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PREPARATION AND CHARACTERIZATION OF CATALYST FOR REDUCTION AMINATION OF ETHANOLAMINE BY DIFFERENT METHOD

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ABSTRACT

The NiO-CuO-CaO/Al_2O_3 composite oxide catalyst was prepared by impregnation method, CO-precipitation method and grinding microwave method with Al_2O_3 as carrier, Ni-Cu bimetal as active component and Ca as additive. And their performances were characterized by XRD, SEM, BET and IR. The results show that impregnation method is a suitable method for the preparation of composite oxide catalyst, and the WNiO:WCuO:WCaO =15:3.5:2.0 is determined by EDS analysis. The relatively large BET specific surface areas of 22.08 cm^2/g and 31.72 cm^2/g can be obtained by impregnation and microwave grinding, separately, while the CO-precipitation yield is only 2.49 cm^2/g. The BJH pore volume of the composite oxide obtained by the above three methods is not very different. The BJH pore size of the composite oxide obtained by impregnation is 2.070 nm, which is relatively small, in theory, it is more suitable for the catalytic reaction of ethanediamine from ethanolamine by reduction amination.

KEYWORDS

Ethanolamine, reduction amination, ethanediamine, composite oxide, catalyst, preparation

1. INTRODUCTION

Ethylenediamine (EDA)is an important chemical raw material and fine ch emical intermediate. It is widely used in the fields of pesticides, pharmace uticals and additive. It can be used to produce chelating agents, insect rep ellents, soil conditioners, lubri cants, rubber accelerators, emulsifiers [1-3]. The synthesis methods of ethylenediamine mainly include dichloroetha ne method, ethanolamine method, ethylene amination, formaldehyde-hyd rocyanic acid method, etc [4-6]. In recent years, the application of EDA in China has developed rapidly. Its annual growth rate of demand has reach ed 20%,which is one of the fine petrochemical intermediates urgently to b e developed in China [7-9]. At present, the main routes for the production of EDA in industry are dichloroethane (EDC)and ethanolamine (MEA)met hods [10]. Between them, the EDC route has serious pollution and high in vestment costs; while compared with the EDC route, the MEA route show s less pollution and lower investment costs [11-13]. Currently, the EDC ro utes employed are about 61%of the EDA production facilities in the world , and they will be substituted by the MEA routes, Which will be the genera l trend of development [14-16].

MEA has two reactive functional groups, the reaction with ammonia is m ore complex. In which, tandem reaction between intramolecular or interm olecular is occurred, and a series of chain or cyclic by-products are genera ted. Above of these results in the reduced selectivity of ethylenediamine [17-20]. Therefore, on the process route of EDA from MEA, high-activity an d high-selectivity catalysts have always been the focus of researchers. In o ur study, the reduction amination catalyst for MEA route was designed an d prepared. Using Al_2O_3 as the carrier, Ni-Cu as dual active component and Ca as the additive, the effect of different preparation methods on the perf ormance of the catalyst was investigated. It is hoped that this study will p rovide a useful reference for the research work of catalytic synthesis of E DA.

2. EXPERIMENT

2.1 Materials

Active aluminum hydroxide, $Al(OH)_3$,analytically pure (99.0%),Tianjin Yongda Chemical Reagent Co, Ltd; Aluminum nitrate, $Al(NO_3)_3 \bullet 9H_2O$,analytically pure(99.0%),Tianjin hengxing chemical reagent manufacturing co.LTD;Nickel nitrate,$Ni(NO_3)_2 6H_2O$,analyticallypure(98.0%),Tianjin Yongda Chemical Reagent Co.,Ltd;Copper nitrate,$Cu(NO_3)_2 \bullet 3H_2O$,analytically pure(99.0%),Tianjin Ruijinte Chemical Co.,Ltd.;Calcium nitrate,$Ca(NO_3)_2 \bullet 4H_2O$,analytically pure(99.0%),Tianjin Ruijin Special Chemicals Co.,Ltd.;Anhydrous sodium carbonate,Na_2CO_3,analytically pure(99.8%),Tianjin City Northern Tianyi Chemical Reagent Factory. All reagents were not further purified before use.

2.2 Instruments

D8 ADVANCE powder X-ray diffractometer, Bruker AXS Corporation, Germany; JSM-6490LV Scanning Electron Microscope, Japan Electronics Corporation, Japan;Gemini VII 2390 Automatic Surface Area Analyzer, Micromeritics Corporation,USA;Nicolet-6700 Fourier infrared spectrometer, USA Nicolet Corporation, USA.

2.3 Preparation of catalyst

2.3.1 Preparation of carrier

The active aluminum hydroxide raw materials are clained by a temperature program, the process is as follows: the first stage, heating for 24 min from room temperature to 260°C;the second stage, keeping the temperature of 260°C for 1 h; the third stage, another heating for 69 minutes, and the temperature was increased to 950°C;the fourth stage, running to maintain at 950°Cfor 4 h; finally, natural cooling to room temperature. According to above program, he catalyst carrier transition state Al_2O_3 is obtained.

2.3.2 Impregnation (IMP)

The above catalyst carrier is added to an ethanol solution of Ni $(NO_3)_2$•6H2O,Cu $(NO_3)_2$•3H_2O,Ca$(NO_3)_2$•4H_2O in proportion. After magnetic stirring for 2 h, removing the ethanol by rotary evaporator, and then drying at 105℃for 4 h, grinding to micron level. The catalyst samples was prepared according to the calcination process of temperature program, and the sample was recorded as No (IMP) [21].

2.3.3 Coprecipitation (COP)

Al$(NO_3)_3$•9H_2O(10.3034g),Ni$(NO_3)_2$•6H_2O(1.1682g),Cu$(NO_3)_2$•3H_2O(0.6074g),and Ca$(NO_3)_2$•4H_2O(0.4262g)were mixed to form a homogeneous aqueous solution. Above solution was added a concentrated solution of Na_2CO_3(9.6116 g). After magnetic stirring for 2 h, the obtained suspension was filtered. Then drying the filter cake, grinding and calcination according to the above method, the catalyst sample was prepared as No (COP) [22].

2.3.4 Microwave grinding (MWG)

Al$(NO_3)_3$•9H_2O(10.3034g),Ni$(NO_3)_2$•6H_2O(1.1682g),Cu$(NO_3)_2$•3H_2O(0.6074g),and Ca$(NO_3)_2$•4H_2O(0.4262g)four kinds of nitrate solid were mixed in proportion. After grinding, the mixture was placed into the microwave synthesizer, and reacted under 300W microwave for 15 min. After calcinations and grinding, the catalyst was obtained, and recorded as No (MWG) [23].

2.4 Characterization of catalyst

2.4.1 Powder X ray diffraction analysis (XRD)

About 1g catalyst sample was ground into powder, loaded the sample plate, pressed flat with glass and placed on the sample rack. Used CuKαas the ray source(Kα=0.15416 nm),NaI Scintillation counter, scan voltage and current were set to 40 kV and 40 mA respectively.2θscanning range was 4 to 65°,step scan mode was employed and step width was 0.02°.The analysis was carried out with 0.1 s/step speed. The software of Jade 5.0 was used for corresponding calculations.

2.4.2 Scanning electron microscopy-energy dispersive spectrometer analysis (SEM-EDS)

A little powder of catalyst sample was added to the anhydrous ethanol, dispersed under ultrasonic oscillation. And then it was dropped onto a piece of iron attached with a conductive tape. After anhydrous ethanol volatilized, the morphology was observed by using scanning electron microscopy. The operating conditions are as follows: working distance 10 mm, objective lens aperture 100μm, sample current 50×10-10 mA, and acceleration voltage 20 kV.Si (Li)detector was used on the energy spectrometer, the resolution was better than 133 eV, the effective detection area was10 mm^2,and the energy spectrum element analysis range was B5～U92.

2.4.3 BET surface area, BJH pore volume, and BJH size analysis (BET)

The sample tube was weigh accurately, and about 0.25g of the catalyst put in the sample tube. Then the sample was treated under the condition of 90℃for 1 h and 340℃ for 3 h in the presence of nitrogen, and the total weight was weigh accurately. The sample tube was fixed to the full automatic surface area meter. Used 99.99% of He as carrier gas and 99.999% of N_2 as adsorbent, the average adsorption and desorption time for each sample at P/P_0 was 5 min. Empty rate was 300 mmHg/min, balance time was 5 s, and 9-point analysis was run. The specific surface area was calculated by BET method, the pore size and distribution of samples and the pore volume of samples were analyzed by BJH method.

2.4.4 Infrared spectroscopic analysis (IR)

The sample was dried in a vacuum and ground into a powder, determined by solid KBr pressing method (the mass ratio of KBr to sample = 100:1), and detected by DTGS medium infrared detector with a resolution of 0.1 cm^{-1} and measured in the range of 4000 to 450 cm^{-1}, Wave number accuracy 0.01 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction results

On the basis of Al_2O_3:NiO:CuO:CaO=70:15:10:5 (mass percentage) in the catalyst of NiO-CuO-CaO/Al_2O_3 composite oxide, the XRD patterns of different catalysts prepared by three methods in the article were shown in Fig.1.The XRD patterns of the individual oxide components were shown in Figure 2.As can be seen from Figure 1 and Figure 2,the complex oxides prepared by the IMP and MWG methods had amorphous phase, separately, while the MGW method was more obvious. Additionally, the characteristic peaks of the oxide crystals can be observed by above two methods, and their crystallinity was similar. However, the composite oxide obtained by COP method was significantly different from the above, the crystallinity was relatively high, and the characteristic peaks of slight oxides can be observed. Some new characteristic peaks appeared indicated that special new phase was generated in the co-precipitation process. It was further confirmed that a large amount of NaAlO2 metal salt was occurred during precipitation. We can see from the above that, compared with the COP and MGW methods, the IMP method is a suitable method for preparing a composite oxide.

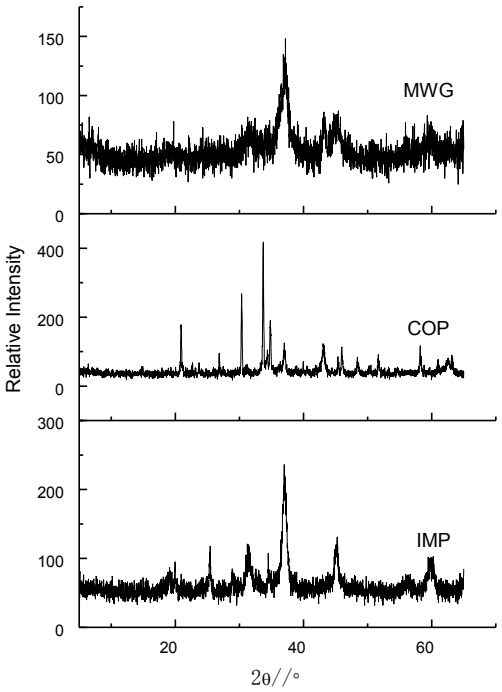


Figure 1: XRD patterns of composite oxides prepared by different methods

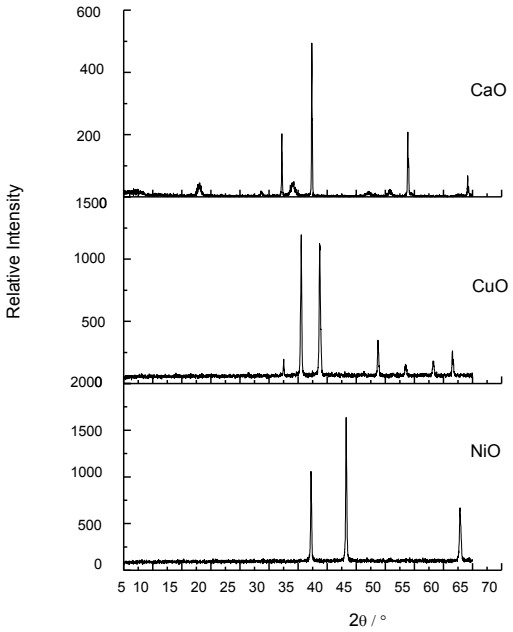
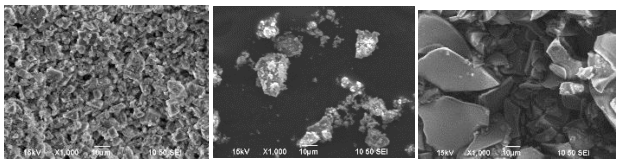


Figure 2: XRD patterns of single oxide

3.2 Scanning electron microscope - energy spectrum results

The SEM images of different composite oxides catalysts prepared by above different methods were shown in Figure 3, and the results of the composite oxides data of EDS analysis were shown in Table 1.



IMP COP MWG

Figure 3: SEM images of composite oxides prepared by different methods

As shown in Figure 3, there were significant differences in the structure of composite oxides prepared by the three methods. The composite oxides obtained by the IMP method had uniform size, clear contours, loose structure, and rare aggregates. But, by the MWG method, resulted in an extremely inhomogeneous lamellar aggregate structure. While, by the COP method, resulted in larger bulk crystals, and some small particles and flocs were grown on the surface of the bulk crystals.

Table 1: Data of composition of oxides except carriers determined by EDS

Preparation	Elemental mass percentage			Calculate oxide mass ratio		
	Ni	Cu	Ca	W_{NiO}	W_{CuO}	W_{CaO}
MWG	12.509	6.808	2.571	15.0	4.9	2.1
COP	11.616	2.127	5.347	15.0	1.1	4.5
IMP	17.017	7.906	3.728	15.0	3.5	2.0

As can be seen from Table 1, the comparison of the $W_{(NiO)}$:$W_{(CuO)}$:$W_{(CaO)}$and the originally designed 15:10:5 in the composite oxides, there was a deviation obtained by the MGW and IMP methods, W_{CuO} and W_{CaO} were decreased by more than 50%relative to the designed specific loading, but the relative mass ratio of W_{CuO}: W_{CaO} was in line with expectations. The composite oxides obtained by the COP method contained almost no auxiliary catalytic component CuO, while the additive component CaO maintains the intended design mass ratio. This was related to the crystallization properties of the metal carbonate or the basic carbonate, and the solubility product constant in water. It's also related to pH, and temperature, etc. Further in-depth studies will be discussed later.

Combined with the SEM-EDS results, although the amount of co-components and auxiliary components has been reduced, and the relative ratio still remains expected, thus, we can know that the IMP method is a good method for preparing composite oxides.

3.3 BET surface area, BJH pore volume, BJH pore size results

The results of the BET specific surface area, BJH pore volume, and BJH pore size of the different composite oxides catalysts prepared by above different methods were shown in Table 2.

From Table 2, it can be seen that MGW and IMP method have a larger specific surface area than COP method and they were more suitable for catalytic application; The BJH pore volumes of the composite oxides obtained by the three methods were not very different; The BJH pore diameters of the composite oxides obtained by the MGW and IMP methods were very small, and smaller than those of the COP method. From the viewpoint of molecular size, considered reduction amination of ethanolamine to ethylenediamine, the smaller pore size of the catalyst was the better for promoting selectivity of ethylenediamine. Therefore, we believe that the IMP method is a relatively suitable method for preparing composite oxides catalysts.

Table 2: Data of BET surface, BJH pore volume, and BJH pore diameter of oxides except carriers

Preparation	BET specific surface area/cm^2/g	The BJH pore volume/cm^3/g	BJH pore size /nm
MWG	31.72	10.010	2.074
COP	2.49	10.002	2.165
IMP	22.08	10.006	2.070

3.4 Infrared spectrum results

The infrared spectrum (IR)results of different composite oxides catalysts prepared by above different methods are shown in Figure 4. As can be seen from Figure 4,a wide-dispersion infrared characteristic absorption peak of the metastable isomer-Al_2O_3 in the composite oxides obtained by the IMP and MWG methods was shown, clearly. Due to its amorphous bulk structure, there is no single bond vibrational absorption. Comparision with the MWG method, IMP absorption slightly reduces the tendency of single peak formation, it can be seen that the relative amorphous content was reduced. There are four distinct absorption peaks of $NaAlO_2$ on the IR absorption curve of the COP method:902 cm^{-1} Al-OH vibration band,729 cm^{-1},626 cm^{-1} $Al(OH)^{4-}$vibration zone,529 cm^{-1} Al-O-Al vibration zone. Summarizing the above, IR analysis can tell that the IMP method is a more suitable method for preparing the catalyst.

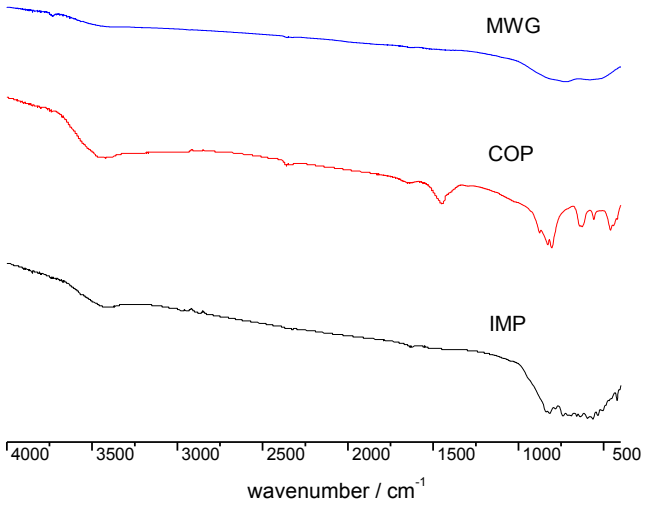


Figure 4: IR patterns of composite oxides prepared by different methods

4. CONCLUSION

Among the three methods of impregnation, co-precipitation and microwave-grinding, XRD,IR and SEM images show that impregnation was a suitable method for the preparation of metal composite oxides catalysts for the reduction amination of ethanolamine to ethylenediamine. According to Al_2O_3:NiO:CuO:CaO=70:15:10:5(mass percentage)in the NiO-CuO-CaO/Al_2O_3 composite oxides catalyst designed, the actual ratio was confirmed by EDS data analysis. During the impregnation process, although the amounts of auxiliary components and co-ingredients compared to the expected design have been reduced, the relative proportions of CuO and CaO remain unchanged. The concentration of impregnating solution can be increased to increase its oxides content in catalysts.

In addition, relatively large BET specific surface areas of 22.08 cm^2/g and 31.72 cm^2/g were obtained by the impregnation method and the microwave grinding method, respectively. And the specific surface area of only 2.49 cm^2/g was obtained by coprecipitation method. The difference of BJH pore volume of the composite oxides obtained by the three methods was not large; The BJH pore diameter of the composite oxide obtained by the impregnation method is 2.070 nm, which is relatively small compared to other methods. Theoretically, it was more suitable for the catalytic reaction of ethanolaminer eduction amination to ethylenediamine. The investigation of the catalytic performance of the catalyst and the design of the catalytic process are being studied.

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