Direct Dehydrogenation of Methanol to Formaldehyde over Novel Ag-Containing Ceramics

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A novel silver-ceramics supported catalyst showing excellent activity and selectivity in the direct dehydrogenation of methanol to formaldehyde was prepared. The selectivity was as high as 100% and the yield of formaldehyde reached 70%.

Formaldehyde is a very important product with an annual worldwide production capacity of (2–3) × 10^7 tons. A vast majority of formaldehyde is produced from partial oxidation of methanol by air in the presence of a silver catalyst or an iron-molybdenum catalyst.[1,2] Both processes produce aqueous solution of formaldehyde. In recent years, water free formaldehyde has been paid more and more attention due to its important applications in many fine organic chemical processes, e.g., the synthesis of polyacetal plastics via trioxane. However, the removal of water from the formaldehyde solution is cumbersome and expensive due to negative deviation from ideal solution and formation of azeotropes.[3] An alternative route is the direct catalytic dehydrogenation of methanol. Many materials, which showed potential applications as catalysts in this process, were listed in literature[4] and were classified as: transition metal based catalysts, sodium carbonate catalysts, metal oxides and zeolites. Among them, some transition metal based catalysts (containing Cu, Ag, etc.) exhibited higher selectivity toward formaldehyde ~ 70%.[4] Nevertheless, the applications of these catalysts were restricted by the gas phase decomposition of methanol and formaldehyde to carbon monoxide and hydrogen under elevated temperature.

The present study reports a 20 wt% silver-containing ceramics catalyst, which exhibited extremely high activity and selectivity in the direct dehydrogenation of methanol to formaldehyde. The selectivity toward formaldehyde over this novel catalyst is 100%, and the yield of formaldehyde is ~70% at the reaction temperature of 600 °C. No side product such as carbon monoxide was detected. To our knowledge of the direct catalytic dehydrogenation of methanol to formaldehyde, this novel silver-containing ceramics catalyst shows the highest selectivity and excellent catalytic performance.

Finely powdered natural kaolin ($Al_4Si_4O_{10}(OH)_8$, China) and silver nitrate ($AgNO_3$) were used as the precursors for the catalyst. The kaolin powder was boiled with aqueous solution of 3 M HNO_3 to remove metallic impurities and then rinsed with distilled water until pH = 5.0. Then, the treated kaolin powder was impregnated with aqueous solution of $AgNO_3$. The resulting mixture was dried at 120 °C for 24 h, calcined at 1200 °C for 9 h in air and finally ground to grain size of 40–60 meshes for catalytic test. The BET surface area of the catalyst is 0.94 m^2/g and the silver content is determined as 19.9 wt%, implying that there is virtually no silver loss present during the high temperature calcination process.

The dehydrogenation reaction was carried out in a fixed-bed flow-type quartz reactor. Before feeding methanol into the reactor, the catalyst was treated in situ with high purity argon (double oxygen trapped, Oxygen Trap, ALLTECH, U.S.A.) flow at 600 °C for 3 h to get rid of any influence of the adsorbed oxygen in the catalyst. Methanol was also bubbled with the above-mentioned argon to exclude dissolved oxygen. Products were analyzed by an online gas chromatography. Reaction product mixture was consisted of HCHO, H_2, trace H_2O and the residual methanol.

Figure 1 shows the yield of formaldehyde and the selectivity towards formaldehyde as function of the reaction temperature. Direct dehydrogenation of methanol occurred with the selectivity near 100% below and at 600 °C. When the reaction temperature was increased to 600 °C, the yield of HCHO reached its maximum of ~ 70%. Since the direct dehydrogenation of methanol was endothermic, a higher conversion of methanol was obtained at a higher reaction temperature. It should be noted that the yield of HCHO along with the conversion of methanol decreased with the increment of the temperature. This result can be well explained by the appearance of the CO by-product and the deposited carbon on the surface of the catalyst owing to the decomposition of HCHO and methanol under elevated temperature. Therefore, an appropriate reaction temperature should be chosen.

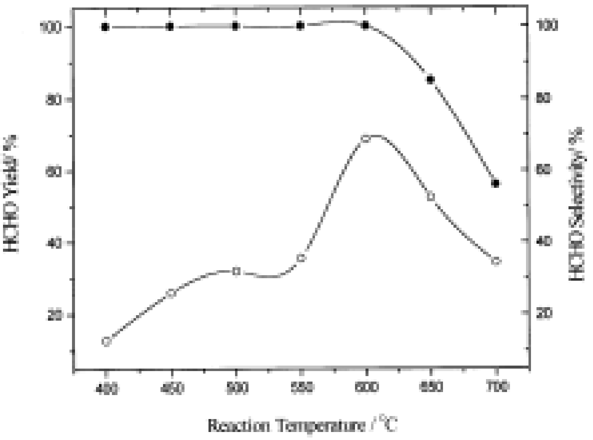

Figure 1. The temperature dependence of the yield (○) and selectivity (●) of formaldehyde over silver containing ceramics. Reaction conditions: 0.5 g catalyst; carrier gas, argon; flow rate = 20 mL /min(STP); CH_3OH, v/v% = 10%.

Chemical analysis and some modern analytical methods such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and UV–visible diffuse reflectance spectroscopy (UV–vis. DRS) were used to characterize the catalysts. In the chemical analysis experiments, the total content of silver was determined by titration after dissolving the sample with the hydrofluoric acid/nitric acid mixture. The content of Ag^+ could be obtained by pre-separation of Ag^+ from Ag^0 with hydrofluoric acid and no Ag^0 could be detected in the prepared Ag/ceramics sample. Both the Ag $3d_{5/2}$ chemical shift (368.6 eV as referenced to Ag^0: 368.2 eV) in the XPS spectra and the presence of a unique absorption band at 250 nm typical of Ag^+ in the UV–vis. DRS revealed that all silver was present as ionic state in the catalysts before the dehydrogenation. Figure 2 shows the XRD patterns of silver containing ceramics catalysts before and after reaction. As shown in Figure 2(a), the XRD pattern of catalysts before reaction was not significantly different from that of the blank. No diffraction peaks corresponding to crystalline silver or any other silver-containing crystalline phases were observed even at high silver content up to 20%, indicating that all silver species were present in ionic state. After treatment with reaction mixture for 2 h, four small diffraction peaks at 2θ of 38.1, 44.5, 64.6, and 77.5° attributable to metallic Ag (111), (200), (220) and (311) appeared, as shown in Figure 2(c). The result indicated that some of the Ag^+ was reduced to metallic silver after the reaction, as has also been confirmed by chemical analysis.

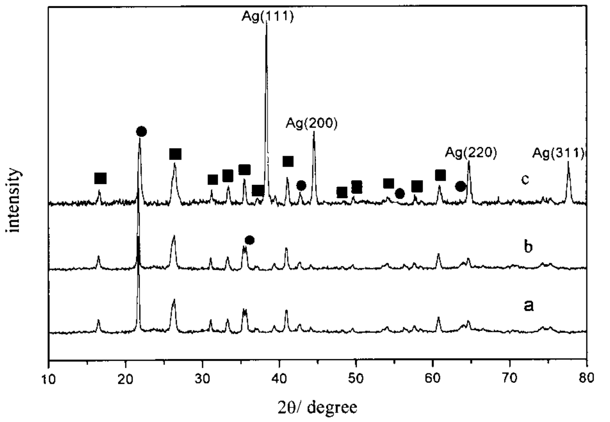

Figure 2. The XRD patterns of silver containing ceramics under different conditions: (a) before the reaction; (c) after the reaction for 2 h, and (b) the deactivated catalyst after regeneration under oxygen atmosphere at 650 °C for 1 h. (■) Mullite, (●) α-cristobalite.

It should be noted that the conversion of methanol decreased along with the process of the direct dehydrogenation, suggesting that the activity of the catalyst dropped with reaction time, which can be ascribed to partial consumption of the Ag^+ active sites during the reaction as mentioned above. It is also interesting to find that the lifetime of the catalyst with a steady high activity could be more than 1 h and the yield of another product—hydrogen was almost the same as formaldehyde. The molar ratio of the resulting HCHO to Ag^+ in the novel Ag/ceramics catalyst is more than 500, meaning that 1 g 20% Ag/ceramics can catalyze more than 25 g CH_3OH to HCHO. However, the deactivated catalyst could be easily regenerated after oxygen treatment at 650 °C for 1 h. Therefore, the lifetime of the present catalyst could be greatly extended by discontinuous operations. As shown in a discontinuous lifetime test, the catalytic activity remained virtually invariable in a 100-h activity test. On the other hand, there was no increase of carbonaceous species on the surface after the lifetime test as determined by means of XPS and scanning electron microscopy (SEM). All the results mentioned above showed that the novel silver containing ceramics catalyst not only exhibited excellent selectivity and activity at a temperature of 600 °C, but also can be regenerated by high temperature treatment under oxygen atmosphere. Hence, this novel catalyst showed promising potential application in industrial manufacture of water-free formaldehyde.

Figure 2(b) shows the XRD pattern of the resulting catalysts after treatment by oxygen at high temperature. The peaks corresponding to metallic silver disappeared, indicating that metallic silver was oxidized to Ag^+ again. Chemical analysis and XPS also verified the transformation of $Ag^0 \rightarrow Ag^+$. Thus, an $Ag^+ \leftrightarrow Ag^0$ cycle was present in this silver-containing ceramics catalyst under different atmosphere.

The direct dehydrogenation experiments were also carried out over the blank ceramics and over electrolytic silver powders. The results showed that pure ceramics exhibited no dehydrogenation activity, and electrolytic silver treated in oxygen atmosphere at 650 °C gave initial yield of formaldehyde lower than 5% and was deactivated in 0.5 h. As mentioned above, ionic silver predominated in the active catalyst and the deactivation of catalyst was accompanied by the decrease of ionic silver amount. Therefore, Ag^+ or Ag^+-related structure is supposed to be the active center of this silver containing ceramics in methanol dehydrogenation. The extraordinary stability of Ag^+ in the ceramics catalyst under the reducing ambient can be explained by the magic angle spinning nuclear magnetic resonance (MAS NMR). In the ^{27}Al spectra, there is a peak at 44.5 ppm due to the existence of $[AlO_4]$ tetrahedral unit.[5] The $[AlO_4]$ tetrahedron and silver cation formed ion pairs, and the strong static interaction between them could stabilize the ionic state of silver, and, as a result, maintained the high catalytic activity of the catalyst.

As a conclusion, the present study is the first report on a novel silver-containing catalyst used in the direct dehydrogenation of methanol to formaldehyde without any side-products. The catalyst can be easily regenerated with oxygen at high temperature, which leads to longer lifetime. The dehydrogenation process can be performed in a riser reactor in which deactivated catalysts could be regenerated while not influencing the continuity of the reaction. Moreover, considering the cheapness of the natural kaolin support and the simpleness of the preparation procedure, this novel catalyst is a promising potential candidate for water-free formaldehyde manufacture. Further study on its detailed mechanism is under way.

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