$\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /堇青石整体式催化剂的制备及其催化甲苯燃烧性能

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摘要: 以堇青石蜂窝陶瓷为基底, Al_2O_3 浆料为过渡胶体, Cu 和 Co 为催化活性组分, 制备了一系列 $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /堇青石 ($x = 0\sim 1$) 整体式催化剂. 采用 X 射线衍射、X 射线光电子能谱、扫描电镜和程序升温还原等手段对催化剂进行了表征. 以甲苯为模型化合物, 在微型固定床反应器上评价了催化剂的催化性能. 结果表明, 当 Cu 含量较低时, 在整体式催化剂上形成了 Cu-Co-O 固溶体; 当 Cu 含量较高时, 可以检测到 CuO. 在催化剂表面, Co 以 Co^{2+} 和 Co^{3+} 形式存在, 而 Cu 主要以 Cu^{2+} 形式存在. 适量 Cu 的加入可以改善催化剂中 Co 的氧化还原性能, 有利于催化剂活性的提高. 在所制备的催化剂中, $\text{Cu}_{0.5}\text{Co}_{0.5}/\text{Al}_2\text{O}_3$ /堇青石整体式催化剂活性最高, 在 315 °C 可以完全催化燃烧消除甲苯.

关键词: 铜; 钴; 堇青石; 整体式催化剂; 甲苯; 催化燃烧

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Preparation of $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /Cordierite Monolithic Catalysts and the Catalytic Combustion of Toluene

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Abstract: A series of $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite ($x = 0\sim 1$) catalysts were prepared using cordierite as a support, a boehmite primer sol as the first washcoat layer and copper as well as cobalt oxides as the activity washcoat layer. The structure of the catalysts was characterized using X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and temperature-programmed reduction. Toluene was chosen as a model compound to evaluate the catalytic activity in a conventional fixed-bed quartz reactor. The results indicate that Cu-Co-O was present when the Cu content was low. CuO diffraction peaks were observed when the Cu content was high. Both Co^{2+} and Co^{3+} exist on the surface of the obtained monolithic catalysts while Cu^{2+} is the main Cu species. The addition of a certain amount of copper oxide improved the reducibility of the cobalt oxide, which enhanced the catalytic activity of the catalysts. All the obtained catalysts showed good activity for the catalytic combustion of toluene. The $\text{Cu}_{0.5}\text{Co}_{0.5}/\text{Al}_2\text{O}_3$ /cordierite catalyst showed the best catalytic activity. Toluene was completely oxidized at 315 °C.

Key words: copper; cobalt; cordierite; monolithic catalyst; toluene; catalytic combustion

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Volatile organic compounds (VOCs) are emitted from numerous industrial sources and they have long been a typical source of air pollution [1]. Their release into the atmosphere causes serious environmental problems [2]. Therefore, the removal of these pollutants has been an important research topic over the last 30 years [3]. Catalytic combustion is one of the most promising technologies for the removal of VOCs because of the low temperature required for combustion ignition, high selectivity, and high energy efficiency [4,5]. Supported noble metals and metal oxides are two types of catalysts used widely for the catalytic combustion of VOCs. Various reports have shown that supported Pt and Au have excellent activity for the complete oxidation of VOCs [6]. However, the high cost of noble metals has led to the development of base metal catalysts for this application.

Recently, many reports have been published on copper-containing catalysts for the catalytic oxidation of VOCs. Karthik et al. [7] reported the catalytic oxidation of VOCs over a Cu-Al-MCM-41 catalyst and found that Cu-Al-MCM-41 was an efficient catalyst because of the presence of well dispersed and isolated Cu^{2+} ions on the catalyst. Chen et al. [8] synthesized a series of CuO catalysts supported on cerium-modified and zirconium-pillared montmorillonite (CuO/CZM) and studied their performance for the total oxidation of toluene. Their results showed that the CuO/CZM catalyst is a promising candidate for industrial-scale VOC elimination. Lu et al. [9] prepared a series of transition-metal catalysts using activated carbon (AC) as the support material and copper, cobalt, iron, nickel as the catalytic active phases.

Monolithic catalysts have increasingly attracted the attention of researchers. They are used in many new reactor applications such as chemical processing, refining industries, and in catalytic combustion [10]. Compared with conventional catalysts, the monolithic catalysts have distinct advantages such as better mechanical strength, lower mass and heat transfer capacity, and lower thermal expansion coefficients [11]. Therefore, monolithic catalysts are promising for reactions with a high space velocity and a large amount of heat exchange such as the toluene combustion reaction.

In this work, a series of copper-cobalt mixed oxide catalysts with different Cu/Co ratios and washcoated on cordierite monoliths were investigated. The performance of the obtained catalysts for toluene catalytic combustion was evaluated and the catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and temperature-programmed reduction (H_2 -TPR).

1 Experimental

1.1 Catalyst preparation

Commercial cordierite with a cell density of 400 cpsi (62 cells/cm^2) was cut to obtain samples with a diameter of 8 mm and a length of 50 mm. The obtained cordierite samples were then pre-treated with a 20% oxalic acid solution and boiling for 3 h. The samples were washed with deionized water and finally calcined at 300°C for 3 h. The $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3/\text{cordierite}$ ($x = 0-1$) catalysts were prepared as follows: solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed in appropriate ratios. The mixture was added to the boehmite primer sol to obtain a total 40 wt% metal content in the slurry. The cordierite was then inserted into the above slurry and held for 10 min. It was then dried at room temperature in air and thereafter at 120°C for 3 h and then calcined at 500°C for 4 h. The coating procedure was repeated to achieve the desired amount of coating. Finally, the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3/\text{cordierite}$ monolithic catalysts were obtained.

1.2 Catalyst characterization

The phase structure of the samples was characterized by XRD using a Rigaku D/Max 2500 VB2+/PC diffractometer with Cu K_α radiation operating at 200 mA and 40 kV. XPS experiments were carried out on a Thermo Electron ESCALAB 250 instrument using Mg K_α as the excitation radiation at a constant pass energy of 30 eV. Binding energies were calibrated using the carbon that was present as a contaminant ($\text{C } 1s = 285.0 \text{ eV}$). The surface atomic compositions of all the samples were calculated from the photoelectron peak areas for each element after a correction for instrument parameters. The morphology of the samples was observed using a Japan HITACHI S-4700 scanning electron microscope. H_2 -TPR measurements were carried out using a Thermo Electron TPD/R/O 1100 series catalytic surfaces analyzer equipped with a TCD detector. The sample (0.08 g) was loaded and preheated with a 10% O_2 -90% He mixture at 500°C for 1.5 h. After cooling to room temperature, a 5% H_2 -95% N_2 mixture was introduced into the instrument and the temperature was increased to 800°C at a heating rate of 5°C/min . The water produced by the sample reduction was condensed in a cold trap before reaching the detectors. Only H_2 was detected in the outlet gas confirming the effectiveness of the cold trap.

1.3 Catalytic activity measurements

Catalytic combustion experiments were performed in a conventional fixed-bed quartz reactor at atmospheric pressure. The reactant gas mixture was prepared by passing air through a conical flask filled with liquid toluene, which was

kept at 0 °C. The reaction feed consisted of 0.1% toluene in dry air and the space velocity was 5.6×10^4 ml/(g·h). The reaction was stabilized for 20 min at the required temperature and the outlet products were measured using on-line gas chromatography (Beijing East & West Electronics Institute, GC-4000A) equipped with a flame ionization detector (FID). The temperature was controlled with a K-type thermocouple placed in the vicinity of the catalyst bed. Carbon dioxide and water were always the only reaction products detected during these experiments.

2 Results and discussion

2.1 XRD

The XRD patterns of the pretreated cordierite and $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite monolithic catalysts are shown in Fig. 1. For the pretreated cordierite support, the characteristic peaks at $2\theta = 10.4^\circ$, 18.0° , 19.0° , 21.6° , 26.3° , 28.4° , 29.4° , 33.9° , 36.8° , and 54.2° were present and these correspond to the ceramic structure [12]. The Co_3O_4 phase cannot be detected by XRD because of the congruence of the

Fig. 1. XRD patterns of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite samples.

Fig. 2. XRD patterns of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ samples.

Co_3O_4 and cordierite diffraction peaks.

To further confirm the phase of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite catalysts, the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ sol was characterized by XRD and the result is shown in Fig. 2. The position of the main diffraction peaks at $2\theta = 31.20^\circ$, 36.84° , 44.63° , 59.46° , and 65.35° correspond to Co_3O_4 (JCPDS 42-1467) for $x = 0$. With the addition of Cu the main diffraction peaks showed a small shift. Using the intensity 2θ peak at 36.84° as an example: the d value for the (311) plane is 0.24428 nm for $x = 0$ (Table 1); for $x = 0.5$ the d value for the (311) plane is 0.24519 nm; for $x = 0.75$ the d value for the (311) plane is 0.24534 nm. This is because the radius of Cu^{2+} (0.062 nm) is bigger than that of Co^{3+} (0.052 nm), which leads to an expansion of the Co_3O_4 lattice when Cu^{2+} migrates partially into the cubic structure. Therefore, changes in the d_{311} value around 0.001 nm for the samples indicate that the missing CuO phase at low Cu loading is incorporated into the Co_3O_4 lattice to form a Cu-Co-O solid solution [13]. The formation of the Cu-Co-O solid solution has been frequently reported in the literature [14,15]. When $x > 0.5$, the most intense peaks of bulk CuO at $2\theta = 35.5^\circ$, 38.7° , and 48.6° [16] were detected.

Table 1 XPS and XRD results of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite catalysts

Sample	Banding energy ^a (eV)				Atomic concentration (%)				d_{311}^b /nm
	Cu 2p _{3/2}	Co 2p _{3/2}	Al 2p	O 1s	Cu 2p _{3/2}	Co 2p _{3/2}	Al 2p	O 1s	
$x = 1$	932.9	—	74.2	531.0	3.24	—	42.70	54.06	—
$x = 0.9$	933.1	780.5	74.2	530.9	3.06	1.52	43.52	51.90	—
$x = 0.75$	932.8	780.2	74.3	531.0	2.72	1.03	40.40	55.85	0.24534
$x = 0.5$	932.8	780.3	74.2	531.0	3.53	2.51	44.89	49.07	0.24519
$x = 0.25$	933.0	780.4	74.4	531.1	2.13	1.71	40.42	55.74	0.24467
$x = 0.1$	933.1	780.5	74.5	531.1	0.71	1.71	42.64	54.94	0.24441
$x = 0$	—	781.8	74.3	531.3	—	1.98	40.80	57.22	0.24428

^aCorrected using the C 1s peak at 285.0 eV. ^bThe d_{311} values of Co_3O_4 were obtained from XRD.

2.2 XPS

The XPS spectra of Cu 2*p* for the catalysts with $x = 1$, 0.25, and 0.1 are shown in Fig. 3(a). The peak centered at about 933.1 eV represents Cu 2*p*_{3/2}. The presence of a higher Cu 2*p*_{3/2} binding energy (933.0–933.8 eV) and the pronounced shake-up peak (940.0–945.0 eV) are two major characteristics of CuO while a lower Cu 2*p*_{3/2} binding energy (932.2–933.1 eV) and the absence of the shake-up peak are characteristic of Cu₂O [17,18]. After the Gauss model fitting of our catalysts, we noticed that the given catalysts had a Cu 2*p*_{3/2} main peak at about 933.2 eV with a characteristic shake-up peak, which indicates the existence of a Cu²⁺ species in the catalysts.

The Co 2*p* spectra of the catalysts with $x = 0.1$, 0.5, and 0 are shown in Fig. 3(b). All the Co species in these samples are characterized by two main peaks (2*p*_{3/2} at about 780.5 eV and 2*p*_{1/2} at about 796.2 eV) with a spin-orbit splitting of about 15.0 eV. Since the Co 2*p* binding energies of Co²⁺ are similar to that of Co³⁺, satellite peak information must be considered to distinguish the two oxidation states of cobalt. It is generally accepted that energy gaps between the Co 2*p* main lines and the satellite peaks are highly related to the oxidation states of the Co cation. According to previous

reports, the high spin Co²⁺ compounds have strong satellite peaks and the binding energies are located at about 5–6 eV above the Co 2*p*_{3/2} main line. Low spin Co³⁺ compounds have very weak satellite peaks and these shift to higher binding energies by about 10–11 eV from the main peak [19,20]. Based on the binding energies of the Co 2*p* main lines and the energy gaps between the main lines and the satellite peaks, we conclude that both Co²⁺ and Co³⁺ exist on the surface of the obtained monolithic catalysts.

Table 1 lists the binding energies of Cu, Co, Al, O and the surface atomic percentages of all the samples. Mg and Si elements are not present in the cordierite support according to the XPS results, which means that the cordierite surface was fully covered by the active coating. For the Cu/Al₂O₃/cordierite catalyst, the surface atomic content of Cu was found to be 3.24% and it shows a small decrease with an increase in Co. For $x = 0.5$, the surface atomic content of Cu was found to be the highest among the prepared catalysts. Additionally, the surface atomic content of Co was also the highest. No significant differences among the binding energies of the different samples were observed for Al and O but the surface composition varied among the different samples.

2.3 Surface morphology of the samples

Figure 4 shows the morphology of the Cu_xCo_{1-x}/Al₂O₃/cordierite monolithic catalysts. The surface morphology changed significantly with the x value. For the catalyst with $x = 1$, namely Cu/Al₂O₃/cordierite, the surface was quite homogenous. The particle sizes were almost equivalent. However, the surface morphology of the catalysts changed greatly with a decrease in Cu content.

For $x = 0.9$, the surface was smoother and the particles were smaller. For $x = 0.75$, the catalyst also had a smooth surface but several cracks were found. For x from 0.5 to 0.1, the surface was very smooth and no cracks were found. For an x of 0, the surface was found to differ from the other catalysts and the dispersion was inhomogeneous while the particle heap was loose.

2.4 Catalytic activity

Figure 5 shows the catalytic activities of toluene oxidation with reaction temperature for the Cu_xCo_{1-x}/Al₂O₃/cordierite catalysts. The Cu/Co ratio has a significant influence on the catalytic activity of the catalysts. The catalytic activity of toluene oxidation over either Cu/Al₂O₃/cordierite ($x = 1$) or Co/Al₂O₃/cordierite ($x = 0$) was quite low. For $x = 1$, T_{10} (the temperature for 10% conversion of toluene) and T_{90} (the temperature for 90% conversion of toluene) was 242 °C and 339 °C, respectively, while for $x = 0$, T_{10} and T_{90} were 265 °C and 353 °C, respectively. Wang [21] reported on the

Fig. 3. Cu 2*p* (a) and Co 2*p* (b) XPS spectra of the Cu_xCo_{1-x}/Al₂O₃/cordierite catalysts.

Fig. 4. SEM images of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite samples. (a) $x = 1$; (b) $x = 0.9$; (c) $x = 0.75$; (d) $x = 0.5$; (e) $x = 0.25$; (f) $x = 0.1$; (g) $x = 0$.

catalytic combustion of toluene over $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts. They found that 5% $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ showed the highest catalytic activity and its T_{90} was 320 °C at a space velocity of 3600 ml/(g·h). Considering that the space velocity in our experiment was 5.6×10^4 ml/(g·h), the $\text{Cu}/\text{Al}_2\text{O}_3$ /cordierite monolithic catalyst gave much better catalytic performance.

The $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite ($x = 0.1\text{--}0.9$) catalysts gave higher catalytic activities than the $x = 1$ or $x = 0$ catalysts. This indicates a synergistic effect between CuO and Co_3O_4 , which implies that the Cu-Co-O solid solution is the active phase for toluene oxidation. Li et al. [22] also suggested that Cu-Mn-O was responsible for the toluene combustion reaction in Cu-Mn/MCM-41 catalysts. For $x = 0.5$, the catalyst gave the best catalytic activity with a toluene conversion of 10% at 234 °C. The toluene was completely oxidized at 315

°C. However, a further increase in the Cu content ($x > 0.5$) resulted in a decrease in catalytic activity. XRD showed that CuO peaks were present at $x > 0.5$, which suggests that the presence of bulk CuO depressed the catalytic activity.

2.5 H_2 -TPR

Figure 6 shows the H_2 -TPR profiles of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite monolithic catalysts. Three reduction peaks are present at about 206, 260, and 318 °C for the $\text{Cu}/\text{Al}_2\text{O}_3$ /cordierite catalyst ($x = 1$). The reduction temperature is markedly lower than that of pure CuO , which has a reduction peak at about 420 °C, suggesting that the redox properties of CuO are significantly affected by the interaction with the support. Based on a previous report, the two lower reduction peaks represent the reduction of small CuO clusters

Fig. 5. Catalytic activity of $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite for toluene combustion. Reaction conditions: GHSV = 5.6×10^4 ml/(g·h), $\varphi_0(\text{toluene}) = 0.1\%$.

Fig. 6. H_2 -TPR profiles of the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3$ /cordierite catalysts.

and the peak at 286 °C is attributed to the reduction of bulk CuO particles [23].

It is obvious that a different reduction profile is observed with an increase in cobalt oxide loading suggesting that the strong interaction between surface cobalt oxide and surface copper oxide improves the reducibility of the copper oxide. For the sample with $x = 0.9$, the two reduction peaks at lower temperature may be attributed to the stepwise reduction of Cu^{2+} , and the two higher temperature peaks are assigned to the stepwise reduction of Co^{3+} [24]. For the samples with $x = 0.75\text{--}0.1$, the low-temperature peaks resulted because of surface copper oxide reduction and the high-temperature peaks are assigned to surface cobalt oxide reduction. Three reduction peaks were present for the $\text{Co}/\text{Al}_2\text{O}_3/\text{cordierite}$ catalyst ($x = 0$). The peak at 372 °C should correspond to the reduction of highly dispersed or small crystallite Co_3O_4 to CoO , and the peak at 477 °C is due to the reduction of CoO to metallic Co . The peak at 608 °C represents the reduction of well-defined bulk Co_3O_4 to metallic Co [25].

3 Conclusions

$\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3/\text{cordierite}$ monolithic catalysts were prepared using cordierite as a support and with Al_2O_3 as a washcoat. In the $\text{Cu}_x\text{Co}_{1-x}/\text{Al}_2\text{O}_3/\text{cordierite}$ monolithic catalysts, the catalytic activities of the catalysts were strongly influenced by the Cu/Co ratios. $\text{Cu}_{0.5}\text{Co}_{0.5}/\text{Al}_2\text{O}_3/\text{cordierite}$ showed the highest catalytic activity. Toluene was completely oxidized at 315 °C with a GHSV of 5.6×10^4 $\text{ml}/(\text{g}\cdot\text{h})$. Using cordierite as a support benefited the dispersion of Cu . A CuO phase was observed at a higher Cu content. When $x < 0.5$, the Cu-Co-O solid solution formed on the monolithic catalysts and was responsible for the catalytic combustion of toluene. The XPS results showed that both Co^{2+} and Co^{3+} existed in the obtained monolithic catalysts and Cu existed mainly as the Cu^{2+} species. Since no Mg or Si was found in the cordierite support using XPS, the cordierite surface was fully covered by the active coating. The introduction of copper oxide changed the reduction profile of cobalt substantially suggesting that the strong interaction between surface cobalt oxide and copper oxide improved the reducibility of the cobalt oxide.

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