



## Short communication

A new type Ni-MOF catalyst with high stability for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>Xiaoyu Sun<sup>a</sup>, Yong Shi<sup>a,\*</sup>, Wang Zhang<sup>a</sup>, Chunyan Li<sup>a</sup>, Qidong Zhao<sup>b</sup>, Jinsuo Gao<sup>a</sup>, Xinyong Li<sup>a</sup><sup>a</sup> Key Laboratory of Industrial Ecology and Environmental Engineering and State Key Laboratory of Fine Chemicals, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, PR China<sup>b</sup> School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin Campus, Post Code 124221, NO.2 Dagong Road, New District of Liaodong Bay, Panjin City, PR China

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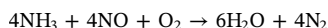
Active temperature

## ABSTRACT

A crystalline porous Ni-MOF catalyst was fabricated successfully through hydrothermal method and shown to exhibit excellent catalytic performance for NH<sub>3</sub>-SCR. This prepared Ni-MOF showed better thermal stability than other reported Cu-BTC or MIL-100(Fe) SCR catalyst material. It could keep a satisfactory stable crystalline structure when the reaction temperature reached up to 440 °C. Moreover, it was found that the catalytic activity of Ni-MOF was significantly improved after preheat treatment in N<sub>2</sub> atmosphere. The Ni-MOF catalyst activated at 220 °C achieved more than 92% NO conversion efficiency with a large operating-temperature window from 275 to 440 °C.

## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) from flue gas have been a major air pollutants causing acid rain and photochemical smog ever since. According to the different stages of NO<sub>x</sub> formation, the commonly used approaches for reducing NO<sub>x</sub> production can be divided into two categories: post-treatment technology and low nitrogen combustion technology. Of the two processes, selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> (NH<sub>3</sub>-SCR), which can catalytically convert NO to nitrogen and water vapor, has been considered as a leading post-treatment technology for NO<sub>x</sub> emissions control. The conversion process from NO to N<sub>2</sub> can be expressed by the following SCR reaction:



In general, different metal oxides catalysts have been investigated and applied for NH<sub>3</sub>-SCR reaction, such as vanadium [1, 2], manganese [3, 4], cobalt [5], copper [6, 7] and oxides etc. The V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst has been found to be most commercially available as a long-term stable catalyst material. However, vanadium catalyst also has some drawbacks, such as the toxicity of vanadium and formation of N<sub>2</sub>O at high temperature. Therefore, developing new NH<sub>3</sub>-SCR catalyst with good catalytically activity and high hydrothermal stability is still desirable for SCR DeNO<sub>x</sub> application.

Recently, the metal organic frameworks (MOFs), also known as Porous Coordination Polymers (PCPs), have generated significant

interest as a novel kind of functional catalytic material. MOFs exhibit many unique properties such as low density, high porosity, conductivity and large surface area. These unique properties make them very promising for different applications such as gas separation [8, 9], storage [10, 11] and catalysis [12]. Recognizing that the pore structure of MOFs is beneficial to gas adsorption based on the combination between their ionic crystals and discrete organic monomer [13]. In addition, numerous MOFs have been developed for various catalytic reactions due to their customizable and desirable chemical functionalities [4, 14].

Nowadays, a few MOFs have been reported to apply in NH<sub>3</sub>-SCR process. For example, both copper-based Cu-BTC and iron-based MIL-100(Fe) have displayed good NH<sub>3</sub>-SCR activity in a suited reaction temperature range. However, thermal stability is still a weakness for these MOFs materials as their stability is usually no more than 350 °C in such SCR process. In addition, it has been reported that nickel-based MOFs can exhibit excellent thermal stability up to 440 °C, which is higher than that of Cu-BTC and MIL-100(Fe) [15–18]. On the other hand, since nickel-based oxide catalyst possess excellent SCR catalytic performance [6], we supposed that Ni-based MOF material would exhibit good denitrification capacity with desired stability in NH<sub>3</sub>-SCR performance. To the best of our knowledge, there has still no report about Ni-MOF material applying in the SCR reaction.

In this work, a series of Ni-MOF catalysts were successfully synthesized via a direct solvothermal method and were used for selective catalytic reduction of nitrogen oxide (NO<sub>x</sub>) with NH<sub>3</sub> for the first time.

\* Corresponding author.

E-mail address: [sys-99@163.com](mailto:sys-99@163.com) (Y. Shi).

After activated under different temperatures by N<sub>2</sub> purging, the catalytic performance of Ni-MOF was systematically investigated. As expected, the Ni-MOF catalyst not only showed powerful catalytic properties for NH<sub>3</sub>-SCR, but also showed good stability which was higher than that of other reported MOFs. The effects of activation temperatures on the SCR activity and physicochemical properties of the prepared catalyst were discussed in details.

## 2. Experiment

### 2.1. Synthesis of Ni-MOF catalysis

All chemicals were of analytical grade and used without further purification. Typically, nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.96 g)) and PTA (H<sub>2</sub>BDC, 1.66 g), were dissolved into 60 ml *N,N*-dimethylformamide (DMF) with magnetic stirring [18]. The as-prepared solution were slowly added with 4 ml NaOH solution (4 M) and ultrasonically treated for 30 min to accelerate such dissolution process. Then the mixtures were transferred into a 100 ml Teflon-lined autoclave, which were sealed and maintained at 120 °C for 24 h. After hydrothermal processing, the obtained samples were collected and washed with ethanol and DMF by centrifuging at 10,000 rpm for 10 min, and finally the light green samples were dried in a vacuum oven at 100 °C for 12 h.

### 2.2. Characterization

Powder X-ray diffraction patterns (PXRD) of the prepared materials were recorded on a Empyrean X-ray diffraction meter using Cu K $\alpha$  radiation (range of 5–30). Fourier transform infrared (FTIR) spectrum was recorded on an FTIR spectrometer (Bruker VERTEX 70-FTIR) with a standard KBr pellet method. All spectra were collected over accumulative 64 scans with a resolution of 4 cm<sup>-1</sup> in the range of 4000–400 cm<sup>-1</sup>. N<sub>2</sub> adsorption-desorption isotherms were measured on a Micrometrics ASAP2020M instrument at 96 °C (BET model in Quanta chrome SI). NH<sub>3</sub>-TPD was carried out by a Chembet PULSAR TPR/TPD. The surface topography of Ni-MOF materials were investigated with a scanning electron microscopy (SEM, Hitachi SU8010). Thermogravimetric analysis (TGA) were performed on a TGA SDTA850 thermogravimetric analyzer in a nitrogen flow from 30 to 600 °C. X-ray photoelectron spectra (XPS) measurements were carried out by a VG ESCALAB250 Electron Spectrometer with monochromatic Al K $\alpha$  (1486.6 eV) at 15 kV and 10 mA.

### 2.3. Catalysts performance test

The NH<sub>3</sub>-SCR of NO reaction was carried out in a fixed-bed quartz tube reactor (inner diameter 8 mm) loaded with the catalyst (0.20 g). The pressure of the SCR reaction was 101.3 Kpa and the powder catalyst was pressed into sheets of about 1 mm thickness. Catalytic activity of the prepared catalysts was evaluated from 100 °C to 500 °C and continually monitored by a flue gas analyzer (Testo 350). The samples were then activated under nitrogen flow at temperatures ranging from 180 °C to 220 °C before catalytic performance test.

The total flow rate was 100 ml·min<sup>-1</sup> and the gas hourly space velocity (GHSV) was 15,000 h<sup>-1</sup>. The reactant gas composition was set as follows: 500 ppm NO, 5 vol% O<sub>2</sub>, 500 ppm NH<sub>3</sub>, and N<sub>2</sub> as balance gas. While the NH<sub>3</sub>-SCR reaction reaches a steady-state condition, data were collected and analyzed. The NO<sub>x</sub> conversions can be calculated by the following equation:

$$\text{No}_x\text{conversion} = \frac{\text{No}_x\text{inlet} - \text{No}_x\text{outlet}}{\text{No}_x\text{inlet}} \times 100\%$$

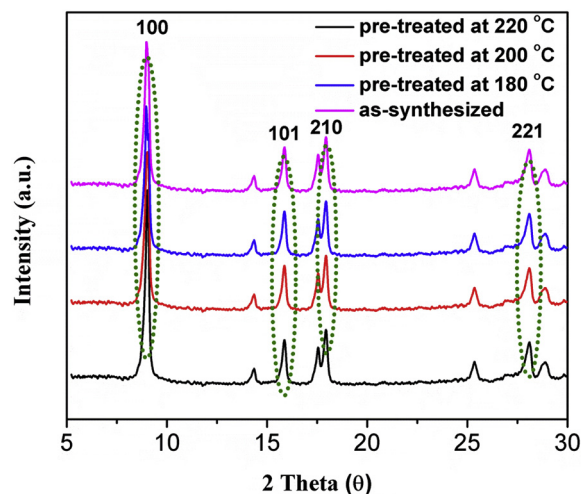


Fig. 1. The XRD patterns of as-synthesized Ni-MOF and pre-treated samples at different temperatures: 180 °C, 200 °C, 220 °C.

## 3. Results and discussion

### 3.1. Structure and properties of Ni-MOF catalyst

The crystalline phases of the synthesized Ni-MOF samples were identified by XRD. As shown in Fig. 1, main characteristic peaks of Ni-MOF have been detected, in which the peaks at 8.9°, 15.9°, 17.9° and 28.1° are corresponding to the diffraction peaks of (100), (101), (210) and (221) crystal planes of [Ni<sub>3</sub>(OH)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O (CCDC no.638866) [19]. It can be seen that the Ni-MOF powders obtained from the solvothermal synthesis possessed a high crystallinity and no impurity peaks were observed. Furthermore, diffraction peaks positions and intensities for activated Ni-MOF showed high similarity to as-synthesized sample, indicating that Ni-MOF could keep a stable crystal structure during active process.

### 3.2. DeNO<sub>x</sub> catalyst activity

The catalytic performance of Ni-MOF pre-treated at different temperatures for NH<sub>3</sub>-SCR was measured and the obtained NO<sub>x</sub> conversion results were shown in Fig. 2. At temperatures below 80 °C, there is a nearly 10% NO conversion for all the sample which may mainly due to physical adsorption of NO to catalyst surface. When temperature above 100 °C, the N<sub>2</sub> yields for all samples ascend with reaction temperature to a maximum values (more than 90%) and keep stable in a certain temperature range of 275 °C to 400 °C. Moreover, it could be observed that N<sub>2</sub> yields obviously increased with activation temperature, which indicated catalytic activity of Ni-MOF was promoted at higher activation temperature. This result can be explained that thermal treatment is beneficial to producing more nickel active sites by removing residual water molecules connected to carbonylate nickel-clusters [20]. Especially, the catalyst pre-treated at optimum temperature (220 °C) displayed a nearly 92% NO conversion with large operating-temperature window from 275 to 400 °C. This result also demonstrates that Ni-MOF was more stable than reported Cu-BTC and MIL-100(Fe) [16, 17]. Compared with reported literature, the nickel hydroxide from Ni-MOF may be possessed both highly catalytic functionalities and inherit the high structure stability [21–23].

When reaction temperature rose to 440 °C, the NO conversions for all samples decreased sharply. This decline is associated with the destruction and destabilization of Ni-MOF framework, which is also evidenced by the following TGA result (Fig. 4).

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