Potassium-Promoted Ag/Al$_2$O$_3$ for Catalytic Oxidation of Formaldehyde at Low Temperature

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Abstract: Ag/Al$_2$O$_3$ catalyst and K-Ag/Al$_2$O$_3$ catalysts with different K doping amount were prepared by an impregnation method and subsequently tested for the catalytic oxidation of formaldehyde (HCHO) at low temperature. It is observed that K doping has a dramatic promotion effect on the Ag/Al$_2$O$_3$ catalyst. Based on the characterization results, it is suggested that K species addition increased the content of metallic Ag species in Ag/Al$_2$O$_3$ catalysts and promoted the adsorption and activation for oxygen species, while the excessive doped K$^+$ resulted in agglomeration of Ag particle and then lost some of active site.

Keywords: HCHO oxidation, Potassium ions, Ag/Al$_2$O$_3$.

1. Introduction

Formaldehyde (HCHO) is one of the major indoor air contaminants, leading to serious and hazardous effects on human health. Among various methods for formaldehyde removal, the catalytic oxidation is regarded as the most promising method for its high effectiveness in achieving total conversion of HCHO into harmless CO$_2$ and water. Currently, the conventional catalysts used in catalytic oxidation of HCHO include transition-metal oxides (Co, Cu, Ce, and Mn) and the supported precious metal (Pt, Pd, Au and Ag) catalysts. In general, the transition-metal oxides need much higher temperatures to complete combustion of HCHO, while the supported noble metal catalysts such as Pt-, Pd-, and Au-based catalysts exhibited excellent activity for HCHO oxidation at ambient temperature. However, the wide application of Pt, Au, Pd are limited due to their high costs. In comparison, Ag-based catalysts are much less expensive and shows considerable efficiency for HCHO oxidation in low temperature. Previously, we have demonstrated that the addition of alkali ions (such as Li$^+$, Na$^+$, and K$^+$) on Pt- and Pd-based catalysts can dramatically promote the catalytic efficiency for HCHO while the specific role of alkali ions on Ag-based catalysts remains to be ambiguous. Al$_2$O$_3$ is a stable and irreducible support, and generally not directly involved in the catalytic reaction. Therefore, in this paper, we prepared Ag/Al$_2$O$_3$ catalyst and K-Ag/Al$_2$O$_3$ catalysts to investigate how K addition affect the performance of Ag-based catalysts in HCHO oxidation. The series of catalysts were tested and the results verified that the K also had a dramatic promotion effect on the Ag/Al$_2$O$_3$ catalyst. The catalysts were next characterized by XRD, BET, TEM, H$_2$-TPR, XPS, UV-vis and XAFS methods. Based on the characterization results, the specific role of K doping in promoting the performance of Ag/Al$_2$O$_3$ were clearly elucidated.

2. Experimental

The 8 wt % Ag/Al$_2$O$_3$ catalyst and K-8 wt % Ag/Al$_2$O$_3$ samples with different K doping quantities (0.5, 1, 1.5, 2, and 4 wt %) were prepared by co-impregnation of Al$_2$O$_3$ (Aladdin, BET surface area 187.8 m$^2$g$^{-1}$) with aqueous AgNO$_3$ and KNO$_3$ (Aldrich). After stirring for 1 h, the excess water was removed in a rotary evaporator at 55 °C. Then, the samples were dried at 100 °C for 4 h and calcined at 450°C for 3 h afterwards. The samples were denoted as Ag/Al$_2$O$_3$ and 0.5 ~ 4K-Ag/Al$_2$O$_3$.

The activity tests for the catalytic oxidation of HCHO over the catalysts (60 mg) were performed in a fixed-bed quartz flow reactor (i.d. = 4mm) in an incubator. Gaseous HCHO was generated by flowing helium through the paraformaldehyde container in a water bath kept at 35 °C. Water vapor was generated by flowing helium through a water bubbler at 25 °C. The feed gas composition is 110 ppm of HCHO, 20% O$_2$ and balanced by helium. The total flow rate was 100 mL min$^{-1}$, corresponding to a gas hourly space velocity (GHSV) of 100 000 mL/(g$_{cat}$ h).

3. Results and discussion

As shown in Figure 1, 100% HCHO conversion was attained at 80 °C for Ag/Al$_2$O$_3$ catalyst in the space velocity of GHSV = 100,000 mL/(g$_{cat}$ h). Remarkably, K addition demonstrated a dramatic promotion
effect on the Ag/Al₂O₃ catalyst. When the theoretical doping amount of K reached 1.5%, the 1.5K-Ag/Al₂O₃ catalyst showed the best low temperature activity and completely oxidized HCHO at 65 °C. Further increasing the K content to 4 wt % significantly decreased the HCHO conversion in the low temperature range. Thus, we can conclude that potassium doping improved the activity of Ag/Al₂O₃ catalyst for formaldehyde catalytic oxidation, but there was an optimal doping amount.

H₂-TPR was conducted to study the reducibility of the catalysts, and the TPR profiles of fresh and K doped Ag/Al₂O₃ catalysts are shown in Figure 2. The pattern of Ag/Al₂O₃ sample showed only one reduction peak at 75 °C which should be ascribed to reduction of oxygen species absorbed on the dispersed Ag surface. Similarly, the peak located at about 75 °C appeared on all K-Ag/Al₂O₃ catalysts, and H₂ consumption amount arose with increasing addition amount of K⁺, indicating the presence of K⁺ ions promoted abilities to oxygen adsorption for Ag/Al₂O₃ catalysts. In accordance with the literature, when oxygen associatively chemisorbed on the Ag surface, partial charge transfer can be expected due to the overlap of the π* antibonding orbitals of O₂ with Ag orbitals. The addition of allaki partly covered the surface of Ag, charge polarization at the surface changed the local electronic structure and status. This may enhance orbital coupling between O₂ and Ag, thus accounting for the increased adsorption and activation for O species. For 2K-Ag/Al₂O₃ and 4K-Ag/Al₂O₃ catalysts, another reduction peak respectively located at 139 °C and 160 °C should be assigned to the reduction of K species.

4. Conclusions

In summary, this work demonstrated that the K addition had a dramatic promotion effect on Ag/Al₂O₃ catalyst for HCHO oxidation, while there existed an optimal doping amount. The addition of K⁺ ions further increased the content of metal Ag in Ag/Al₂O₃ catalyst. Besides, when K partly covered on the surface of Ag, the local electronic structure and status were changed because of charge polarization at the surface, thus accounting for the increased adsorption and activation for oxygen species. Nevertheless, K could penetrate the Ag lattice due to their similar atomic sizes, resulting in the structural reforming of Ag. The interaction between Ag and subsurface K⁺ led to agglomeration and loss of active sites of Ag when excessive doped K⁺. This work further confirmed the potassium promotion effect on the catalytic activity of Ag-based catalysts.

References