Cu₃₀Cr₅/碱性氧化铝催化 2,2,6,6-四甲基哌啶酮加氢

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摘要: 在2,2,6,6-四甲基哌啶酮连续化加氢生成2,2,6,6-四甲基哌啶醇的反应中, Cu₃₀Cr₅/碱性氧化铝比Cu₃₀Cr₅/γ-Al₂O₃具有更优异的催化性能, 反应的转化率和选择性分别高达99.0%和97.2%。N₂物理吸附-脱附、X射线光电子能谱、X射线衍射和氨气程序升温脱附结果表明, Cu⁰作为催化加氢反应的活性中心, 在Cu₃₀Cr₅/碱性氧化铝中具有更好的分散性, 且随着碱性氧化铝的引入, 催化剂酸性大幅下降, 从而有效抑制副产物2,6-二甲基-4-庚酮的生成, 因而产物2,2,6,6-四甲基哌啶醇的选择性显著提高。

关键词: 2,2,6,6-四甲基哌啶酮; 2,2,6,6-四甲基哌啶醇; 碱性氧化铝; 2,6-二甲基-4-庚酮; 铜; 铬; 伽马氧化铝

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Hydrogenation of 2,2,6,6-Tetramethylpiperidin-4-one over Cu₃₀Cr₅/Basic Alumina

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Abstract: Alumina B (basic alumina, pH > 8) was used as the support of copper-chromium catalysts for continuous hydrogenation of 2,2,6,6-tetramethylpiperidin-4-one (TAA) to 2,2,6,6-tetramethylpiperidin-4-ol (TMP). It was found that Cu₃₀Cr₅/alumina B exhibited better catalytic performance than Cu₃₀Cr₅/γ-Al₂O₃. 99.0% conversion of TAA and 97.2% selectivity for TMP were obtained over Cu₃₀Cr₅/alumina B under optimized conditions. Cu₃₀Cr₅/γ-Al₂O₃ and Cu₃₀Cr₅/alumina B were characterized by N₂ adsorption-desorption, X-ray diffraction, X-ray photoelectron spectroscopy, and NH₃ temperature-programmed desorption. The results showed that Cu particles dispersed better in Cu₃₀Cr₅/alumina B than in Cu₃₀Cr₅/γ-Al₂O₃.

Key words: 2,2,6,6-tetramethylpiperidin-4-one; 2,2,6,6-tetramethylpiperidin-4-ol; basic alumina; 2,6-dimethyl-4-heptanone; copper; chromium; γ-alumina

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2,2,6,6-Tetramethylpiperidin-4-ol (TMP, m.p. 127–129 °C, b.p. 214 °C) is a key intermediate of hindered amine light stabilizers (HALS) [1–4]. Traditionally, it is mainly manufactured in autoclaves from the hydrogenation of triacetoneamine (TAA, 2,2,6,6-tetramethylpiperidin-4-one) [1,3,5–8]. However, these batch processes in autoclaves are

energy inefficient and labor intensive. The proposed work therefore is to develop a continuous process for the production of TMP from hydrogenation of TAA. In our previous work [9], a continuous process was established for the production of TMP from hydrogenation of TAA catalyzed by Cu₃₀Cr₅/γ-Al₂O₃. This continuous process had reached a

high yield and could save energy and decreased environmental pollution. Nevertheless, the deamination of TAA occurs as a side reaction. 2,6-Dimethyl-4-heptanone is produced as a by-product (Scheme 1). For the mechanism of this side reaction, two factors have been proposed. One is the special structure in which the amino group is bonded to two tertiary carbon atoms that weakens the C–N bonds in TAA. The other one is that the acidic centers of γ -Al₂O₃ could easily adsorb TAA molecules from “N” moiety, which leads to breaking the C–N bonds catalyzed by Cu₃₀Cr₅/ γ -Al₂O₃.

Scheme 1. The reaction pathway for catalytic hydrogenation of TAA.

As mentioned above, hydrogenolysis may cause side reaction. Thus, modifying the support of the catalyst might decrease the side reaction and improve the selectivity for TMP. In this paper, alumina B (basic alumina, pH > 8) was performed instead of γ -Al₂O₃. The effects of alumina B were studied through N₂ adsorption-desorption (Brunauer-Emmet-Teller method; BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and NH₃ temperature-programmed desorption (NH₃-TPD).

1 Experimental

1.1 Preparation of the catalyst

All the catalysts used in this study were prepared by co-precipitation-kneading method. Taking Cu₃₀Cr₅/alumina B as an example, under mechanical stirring, a solution of 22.73 g Cu(NO₃)₂·3H₂O and 7.69 g Cr(NO₃)₃·9H₂O in 300 ml H₂O, and a solution of 13.08 g sodium carbonate in 300 ml H₂O were added together into a beaker containing 300 ml H₂O at 75 °C over 1 h. The mixture was aged for 1 h. The obtained precipitates were washed with water until NO₃[−] could not be detected, then, dried in air at 110 °C for 6 h. The obtained solid was ground into powder. The powder was kneaded with a mixture of 32.94 g alumina B (Tianjin Fine Chemical Research Institute) and 60 ml water and molded to bar by an extruder. After drying in air at 110 °C for 6 h, the catalyst was calcined at 500 °C for 4 h, and then

activated at 150 °C in hydrogen steam (0.7 MPa) before use.

1.2 Characterization of the catalyst

The composition of the catalyst was measured with an ICP instrument. The BET specific surface area and pore size measurements were performed by adsorption/desorption of N₂ at liquid nitrogen temperature on a NOVA 2200e automatic surface analyzer. XPS measurements were recorded with a PHI 1600 spectrometer using a Mg-K α X-ray excitation source (1486.6 eV, 15 kV, 400 W). The XRD patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu-K α radiation (40 kV, 100 mA) in the range of $2\theta = 10^\circ$ – 90° . NH₃-TPD was carried out on a Micromeritics 2910 apparatus equipped with a TCD detector. The calcined samples were heated up to 500 °C with helium blowing at a speed of 40 ml/min for 2 h. Then, after the temperature decreased to 120 °C, NH₃ were introduced with a speed of 20 ml/min for 0.5 h. Finally, the catalyst was treated with helium gas with a speed of 40 ml/min again. At the same time the temperature rose to 700 °C at a speed of 5 °C/min.

1.3 Activity test

The activity of the catalysts was tested in a tubular fixed-bed reactor with an inner diameter of 15 mm and a length of 700 mm, which contained 15.0 g catalysts. A solution of TAA (95%, m.p. 35–39 °C, b.p. 205 °C, Tiangang Auxiliary Co. Ltd) in ethanol (mass concentration of TAA in solution = 20%) was dosed into the reactor at a speed of 0.5 ml/min by a syringe pump. The temperature in the reaction zone was measured by a thermocouple located in the center of the tube and regulated by a PID cascade controller. The hydrogen pressure in the reaction system was controlled by a hydrogen pressure reducing valve. The reaction mixtures were analyzed by GC equipped with a 30 m SE-54 capillary column every 4 h. The components of the mixtures were confirmed by a HP 5971A GC-MS instrument with a 30 m SE-54 capillary column.

2 Results and discussion

2.1 Modification of the catalyst support

As mentioned above, the reason for the generation of 2,6-dimethyl-4-heptanone might be the acidic capacity of the catalyst support. Therefore, in order to prevent producing the by-products, alumina B was performed as the catalyst support. The results are summarized in Table 1. As shown in Table 1, the conversion of TAA and selectivity for TMP were improved compared to those over Cu₃₀Cr₅/

Table 1 Hydrogenation of TAA catalyzed by $\text{Cu}_{30}\text{Cr}_5$ /alumina B and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
$\text{Cu}_{30}\text{Cr}_5$ /alumina B	99.0	97.2	96.2
$\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$	97.1	92.4	89.7

Reaction conditions: 140 °C, 4.0 MPa hydrogen, flow rate of TAA in ethanol = 0.5 ml/min (concentration of solution = 20%).

$\gamma\text{-Al}_2\text{O}_3$, which implied that $\text{Cu}_{30}\text{Cr}_5$ /alumina B exhibited an excellent catalytic performance.

2.2 Characterization results

As shown in Fig. 1, NH_3 -TPD profiles of $\text{Cu}_{30}\text{Cr}_5$ /alumina B and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$ were carried out for comparison. Three peaks at 200, 300, and 510 °C existed in both of the NH_3 -TPD profiles. It can be found that the amount of acidic sites in $\text{Cu}_{30}\text{Cr}_5$ /alumina B was less than those in $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$. Based on the results of Fig. 1 and Table 1, we can conclude that the selectivity for TMP was improved with decreasing the amount of acidic sites.

Fig. 1. NH_3 -TPD profiles of reduced $\text{Cu}_{30}\text{Cr}_5$ /alumina B (1) and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$ (2).

The XRD patterns of the catalysts are shown in Fig. 2. It can be seen that the components of the two catalysts were

Fig. 2. XRD patterns of reduced $\text{Cu}_{30}\text{Cr}_5$ /alumina B (1) and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$ (2).

similar. CuCr_2O_4 signal could be found in XRD patterns of the catalysts. It indicated that the added chromium interacted with the copper to form CuCr_2O_4 . Additionally, the diffraction peaks demonstrated that Cu presented as copper crystals. It implied that Cu^0 was the major form in both catalysts.

The mean diameter of Cu crystals was calculated from the different diffraction lines at different 2θ using Scherrer equation. The results are shown in Table 2. It can be found that the average diameter of the Cu crystals in $\text{Cu}_{30}\text{Cr}_5$ /alumina B was smaller than that in $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$ at different 2θ . It indicated that the dispersion of Cu crystals in $\text{Cu}_{30}\text{Cr}_5$ /alumina B was better than that in $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$. Thus, compared with $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$, $\text{Cu}_{30}\text{Cr}_5$ /alumina B could provide more active centers, which might be the reason that the reaction achieved a high conversion over $\text{Cu}_{30}\text{Cr}_5$ /alumina B.

Table 2 The mean diameter of Cu crystals in reduced $\text{Cu}_{30}\text{Cr}_5$ /alumina B and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$

hkl	$2\theta/^\circ$	Crystal spacing (d, nm)	Mean diameter (nm)	
			$\text{Cu}_{30}\text{Cr}_5$ /alumina B	$\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$
111	43.2	0.20895	15.9	18.2
200	50.3	0.18092	10.6	12.0
220	74.0	0.12799	12.0	12.9

Active temperature: 150 °C.

In order to further investigate the effects of alumina B, the BET results of reduced $\text{Cu}_{30}\text{Cr}_5$ /alumina B and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$ are displayed in Table 3. Compared with $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$, the surface area of $\text{Cu}_{30}\text{Cr}_5$ /alumina B was increased. It has been reported that a higher surface area favored the dispersion of the active component of the catalysts [10–12]. Thus, the catalytic activity of $\text{Cu}_{30}\text{Cr}_5$ /alumina B was better than $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$, which resulted in a higher conversion of TAA over $\text{Cu}_{30}\text{Cr}_5$ /alumina B than over $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$.

Table 3 BET results of reduced $\text{Cu}_{30}\text{Cr}_5$ /alumina B and $\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
$\text{Cu}_{30}\text{Cr}_5$ /alumina B	135.6	0.3865	11.40
$\text{Cu}_{30}\text{Cr}_5/\gamma\text{-Al}_2\text{O}_3$	124.1	0.3564	11.49

The XPS profiles of $\text{Cu}_{30}\text{Cr}_5$ /alumina B are shown in Fig. 3. The curve of $\text{Cu } 2p_{3/2}$ can be divided into two peaks using Gauss curve fitting method. The peak with the binding energy value at 931.68 eV in $\text{Cu}_{30}\text{Cr}_5$ /alumina B (Fig. 3 (a)) was assigned to Cu^0 , which indicated that the copper element on the surface of the catalyst can be mainly reduced to Cu^0 . The weak signal of the $\text{Cu } 2p_{3/2}$ at 934.13 eV indicated that only trace amount of CuCr_2O_4 was present in the re-

Fig. 3. XPS profiles of the reduced $\text{Cu}_{30}\text{Cr}_5/\text{alumina B}$.

duced $\text{Cu}_{30}\text{Cr}_5/\text{alumina B}$. Meanwhile, the binding energy of Cr $2p_{3/2}$ level at 576.17 eV (Fig. 3 (b)) revealed that Cr existed mainly as CuCr_2O_4 . These results are in agreement with the XRD measurements.

2.3 Effect of reaction conditions

2.3.1 Reaction temperature

The reaction temperature was optimized and the results are shown in Fig. 4. With the increase of temperature, the conversion of TAA is enhanced and the selectivity changes slightly except for an obvious drop at 150 °C. At 140 °C, the

Fig. 4. Effects of temperature on the reaction over $\text{Cu}_{30}\text{Cr}_5/\text{alumina B}$. Reaction conditions: 4.0 MPa hydrogen, flow rate of the TAA in ethanol = 0.5 ml/min (concentration of the solution = 20%).

best yield was obtained. Thus, 140 °C was selected as the reaction temperature.

2.3.2 Hydrogen pressure

The hydrogen pressure has a remarkable effect on the selectivity for TMP, but a slight influence on the conversion of TAA (shown in Fig. 5). With an increase in hydrogen pressure from 1.0 to 4.0 MPa, the selectivity for TMP enhanced dramatically from 78.1% to 97.2%. While the conversion of TAA only increased slightly from 94.1% to 99.0%. Thus, considering the yield and feasibility of operation, 4.0 MPa was selected as the optimum hydrogen pressure.

Fig. 5. Effects of hydrogen pressure on the reaction over $\text{Cu}_{30}\text{Cr}_5/\text{alumina B}$. Reaction conditions: 140 °C, flow rate of the TAA in ethanol = 0.5 ml/min (concentration of the solution = 20%).

2.4 Catalyst lifetime

The lifetime of $\text{Cu}_{30}\text{Cr}_5/\text{alumina B}$ was also tested. The reaction was performed under the optimized conditions over 100 h. During this period, the catalyst performed good stability. The yield of TMP was kept to about 95%.

3 Conclusions

$\text{Cu}_{30}\text{Cr}_5/\text{alumina B}$ was used as the catalyst for the continuous hydrogenation of TAA to TMP. The conversion of TAA was 99.0% and the selectivity for TMP was 97.2%. The active center much dispersed better in alumina B than in $\gamma\text{-Al}_2\text{O}_3$. Meanwhile, the by-products clearly decreased and the selectivity increased with decreasing acidic centers.

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