Synthesis and characterization of Cu-Zn mixed oxide catalysts synthesized by using different precipitants

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Abstract: The copper-zinc mixed oxide catalysts were synthesized via a co-precipitation method using different precipitants, and their physico-chemical properties were analyzed. The solid crystalline phases prepared varied widely depending on the precipitant used, and morphology and textural properties were also strongly influenced.

Keywords: Copper-zinc, precipitant, co-precipitation, malachite, CO oxidation

1. Introduction

In the methanol synthesis reaction, the Cu-Zn-Al composite oxide is the most widely used. In particular, metallic copper acts as an active component for hydrogenation, and thus it is very important to improve the exposed surface area of the copper species. Although it is known that introduction of ZnO component into composite structure results in an increase of copper surface area [1,2], the physico-chemical properties of ZnO depending on synthetic conditions have not been deeply studied. Thus, we synthesized CuO-ZnO (CZ) binary mixed oxide as a simple model structured catalyst, and physico-chemical properties depending on precipitant and aging temperature were carefully investigated.

2. Experimental

The CZ catalysts were synthesized via a co-precipitation method with different precipitants of 1 M of KOH , NaOH, Na_2CO_3, $NaHCO_3$, and NH_4OH. The precursors of copper and zinc were $Cu(NO_3)_2·3H_2O$ and $Zn(NO_3)_2·6H_2O$, respectively. The molar ratio of copper to zinc was fixed to 3/1. The pH of solution was controlled to 7.0, and the resulting solution was aged at room temperature for 24 h. The precipitate filtered was washed and dried at 100 ºC for overnight. Finally, dried samples were calcined at 350°C for 12 h. To characterize the catalysts, N_2 sorption, IPA-TPD, XRD, SEM, H_2-TPR, and CO oxidation were carried out.

3. Results and discussion

Fig. 1 shows XRD patterns of as-made and calcined Cu-Zn compounds. The as-made XRD pattern of the $NaHCO_3$ precipitant was malachite $Cu_2(OH)_2(CO_3)$ (JCPDS No.; 41-1390) which is very similar to $CuZn(CO_3)(OH)_2$ (JCPDS No.; 36-1475), and all other cases showed $Cu_2(OH)_3(NO_3)$ (JCPDS No.; 75-1779) and $Zn_3(OH)_4(NO_3)_2$ (JCPDS No.; 52-0627). The XRD patterns of $Cu_2(OH)_3(NO_3)$ and $Zn_3(OH)_4(NO_3)_2$ were very similar to each other. The XRD patterns after calcination showed mixed phases of CuO (JCPDS

No.; 48-1548) and ZnO (JCPDS No.; 36-1451), not Cu-Zn single phase. The textural properties of Cu-Zn mixed oxides calcined at 350 °C for 12 h are shown in Table 1. The BET surface area increases in the order of $NaHCO_3$, Na_2CO_3, KOH, NaOH, and NH_4OH. As-made malachite type has a larger BET surface area than the others. No acid sites were observed in the IPA-TPD for acid-base characterization due to the effect of ZnO, which is generally known to have a basic property. Catalytic activity of CO oxidation was found to be the best activity of the catalyst prepared using KOH precipitant, but no correlation was found between activity and BET surface area. These changes in activity are probably due to the effects of K and Na, which are present as residual components.

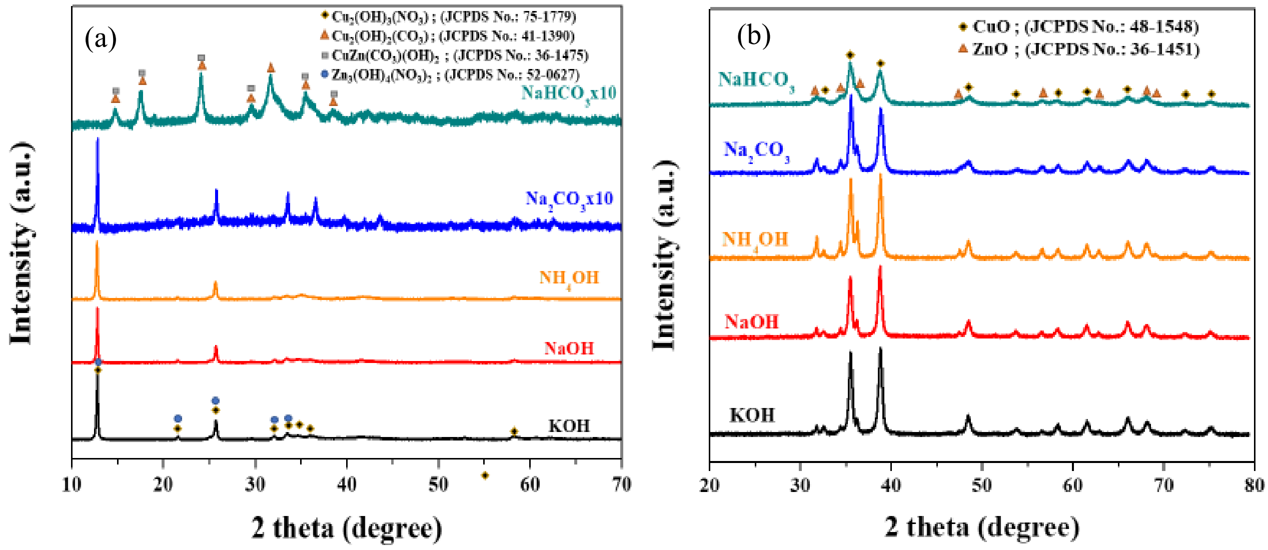

Fig. 1. XRD patterns of Cu-Zn mixed oxide; (a) as-made and (b) calcined at 350 °C for 12 h.

Table. 1. Textural properties of Cu-Zn mixed oxide calcined at 350 °C for 12 h and their catalytic activities in CO oxidation.

Precipitant	S_{BET} ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)	Temperature in CO oxidation (°C)		
				T10%	T50%	T90%
$NaHCO_3$	35.3	0.333	31.5	89	133	167
Na_2CO_3	20.5	0.105	22.3	95	143	160
NH_4OH	12.6	0.051	18.1	103	127	139
NaOH	17.2	0.076	19.7	96	119	130
KOH	20.2	0.077	16.7	85	117	128

4. Conclusions

In the synthesis of Cu-Zn mixed oxide, the precipitant for pH control had a great effect on catalytic activity and textural properties. The highest BET surface area was obtained when the KOH precipitant was used, but the catalyst prepared using KOH exhibited the best activity for the catalytic activity of CO oxidation reaction.

References

[1] H. Knozinger, P. Ratnasamy, Catal. Rev. Sci. Eng. 17 (1978) 31.

[2] C. Jeong, H. Ham, J. W. Bae, D.-C. Kang, C.-H. Shin, J. H. Baik, Y.-W. Suh, ChemCatChem 9 (2017) 4484-4489.