

Characterization and catalytic activity for the NO decomposition and reduction by CO of nanosized Co_3O_4

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Abstract

Nanosized Co_3O_4 prepared by a precipitation method was characterized by TEM, XRD, BET and TPD techniques, and studied for NO decomposition and reduction by CO. It is found that Co_3O_4 thus obtained has a specific surface area of $23.4 \text{ m}^2/\text{g}$ and an average particle size of 26 nm. Catalytic tests showed that full NO conversion to N_2 was obtained above 300°C . A redox mechanism between Co^{3+} and Co^{2+} ions based on NO decomposition is proposed.

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1. Introduction

Cobalt oxides have been extensively studied for a long time in the field of air pollution control. Co_3O_4 [1] and cobalt oxides doped with Cu [2], Fe [3], or supported on $\gamma\text{-Al}_2\text{O}_3$ [4], are well known to be active catalysts for CO oxidation at low temperatures. CoMgO solid solution [5] and LaCoO_3 composite oxide [6] are used for methane oxidation and VOCs combustion, respectively. Besides, bulk Co_3O_4 is one of the most active single component metal oxides for NO decomposition, and its activity can also be enhanced by addition of Ag and Na [7]. Accordingly, bulk and supported cobalt oxides have revealed high activity for the reduction of NO by CO [8] and hydrocarbons [9]. The reduction of NO by CO is an important reaction for exhaust gas depollution because the two pollutants are simultaneously eliminated in one step. Panayotov et al. [2] reported the interaction between NO and CO over Co_3O_4 , which was prepared from the decomposition of cobalt nitrate, with a surface area as low as $9 \text{ m}^2/\text{g}$. Simonot et al. [8] found a unique phenomenon on Co_3O_4

for the NO + CO reaction, that is, at 300°C , 100% NO conversion is reached, but when the temperature increased the conversion fell to 70% before increasing again to reach 100% above 535°C . Unfortunately, we did not find this. Precipitation is one of the most widely employed preparation methods to obtain nanosized materials, which is very easy and cheap as regards industrialization and commercialization. In this paper, the nanosized Co_3O_4 was prepared by precipitation and characterized by TEM, XRD, BET and TPD techniques. Its catalytic activity in the reduction of NO by CO is checked and discussed.

2. Experimental

Co_3O_4 were prepared by a precipitation method. The stoichiometric solutions of $\text{Co}(\text{NO})_2 \cdot 6\text{H}_2\text{O}$ and ammonia were simultaneously dropped into de-ionized water under vigorous agitation, and then the solution was aged for 30 min. The resultant precipitates were dried at 120°C overnight and calcined at 500°C for 5 h in air.

A U-shaped quartz reactor (i.d. = 6 mm) with a porous quartz frit supporting the catalyst was used for reaction tests

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under atmospheric conditions. The model flue gases employed are 1025 ppm NO and 2085 ppm CO in Ar. The total flow rate was 40 cm³/min, and 300 mg of catalyst was placed in the reactor leading to a space velocity of 8000 ml/(h g). The products in the effluent stream were analyzed by an online quadrupole mass spectrometry (LZL-204, Beijing Analytical Instrument Plant). The NO conversion was calculated on the basis of the differences between the inlet and outlet NO intensities. The data for steady-state activity of the catalyst were collected after 2 h testing.

Conversion of NO (%):

$$X_{\text{NO}} = \frac{[\text{NO intensity}]_{\text{in}} - [\text{NO intensity}]_{\text{out}}}{[\text{NO intensity}]_{\text{in}}} \times 100$$

The morphology of the nanosized particles was examined with a JEM-2010 (JEOL) transmission electron microscopy at an accelerating voltage of 200 kV.

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max 2000 diffractometer employing Cu K α radiation. The BET specific surface area and pore structure were measured in a Micromeritics ASAP-2010 instrument.

The temperature-programmed desorption of NO was carried out on the above equipment. A sample of 100 mg was first heated in 20 ml/min Ar flow to 500 °C with a 15 °C/min ramp, followed by cooling to ambient temperature in the same flow. After a short purging, the flow was switched to a mixture of 2050 ppm NO in Ar at a flow of 20 ml/min and maintained for 60 min, then the flow was switched back to Ar at 20 ml/min, and the sample was purged for 1 h. A NO-TPD profile was registered in the same flow while the temperature was increased to 500 °C at 10 °C/min.

The transient response technique is used to elucidate NO decomposition and reaction mechanism. First, Ar flowed through the catalyst at the desired temperature, and then the concentration step change from Ar to 2050 ppm NO in Ar was enforced by switching a four-way valve. The mass-to-charge (*m/e*) ratios were monitored by MS as follows: NO (30), O₂ (32), CO and N₂ (28), CO₂ and N₂O (44), NO₂ (46).

3. Results and discussion

3.1. TEM characterization

The transmission electron microscope images of Co₃O₄ prepared by precipitation and calcined at 500 °C are shown in Fig. 1. It can be seen that there exists a certain extent of coagulation. The particle size was between 20 and 40 nm (Fig. 1a). High-magnification image showed clear lattice strings of crystalline phases and pseudo-hexagonal morphology of the nanoparticles (Fig. 1b).

3.2. Catalytic activity

The catalytic activity of Co₃O₄ for NO reduction by CO was measured as a function of reaction temperatures from

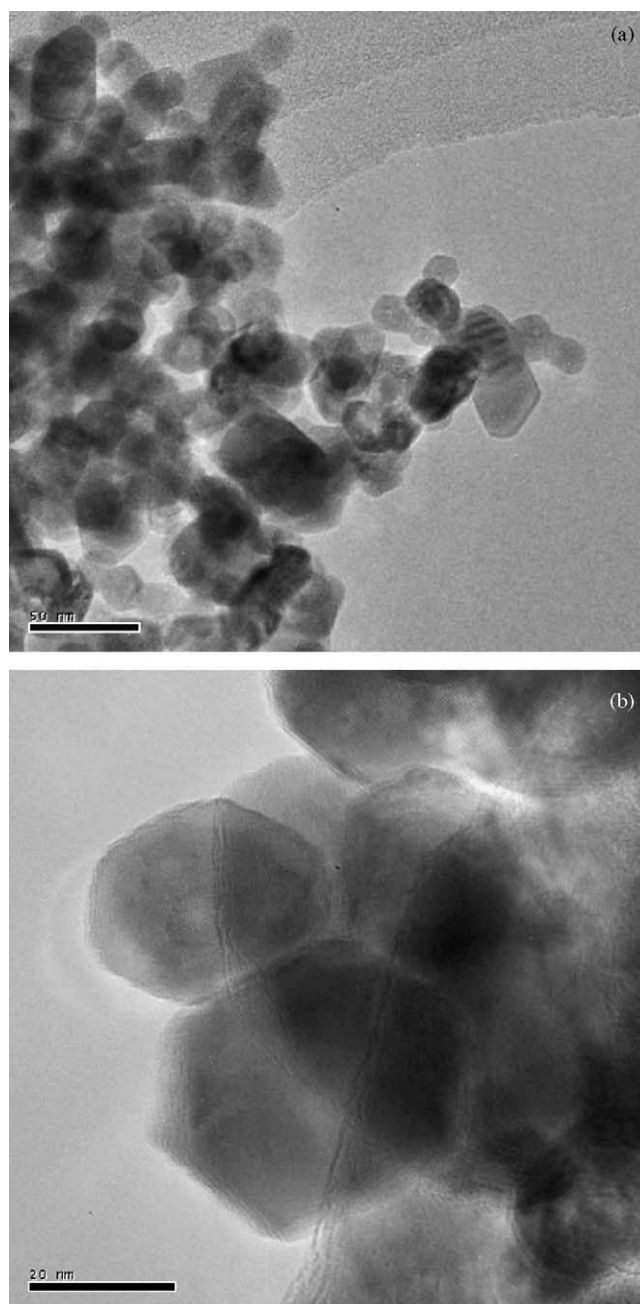


Fig. 1. (a) and (b) TEM images of Co₃O₄ nanoparticles.

ambient temperature to 500 °C, as shown in Fig. 2. During the whole range, nearly complete NO conversion to N₂ with negligible amount of N₂O formation was achieved. The NO conversion showed a S-shape curve with temperature change. The light-off temperature, at which 50% NO conversion was reached, is about 110 °C. Almost complete NO conversion could be achieved at 300 °C, and no activity decrease was detected thereafter. The CO/NO ratio used was twice the stoichiometric ratio in this reaction [10].

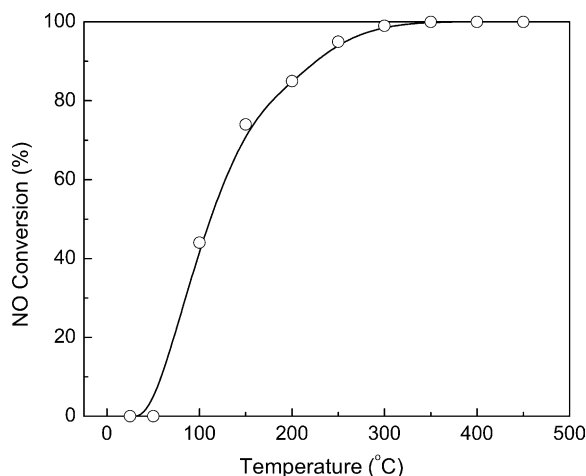


Fig. 2. NO conversions in the NO + CO reactions.

3.3. XRD characterization

Fig. 3a shows the XRD pattern of the fresh catalyst. The peak positions agree well with the reflections of bulk spinel Co_3O_4 . According to the Scherrer equation $D = k\lambda/(\beta \cos \theta)$, where k is a constant, λ the X-ray wavelength, β the breadth at half-maximum intensity and θ is the Bragg angle in the diffraction pattern, the crystallite size D is equal to 26 nm in diameter, which is in a reasonable agreement with the TEM results. The surface characteristics of the resultant Co_3O_4 , namely specific surface area (S_{BET}), total pore volume and average pore radius were determined from nitrogen adsorption isotherms measured at -196°C . The results obtained are given in Table 1, which shows a BET surface area of $23.4\text{ m}^2/\text{g}$, a pore volume of $0.1338\text{ cm}^3/\text{g}$ and an average pore diameter of 228.5 \AA . These data meant that the pores were the voids among the dense coagulation of original particles, as shown in Fig. 1a. For comparison, the XRD pattern of the used catalyst after NO + CO reactions is shown in Fig. 3b. In accordance with the previous work [11], Co_3O_4 was partly

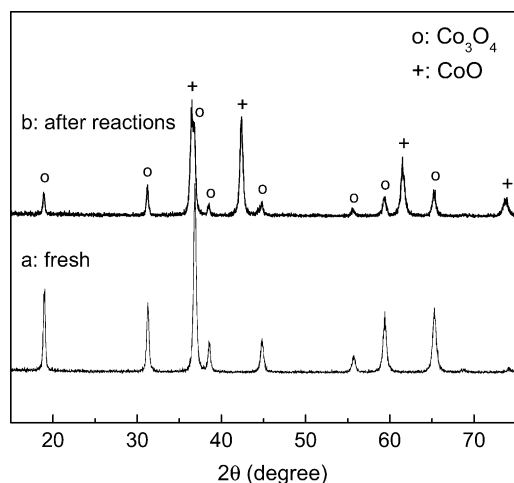


Fig. 3. XRD patterns of the catalyst before and after NO + CO reactions.

Table 1
Characterization of calcined Co_3O_4 at 500°C for 5 h

Characteristics	Values
BET surface area (m^2/g)	23.4
Pore volume (cm^3/g)	0.1338
Average pore diameter (\AA)	228.5
Crystallite size (nm)	26

reduced to CoO , an oxygen deficient phase, even though the ratio of the reacting molecules of NO and CO equals unit. This observation is evidence that the reaction occurred not only via the surface but also via an intrafacial process.

3.4. Transient studies

NO decomposition is checked using the transient response method, which is based on recording the response of a given parameter of the reaction system to a sharp change in the steady state. It is traced until a new steady state is attained. Fig. 4 shows the transient responses obtained at 350°C on Co_3O_4 after switching from Ar to 2050 ppm NO in Ar. The instantaneous N_2 response curve concomitant with the formation of a small fraction of N_2O indicated the catalyst was active in the NO decomposition in the absence of CO in the gas phase, and that NO dissociated upon adsorption. However, as no oxygen desorbed from the catalyst, the catalyst surface would become oxidized. The catalytic activity of NO decomposition into N_2 gradually decreased to zero after 40 min. Alternatively, about 9% NO conversion to N_2O was observed.

3.5. NO-TPD

NO-TPD was performed on Co_3O_4 for three times, showing that a large amount of NO can adsorb and desorb reversibly. Unfortunately, reproducible spectra were never obtained (not shown here). Moreover, an increasing NO desorption was recorded after the former cycle. From transient studies, we know that the interaction between NO and Co_3O_4 is the process of Co_3O_4 oxidation by NO, which will result in a change in oxidation state of some low-valent Co ions or a surface reconstruction [12] after NO-TPD, thus different desorption spectra with respective desorption temperatures and amounts were observed. It is confirmed that there was more NO sorption capacity on the oxidized catalyst surface [2], which can explain more NO desorption for the later NO-TPD cycle than the former.

3.6. Reaction mechanism

It was previously observed that preoxidized cobalt oxide catalysts show high low-temperature activity for CO oxidation. While the activity over pre-reduced cobalt oxide is much lower. Therefore, CO was suggested to be adsorbed on an oxidized cobalt site, probably Co^{3+} [4]. The adsorbed CO reacts with oxygen linked to the active Co^{3+} ; CO_2 is formed and desorbed quickly. The result is a partially reduced site,

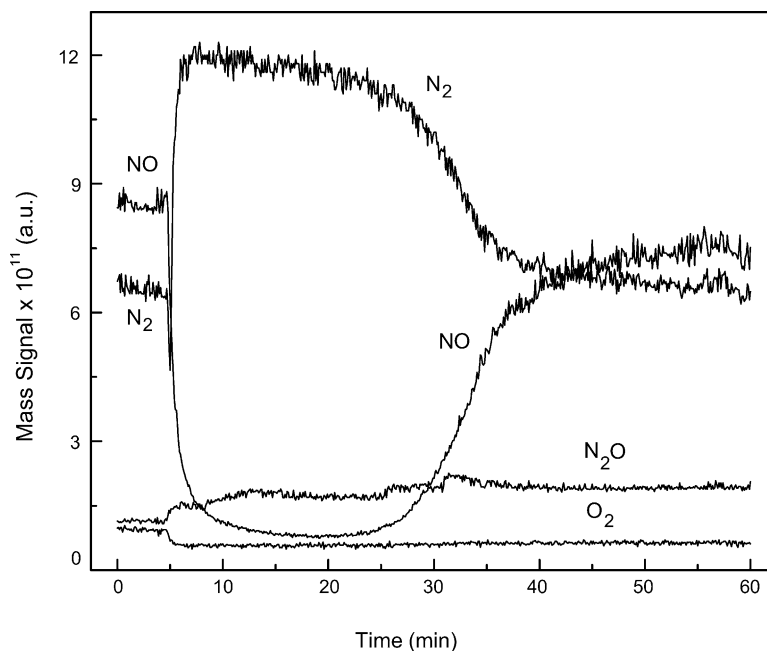
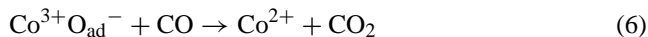
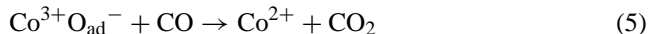
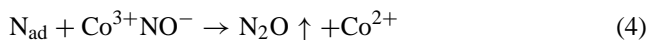
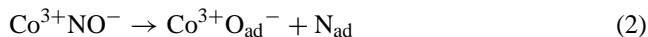


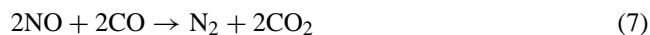
Fig. 4. Transient response curves obtained over Co_3O_4 at 350°C after switching from Ar to 2050 ppm NO in Ar.

which may consist of two Co^{2+} ions or may be regarded as an oxygen vacancy. On the basis of the mechanism of NO decomposition on metal oxides, it is reasonable to deduce that NO adsorbed on Co^{2+} or oxygen vacancy sites. Thus, the following elementary steps are proposed for NO decomposition and reduction by CO on Co_3O_4 , in which stands for oxygen vacancies, “ad” and “L” are the abbreviations of adsorption and lattice, respectively:



In the absence of CO, when the oxygen vacancies were not enough or depleted by the reaction, there was not sufficient N_{ad} to ensure the occurrence of reaction (3). On the contrary, reaction (4) will prevail, as shown by the NO decomposition (Fig. 4). However, because O_{ad} would not be desorbed, Co_3O_4 shows no sustainable activity for NO decomposition to N_2 and/or N_2O . When CO was added, that is, the reduction of NO by CO, reaction (5) produced enough oxygen vacancies for NO adsorption and decomposition, and thus a reaction cycle was constructed. Simultaneously, reaction (6) would result in the production of oxygen vacancies available for reaction (1) and in a partial catalyst reduction to CoO.

Overall, the reaction between NO and CO can be written as



4. Conclusions

Nanosized Co_3O_4 was prepared by precipitation of a solution of cobalt nitrate using ammonia, which is easy and cheap as regards industrialization and commercialization. A crystallite size of 26 nm and BET surface area of $23.4\text{ m}^2/\text{g}$ were reached.

Using CO as a reducing agent, Co_3O_4 showed complete NO conversion to N_2 above 300°C . The reaction took place simultaneously with a reduction of Co_3O_4 into CoO. A redox mechanism between Co^{3+} and Co^{2+} ions based on NO decomposition was proposed.

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