

Novel sol–gel-derived Ag/SiO₂–Al₂O₃ catalysts for highly selective oxidation of methanol to formaldehyde

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Novel Ag/SiO₂–Al₂O₃ catalysts with low silver content prepared by the sol–gel method exhibit excellent catalytic properties in the catalytic oxidation of methanol to formaldehyde. The silver content was as low as 2% and the yield of formaldehyde was achieved as 90.3%, which is 16% higher than that of pumice-supported silver and even 5–6% higher than that of a commercial electrolytic silver catalyst. XRD, XPS and SEM results reveal that all silver was present as Ag⁺ before catalytic reaction and was partially reduced to the metallic state after the reaction. It was also found that silver was aggregated on the surface after its reduction.

Keywords: sol–gel method, SiO₂–Al₂O₃-supported silver catalyst, formaldehyde, oxidation of methanol

Formaldehyde, a very important chemical in business with an annual worldwide production capacity of 2–3 × 10⁷ tons, is produced mainly on the basis of methanol oxidation [1]. For its moderate operation conditions and simplicity of reactor design, the commercial process using a silver catalyst is the preferred route to the iron–molybdate one [2]. However, the short lifetime of the crystalline silver catalyst and the low formaldehyde yield of pumice-supported silver have severely limited the wide use of silver-based catalysts [3]. In recent years, various silica or silica–alumina mixed oxides are used as supports for their good catalytic properties [4–10]. In the present report, a silica–alumina–silver catalyst with as low as 2 wt% content of silver prepared by the sol–gel method exhibits extremely high catalytic activity and selectivity in the catalytic oxidation of methanol to formaldehyde. The yield of formaldehyde on this novel catalyst is 16% higher than that of pumice-supported silver and even 5–6% higher than that of the electrolytic silver catalyst. To the best of our knowledge about the silver-based catalysts, our novel catalyst exhibits the highest formaldehyde yield at the lowest silver loading, and seems to be the promising candidate for application in the current formaldehyde manufacturing industry.

Tetraethoxysilicon (TEOS), aluminum nitrate (Al(NO₃)₃·9H₂O) and silver nitrate (AgNO₃) were employed as the precursors of the catalyst. Briefly, 0.63 g AgNO₃ and 7.36 g Al(NO₃)₃·9H₂O were dissolved in 20 ml distilled water and 67 ml TEOS was added dropwisely to this solution, and finally a drop of 1 M HNO₃ solution was added. The mixture was maintained at 80 °C under continuously magnetic stirring. The resulting gel was dried in air at 110 °C for 24 h, then calcined at 950 °C in air for 6 h. Then, the catalyst

was ground to grain size of 40–60 meshes for the catalytic activity test.

The catalytic oxidation of methanol over the catalyst was carried out in a flow-type quartz reactor (i.d. = 16 mm) at a reaction temperature of 550–700 °C with the space velocity (GHSV: at the typical reaction conditions) at 1.2 × 10⁵ h^{−1}. 60 wt% aqueous solution of methanol was fed to the reactor by a micropump. Reaction products were found as: HCHO, CO₂, H₂, H₂O and traces of CO and HCOOH. Formaldehyde and residual methanol were analyzed by traditional titration and gas chromatography (GC). The tail gas was analyzed by GC. The catalyst showed excellent properties in the catalytic oxidation of methanol to formaldehyde. Figure 1 illustrates the yield of formaldehyde as a function of the molar ratio of O₂/MeOH and reaction temperature, contrasted with that of a commercial electrolytic silver catalyst (Shanghai Petrochemical Co. LTD, PR China). Under the optimum reaction conditions (O₂/MeOH molar ratio ~0.38, temperature ~650 °C), the yield of HCHO was found to exceed 90%. Table 1 shows the optimum reaction conditions and the amount of Ag used in electrolytic silver, pumice-supported silver and the Ag/SiO₂–Al₂O₃ catalyst. It should be also noted that all data in figure 1, table 1 and the lifetime test are collected after the 2 h induction period. Our catalyst achieves the high yield of 90% at only 1/20 silver content compared with the pumice-supported catalyst (40 wt%). Superior to electrolytic silver, the effects of the variation of the reaction temperature and the O₂/CH₃OH molar ratio on the formaldehyde yield are very small, the yield stays above 88% in the range of 550–700 °C and 0.38–0.45, respectively. To examine the stability of this catalyst, a 100 h lifetime test has been processed under its optimum reaction conditions and no drop of the activity for the catalyst was observed. All the results indicate that the novel Ag/SiO₂–Al₂O₃ catalyst reported in this paper shows

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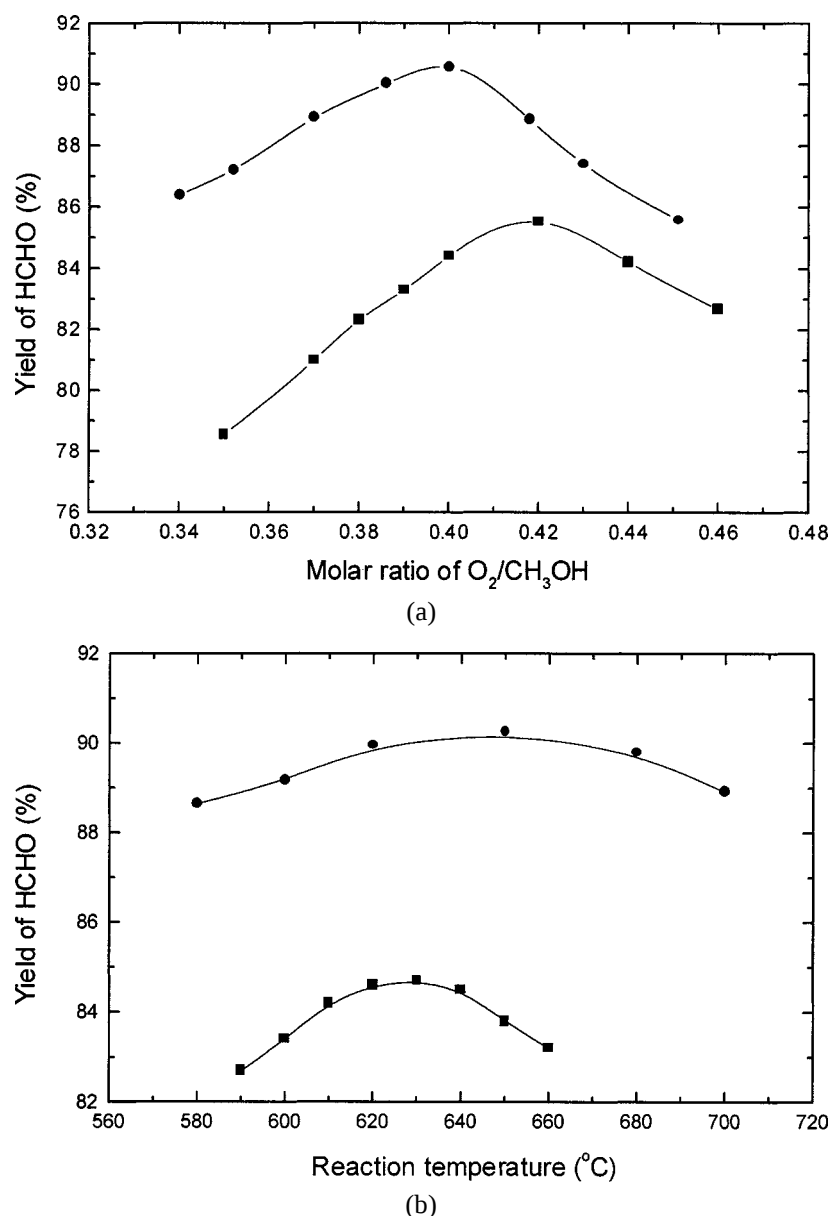


Figure 1. The effects of reaction conditions on the yield of HCHO: (a) molar ratio of O₂/CH₃OH (reaction temperature = 640 °C) and (b) reaction temperature (O₂/CH₃OH = 0.41); (■) electrolytic silver, (●) Ag/SiO₂-Al₂O₃. Reaction conditions: GHSV = 1.2 × 10⁵ h⁻¹, height of catalyst bed = 10 mm, feed liquid = 60% (w/w) CH₃OH water solution.

Table 1
Silver contents and reaction results of different silver catalysts.

Catalyst	Ag content (w/w%)	GHSV (h ⁻¹)	T (°C)	O ₂ /CH ₃ OH	Yield of HCHO (%)	Yield of (CO + CO ₂) (%)	Selectivity of HCHO (%)
Ag/SiO ₂ -Al ₂ O ₃	2	1.2 × 10 ⁵	640	0.51	90.3	7.6	92.5
Electrolytic silver	100	1.2 × 10 ⁵	640	0.41	84.4	9.2	88.8
Ag/pumice	40	3.0 × 10 ⁴	700	0.32	74.2	10.7	84.5

not only outstanding catalytic activity but also much longer lifetime during the oxidation of methanol in a microreactor. In addition, the easy operating conditions mentioned above along with these two excellent characteristics all make this novel catalyst a promising one to be employed in industrial process.

The superior properties of this novel catalyst also attract our interest. Firstly, all silver is present as ionic state in this novel catalyst, even after a high-temperature calcination process at 1100 °C. This has been confirmed by traditional chemical analysis and some other modern analytical methods, such as X-ray photoelectron spectroscopy

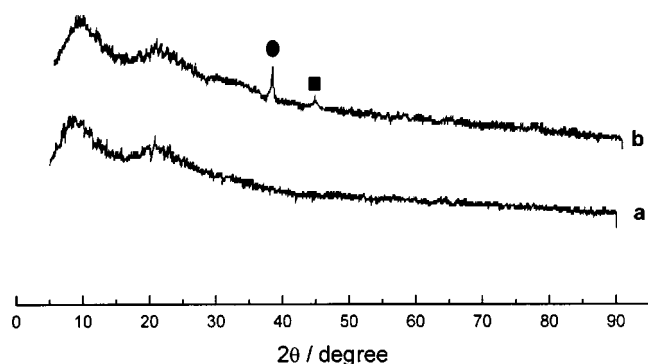


Figure 2. XRD spectra of 2% Ag/SiO₂–Al₂O₃ catalyst: (a) before and (b) after reaction for 2 h; (●) Ag(111), (■) Ag(220).

(XPS), temperature-programmed reduction (TPR) and diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis). XPS showed an obvious chemical shift in the binding energies of Ag 3d_{5/2}, suggesting the presence of silver ions (Ag⁺). TPR experiments resulted in a conclusion that there was a stoichiometric reaction between Ag⁺ and the consumed hydrogen, which was in good accordance with the chemical analysis results, meaning that all silver was present as Ag⁺. DR-UV-Vis confirmed that all silver existed as isolated Ag⁺ referenced to standards since they all had an absorption band at 250 nm in the spectra characteristic of Ag⁺. Secondly, the silver ions in the silica–alumina support can easily be reduced to metals by hydrogen or a reaction gas mixture (a reducing mixture containing CH₃OH, H₂O, N₂ and O₂). It is obvious that there are remarkable structural changes from the X-ray diffraction (XRD) spectra when this novel Ag/SiO₂–Al₂O₃ catalyst undergoes reaction (see figure 2). According to figure 2(a), no sharp diffraction peaks are observed. Two big broad peaks at 2θ of 9.5° and 22° are attributed to the diffraction peaks of the amorphous silica. Two small broad diffraction peaks at 2θ of 38.1° and 44.3° ascribed to the diffraction peaks of metallic Ag(111) and Ag(220) appeared, as shown in figure 2(b), after treatment with the reaction gas mixture for 2 h. The results indicate that silver is highly dispersed on the supports as ionic state in the fresh catalyst but transformed to free metal clusters after 2 h reaction. Figure 3 shows the scanning electron micrograph (SEM) of the morphology of this novel catalyst before and after reaction. No silver particles were present on the silica–alumina support before reaction, while a great many of isolated metallic silver particles with mean size of ca. 200 nm appeared on the support after reaction. Those silver particles are directly incorporated into the framework of the mixed oxides of silica–alumina. Novel Ag/SiO₂–Al₂O₃ catalysts with some other silver contents are prepared and a similar phenomenon can also be observed. This suggests that silver ions are reduced and migrated to the surface from the bulk during the reaction process. XPS results reveal that the surface concentration of silver after reaction increased ca. 100 times compared to that before reaction, which is in good consistency with the SEM results. All

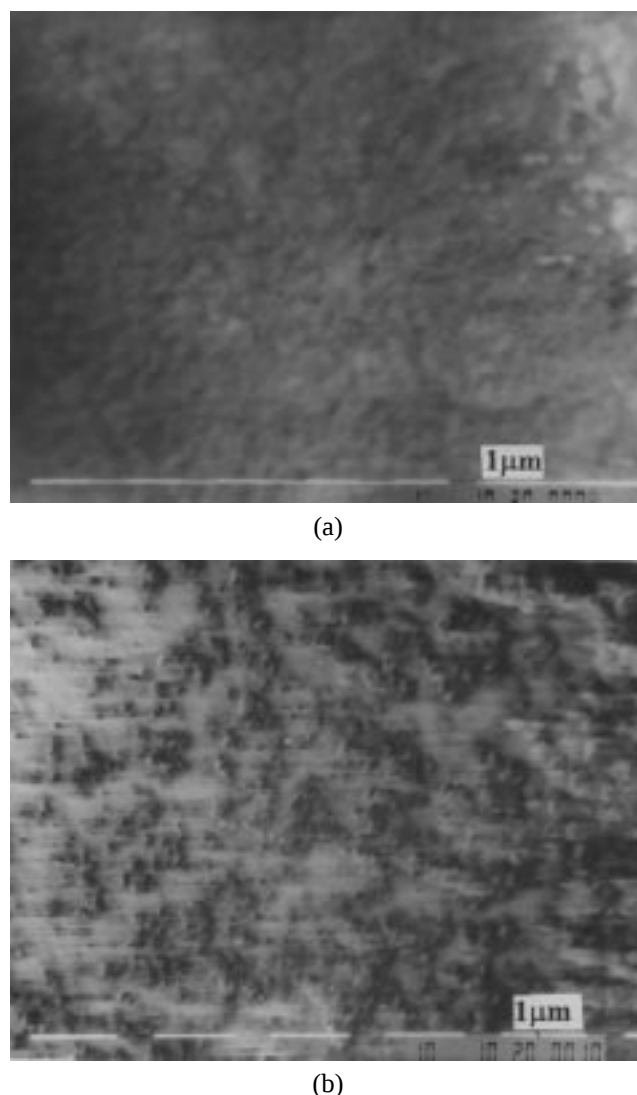


Figure 3. SEM photos of 2% Ag/SiO₂–Al₂O₃ catalyst: (a) before reaction and (b) after reaction for 2 h.

the experimental results represent that silver will be enriched and dispersed on the surface of the support after its reduction, which suggests that the highly efficient catalytic oxidation of methanol to formaldehyde occurs on the *in situ* derived free silver clusters accumulated on the catalyst surface. The third interesting feature of this novel catalyst is that the metallic silver derived from the reduction of H₂ or the reaction mixture can be oxidized to silver ions again by oxygen after a high-temperature treatment process. Accordingly, a Ag⁺ ⇌ Ag cycle is supposed to be present in this novel catalyst under different atmosphere.

As a summary, a novel low silver-loaded silica–alumina catalyst prepared by the sol–gel method showed excellent catalytic activity and selectivity compared with the pumice-supported catalyst and even the commercial electrolytic silver catalyst. The silver content of the catalyst was reduced to a lowest value of 2 wt%. The superior properties of this novel Ag/SiO₂–Al₂O₃ catalyst lead to its excellent catalytic

activities and detailed correlation of the structural properties with the catalytic performance will be reported in our following work.

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