into the above process with an *in situ* confocal microprobe Raman spectroscopy. As we know, *in situ* Raman studies on silver catalysts provide unique opportunities to investigate surface oxygen species under reaction conditions [26,27]. In the present work, unique properties over polycrystalline silver catalyst have been observed after the oxygen treatment at elevated temperature as 650 °C. To our great surprise, the specially pre-treated catalyst shows excellent activity and selectivity in the direct dehydrogenation of methanol, i.e., both the conversion of methanol and the selectivity toward formaldehyde reaches 100%. Thus, this system is a typical and model one for the observation of active sites on the silver surface because there is only one reaction occurred ($CH_3OH \rightarrow HCHO + H_2$). In addition, although the conversion of methanol decreased along with time-on-stream of the dehydrogenation, the selectivity toward formaldehyde was still equal to 100%. Hence, the time-resolved Raman spectroscopy may be an especially appropriate tool to monitor the change on the catalyst surface under the reaction conditions. This paper reported, for the first time, the perfect results of the catalytic performance of the direct dehydrogenation of methanol to formaldehyde as well as the confirmation of the active oxygen species on the commercial polycrystalline silver surface by using *in situ* Raman scattering method.

2. Experimental

The triply refined polycrystalline silver catalyst (40–60 mesh, purity >99.999%) is purchased from Shanghai Petroleum Chemical Engineering Co. Ltd. (China) without further purification, which was firstly treated with high-pure oxygen at 650 °C for 10 h and then pressed to a 10 mm × 10 mm circular disk with a tablet

* To whom correspondence should be addressed.
   E-mail: wldai@fudan.edu.cn;
** To whom correspndence should be addressed.
   E-mail: knfan@fudan.edu.cn

machine under 22 ton pressure to get a pre-treated silver surface for the *in situ* Raman study. The direct dehydrogenation activity test of methanol to formaldehyde was carried out over the polycrystalline silver catalyst after pre-treated with pure oxygen at 650 °C for 10 h.

The direct dehydrogenation reaction of methanol was carried out in a flow-type quartz reactor (i.d. = 4.5 mm) at a reaction temperature range of 300–700 °C with the space velocity (GHSV) at 1×10^4 h^{-1}, and the weight of the catalyst was 0.5 g. Anhydrous methanol was evaporated and then fed into the reactor with high purity argon (>99.999%) flow. The weight ratio of methanol in argon flow was determined as 19.3%. The products were analyzed by on line gas chromatography (GC) and mass spectroscopy (MS). CH_3OH, HCHO, di-methyl ether (DME) and water were determined by using thermal conductivity detector (TCD) method with a Porapak-N column, while H_2, CO, CO_2 were analyzed also by TCD method with a TDX column. Carbon balance was tested as 0.98–1.02.

Scanning electron microscope (SEM) images of the samples were measured by using a Philips XL30 SEM. *In situ* Raman spectra were recorded on a Jobin Yvon LabRam Infinity confocal microprobe Raman spectrometer equipped with a holographic notch filter and a CCD detector. The Raman spectra were recorded based on an Olympus BX40 system using a 50× long working-length objective (8 mm). The exciting wavelength was 514.5 nm from an Ar$^+$ laser with a power of 9.6 mW at the surface of the sample and a spot of ca. 3 μm on the sample surface. Powdered sample was put in a set of specially designed quartz *in situ* Raman cell. The surface of the sample was extensively cleaned at 550 °C under purified air flow for about 30 min. Methanol (A.R.) was used as purchased without additional treatments. Gaseous methanol was introduced into the Raman cell by bubbling high purity argon through the solution at 25 °C under atmospheric pressure.

3. Results and discussion

Figure 1 shows the SEM images of the polycrystalline silver catalyst before (a) and after (b) pre-treatment,

which reveals that the silver catalyst undergoes great change of appearance during the pre-treatment process. A rough silver surface by large-scale surface reconstruction can be easily observed after the treatment, which is in well accordance with that from Bao *et al.* and Millar *et al.* [9,23,28]. However, the silver catalyst used and the pre-treatment conditions are different in different groups, resulting in the difference of the morphology of the silver samples. Waterhouse *et al.* [22] also reported a similar system related to silver–oxygen interaction at elevated temperature. However, there are massive structural changes of morphology between the silver samples, which may be resulted in the difference of the sample sources, i.e., Johnson and Matthey and Shanghai Petroleum Chemical Engineering Co. Ltd.

The direct dehydrogenation of methanol was carried out over the polycrystalline silver catalyst before and after pretreatment. It is of great amazement to find that there is tremendous difference with their activity results. Table 1 shows the initial activity data of these two samples. The as-received one only shows a 73.2% conversion and 82.8% selectivity. After the pre-treatment, the crystalline silver catalyst shows superior results, in which both the conversion and the selectivity almost equal to 100% as detected by online GC and MS. The most important is that the amount of HCHO and H_2 produced are quite equivalent, indicating the existence of the direct dehydrogenation process of methanol

Table 1
Catalytic performance of the silver catalyst under different conditions

Polycrystalline Silver Catalyst	Methanol Conv. (%)	Selectivity (%)					
		HCHO	DME	H_2O	H_2	CO	CO_2
Original	73.2	82.8	0	8.9	48.6	14.2	3.0
Pretreated (min)							
0	100	99.9	0	0	99.8	0	0
20	74.3	99.9	0	0	99.8	0	0
40	37.5	99.9	0	0	99.8	0	0
60	11.9	99.8	0	0	99.9	0	0

Reaction temperature, 600 °C; GHSV 1×10^4 h^{-1}; height of the catalyst bed 30 mm.
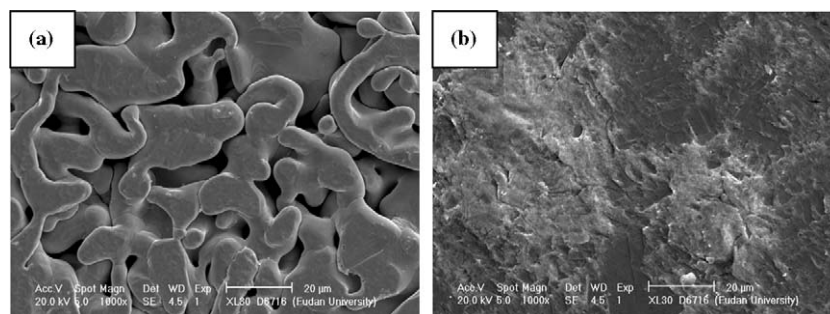

Figure 1. SEM images of the polycrystalline silver catalyst before (a) and after (b) pre-treatment.

to formaldehyde. In addition, no by-products, such as CO, CO_2, DME, could be detected. To the best of our knowledge, this catalyst shows one of the best results in this process because the highest yield of formaldehyde in the direct dehydrogenation of methanol was only about 70% as in the literature reports [25].

Although the short life-time of the pre-treated silver restricts its direct application in industry, the following advantages still make this system an interesting one both in the fundamental and the industrial fields. Firstly, the selectivity still keeps at near 100% with the time, suggesting that there were no other active sites present in the surface except for the dehydrogenating sites, which provides a suitable system for the mechanism study by using *in situ* Raman method. Secondly, the deactivated catalyst can be easily recovered after a simple treatment process same as the initial one, which may prolong its lifetime dramatically when used in industry. Thirdly, the catalyst can be reused for at least 10 times and no deactivation could be observed after the same treating process. Table 1 also shows the activity data at different reaction time. It is obvious that the selectivity still kept at ca. 100% although the conversion of methanol decreased to near 12% after a 60 min reaction.

In situ Raman studies on the oxygen species of the pre-treated silver catalyst at different temperature from 300 to 700 °C under argon flow are shown in figure 2(a). The intensity of the laser excitation (λ_{ex} = 514.5 nm) was reduced to 9.6 mW in order to exclude the light-induced changes of the sample and further resulted in a stable and repeatable Raman spectrum. It can be seen that a rather strong Raman feature at 805 cm^{-1} and three relatively weaker ones at 342, 645 and 1610 cm^{-1} are also present in the spectrum at 300 °C. Differences between the spectra at different temperatures reflect the chemical heterogeneity exhibited by the catalyst surface. All other three bands decreases in intensity with the temperature except for that at 645 cm^{-1}, which keeps stable with temperature increasing from 300 to 400 °C. Once the temperature is further increased to 500 °C, this band disappears. The intense feature and stability at 645 cm^{-1} is typical for atomic oxygen, and is a v(Ag–O) stretching vibration (denoted as O_β) [22,29]. The intensity of the other three bands at 342, 805 and 1610 cm^{-1} decreases sharply with temperature increasing from 300 to 400 °C and almost maintains their intensity at 500 °C and then attenuates slightly with temperature further increasing. The proportionality observed for the three bands inclines that they are all associated with the same adsorbed species. The associated feature at 1610 cm^{-1} is likely to represent an overtone band of the 805 cm^{-1} one [22,28]. According to its super thermal stability, the Raman band at ~805 cm^{-1} can be naturally assigned to the sub-surface oxygen species, denoted as O_γ [22,30,31]. Therefore, the two bands observed at 342 and 805 cm^{-1} are assigned to the v(Ag–O) bending and stretching mode of O_γ, respectively [22,32], since the Ag–O stretching mode will appear at a higher frequency than the bending mode [22,33].

In situ Raman study was also conducted over the pre-treated polycrystalline silver at 600 °C under the same conditions as the reaction conditions of methanol dehydrogenation. Figure 2(b) represents the time resolved Raman spectra on the silver surface with the introduction of methanol. With time prolonging, one can easily find that the O_γ species on silver surface decreases its intensity abruptly, which accords well with that obtained from the activity results. That is, methanol can consume the active oxygen species on the surface gradually. On the grounds of the activity results, such conclusion can be naturally drawn: O_γ species on silver represents the active oxygen species that catalyze the direct dehydrogenation of methanol to formaldehyde. With time going on, part of the O_γ species may react with the active hydrogen and form the OH species with
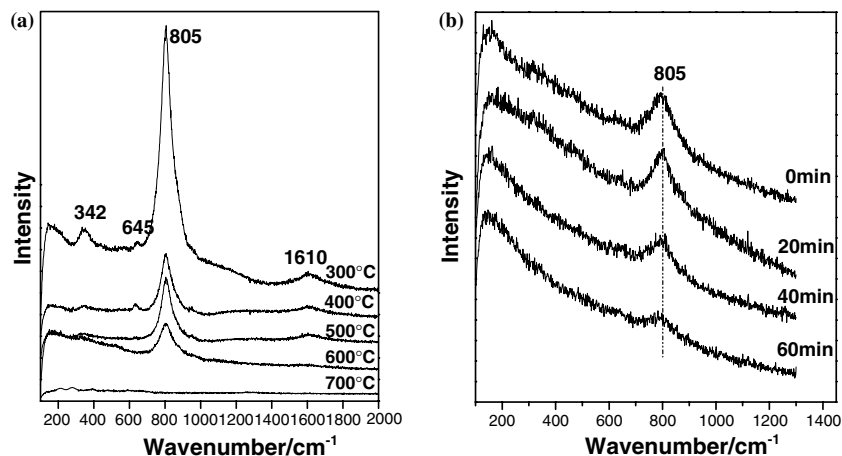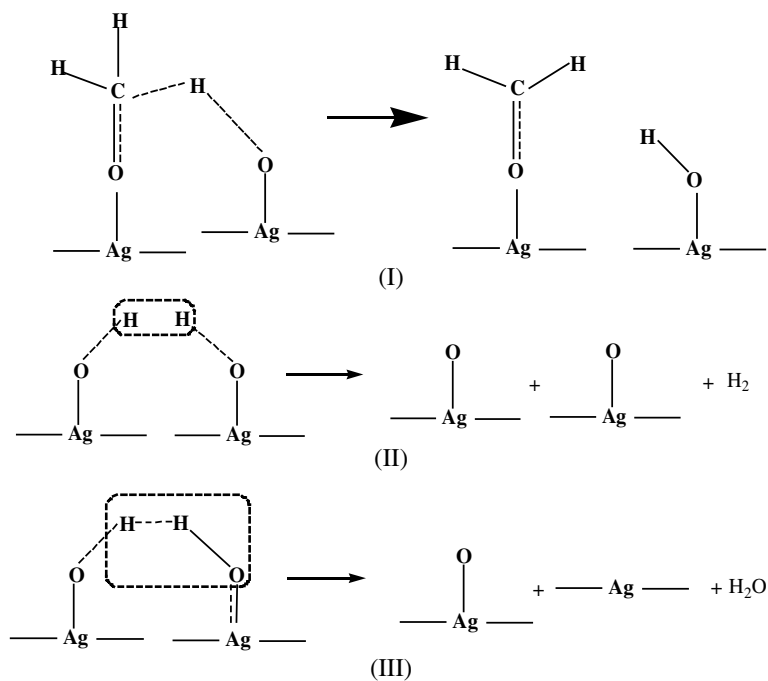

Figure 2. (a) *In situ* Raman spectra collected with heating of the silver catalyst from 300 to 700 °C under an argon purge; (b) *In situ* Raman spectra of pre-treated silver catalyst obtained upon exposure to methanol at 600 °C.

Scheme 1. Schemetic reaction route for the direct dehydrogenation of methanol.

the presence of methanol and then desorbs from the surface as the form of water, which leads to the ultimately disappearance of the O_γ species on the silver surface [22,34].

The combination study of the activity test and the Raman studies reveals that the possible mechanism for the direct dehydrogenation of methanol to formaldehyde may be illustrated as following:firstly, methanol is chemi-adsorbed on the surface to form a methoxyl group, which is commonly accepted by all the researchers; secondly, the adsorbed methoxyl group reacts with the adjacent O_γ center to form a adsorbed formaldehyde species and hydroxyl group, as showing in step (I); after that, two hydroxyl groups will combine to form a molecular H_2 and desorb from the surface, and the Ag–O_γ will be recovered. However, the side-reaction, which will result in the consumption of the active centers (Ag–O_γ), will also occur under the same reaction conditions. As illustrated in step (III), the hydrogen in one hydroxyl group will react with the–OH group of the other one to form H_2O, which will inevitably lead to the decrease of the activity. Scheme 1 clearly explains the process of the direct dehydrogenation and the deactivation of the catalyst.

4. Conclusions

In conclusion, the pre-treated polycrystalline silver catalyst was applied in the direct dehydrogenation process of methanol to formaldehyde and an excited activity result was obtained for the first time. On the same time, the active sites on the polycrystalline silver catalyst for the title reaction were proved to be the O_γ species by using *in situ* Raman spectroscopy.

References

[1] H. Sperber, Chem. Eng. Technol. 41 (1969) 962.
[2] R.A. van Santen and H.P.C.E. Kuipers, Adv. Catal. 35 (1987) 265.
[3] C.V. Andre, H. Olaf and M. Martin, J. Catal. 210 (2002) 53.
[4] S.R. Bare, K. Griffiths, W.N. Lennard and H.T. Tang, Surf. Sci. 342 (1995) 185.
[5] A. Andreasen, H. Lynggaard, C. Stegelmann and P. Stoltze, Surf. Sci. 544 (1) (2003) 5.
[6] L. Lefferts, J.G. van Ommen and J.R.H. Ross, Appl. Catal. A 23 (1986) 385.
[7] C.T. Au, S. Singh-Boparai, M.W. Roberts and R.W. Joyner, J. Chem. Soc. Faraday Trans. 79 (1983) 1779.
[8] G. Rovida, F. Pratesi, M. Maglietta and E. Ferroni, Surf. Sci. 43 (1974) 230.
[9] X. Bao, J.V. Barth, G. Lehmpfuhl, R. Schuster, Y. Uchida, R. Schlögl and G. Ertl, Surf. Sci. 283 (1993) 14.
[10] A. Nagy, G. Mestl, D. Herein, G. Weinberg, E. Kitzelmann and R. Schlögl, J. Catal. 182 (1999) 417.
[11] J.-H. Wang, W.-L. Dai, J.-F. Deng, X.-M. Wei, Y.-M. Cao and R.-S. Zhai, Appl. Surf. Sci. 126 (1998) 148.

[12] J.-H. Wang, X.-H. Xu, J.-F. Deng, Y. Liao and B.-F. Hong, Appl. Surf. Sci. 120 (1997) 99.

[13] B. Pettinger, X. Bao, I. Wilcock, M. Muhler, R. Schlögl and G. Ertl, Angew Chem. 106 (1994) 113.

[14] A. Nagy and G. Mestl, Appl. Catal. 188 (1999) 337.

[15] C.-B. Wang, G. Deo and I.E. Wachs, J. Phys. Chem. B 103 (1999) 5645.

[16] G.J. Millar, J.B. Metson, G.A. Bowmaker and R.P. Cooney, Appl. Catal. 147 (1994) 385.

[17] X.-D. Wang, W.T. Tysoe, R.G. Greenler and K. Truszkowska, Surf. Sci. 258 (1991) 335.

[18] M. Voß, D. Borgmann and G. Wedler, Surf. Sci. 465 (2000) 211.

[19] L. Lefferts, J.G. van Ommen and J.R.H. Ross, Appl. Catal. A 31 (1987) 291.

[20] X. Bao, M. Muhler, T. Schedel-Niedrig and R. Shlogl, Phys. Rev. B 54 (1996) 2249.

[21] L. Lefferts, J.G. van Ommen and J.R.H. Ross, J. Catal. 144 (1988) 303.

[22] G.I.N. Waterhouse, G.A. Bowmaker and J.B. Metson, Appl. Surf. Sci. 214 (2003) 36.

[23] G.J. Millar, M.L. Nelson and P.J.R. Uwins, J. Catal. 169 (1997) 143.

[24] M. Qian, M.A. Liauw and G.. Emig, Appl. Catal. A 238 (2) (2003) 211.

[25] S. Ruf, A. May and G. Emig, Appl. Catal. A 213 (2001) 203.

[26] R.K. Chang and T.E. Furtak, eds. *Surface Enhanced Raman Scattering* (Plenum Press, New York, 1982).

[27] W.L. Dai, Y. Dong, Y. Cao, K.N. Fan, J.F. Deng, Y.Y. Liao and B.F. Hong, J. Raman Spectr. 33 (5) (2002) 318.

[28] G.J. Millar, J.B. Metson, G.A. Bowmaker and R.P. Cooney, J. Chem. Soc. Faraday Trans. 91 (1995) 4149.

[29] S.J. Lee and K. Kim, Chem. Comm. 2 (2003) 212.

[30] C.B. Wang, G. Deo and I.E. Washs, J. Phys. Chem. B 103 (1999) 5645.

[31] X. Bao, B. Pettinger, G. Ertl, R. Schlogl and Ber. Bunsen-Ges, Phys. Chem. 97 (1993) 322.

[32] D.I. Kondarides, G.N. Papatheodorou, C.G. Vayenas and X.E. Verykios, Ber. Bunsen-Ges. Phys. Chem. 97 (1993) 709.

[33] A. Campion, Annu. Rev. Phys. Chem. 36 (1985) 549.

[34] B. Pettinger, X. Bao, I.C. Wilcock, M. Muhler and G. Ertl, Phys. Rev. Lett. 72 (1994) 1561.