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Effect of doping rare earth oxide on performance of copper-manganese catalysts for water-gas shift reaction

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Abstract: Rare earth-doped copper-manganese mixed oxide catalysts were prepared by coprecipitation and mechanical mixing using copper sulfate, manganese sulfate, and rare-earth oxides REO (REO indicates La_2O_3, CeO_2, Y_2O_3, or Pr_6O_{11}) as raw materials. The samples were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed reduction of oxidized surfaces (s-TPR), and temperature-programmed desorption (TPD). Catalytic activities were tested for a water-gas shift reaction. Doping rare earth oxides did not alter the crystal structure of the original copper-manganese mixed oxides but changed the interplanar spacing, adsorption performance and reaction performance. Doping with La_2O_3 enhanced the activity and stability of Cu-Mn mixed oxides because of high copper distribution and fine reduction. Doping with CeO_2 and Y_2O_3 also decreased the reduction temperatures of the samples to different degrees while improving the dispersion of Cu on the surface, thus, catalytic activity was better than that of undoped Cu-Mn sample. The Pr_6O_{11}-doped sample was difficult to reduce, the dispersion of surface coppers was lowered, resulting in poor activity.

Keywords: rare earth oxide; copper-manganese catalyst; water-gas shift reaction; stability

The water-gas shift reaction (WGSR) is used in industrial catalytic processes to control the H_2/CO ratio in syngas or reduce CO. Traditional shift catalysts include Fe_2O_3-Cr_2O_3 and $CuO/ZnO/Al_2O_3$ catalytic systems. In recent years, investigations on new catalyst have received considerable attention at home and abroad[1–4]. Cu-Mn catalysts have been extensively examined[5–9]. Since the beginning of 1920, Cu-Mn catalysts have been used for many catalytic processes, such as the oxidation of carbon monoxide[10], VOC removal, low-temperature NO reduction, and other industrially important hydrogenation and oxidation reactions including the WGSR[11] because of their excellent catalytic oxidation. The different preparation methods and conditions for Cu-Mn catalysts lead to substantial differences in their composition, structure, and catalytic performance[12,13]. Many studies have focused on optimizing preparation conditions, such as the type and concentration of precipitators, temperature, pH of the precipitation process, and aging time, because these factors significantly affect the precipitation reaction and catalyst performance[14,15]. Mirzaei et al.[16,17] found that other preparation factors such as solution pH and temperature significantly influence the composition, structure, and valence of Cu and Mn ions in Cu-Mn catalysts. Their calcined sample is $Cu_xMn_{3−x}O_4$, and the x

and phase structure (e.g., $CuMn_2O_4$, $Cu_{1.4}Mn_{1.6}O_4$, $Cu_{1.5}Mn_{1.5}O_4$, and so on) differ with different aging conditions. The activity and thermal stability are also markedly different. Tanaka et al.[12,13] studied the effect of preparation conditions, concentrations of gas species, Cu/Mn ratio, and calcination temperature on the catalytic activity of Cu-Mn spinel oxide for the WGSR. Their results reveal that the highest activity is produced when the Cu/Mn ratio is approximately 1:2 and the Cu-Mn catalyst is calcined above 900 °C. The citric acid method is a good way of preparing a high-activity catalyst, in which the partial substitution of Fe or Al for Mn enhances the catalytic activity of the Cu-Mn spinel. Tabakova et al.[18] reported that the catalyst stability could be improved by applying novel preparation methods and using an appropriate support. They used urea-nitrate combustion to prepare Cu-Mn catalysts and found that this method is more appropriate than coprecipitation for the preparation of active and stable Cu-Mn catalysts for the WGSR.

Rare earth elements are often used as co-catalysts because of the paramagnetism and mobility of the lattice oxygen and variable valence, their excellent oxygen storage and release activity during oxidation-reduction reactions, and their ability to significantly improve the

electron transmission and transfer ability of catalysts. Many studies have examined the effects of rare-earth-doping on WGSR catalyst. Andreeva et al.[19] prepared Au/CeO_2 catalysts doped with the rare-earth elements La, Sm, Gd, Yb, and Y by deposition-precipitation and found that catalysts doped with Yb and Sm exhibited high water-gas shift reactivity. In a previous study[20], doping Cu-Ce catalysts with La is found to improve the catalytic activity of Cu-Mn catalysts and promote their oxidation selectivity. Tabakova et al.[21] studied the effect of additives on the structural and catalytic properties of Cu/CeO_2. They found that adding Sm significantly increases catalytic activity. However, studies on rare-earth-doped Cu-Mn catalysts are limited. Zhang et al.[22] prepared Cu-Mn catalysts through coprecipitation and studied the effects of doping with Al_2O_3, BaO/Al_2O_3, ZrO_2/Al_2O_3 and CeO_2/Al_2O_3. They found that the CeO_2/Al_2O_3-doped catalysts have higher catalytic activity. He et al.[23] examined Cu-Mn catalysts doped with La and found that a doping amount of 0.5 mol.% on the samples is easier to reduce and that the adsorption of CO_2 is strong, thereby exhibiting the highest activity and stability. Du et al.[24] investigated the effect of a third metal (i.e., Ce, Zr, Zn, Fe, and Al) on WGS activity and stability. They found that WGS activities strongly depend on the nature of the dopant used and follow the order Zr>Fe>non-doped>Ce>Al>Zn. This finding indicates that a metal dopant is a good promoter for Cu-based catalysts. Furthermore, the additives Zr, Li, and Na change the particle size of the active metal and the distribution of the active site, thereby significantly altering the properties of Cu-Mn catalyst[24,25].

After years of research, the catalytic performance of Cu-Mn catalysts has been greatly improved. However, their application still has several gaps. The main problem is that Cu-Mn catalysts show poor activity at a low temperature, whereas their stability is expected to be further promoted.

Based on preliminary experiments in our laboratory, Cu-Mn catalysts were prepared in this work with Cu and Mn sulfates and rare-earth oxides (i.e., La_2O_3, CeO_2, Y_2O_3, and Pr_6O_{11}) as starting materials. To take advantage of the unique physical and chemical properties of rare earth elements, Cu-Mn catalysts were modified to improve their activity and thermal stability.

1 Experimental

1.1 Catalyst preparation

Cu-Mn catalysts were prepared by coprecipitation and mechanical mixing with $CuSO_4 \cdot 5H_2O$ and $MnSO_4 \cdot H_2O$ as starting materials. The molar ratio of Cu to Mn in the form of $CuSO_4 \cdot 5H_2O$ and $MnSO_4 \cdot H_2O$ was fixed at 1:1. Desired amounts of $CuSO_4 \cdot 5H_2O$ and $MnSO_4 \cdot H_2O$ were

dissolved to obtain a 0.225 mol/L mixed solution. NaOH solutions were prepared at 4 mol/L (1.2 times the theoretical calculated amount of NaOH) and pumped into a flask containing the $CuSO_4 \cdot 5H_2O$ and $MnSO_4 \cdot H_2O$ mixed solution at 45 °C with stirring at 300 r/min. The precipitate obtained after washing was dried in an oven at 80 °C for 4 h and then mechanically mixed with 3 mol.% La_2O_3, CeO_2, Y_2O_3, and Pr_6O_{11} in a mortar. After grinding for 0.5 h until good distribution is achieved, the samples were calcined in air at 550 °C for 4 h. The prepared catalyst samples were designated as Cu-Mn and CuMn-REO (REO indicates La_2O_3, CeO_2, Y_2O_3, or Pr_6O_{11}).

1.2 Catalyst tests

The catalytic activities and thermal stabilities of the Cu-Mn mixed oxide catalysts for the WGSR were examined using a plug-flow stainless-steel reactor (ID=6 mm). The WGSR was conducted at 200 to 450 °C, atmospheric pressure, and constant space velocity of 20 000 mL/g/h. The steam/gas ratio was 4. The amount of catalyst used to test catalytic activity was 0.5 g. Before the WGSR, the Cu-Mn mixed oxide catalysts were reduced using feed gas under the conditions described above. The standard composition of feed gas was 65.6 vol.% CO, 31.72 vol.% H_2, and 1.76 vol.% CO_2, and the balance was Ar. The feed gas and reaction tail gas were analyzed online using a gas chromatograph with a thermal conductivity detector (SP3420, BeifenRuanli, China). Unreacted water in the tail gas was removed using silica gel before gas chromatography sampling. Reactor temperature was increased by 2 °C/min. Catalytic activity was measured at 200 to 450 °C at 50 °C intervals and then at 450 °C for 3 h. Reaction temperature was then cooled to 200 °C, and catalytic activity was measured at 50 °C intervals. The reported data consisted of the average of three tests.

1.3 Catalyst characterization

The crystalline phase of the samples was analyzed by XRD (D8 Advance, Bruker, Germany) with Cu Kα (λ= 0.1541 nm) radiation operating at 40 kV and 40 mA with 2θ angles ranging from 20° to 80°. The scan rate was 2(°)/min.

Temperature-programmed reduction (TPR) and desorption (TPD) were performed with a chemical adsorption equipment (AutoChem2920, Micromeritics, USA) and determined using a thermal conductivity detector (TCD).

A 20 mg sample was loaded into a quartz U-tube reactor. Reduction was performed in a 5% H_2 or CO-Ar mixture gas flow (60 mL/min). The catalyst sample was purged in He (99.99%) flow (60 mL/min) at 120 °C for 60 min and then cooled to 40 °C under He stream. When the TCD signal was stable, a 5% H_2-Ar or CO-Ar mixture gas was switched to the reactor until the system