

Letter

The oxidative dehydrogenation of methanol over a novel Ag/SiO₂ catalyst

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Abstract

Catalytic oxidative dehydrogenation of methanol to formaldehyde was carried out over a novel Ag/SiO₂ catalyst prepared by the sol–gel method. The yield of formaldehyde over this catalyst was ~10% higher than that over conventional pumice-supported silver and even ~1% higher than that over commercial electrolytic silver. When the yields were compared under the optimum conditions, the catalytic activity was measured at 820–920 K, O₂/CH₃OH molar ratio of 0.35–0.55 and at the space velocity of 1.2×10⁵ h⁻¹. The thermal behavior and structure of the catalyst were characterized by TG–DTG, DTA and XRD. It was found that this catalyst was thermally stable and silver was present in a crystalline state. SEM was used to determine its morphology and particle size. The silver particle size range was found to be 200–700 nm. XPS results indicated that two different kinds of silver in aggregated and highly dispersed metallic states, were present on the surface of the catalyst.

Keywords: Supported silver catalyst; Formaldehyde; Methanol oxidation; Sol–gel method

1. Introduction

The commercial production of formaldehyde is mainly based on methanol oxidation [1]; its annual production has come up to 5.3×10⁶ tons. The methanol-rich process using a silver catalyst is preferred for its moderate operating conditions and simplicity of reactor design over the oxygen-rich process using an iron–molybdate catalyst [2]. The silver catalyst has been used in the form of either a bulk metal or a dispersed metal supported on various supports. In general, the widely used pumice-supported catalyst has a longer life than a bulk metal catalyst such as an electrolytic silver catalyst, but gives a relatively low formal-

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dehyde yield ($\sim 75\%$) [3]. Some other supports, which are obtained by the thermal treatment of various materials used in ceramic production [4,5] have also been proposed for improving the catalytic activity. As a result, silica–alumina-supported catalysts have been found to exhibit a much higher catalytic activity even at a lower content of silver as compared with the pumice-supported catalyst, but the preparation process of these catalysts is rather complicated. Recently, a sol–gel method has attracted much attention because it provides a new approach to prepare highly dispersed supported catalysts, which may even have an excellent resistance to sintering [6–8]. This paper demonstrates that a novel silica-supported silver catalyst prepared by a sol–gel method exhibits a high activity and selectivity in the catalytic oxidative dehydrogenation of methanol to formaldehyde. The catalyst was also characterized by TG–DTG, DTA, XRD, SEM and XPS.

2. Experimental

2.1. Catalyst preparation

The Ag/SiO₂ catalyst was prepared according to the following procedures. 36 ml (159 mmol) of silicon tetraethoxide (TEOS) was mixed with 6 ml of 0.10 M HNO₃ (334 mmol) in 20 ml of ethanol at 70°C for 1.0 h to obtain a silica sol solution. The solution was refluxed by agitating with a magnetic stirrer in an oil bath for 2.0 h, and to the refluxing solution was added 3.15 g (18.5 mmol) of silver nitrate (AgNO₃), followed by 25 ml of distilled water. The resulting solution was then left at room temperature in an open beaker for one day, which allowed the gradual and almost complete evaporation of the solvent ethanol, leaving a transparent xerogel in the vessel. The xerogel was further dried at 110°C for 24 h and calcined at 650°C in a muffle-oven for 10 h. The brown colored Ag/SiO₂ catalyst thus obtained was then ground to a grain size of 40–60 mesh and used as a catalyst in this work.

2.2. Characterization of catalysts

X-ray diffraction (XRD) was executed on a Rigaku Dmax-rA powder diffractometer. The radiation used was from Cu K α . Scanning electron micrographs (SEM) were obtained on a Hitachi H600 electron micrograph. Thermogravimetry–Differential Thermogravimetry (TG–DTG) and Differential Thermal Analysis (DTA) were performed on a Perkin-Elmer 7 Series Thermal Analysis System in the temperature range 25–1000°C at a heating rate of 10.0 K/min under a nitrogen atmosphere at a rate of 15 ml/min. X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Perkin-Elmer PHI 5000C ESCA System. The base pressure of the test chamber was 1×10^{-9} torr. All the binding energy values were calibrated using the contaminant carbon (C1s=284.6 eV).

2.3. Reaction procedure

The oxidative dehydrogenation of methanol on the catalyst under study was carried out in a flow-type quartz reactor (i.d.=16 mm) at 500–700°C. The molar ratio of oxygen to methanol (O₂/MeOH) in the reactant mixture was varied from 0.30 to 0.55. The height of the packed catalyst-bed was 10 mm (2.0 g for Ag/SiO₂) and the space velocity (GHSV) was kept at 1.2×10⁵ h⁻¹. The reaction products were analyzed for methanol, formaldehyde, formic acid, carbon monoxide and dioxide, hydrogen and oxygen in conventional ways as follows. The yields of the gaseous products (CO₂, CO, H₂ and O₂) were determined with the aid of a QF-1903 gas analyzer, while that of formaldehyde was determined by the sulfite titration method, and that of methanol by gas chromatography (GC) with an FID detector. No appreciable formic acid was found.

3. Results and discussion

3.1. Morphology and structure

The XRD patterns of the silica xerogel and Ag/SiO₂ are shown in Fig. 1. There are no sharp peaks for the pure silica xerogel; the two broad peaks at 2θ of 10° and 22° are based on the amorphous silica. On the other hand, there are eight sharp diffraction peaks for the Ag/SiO₂ sample prepared by the sol–gel method. The peaks at 20.6° and 49.5° can be ascribed to the silica O (syn), those at 21.9° and

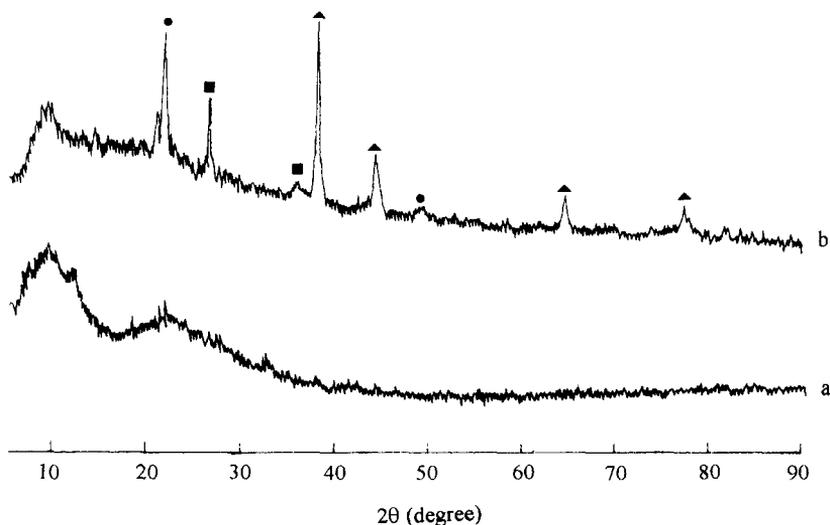


Fig. 1. XRD patterns of the as-prepared samples: (a) pure support; (b) 20% (w/w) Ag/SiO₂. (●) – Silica O (syn), (■) – Crystaobalite (low syn), (▲) – Crystalline silver.

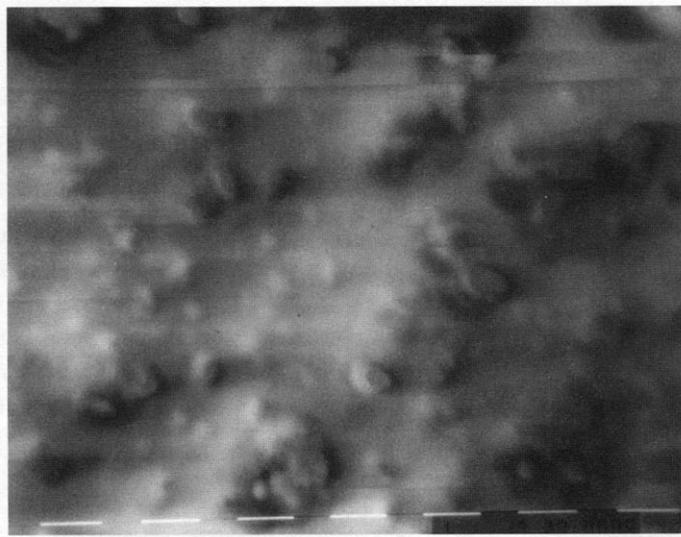


Fig. 2. SEM photograph of the Ag/SiO₂ catalyst.

36.1° to the cristobalite (low syn). The additional peaks at 38.1°, 44.3°, 64.4° and 77.5° were identified as those from the crystal faces of Ag(1 1 1), (2 0 0), (2 2 0), and (3 1 1), respectively (see also Fig. 1(b)). These results indicate that when silver was introduced into the pure silica xerogel, two crystalline phases of SiO₂·*x*H₂O were formed and no crystalline phases corresponding to the compounds of Ag_{*x*}(SiO₂)_{*y*}·*z*H₂O were observed.

The SEM photograph of the fresh Ag/SiO₂ catalyst is shown in Fig. 2. Some aggregates of silver can be seen on the surface of the catalyst. The size of these silver particles was estimated to be in the range 200–700 nm.

Fig. 3 shows the XPS peaks of Ag 3d_{5/2} for the fresh Ag/SiO₂ sample, where the original peak (solid line) observed has been resolved into a couple of peaks (broken line). The binding energies for these two peaks are 368.2 and 370.4 eV, respectively. This suggests that there are two different states of metallic silver on the surface, where the difference in binding energy (2.2 eV) between the two states can be explained by the difference of the charge effect [10]. The one at the binding energy of 368.2 eV was attributed to an aggregated state of silver metal (large particles) because of its small charge effect, while the other at 370.4 eV was ascribed to a highly dispersed metallic silver because of its big charge effect [9,10]. The ratio of the area of these two peaks was about 1 : 9; this indicated that the aggregated state was about 10% in the total silver on the surface.

The thermal behavior of the xerogel containing 20% (w/w) silver was investigated by TG–DTG and DTA as shown in Fig. 4. In the TG–DTG spectra, there were two weight loss peaks. One is at 77.5°C, corresponding to the loss of the solvent, and the other is a very broad peak ranging within 200–500°C, which can be

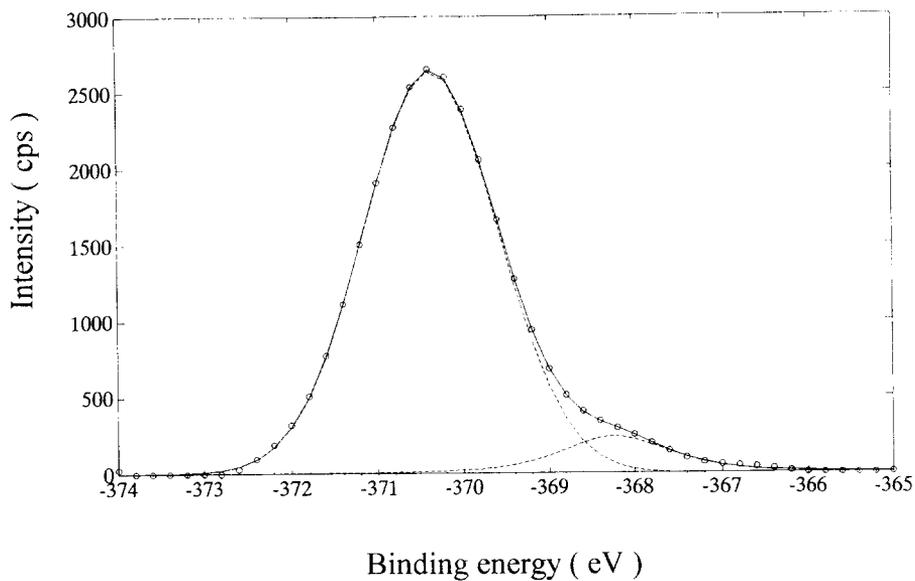
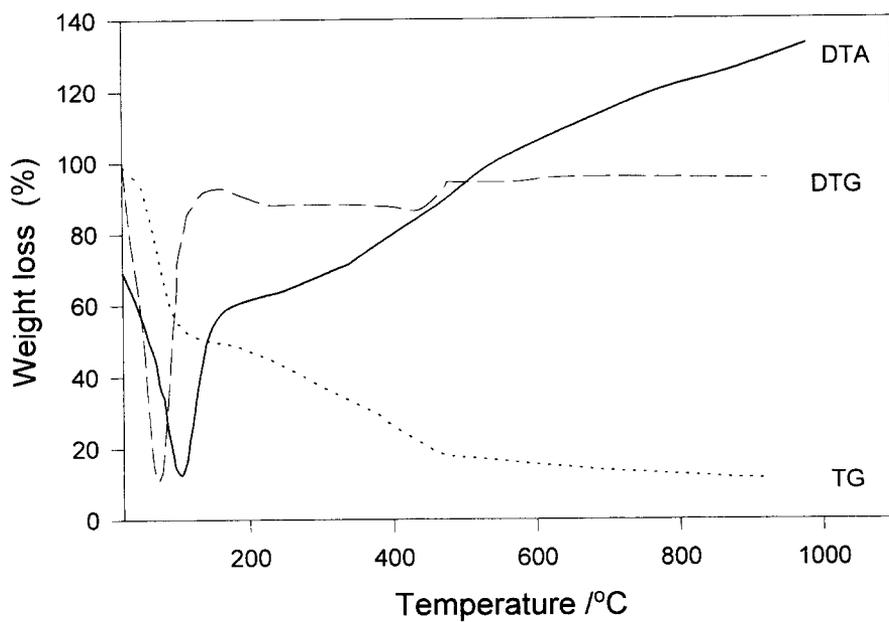
Fig. 3. XPS spectra of Ag 3d_{5/2}.

Fig. 4. TG–DTG and DTA curves of the silica gel containing 20% (w/w) silver: (—) – DTA; (---) – DTG; (···) – TG.

Table 1

The optimum reaction conditions and results of selective methanol oxidation for the three silver catalysts

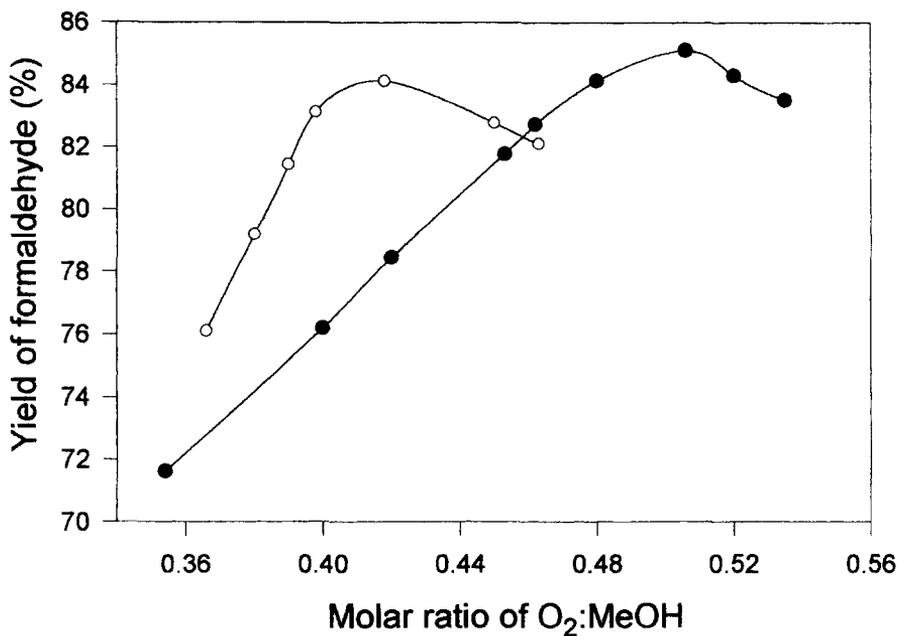
Catalyst	Temperature (°C)	O ₂ /MeOH (mol ratio)	HCHO yield (%)	CO ₂ +CO yield (%)	HCHO select. (%)	SV (h ⁻¹)
Ag/SiO ₂ , 20% (w/w)	640	0.51	85.49	7.59	89.05	1.2×10 ⁵
Electrolytic silver	640	0.41	84.44	9.19	88.75	1.2×10 ⁵
Ag/Pumice, 40% (w/w)	700	0.32	75.21	10.71	84.51	3.0×10 ⁴

ascribed to the weight loss due to the dehydration of the xerogel and the decomposition of AgNO₃. No obvious changes were observed during the heating process from 600°C to 1000°C, which revealed that this catalyst was thermally stable. DTA gave the same results.

3.2. Methanol oxidation

The catalytic activity and selectivity of the novel silver catalyst Ag/SiO₂ for the selective oxidation of methanol under the optimum reaction conditions and those of conventional catalysts, Ag/Pumice and electrolytic silver [11] are compared in Table 1. As Table 1 shows, this novel Ag/SiO₂ catalyst, despite its lower silver content, was found to give much higher activity and selectivity than Ag/Pumice. It also gave better results than the electrolytic silver catalyst. The yield of formaldehyde for the Ag/SiO₂ catalyst was about 10% and 1% higher than those by Ag/Pumice and the electrolytic silver catalyst, respectively. It is expected that even such a small increment of the formaldehyde yield would result in great economic benefits in the industrial process because of the current huge output of formaldehyde [1]. Fig. 5(a) and (b) show the effects of the feed composition O₂/CH₃OH and reaction temperature on the yield of formaldehyde in the methanol oxidation over this novel catalyst and the electrolytic silver. In Fig. 5(a), the optimum molar ratio of O₂/CH₃OH that maximizes the formaldehyde yield is 0.41 for the electrolytic silver and 0.51 for Ag/SiO₂. Fig. 5(b) indicates that Ag/SiO₂ always gives higher yield of formaldehyde in the wide temperature range around the optimum temperature. Although the optimum temperatures were almost the same (630–640°C) for the two catalysts, the curve of formaldehyde yield versus temperature was much more smooth for this novel catalyst. This suggests that this novel catalyst can effectively be used over a broader temperature range than the conventional catalyst. In addition, it is noted that the conventional electrolytic silver has a poor resistance to sintering at high temperature above 680°C. So, the deactivation of the bulk silver catalyst would not be avoided. On the other hand, this novel silica-supported silver catalyst has an outstanding thermal stability even in the temperature range 600–1000°C, as mentioned above. The long life test for selective oxidation of methanol was performed over the novel Ag/SiO₂ catalyst in the micro-reactor mentioned above: no deactivation was found during the 100 h performance.

(a)



(b)

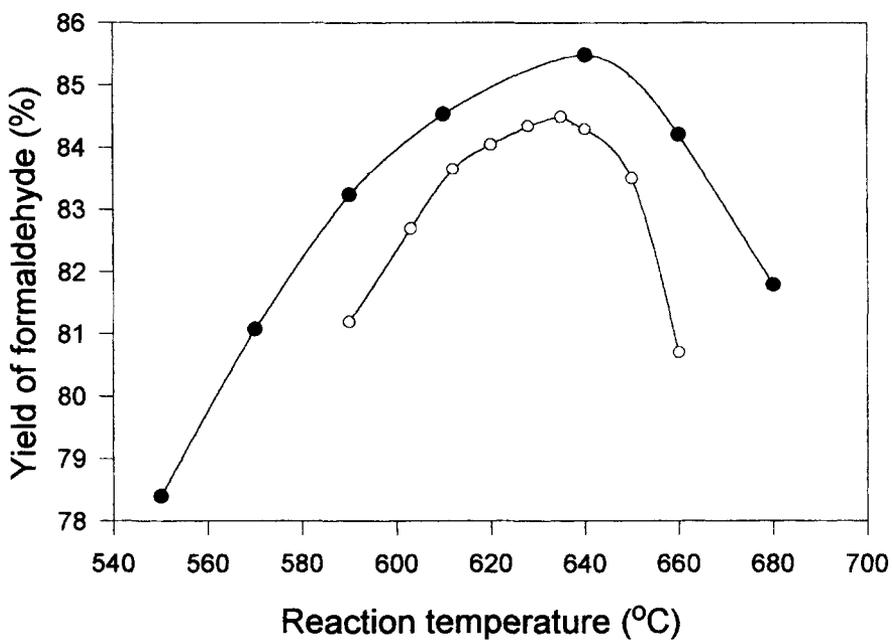


Fig. 5. The effects of the reaction conditions on the yield of formaldehyde: (a) molar ratio of O_2/CH_3OH (reaction temperature= $640^\circ C$); (b) reaction temperature ($O_2/MeOH=0.41$ for electrolytic silver and 0.51 for Ag/SiO₂). (●) - Ag/SiO₂, (○) - Electrolytic silver.

By comparing the SEM photographs of this catalyst before and after the reaction, it was confirmed that no sintering was observed during the reaction at such high temperature. Therefore, this catalyst prepared by the sol–gel method is expected to be much more conveniently and safely applied in industries.

In this paper, we described a novel Ag/SiO₂ catalyst prepared by the sol–gel method. It showed a very high activity and selectivity in the oxidative dehydrogenation of methanol to formaldehyde. Further works are still in progress.

Acknowledgements

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