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Enhanced activity and stability of a Cu/SiO$_2$ catalyst for the reverse water gas shift reaction by an iron promoter

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An Fe promoter inhibits the sintering of Cu particles and oxidation of the Cu surface, resulting in high catalyst activity and stability.

Carbon dioxide has been attributed to be the main source of the greenhouse effect. The increase of carbon dioxide concentration will strongly influence the global weather. Conversion of CO$_2$ to CO by catalytic hydrogenation has been recognized as one of the most promising processes for CO$_2$ utilization. Synthesis gas, H$_2$ and CO, can be used to produce long-chain hydrocarbons *via* the Fischer–Tropsch reaction.[1,2] The reverse water gas shift (RWGS) reaction is one of the available methods for the production of CO.

Generally, copper catalysts are used for both the water gas shift reaction and the reverse water gas shift reaction.[3–10] There have been many papers reporting the enhanced activity by promoters and the reaction mechanism;[3–7] however, the stability of copper catalysts is little mentioned. The RWGS reaction is an endothermic reaction; therefore, high temperature will facilitate the formation of CO. Nevertheless, copper-based catalysts are not suitable for operation at high temperature because they are significantly deactivated by sintering. In this study, iron is used as a promoter for copper catalysts in order to improve the stability of the catalysts at high temperature.

The 10 wt% Cu/SiO$_2$ and 0.3 wt% Fe/SiO$_2$ samples were prepared by impregnating Cab-O-Sil M-5 SiO$_2$ with an aqueous solution of Cu(NO$_3$)$_2$ and Fe(NO$_3$)$_3$, respectively. The Cu–Fe/SiO$_2$ (Cu:Fe = 10:0.3) was prepared by the addition of an aqueous solution of Fe(NO$_3$)$_3$ to dried Cu/SiO$_2$ before calcination and/or reduction. These catalysts were calcined in air and reduced in pure H$_2$ at 873 K for 5 h before reaction. Carbon dioxide hydrogenation was carried out over a fixed bed reactor at atmospheric pressure. 0.1 g samples of catalysts were used for the RWGS reaction by feeding a stream of H$_2$/CO$_2$ at 100 ml min^{-1} in a 1:1 feed ratio. Temperature programmed reduction (TPR) of catalysts was performed at atmospheric pressure in a conventional flow system. Samples of 0.06 g of the catalysts were placed in a U-shaped tube reactor and heated in a 5% H$_2$/N$_2$ mixed gas stream flowing at 30 ml min^{-1} at a heating rate of 10 °C min^{-1} from 25 to 973 K. The area of the copper surfaces was determined by using TPR of Cu oxidized by N$_2$O.[11]

The dependence of CO$_2$ conversion on time on stream for comparison of the RWGS reaction over Cu/SiO$_2$, Cu–Fe/SiO$_2$ and Fe/SiO$_2$ are shown in Fig. 1. It was found that the reaction conversion using Cu/SiO$_2$ was drastically decreased within 120 h: the catalytic activity decreased from 8.5 to 0.3%. The 0.3% Fe/SiO$_2$ catalyst offered low catalytic activity: its conversion decreased from 2.5 to 0.4% within 120 h. However, when the same experiment was run over the Cu–Fe/SiO$_2$ (Cu:Fe = 10:0.3) catalyst, it was found that CO$_2$ conversion was significantly increased and initial conversion increased from 8.5 to 15%. On the other hand, the deactivation of Cu–Fe/SiO$_2$ decreased only from 15 to 12% within 120 h. After 40 h, the catalytic activity fluctuated at about 12%. This shows that the Cu-based catalyst could be kept in a stable state by the Fe promoter.

Fig. 2 shows the comparison of surface area of Cu/SiO$_2$ and Cu–Fe/SiO$_2$ catalysts before and after the reaction. The fresh Cu/SiO$_2$ and Cu–Fe/SiO$_2$ catalysts were pretreated by calcination and reduction at 873 K for 5 h. Obviously, the copper surface area in Cu–Fe/SiO$_2$ was twice as large as that in Cu/SiO$_2$ [Fig. 2(a) and (b)]. When both catalysts were exposed to the H$_2$/CO$_2$ feed at 873 K for 120 h, the copper surface area in Cu/SiO$_2$ was significantly decreased, but Cu–Fe/SiO$_2$ retained a copper surface area as high as that of a fresh catalyst.

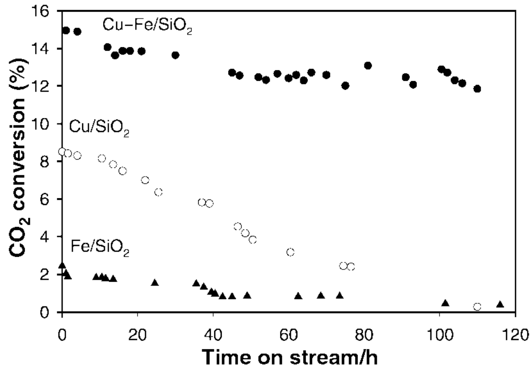

Fig. 1 The dependence of CO$_2$ conversion on time for H$_2$/CO$_2$ with 1:1 ratio over Cu/SiO$_2$, Cu–Fe/SiO$_2$ and Fe/SiO$_2$ catalysts at 873 K.

TPR was used to characterize the Cu/SiO$_2$ and Cu–Fe/SiO$_2$ after H$_2$/CO$_2$ reaction at 873 K for 120 h (see Fig. 3). The TPR profile of the Cu/SiO$_2$ catalyst shows a typical Cu$_2$O reduction peak at 503 K. A similar result was found in our previous paper, showing that copper can be oxidized in the process of the RWGS reaction.[7] Two peaks are observed in the Cu–Fe/SiO$_2$ catalysts at 723 and 853 K, respectively. The TPR profile of the Fe/SiO$_2$ catalyst through H$_2$/CO$_2$ reaction at 873 K for 120 h was performed to confirm the assignment of iron reduction peaks in the Cu–Fe catalyst. Two peaks are also observed at 723 and 853 K. Comparing these features with earlier literature reports,[1,12] the first peak could be due to reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$. The second peak is due to reduction of Fe$_3$O$_4$ to FeO. Surprisingly, no reduction peak of copper is found in the TPR profile of Cu–Fe/SiO$_2$. The reduced copper particles in Cu–Fe/SiO$_2$ catalyst cannot be oxidized during the reaction process.

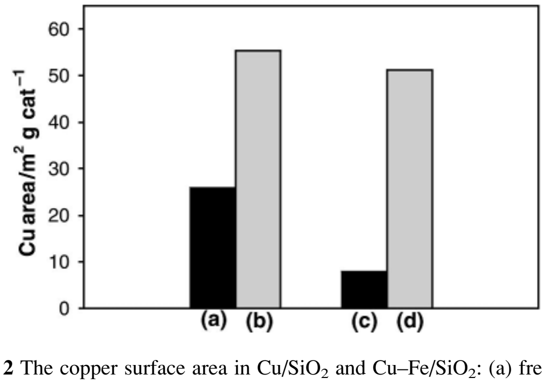

Fig. 2 The copper surface area in Cu/SiO$_2$ and Cu–Fe/SiO$_2$: (a) fresh Cu/SiO$_2$, (b) fresh Cu–Fe/SiO$_2$, (c) Cu/SiO$_2$ after exposure to H$_2$/CO$_2$ feed at 873 K for 120 h, (d) Cu–Fe/SiO$_2$ after exposure to H$_2$/CO$_2$ feed at 873 K for 120 h.

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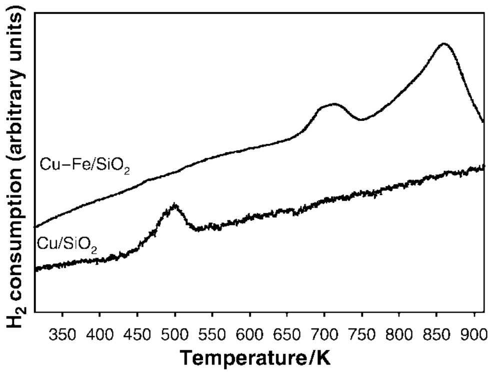

Fig. 3 TPR profiles of Cu/SiO$_2$ and Cu–Fe/SiO$_2$ catalysts after exposure to H$_2$/CO$_2$ feed at 873 K for 120 h.

Two models, redox and formate decomposition mechanisms, were proposed to explain the mechanism of CO formation in the RWGS reaction.[3–7] Cu^0 may be attributed to be the major active site for the RWGS reaction. The higher activity of Cu–Fe/SiO$_2$ compared with Cu/SiO$_2$ can be explained by the difference in copper surface area values between these two catalysts. When the pretreatment of Cu/SiO$_2$ was conducted at 773 K for 5 h, the copper surface area was 55 m^2 g cat^{-1}. When the temperature of calcination and reduction increased to 873 K, the surface area of copper decreased markedly due to sintering. By adding 0.3% iron onto the copper catalyst, the sintering of the copper catalyst was successfully inhibited under these high temperature conditions.

A decrease of the copper surface area together with the oxidation of copper caused the decay in catalytic activity for Cu/SiO$_2$. Iron additives obviously suppressed the decrease of copper surface area and catalyst deactivation. The small surface energy of copper would easily lead to migration of copper under high temperatures. The TPR study showed that iron was oxidized under the reaction conditions. Fe oxides may act as textural promoters which effectively suppress the sintering of Cu.

Instead of the oxidation of copper, an Fe species in the Cu–Fe catalyst was oxidized by the H$_2$/CO$_2$ stream. The TPR profile of an Fe$_2$O$_3$/zeolite catalyst has been reported: three reduction steps appeared at 695, 850 and 1000 K, respectively, when the catalyst was calcined at 773 K.[12] The lower temperature peak at 695 K corresponds to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$; the middle temperature peak at 850 K is due to the reduction of Fe$_3$O$_4$ to FeO; and the higher temperature peak at 1000 K is for the reduction of FeO to Fe^0. FeO can reasonably be deduced to be the major species in the Cu–Fe catalyst after the reduction treatment at 873 K for 5 h in this study. The TPR profile of our Cu–Fe/SiO$_2$ catalyst in Fig. 3 provides strong evidence that FeO can be oxidized to Fe$_3$O$_4$ and/or Fe$_2$O$_3$ during the reaction.

In summary, we have shown that Fe-promoted Cu/SiO$_2$ exhibits high activity and stability for the RWGS reaction. The Cu surface area was significantly improved at high temperature by Fe additives. The Fe promoter inhibits the sintering of Cu particles and oxidation of Cu, resulting in high catalytic activity and stability.

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