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The preparation and activity of Cu-Fe-Zr-Ce based catalysts for water gas shift

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Abstract. CeO₂-ZrO₂ composite oxide was synthesized with precipitation method as support and Cu₅Fe₆(ZrCe₄)₈Oₓ catalysts were prepared by impregnation; X-ray diffraction, H₂ temperature program reduction, and scanning electron microscope techniques were jointly used to characterize the crystal phases and reduction properties of catalysts. Then the activity of catalysts in water gas shift was studied; thus investigated how catalyst composition impacted the water gas shift. Conclusions drew from the results can be briefly stated. Cu₅Fe₆(ZrCe₄)₈Oₓ was provided with stable cubic crystalline framework and Cu and Fe, as the active components, was highly dispersed on the surface of supports in the form of CuO and Fe₂O₃ respectively. The strong interactions between copper and iron component enhanced the reducing capacity of CuO and Fe₂O₃. Cu₅Fe₆(ZrCe₄)₈Oₓ catalysts exhibited high catalytic activity and selectivity while the main active components were Cu and Fe₃O₄. The CO conversion rate reached 96% when Cu₇Fe₃(ZrCe₄)₈Oₓ catalysts was used in water gas shift at 623K and the only products were H₂ and CO₂. The activity was still desirable even the catalysts was applied at 723K.

1. Introduction

Water Gas Shift (WGS) is widely used in industrial manufacturing processes such as the synthesis of ammonia, purification of automotive exhaust, exploitation of hydrogen resource. From a thermodynamic point of view, this shift (CO+H₂O→H₂+CO₂) is a reversible exothermic reaction, and a lower reaction temperature is more favorable to the positive occurrence of the reaction which means catalysts with high activity at low temperature are required [1]. Cu-Zn catalyst is well accepted in WGS, however sintering deactivation makes it hard to dedicate in long-term reaction which leads to the development of other WGS catalysts including noble metals and transition metals as active components such as Pt, Ru and Au [2, 3]. Even though high activity and stability at low temperature are exhibited in the WGS, the high cost and scarcity of resources have limited the application of precious metal based catalysts. Due to the reasons above, low-cost catalysts with high activity and stability at low temperature have become the focus of the research.

It was reported that the CeO₂ crystal structure contains rich oxygen vacancies which is ideal for oxygen storage and oxygen evolution, thus makes it possible to promote a fast redox conversion [4, 5]. Also the high probability of strong interaction with other metal can improve the activity and selectivity of catalysts thus makes ceria a popular support of catalysts. Unfortunately, the stability of pure CeO₂ needs to be improved since it would be sintered at high temperature [6]. Recent researches shown that catalytic activity and thermal stability of catalysts could be dramatically improved by mixing stable
cation such as Zr\textsuperscript{4+} into Ce\textsubscript{2}O\textsubscript{3} [7]. Other studies suggested relatively approving catalytic activity of copper-based catalyst and iron-based catalyst when they were applied in WGS [8, 9], yet less reports about Cu-Fe-Ce-Zr based catalysts in WGS had been found. Based on this, preparation method, characterization results and catalytic performance of catalysts in WGS will be introduced in this article.

2. Experiment
Catalyst support was prepared by coprecipitation method and the active component is loaded by impregnation method. The catalyst activity was evaluated in a fixed bed microreactor. Then X-ray Powder Diffraction Method (XRD) was used to determined the crystal structure of catalyst. And at last the reduction characteristics of catalysts were studied by temperature-programmed reduction (TPR).

2.1. Catalyst preparation
The Ce\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} composite oxide supports, molar ratio of Zr:Ce were 1:4, were prepared by co-precipitation method with starting material of cerous nitrate - zirconium nitrate aqueous solution and precipitant of ammonium carbonate. A certain amount of cetyltrimethylammonium bromide (CTAB) was added separately into the prepared ammonium carbonate aqueous solution with a concentration of 0.5mol·L\textsuperscript{-1} and mixed solution of Zr(NO\textsubscript{3})\textsubscript{4} and Ce(NO\textsubscript{3})\textsubscript{3} with a Ce\textsuperscript{3+} + Zr\textsuperscript{4+} ion concentration of 0.5mol·L\textsuperscript{-1}. Added dropwise the mixed solution of Zr(NO\textsubscript{3})\textsubscript{4} and Ce(NO\textsubscript{3})\textsubscript{3} into aqueous ammonium carbonate solution with vigorous stirring, and kept the stirring for a time. After filtration, the filtrate cakes were washed by deionized water and anhydrous ethanol separately for several times, and then dried at 80\degree C for 8h. Catalyst supports were obtained after calcination at 400\degree C and 600\degree C each for 4h. Copper nitrate and iron nitrate were loaded by impregnation method and after a desiccation and calcinations at 600\degree C for 3h Cu\textsubscript{6}Fe\textsubscript{6} (ZrCe\textsubscript{4})\textsubscript{8}O\textsubscript{20} catalyst was obtained with the Cu:Fe molar ratios of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 2:8.

2.2. Evaluation of Catalytic activity
Water Gas Shift reaction was carried out in a down flow fixed bed quartz tubular reactor (inner diameter 10 mm) under atmospheric pressure and 500 mg catalyst (particle diameter 0.4~0.8 mm) was loaded. Before the reaction, the catalyst would be reduced with H\textsubscript{2} (30 mL·min\textsuperscript{-1}) at 400\degree C for 1h. Then the reactor with the sample was cooled down to room temperature swept with CO (10 mL·min\textsuperscript{-1}). Using a micro-pump at the rate of 0.036 mL·min\textsuperscript{-1}, highly purified water was infused in to a vaporizer heated to 200\degree C and then introduced to the reactor. The obtained gas mixture was cooled at 0\degree C using a condenser and the dry gas mixture was analyzed by a SP-6800A equipped with TCD detector. Afterward, the calibrated gas mixture of known composition was used for quantification.

2.3. Catalyst characterization
The examined sample was pretreated in situ in Ar stream (600\degree C, 20 mL·min\textsuperscript{-1}, 40min) before the TPR test. Then the reactor with the sample was cooled down to room temperature, after which the stream was replaced with H\textsubscript{2} (5%)-Ar (95%) mixtures with the rate of 40 mL·min\textsuperscript{-1}. Generally, the TPR measurements were carried out at 10\degree C·min\textsuperscript{-1}. X-Ray Diffraction (XRD) patterns were collected on a 8D ADVANCE powder diffractometer using Cu K\alpha radiation (Germany, 60KV, 300mA).

3. Results and discussion
It was characterized by XRD measurements that ZrCe\textsubscript{4}O\textsubscript{20} composite oxide, as the support of catalyst, retained the lattice characteristics of Ce\textsubscript{2}O\textsubscript{3} which was the cubic crystalline phase. The lattice structure of this support was stable as catalyst was subjected to a hydrogen reduction process and applied in the WGS reaction process. The active component of the catalyst, such as copper and iron, was highly dispersed on the surface of the support. The copper component mainly existed as Cu. In the meanwhile, no diffraction peaks of iron component were detected which indicated that the iron component was highly dispersed on the surface of the support, as stated above. The results of TPR measurements exhibited strong interactions between these two components which might lead to partial reduction of
CuO and Fe₂O₃ by hydrogen at lower temperature. Thereinto CuO could be reduced to Cu₂O in the above-mentioned reduction at temperature lower than 100°C, while Fe₂O₃ could be reduced to Fe₃O₄ at around 225°C. Besides, as Cu₉Fe₈ (ZrCe₄)Oₓ catalysts had better performance in catalytic activity of WGS when the temperature was between 400°C~500°C, it seemed that the Cu and Fe₃O₄ were the active component in WGS reaction. The loading of active component and the ratio of Cu to Fe, moreover, indicated their impacts on catalytic activity to some degree.

### 3.1. XRD analysis

Figure 1-L1 shows XRD patterns of ZrCe₄Oₓ support. In the case of ZrCe₄Oₓ, the diffraction patterns are in good agreement with those of single ceria typical cubic structure (2θ=28.56°, 33.08°, 47.48°, 56.33°; 59.09°; 69.40°; 76.70°; 79.07°; 88.41°; JCPDS:34-0394). Moreover, no characteristic diffraction peaks of the doped zirconium or zirconia appear, which means Zr⁴⁺ ion has permeated the lattice of CeO₂. Figure 2 and figure 3 illustrating the XRD patterns of cubic-phase CeO₂ have no significant change in all Cu₉Fe₈(ZrCe₄)Oₓ catalysts which indicates a stable crystal structure of cubic-phase CeO₂ in support after high temperature reduction.

Figure 2 demonstrates XRD patterns of several fresh catalysts of Cu₉Fe₈(ZrCe₄)Oₓ. No characteristic diffraction peak of CuO is observed when copper content is relatively low (see figure 2-a1), which suggests its high dispersion over the supports. However with the increase of copper content, the characteristic diffraction patterns of monoclinic structure CuO (2θ=35.5°; 38.73°; JCPDS: 45-0937) appear clearly and their intensity grows with copper content. This phenomenon implies that CuO nanocrystallite grows up progressively with the amount of copper. Figure 3 shows XRD patterns of catalysts with different molar ratios of Cu:Fe after the reaction under temperature of 400°C. No diffraction peak of CuO can be observed in this picture which means CuO has been reduced to Cu. However, there is no diffraction peak of “Cu” phase recorded by XRD when copper content is lower (see figure 3-a2), because copper components are highly dispersed over the supports. But diffraction peak of cubic Cu appears with increasing percentage in composition of Cu (2θ=43.4°, 50.8°; JCPDS: 65-9743). The experimental results shown that XRD peaks were strengthened with the increasing percentage of Cu in composition. The used catalyst was analyzed by XRD so that the existence form of copper components in water gas shift reaction could be investigated. Two phases, cubic Cu and monoclinic CuO (small-signal), were observed by XRD, as presented in figure 1-L2. The figure demonstrated the transition of Cu to CuO after the reaction with water (Cu + H₂O → CuO + H₂).

![Figure 1. XRD patterns of catalyst used and fresh support.](image1.png)

![Figure 2. XRD patterns of fresh catalyst.](image2.png)
Figure 3. XRD patterns of after 400 °C reduction.

a2: (Cu2Fe5)(ZrCe8)O13  b2: (Cu6Fe5)(ZrCe8)O13
c2: (Cu2Fe5)(ZrCe8)O13  d2: (Cu6Fe5)(ZrCe8)O13
e2: (Cu6Fe5)(ZrCe8)O13  α:CeO2, β:Cu, γ:CuO

Figure 2 and 3 do not imply any characteristic diffraction peaks of the doped iron or ferric oxide, which might due to the high dispersion of Fe2O3 on the supports promoted by the coexistent copper species and the overlapping effect of copper species on iron species. In fact, the 120 °C decomposition temperature of ferric nitrate is lower than copper nitrate’s 170 °C which means during the calcination, Fe(NO3)3 will be decomposed prior to Cu(NO3)2 and the products will exist as Fe2O3 in crystalline form on the surface of supports. With the increase of calcination temperature, CuO, as the decomposition product of Cu(NO3)2, will be mixed with Fe2O3 and adhere to the surface of Fe2O3 crystalline grain and become a disincentive of grain growth [10, 11]. As the grain size of Fe2O3 is too small to be detected, there is no record during the XRD analysis process of iron oxide phase. On the contrary, CuO which exists on the surface of complex oxide, has much lower growth activation energy and higher growth rate. These features make it easy to shape larger size crystals so that produce a diffraction peaks during XRD analysis.

3.2. TPR analysis

Figure 4 indicates the TPR profiles of Cu2Fe5(ZrCe8)O13 catalysts. In the figure demonstrating H2-TPR process under the condition of 10 °C·min–1, catalysts with higher level of iron components content (see curve b, c, d, e in figure 4) present three reduction peaks of copper components under the stage of low temperature (marked as t1, t2, t3 in figure 4), and the peak temperatures are 108 °C, 150 °C, 200 °C respectively. However, with the decrease of iron content, t1 become lower and lower and it even disappear in the TPR of the catalysts with the lowest iron content such as (Cu2Fe5)(ZrCe8)O13 (see curve f in figure 4). Concerning the fact that no diffraction peaks of CuO in XRD result of (Cu2Fe5)(ZrCe8)O13 (figure 2-a1), its t1 peak can be attributed to reduction peak of CuO which has the characters of high dispersion and strong interaction with Fe2O3 (2CuO + H2 → Cu2O + H2O). While t2 can be cataloged to reduction peak of CuO with larger crystalline grain (2CuO + H2 → Cu2O + H2O) and t3 goes to overlapping reduction peaks of Cu2O (Cu2O + H2 → 2Cu + H2O) and the remaining CuO.

The attribution of t3 peak can be obtained by analyzing the sum of three reduction peak areas of copper components (figure 4). In figure 4, it is obvious that the sum of t1 and t2 peak areas is smaller than that of t3, which indicates the incomplete reduction of CuO→Cu2O under 150 °C, while the reaction of Cu2O→Cu has already begun at the temperature lower than 200 °C. To have a better understand of to what extent the reduction of CuO→Cu2O takes place under 150 °C, TPR experiment is implemented at the heating rate of 1 °C·min–1 (see figure 5). It is observed that the temperature of three reduction peaks of copper component all move toward a low temperature zone and the peak temperature of t1, t2, t3 are 65 °C, 110 °C, 150 °C respectively. The same phenomenon that sum of t1 and t2 peak area is lower than t3 peak area appears at this stage. Afterward, these two figures with controlled catalysts in reduction reactions for 2h under 150 °C and 200 °C was reexamined respectively, and the reduction peak area of the former (150 °C) was still smaller than the latter one (200 °C). The
results above verify the fact that the reduction of CuO→Cu₂O cannot transform completely under 150°C, however the process of Cu₂O→Cu has taken place before 200°C (the temperature would be 150°C with a heating rate of 1°C·min⁻¹), that means there is a cross phenomenon between the two reduction. The above-mentioned can be explained by the overlapping effect of the outside Cu₂O on the inside CuO. As Cu₂O is reduced by H₂ and transform into Cu under a relatively high temperature, without the coverage of Cu₂O, the left CuO can be reduced by H₂. Previous study [12] asserts that during the reduction process, CuO transform into Cu⁺ which is easy to absorb H₂, thus stimulates the electron transfer in the catalyst system and reduction of the inside CuO, and makes t₃ peak far more bigger than t₂ peak.

![Figure 4. TPR profiles of (Cu₄Fe₆)(ZrCe₈)Oₓ](image)

There are two reduction peaks at the high temperature zone in the TPR profile of Cu₄Fe₆(ZrCe₈)Oₓ, marked as δ and ε respectively (see figure 4(b, c, d, e, f)) and they can be attributed to reduction hydrogen consumption peak of iron component in catalysts. δ, as the shoulder peak, its peak temperature is around 225°C and is regarded as the reduction hydrogen consumption peak of Fe₂O₃→Fe₂O₃ reduction step. The other broad peak (ε) with peak temperature of 520°C is attributed to the reduction hydrogen consumption peak of the transition Fe₃O₄→(FeO)→Fe. It is also observed that there are three-step mechanism in TPR of pure Fe₂O₃ [13], as the reduction peaks at 400°C, 500°C and 655°C could be assigned to the step reductions of Fe₂O₃→Fe₂O₃→FeO→Fe. Apparently, there are two significant differences between our TPR results of Cu₄Fe₆(ZrCe₈)Oₓ and early research. One is that the reduction process of Fe₂O₃→FeO appears in a relatively low temperature zone of Cu₄Fe₆(ZrCe₈)Oₓ’s TPR curve. The other is that there is only one broad peak of Fe₂O₃→(FeO)→Fe which is a two-step reaction on Cu₄Fe₆(ZrCe₈)Oₓ’s TPR curve. A TPR test of (Fe₁₉) (ZrCe₈)Oₓ is implemented in order to find out what leads to these discrepancies (see figure 4-a). Three reduction peaks of (Fe₁₉) (ZrCe₈)Oₓ appear at 400°C, 520°C and 630°C, and the XRD results of these three peaks (figure 6) indicate three steps reduction of Fe₂O₃→Fe₂O₃→FeO→Fe. It is clear that during the whole TPR test of Cu₄Fe₆(ZrCe₈)Oₓ, δ peak appears at a much lower temperature (225°C) than the first reduction peak temperature (400°C) of (Fe₁₉) (ZrCe₈)Oₓ, because copper has a dispersion effect on Fe₂O₃ and there are interactions between them which strengthen Fe₂O₃’s ability of being reduced, thus lower the required temperature of reduction. Again, copper component plays the vital role in the Fe₂O₃→(FeO)→Fe process, which make ε a broad peak in Cu₄Fe₆(ZrCe₈)Oₓ’s TPR test and is similar to what has been reported [14].

![Figure 5. TPR profiles of (Cu₄Fe₆)(ZrCe₈)Oₓ.](image)
3.3. Catalytic activity

It was found that (Cu₇Fe₃)(ZrCe₄)Oₓ catalyst showed good catalytic activity in the reaction of water gas shift and no obvious inactivation was detected which suggests a good stability. Gas phase product only contains CO, H₂, CO₂, but no CH₄, indicating that the methanation reaction did not happen in the process of catalytic reaction. Methanol, formaldehyde, formic acid and carbon-containing organic was not observed in liquid product detection. Figure 7 and figure 8 illustrate the relationship between conversion rate of CO and the catalyst composition under different temperature.

![Figure 6. XRD spectras of (Fe₁₀)(ZrCe₄)Oₓ.](image)

h1: catalyst after 400°C reduction  
h2: catalyst after 520°C reduction  
h3: catalyst after 630°C reduction

\(\alpha: CeO_2, \mu: FeO, \rho: FeO\)  
\(\nu: Fe_3O_4\)  
\(\phi: Fe_2O_3\)

![Figure 7. The influence of Cu:Fe molar ratio on catalytic activity.](image)

![Figure 8. Effects of active component load amount.](image)

Figure 7 displays that loaded Cu:Fe ratio has certain influences on the catalytic activity, and the catalytic activity reaches the top when the Cu:Fe ratio is 7:3, while the conversion rate of CO reached to 89% under 400°C. However, the catalytic activity will decrease no matter the Cu:Fe>7:3 or Cu:Fe<7:3. This result indicates that iron is a vital active component and there is a synergistic effect between iron and copper species during the water gas shift reaction. Such effects would change with the Cu/Fe ratio which ensured a proper proportion of active component that effectively increased catalytic activity [15].

Figure 8 presents the activity of catalysts in water gas shift with different loading amount of active component. It is clear that with the increase of active component’s loading amount, the activity of the catalyst enhanced gradually, but excess active component can also decrease catalytic activity. (Cu₇Fe₃)(ZrCe₄)Oₓ is the one with the highest catalytic activity. At 350°C, CO conversion rate reaches 96%, which can maintain a high catalytic activity even in the period of high temperature up to 450°C. The effects of loading amount of active component on the catalytic activity has also been reported in literature [16, 17]. Research on oxidation mechanism of CO indicated that the activated
CO adsorbed on the surface of active components (such as Cu, Fe, Ni) would be transformed into CO$_2$ when reacted with active oxygen species or active hydroxyl groups on the surface of the supports (such as CeO$_2$) [15, 18]. Thus there would be a satisfactory conversion rate from CO to CO$_2$ when the activated CO concentration of the catalyst surface matched the concentration of active oxygen or active hydroxyl groups. For this reason, when the amount of active component on the carrier surface was too large, the surface of the carrier would be overcovered and the concentration of active oxygen species or active hydroxyl groups on the surface of catalysts would decrease, leading to the decrease of the catalyst activity. The recently released report [19] further proved that the oxygen vacancy of the doped ceria carrier was often larger than that of the pure ceria, therefore there was a higher concentration of the surface active oxygen or active hydroxyl oxygen of the doped carrier.

4. Conclusion

The ZrO$_2$-CeO$_2$ composite oxide prepared by coprecipitation method was provided with stable cubic crystalline skeleton. Copper and iron, as the active components, having been loaded by impregnation method to obtain catalysts, was highly dispersed on the surface of supports in the form of CuO and Fe$_2$O$_3$ respectively. The strong interactions between copper and iron component enhanced the reducing capacity of CuO and Fe$_2$O$_3$. The elemental copper(Cu$^{0}$) and Fe$_2$O$_4$ were the main active components in WGS and the activity of catalyst would be affected by active component loading amount and Cu/Fe ratio. The prepared Cu,Fe$_x$(ZrCe)$_{1-x}$O$_2$ catalysts exhibited high catalytic activity and stability in WGS when temperature was between 400℃~500℃. The only two products, H$_2$ and CO$_2$, indicated favorable selectivity of this catalyst series.

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