



Synthesis of a novel catalyst with nano metal core/carbon shell by a facile pre-complexation strategy and its application in enhanced catalytic decomposition of nitric oxide



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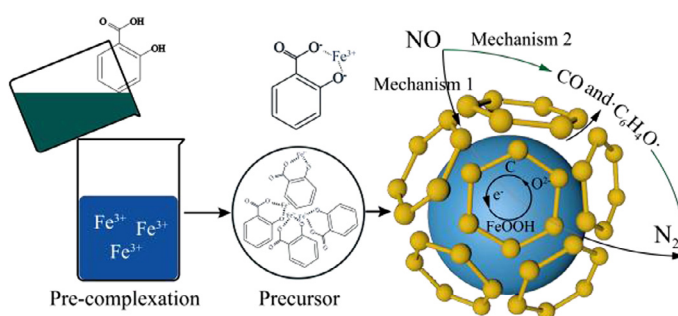
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HIGHLIGHTS

- A pre-complexation strategy was used to synthesize catalyst.
- A nano metal core/carbon shell catalyst was obtained.
- The catalyst removed ~100% of NO for more than 1000 min.
- The NO was catalytically removed by dual mechanisms.
- Solid and gaseous active species accounted for the enhanced activity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a novel and facile pre-complexation strategy was reported for the synthesis of carbon-metal catalyst for the first time. The carbon-metal catalyst (SF₂₅₀) was obtained by thermal-activating pre-complexation of ferric chloride and sodium salicylate. The HRTEM and XRD showed that SF₂₅₀ contained nanometer particles with core of FeOOH and shell of carbon species. When SF₂₅₀ was applied in selective catalytic reduction of nitric oxide (NO), it resulted in outstanding efficiency and long-term stability: the removal of NO was 99.8% with a fluctuation of 0.8%; moreover, the SF₂₅₀ maintained high efficiency of removal for more than 3000 min at 400 °C. The analyses of EELS and TG-MS suggested that solid-phase and gas-type carbons both participated in reduction of NO, thus resulting in the excellent activity at low temperature. The solid-phase carbon included the active species with great reducibility distributed on the core-shell interface. The gas-type carbon included CO and benzene radicals. Therefore, our work has suggested a novel method for the synthesis of catalyst with core-shell structure by simple operation and low-cost precursors, together with excellent activity toward catalytic reduction of NO.

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1. Introduction

Carbon-metal catalyst has attracted worldwide attentions in recent years. In this hybrid structure, carbon material has excellent conductivity and rich chemical active sites [1–3]; metal species functions as the centre of catalytic reaction and plays the role of

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electron transport and material transfer [4]. Carbon-metal catalyst thus showed excellent catalytic activities toward various reactions, including photocatalysis, electrocatalysis and asymmetric catalysis [5–8]. On the other hand, nitrogen oxide (NO_x) is one of the most toxic and abundant air pollutants produced by combustion, such as automotive engine, power plant and other industrial processes [9]. Until recently, selective catalytic reduction of NO_x (NO_x-SCR) is considered to be the most efficient and widely used technology for reducing emission of NO_x. Basically, catalyst is a key factor in NO_x-SCR [10], and carbon-metal composite showed enhanced catalytic activity [11–18].

To prepare carbon-metal composite with outstanding activity of NO_x-SCR, a variety of technologies have been employed, including impregnation, co-precipitation, sol-gel, chemical bath deposition and hydrothermal methods [14–18]. For instance, coal char loaded with Ca and Fe was prepared by impregnation, and applied in NO_x-SCR. The conversion of NO_x reached 100% at 750 °C [17]; the V₂O₅/TiO₂-carbon nanotubes (CNTs) synthesized by sol-gel method showed a removal of 89% at 300 °C; the CNTs supported MnO₂ fabricated by co-precipitation removed 89.5% of NO at 180 °C. It showed better efficiency of NO_x-SCR than the MnO_x/CNTs obtained by impregnation [18]; chemical bath deposition was utilized to prepare a core-shell structural MnO_x@CNTs, which removed >90% of NO in a wide temperature from 165 to 325 °C [14]; the MnO_x-CeO₂/graphene catalyst prepared by hydrothermal method exhibited good catalytic performance, up to 100% of NO at 140 °C [15]. Thus, carbon-metal catalysts prepared by different methods exhibit different catalytic activities.

However, although low-temperature catalyst of NO_x-SCR could be synthesized by above technologies, these common methods had many shortcomings, especially harsh conditions, complex processes, long time-consuming and large energy consumption. Moreover, they usually used expensive carbon material. For example, CNT and graphene. Otherwise, low-temperature activity was not ensured, such as using coal char-based catalyst [17]. These problems hindered the industrialization of effective catalyst of NO_x-SCR. Therefore, it is necessary to explore a method to overcome these disadvantages, and synthesize carbon-metal catalyst with specific structure and high activity.

Herein, we reported a novel, facile strategy for the synthesis of carbon-metal catalyst. The catalyst with specific nanometer core-shell structure was synthesized by pre-complexation of organic and metal ion. The nanomaterial was then applied in reduction of NO_x, resulting in outstanding efficiency and long-term stability. Its physicochemical properties and mechanism for effective NO_x-SCR were systematically investigated. To the best of our knowledge, this was the first report discussing the pre-complexation strategy for the synthesis of carbon-metal catalyst with great catalytic activity and stability.

2. Materials and methods

2.1. Catalyst preparation

The novel carbon-metal catalyst was synthesized by pre-complexation of ferric chloride (FeCl₃·6H₂O) and sodium salicylate. In detail, two solutions were first prepared. Solution A contained 1 mol/L of sodium salicylate; solution B contained 1 mol/L of FeCl₃·6H₂O. Secondly, 10 mL of solution A was mixed with 10 mL of solution B. The carbon-metal complex was then obtained after adjusting the mixture to an acidic pH (<4) [19]. The mixture was dried at 100 °C in vacuum. The obtained solid was denoted by SF. Prepared SF was then activated at different temperature (200, 250, 300, 350, 400 °C) under nitrogen atmosphere. These activated carbon-metal catalysts were simplified as SF_x, and the x stood for

the activated temperature. For example, the SF₂₀₀ indicated the sample activated at 200 °C. All catalysts were milled through 100 meshes for further use.

2.2. Experiment setup and NO removal

A fixed bed reactor was used in this work, which was detailedly described in our previous report [20]. Prior to each measurement, a certain amount of catalyst was filled in the middle part of a quartz reactor with an inner diameter of 4 mm, with a packing density of ~1.27 g/cm³. At first, a flow of Ar flushed the reaction system for 30 min to clean residual air. Then NO (990 ppm, balance Ar) was introduced into the reactor at a flow rate of 30.0 mL/min for 30 min to stabilize gas flow. The outlet stream was diluted with Ar by mass flowmeters (D07-B, D07-19B Beijing Seven-star Electronics Co., Ltd.) to gain a concentration of 51.2 ppm (NO). The concentration of NO was detected by Chemiluminescence NO-NO₂-NO_x Analyser (Thermo Scientific 42i). When 0.16 g of catalyst was used, gas hourly space velocity was about 14400 h⁻¹ (=30.0 mL/min × 60 min/(0.16 g/1.27 g/cm³)). After the detected concentration became steady, the temperature of tube furnace increased to the designed temperature. The concentration of NO was monitored by NO-NO₂-NO_x Analyser during the whole process.

2.3. Characterizations

Fourier Transform Infrared (FTIR) was used to characterize sample in the range of 400–4000 cm⁻¹ on a Nicolet 380 spectrometer. It was get by measuring the absorbance of KBr pellet after scanning 64 times. The XRD was obtained using a Rigaku D/max RBX X-ray diffractometer at 6°/min in range of 10–80° with Cu-Kα radiation (λ = 0.154 nm). The HRTEM was recorded at an operating voltage of 200 keV (JEOL JEM2010, Japan) together with electron energy-loss spectroscopy (EELS) (Model PEELS-666, Gatan, USA). The TG-MS was used to characterize the mass loss together with evolved gases from catalyst by NETZSCH thermogravimetric analyser (STA 449C) coupled with a quadrupole mass spectrometry (MS 403C).

3. Results and discussions

3.1. DeNO_x activity and durability

Fig. 1A shows the catalytic performances of NO by SF_x (x = 200, 250, 300, 350, 400) at the reaction temperature of 400 °C. The column chart clearly exhibited the catalytic activities of prepared carbon-metal catalysts at different activated temperature. The error bar indicated the stability of each catalyst. When the activation temperature was less than 300 °C, a high activity and good stability were obtained. For example, the SF₂₅₀ removed 99.8% of NO with a fluctuation less than 0.8%; the SF₃₀₀ removed more than 98.9% of NO, together with a fluctuation of 0.8%. However, when the activation temperature continued to increase, both activity and stability of the catalyst decreased sharply. Compared with SF₂₅₀ and SF₃₀₀, the sample activated at 400 °C (SF₄₀₀) removed less than 60% of NO. In addition, its ability was quite unstable, with a fluctuation of about 20%. The SF₃₅₀ showed similar activity and stability to SF₄₀₀. Thus, the activation temperature seemed to control ability of NO-SCR.

Fig. 1B compares conversions of NO by SF₂₅₀ and SF₃₀₀ at various catalytic temperatures. In general, for both SF₂₅₀ and SF₃₀₀, the conversion of NO increased with the increase of temperature. The removal of NO by SF₂₅₀ increased from 10.0 to 65.3%, when the temperature increased from 320 to 360 °C. After the catalytic

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