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Low-temperature catalytic oxidation of formaldehyde over Co₃O₄ catalysts prepared using various precipitants



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ABSTRACT

Co₃O₄ catalysts prepared with different precipitants (NH₃·H₂O, KOH, NH₄HCO₃, K₂CO₃ and KHCO₃) were investigated for the oxidation of formaldehyde (HCHO). Among these, KHCO₃-precipitated Co₃O₄ (KHCO₃-Co) was the most active low-temperature catalyst, and was able to completely oxidize HCHO at the 100-ppm level to CO₂ at 90 °C. In situ diffuse reflectance infrared spectroscopy demonstrated that hydroxyl groups on the catalyst surface were regenerated by K⁺ and CO_{3²⁻}, thus promoting the oxidation of HCHO. Moreover, H₂-temperature programmed reduction and X-ray photoelectron spectroscopy showed that employing KHCO₃ as the precipitant increased the Co³⁺/Co²⁺ molar ratio on the surface of the Co₃O₄ 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 Co₃O₄ 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 Co_3^{+}/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, Co₃O₄ 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 Co₃O₄ 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 (Co_3O_4/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 HT > DP > 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 $Mn_xCo_3.xO_4$ 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 NH₃-Co, KOH-Co, NH₄HCO₃-Co, K₂CO₃-Co, and KHCO₃-Co catalysts were prepared using a precipitation method, employing five precipitants: NH₃·H₂O, KOH, NH₄HCO₃, K₂CO₃, and KHCO₃. In this method, a solution of the chosen precipitant (2 mol/L) was added dropwise (10 mL/min) to a solution of Co(NO₃)₂·6H₂O (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 HN₄HCO₃-Co in a K₂CO₃ 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 Cu K_{α} radiation. The K content of each sample was determined by atomic absorption spectroscopy (AAS). N₂ adsorption-desorption isotherms were obtained used 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 Mg K_{α} excitation. H₂ temperature-programmed reduction (TPR) data were obtained with a Chemisorb 2720 TP_x apparatus (Micromeritics). In these tests, a 0.1-g sample (40-60 mesh) was pretreated under a N2 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% H₂ 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% O2 in N2 at 100 mL/min total flow. Prior to the FTIR characterization, catalysts were pretreated under N2 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 N₂ through a paraformaldehyde (99%, SCRC) solution in a container within a water bath. The concentration of HCHO was adjusted by varying the N₂ flow rate and/or the temperature of the water bath. By mixing this N₂ stream with a flow of O₂ in N₂, a typical feed gas composition (100 mL/min, GHSV of 69000 h⁻¹) containing 100 ppm HCHO and 21 vol% O₂ was obtained.

The concentrations of CO and CO₂ in the outgoing gas stream were measured by gas chromatography (GC 9560, HUAAI, flame ionization detector with a CH₄ conversion oven, 5Å 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

HCHO conversion = $[CO_2]_{out}/[HCHO]_{in} \times 100\%$ where $[CO_2]_{out}$ is the CO₂ concentration in the outlet stream (vol%), and $[HCHO]_{in}$ 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 CO₂ over the KHCO₃-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 NH₃-Co catalysts achieved 100% HCHO conversion at 120 and 130 °C, respectively. The light off temperature (T_{10}) obtained with the KHCO₃-Co was only 60 °C, much lower than the values for the NH₄HCO₃-Co (90 °C) and NH₃-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% O_2/N_2 , 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 2θ = 31.3°, 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 (FMWH of the (311) peak) using the Scherrer equation, ranged from 17 to 23 nm (Table 1).

The N_2 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 cata	lysts	prepared	with	differei	nt
precipita	nts.								

Sample	BET surface area	BJH pore volume	BJH pore size	Ka	Crystallite size ^b
oumpio	(m^2/g)	(m^2/g) (cm^3/g) (nm^3/g)		(wt%)	(nm)
NH3-Co	67.7	0.135	7.6	0	17.6
КОН-Со	54.8	0.105	7.6	0	18.6
NH4HCO3-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
КНСО3-Со	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 Co_3O_4 or replace the Co^{2+} ions because of the space ($r_{K+} = 0.152$ nm, r_{Co2+} (*hs*) = 0.0885 nm and r_{Co3+} (*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. N_2 adsorption-desorption isotherms of catalysts prepared with different precipitants.



Fig. 4. H_2 -TPR profiles of NH₃-Co (1), KOH-Co (2), NH₄HCO₃-Co (3), K₂CO₃-Co (4), KHCO₃-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. H₂-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 Co₃O₄. Arnoldy et al. [31] stated that the reduction of Co₃O₄ consisted of only a single step, while many other researchers [32–34] regarded the reduction of Co₃O₄ as a two-step process involving the intermediate reduction of CoO. In the low temperature region, the Co³⁺ in Co₃O₄ was presumably reduced to Co²⁺ 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 Co³⁺ to Co²⁺, while peak II (at 400 °C) resulted from the reduction of CoO to Co. The KHCO₃-Co showed the lowest reduction temperature (266 °C) among all the samples

Table 2

Surface chemical compositions and element molar ratios of different catalysts.

Comulo	Surface content (at%)			Surface molar ratio		
Sample	Со	0	К	Co ³⁺ /Co ²⁺	O_{ads}/O_{latt}	
NH ₄ HCO ₃ -Co	39.1	56.7	0	0.24	1.08	
KHCO3-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 NH₃-Co had the highest peak. The reduction temperatures of the others were in the order of KOH-Co > NH₄HCO₃-Co > K₂CO₃-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 Co³⁺ 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 K₂CO₃ (2 wt%) on the NH₄HCO₃-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 KHCO₃-Co, NH₄HCO₃-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 KHCO₃-Co and PC/AHC-Co, but not in the NH₄HCO₃-Co. The amounts of K on the surfaces of the KHCO₃-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 0 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 (Oads) [39]. The Oads/Olatt ratio in the KHCO₃-Co was 0.96 (Table 2), a value that is slightly lower than that of the NH4HCO3-Co (1.08). The Oads/Olatt 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 NH₄HCO₃-Co (1), KHCO₃-Co (2), and PC/AHC-Co (3) catalysts.

the hydrolysis of K₂CO₃ [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 2pspin-orbit splitting value of the Co₃O₄ catalysts was 14.9 eV, which is close to that of $Co^{3+}(15.0 \text{ eV})$ [41], therefore, the catalysts likely consisted of Co₃O₄. The Co³⁺/Co²⁺ ratio for the NH₄HCO₃-Co was 0.24, a value that is less than that of the PC/AHC-Co (0.42), indicating that a greater amount of Co³⁺ was present on the PC/AHC-Co surface exposed after the K2CO3 immersion. This could explain the shift in the reduction temperature, which decreased from 300 to 283 °C when K₂CO₃ was coated onto the NH₄HCO₃-Co catalyst. The Co³⁺/Co²⁺ ratio of the KHCO₃-Co was 0.35, which is between the values for the NH₄HCO₃-Co and PC/AHC-Co. It appears that less of the KHCO₃-Co surface was covered with K₂CO₃ compared with the PC/AHC-Co. Despite the much higher Co³⁺/Co²⁺ 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 KHCO₃-Co.

3.2.4. FT-IR

Figure 6 shows the *in situ* DRIFT spectra acquired during HCHO oxidation over the NH₄HCO₃-Co and KHCO₃-Co catalysts. In Fig. 6(a), no peaks associated with adsorbed HCHO are seen

in the NH₄HCO₃-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 O₂ 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 NH₄HCO₃-Co, and during HCHO adsorption (c) and HCHO oxidation (d) on KHCO₃-Co.

The behavior of the KHCO₃-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 $(1593 \text{ and } 1376 \text{ cm}^{-1})$ initially increased in intensity and then decreased on going from 40 to 160 °C, while the peaks due to DOM decreased continuously. At 200 °C, the KHCO3-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 °C), few DOM species could be converted to formate species due to absence of hydroxyl groups on the NH₄HCO₃-Co. In contrast, at higher temperatures (> 80 °C), the decomposition of formate species became the key step. In the case of the KHCO₃-Co, the DOM species generated via the adsorption of HCHO could be converted to formate species in the presence of K₂CO₃, 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 K₂CO₃, and are then consumed during the reaction. Subsequently, these hydroxyl groups are replaced by the H₂O generated by the reaction. Thus, surface alkaline hydrolysis is continued and accelerates the HCHO oxidation process.

4. Conclusions

Co₃O₄ catalysts prepared using various precipitants were studied with regard to low-temperature HCHO oxidation. It was

found that the KHCO₃ precipitated material (KHCO₃-Co) exhibits the best catalytic efficiency, and is able to provide 100% conversion of HCHO to CO₂ at 90 °C. The AAS and XPS data indicate that the KHCO₃-Co surface holds residual K. The structures of the Co₃O₄ catalysts obviously vary with different types of precipitants, such that those catalysts precipitated using reagents containing CO₃²⁻ or HCO₃⁻ ions have higher BET surface areas and BJH pore sizes. H₂-TPR and XPS analyses show that the KHCO₃-Co and PC/AHC-Co have higher oxidizing abilities due to their relatively high surface Co³⁺/Co²⁺ 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 CO₃²⁻ loaded on the surface of the Co₃O₄.

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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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