

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

Yingchun Ye, Lei Wang,§ Shiran Zhang, Yuan Zhu, Junjun Shan and Franklin (Feng) Tao*

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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 Fe₃O₄ and a metallic Cu layer below it upon pretreatment at 350 °C. The strong metal (Cu)–oxide (Fe₃O₄) interface effect of this double layer structure enhances the catalytic activity of Fe₃O₄ 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.¹ For example, potential promotional roles of Co, Bu, Ag, Ba, Ce for Fe–Cr–O catalysts were examined.^{2–10}

Fe–Cu–Al–O catalysts^{2,3,9} reported recently exhibit a comparable catalytic performance to Fe–Cr–O and other Fe-based catalysts.⁸ 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. Another argument is that the integration of CuO into Fe₃O₄ could aid charge transfer since an effective charge transfer between Fe²⁺ and Fe³⁺ coordinating with octahedral oxygen atoms in Fe₃O₄ was proposed as the mechanism taking place on Fe₃O₄^{1,11} for high temperature WGS. Elucidation of the promotional effect of Cu in Fe-based WGS catalysts including Fe–Cu–Al–O need to identify oxidation states of copper and iron and measure their surface compositions. Active phase can be oxidized readily once they are exposed to

an ambient environment. Thus, it is necessary to carry out *in situ* studies which track the oxidation state of catalytic sites and measure the composition of the catalyst with high surface sensitivity during catalysis. Due to the technical challenge in such a surface analysis during catalysis, exploration of the promotional effect of Cu for WGS in Fe-based catalysts has been behind the advance^{2,3,9} in catalyst synthesis and experimental evaluation of their catalytic performances.

Here we synthesized an Fe–Cu–Al–O catalyst with an atomic ratio of Fe : Cu of 4 : 1. *In situ* studies using in-house ambient pressure XPS (AP-XPS)¹² in our group and measurement of catalytic performances were carried out under similar conditions. Surface composition and oxidation state of Cu and Fe were tracked and studied under reaction conditions. A correlation between surface chemistry and catalytic performance was built. This correlation suggests a strong metal (Cu) and oxide (Fe₃O₄) interaction which is responsible for the promotional effect of Cu on Fe₃O₄ in the Fe–Cu–Al–O catalysts for WGS.

Fe–Cu–Al–O was synthesized using a method reported by Ozkan *et al.*⁹ X-ray diffraction patterns of the as-synthesized Fe–Cu–Al–O catalyst were readily assigned to hematite phase (γ -Fe₂O₃, ICDD#04-0755). Although magnetite (Fe₃O₄, ICDD# 11-0614) has very similar diffraction patterns in the range of 20°–70°, we do not think this is a magnetite phase since the last step of the preparation of these catalysts is calcination in air. In fact, only hematite phase was identified in the as-synthesized catalyst. Notably, there is neither metallic Cu nor oxide phase such as Cu₂O or CuO. XRD patterns suggested that copper does not exist as a separate phase; alternatively, Cu²⁺ is incorporated into the lattice of Fe₂O₃. The valence states of copper and iron in those catalysts were confirmed by our XPS studies and will be discussed in the following paragraphs.

Fig. 1 shows the catalytic performances of Fe–Cu–Al–O (0.15 mmol iron and 0.0375 mmol copper) upon different pretreatments (Fig. 1a and b) and a physical mixture of Fe–Al–O (0.15 mmol iron) and Cu–Al–O (0.0375 mmol copper) (Fig. 1c) upon a pretreatment at 350 °C in H₂ for one hour. All these catalysts have the same amount of iron (0.15 mmol). The difference in catalytic activity between Fe–Cu–Al–O and a physical mixture of Fe–Al–O and Cu–Al–O is distinct. At 300 °C, Fe–Cu–Al–O (0.15 mmol) pretreated at 350 °C exhibits a higher conversion by ~40% in contrast to a physical mixture of Fe–Al–O (0.15 mmol) and Cu–Al–O

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA. E-mail: ftao@nd.edu

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§ Current address: Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

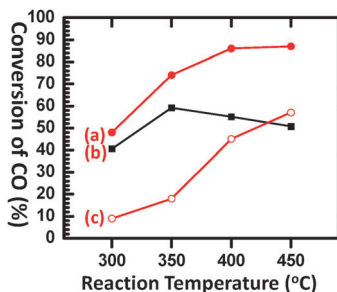


Fig. 1 Conversion of CO in WGS on Fe–Cu–Al–O upon pretreatment at 350 °C in H₂ (a) and 400 °C in H₂ (b) and on the physical mixture of Fe–Al–O and Cu–Al–O upon pretreatment at 350 °C in H₂ (c).

(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 K α 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 K α 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

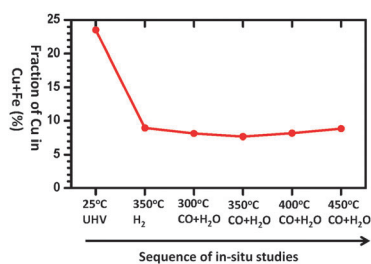


Fig. 2 Atomic fraction of Cu in the total of Cu and Fe measured with AP-XPS under reaction conditions (pretreatment and catalysis).

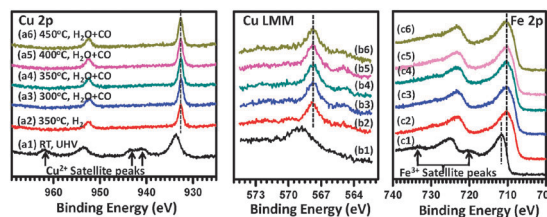


Fig. 3 AP-XPS studies of Cu 2p, Cu LMM and Fe 2p of the Fe–Cu–Al–O catalyst under reaction conditions upon pretreatment at 350 °C in H₂.

pretreatment and catalysis. Cu²⁺ was clearly identified since the satellite peaks of Cu 2p_{3/2} at 941.0 eV and 943.4 eV and Cu 2p_{1/2} at 961.8 eV^{15,16} 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⁺/Cu^{15,16} 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 Fe₂O₃ instead of Fe₃O₄. Upon pretreatment at 350 °C in H₂, Cu 2p satellite peaks disappeared and the peak position of Cu 2p_{3/2} down-shifted to 932.7 eV. Clearly, Cu²⁺ was reduced. Further analysis using the Auger parameter^{15,16} showed that the reduced copper is in fact metallic copper instead of Cu⁺ (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 Fe₂O₃ for WGS is Fe₃O₄.¹ 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 Cu⁰ 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

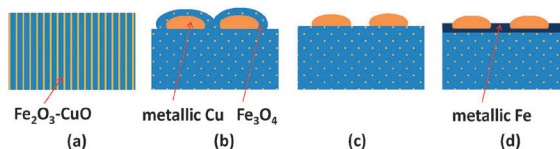


Fig. 4 Schematics showing surface structures under different conditions. (a) As-synthesized. (b) Fe₃O₄–Cu double layers during catalysis pretreatment at 350 °C in H₂. (c) Potential Cu–Fe₃O₄ structure. (d) Surface layer consisting of Cu and Fe nanoclusters during pretreatment at 400 °C in H₂.

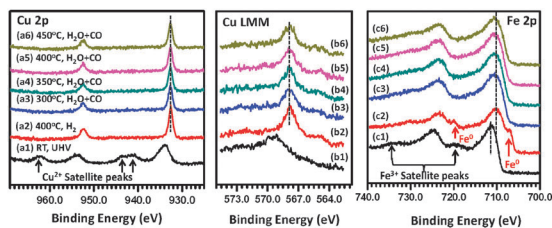


Fig. 5 AP-XPS studies of Cu 2p, Cu LMM and Fe 2p of the Fe–Cu–Al–O catalyst under reaction conditions upon pretreatment at 400 °C in 1 Torr H₂ for 1 h.

formed during pretreatment at 350 °C and when located below the Fe₃O₄ 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 Fe₃O₄ (Fig. 4c) was not supported. As AP-XPS showed that Fe₂O₃ was reduced to Fe₃O₄ and Cu²⁺ to Cu during the pretreatment, we suggest that Fe₃O₄ 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 Fe₃O₄ 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 H₂ 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 H₂ 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 H₂. Similar to the catalyst pretreated at 350 °C, Cu²⁺ was reduced to metallic Cu. However, it is noted that Fe₃O₄ was partially reduced to metallic Fe upon pretreatment at 400 °C in H₂, 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 H₂ (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. Fe₃O₄ 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 H₂O 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 H₂ at 400 °C can be changed to an oxidizing state of iron such as FeOOH.¹⁸ We excluded the possibility of oxidizing metal Fe to Fe₃O₄ since its catalytic performance is quite different from that pretreated 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

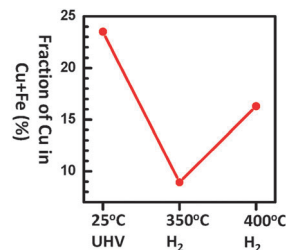


Fig. 6 Evolution of the Cu fraction in the total of Cu and Fe upon pretreatment at 350 °C and a followed one at 400 °C in 1 Torr H₂ for 1 h.

catalyst upon pretreatment at 400 °C. Due to the lack of a Fe₃O₄ 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 H₂ copper is reduced to metallic Cu at the subsurface below a layer of Fe₃O₄ which is preserved during WGS reaction. This strong Cu–Fe₃O₄ interface interaction significantly promotes the WGS on Fe₃O₄.

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