

The oxidative dehydrogenation of methanol over a novel low-loading Ag/SiO₂–TiO₂ catalyst

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Catalytic oxidation of methanol to formaldehyde was carried out over Ag/TiO₂–SiO₂ catalysts prepared by chemical reduction. The catalytic activity was measured at the temperature interval 820–920 K, O₂/CH₃OH molar ratio between 0.35 and 0.50 and at the space velocity of 1.2×10^5 h⁻¹. The optimal content of silver determined by chemical analysis was about 1.7 wt%. The yield of formaldehyde over this catalyst was ~13% higher than that of the industrial pumice-supported silver catalyst and even ~3.5% higher than that of electrolytic silver. The XRD patterns for silver particles supported on TiO₂–SiO₂ are corresponding to Ag(111), (200) and (220), respectively. SEM was used to determine its morphology and particle size. Isolated silver particles were observed on the surface of the catalyst. O₂ chemisorption by using the pulse technique was carried out to determine the free silver surface areas. The average silver particle size from the calculation of selective oxygen chemisorption was found to be in good agreement with that observed from SEM.

Keywords: TiO₂–SiO₂-supported silver catalyst, formaldehyde, oxidation of methanol, chemical reduction

1. Introduction

In modern industry, both the metallic and supported silver-based catalysts are widely used in the partial oxidation of methanol to formaldehyde [1–4]. Supported silver catalysts by using inert materials as supports (such as pumice, corundum or SiC, etc.) have much longer lifetime, but the low yield of formaldehyde greatly limits their further applications in industry. The more widely used electrolytic silver catalyst is favored in industry for its easy recyclability and regeneration [5], but its short lifetime (~3–4 months) makes this process more inconvenient. Therefore, intensive research has been dedicated to finding new series of supported catalysts with higher catalytic performance as well as longer lifetime. Previously, we reported a novel Ag/SiO₂ catalyst via the sol–gel method achieving a high yield of formaldehyde of 85.49% at low silver content (~20 wt%) [6]. However, the yield of formaldehyde was not very high compared to that over a commercial electrolytic silver catalyst. In addition, the sol–gel method is always suffering from the disadvantages of a low solid yield and a very high shrinkage [7], which always restricts its further application in the preparation of catalysts. Batyan et al. reported a ceramic supported catalyst with a 87.0% yield of formaldehyde at a relatively low content of silver (~6 wt%) during the oxidative dehydrogenation of methanol at 650 °C [8]. However, this catalyst needed an extremely high treating temperature up to 1400 °C. In this paper, a mixed oxides support, TiO₂–SiO₂, is prepared by a method just like the formation of ceramics, and a low

content of silver is introduced on the support by chemical reduction of Ag(NH₃)₂⁺. The Ag/TiO₂–SiO₂ catalyst thus prepared exhibits significantly high catalytic activity and selectivity in the partial oxidation of methanol to formaldehyde at substantially low silver content (~1.7 wt%). BET, selective O₂ chemisorption, XRD and SEM were used to correlate its activity to the structural features.

2. Experimental

2.1. Catalyst preparation

Titania powder (0.5 μm) and colloidal silica sol (40 wt% of silica particles of 50–100 nm in diameter) are used as precursors of the preparation of TiO₂–SiO₂ support (TiO₂:SiO₂ = 2:1 w/w). First, the pH of the colloidal sol is adjusted from 9.0 to 2.0 with dilute HNO₃. The desired amount of titania powder is then dispersed into the sol with magnetic stirring at 80 °C. The gel was obtained after gelling for 120 min and dried at 110 °C for 48 h. Finally, the grains of TiO₂–SiO₂ (ground to 20–40 mesh) were calcined in air at 1200 °C for 5 h.

The as-prepared titania–silica support was suspended in an aqueous solution containing different amounts of Ag(NH₃)₂⁺ ions at 50 °C, to which a solution of formalin was added dropwise with vigorously agitating within 30 min and kept for another 60 min [9]. Then, the sample was filtered and washed five times with 70 °C distilled water, followed by drying at 110 °C for 24 h and calcining at 800 °C for 4 h. Through these procedures, the Ag/TiO₂–SiO₂ catalysts were finally obtained.

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2.2. Catalyst characterization

The specific surface areas were determined by BET methods by using a Micrometric ASAP 2000 adsorption apparatus with nitrogen at 77 K. The active surface area of silver was determined by selective chemisorption of oxygen at 200 °C with a pulse chemisorption apparatus according to the procedure described by Lemaitre et al. [10] and a site density of $1.15 \times 10^{15} \text{ Ag}_s \text{ cm}^{-2}$ [11] was used to calculate the active surface areas. X-ray diffraction (XRD) was executed on a Rigaku Dmax-rA powder diffractometer at the 2θ range of 10–80° using Cu K α radiation. Scanning electron microscopy (SEM) was performed on a Hitachi H600 electron micrograph.

2.3. Activity test

The partial oxidation of methanol was carried out in a fixed-bed reactor, operating at a pressure slightly above atmospheric pressure. The reactor, a quartz tube with an i.d. of 16 mm [12], was loaded with 3 g catalyst (20–40 mesh, ~10 mm high). An aqueous solution of methanol (60 wt%) was pumped into a quartz evaporator through a micro-pump and mixed with air before entering the reactor. The vaporization temperature was kept at 220 °C. The temperature of the reactor was controlled at about 580–680 °C by a DWK-702 temperature controller (± 0.5 °C) and the space velocity was controlled at about $1.2 \times 10^5 \text{ h}^{-1}$ (under the reaction temperature). The product mixture was firstly quenched to near room temperature with a sudden water cooling and then collected through an absorption column (height ~1.5 m) packed with ceramic rings with distilled ice-water. The reaction products were analyzed for methanol, formaldehyde, formic acid, carbon monox-

ide and dioxide. No significant formic acid was detected. Formaldehyde was determined by the traditional sulfite titration method. The residual methanol was detected by a 102-GD gas chromatograph (GC) with FID detector. The contents of CO₂ and CO in the tail gas were analyzed by using a QF-1903 gas analyzer.

Mass balances for carbon before and after the reactor were in agreement with $\pm 1\%$ in almost every experiment.

3. Results and discussion

3.1. Catalyst characterization

Figure 1(a) shows the XRD patterns of the as-prepared TiO₂-SiO₂ mixed oxides. The sharp peaks at 2θ of 27.4, 36.1, 41.3, 54.6, 56.7 and 69.2° are attributed to rutile(110), (101), (111), (211), (220) and (112), respectively. Also, the sharp peak at 2θ of 22° is based on α -cristobalite(100). No diffraction peaks of anatase can be found due to the high-temperature calcination (~1200 °C) for the mixed oxides. Figure 1(b) gives the XRD patterns of the Ag(1.7 wt%)/TiO₂-SiO₂ catalyst. By subtracting the background of the TiO₂-SiO₂ support, the additional diffraction peaks at 2θ of 38.1, 44.3 and 64.4° are identified as those from the crystal planes of Ag(111), (200) and (220), respectively.

The SEM photographs of Ag(1.7 wt%)/TiO₂-SiO₂ catalyst before and after a long performance in the reaction are shown in figure 2. Each of them displays isolated silver particles on the surface. According to figure 2(a), the average silver particle size is estimated to be ~1 μm , which is in good agreement with the results calculated from the selective O₂ chemisorption. There is also no obvious growth

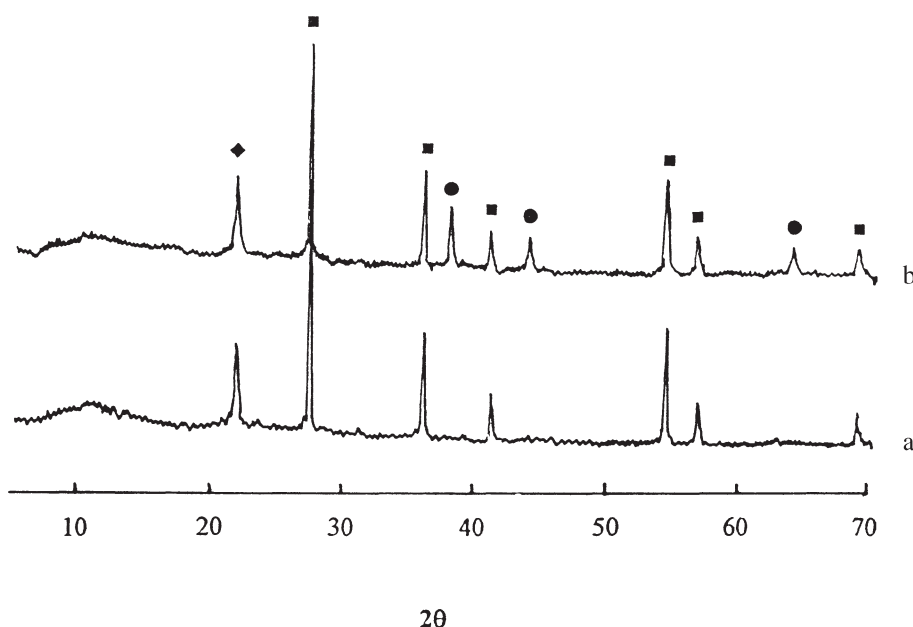


Figure 1. XRD patterns of as-prepared samples: (a) support of TiO₂-SiO₂, (b) Ag(1.7 wt%)/TiO₂-SiO₂. (♦) α -cristobalite, (■) rutile, (●) crystalline silver.

of the silver particle after 100 h performance, as shown in figure 2(b). It is well known that the catalytic activity is correlated strongly to the particle size of metals on the supports. So the result is also in agreement with the fact that the catalyst maintained nearly the initial high activity during about 100 h.

As we know, supported silver catalysts with low BET surface area ($<5 \text{ m}^2/\text{g}$) have good catalytic activity in the conversion of methanol to formaldehyde [7]. The as-prepared TiO₂-SiO₂ support, of which the BET surface area is $1.17 \text{ m}^2/\text{g}$, which is about two times higher than the commercial pumice-supported silver catalyst, is a suit-



(a)



(b)

Figure 2. SEM photographs of the Ag(1.7 wt%)/TiO₂-SiO₂ catalysts: (a) fresh catalyst, (b) catalyst used for 100 h.

able support to prepare silver catalysts. Table 1 lists BET surface areas of those Ag/TiO₂-SiO₂ catalysts with different silver loading. It is obvious that BET surface areas decreased with increasing silver content, which might be ascribed to the fact that many micro-pores were covered with silver particles. The selective O₂-chemisorption experiments were performed at 200 °C, at which temperature oxygen monolayer coverage of silver occurs and the stoichiometry of chemisorption corresponds nearly to one oxygen atom per surface silver atom [13]. The free silver surface areas, dispersions and average silver particle sizes for both electrolytic silver and Ag/TiO₂-SiO₂ catalysts determined by selective O₂ chemisorption are also listed in table 1. The free silver surface area of electrolytic silver is $5.4 \times 10^{-3} \text{ m}^2/\text{Ag/g-cat}$, which is smaller than the BET area obtained by the N₂ adsorption. Corresponding dispersion and average silver particle size are calculated as 1.19×10^{-5} and 105–200 μm, respectively. These results coincide very well with those obtained by Mao et al. on silver powder performed in a stainless steel adsorption system [14]. The average silver particle size on the Ag/TiO₂-SiO₂ catalysts increased with the increase of the silver contents, while the dispersion of these catalysts varied in an opposite way. It is interesting that the free silver surface area of these Ag/TiO₂-SiO₂ catalysts firstly increased with the increase of the silver contents, then it gradually decreased with the further increase of the silver content, which could be easily understood by considering the change of the average silver particle size and dispersions on the Ag/TiO₂-SiO₂ catalysts with different silver contents. At low silver contents, the newly added silver mainly led to the formation of new particles [15], so the free silver surface area increased with the increase of silver contents. While there are significant crystallite migration and coalescence at higher contents, so the newly added silver mainly forms larger silver particles. This may lead to the decrease of the free silver surface areas.

3.2. Catalytic properties

A set of silver contents, such as 0.2, 0.5, 1.7, 3.6 and 6.0 wt%, were firstly chosen to investigate the relationship

Table 1
The free silver surface areas, average particle size and dispersion based on O₂ chemisorption for both electrolytic silver and TiO₂-SiO₂-supported catalysts.

Catalyst ^a	Ag (wt%)	Specific surface area (m ² /g)	Silver surface area (10 ⁻³ m ² -Ag/g-cat)	d_{Ag} (μm)	Dispersion
Electrolytic silver	99.999	0.10 ^b	5.4	105	1.19×10^{-5}
AGTS-01	0.2	0.98	2.2	0.52	2.26×10^{-3}
AGTS-02	0.5	0.85	4.7	0.60	1.84×10^{-3}
AGTS-03	1.7	0.77	7.0	1.16	8.67×10^{-4}
AGTS-04	3.6	0.66	6.5	3.05	3.86×10^{-4}
AGTS-05	6.0	0.57	6.0	5.35	2.35×10^{-4}

^a AGTS-01–05 are corresponding to those Ag/TiO₂-SiO₂ catalysts with different silver loading (wt%): 01 – 0.2%, 02 – 0.5%, 03 – 1.7%, 04 – 3.6%, 05 – 6.0%.

^b Determined with helium at 4 K.

between the silver content and the yield of formaldehyde. Figure 3 shows that the formaldehyde yield increases significantly with the increasing of silver loading from 0.2 to 1.7 wt%, but decreases slightly with the further increase of silver loading. Therefore, the optimum content is 1.7 wt%, much lower than for any reported supported silver catalyst [6,7]. The relationship between the free silver surface area and the catalytic activity could be obtained by combining the BET and the active silver surface area of those catalysts in table 1 with the results in figure 3. The larger the active silver surface areas those catalysts have, the more active centers there would be. Therefore, it is not strange that the catalyst with a 1.7 wt% silver content has the highest catalytic activity owing to its highest active silver surface area. Such a conclusion could also be used to explain the higher yield of HCHO over 1.7 wt% Ag/TiO₂-SiO₂ (88.16%) than that over the electrolytic silver (84.44%), since the free silver surface area increased from 5.4×10^{-3} to 7.0×10^{-3} m²-Ag/g-cat.

Some experimental data for 1.7 wt% Ag/TiO₂-SiO₂, pumice-supported silver and electrolytic silver catalysts are listed in table 2. Though the silver content of the Ag/TiO₂-SiO₂ (1.7 wt%) catalyst was much lower than that of the pumice-supported silver (40 wt%), the yield of formaldehyde over Ag/TiO₂-SiO₂ was about 13.0% higher than that over Ag/pumice catalyst [3] and also about 3.5% higher than that of electrolytic silver [5]. Those results may be caused by the increment of free silver surface area of the Ag/TiO₂-SiO₂ compared to electrolytic silver. As to this

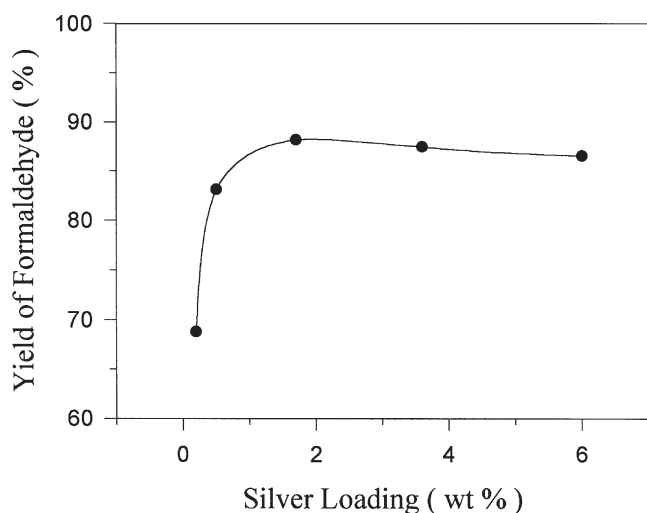
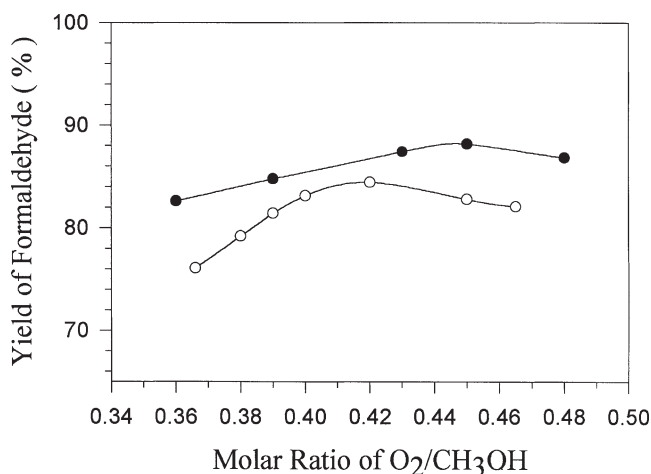


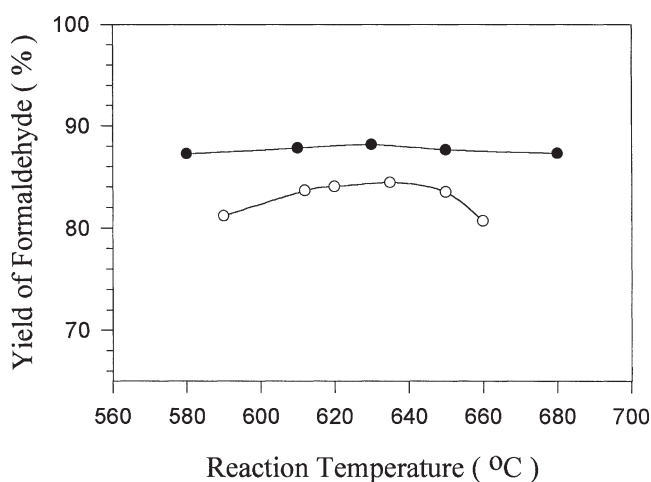
Figure 3. The effect of silver content on the yield of formaldehyde.

partial oxidation, catalysts with excess large free silver surface area will always lead to more side reactions. Therefore, the free silver surface area played a key role in determining the catalytic activity and selectivity, i.e., the yield of HCHO.

Figure 4(a) shows the influence of O₂/CH₃OH molar ratio on the conversion of methanol to formaldehyde at 630 °C over both Ag/TiO₂-SiO₂ (1.7 wt%) and electrolytic



(a)



(b)

Figure 4. The influence of reaction conditions on the yield of formaldehyde: (a) O₂/CH₃OH on the formaldehyde yield, reaction temperature ~630 °C; (b) reaction temperature on the yield of formaldehyde, O₂/CH₃OH ~ 0.45 for Ag(1.7 wt%)/TiO₂-SiO₂ catalyst and O₂/CH₃OH ~ 0.41 for electrolytic silver catalyst. (●) Ag(1.7 wt%)/TiO₂-SiO₂; (○) electrolytic silver catalyst.

Table 2
The optimum reaction conditions and results.

Catalyst	T (°C)	O ₂ /MeOH (mol ratio)	HCHO yield (%)	CO ₂ + CO yield (%)	HCHO select. (%)	SV (h ⁻¹)
Electrolytic silver	640	0.41	84.44	9.19	88.75	1.2×10^5
Ag/pumice (40 wt%)	700	0.32	75.21	10.71	84.51	3.0×10^4
Ag/TiO ₂ -SiO ₂ (1.7 wt%)	640	0.44	88.16	6.88	91.83	1.2×10^5

silver catalyst. Ag/TiO₂-SiO₂ exhibits strikingly higher catalytic activity and selectivity than the other. The optimum O₂/CH₃OH molar ratio for the electrolytic silver is 0.41, while 0.45 for the Ag/TiO₂-SiO₂. The yield of HCHO over Ag/TiO₂-SiO₂ achieves 88.16% at its optimum O₂/CH₃OH molar ratio, which is nearly 4% higher than over electrolytic silver.

Figure 4(b) indicates that at their corresponding optimum O₂/CH₃OH ratios, the yield of formaldehyde over Ag/TiO₂-SiO₂ catalyst is always higher than over the conventional catalyst within the wide temperature range of 580–700 °C. In addition, the Ag/TiO₂-SiO₂ catalyst could maintain its high activity even at temperatures up to 680 °C, which is much higher than the up-limited temperature used for electrolytic silver. This could be ascribed to the low silver content on the TiO₂-SiO₂ support. Those silver particles show good resistance to sintering at such high reaction temperatures owing to the high dispersion and the interaction between the metal and the support. A lifetime test was also purposely performed for 100 h. No appreciable deactivation was observed, revealing the excellent thermal stability of the as-prepared Ag/TiO₂-SiO₂ catalyst. Therefore, this Ag/TiO₂-SiO₂ catalyst could be much more conveniently and safely employed in industries. Also, the significant enhancement of the yield of formaldehyde would lead to great economic benefits in industry because of the huge output of formaldehyde [1].

4. Conclusions

Chemical reduction of Ag(NH₃)₂⁺ onto TiO₂-SiO₂ support was employed to develop novel Ag/TiO₂-SiO₂ catalysts. SEM and selective O₂ chemisorption showed that the average particle size of silver is about 1 μm. Higher free silver surface area was obtained on this novel catalyst in comparison with that on the electrolytic silver. The catalyst exhibited significantly high activity and selectivity

in the conversion of methanol to formaldehyde at a silver content of only ~1.7 wt% which is lower than all known supported silver catalysts. The 100 h life-time test shows no significant deactivation, implying its promising industrial application.

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