

Preparation and Application of Metal Oxides/SBA-15 Mesoporous Composites as Catalysts for Selective Oxidation of benzyl alcohol

Xuan Yu^{1,2}, Haojie Li¹, Tianhao Yu¹, Zhixin Xia, Qiqi Weng¹ and Zhengping Zhao^{1,2,*}

¹ Zhijiang College, Zhejiang University of Technology, Hangzhou 310014, P.R. China

² College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China

*E-mail: sjzhaolei@163.com

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In this project, SBA-15 with a mesoporous pore channel structure was synthesized by a hydrothermal method and its characterization by XRD, SEM and TEM proved that the mesoporous channels had highly ordered. Ordered mesoporous supported composite metal oxide catalysts NiO_x-CuO_x/SBA-15 was prepared by Nanocasting using nickel nitrate and Copper nitrate as precursors. The influence of ratio of the mesoporous precursor Ni(NO₃)₂ and Cu(NO₃)₂ (1: 0, 3: 1, 2: 3, 2: 1, 1: 1, 2: 3, 0: 1), roasting temperature (300°C, 400°C, 500°C, 600°C, 700°C) and other influencing factors of mesoporous precursors for the selective oxidation of benzyl alcohol by supported composite metal oxides was investigated. The results represent that 88.85% could be achieved with the optimal calcination temperature of 500°C, nickel copper ratio of 2:1, Catalyst dosage of 1 g, reaction temperature of 90°C, reaction time of 5 h, 2.5 ml of Bnoh, 76.34% selectivity and 67.62% yield of Bzh. In the oxidation reaction with alcohol, reaction is difficult when there are electron withdrawing groups on aromatic rings; when there were no groups or electron groups on aromatic rings, active group containing alcohols had a higher conversion rate than that of Benzyl alcohol. In this composition, Ni-Cu composite oxides and their support catalysts with low raw material, simply preparation process and easy recovery were synthesized, furthermore under mild conditions, selective oxidation of benzyl alcohol in organic solvents has high catalytic activity and no environmental contamination. This manner is easy to operate, has high yield and high utilization rate of raw material that has certainly application value in chemical production of benzaldehyde.

Keywords: Catalyst, Mesoporous supported, Compound metal oxidate, Selective oxidation.

1. INTRODUCTION

Environmental contamination is an urgent issue to be solved by mankind. In industry, benzyl chloride is mainly chlorinated from toluene and secondarily hydrolyzed to get

benzaldehyde. Nevertheless, this method requires a large amount of chlorine gas, acid and base, the yield of benzaldehyde is low, and contains trace chlorine, which will seriously pollute the environment. With the improvement of the quality requirement and the increase of the demand for benzaldehyde in the domestic market, the technology of enterprises producing benzaldehyde still required improving which the production of high-quality environmental benzaldehyde has become the trend of the current market [1]. The demand for high-quality benzaldehyde is increasing, the requirements for environmental protection are becoming more and more stringent. Research on economic benzaldehyde production technology to cope with the contamination dilemma of pollutants in the synthetic production process and improve its conversion rate has become an urgent trouble to be solved in benzyl alcohol production.

Humans have used catalytic processes to get desired target products for thousands of years, and among supported catalysts, which mesoporous materials can serve as excellent support materials [2]. Copper catalyzed oxidation of alcohol has been reported in quite a few articles [3]. Bimetallic catalysts have been one of the hot spots in catalytic research due to the synergy between their constituent metals, which makes them more catalytically active than the corresponding monocomponent metals occur in many reactions. The mesoporous materials refer to porous materials with pore diameters in 2-50 nm, including carbon materials, carbonitrile, metal oxides, metal sulfide, the metal nitride and composites, among others [4, 5, 6]. Because of their homogeneous porous structure, large specific surface area, good chemical and thermal stability, tunable pore size, and low density, mesoporous materials have found great applications in many fields, such as gas storage, analytical chemistry, catalysis, optical devices, and drug deliveries.

In long-term practical applications, there are two classes of heterogeneous catalysts that have gained increasing attention heterogeneous catalysts are considered a more preferential option than homogeneous catalysts due to convenient operation [7]. Ordered mesoporous materials were chosen as catalyst support for our experiments. Ordered mesoporous materials have the following advantages: high specific surface area, which is conducive to mass transfer and diffusion, and large pore size that can be used for the reaction of larger molecules. The pore size and the shape of the pore is tunable, which can optimize various special effects brought by the restricted space of the pore channel. The pore surface is easily transformed, and we can regulate the microenvironment inside the pores for the reaction system. The morphologies are diverse and controllable, so that structural morphologies such as large particles, fibers, and films can be formulated as required for catalytic reaction engineering [8].

In traditional oxidation reactions, inorganic oxidants usually used are permanganate, nitrate, chromate, periodate, etc.. These substances have severe corrosion on equipment, poor reaction selectivity, and many safety concerns in the generation process [9]. Therefore, in this paper, mesoporous materials were used as excellent support materials to prepare the composite metal for the oxide catalyst $\text{NiO}_x\text{-CuO}_x/\text{SBA-15}$, which air was used as clean oxidant, and the optimized catalytic conditions applied to realize the selective reaction of benzylic alcohol, and this method conformed to green chemistry. At present, the research on improving the catalytic performance of nickel copper oxide catalysts only staying on the amount of doping, and there is not a systematic study. In this paper, we investigated the influence of hydrothermal synthesis of silica SBA-15 with ordered mesoporous pore structures as catalyst support and investigated the oxidation of benzyl alcohol to benzaldehyde by using different mesoporous precursors $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ doping ratios, different calcination temperatures,

reaction temperatures, and reaction times to comprehensively oxidize the selected catalysts NiO_x-CuO_x/SBA-15, to provide a more cost-effective and efficient technical method for printing and dyeing wastewater treatment.

2. EXPERIMENTAL

2.1 Materials

Nickel nitrate, copper nitrate, benzyl alcohol, 4-methyl benzyl alcohol, 4-chlorobenzyl alcohol, 4-methylthiobenzyl alcohol, acetonitrile, surfactant P123 (Aldrich, EO₂₀PO₇₀EO₂₀, M_a = 5800), ethylene orthosilicate (TEOS), concentrated hydrochloric acid, silica gel of color change were of analytical grade and purchased from Shanghai Alain Biochemical Technology Co., Ltd.

Beakers, centrifuge cattle horn tubes, pH test strips, glass bars, 2XZ-2 rotary vane vacuum pump, FA2204B electronic balance, DF-101S collector type thermostatically heated magnetic stirrer, HJ-3 number manifest thermostatic magnetic stirrer, HJ-6 multi headed magnetic heating stirrer, electric thermostated blast drying oven, KQ2200E ultrasonic cleaner, TG16-WS table top high-speed centrifuge, DZF-6050 vacuum drying oven, Agilent 700 ICP emission spectrometer, Perkin Elmer 2400 II elemental analyzer, USA, Perkin Elmer 950 UV spectrometer, Perkin Elmer frontier infrared spectrometer, HORIBA Fluomax-4 fluorescence spectrometer, Switzerland, Mettler TGA/DSC₃ thermogravimetric analyzer, Czech FEI Nova Nano SEM field emission scanning electron microscope, etc.

2.2 Hydrothermal synthesis of SBA-15

References of synthesis process of mesoporous molecular sieve SBA-15 [9]. Ml of deionized water at 35-40 °C, to which ethyl orthosilicate (TEOS), hydrochloric acid (HCl) was added with constant vigorous stirring for over 24 h, loaded into an ethylene bottle and crystallized for more than 24 h, filtered, washed and dried, and finally calcined at 550 °C for over 5 h to remove the template agent or washed the template agent with solvent reflux followed by filtration, washing and drying, the resulting white powder is SBA-15. The molar ratio of EOS:P123:HCl:H₂O of each raw material used in the experiment was 1: 0.017: 5.88: 136.

2.3 Preparation of Ni-Cu based supported catalysts

A Ni-Cu based supported catalyst [10] was prepared by nano casting method: 1 g of Ni(NO₃)₂·6H₂O 1.16 g and 0.48 g of Cu(NO₃)₂·3H₂O dissolved in 100 ml of absolute ethanol to make an ethanol solution containing Ni(NO₃)₂ 0.04 mol/L and Cu(NO₃)₂ 0.02 mol/L, to which 1 g of SBA-15 was added and labeled. After 24 h of magnetic stirring at room temperature, they will perform suction filtration, washing, which cake was ground after being put into an oven for drying, and the ground powder was calcined in a muffle furnace at 500 °C for 3 hours. Namely, Ni/Cu based supported catalyst NiO_x-CuO_x/SBA-15 was obtained.

2.4 Oxidation of benzyl alcohol to benzaldehyde

Put 1g of Ni Cu based supported catalyst into a 100ml flask and add 2.5ml (23.8 mmol) of benzyl alcohol (BnOH). When the magnetic stirring water bath is heated to 90 °C, it carried the reaction out in an air atmosphere and under the constant temperature of 90°C for 5 hours. After the reaction, it is cooled at room temperature. After separating the catalyst in the cooled reaction system, we extracted the remaining liquid mixture three times with 10 ml acetonitrile, when the organic layer was collected, and detect it by GC and GC-MS.

2.5 Detection of Benzaldehyde

The samples to be tested after benzaldehyde extraction were subjected to gas chromatography (GC9890A gas chromatograph, Shanghai Linghua Instrument Co., Ltd.). Instruments needed were: air pump (SGK-21B low-noise air pump produced by Beijing Oriental seiyan Technology Co., Ltd.), the hydrogen generator (SGH-300 high pure hydrogen generator produced by Beijing Oriental seiyan Technology Co., Ltd.), high pure nitrogen (carrier gas). Test conditions for chromatography which the chromatographic column was a capillary column of 30 m and 0.32 mm in diameter: injector temperature 300°C, and detector (flame ion detector) temperature 320 °C; nitrogen pressure 10 psi; after ignition, the signal was adjusted to around 33. The programmed temperature was: in the first segment, 54 °C to 110 °C per min for 15 minutes, in the second segment, 110 °C to 250 °C per minute for 20 °C, and was kept for 5 minutes when raised 250 °C; the maximum level was set to 1000 MV, and the minimum level was set to -15 MV. Injection volume was 0.5µm.

Nitrobenzene was used as internal standard for quantitative analysis of oxidation products and unreacted substrates [11]. The calculation method is as follows:

$$\text{Con}(\text{benzyl alcohol})\% = \frac{\text{The Moles of benzyl alcohol consumed}(\text{mol})}{\text{The amount of benzyl alcohol that was added}(\text{mol})} \times 100\% \quad (1)$$

$$\text{Sel}(\text{benzyl alcohol})\% = \frac{\text{The Moles of benzyl alcohol consumed}(\text{mol})}{\text{The amount of benzyl alcohol subatance sonsumed}(\text{mol})} \times 100\% \quad (2)$$

$$\text{Yied}(\text{benzyl alcohol})\% = \frac{\text{The Moles of benzyl alcohol consumed}(\text{mol})}{\text{The amount of benzyl alcohol that was added}(\text{mol})} \times 100\% \quad (3)$$

$$\text{The Moles of benzyl alcohol consumed}(\text{mol}) = \frac{A}{A_s} \times \frac{W_s}{M} \times f \quad (4)$$

In Equation 4, A is the peak area of benzaldehyde. Ws is the mass of internal standard nitrobenzene. As is the peak area of internal standard nitrobenzene. M is themolar mass of benzaldehyde. f is the correction factor of benzaldehyde.

3. RESULTS AND DISCUSSION

3.1. Structural characterization and analysis of ordered mesoporous SBA-15

3.1.1 SBA-15 XRD characterization test

The XRD characterization test of SBA-15 is shown in Figure 1. The minor angle X-ray diffraction curve of SBA-15 molecular sieve synthesized by the hydrothermal method that four characteristic diffraction peaks in the curve, which belonged to the peaks got by (100), (110), (200) and (210) crystal plane diffraction, respectively. The results represent that the SBA-15 molecular sieve has a two-dimensional hexagonal pore structure, which can be inferred from the intensity of the diffraction peak that the SBA-15 molecular sieve maintains a highly ordered state [12]. According to the formula, SBA-15 molecular sieve is $d_{100}=10.52\text{nm}$, $a_0=12.15\text{nm}$. The synthesis of SBA-15 was further verified.

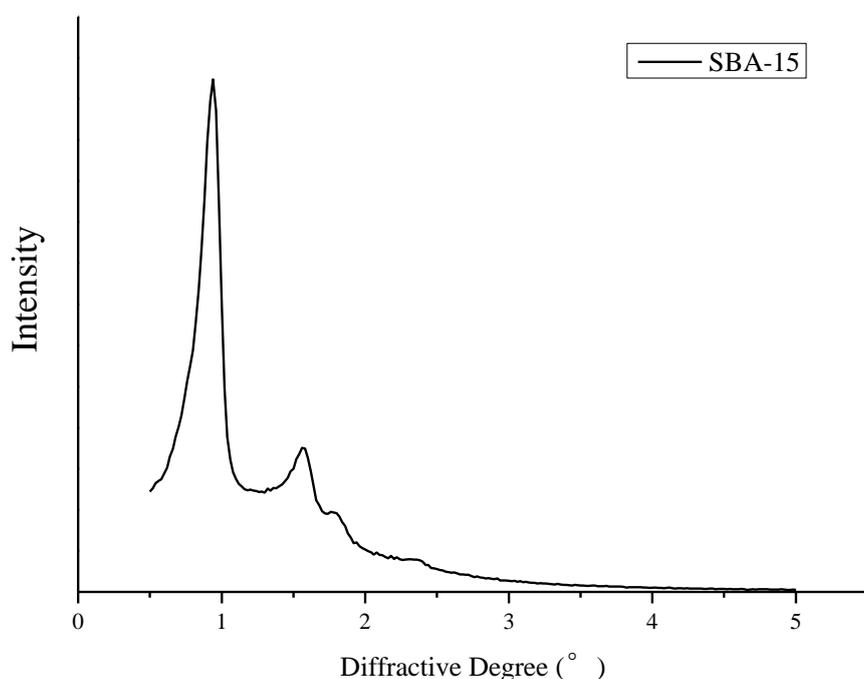


Figure 1. XRD spectrum of SBA-15

3.1.2 SEM characterization test of SBA-15

Figure 2 shows the SEM spectrum of SBA-15. We can see it from the figure that the grain shape of SBA-15 sample synthesized by the hydrothermal method mainly presents fibrous crystal structure. The diameter of grain fiber is about 333 nm, the single length is about 500 nm, and the length of some fiber adhesion can reach the micron level.

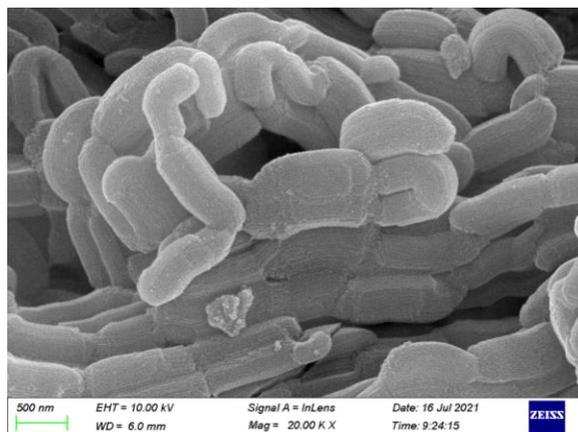


Figure 2. SEM spectrum of SBA-15

3.1.3 TEM characterization test of SBA-15

Figure 3 shows the TEM photos of SBA-15 and its parallel to the channel direction. The molecular sieve prepared in this test has highly ordered planar hexagonal mesoporous channels and neat transverse structure patterns parallel to the channel direction. It is further to prove that SBA-15 has a two-dimensional planar hexagonal mesoporous structure.

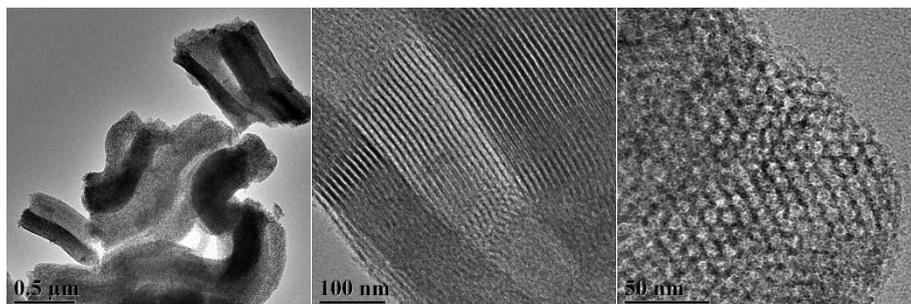


Figure 3. TEM spectrum of SBA-15

3.1.4 SBA-15 nitrogen adsorption desorption test

Figure 4 shows the low temperature nitrogen adsorption desorption isothermal curve of SBA-15 molecular sieve sample synthesized by the hydrothermal method. It can be seen from the figure that SBA-15 presents a typical irreversible IV Adsorption-desorption isotherm and has an obvious H1 hysteresis loop, which is the characteristic of the Adsorption-desorption isotherm of mesoporous materials with one-dimensional cylindrical pore structure [13]. At relatively low partial pressure, monolayer adsorption dominates the adsorption behavior of SBA-15. In this case, in the process of desorption, the narrow pore structure has no pore resistance to hinder the gas desorption, so that capillary condensation can not occur at a relatively low partial pressure. In data, the dissociative adsorption process did not lag behind, the adsorption process and dissociative adsorption process were reversible, and there were no evident adsorption branches and dissociative branches in the adsorption dissociative

isotherms. After that, with the gradual increase of relative partial pressure and the volume of gas adsorbed in the channel, the adsorption behavior is mainly multimolecular layer adsorption. From this moment, the volume of gas adsorbed by the pores of the prepared mesoporous materials increased. For SBA-15 molecular sieve synthesized by conventional method, when its relative partial pressure (p/p_0) reaches 0.73, the adsorption branch and the desorption branch of its adsorption desorption isotherm appeared abrupt phenomenon. The main reason for this phenomenon is that when the relative partial pressure rises to a certain value, capillary condensation can occur, which leads to the sudden increase of adsorption volume of adsorption branch and the desorption branch. There is an obvious hysteresis loop in the nitrogen adsorption desorption isotherm. This hysteresis phenomenon shows that the adsorption process and the desorption process are different, the adsorption process and desorption process are irreversible, and the desorption process lags the adsorption process. The phenomenon that the dissociative adsorption of process lags the adsorption process can be attributed to the shrinkage of the cylindrical channel of mesoporous materials, and the direct consequence of the shrinkage of the cylindrical channel is to delay the capillary evaporation process. Therefore, the adsorption process and dissociative adsorption of process can be carried out under the different relative to partial pressure. In materials with mesoporous channels, the relative pressure of capillary condensation (capillary condensation) is an increasing function of mesoporous channel diameter. The larger the mesoporous channel diameter of the material, the higher the relative pressure that can produce capillary condensation [14]. From the nitrogen adsorption desorption isotherm of the prepared material, it can also be seen that for the synthesized SBA-15 molecular sieve, when its relative to the partial pressure (P/P_0) reaches 0.85, the adsorption branches and desorption branches of the adsorption desorption isotherm overlap again, the phenomenon that the desorption branch of the adsorption desorption isotherm lags the adsorption branch no longer emerges.

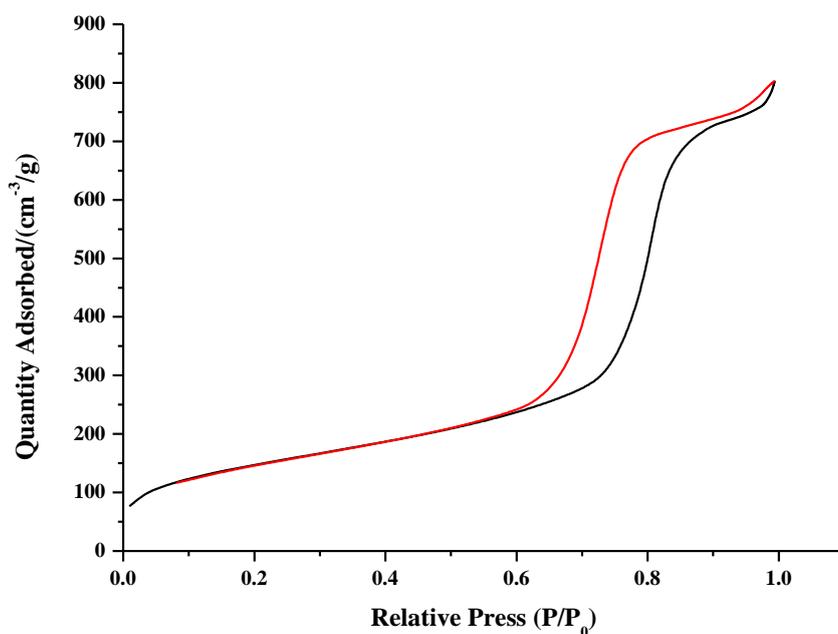


Figure 4. Nitrogen adsorption desorption isotherm of SBA-15

3.2 Structural characterization and analysis of Ni-Cu based supported catalysts

3.2.1 XRD characterization of Ni-Cu based supported catalysts

Figure 5 shows the small angle XRD spectra of NiO_x/SBA-15, NiO_x-CuO_x/SBA-15 and CuO_x/SBA-15 prepared in the test. It can be seen from the figure that the three supported metal oxide SBA-15 molecular sieves prepared in this study have four diffraction peaks, which belonged to the peaks got by (100), (110), (200) and (210) crystal plane diffraction respectively, which is consistent with the characteristic peaks of SBA-15 [15]. It is showing that after the metal oxide guest material is assembled in the SBA-15 molecular sieve channel, the two-dimensional planar hexagonal pore structure of SBA-15 molecular sieve is kept intact, which perfectly maintain the ordered state of molecular sieve structure.

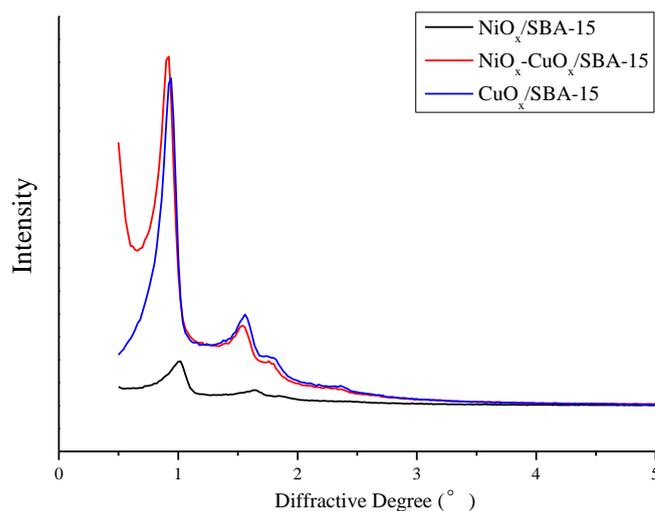


Figure 5. XRD spectra of NiO_x/SBA-15, NiO_x-CuO_x/SBA-15 and CuO_x/SBA-15

3.2.2 SEM characterization test of Ni Cu based supported catalyst

Figure 6, Figure 7 and Figure 8 show the SEM photos of NiO_x/SBA-15, NiO_x-CuO_x/SBA-15 and CuO_x/SBA-15. It can be seen from the figure that SBA-15 molecular sieve shows that an enormous amount of Ni, Cu metals and their oxides were deposited, and the test product results are verified.

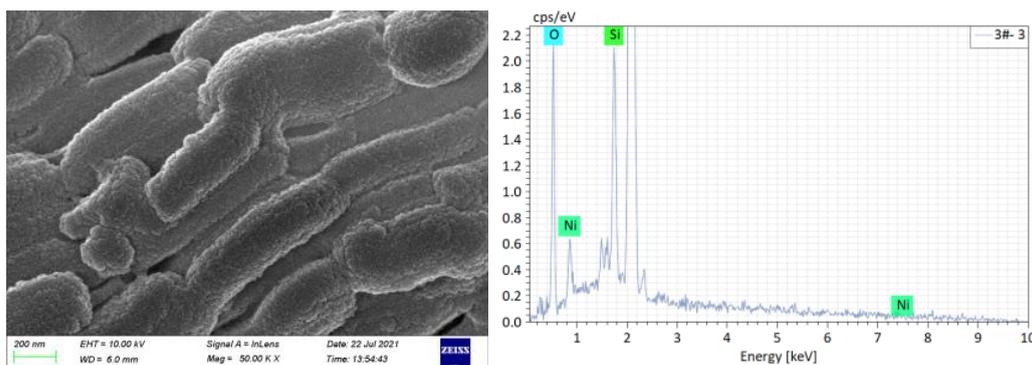


Figure 6. SEM and EDS spectra of NiO_x/SBA-15

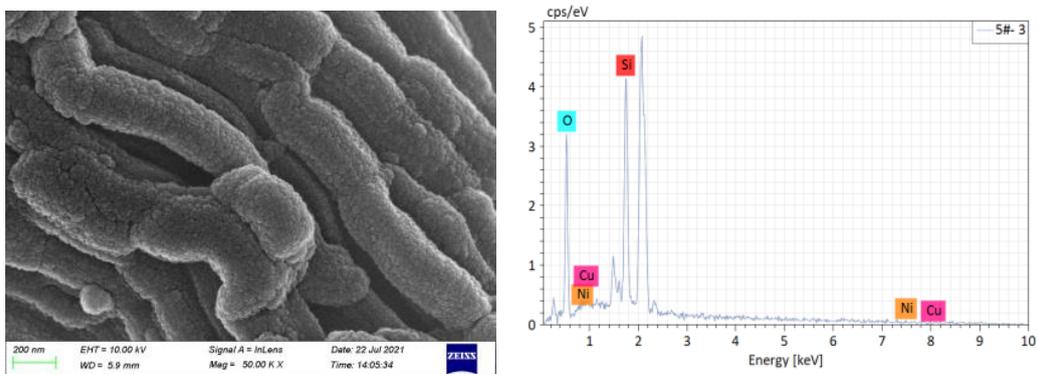


Figure 7. SEM and EDS spectra of NiO_x-CuO_x/SBA-15

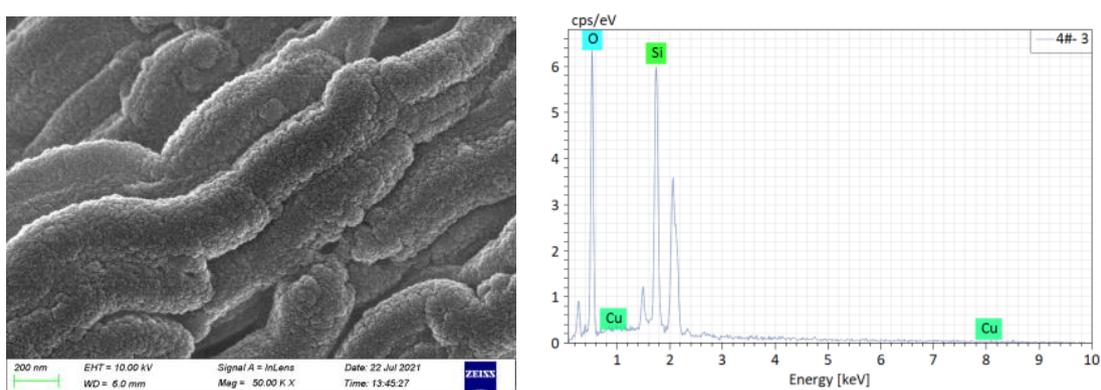


Figure 8. SEM and EDS spectra of CuO_x/SBA-15

3.2.3 TEM characterization test of Ni-Cu based supported catalyst

Figure 9 shows the TEM spectrum of NiO_x-CuO_x/SBA-15. It can be seen from the figure that Ni and Cu are evenly distributed on the surface or mesoporous of SBA-15 in the particle package, and the ordered pipeline of SBA-15 does not collapse.

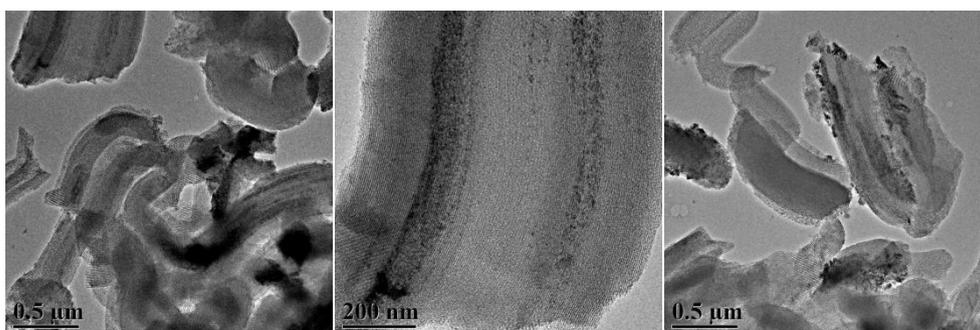


Figure 9. TEM spectrum of NiO_x-CuO_x/SBA-15

3.2.4 XPS characterization of Ni-Cu based supported catalysts

Figures 10, 11, 12 and Table 1 are the XPS spectra and the data sheet of NiO_x/SBA-15, NiO_x-CuO_x/SBA-15 and CuO_x/SBA-15, respectively. It can be seen from the charts that Ni, Cu and Ni Cu composite metals are distributed as oxide, and the results of testing the product are verified. Therefore that the nano casting process, the content of Ni and Cu is directly relevant to the concentration of the prepared solution. Under the experimental concentration, content of Ni and Cu is relatively insignificant, but NiO_x-CuO_x/SBA-15 catalyst material can still be prepared.

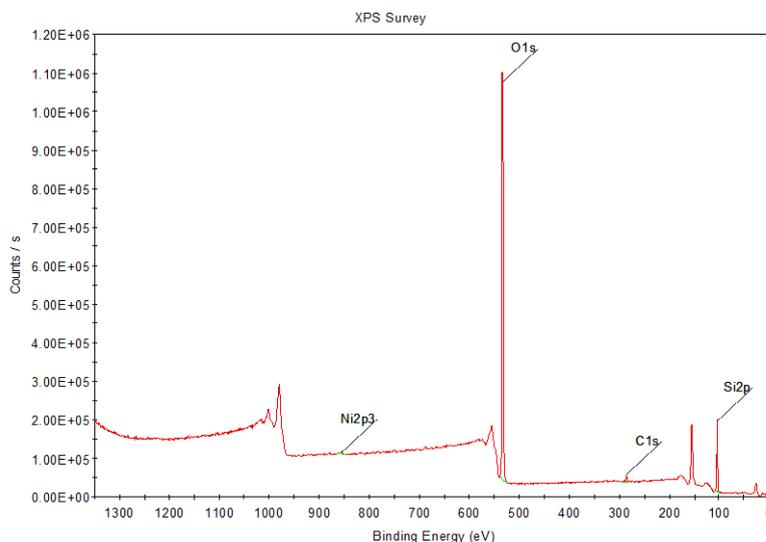


Figure 10. XPS spectrum of NiO_x/SBA-15

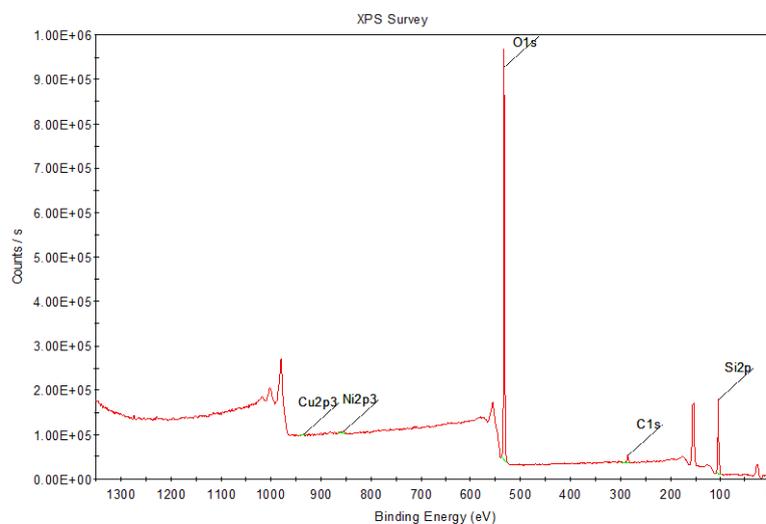


Figure 11. XPS spectrum of NiO_x-CuO_x/SBA-15

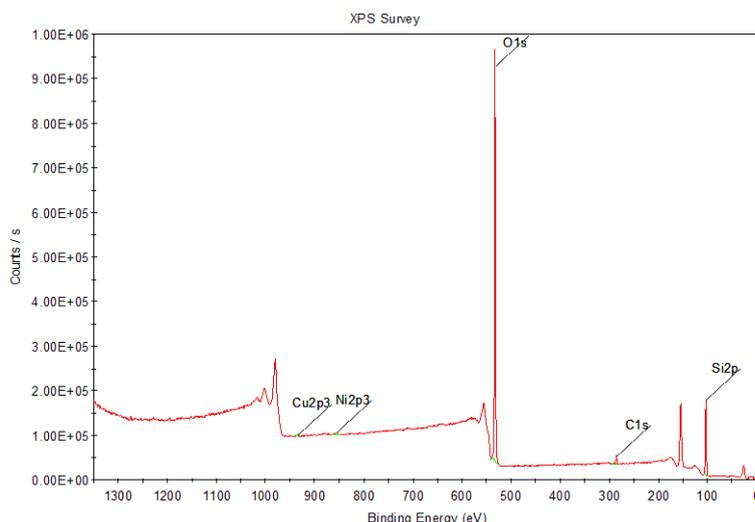


Figure 12. XPS spectrum of CuO_x/SBA-15

Table 1. XPS data sheet of NiO_x-CuO_x/SBA-15

NiO _x /SBA-15	Elemental content (%)	NiO _x -CuO _x /SBA-15	Elemental content (%)	CuO _x /SBA-15	Elemental content (%)
Si2p	30.68	Si2p	30.32	Si2p	30.43
C1s	3.72	C1s	4.25	C1s	4.33
O1s	64.98	O1s	64.45	O1s	64.88
Ni2p	0.61	Cu2p	0.28	Cu2p	0.36
		Ni2p	0.7		

3.3 Oxidation catalyzed by NiO_x-CuO_x/SBA-15 complex oxides

3.3.1 Effect of calcination temperature on catalytic activity of mesoporous supported Ni-Cu oxide catalysts

The relationship between the catalytic activity of catalyst calcination at different temperatures and the selective oxidation of Bnoh to Bzh in solvent-free condition was investigated, and the results are shown in Figure 13. In this experiment, the prepared catalyst was loaded with SBA-15 molecular sieve and calcined below 500°C, but its catalytic activity in benzyl alcohol oxidation did not transform much. While the calcination temperature used once it exceeded 500 °C, its catalytic activity then decreased sharply, which might be caused by the too high temperature particle coacervation and the destruction of the internal structure of analytical sieves because of the high temperature, pore channel structure collapse [16].

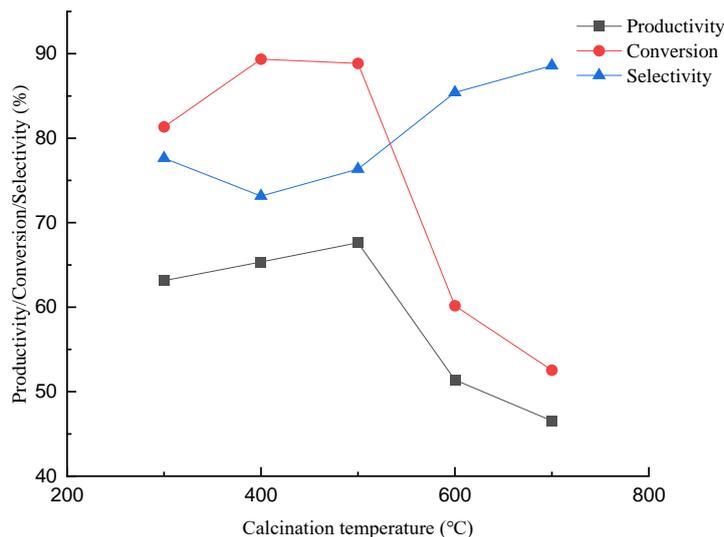


Figure 13. Catalytic activity of NiO_x-CuO_x/SBA-15 with different calcination temperatures. Reaction conditions: BnOH 2.5ml, catalyst dosage 1g, reaction temperature 90 °C and reaction time 5h.

3.3.2 Effect of different nickel copper composite oxide doping ratios on catalyst activity by mesoporous Loading

Examined the catalytic activity of various oxide catalysts with different negative mesoporous supported nickel copper ratios in benzyl alcohol oxidation (shown in Figure 14), the oxide with solely mesoporous supported copper showed the lowest catalytic activity, which increased with the nickel phase gradually. When the ratio of the amount of mesoporous supported Ni to Cu species was 2:1, the conversion reached 88.85%, and the selectivity was 76.34%, which the reaction had the highest yield, and the Ni/Cu composite oxide catalyst catalyzed alcohol oxidation with good activity. Therefore, this study was used to determine the optimal Ni/Cu ratio, and the following a discussion was given to the mesoporous supported Ni: Cu=2:1 catalytic system.

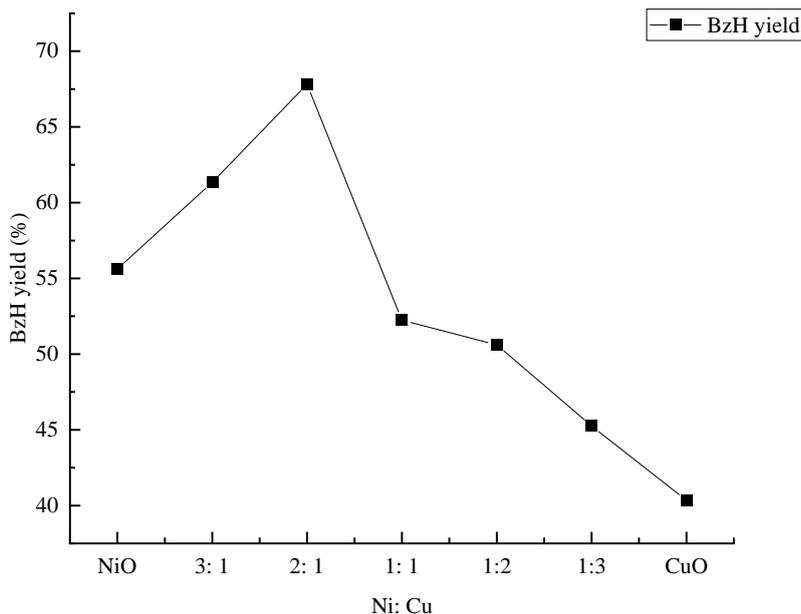


Figure 14. Catalytic activity of NiO_x-CuO_x/SBA-15 with different loading ratios. Reaction conditions: Catalyst calcination temperature 500 °C, BnOH 2.5ml, catalyst dosage 1g, reaction temperature 90 °C and reaction time 5h.

Compared with the known catalysts reported in the literature, the catalytic values are shown in Table 2. NiO_x-CuO_x/SBA-15 has the advantages of high efficiency, environmental protection and low cost, and will behave the potential industrial application value.

Table 2. Catalytic reaction of alcohol oxidation with different catalyst

Code	Conversion rate	selectivity	productivity
NiO _x -CuO _x /SBA-15	88.85%	76.34%	67.62%
Co/Mn[17]	39.42%	5.39%	25.26%
Mn ₃ O ₄ [18]	59.34%	89.31%	36.06%
La-OMS-2-A [19]	61.45%	63.83%	56.29%
VO _x /γ-Al ₂ O ₃ [20]	30.73%	79.03%	28.14%
Fe/KIT-PS[21]	80.40%	53.55%	56.38%

3.3.3 Effect of catalyst dosage of mesoporous supported Ni Cu oxides on reaction activity

Figure 15 shows the effect of mesoporous supported Ni/Cu oxide catalyst dosage from 0.25 g to 1.50 g on benzyl alcohol selective catalytic oxidation performance.

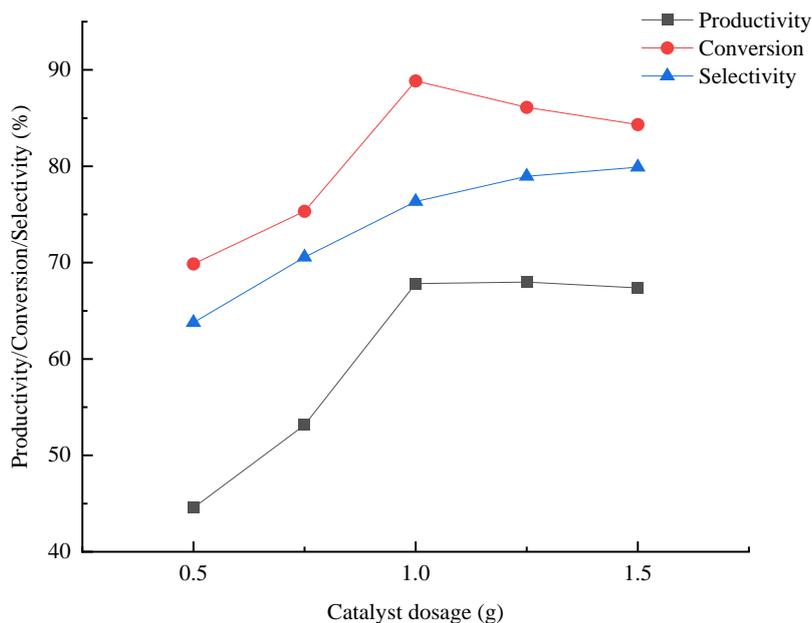


Figure 15. Catalytic activities with different catalyst dosages of NiO_x-CuO_x/SBA-15. Reaction conditions: Catalyst calcination temperature 500 °C, Nickel copper ratio 2:1, BnOH 2.5ml, reaction temperature 90 °C and reaction time 5h.

As seen from the figure, when the dosage of NiO_x-CuO_x/SBA-15 catalyst was less than 1.0 g, the conversion of Bnoh and the yield of Bzh in the reaction both rose with the increasing dosage of catalyst. This may be for the contributor that, as the dosage of catalyst increases, so does the number of catalytically active centers it can provide, when the catalyst dosage was 1.0 g, the benzyl alcohol conversion reached the maximum. However, when the dosage of NiO_x-CuO_x/SBA-15 Catalyst was over 1.0 g, the conversion of Bnoh and the yield of Bzh slightly decreased. This may lead to a fall in oxygen content due to too many catalytically active sites and insufficient benzyl alcohol oxidation, so 1.0 g was the optimum dosage of catalyst.

3.3.4 Effect of reaction temperature on catalytic activity of mesoporous supported Ni-Cu oxide catalysts

Usually, the number of activated molecules in the reaction is closely related to the reaction temperature, so the change of temperature is also one of the important factors affecting the catalytic activity of the reaction. Figure 16 examined the effect of temperature from 70 °C to 110 °C on the reaction of selective oxidation of Bnoh to produce Bzh. As seen from the figure, when the reaction temperature is lower than 90 °C, the number of activated molecules increases as the reaction temperature increases, and the conversion of Bnoh, as well as the yield of Bzh, increases dramatically. But after the reaction temperature exceeded 90 °C, the conversion of Bnoh slightly decreased while the selectivity of

Bzh almost unchanged, thus leading to a decrease in yield. We thus identified 90 °C as the most suitable temperature for this reaction.

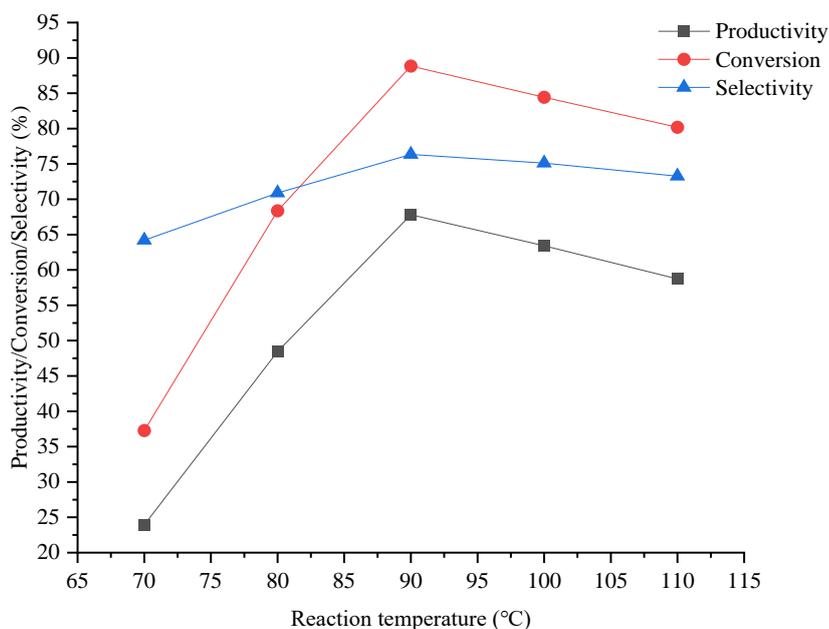


Figure 16. Effect of reaction temperature on activity of NiO_x-CuO_x/SBA-15 Catalysts. Reaction conditions: Catalyst calcination temperature 500 °C, BnOH 2.5ml, catalyst dosage 1g, and reaction time 5h.

3.3.5 Effect of reaction time on catalytic activity of mesoporous supported Ni Cu oxide catalysts

Figure 17 shows the effect of different reaction times on the Bnoh conversion and Bzh yield using NiO_x-CuO_x/SBA-15 as catalysts. It can be seen that when the reaction time is less than 5 h, the conversion of benzyl alcohol and the yield of benzaldehyde are both increasing with the extension of the reaction time, and it reached the maximum value at 5 h. While after the reaction time was over 5 h, the conversion of benzyl alcohol basically did not change, but with the extension of the reaction time. It promoted the occurrence of side reactions and increased the chance that the excessive oxidation of benzaldehyde to benzoic acid, so the selectivity of benzaldehyde decreased throughout the reaction. So 5 h was determined as the optimal time of reaction.

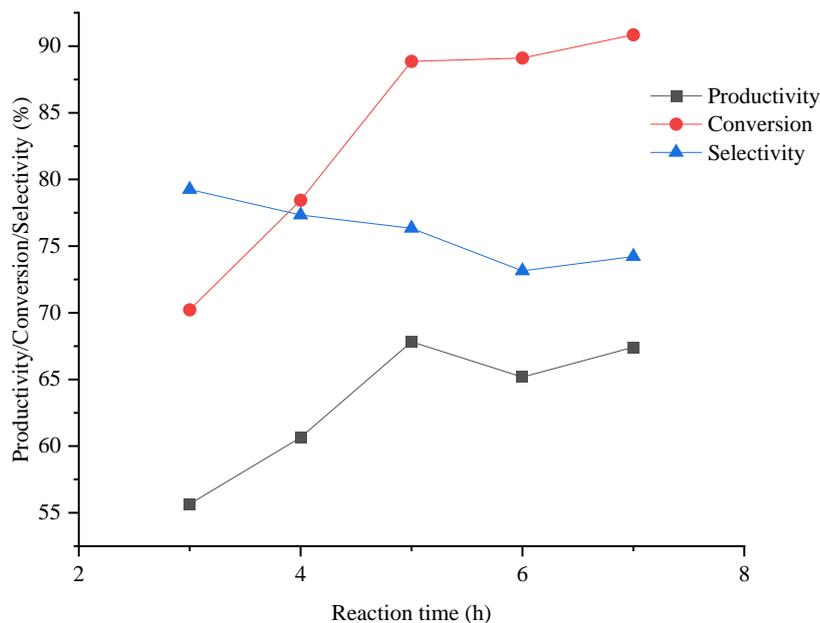


Figure 17. Effect of reaction time on the activity of NiO_x-CuO_x/SBA-15 catalysis. Reaction conditions: Catalyst calcination temperature 500 °C, BnOH 2.5ml, catalyst dosage 1g and reaction temperature 90 °C.

3.3.6 NiO_x-CuO_x/SBA-15 catalyzed alcohol oxidation with different substituents

To further test the effect of other substituent groups in NiO_x-CuO_x/SBA-15 on the catalytic performance in the alcohol oxidation reaction, benzyl alcohol, 4-methylbenzyl alcohol, 4-chlorobenzyl alcohol and 4-methylthiobenzyl alcohol were selected as references (show in Table 3). By comparison, it can be concluded that the substituent groups on the phenyl ring of benzyl alcohol compounds are different, and there is an obvious difference in oxidation effect under this oxidation system. Benzyl alcohol with no substituent groups could be quantitatively and highly selectively converted into the corresponding product, benzaldehyde. When an electron donating group (methyl or methoxy) was substituted at the para position on the phenyl ring of the substrate, both could be oxidized quantitatively with high selectivity to generate the corresponding aldehydes. However, when there is an electron-withdrawing group substitution on the benzene ring of the substrate, the effect on the oxidation of P-chlorobenzyl alcohol is not very ideal. When the substrate alcohol contains a sulfur heteroatom, the substrate can oxidize to the corresponding aldehyde in a shorter time. Also oxidizes to 4-methylthio benzaldehyde in a shorter time when there is a methyl thio substitution at the para position of the substrate.

Table 3. Catalytic reaction of alcohol oxidation with different substituents by NiO_x-CuO_x/SBA-15

Code	Conversion rate	selectivity	productivity
Benzyl alcohol	88.85%	76.34%	67.62%
4-methylbenzyl alcohol	85.32%	65.23%	65.78%
4-chlorobenzyl alcohol	79.51%	63.94%	56.82%
4-methylthiobenzyl alcohol	85.92%	73.26%	66.35%

Remark: catalyst calcination and catalytic process selection, calcination temperature of 500 °C, catalyst 1g, alcohol 23.8 mmol, 90 °C, 5h.

The resulting product after the catalysis of four benzyl alcohols was isolated by column chromatography to obtain a pure product, the yield was calculated, and the product composition was resolved with nuclear magnetic spectroscopy [22-23]. Raw material conversion and product selectivity were also determined by area normalization by ¹H-NMR, with partial product characterization data presented below:

Benzaldehyde: pale yellow liquid, ¹H-NMR (500MHz, CDCl₃) δ is 9.97 (s, 1H), 7.84 (d, J=4.9 Hz, 2H), 7.56-7.58 (m, 1H), 7.46-7.49 (m, 2H), MS (EI), m/z is 114.02 [M⁺].

4-methylbenzaldehyde: pale yellow liquid, ¹H-NMR (500MHz, CDCl₃) δ is 9.98 (s, 1H), 7.79 (d, J=8.1 Hz, 2H), 7.35 (d, J=8.0 Hz, 2H), 2.46 (s, 3H), MS (EI), m/z is 120.06 [M⁺].

4-Chlorobenzaldehyde: white solid, ¹H-NMR (500MHz, CDCl₃) δ is 9.99 (s, 1H), 7.86 (t, J=1.8 Hz, 1H), 7.79 (d, J=7.5 Hz, 1H), 7.61-7.63 (m, 1H), 7.87 (t, J=7.7 Hz, 1H), MS (EI), m/z is 140.03 [M⁺].

4-methylthiobenzaldehyde: pale yellow solid, ¹H-NMR (500MHz, CDCl₃) δ is 9.92 (s, 1H), 7.76-7.79 (m, 2H), 7.26-7.32 (m, 2H), 2.55 (s, 3H), MS (EI), m/z is 152.07 [M⁺].

4. CONCLUSIONS

In this paper, the selective oxidation of benzyl alcohol (BnOH) to produce benzaldehyde (BzH) was carried out to explore the optimal nickel copper based supported oxide catalyst for the development of NiO_x-CuO_x/SBA-15 with excellent catalytic performance, and the effects of various factors, such as the catalyst dosage, reaction temperature, and reaction time, on the catalytic activity of the reaction were discussed, the catalytic activity of catalysts in other alcohol oxidation reactions was also investigated. The following conclusions were drawn:

SBA-15 prepared by the hydrothermal method had ordered mesoporous pore channel structure, which was confirmed to be highly ordered by XRD, SEM, TEM, nitrogen desorption and so on. Supported the nickel copper composite oxide catalysts were synthesized by nano casting method using SBA-15 molecular sieves as support. Examination of the calcination temperature and the catalytic activity of various Ni and Cu loadings of NiO_x-CuO_x/SBA-15 Catalysts in benzyl alcohol oxidation showed that when the calcination temperature was 500 °C, the catalyst with Ni: Cu = 2:1 showed the best catalytic effect. The NiO_x-CuO_x/SBA-15 Supported Catalysts maintained the framework structure of SBA-15. The optimal conditions for catalyst use were 1.0 g of NiO_x-CuO_x/SBA-15 Supported

catalyst, 2.5 ml of benzaldehyde, 90 °C reaction temperature, and 5 h reaction time. Under these reaction conditions, 88.85% conversion of benzyl alcohol and 76.34% benzaldehyde selectivity, as well as 67.82% reaction yield, was obtained. Its catalytic performance is better than pure nickel or copper composite oxides.

The NiO_x-CuO_x/SBA-15 Catalyst could quantitatively and highly selectively convert benzyl alcohol with no substituents to the corresponding product benzaldehyde in other alcohol oxidation reactions. The electron donating group (methyl or methoxy) was substituted at the para position on the phenyl ring of the substrate, both could be oxidized quantitatively with high selectivity to generate the corresponding aldehydes. However, when there is an electron-withdrawing group substitution on the benzene ring of the substrate, the effect on the oxidation of P-chlorobenzyl alcohol is not very ideal. When the substrate alcohol contains sulfur heteroatom, the substrate can oxidize to the corresponding aldehyde in a shorter time. Also oxidizes to 4-methylthio benzaldehyde in a shorter time when there is a methylthio substitution at the para position of the substrate. The NiO_x-CuO_x/SBA-15 Catalyst synthesized in this paper is inexpensive, easy to get, and easy to recycle. In the process of selective oxidation of benzyl alcohol under mild conditions without organic solvent, the catalytic activity is high, and the environment is not polluted, which met the demands of "green chemistry". The production of Benzaldehyde by this method is simple, less time -consuming, provides high yield and high utilization of raw materials.

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