

Fabrication of Dispersing Co_3O_4 and Application in the Elimination of Carbon Monoxide

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ABSTRACT

Carbon monoxide (CO) is a colorless and odorless poisonous gas, which is very harmful to humans indoors. Therefore, how to quickly eliminate it is an important issue. In this study, activated cobalt oxide (Co_3O_4) catalysts were prepared by a precipitation-dispersion method, named A-CoDP, F-CoDP, and O-CoDP. In this experiment, the effects of CO elimination activity and three chelating dispersants, acetic acid, formic acid, and oxalic acid, on the catalytic activity were investigated. The research results show that oxalic acid dispersants with di-chelate teeth are more suitable for a neutral environment, and the activity will decrease with the decrease of pH value. The sample of O-CoDP-7 has the best CO elimination activity among a series of dispersed catalysts, and its T_{50} is 120 °C.

Keywords: Dispersion-precipitation, Chelating dispersant, Co_3O_4 , Abatement of CO

分散型 Co_3O_4 製備及其在一氧化碳消除之應用

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摘 要

一氧化碳 (Carbon Monoxide, CO) 為無色、無味的有毒氣體，在室內對人類危害非常大，因此如何快速消除為一重要課題，本研究採用沉澱-分散 (precipitation-dispersion) 法製備活性氧化鈷 (Co_3O_4) 催化劑，命名為 A-CoDP、F-CoDP 和 O-CoDP。本實驗探討 CO 消除活性與三種螯合分散劑乙酸 (acetic acid)、甲酸 (formic acid) 和草酸 (oxalic acid) 對催化活性的影響；研究結果顯示具二螯合齒的草酸分散劑則較適合中性環境，活性會隨 pH 值遞減而降低；O-CoDP-7 樣品在系列分散型觸媒中具最佳消除 CO 的活性，其 T_{50} 為 120 °C。

關鍵詞：分散劑、螯合分散劑、四氧化三鈷、一氧化碳消除。

I. INTRODUCTION

Catalytic oxidation is considered to be one of the most effective methods for removing pollutants such as volatile organic compounds (VOCs) and carbon monoxide (CO) [1, 2]. In the past, precious metal catalysts were often used to remove pollutants such as CO from the exhaust gas to reduce air pollution. However, in recent years, various types of catalysts, including transition metal and noble metal oxides, have been tested to replace more expensive noble metal catalysts [3-5]. Among them, Co₃O₄ is regarded as one of the most promising catalysts due to its advantages of high conversion rate and low cost compared with noble metals and noble metal catalysts [6, 7]. Several studies have confirmed that the CO oxidation ability of Co₃O₄ is affected by grain size and redox ability. The smaller crystallite size results in a higher surface area than bulk Co₃O₄ and increases its oxidizing power [8]. In addition, the oxidizing ability is also affected by the redox properties of Co₃O₄, since higher magnetoresistance increases the formation of oxygen vacancies, which usually leads to good oxidation performance [3, 4, 6, 9].

In summary, the enhancement of CO oxidation ability can be achieved by improving its redox ability and reducing its particle size. Base-induced precipitation is considered to be one of the most convenient and commonly used methods because the process can be performed at room temperature and atmospheric pressure [10-14]. However, the particle size of catalysts prepared by this method is often difficult to control. For better oxidizing power, dispersants can be added during preparation to prevent severe crystal agglomeration, thereby reducing particle size and increasing surface area. In recent studies [15-18], acetic acid was used as a dispersant to disperse Co₃O₄ particles into smaller particles through the chelation effect to form a colloidal dispersion. Other studies confirmed that excess water can be used to destabilize colloidal dispersions and form nano-sized Co₃O₄ precipitates [19, 20].

Previously, we studied three chelating dispersants, formic acid, acetic acid and oxalic acid, to modify Co₃O₄ to form catalysts with different morphologies. Among them, the nanorod catalyst modified with oxalic acid had the best carbon monoxide oxidation activity [21]. Further, in this study, the effect of three chelating

dispersants, for dispersing Co₃O₄ particles in different pH environments was investigated, and the ability of CO oxidation was evaluated.

II. EXPERIMENTAL

2.1 Catalysts preparation

In this experiment, NaOH was used as the precipitating agent, while three organic acids (formic acid, acetic acid, and oxalic acid) were used as the dispersing agent. Under magnetic stirring, 80 mL of 0.5 M aqueous Co(NO₃)₂·6H₂O was added dropwise to 80 mL of 1.5 M NaOH_(aq). After stirring for 3.5 hours, the hydroxide precipitate was isolated by centrifugation and washed with deionized water. Next, 0.12 mol of dispersant were added to the wet cake and the resulting mixture was stirred for 1 hour until the hydroxide was completely dispersed and a stable dark brown gummy dispersion was formed. Subsequently, 140 mL of deionized water was added to the colloidal dispersion at room temperature with constant stirring to induce destabilization, while the suspension was adjusted to different pH environments (1, 3, 5, 7) with 1 M NaOH_(aq). After aging for 12 hours, the pellet was collected by centrifugation.

It was dried in air at 80 °C, and finally calcined in a high-temperature furnace at 300 °C (10 °C·min⁻¹) for 2 hours to obtain a series of dispersed Co₃O₄. Its nomenclature, reducing properties and CO elimination activities are listed in Table 1.

Table 1. The CO oxidation and characterization on the cobalt oxide by the different pH values.

Catalysts*	pH value	TPR (°C)	CO Oxidation(T ₅₀)
F-CoDP-1	1	274, 338	128
F-CoDP-3	3	259, 854	209
F-CoDP-5	5	253, 877	241
F-CoDP-7	7	246, 879	191
A-CoDP-1	1	320, 348	135
A-CoDP-3	3	300, 377	170
A-CoDP-5	5	311, 376	177
A-CoDP-7	7	370, 888	197
O-CoDP-1	1	331, 360	161
O-CoDP-3	3	277, 341	130
O-CoDP-5	5	266, 347	140
O-CoDP-7	7	261, 334	120

*The chelating dispersant were the acetic acid, formic acid and oxalic acid, respectively.

2.2 Catalysts Characterization

XRD analysis was performed using a Bruker D2 PHASER and the samples were run with $\text{CuK}\alpha_1$ radiation ($\lambda = 0.154 \text{ nm}$). Temperature-programmed reduction (TPR) analysis of the catalyst in hydrogen was performed using a self-assembled instrument, and hydrogen consumption was measured by a thermal conductivity detector. In each test, 0.02 g of catalyst was pretreated at room temperature for 30 min with an N_2 flow rate of $40 \text{ mL}\cdot\text{min}^{-1}$, then the gas was replaced with an H_2/N_2 mixture (10 vol % H_2 in N_2) with a flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$, the catalyst was heated from room temperature to 900°C at a heating rate of $7^\circ\text{C}\cdot\text{min}^{-1}$. Fourier-transform infrared spectroscopy (FTIR) used Bomem DA-8 FT-IR, the sample was uniformly mixed with 0.1 g KBr powder at a weight ratio of 1:200 and pressed into a circular disk at a pressure of 6 tons. The detector used is MCT, the scanning wavelength range is from 4000 to 400 cm^{-1} , the resolution is set to 4 cm^{-1} , and the spectrum is accumulated over 100 scans to improve the S/N ratio.

2.3 Carbon monoxide oxidation test

The catalytic performance of the Co_3O_4 catalyst for CO oxidation was carried out in a continuous flow micro-reactor. The reaction gas (a mixture of 4 % vol. O_2 , 1 % CO, and 95 % He) was fed into a catalyst bed of 0.02 g catalyst at a rate of $50 \text{ mL}\cdot\text{min}^{-1}$. Steady-state catalytic activity was measured at each temperature, and the reaction temperature was increased from room temperature to 200°C . Effluent gases were analyzed online using a China Chromatography GC1000 TCD. Before the reaction, the catalyst was pretreated in flowing pure helium for one hour to remove pre-adsorbed molecules from the sample in the atmosphere.

III. RESULTS AND DISCUSSION

3.1 XRD structure analysis

The structure of the catalyst was characterized according to XRD, and the XRD pattern of the prepared Co_3O_4 sample is shown in Figure 1. The peaks at 2θ 31.3° , 36.8° , 38.5° , 44.8° , 55.6° , 59.5° , 65.2° , and 77.3° of the pattern

in Fig. 1 correspond to (220), (311), (222), (400), (422), (511), (440) and (533) planes, all of which are consistent with those of spinel Co_3O_4 (JCPDS 65-3103).

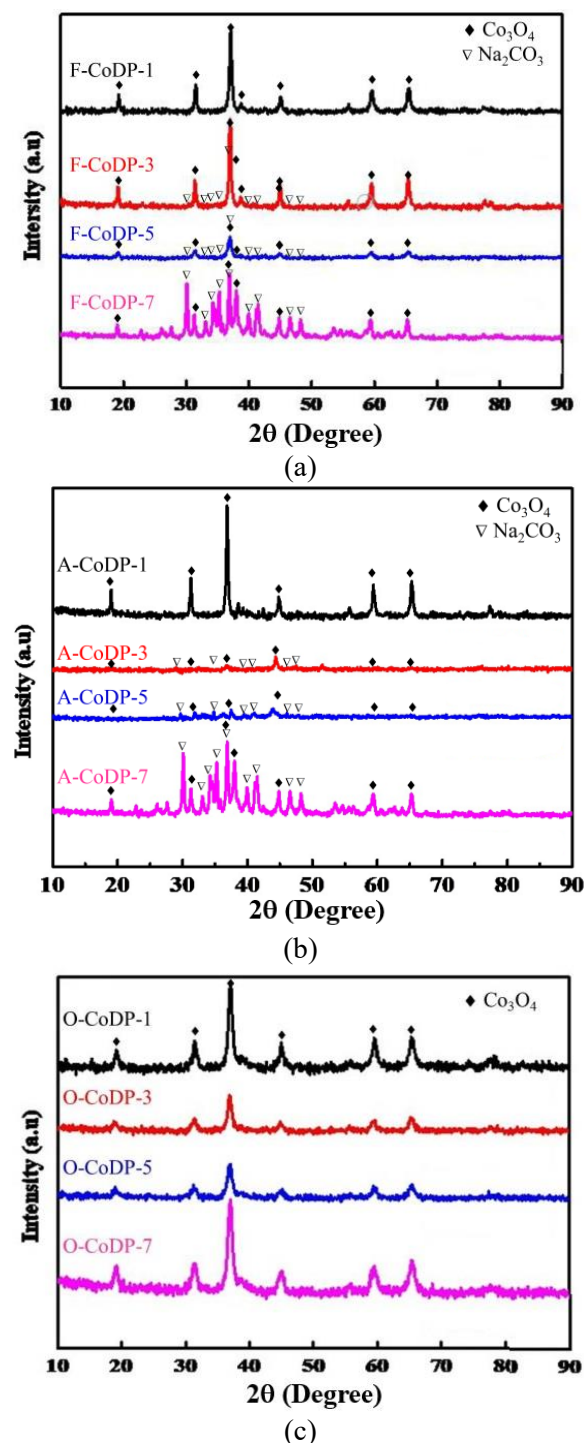


Fig.1. The XRD patterns of Co_3O_4 prepared from (a) formic acid, (b) acetic acid, (c) and oxalic acid.

However, the figure also shows that, with the effect of adjusting the pH value, F-CoDP and

A-CoDP also show that in the activated Co₃O₄ prepared by the precipitation-dispersion method, except for the pH value of 1, there are crystalline Na₂CO₃, the corresponding XRD peaks have different degrees of crystallinity [22-24].

3.2 Analysis Spectrum of TPR

H₂-TPR was performed to determine the redox performance of the catalyst (as shown in Fig. 2), the reduction of Co₃O₄ occurred through a two-step process: the first (T_{r1}, 200 ~ 350 °C) low-temperature reduction peak was attributed to the reduction of Co³⁺ to Co²⁺ (Co₃O₄ → CoO); the larger reduction peak of the second (T_{r2}, 300 ~ 450 °C) is caused by the reduction of Co²⁺ to the metal of Co (CoO → Co). O-CoDP series catalysts are easier to reduce than A-CoDP and F-CoDP series catalysts, and the reduction temperature will decrease with the increase of pH value. The O bond is weaker and contributes to the oxidation of CO. The other weak peaks around 100 °C may be highly reactive oxygen species adsorbed on the surface oxygen vacancies.

Some studies have shown that the oxidative ability of Co₃O₄ is strongly affected by its reducibility [3, 4], also, the reducibility of Co₃O₄ is greatly affected by the particle size and dispersion state of cobalt [6, 10]. According to research, it was found that smaller nanocrystals have more exposed areas and more reducible points on the surface [7]. In addition to the reduction signal of T_{r1}, A-CoDP-3, A-CoDP-5, A-CoDP-7, and F-CoDP-7 catalysts also have a reduction peak in the high-temperature region (T_{r3}, 800 ~ 900 °C). A comparison of the XRD patterns (Fig. 1) shows that the four catalysts all have Na₂CO₃ species.

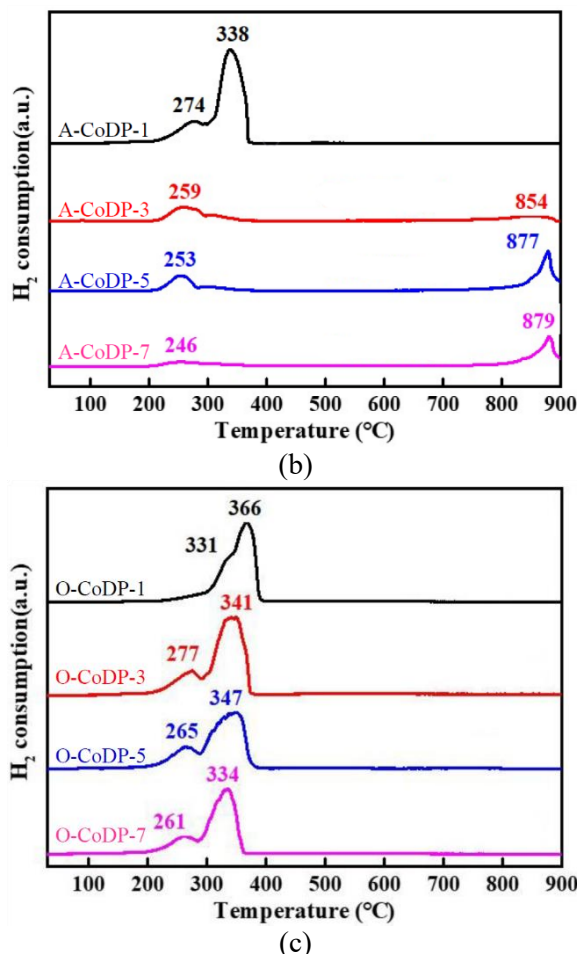
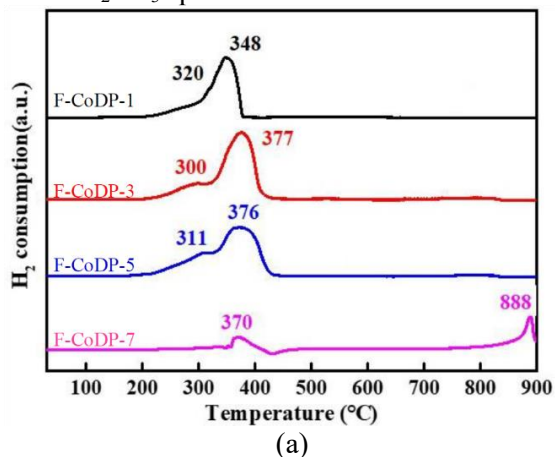
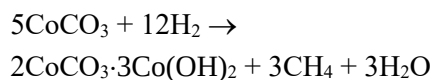


Fig.2. H₂-TPR profiles of Co₃O₄ prepared from (a) formic acid, (b) acetic acid, (c) and oxalic acid.

When Co₃O₄ is reduced to CoO in a hydrogen environment, it will form CoCO₃ with the CO₂ released by Na₂CO₃, and it will become alkaline as the temperature rises to 800 °C. Cobalt carbonate [2CoCO₃·3Co(OH)₂], part of C is reduced to CH₄.



Only catalysts containing Na₂CO₃ species can easily coat Co₃O₄ or form CoCO₃, which will affect the oxidation of CO.

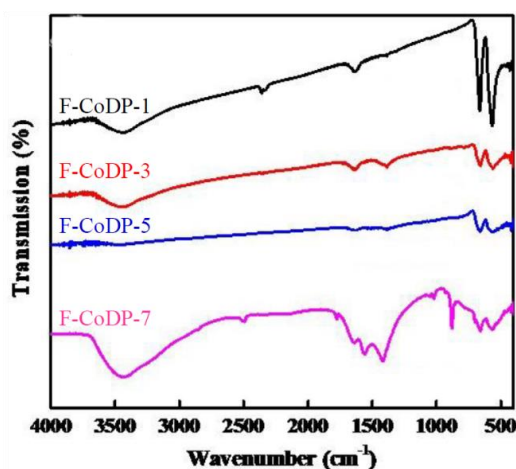
3.3 Infrared spectroscopy identification

Observing the FT-IR spectra of A-CoDP, F-CoDP, and O-CoDP (Fig. 3), the series of catalysts all exhibit ν_{-OH} stretching vibration at 3000 ~ 3500 cm⁻¹ and bending vibration at 1500

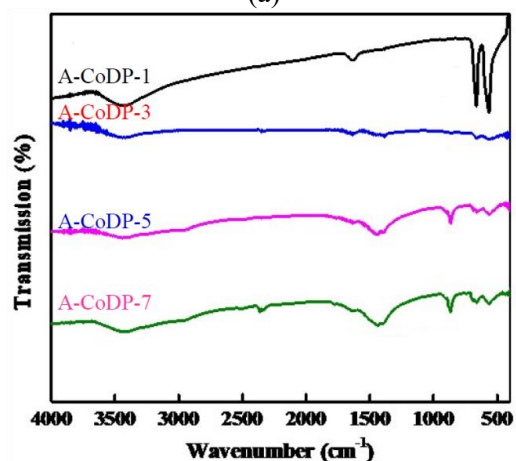
$\sim 1400\text{ cm}^{-1}$ ν_{OH} shows that the catalyst is porous and easy to adsorb water molecules. In addition, the O-CoDP series catalysts exhibit two strong absorption peaks at 559 cm^{-1} (ν_1) and 658 cm^{-1} (ν_2), which are the $\nu_{\text{Co-O}}$ stretching vibrations in the Co_3O_4 spinel structure.

The strong spectral peak (ν_1) is the $\nu_{\text{Co-O}}$ characteristic vibration peak of OB^{Oh}_3 (B^{Oh} represents the position of Co^{3+} located in the octahedral hole); The strong spectral peak of ν_2 is the $\nu_{\text{Co-O}}$ characteristic vibration peak of $\text{A}^{\text{Td}}\text{B}^{\text{Oh}}\text{O}_3$ (A^{Td} represents that Co^{2+} is located in the position in a tetrahedral hole) [25-27].

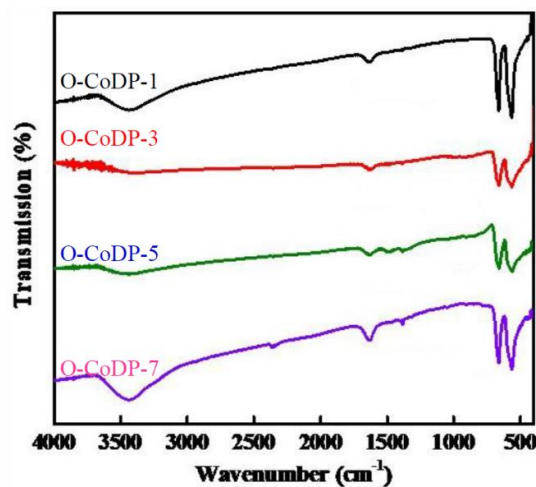
In addition to the vibrational peaks of ν_{OH} and $\nu_{\text{Co-O}}$, A-CoDP-3, A-CoDP-5, A-CoDP-7, and F-CoDP-7 catalysts also showed broad vibrational peaks at 1426 cm^{-1} , 878 cm^{-1} presents a sharp vibrational peak, which is the vibrational peak of CO_3^{2-} [28, 29], which is consistent with the identification of the XRD pattern (Fig. 1) confirming that the four catalysts all have Na_2CO_3 species.



(a)



(b)



(c)

Fig.3. FT-IR spectrum of Co_3O_4 prepared from (a) formic acid, (b) acetic acid, (c) and oxalic acid.

3.4 Assessment of carbon monoxide oxidation activity

The catalytic activity of a series of samples prepared at different pH values of Co_3O_4 was evaluated by carbon monoxide oxidation. Figure 4 shows the CO catalytic activity of Co_3O_4 sample catalysts prepared at different pH values as a function of reaction temperature. Comparing all samples, the conversion rate of carbon monoxide oxidation is 50 %. Among the O-CoDP series samples, the sample of O-CoDP-7 is 120°C as the lowest conversion temperature. In addition, in the F-CoDP and A-CoDP series samples, F-CoDP-1 at 128°C and A-CoDP-1 at 135°C . The results also showed that the oxidative ability of A-CoDP series samples decreased with the increase of pH value during the preparation process.

When the pH value of the sample preparation process was 1, the temperature sequence of its T_{50} catalytic activity was: A-CoDP-1 (128°C), F-CoDP-1 (135°C), and O-CoDP-1 (161°C). When the pH values were 3 and 5 during the preparation of the samples, the temperature sequence of their T_{50} catalytic activities was: O-CoDP-3 (130°C), A-CoDP-3 (170°C) and F-CoDP-3 (209°C) with O-CoDP-5 (140°C) and A-CoDP-5 (177°C), and F-CoDP-5 (241°C).

Finally, when the pH value of the sample preparation was neutral at 7, the temperature sequence of its T_{50} catalytic activity was:

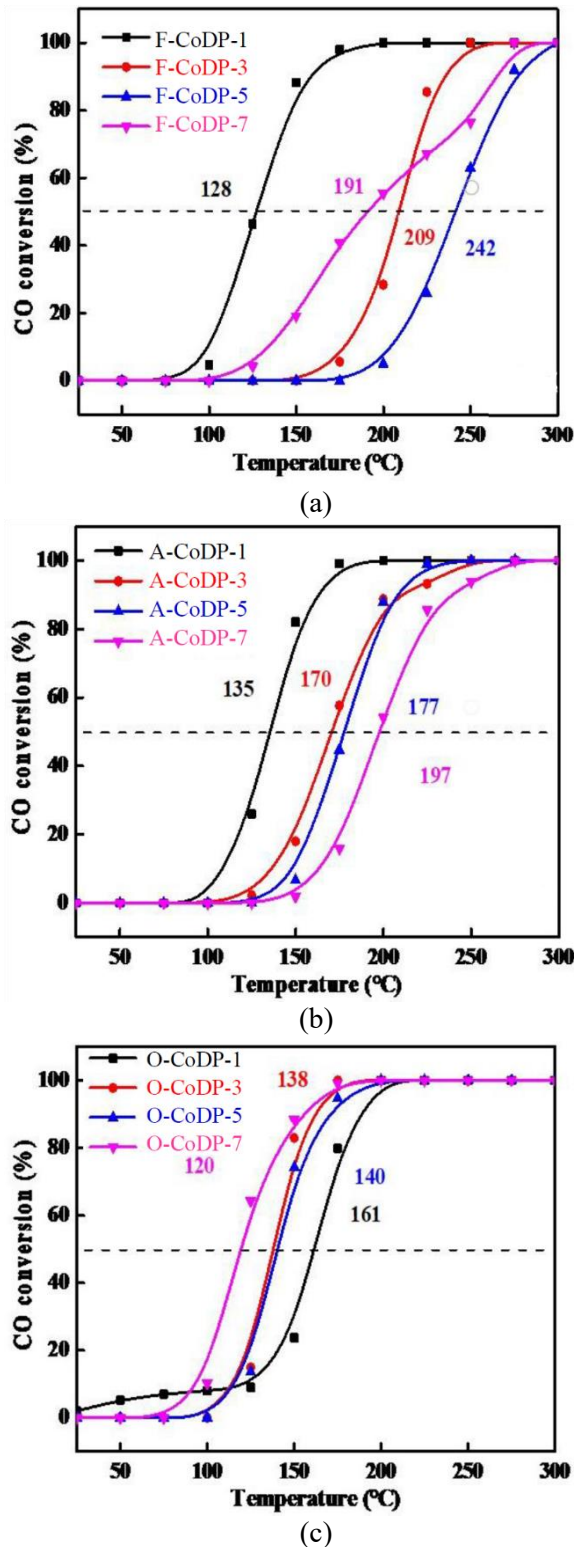


Fig.4. Conversion profiles for CO oxidation over the series Co₃O₄ from (a) formic acid, (b) acetic acid, (c) and oxalic acid.

O-CoDP-7 (120 °C) and F-CoDP-7 (191 °C), and A-CoDP-7 (197 °C).

Among a series of dispersed Co₃O₄ catalysts,

O-CoDP series samples are better than F-CoDP and A-CoDP series samples in carbon monoxide oxidation catalysis. The 50% conversion (T₅₀) of carbon monoxide oxidation was used to compare the catalytic activity of the samples (Table 1 and Fig. 5). The results showed that Co₃O₄ modified with formic acid and acetic acid had the best activity under strong acid conditions, and the catalyst modified with oxalic acid had no obvious effect under acidic conditions. Also found in the literature, LaFeO₃ (LFO) perovskite, the acid-treated catalyst showed higher activity in CO oxidation than the un-modified LFO. The exposed La ions of the LFO were slightly etched by dilute nitric acid. The corresponding surface area, surface oxygen vacancies and reducibility were also improved after acid treatment, obtained its higher catalytic activity. [30]

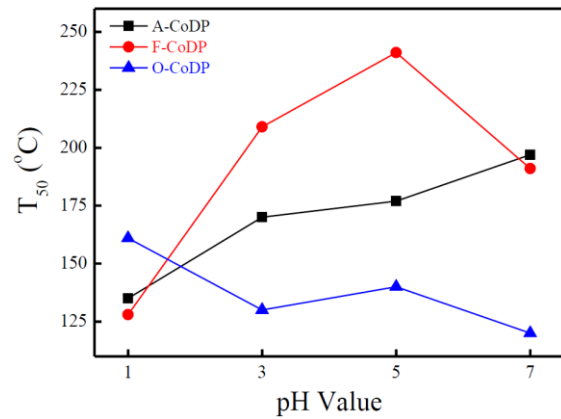


Fig.5. The T₅₀ versus the pH ranges for series Co₃O₄ catalysts.

IV. CONCLUSION

Based on the above experimental results, it is found that the O-CoDP-7 sample has the highest CO conversion rate among the O-CoDP series samples, and its T₅₀ catalytic activity temperature is 120 °C, but this was not the case for A-CoDP-1 and F-CoDP-1 catalysts. Because the pH is 1, its carbon monoxide oxidation conversion rate is the highest. The results showed that the activity of A-CoDP and F-CoDP series catalysts increased with the increase of acidity during the preparation process; as for the O-CoDP and F-CoDP samples when the pH value was 7 neutrals during the preparation process, the activity increased.

This is because Na₂CO₃ covers the surface and the content of Co₃O₄ decreases, resulting in

an increase in the conversion of carbon monoxide. In addition, the TPR spectrum of the O-CoDP sample has a large reduction area and a low reduction temperature, and it is easy to provide oxygen to participate in the catalytic reaction, so its catalytic activity is better.

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