Synthesis and characterization of Cu/MgO with controllable interface based on Raney Cu by wet-mixing method

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A Cu/MgO composite was prepared through wet mixing method with modified Raney Cu with MgO. The texture of the Cu/MgO composite was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller (BET). The hydrogen adsorption and acid-base properties of the composite were tested by Hydrogen Temperature Programmed Desorption (H_2-TPD), CO_2-TPD and NH_3-TPD. Results showed that MgO was well dispersed within the pores of Raney Cu, and the contact interface of Cu and MgO was enhanced based on the large specific surface area of Raney Cu. A new phase of Cu-MgO was formed, and the surface properties of Raney Cu were modified.

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1. Introduction

Some composites produced by dispersing metals on oxides have special properties on the metal-oxide interface. These composites are widely applied in catalysis, microelectronics, metal matrix ceramics, gas sensors, recording media, corrosion protection coatings and other fields [1-3]. Cu/MgO is receiving widespread interest [4-8], because of its excellent interfacial properties, such as good electric conductivity and microstructure stability of Cu [9-11] and porous MgO with special optical, electrical, thermal, chemical, and mechanical properties [12]. The special properties of Cu-MgO interface are to some extent caused by the changes in the surface properties because of the interfacial interactions. Besides the intrinsic properties of the matrix, they are also closely related to the preparation methods of composite. The two types of preparation methods of Cu/MgO composites are high-temperature melting and grinding-calcination methods in the field of physical materials [2], and impregnation and co-precipitation methods within the range of chemical materials [13]. When preparing the composite under high temperature, the particle will be uniformly dispersed and its size will be relatively large, resulting in an even but small interface. During chemical processes, copper is dispersed unevenly and is thus difficult to control. Therefore, the preparation approaches of Cu/MgO composite must be improved by developing new surface properties and interfacial properties.

Raney Cu, which is prepared from Cu (Al) alloy, has a sponge-like structure and a large specific surface area with high activity. This composite lays the foundation for the preparation of a large interface composite at low temperature. The present study used Raney Cu as active ingredient template and modified Cu with MgO. A controllable, well-dispersed Cu/MgO composite was successfully prepared, and its texture and basic surface physicochemical properties were investigated.

2. Experimental details

The preparation process of Cu/MgO composite by wet mixing method is as follows. Raney Cu was mixed with MgO (1:1 molar ratio) into a single-necked flask. Deionized water, which was four times the volume of the mixture, was added. The mixture was stirred at room temperature for 24 h and filtered. The wet solid was collected into a three-necked flask, which was then vacuum- pumped. The solid was treated in nitrogen atmosphere at 200 °C for 4 h and cooled to room temperature. Then, Cu/MgO fine powder was obtained.

XRD patterns were recorded on a Rigaku D/Max 2500 PC X-ray diffractometer (Japan Science) with Cu/K radiation. The pattern was collected over the 2θ range of 10 to 80°. Specific surface areas were measured by N_2 adsorption/desorption using the BET method on a Micromeritics Autochem 2910 analyzer. TEM images were acquired using a JEOL JEM-1230 transmission electron microscope (Japan Electronics Corporation).

TPD tests were conducted on a self-made device. In the NH_3-TPD test, after vacuum desorption at low

temperature, the sample (300 mg) was placed in a reaction tube and heated at a rate of 20 °C /min from room temperature to 400 °C under N_2 gas flow. After a 30 min pretreatment, the sample was cooled to room temperature and then exposed to NH_3 for 30 min and heated at a rate of 5° C /min to 100 °C. After reaching stability, the sample was heated to 660 °C at the same rate. The NH_3-TPD spectrogram was obtained through the TCD test.

3. Results and discussion

The texture of the composite is characterized by XRD, TEM and BET.

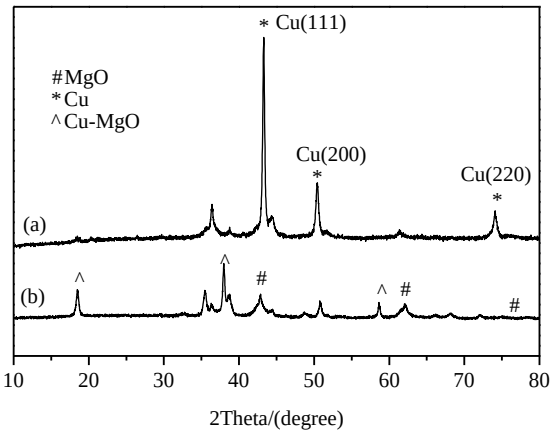

Fig. 1. XRD patterns of Raney Cu (a) and Cu/MgO (b).

Fig. 1 shows the XRD patterns of Raney Cu (a) and Raney Cu/MgO (b). Fig. 1a shows that the characteristic diffraction peaks of Cu^0 appeared at the double diffraction angles of 43.2°, 50.5°, and 73.3°. Fig. 1b shows that in the XRD pattern of Cu/MgO, the characteristic diffraction peaks of MgO and Cu^0 appeared at corresponding places. However, the XRD of crystal face significantly weakened, especially the Cu (220) plane, which had no diffraction peak. This result indicated that the Cu surface was strongly modified by MgO. Meanwhile, new diffraction peaks appeared at 18.7° 37.8°, and 58.2°, indicating that a new phase was formed during the preparation of Cu/MgO. The new phase Cu-MgO [14] may be generated by the reaction between Raney Cu and MgO, which has structural defects [9, 13]. Comparing the peak intensity in Figs.1a and b, Raney Cu modified by MgO became finer with decreased crystallinity. Based on calculations using the half-peak width, the mean particle size was approximately 8.3 nm.

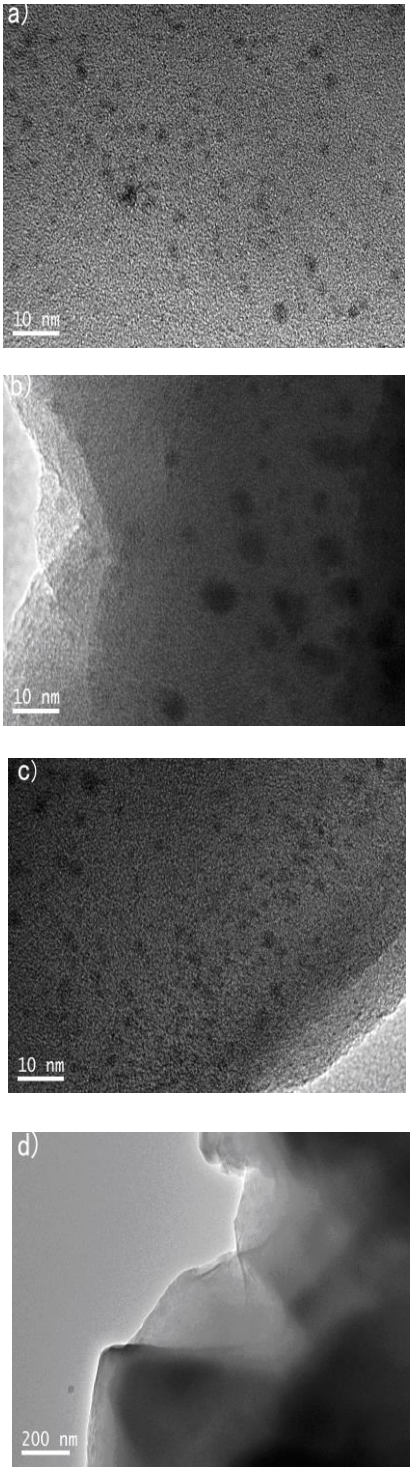

Fig. 2. TEM images of Cu/MgO.

Fig. 2 shows the TEM images of Raney Cu/MgO. Figs.2a and c show that Cu metal particles (black spots in figures) were more uniformly embedded in MgO, after catalyst preparation, with a mean particle size of approximately 2nm. As shown in Figs. 2b and d, some Cu particles exhibited irregularly shaped granules, whereas others were aggregated. This finding is related to the original structure of Raney Cu. The pore distribution of Raney Cu was uneven. Therefore, with an optimized

synthetic method of Raney Cu, the ideal Raney Cu/MgO composite can be evenly obtained by dispersing Al in Cu (Al) alloy. Based on the dispersion of Cu, the internal surface of Raney Cu pores was taken up by MgO. In contrast to the co-precipitation method [15-16], this method regulated the interaction between Cu and MgO and the distribution of MgO based on Raney Cu with the sponge pores derived from the preparation.

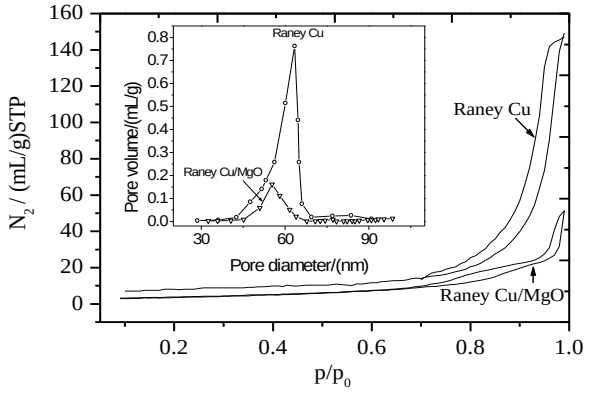

Fig. 3. N_2 adsorption-desorption isotherms and the pore-size distribution of Cu/MgO (inset).

The BET analysis of Raney Cu and Raney Cu/MgO showed the changes in the pore-size distribution of Raney Cu before and after modification (Fig. 3). Both present the type IV O-ring, indicating that Raney Cu has mesoporous structure before and after modification. The mesoporous characteristics of Raney Cu/MgO were attributed to the contribution of Raney Cu because MgO is a non-mesoporous material. Compared with the original Raney Cu, the Raney Cu modified by MgO had smaller surface area and pore size, with a 21.5% decrease of the surface area from 30.40 m^2/g to 23.87 m^2/g. This finding demonstrates the increase in the contact area of Cu and MgO. As MgO occupies the pore surface of Raney Cu, the mean size of Cu/MgO pore reduces to 25 nm, about half of the original value. MgO is a porous material with small density and therefore there is no possibility of MgO blocking the pores of Raney Cu.

The interfacial properties of the composite were tested by H_2-TPD, CO_2-TPD and NH_3-TPD.

The surface adsorption activity of Raney Cu and Raney Cu/MgO is shown in H_2-TPD (Fig. 4). Fig. 4 shows that the adsorption of H_2 on Raney Cu and Raney Cu/MgO was mainly physical absorption with a main peak. Compared with the H_2 desorption from Raney Cu, desorption from the modified Raney Cu occurred at a temperature higher by 21 °C. The formed peak was more symmetrical, which showed that the interface of Raney Cu modified by MgO became even. Different sites of Raney Cu showed varied adsorption ability on H_2 because of the surface defects. After modification by MgO, H_2 desorption from Cu/MgO occurred at a higher temperature because of the interaction between MgO and the defect sites of Raney Cu, as well as the hindering effect of MgO to H_2 desorption. This finding agrees well with the results of BET analysis, confirming the generation of new phase Cu-MgO by XRD analysis because the effect of H_2 on MgO could not be explained from the energy perspective [17].

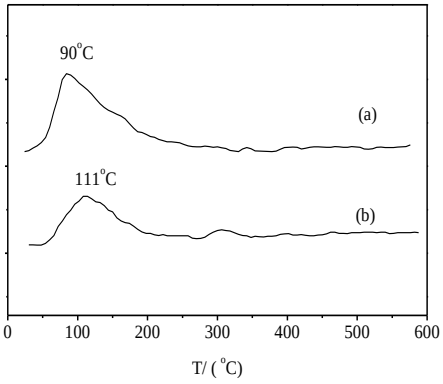

Fig. 4. H_2-TPD profiles of Raney Cu (a) and Cu/MgO (b).

The acidic Cu/MgO surface can be observed from NH_3-TPD (Fig. 5a). Cu/MgO presented a diffused acidity distribution, especially after the adsorption by Mg^{2+} of NH_3 when the temperature reached to 250 °C. The acidity distribution was uneven, and the acid strength was below 0.05 mmol /g.

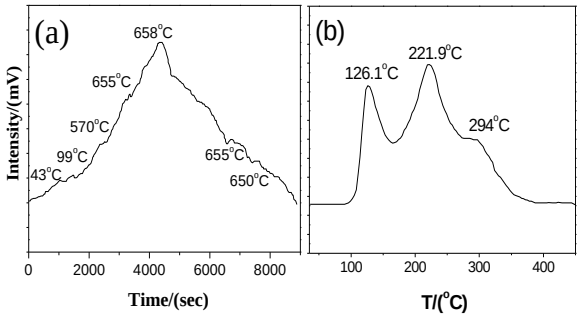

Fig. 5. NH_3-TPD (a) and CO_2-TPD (b) profiles of Cu/MgO.

The Cu/MgO surface had strong basic sites (Fig.5b). As shown in the figure, three CO_2 desorption peaks existed: one main peak and two shoulder peaks. The desorption peak at 126.1 °C was attributed to the weak physical adsorption of ammonia and -OH, whereas the desorption peak at 221.9 °C was due to the strong adsorption of CO_2 and MgO (Mg-O^{2-} pair). The intensity varied according to the position of MgO. A strong adsorption occurred on MgO at 294 °C (O^{2-} ion). Cu/MgO had different basic sites, and the overall alkalinity was 30 times higher than the acidity, which is similar to the results of other preparation methods [18-19]. This finding was ascribed to the

alkalinity which was mainly from the surface of MgO. However, the three alkalinity intensities of Raney Cu/MgO were not so distinctively different, probably because the interface affected CO_2 desorption during the characterization process.

4. Conclusion

Using Raney Cu with pores and large surface as template, a stable Cu/MgO composite could be effectively prepared by wet mixing method with MgO for modification. The materials prepared could retain the original structure of Raney Cu, but with the surface properties of modified Raney Cu. Moreover, the interfacial interaction of Cu and MgO was enhanced, and the new phase Cu-MgO was produced, which makes the Raney Cu surface become even, and the prepared method may regulate the interaction between Cu and MgO based on Raney Cu with the sponge pores. As changes of interface chemical properties will inevitably lead to changes of physical properties, Cu/MgO as the functional material prepared by wet mixing method has extensive applications in catalysis, electronics, and so on. Further, its other attributes, such as photoelectric properties, require tests.

Acknowledgements

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