Study on catalytic performance of MnO$_x$ nanoparticles for CO oxidation

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Abstract. As a kind of toxic gas, carbon monoxide is often found in industrial waste gas, automobile exhaust, confined space such as submarines, etc. In recent years, the purification of carbon monoxide has attracted more and more attention. Catalytic oxidation has become a widely used method for carbon monoxide purification. In this paper, manganese oxide nanoparticles were synthesized by emulsion self-assembly method and characterized by X-ray powder diffraction (PXRD) and high-resolution transmission electron microscope (HRTEM). The activity of the oxide nanoparticle catalysts were evaluated on the fixed bed tubular quartz microreactor at atmospheric pressure. The effects of KMnO$_4$ dosage, flow rate and temperature were investigated and the reaction kinetics range was determined.

1 Introduction

Carbon monoxide (CO) is a typical flammable and toxic compound. The toxic characteristics of CO are colorless, tasteless and odorless, which makes it difficult to detect its existence. Low concentration can cause chronic poisoning, and high concentration can cause asphyxia death. The incomplete combustion of fossil fuels, chemical industry and motor vehicle use have caused a large amount of CO emissions, which has become a serious environmental problem and has attracted widespread attention [1]. Catalytic oxidation is a widely used method for CO purification among which non-noble metal catalysts have made great progress in CO purification due to their abundant resources and low price [2].

There are two kinds of non-noble metal catalysts for CO oxidation reaction: p-type oxide with metal ion vacancy and n-type oxide with metal ion excess. Non-noble metal catalysts generally require high reaction temperature [3]. In order to improve the conversion efficiency at low temperature, non-noble metal catalysts with smaller particle size have been studied. The experiments showed that the oxidation activity of nano-sized catalysts with good dispersion and large specific surface area was much higher than that of conventional types [4], but the catalytic activity of nano-sized manganese oxide for CO was not well understood.

This paper mainly studies the catalytic performance of manganese oxide nanoparticles for CO oxidation. Firstly, manganese oxide nanoparticles were prepared in their emulsion self-assembly synthesis and then the samples were characterized. The effects of flow rate and temperature on CO conversion rate were investigated in a micro fixed-bed reactor by using the method of dynamic tube experiment, so as to screen out the optimal conditions for CO catalysis by MnOx nanoparticles.

2 Experiment

2.1 Synthesis

Potassium permanganate (KMnO$_4$), oleic acid and ethanol were purchased from Beijing Chemical Reagent Company. A certain amount of KMnO$_4$ was dissolved in 200 mL of water, and the mixture was fleetly stirred for 30 min. Then 4.0 mL of oleic acid was added and a steady emulsion was formed after continuous stirring for 2 h. The brown-black products were collected and washed three times with water and ethanol by vacuum filtration. The washing time is about 8 h to remove the possible residual reactants. The product was dried in air at 80 °C for 10 h. The precursor was calcined at different temperature (200 °C or 300 °C) for 5 h in muffle furnace. Finally, grind thoroughly and set aside.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max-2000, equipped with a Cu Kα on the diffracted beam. The XRD data was collected in the 2θ range of 10-80°and the scan rate was 4°·min$^{-1}$. The morphology was measured by JEOL JEM-2100F high-resolution transmission electron microscope.

2.3 Experimental device construction and flowmeter calibration

In this experiment, an experimental device for measuring
the activity of MnO$_x$ based on the power tube experiment was established, as shown in Figure 1.

![Figure 1. The testing device for the activity of MnO$_x$.](image)

The device is divided into three parts, namely the gas distribution part, the reaction furnace part and the detection part. The gas distribution part is composed of four gas cylinders and a gas distribution box, which is mainly used for flow control and gas mixing. There are four mass flowmeters in the gas distribution box, corresponding to four kinds of gas MFC1-oxygen, MFC2-carbon oxide, MFC3-helium and MFC4-air. The reactor part is a fixed bed reactor, and the reaction temperature can be controlled by the connected secondary table when loading the diluted sample for activity test.

In this experiment, mass spectrometry was used for quantitative test, and internal standard method was used to add internal standard gas Ar into the reaction gas, so as to accurately and quantitatively determine the activity.

After the completion of all the devices, the air pressure method and soap bubble method should be used to detect the leakage of the connecting parts of the air path one by one. Due to the difference between the experimental gas and the calibration gas from the factory, it is necessary to calibrate them before the experiment. Each flowmeter needs a soap film flowmeter to calibrate its actual flow rate.

2.4 Test of CO oxidation

The activity of MnO$_x$ catalysts were evaluated on the fixed bed microreactor and the reaction tube was a quartz tube with outer diameter of 8 mm, inner diameter of 6 mm and length of 500 mm which contained a sieve. 0.05 g of catalyst was mixed with 0.15 g of quartz sand. Before the activity test, the catalysts were in situ pretreated with air (30 mL·min$^{-1}$) for 2 h at different temperature (200 °C or 300 °C) and then cooled to room temperature. After pretreatment, the reactant feed was composed of 1% CO, 24% O$_2$, and 4% Ar and the rest is He. The total flow was 100 mL·min$^{-1}$. The catalytic reaction was carried out at different flow rates and temperatures, and the concentrations of CO and CO$_2$ in the effluent gas were analyzed online by OminiStarTM mass spectrometer.

3 Results and Discussion

3.1 Characterization results

Figure 2 shows PXRD patterns of MnO$_x$. There were obvious characteristic diffraction peaks at $2\theta = 18.0^\circ$, 29.0$^\circ$, 32.5$^\circ$, 36.2$^\circ$, 44.6$^\circ$, 58.8$^\circ$ and 60.0$^\circ$, and the corresponding diffraction planes were 101, 112, 103, 211, 220, 321 and 224. The corresponding crystal is quartet pyrolusite Mn$_3$O$_4$ (JCPDS card number: 01-1127).

According to Sherrer equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

The particle size of MnO$_x$ is calculated at 16.5 nm from the half-width of the diffraction peak at $2\theta = 36.2^\circ$.

Figure 3 shows the PXRD spectra of products without calcination (a), calcined at 150 °C (b) and 500 °C (c) in the literature [5]. The calcination temperature of the prepared sample was 200 °C, and the PXRD spectra of the two samples were compared. The positions of the diffraction peaks were basically overlapped, and the synthesized samples had similar crystal structure with the sample in the literature (tetragonal pyrolusite Mn$_3$O$_4$).

In order to further confirm the particle size of the sample, HRTEM was used to preliminarily characterize the MnO$_x$ nanoparticles. The result of HRTEM images is shown in Figure 4.

The particle sizes of MnO$_x$ nanoparticles are uniform. Statistical results show that the average particle diameter of MnO$_x$ nanoparticles is 15.0±1.1 nm, which is consistent with the XRD results.
3.2 Effects of conditions on the activity of MnOx

3.2.1 Effect of KMnO₄ dosage

Firstly, samples No.1 (2.0 g KMnO₄), No.2 (3.0 g KMnO₄) and No.3 (4.0 g KMnO₄) were selected for the test to investigate the effect of KMnO₄ dosage on the activity of samples. The relationship between KMnO₄ dosage and CO conversion rate under the same test conditions is shown in Figure 5.

Compared with the samples with different KMnO₄ dosages at the same temperature, the order of CO conversion rate in the test temperature range of 40-90 °C was 3 g > 4 g > 2 g. But at the low temperature, the CO conversion rate is low due to the low activity of the samples. The activity of samples No.1,2 and 3 at 40 °C were 0.05 %, 0.49 % and 0.17 % respectively. Therefore, there was no significant difference in the activity of the samples synthesized with three different amounts of KMnO₄. The above data show that the sample synthesized with 3 g KMnO₄ has higher catalytic activity. Therefore, the samples synthesized with 3 g KMnO₄ were selected in the following tests.

3.2.2 Effects of flow rate

Figure 6 shows the relationship between the reaction flow rate and CO conversion rate.

With the increasing flow rate, the CO conversion rate gradually decreased from 33.9 % to 11.8 %, and the catalyst activity significantly decreased. There was a linear relationship between CO conversion and flow rate except for 25 mL·min⁻¹. The conversion rate under the suspicious value-25 mL·min⁻¹ was selected by 4d method. The calculation shows that x = 15.9%, d = 0.028. So | 33.9% - x | = 33.9% - 15.9% = 0.180 > 4d = 0.113, the conversion rate of 33.9% under 25 mL·min⁻¹ flow rate should be abandoned. Under the flow rate of 25 mL·min⁻¹, the CO conversion rate is quite big and the detection concentration may be below the detection line of the mass spectrometer analyzer, resulting in data deviation.

The above activity data shows that the effect of flow rate on the activity of CO oxidation is existed, and the reaction kinetics range of linear relationship between flow rate and CO conversion rate is clarified. The effect of diffusion can be excluded in this range. The effect of other factors on the activity of the sample is carried out in the flow range.

3.2.3 Effects of temperature

Figure 7 shows the variation of catalyst activity with reaction temperature.

With the increase of reaction temperature, the CO conversion increased gradually, and the catalyst activity increased significantly. The reaction temperature with the highest catalyst activity was 90 °C, and its activity was 67.8 times that of the lowest active catalyst. It’s found that the two basically conformed to the exponential relationship:

\[ T_{\text{CO}} = 0.0474e^{0.0839t} \]
Next, the apparent activation energy of the reaction was calculated. The compression factor $Z \approx 1$ can be obtained from the two-parameter generalized compression factor diagram. Therefore, the ideal gas equation of state (equation (1)) can be used to calculate the CO concentration, and then the rate constant of the catalytic reaction can be calculated by the equation 2. The $\ln k$ vs $1/T$ is used to plot (see figure 8). The apparent activation energy $E_a = 81.7 \text{ kJ mol}^{-1}$ and pre-exponential factor $A = 124.0 \text{ kmol s}^{-1}$ were calculated by Arrhenius equation (equation 3):

$$C_{CO} = \frac{V \times C_{CO}}{RT} = \frac{100}{RT}$$  
$$k = k_0 \times V \times C_{CO}$$  
$$\ln k = -\frac{E_a}{R} + \ln A$$

In the equation, $C_{CO}$ represents CO concentration in the reaction gas and the unit is mol·m³. $V$ represents reaction gas volume and the unit is mL·mol⁻¹. $P$ represents pressure and the value is 100 kPa. $T$ represents temperature and the unit is K. $R$ represents molar gas constant and the value is 8.314 Pa·m³·mol⁻¹·K⁻¹. $k$ represents rate constant and the unit is mol·s⁻¹. $k_0$ represents pre-exponential factor and the unit is kmol·s⁻¹·A represents activation energy and the unit is kJ·mol⁻¹.

![Figure 8. The relationship between k and 1/T.](image)

**3.2.4 Effect of pretreatment conditions**

The samples which were pretreated at two different temperatures were compared with the samples without pretreatment. The relationship between pretreatment temperature and CO conversion was shown in table 1.

**Table 1. Relationship between pretreatment temperature and CO conversion rate**

| reaction temperature/°C | CO conversion rate/% Without | 200 °C | 200 °C |
|-------------------------|----------------------------|-------|-------|
| 40                      | 0.3                        | 0.1   | 1.0   |
| 50                      | 0.7                        | 0.5   | 2.4   |
| 60                      | 1.2                        | 1.3   | 6.2   |

Table 1 shows the effect of pretreatment temperature on catalyst activity. By comparing the activity of samples with different pretreatment conditions at the same reaction temperature, it was found that the reaction activities without pretreatment and those with pretreatment at 200 °C at 40 °C, 50 °C and 60 °C were not significantly different, and the CO conversion rates were 1.2 % and 1.3 % at 60 °C, respectively. The reaction activities of samples with pretreatment at 300 °C at 40 °C, 50 °C and 60 °C were significantly higher than those of samples under the other two conditions, and the CO conversion rate reached 1.0 % at 40 °C.

The above activity data indicated that at the same reaction temperature, the samples without pretreatment or pretreated at 200 °C began to have activity at 60 °C, while the samples pretreated at 300 °C began to have activity at 40 °C. However, according to the theoretical inference, the activity of the sample pretreated at 200 °C should be higher than that of the sample without pretreatment. There is little difference between the two, probably because the CO conversion rate is low at this time, which is close to the detection limit of mass spectrometer. Therefore, there is some error in the experimental data.

**4 Conclusion**

In this paper, MnO₉ nanoparticles were synthesized, and the effect of KMnO₄ dosage and reaction conditions on the catalytic CO oxidation performance was investigated. The PXRD characterization results showed that the synthesized samples had similar crystal structure with a size of about 16.5 nm compared with the samples in the literature (tetragonal pyrolysite Mn₉O₄ type). Under the condition of 100 mL·min⁻¹ flow rate and 40 °C temperature, the MnO₉ nanoparticles exhibited catalytic activity for CO oxidation reaction. The reaction kinetic range (40 mL·min⁻¹-125 mL·min⁻¹) was determined. The apparent activation energy was 81.7 kJ·mol⁻¹.

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