A Novel Silver-Silica Catalyst Used for the Manufacture of Formaldehyde

Wei-Lin Dai, Yong Cao, He-Xing Li, and Jing-Fa Deng*
Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

(Received November 11, 1996)

Several novel silver-silica catalysts were prepared by means of sol-gel method, which exhibited high activity and selectivity in the catalytic oxidation of methanol to formaldehyde. The optimum content of silver was determined as 20%(w/w.), which showed 97% conversion and 85.5% yield of formaldehyde. Some other superiority of the as-prepared silver catalysts was observed by comparing with the commercial silver catalysts, including pumice-supported silver and electrolytic silver. XRD patterns reveal that silver is present as a crystalline state in the Ag-SiO_2 catalysts.

Because of great and increasing demand of formaldehyde in industries, [1] the catalyst used for its manufacture has caused an extensive interest. Silver-based catalyst, which is one of important catalysts used for the manufacture of formaldehyde by the oxidation of methanol, can be used both in the form of bulk silver(*e.g.* electrolytic silver) [2] and supported one (*e.g.* pumice-supported silver) [3]. Because of the short lifetime of the electrolytic silver and the low formaldehyde yield for the pumice-supported silver, the silver catalyst cannot completely replace another important catalyst — iron-molybdate catalyst, [4] which also takes a relatively big proportion in the industries. Therefore, many researchers devote themselves to searching for new types of silver catalysts to improve the catalytic properties. However, only very few works have been reported so far. [5] In this paper, we report a set of novel silver catalysts obtained by sol-gel method. This set of silver catalysts not only show higher activity and selectivity than pumice-supported silver, but also show some excellent properties relative to electrolytic silver. It has thus great potential economic benefits in industries.

Sol-gel method is employed to prepare the new type silver-based catalysts. Firstly, 36 ml (159 mmol) tetraethoxysilane (TEOS) was mixed with 6 ml 0.1 M HNO_3 (334 mmol). Then a certain amount of silver nitrate ($AgNO_3$) was added followed by addition of 25 ml distilled water. The resulting gel was dried and calcined at 600 °C for 6 h. The catalysts of the as-prepared sample with the size of 40-60 mesh were used in the experiments. The catalysts were characterized by XRD, SEM, TG-DTG and DTA. The catalytic oxidation of methanol over the Ag-SiO_2 catalysts was carried out on a flow-type quartz reactor (i.d.=16 mm). 60% (w/w.) aqueous solution of methanol was pumped to the vaporizer (keeping at 250 °C) through a micro-pump and mixed with the compressed air to pass through the reaction bed. The product mixture was cooled to 300 °C with a sudden water cooling and collected through a absorption tower(height 1.5 m, packed with ceramic rings). The tail gas was analyzed by a QF-1903 gas analyzer for the content of CO_2, CO, O_2 and H_2, the yield of formaldehyde and formic acid were analyzed by titration method and the residual methanol concentration was analyzed through gas chromatography method.

A set of silver contents, such as 5, 10, 15, 20, 30 and 40%(w/w.), were chosen to investigate the relationship between the silver content and the yield of formaldehyde. Figure 1

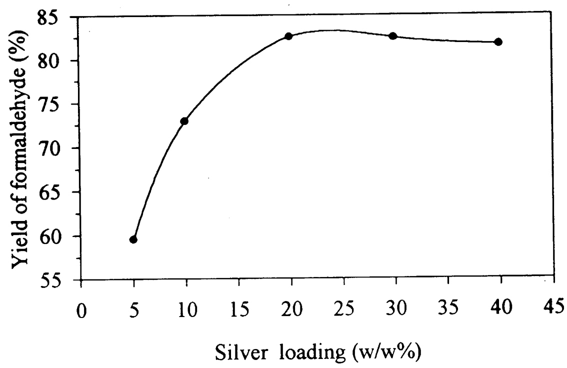

Figure 1. The relationship between the yield of formaldehyde and the silver loading. Reaction conditions: Temperature 640 °C, O_2/CH_3OH molar ratio 0.50, GHSV 1.2×10^5 h^{-1}, height of the catalyst bed 10 mm.

shows the results which indicate that the optimum content of silver is 20%. So the study was focused on this catalyst. With keeping some reaction conditions as: GHSV~$1.2\times10^5 h^{-1}$, height of the bed~10.0 mm and the vaporizer temperature ~250 °C, the effects of the reaction temperature and the O_2/CH_3OH molar ratio on the yield of formaldehyde are shown in Figure 2. Under similar reaction conditions, to electrolytic silver, those effects are also indicated in Figure 2. The optimum reaction conditions of this silver-silica catalyst were found as: reaction temperature at 640 °C and molar ratio of O_2/CH_3OH at 0.51, and a 97% methanol conversion and a 85.5% formaldehyde yield could be achieved. At

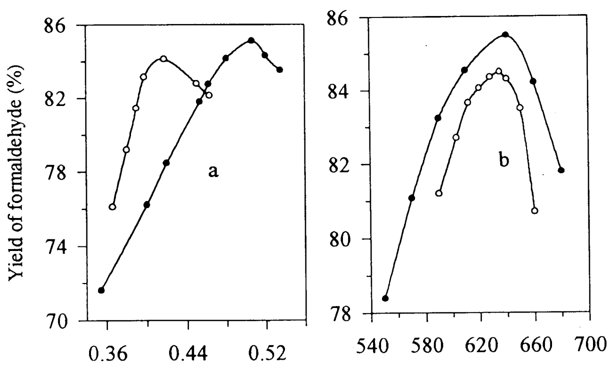

Figure 2. The effects of the reaction conditions on the yield of formaldehyde. a, O_2/CH_3OH molar ratio; b, temperature.
Reaction conditions: GHSV 1.2×10^5 h^{-1}, Height of the catalyst bed 10 mm. To a, temperature 640 °C; to b, O_2/CH_3OH at 0.50.
○-----Electrolytic silver, ●----Silver silica.

the optimum reaction condition, the reaction results of silver-silica catalyst, pumice-supported silver and electrolytic silver are listed in Table 1. It is found that this catalyst shows a much higher yield of formaldehyde (>10%) than pumice- supported silver and

Table 1. The reaction results of the oxidation of methanol

Catalyst	HCHO Yield (%)	CO_2+CO Yield (%)
Ag-SiO_2[a]	85.5	7.6
Electrolytic Ag[b]	84.4	9.2
Ag-Pumice[c]	75.2	10.7

Reaction Conditions: a, GHSV 1.2×10^5 h^{-1} , height of the catalyst bed 10mm, temperature 640 °C, O_2/CH_3OH 0.51; b, GHSV 1.2×10^5 h^{-1}, temperature 625 °C, O_2/CH_3OH 0.40; c, GHSV $3.1\times10^4 h^{-1}$, temperature 680~700 °C, O_2/CH_3OH 0.28~0.32.

also even 1% higher than electrolytic silver. Because of the huge production (5.3×10^6 ton annually) of formaldehyde, a little increment of the formaldehyde yield will bring about great economic benefits. Figure 2 also shows the effect of reaction conditions on the formaldehyde yield over the silver-silica catalyst and electrolytic silver. Comparing these two catalysts, there is a much more broad operation range to silver-silica catalyst. Therefore, this catalyst may be easily and safely used in industries.

TG-DTG and DTA curves reveal that there were no weight loss, endothermic or exothermic peaks in the temperature range from 600 to1000 °C, indicating the thermal stability of the silver-silica catalyst. This result was also supported by SEM photograph, as no significant sintering was observed during the same heating process. In the case of electrolytic silver, when heated up to 680 °C, the sintering took place obviously and irreversibly. This is a fatal shortcoming to electrolytic silver. Also, a life time test of this silver-silica catalyst was carried out. During a 100 hours' time, no obvious change of the yield of formaldehyde was observed. Therefore, if electrolytic silver is replaced by this catalyst, it will be much convenient to the industrial production.

The XRD patterns of those as-prepared catalysts are shown in Figure 3. Only diffraction peaks of crystalline silver are observed in the catalyst. It also reveals that either one or two silica crystalline phases could be identified depending on the silver content.

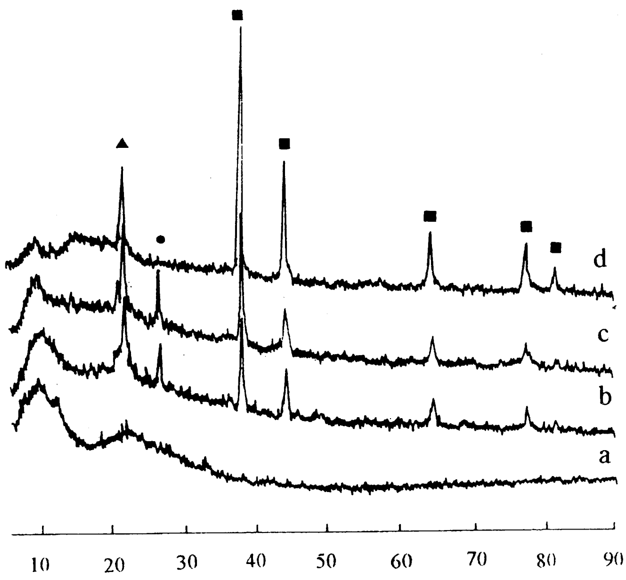

Figure 3. XRD patterns of the as-prepared samples. (a) blank, (b) 5%(w/w.), (c) 20%(w/w.), (d) 40%(w/w.). ■----Crystalline silver, ▲----Silica O(syn), ●----Cristobalite(syn)

We are grateful to the financial support from SINOPEC.

References

1 M. V. Twigg, *Catalyst Handbook*, Wolfe Publishing Ltd. (1989) p. 490.
2 B. Xinhe and D. Jingfa, *J. Catal.*, **99**, 391(1986).
3 L. A. Manucharova and T. G. Alkhazov, *Zh. Fiz. Khim.*, **60**, 73(1986).
4 C. A. Bazilio, W. J. Thomas, U. Ullah, and K. E. Hayes, *Proc. R. Soc. Lond.* **A399**, 181(1985).
5 E. Yu. Batyan, S. V. Mateveichuk, and G. A. Branitskii, *Kinetics and Catalysis*, **136**, 816(1995).