The role of copper in catalytic performance of a Fe–Cu–Al–O catalyst for water gas shift reaction† ‡

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A Fe–Cu–Al–O water gas shift catalyst with a Fe : Cu atomic ratio of 4 : 1 upon pretreatment at 350 °C in H₂ exhibits a conversion higher than a physical mixture of Fe–Al–O and Cu–Al–O by ~40% over a temperature range of 300 °C–450 °C. In situ ambient pressure X-ray photoelectron spectroscopy studies suggest that the surface region of Fe–Cu–Al–O was restructured into a double-layer structure consisting of a surface layer of Fe₂O₃ and a metallic Cu layer below it upon pretreatment at 350 °C. The strong metal (Cu)-oxide (Fe₂O₃) interface effect of this double layer structure enhances the catalytic activity of Fe₂O₃ in WGS.

The water-gas shift (WGS) reaction is critical in production of H₂ in chemical industries and removal of carbon monoxide in H₂ sources. Until recently there has been a lack of a satisfactory and wholly accepted picture of the mechanism of WGS at the molecular level. For WGS reactions used in chemical industries, Cu catalysts and Fe–Cr–O catalysts are typically used for low temperature and high temperature WGS, respectively. Many efforts have been made to improve the catalytic performance of Fe-based catalysts. For example, potential promotional roles of Co, Cu, Ag, Ba, Ce for Fe–Cr–O catalysts were examined. Fe–Cu–Al–O catalysts reported recently exhibit a comparable catalytic activity to Fe–Cr–O and other Fe-based catalysts. Cu is considered as a promoter for the high temperature WGS catalysts, Fe–Cu–Al–O. The mechanism of promotion by copper in Fe–Cu–Al–O is still unclear. One hypothesis is that CuO is reduced to metallic Cu which provides active sites for WGS even at high temperature WGS. The strong (Cu)-oxide (Fe₂O₃) interface effect of this double layer structure enhances the catalytic activity of Fe₂O₃ in WGS.

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(0.0375 mmol), which underwent the same pretreatment (350 °C in H2). In fact, over the catalytic temperature range of 300 °C–450 °C, conversion of Fe–Cu–Al–O is higher than that of the physical mixture by ~40%. This distinct difference shows the promotional effect of copper for WGS on Fe3O4.

To understand this promotional effect, surface chemistries of the Fe–Cu–Al–O catalyst during catalysis were tracked with our in-house AP-XPS system12 under catalytic conditions. This system has a flow reactor integrated into a monochromated Al Kα source and a differential pumping system. The catalyst is placed in the flow reactor. The volume of reactant/product gases in this reactor is about 10–15 ml. The gas delivery system attached to the flow reactor allows a flow rate of reactant gases of 5–20 ml min⁻¹, which is measured using mass flow controllers. This reactor has a window of Si3N4 to transmit an Al Kα and an aperture installed to engage a differential pumping system. The catalyst sample in a gas environment can be heated up to 600 °C.12–14 The partial pressures of CO and H2O are 1 Torr for each gas in the reactor. The flow rate of each gas is ~6 ml min⁻¹. The Fe–Cu–Al–O catalyst placed in the AP-XPS reactor was pretreated at 350 °C in 1 Torr H2 for one hour and then reactant gases were introduced for WGS reaction. During pretreatment and catalytic reaction, photoemission features of Cu 2p, Fe 2p, and Auger line Cu LMM were collected in the presence of reactant and product gases. The evolution of these photoemission features of Cu 2p, Fe 2p, and Cu LMM can reflect the changes of surface chemistry subject to the change of reaction conditions in terms of different reactants and reaction temperatures.

Fig. 2 presents the evolution of the Cu fraction in the total of Cu and Fe during pretreatment at 350 °C and the following catalytic reactions. A significant decrease of Cu fraction was identified upon pretreatment at 350 °C in H2. The measured fraction of the as-synthesized catalysts at room temperature in UHV is 23.5%; it decreased to only 8.1%. Fig. 3a presents the spectra of Cu 2p during pretreatment and catalysis. Cu2⁺ was clearly identified since the satellite peaks of Cu 2p3/2 at 914.0 eV and 943.4 eV and Cu 2p1/2 at 961.8 eV15,16 were clearly identified in this study. The main peaks of Cu 2p at 933.7 and 953.6 eV were clearly identified. The absence of photoemission peak at 932.7 eV of Cu/O15,16 shows a complete Cu²⁺ valence state of the as-synthesized catalyst. Photoemission features of Fe 2p at 711 eV and 724.1 eV and their satellite peaks (Fig. 3c1) show that the surface phase at room temperature is Fe3O4 instead of Fe2O3. Upon pretreatment at 350 °C in H2, Cu 2p satellite peaks disappeared and the peak position of Cu 2p3/2 down-shifted to 932.7 eV. Clearly, Cu2⁺ was reduced. Further analysis using the Auger parameter15,16 showed that the reduced copper is in fact metallic copper instead of Cu2⁺ (Fig. 3b). The Auger parameter for copper in the catalyst upon pretreatment is 1851.2 eV, which is the same as the value of metallic Cu reported in other studies.15,16 Photoemission features of Fe 2p (Fig. 3c) suggest that Fe2O3 was reduced to Fe3O4 upon pretreatment at 350 °C in H2. Notably, there is no photoemission feature at the peak position of metallic Fe17 at 707.0 eV and 720.1 eV. Thus, there is no metallic Fe formed during the reduction. The in situ studies using AP-XPS showed that Cu2⁺ in the Fe–Cu–Al–O (Fig. 4a) is reduced to its metallic form, and iron exists in the form of Fe3O4 upon pretreatment at 350 °C in H2 for one hour.

The decrease of atomic fraction upon pretreatment (from ~24% to ~8%) does not allow us to suggest a segregation of metallic Cu to the surface since XPS is a surface-sensitive technique. In fact, this in situ surface observation shows that Cu is remained at a region near the surface (or subsurface) as schematically shown in Fig. 4b. The photoemission features of Cu 2p and Fe 2p of the Fe–Cu–Al–O catalyst observed during WGS reactions show the preservation of chemical states of Cu and Fe3O4 during these reaction (Fig. 3).

It is well acknowledged that the active phase of Fe3O4 for WGS is Fe2O4.1 Our in situ studies of a physical mixture of Fe–Al–O and Cu–Al–O are consistent with previous studies. During catalysis, copper and iron of the physical mixture of Fe–Al–O and Cu–Al–O exist in chemical states of Cu²⁺ and Fe3O4, respectively. However, catalytic performance of the physical mixture in terms of conversion are much lower than that of the Fe–Cu–Al–O catalyst. It suggested that the subsurface of metallic Cu in Fe–Cu–Al–O
formed during pretreatment at 350 °C and when located below the Fe$_3$O$_4$ layer plays a critical role in the promotion. As the atomic fraction of metallic Cu is significantly decreased (Fig. 2), a segregation of Cu to the surface and formation of Cu clusters on the surface of Fe$_3$O$_4$ (Fig. 4c) was not supported. As AP-XPS showed that Fe$_2$O$_3$ was reduced to Fe$_3$O$_4$ and Cu$^{2+}$ to Cu during the pretreatment, we suggest that Fe$_3$O$_4$ is located above the subsurface Cu layer, as shown in Fig. 4b. The catalyst upon pretreatment can be considered as a reverse catalyst since oxide layers are supported by metal layers. Based on surface sensitivity of XPS, the thickness of the Fe$_3$O$_4$ layer could be a couple of nm.

On the other hand, the as-synthesized Fe–Cu–Al–O catalyst was pretreated at 400 °C in 1 Torr H$_2$ for one hour. WGS reaction was performed after pretreatment at 400 °C. Fig. 1b presents the conversion of Fe–Cu–Al–O at 300 °C–450 °C upon this pretreatment. AP-XPS studies of Fe–Cu–Al–O upon pretreatment at 400 °C in H$_2$ show that the atomic fraction of Cu is 16.3% instead of the 8.5% of the catalyst pretreated at 350 °C. Surprisingly, it exhibits a quite different catalytic performance in contrast to that pretreated at 350 °C. The conversion at 300 °C is 39.2% (Fig. 1b) which is 6% lower than that pretreated at 350 °C (Fig. 1a). The difference is larger at higher temperature. To understand this difference, in situ AP-XPS studies were performed upon pretreatment at 400 °C. Fig. 5 presents the photoemission features of Cu 2p and Fe 2p of the Fe–Cu–Al–O catalyst upon pretreatment at 400 °C in H$_2$. Similar to the catalyst pretreated at 350 °C, Cu$^{2+}$ was reduced to metallic Cu. However, it is noted that Fe$_2$O$_3$ was partially reduced to metallic Fe upon pretreatment at 400 °C in H$_2$, which is evidenced by the observation of the shoulders at 707.0 eV and 720.1 eV (Fig. 5c2). These peaks were not observed for the catalyst pretreated at 350 °C in H$_2$ (Fig. 3c). The ratio of metallic Fe is about 12% of the total iron element or 10% of the total of iron and copper element. Thus, Fe is almost two thirds of the fraction of Cu in the surface region. Fig. 4d schematically shows the structural model of the surface consisting of metallic Cu and Fe upon pretreatment at 400 °C. Fe$_3$O$_4$ layers are buried below layers of Cu and Fe. The photoemission features of Fe 2p and Cu 2p during catalysis upon pretreatment at 400 °C are presented in Fig. 5. Notably, the peak of metallic Fe disappeared upon exposure to H$_2$O and CO (c3–c6 in Fig. 5), though metallic Cu still remained. Based on the binding energy of the Fe 2p photoelectron, we expect that metallic iron formed during the pretreatment in H$_2$ at 400 °C can be changed to an oxidizing state of iron such as FeOOH. We excluded the possibility of oxidizing metal Fe to Fe$_3$O$_4$ since its catalytic performance is quite different from that from pretreatment at 350 °C (Fig. 1b versus Fig. 1a). As Cu remains in its metallic state over the whole temperature range of 300 °C–450 °C (Fig. 5b), the metallic Cu is suggested to be the active phase on the Fe–Cu–Al–O catalyst upon pretreatment at 400 °C. Due to the lack of a Fe$_3$O$_4$ layer right next to the metallic Cu layer, there is no strong oxide–metal interaction in the Fe–Cu–Al–O pretreated at 400 °C. Conversion of CO is further decreased at 400 °C and 450 °C. It probably results from aggregation of Cu clusters at a higher temperature.

In order to confirm the difference between restructured surfaces, Fe–Cu–Al–O underwent a pretreatment at 350 °C (case 1), a pretreatment at 400 °C (case 2), and a sequential pretreatment at 350 °C and a followed pretreatment at 400 °C (case 3) for the same catalyst, simultaneous in situ studies of the catalyst surface using AP-XPS were performed. Fig. 6 presents the atomic fraction of case 3. Obviously, the atomic fractions of copper in the sequential pretreatments (case 3) in Fig. 6 are identical to those upon pretreatment performed at 350 °C (case 1) or 400 °C (case 2) independently. It confirmed that pretreatment at different temperature regimes forms different surface structures, which significantly influences the following catalytic performance.

In situ AP-XPS studies of Fe–Cu–Al–O suggested that upon pretreatment at 350 °C in H$_2$ copper is reduced to metallic Cu at the subsurface below a layer of Fe$_3$O$_4$ which is preserved during WGS reaction. This strong Cu–Fe$_3$O$_4$ interface interaction significantly promotes the WGS on Fe$_3$O$_4$.

Notes and references