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Low-temperature catalytic oxidation of formaldehyde over Co_3O_4 catalysts prepared using various precipitants

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ABSTRACT

Co_3O_4 catalysts prepared with different precipitants ($\text{NH}_3\cdot\text{H}_2\text{O}$, KOH , NH_4HCO_3 , K_2CO_3 and KHCO_3) were investigated for the oxidation of formaldehyde (HCHO). Among these, KHCO_3 -precipitated Co_3O_4 ($\text{KHCO}_3\text{-Co}$) was the most active low-temperature catalyst, and was able to completely oxidize HCHO at the 100-ppm level to CO_2 at 90 °C. *In situ* diffuse reflectance infrared spectroscopy demonstrated that hydroxyl groups on the catalyst surface were regenerated by K^+ and CO_3^{2-} , thus promoting the oxidation of HCHO. Moreover, H_2 -temperature programmed reduction and X-ray photoelectron spectroscopy showed that employing KHCO_3 as the precipitant increased the $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio on the surface of the Co_3O_4 catalyst, thus further promoting oxidation. Structural characterization revealed that catalysts precipitated with carbonate or bicarbonate reagents exhibited greater specific surface areas and pore volumes. Overall, these data suggest that the high activity observed during the Co_3O_4 catalyzed oxidation of HCHO can be primarily attributed to the presence of K^+ and CO_3^{2-} on the Co_3O_4 surface and the favorable $\text{Co}^{3+}/\text{Co}^{2+}$ ratio.

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1. Introduction

Formaldehyde (HCHO) was classified as a human carcinogen by the International Agency for Research on Cancer in June 2004 [1]. Long-term exposure to parts per million (ppm) HCHO concentrations thus represents a health hazard, and the short-term (30 min) exposure limit recommended by the World Health Organization is 0.1 mg/m³ [2]. HCHO is released from various products, such as chipboard, textiles, and decorative materials, and can also contribute to the formation of photochemical smog [3]. Many efforts have been made to devise methods of reducing indoor HCHO concentrations to satisfy the stringent environmental regulations [4–6]. Conventional absorbents (such as activated carbon) are a ready means of eliminating HCHO, but the associated challenges of waste disposal and frequent replacement cannot be ignored. Photocatalysis

allows the ongoing degradation of low HCHO concentrations, although the limited capacity of this approach and the inevitable formation of undesirable by-products restricts its practical application [7]. As such, high efficiency, low-temperature catalytic oxidation is believed to represent the most promising technology for HCHO removal [8,9].

Initially, supported noble metal catalysts were applied to HCHO oxidation at room temperature [10–13], but the high cost of these metals restricts their large-scale application. Fortunately, oxides of transition metals, including Mn, Co, and Cu, also exhibit outstanding catalytic performance for low-temperature HCHO oxidation. Among these, Co_3O_4 has been widely investigated as a component of heterogeneous catalysts because of its high performance [12–18]. Many researchers have found that the catalytic activity of Co_3O_4 varies depending on the method used to prepare the catalyst. Zhu et al. [19] synthe-

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sized a material consisting of Co_3O_4 supported on ZSM-5 ($\text{Co}_3\text{O}_4/\text{ZSM-5}$) for the oxidation of propane, using impregnation (IM), deposition precipitation (DP), and hydrothermal (HT) methods. The catalytic activities of the resulting materials were in the order of $\text{HT} > \text{DP} > \text{IM}$, and it was also determined that the catalyst prepared with ammonium bicarbonate as the precipitant was superior to one prepared with NaOH. Shi et al. [20] produced a $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ catalyst for HCHO oxidation as a solid solution via both co-precipitation and citric acid methods. They found that the sample prepared by co-precipitation exhibited the best catalytic performance and was able to completely oxidize HCHO at 75 °C. The addition of specific alkali elements, such as K and Na, has also proven to be effective for promoting the catalytic oxidation of HCHO, by increasing the concentration of OH^- on the catalyst surface [21–23].

The precipitation method is popular and also practical with regard to eventual scaled-up applications. Therefore, it is necessary to both research and develop the synthesis of transition metal-based catalysts utilizing different precipitation methods. It would also be beneficial to further research the effect of the precipitation method on catalyst performance for low-temperature HCHO oxidation. Therefore, in the present study, various precipitants were used to generate Co_3O_4 catalysts, and the effects of these precipitants on the subsequent HCHO oxidation performance were discussed.

2. Experimental

2.1. Catalyst preparation

All chemicals used in this work were analytical grade and were purchased from the Sinopharm Chemical Reagent Co. (SCRC). The $\text{NH}_3\text{-Co}$, KOH-Co , $\text{NH}_4\text{HCO}_3\text{-Co}$, $\text{K}_2\text{CO}_3\text{-Co}$, and $\text{KHCO}_3\text{-Co}$ catalysts were prepared using a precipitation method, employing five precipitants: $\text{NH}_3\text{-H}_2\text{O}$, KOH , NH_4HCO_3 , K_2CO_3 , and KHCO_3 . In this method, a solution of the chosen precipitant (2 mol/L) was added dropwise (10 mL/min) to a solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (100 mL, 0.1 mol/L) with rapid stirring at room temperature until the reaction solution had a pH value of 9. After standing for 4 h, the resulting precipitate was removed by filtration and washed with deionized water until the wash water was neutral, then dried at 100 °C for 10 h and calcined at 400 °C for 2 h. For comparison purposes, a sample designated as PC/AHC-Co was prepared by dispersing $\text{HN}_4\text{HCO}_3\text{-Co}$ in a K_2CO_3 solution (2 wt%) with stirring for 30 min, followed by drying of the resulting product overnight at 100 °C.

2.2. Catalyst characterization

All samples were pretreated at 200 °C for 1 h prior to catalytic trials. X-ray diffraction (XRD) patterns of the catalysts were acquired using a D8 ADVANCE (Bruker) X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The K content of each sample was determined by atomic absorption spectroscopy (AAS). N_2 adsorption-desorption isotherms were obtained using the Barrett-Joyner-Halenda (BJH) method with a TriStar II 3020 appa-

ratus (Micromeritics) and X-ray photoelectron spectroscopy (XPS) spectra were acquired on an AXIS Ultra DLD instrument (Kratos) at 300 W using $\text{Mg K}\alpha$ excitation. H_2 temperature-programmed reduction (TPR) data were obtained with a Chemisorb 2720 TPx apparatus (Micromeritics). In these tests, a 0.1-g sample (40–60 mesh) was pretreated under a N_2 flow at 400 °C for 30 min in a quartz reactor. The cooled sample was subsequently reduced under a flow (40 mL/min) of 5 vol% H_2 in Ar from 20 to 700 °C (10 °C/min). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data were acquired on a Nicolet 6700 FTIR spectrometer equipped with an MCT detector and a DRIFTS cell (Harrick), scanning from 4000 to 800 cm^{-1} with a resolution of 4 cm^{-1} . Samples (30 mg) were assessed under a flow of 100 ppm HCHO and 21 vol% O_2 in N_2 at 100 mL/min total flow. Prior to the FTIR characterization, catalysts were pretreated under N_2 for 1 h at 300 °C.

2.3. Catalytic activity measurements

Catalytic reactions were carried out in a U-shape fixed-bed quartz tubular reactor with an inner diameter of 4 mm. The catalyst sample (100 mg, 40–60 mesh) was placed between two quartz wool layers in the tube and mass flow controllers were used to set the gas flow rates. HCHO vapor was obtained by passing a flow of N_2 through a paraformaldehyde (99%, SCRC) solution in a container within a water bath. The concentration of HCHO was adjusted by varying the N_2 flow rate and/or the temperature of the water bath. By mixing this N_2 stream with a flow of O_2 in N_2 , a typical feed gas composition (100 mL/min, GHSV of 69000 h^{-1}) containing 100 ppm HCHO and 21 vol% O_2 was obtained.

The concentrations of CO and CO_2 in the outgoing gas stream were measured by gas chromatography (GC 9560, HUAAL, flame ionization detector with a CH_4 conversion oven, 5 Å molecule sieve and TDX-01 packed columns). Experimental data were recorded beginning at the point at which the reaction stabilized at each reaction temperature and data acquisition continued over the span of 1 h. The HCHO conversion values were calculated using the equation

$$\text{HCHO conversion} = [\text{CO}_2]_{\text{out}}/[\text{HCHO}]_{\text{in}} \times 100\%$$

where $[\text{CO}_2]_{\text{out}}$ is the CO_2 concentration in the outlet stream (vol%), and $[\text{HCHO}]_{\text{in}}$ is the inlet HCHO concentration (vol%).

3. Results and discussion

3.1. Catalytic activity

Figure 1 summarizes the catalytic activities during HCHO oxidation over different catalysts. It is evident that 100% of the HCHO was oxidized to CO_2 over the $\text{KHCO}_3\text{-Co}$ and PC/AHC-Co at 90 °C, and so these two catalysts had the best low-temperature activity in this study. In contrast, the KOH-Co and $\text{NH}_3\text{-Co}$ catalysts achieved 100% HCHO conversion at 120 and 130 °C, respectively. The light off temperature (T_{10}) obtained with the $\text{KHCO}_3\text{-Co}$ was only 60 °C, much lower than the values for the $\text{NH}_4\text{HCO}_3\text{-Co}$ (90 °C) and $\text{NH}_3\text{-Co}$ (110 °C). The PC/AHC-Co performance was significantly better than that of the

Fig. 1. HCHO conversions over catalysts prepared with different precipitants. Reaction conditions: 100 ppm HCHO, 21 vol% O₂/N₂, GHSV = 69000 h⁻¹.

NH₄HCO₃-Co because of the immersion process applied during the preparation of the catalyst.

3.2. Catalyst characterization

3.2.1. Structural characterization

The textures of the catalysts were characterized by XRD and N₂ physisorption, and the XRD patterns of the as-prepared Co₃O₄ samples are shown in Fig. 2. The peaks at $2\theta = 31.3^\circ$, 36.8° , 38.5° , 44.8° , 55.6° , 59.5° , 65.2° and 77.3° correspond to the (220), (311), (222), (400), (422), (511), (440) and (533) planes, respectively. All these diffraction peaks are in good agreement with those of spinel Co₃O₄ (JCPDS 65-3103) and do not indicate any impurity phases. The average crystal sizes of these catalysts, as calculated from the XRD data (FWHM of the (311) peak) using the Scherrer equation, ranged from 17 to 23 nm (Table 1).

The N₂ adsorption-desorption isotherms of the catalysts are shown in Fig. 3. Each catalyst generated a typical IV isotherm

Fig. 2. XRD patterns of catalysts prepared with different precipitants. (1) NH₃-Co; (2) KOH-Co; (3) NH₄HCO₃-Co; (4) K₂CO₃-Co; (5) KHCO₃-Co; (6) PC/AHC-Co.

Table 1

Chemical and physical parameters of catalysts prepared with different precipitants.

Sample	BET surface area (m ² /g)	BJH pore volume (cm ³ /g)	BJH pore size (nm)	K ^a (wt%)	Crystallite size ^b (nm)
NH ₃ -Co	67.7	0.135	7.6	0	17.6
KOH-Co	54.8	0.105	7.6	0	18.6
NH ₄ HCO ₃ -Co	95.4	0.393	16.5	0	18.3
K ₂ CO ₃ -Co	78.7	0.337	14.2	0.07	19.3
KHCO ₃ -Co	97.9	0.411	16.8	1.15	15.1
PC/AHC-Co	88.3	0.216	9.8	1.06	22.4

^a Determined by AAS.

^b Determined using the Scherrer equation.

and a type H1 hysteresis loop, indicating that the catalyst pores had a narrow distribution and that these materials each had a mesoporous (2 to 50 nm) structure [24]. The BET surface areas, total pore volumes and pore sizes were found to vary depending on the precipitant. Comparing the NH₃-Co and KOH-Co with catalysts precipitated using carbonate and bicarbonate reagents, the latter had the higher physical parameters. The significant increase in the adsorption capability indicates that the specific surface area was enhanced due to the decomposition of cobalt carbonate during the calcination process. The PC/AHC-Co catalyst shows reduced structural parameters compared with the NH₄HCO₃-Co, which is attributed to either clogging or covering of the NH₄HCO₃-Co pores after K₂CO₃ loading [16]. The residual K concentration in the KHCO₃-Co was 15 times that of the K₂CO₃-Co, although the peak position demonstrates that the K⁺ cations did not enter the bulk phase Co₃O₄ or replace the Co²⁺ ions because of the space ($r_{K^+} = 0.152$ nm, $r_{Co^{2+}}(hs) = 0.0885$ nm and $r_{Co^{3+}}(hs) = 0.075$ nm) [25] and charge factors. That is, if the Co²⁺ ions in the Co₃O₄ lattice had been replaced by K⁺, the lattice parameters of the Co₃O₄ would have been altered accordingly. These results are similar to those reported previously by Wu et al. [26] and Park et al. [27]. As a result of the formation of carbonic acid and hydroxide ions, a hydrogen carbonate solution will slowly generate CO₂ at room temperature [28]. In the presence of Co²⁺, the hydrolyza-

Fig. 3. N₂ adsorption-desorption isotherms of catalysts prepared with different precipitants.

Fig. 4. H_2 -TPR profiles of NH_3 -Co (1), KOH -Co (2), NH_4HCO_3 -Co (3), K_2CO_3 -Co (4), $KHCO_3$ -Co (4), and PC/AHC -Co (6) catalysts.

tion rate will increase substantially and so more CO_2 will be released. The CO_2 gas bubbles thus produced could provide aggregation centers for the precipitation reaction, creating loose hydroxide carbonate precursors that might include K^+ [29]. During the calcination process, these hydroxide carbonate precursors will decompose to CO_2 and H_2O , refining the particle size and increasing the porosity of the powder [30].

3.2.2. H_2 -TPR results

In Fig. 4, two obvious reduction peaks can be observed in the low (I) and high (II) temperature regions. There are different opinions concerning the reduction mechanism of Co_3O_4 . Arnoldy et al. [31] stated that the reduction of Co_3O_4 consisted of only a single step, while many other researchers [32–34] regarded the reduction of Co_3O_4 as a two-step process involving the intermediate reduction of CoO . In the low temperature region, the Co^{3+} in Co_3O_4 was presumably reduced to Co^{2+} with the sample transitioning to CoO as an intermediate. In the high temperature section, this intermediate was further reduced to metallic cobalt. Peak I (at 290 °C) is therefore attributed to the reduction of Co^{3+} to Co^{2+} , while peak II (at 400 °C) resulted from the reduction of CoO to Co . The $KHCO_3$ -Co showed the lowest reduction temperature (266 °C) among all the samples

Table 2

Surface chemical compositions and element molar ratios of different catalysts.

Sample	Surface content (at%)			Surface molar ratio	
	Co	O	K	Co^{3+}/Co^{2+}	O_{ads}/O_{latt}
NH_4HCO_3 -Co	39.1	56.7	0	0.24	1.08
$KHCO_3$ -Co	36.8	59.8	3.4	0.35	0.96
PC/AHC -Co	36.3	60.4	3.3	0.42	1.33

examined, while the NH_3 -Co had the highest peak. The reduction temperatures of the others were in the order of KOH -Co > NH_4HCO_3 -Co > K_2CO_3 -Co > PC/AHC -Co, which is in good agreement with the observed differences in their catalytic $HCHO$ oxidation activities. There have been several literature reports that the amount of Co^{3+} on the catalyst surface is related to the catalytic activity [35–37]. In the present work, it can be seen that the reduction temperature shifts from 300 to 283 °C upon applying a coating of K_2CO_3 (2 wt%) on the NH_4HCO_3 -Co catalyst. The reason for this shift is explained below, based on XPS analysis.

3.2.3. XPS results

Taking into account the structures and residual K contents of these catalysts, the $KHCO_3$ -Co, NH_4HCO_3 -Co and PC/AHC -Co were chosen to investigate the effect of the precipitant on the surface chemical state. The $Co\ 2p$, $K\ 2p$ and $O\ 1s$ XPS data for these materials are presented in Fig. 5, and associated values are summarized in Table 2. As can be seen from Fig. 5(a) and Table 2, K was found in the $KHCO_3$ -Co and PC/AHC -Co, but not in the NH_4HCO_3 -Co. The amounts of K on the surfaces of the $KHCO_3$ -Co and PC/AHC -Co were both approximately 3.3 at%, demonstrating the presence of residual K following the use of $KHCO_3$ as the precipitant. Fig. 5(b) indicates two major oxygen species with $O\ 1s$ binding energy (BE) values of 529.8 and 530.8 eV. The former results from surface lattice oxygen (O_{latt}) contained in the Co_3O_4 [38], while the latter is attributed to adsorbed surface oxygen (O_{ads}) [39]. The O_{ads}/O_{latt} ratio in the $KHCO_3$ -Co was 0.96 (Table 2), a value that is slightly lower than that of the NH_4HCO_3 -Co (1.08). The O_{ads}/O_{latt} ratio of the PC/AHC -Co (1.33) was relatively high, which is attributed to the presence of surface hydroxyl (OH) groups resulting from

Fig. 5. XPS patterns of NH_4HCO_3 -Co (1), $KHCO_3$ -Co (2), and PC/AHC -Co (3) catalysts.

the hydrolysis of K_2CO_3 [22]. The peaks in the Co 2p XPS spectra (Fig. 5(c)) at 795.0 and 780.1 eV could represent Co 2p_{1/2} and Co 2p_{3/2} spin-orbital peaks [19, 40]. In this work, the Co 2p spin-orbit splitting value of the Co_3O_4 catalysts was 14.9 eV, which is close to that of Co^{3+} (15.0 eV) [41], therefore, the catalysts likely consisted of Co_3O_4 . The $\text{Co}^{3+}/\text{Co}^{2+}$ ratio for the $\text{NH}_4\text{HCO}_3\text{-Co}$ was 0.24, a value that is less than that of the PC/AHC-Co (0.42), indicating that a greater amount of Co^{3+} was present on the PC/AHC-Co surface exposed after the K_2CO_3 immersion. This could explain the shift in the reduction temperature, which decreased from 300 to 283 °C when K_2CO_3 was coated onto the $\text{NH}_4\text{HCO}_3\text{-Co}$ catalyst. The $\text{Co}^{3+}/\text{Co}^{2+}$ ratio of the $\text{KHCO}_3\text{-Co}$ was 0.35, which is between the values for the $\text{NH}_4\text{HCO}_3\text{-Co}$ and PC/AHC-Co. It appears that less of the $\text{KHCO}_3\text{-Co}$ surface was covered with K_2CO_3 compared with the PC/AHC-Co. Despite the much higher $\text{Co}^{3+}/\text{Co}^{2+}$ ratio of the PC/AHC-Co, the relatively low specific surface area of this material (Table 1) might explain why its catalytic activity was similar to that of the $\text{KHCO}_3\text{-Co}$.

3.2.4. FT-IR

Figure 6 shows the *in situ* DRIFT spectra acquired during HCHO oxidation over the $\text{NH}_4\text{HCO}_3\text{-Co}$ and $\text{KHCO}_3\text{-Co}$ catalysts. In Fig. 6(a), no peaks associated with adsorbed HCHO are seen

in the $\text{NH}_4\text{HCO}_3\text{-Co}$ spectrum, thus the HCHO was oxidized as soon as it was adsorbed on the surface of the catalyst. The peaks at 1593 and 1575 cm^{-1} are attributed to the asymmetric (COO) stretching vibration of formate species, while those at 1360, 1315 and 1276 cm^{-1} are assigned to the corresponding symmetric (COO) stretch [42]. The absorbance bands at 1480, 1434, 1132, 1097 and 1055 cm^{-1} are ascribed to dioxymethylene (DOM) species [43,44] and are seen to increase significantly over the first few minutes, while those due to OH species at 3400 and 3342 cm^{-1} increased slightly. In addition, the absorptions at 3633, 3568, 3542, and 3373 cm^{-1} ascribed to other hydroxyl groups decreased to give negative peaks, presumably as these groups were consumed during the oxidation. When O_2 was introduced and the temperature increased, similar spectra were obtained, as shown in Fig. 6(b). The bands resulting from DOM species were significantly weakened as the temperature increased. As well, the monodentate formate species (1593 and 1276 cm^{-1}) appear to have been converted to bidentate formate (1575 and 1360 cm^{-1}) [45] as the temperature was raised to 200 °C, with the simultaneous appearance of a new monodentate species (1506 and 1248 cm^{-1}). Surface carbonate and bicarbonate species (1543, 1335 and 1210 cm^{-1}) [45,46] were formed at 80 °C and the absorbance of the two types of hydroxyl groups returned to their initial values.

Fig. 6. *In situ* DRIFTS spectra obtained during HCHO adsorption (a) and HCHO oxidation (b) on $\text{NH}_4\text{HCO}_3\text{-Co}$, and during HCHO adsorption (c) and HCHO oxidation (d) on $\text{KHCO}_3\text{-Co}$.

The behavior of the $\text{KHCO}_3\text{-Co}$ was simple. As shown in Fig. 6(c), the peak due to one type of hydroxyl group (3623 cm^{-1}) decreased slightly with increasing temperature, while the other type (3373 cm^{-1}) increased greatly during HCHO adsorption. The intensities of the DOM peaks (1434 , 1412 , 1132 , 1099 and 1060 cm^{-1}) increased rapidly in the initial stage, and the peaks from one type of bicarbonate (1593 and 1376 cm^{-1}) also increased rapidly up to 60 min. At the oxidation stage shown in Fig. 6(d), the relative intensities of the surface carbonate species peaks (1543 and 1346 cm^{-1}) were found to change, although no new peaks were generated. The hydroxyl species (3373 cm^{-1}) and the formate species (1593 and 1376 cm^{-1}) initially increased in intensity and then decreased on going from 40 to $160\text{ }^\circ\text{C}$, while the peaks due to DOM decreased continuously. At $200\text{ }^\circ\text{C}$, the $\text{KHCO}_3\text{-Co}$ spectrum indicates the presence of only a few OH groups (3373 cm^{-1}), as well as DOM and carbonate species.

At lower temperatures ($80\text{ }^\circ\text{C}$), few DOM species could be converted to formate species due to absence of hydroxyl groups on the $\text{NH}_4\text{HCO}_3\text{-Co}$. In contrast, at higher temperatures ($> 80\text{ }^\circ\text{C}$), the decomposition of formate species became the key step. In the case of the $\text{KHCO}_3\text{-Co}$, the DOM species generated via the adsorption of HCHO could be converted to formate species in the presence of K_2CO_3 , and so the key step would be the oxidation of formate species to carbonate species. It is thought that hydroxyl groups are formed from the hydrolysis of surface K_2CO_3 , and are then consumed during the reaction. Subsequently, these hydroxyl groups are replaced by the H_2O generated by the reaction. Thus, surface alkaline hydrolysis is continued and accelerates the HCHO oxidation process.

4. Conclusions

Co_3O_4 catalysts prepared using various precipitants were studied with regard to low-temperature HCHO oxidation. It was

found that the KHCO_3 precipitated material ($\text{KHCO}_3\text{-Co}$) exhibits the best catalytic efficiency, and is able to provide 100% conversion of HCHO to CO_2 at $90\text{ }^\circ\text{C}$. The AAS and XPS data indicate that the $\text{KHCO}_3\text{-Co}$ surface holds residual K. The structures of the Co_3O_4 catalysts obviously vary with different types of precipitants, such that those catalysts precipitated using reagents containing CO_3^{2-} or HCO_3^- ions have higher BET surface areas and BJH pore sizes. $\text{H}_2\text{-TPR}$ and XPS analyses show that the $\text{KHCO}_3\text{-Co}$ and PC/AHC-Co have higher oxidizing abilities due to their relatively high surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratios. *In situ* DRIFTS results suggest that few DOM species are converted to formate species due to the absence of OH groups, which can be regenerated by K^+ and CO_3^{2-} loaded on the surface of the Co_3O_4 .

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Graphical Abstract

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The K^+ and CO_3^{2-} on the surface of Co_3O_4 would regenerate hydroxyl groups consumed in the reaction, which would be helpful for catalytic oxidation of HCHO.

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不同沉淀剂制备的 Co_3O_4 低温催化氧化甲醛

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摘要: 室内空气中低浓度甲醛严重危害人类健康, 高效去除甲醛成为人们关注的课题。在各种去除甲醛的方法中, 吸附法简单快速, 但是存在饱和和吸附量的限制; 光催化降解法能够去除低浓度甲醛, 却会产生一些如臭氧等二次污染物; 低温催化氧化甲醛由于其高效和产物矿化完全而成为具有实际应用前景的技术。虽然贵金属负载型催化剂具有室温去除甲醛的能力, 可是高昂的成本使其难以大规模应用。过渡金属氧化物因其良好的催化氧化性能和较低的成本逐渐成为研究重点。

近期研究发现, 含钴的氧化物具有较高的催化氧化甲醛能力, 同时一些碱金属如钠或钾的加入可增加催化剂表面羟基物种, 从而有效促进了甲醛氧化。沉淀法具有操作简单和条件易于控制等特点, 因此本文选取不同的沉淀剂 ($\text{NH}_3\cdot\text{H}_2\text{O}$, KOH , NH_4HCO_3 , K_2CO_3 , KHCO_3) 采用沉淀法制备了 Co_3O_4 催化剂并进行了甲醛催化氧化性能测试。采用 X 射线衍射 (XRD)、原子吸收光谱 (AAS)、氢气程序升温脱附 (H_2 -TPD)、X 射线光电子能谱 (XPS) 和原位漫反射红外光谱 (*in situ*-DRIFTS) 等表征手段探讨了不同沉淀剂制备的催化剂催化甲醛氧化性能差异的原因。

结果显示, 在以 KHCO_3 为沉淀剂制备的 Co_3O_4 催化剂 (KHCO_3 -Co) 上甲醛 (100 ppm) 完全氧化成 CO_2 的温度为 90°C , 明显优于其他样品。在以 NH_4HCO_3 为沉淀剂制备的 Co_3O_4 表面负载 2 wt% 的 K_2CO_3 后 (PC/AHC-Co) 具有和 KHCO_3 -Co 相似的催化性能。XRD 结果表明, 各沉淀剂制备的 Co_3O_4 均为尖晶石型, 晶粒尺寸约为 18 nm, 衍射峰位置无明显偏移说明没有其他金属离子掺杂进 Co_3O_4 晶体。结构表征还表明, 采用含碳酸根或碳酸氢根离子试剂制备的样品具有较高的比表面积、孔体积和孔径, 可能是焙烧阶段碳酸钴分解产生大量 CO_2 形成的, 而负载 K_2CO_3 的样品各参数均大幅降低, 说明表面 K_2CO_3 填补或堵塞了部分孔结构。AAS 结果表明, KHCO_3 -Co 和 PC/AHC-Co 所含 K 离子浓度相近并显著高出其他沉淀剂制备样品, XPS 结果也证明了这一点。这可能是由于在用 KHCO_3 沉淀钴离子的过程中, 钾离子裹挟在沉淀物中不易被洗

涤干净, 并且保留在焙烧后的样品中. H_2 -TPR 和 XPS 结果显示, 用 KHCO_3 作为沉淀剂时可以增加 Co_3O_4 催化剂表面 $\text{Co}^{3+}/\text{Co}^{2+}$ 比例从而提高了氧化能力, 虽然本文 PC/AHC-Co 样品有着最高的 $\text{Co}^{3+}/\text{Co}^{2+}$ 比例, 但相对较低的比表面积和孔径减少了活性中心, 使得其活性与 KHCO_3 -Co 相似. *in situ*-DRIFTS 结果表明, NH_4HCO_3 -Co 催化剂上羟基基团在甲醛吸附阶段会被大量消耗, 并有二氧亚甲基 (DOM) 中间物种大量生成. 在氧化阶段, 随着温度升高, DOM 逐渐减少, 而甲酸盐和碳酸氢盐物种逐渐增多, 最后各物种趋近催化剂的初始状态. 在 KHCO_3 -Co 催化剂上, 甲醛吸附阶段有大量 DOM 和甲酸盐物种生成, 而羟基基团消耗并不明显. 在氧化阶段随着温度升高, DOM 逐渐减少, 甲酸盐逐渐增多并最后消失, 整个过程并未观测到碳酸氢盐物种生成. 这说明 KHCO_3 -Co 样品在催化氧化甲醛反应中能够再生羟基基团, 进而提高了催化氧化甲醛活性.

综上所述, 以 KHCO_3 为沉淀剂制备的 Co_3O_4 样品具有最佳的甲醛催化氧化性能, 其在沉淀过程中样品上会残留一定量钾离子, 其作用与在 Co_3O_4 表面负载相当量的 K_2CO_3 相似. Co_3O_4 催化氧化甲醛活性高的主要原因是催化剂表面存在 K^+ 和 CO_3^{2-} 并且具有适当的 $\text{Co}^{3+}/\text{Co}^{2+}$ 混合价态.

关键词: 甲醛氧化; 催化; 四氧化三钴; 沉淀法; 钾离子

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