

Study on denitration performance of multi element modified MIL-101 (Fe) at low temperature

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Abstract. MIL-101 (Fe) was modified by amino group and doped by Cu and Co elements by microwave hydrothermal method. The effect of SCR denitrification at low temperature was investigated with high concentration of NO_x as adsorption object. The results show that when the flue gas temperature is 200 °C and the NO_x concentration is up to 1640 mg/m³, the removal efficiency of NO_x can reach 86% under the optimal conditions, which is 1.5 times higher than that before modification. In addition, the characterization results indicated that the specific surface area of the modified catalyst increased, the thermal stability was good at low temperature, the selective adsorption capacity of NO was enhanced, and the doping played a synergistic catalytic role. It can be used for flue gas denitration in various industries.

1 Introduction

MIL-101 series is one of the second generation MOFs materials. Because of its super large specific surface area, high stability and easy surface functionalization, it has become a research hotspot in the field of adsorption [1,2]. For the sake of improve the adsorption and selectivity of MOFs materials to adapt to more actual flue gas, metal elements are usually used to modify MOFs materials [3-5]. The MOFs with modified bimetallic sites prepared by Yao Zhuo [6] showed a good catalytic denitration effect when the NO_x concentration was less than 670 mg/m³ at about 240 °C, and the conversion efficiency was only about 55% at 200 °C. Although the conversion efficiency of mil series materials modified by Wang Peng [7] is about 90% when the NO_x concentration is lower than 670mg/m³ at 200 °C, it is unknown whether the conversion efficiency of high concentration NO_x can reach the same high. In addition, functionalized MOFs can be achieved by introducing specific functional groups such as -NH₂, -COOH and -OH [8]. Therefore, it is possible to improve the denitration efficiency at high concentration by optimizing the structure and properties of MIL-101 (Fe) monomer with appropriate modification methods.

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Compared with hydrothermal method, microwave hydrothermal method can greatly shorten the preparation time. Therefore, in this study, microwave hydrothermal method was used to prepare multi-component modified MIL-101 (Fe) material to realize SCR denitration at high concentration and low temperature.

2 Materials and methods

2.1 Chemicals

Anhydrous ethanol (AR), glacial acetic acid (AR), terephthalic acid (AR), N, N-dimethylformamide (AR), 2-Aminoterephthalic acid (AR), copper nitrate trihydrate (AR), cobalt nitrate hexahydrate (AR), N-(1-naphthyl) ethylenediamine hydrochloride (AR), ferric chloride (AR).

2.2 Materials

MIL-101 (Fe) was synthesized from terephthalic acid, N, N-dimethylformamide and FeCl_3 by microwave hydrothermal method.

NH_2 -MIL-101(Fe) can be obtained by replacing terephthalic acid with 2-Aminoterephthalic acid during the preparation of MIL-101 (Fe). In addition, copper nitrate or cobalt nitrate were added before stirring for 30 min. For example, $x\text{Cu-NH}_2$ -MIL-101 ($x\%$ is the mole percentage of Cu or Co and Fe) is used to express the product.

2.3 Characterization

The specific surface area, pore size distribution and structural characteristics of the samples were detected by using the SA3100 specific surface area and porosity analyzer of Beckman Coulter Co., Ltd. The thermal stability of the samples was analyzed using the TGA 4000 thermogravimetric analyzer of Birkin Elmer Instruments.; Infrared test was carried out using the Tensor II Fourier transform infrared spectrometer of Brock Technologies Co., Ltd. to analyze the presence of groups and elements in the sample; The NO adsorption strength of the catalyst was analyzed and detected by the PCA-1200 detector (NO-TPD) of Beijing Piod Electronic Technology Co., Ltd.

2.4 Activity evaluation

During the experiment, the ventilation rate of N_2 : 180mL/min, the ventilation rate of NO: 60mL/min, the ventilation rate of O_2 : 10mL/min, and the temperature was set at 200 °C. To explore the influence of the initial concentration of NO_x on the denitrification effect, the nitrogen ventilation rate was controlled to make the concentration change in 500 ~ 2400mg / m^3 . In the experiment, 0.5g catalyst sample was sampled for 15min. The concentration of each gas after reaction was determined by spectrophotometry with naphthalene ethylenediamine hydrochloride. The denitration efficiency of the sample was calculated by combining with the initial value.

3 Results

3.1 Denitration efficiency of catalyst materials

Table 1. Denitration efficiency under different modification conditions.

Sample	NO removal efficiency (%)	NO ₂ removal efficiency (%)	NO _x removal efficiency (%)
MIL-101(Fe)	22	44	34
NH ₂ -MIL-101(Fe)	51	70	55
NH ₂ - Cu(x%)-MIL-101(Fe)	x=3	69	71
	x=5	70	74
	x=7	63	70
	x=9	59	64
	x=1	75	80
NH ₂ - Cu(5%)- Co(x%)-MIL-101(Fe)	x=3	70	75
	x=5	72	72
	x=7	73	73

The denitration efficiency of catalyst materials before and after modification is shown in Table 1. After the introduction of amino and doping elements, the denitration efficiency is obviously better than that of MIL-101(Fe) monomer. The denitration efficiency of Co and Cu double doped catalyst is obviously better than that of Cu Single doped catalyst. When the Co doping ratio is 1%, the catalyst has the highest denitration efficiency, the removal efficiency of NO is more than 75%, the removal efficiency of total nitrogen oxides is 80%, and the removal efficiency of NO₂ is more than 90%. Therefore, NH₂-Cu (5%)-Co (1%)-MIL-101 (Fe) is the best catalyst for denitration.

3.2 Effect of NO_x initial concentration on denitration efficiency

The initial concentration of NO_x was in the range of 500~2400mg/m³ by adjusting the ventilation rate of NO and N₂. In this range, the denitration efficiency of the catalyst increases with the increase of the initial concentration of NO_x, and the highest denitration efficiency reaches 83% when the initial concentration of NO_x reaches 2100mg/m³. Overall, the denitration efficiency of NH₂-Cu(5%)-Co(1%)-MIL-101(Fe) is more than 70%, indicating that the modified catalyst has good adaptability to low concentration and high concentration of NO_x, and is suitable for flue gas denitration in many industries.

3.3 The influence of continuous use time on denitrification efficiency

Table 2. Effect of continuous use time on denitration efficiency of MOFs materials.

Continuous use time(min)	NO removal efficiency(%)	NO ₂ removal efficiency(%)	NO _x removal efficiency(%)
20	81	97	86
40	74	93	81
60	70	86	75

The experimental results are shown in Table 2. After continuous use for 1 hour, the NO_x removal efficiency only decreases by 11%, and the denitration efficiency can still reach more than 70%. The main reason for the decrease of denitration efficiency may be that the catalyst adsorbs a large amount of gas when it is used continuously at high temperature, which affects

its adsorption performance. Generally speaking, $\text{NH}_2\text{-Cu(5\%)-Co(1\%)-MIL-101(Fe)}$ catalyst has good continuous performance.

3.4 Catalyst anti-interference experiment

In the experiment, pure CO_2 and pure 1% SO_2 were introduced respectively. Under the influence of high concentration of CO_2 , the removal efficiency of total nitrogen oxides was higher than 80%. When the concentration of SO_2 reaches 2280mg/m^3 , the removal rate of NO_2 is still higher than 80%; The total denitration efficiency is still over 70%. Therefore, the modified catalyst has good ability to resist the interference of CO_2 and SO_2 .

3.5 BET characterization

Table 3. Analysis of BET of MOFs.

Sample	BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Average aperture (nm)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)
MIL-101(Fe)	190.19	2.30	0.11
$\text{NH}_2\text{-MIL-101(Fe)}$	300.75	12.98	0.33
$\text{NH}_2\text{-Cu-MIL-101(Fe)}$	268.27	3.23	0.22
$\text{NH}_2\text{-Cu-Co - MIL-101(Fe)}$	260.91	2.67	0.17

Table 3 shows the surface structure parameters of the samples. The BET specific surface area of MIL-101 was $190.19\text{m}^2/\text{g}$, and the specific surface area of amino modified catalyst was increased to $300.75\text{m}^2/\text{g}$. When the specific surface area of bimetallic element doped catalyst was similar, more active sites were provided to promote the catalytic reaction. Therefore, the surface structure of the prepared modified MOFs catalyst is better.

3.6 TGA characterization

The results of thermogravimetric treatment are shown in Figure 1. The quality of the four catalysts decreased in the same way in nitrogen atmosphere, so the modification had little effect on the thermal stability of the catalysts. The first weight loss of the four catalysts at about $150\text{ }^\circ\text{C}$ is mainly due to the loss of a small amount of anhydrous ethanol and water in the catalyst. The catalyst was dried at $80\text{ }^\circ\text{C}$ before use, so the weight loss was less, about 5%. The second stage of weight loss occurs between $150\text{ }^\circ\text{C}$ and $300\text{ }^\circ\text{C}$. The boiling point of DMF is $152.8\text{ }^\circ\text{C}$, so DMF is desorbed after $150\text{ }^\circ\text{C}$. The solvent used in the reaction process of catalyst preparation is pure DMF, which is difficult to remove. The unmodified catalyst may be DMF in the catalyst at this stage, while the modified catalyst may also have low temperature decomposition of $-\text{NH}_2$ group at this stage [9]. The third stage is $300\text{ }^\circ\text{C} \sim 500\text{ }^\circ\text{C}$. In this stage, the quality of the catalyst decreases sharply, mainly because the main framework of the catalyst begins to collapse and the organic structure decomposes rapidly. Therefore, the catalyst prepared in this paper has good thermal stability, which is suitable for denitration reaction below $300\text{ }^\circ\text{C}$, and has a wide range of applications [10].

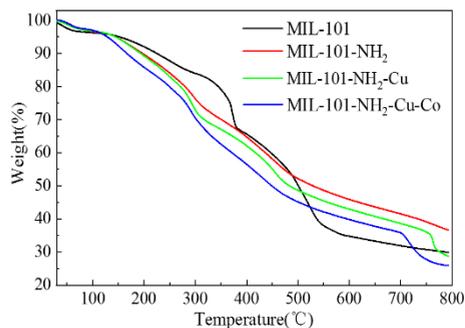


Fig. 1. Analysis of TGA of MOFs.

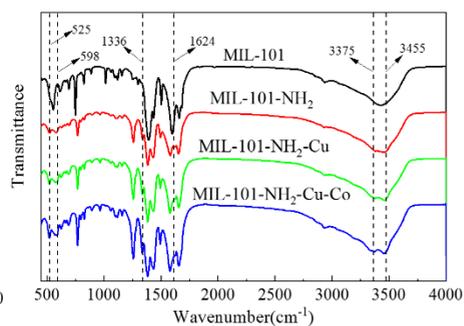


Fig. 2. Analysis of FTIR of MOF.

3.7 FTIR characterization

Four kinds of catalyst samples were tested and analyzed by infrared spectroscopy. It can be seen from Figure 2 that the infrared spectra of three kinds of modified catalysts are basically consistent with those of unmodified catalysts due to the extremely low metal content in the modified catalysts, which indicates that the prepared MIL-101 catalysts are basically consistent. $\text{NH}_2\text{-MIL-101}$ has several more peaks than MIL-101, among which 3455cm^{-1} and 3375cm^{-1} are symmetrical stretching vibration peaks and asymmetric stretching vibration peaks [11, 12], 1624cm^{-1} is bending vibration peak of N-H bond caused by NH_2 group vibration, and 1336cm^{-1} is stretching vibration absorption peak of C=N bond in catalyst [13, 14]. The results showed that there was -NH_2 group on the surface of the catalyst, and the amino modified MIL-101 catalyst was successfully prepared. The vibration absorption peaks at 598cm^{-1} and 525cm^{-1} should be the presence of Cu in the catalyst, corresponding to the peaks related to Cu coordination in the catalyst structure [15].

3.8 NO-TPD characterization

In order to explore the adsorption performance of NO on the catalyst surface, NO-TPD tests were carried out on four kinds of catalysts, and the test results are shown in Figure 3. When the temperature is lower than 250°C , $\text{NH}_2\text{-MIL-101}$ and $\text{NH}_2\text{-Cu-Co-MIL-101}$ both have a no desorption peak, while unmodified MIL-101 has no desorption peak, which indicates that the adsorption capacity of modified catalyst for NO is improved. The desorption peak of $\text{NH}_2\text{-MIL-101}$ for NO is 119.7°C , while the desorption peak of $\text{NH}_2\text{-Cu-Co-MIL-101}$ is about 178.8°C , which indicates that a new low-temperature NO adsorption site is added after modification, and the desorption temperature of the Catalyst Doped with Cu and Co increases, which indicates that the adsorption strength of the Catalyst Doped with Cu and Co increases. In addition, the peak area of the Catalyst Doped with Cu and Co is greatly increased, which indicates that doping Cu and Co can help to improve the ability of the catalyst to adsorb NO at low temperature, which is conducive to the activation of NO on the catalyst surface and the low-temperature SCR catalytic reaction [16].

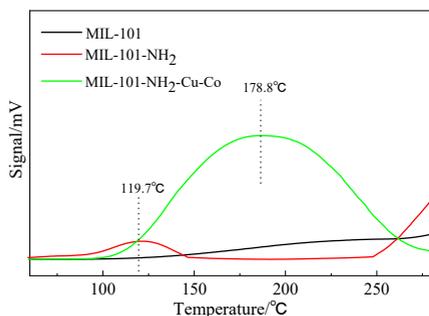


Fig. 3. NO-TPD analysis of MOF.

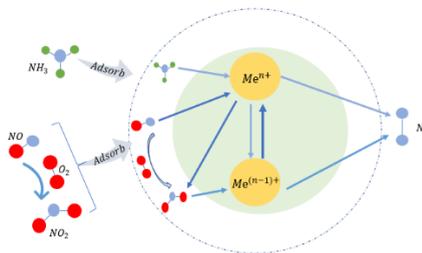


Fig. 4. Process of adsorption and catalysis.

4 Adsorption mechanism

According to the FTIR spectra and BET characterization results, amino groups were successfully introduced and the adsorption performance was improved mainly by increasing the specific surface area of the catalyst. From the experimental results of denitration efficiency before and after modification, it can be inferred that Fe^{3+} in the synthesized MIL-101 (Fe) catalyst material is the active center, and the doping of Cu and Co may occupy part of Fe^{3+} active center, so the catalytic activity of the modified sample is different. However, when the molar ratio of Cu and Co doping exceeds 5% and 1% respectively, the denitration efficiency decreases, which also shows that the key role is still the active host Fe^{3+} , Cu^{2+} and Co^{2+} only play the role of modification and synergistic catalysis, which is consistent with the literature report [17,18] on SCR denitration.

It can be inferred that the SCR catalytic Denitration Process of iron-based MIL-101 catalyst is as follows: NH_3 , O_2 and NO are adsorbed on the catalyst surface, O_2 oxidizes part of NO to NO_2 , Fe^{3+} catalyzes part of NO to NO_2 , NH_3 to N_2 . In this process, Fe^{3+} coordination unsaturated site will be reduced to Fe^{2+} coordination unsaturated site, Fe^{2+} will reduce NO_2 and NO to N_2 , and then Fe^{2+} can be oxidized to Fe^{3+} again by O_2 . The results of BET showed that Cu and Co were successfully doped. Combined with NO-TPD analysis, the doping of Cu and Co enhanced the NO adsorption performance of the catalyst, and could cooperate with Fe^{3+} . The valence state of Cu changed between +1 and +2, and that of Co changed between +2 and +3, which was consistent with the description of related literature [18, 19].

The adsorption catalysis process is shown in Figure 4. In addition, according to the experimental data in Figure 4, As the concentration of NO_x increases, the denitration efficiency of SCR reaction is improved. The NO-TPD characterization analysis diagram also proves that the adsorption strength of NO on the catalyst surface is a key factor affecting SCR reaction, indicating that adsorption is the speed control step of the whole adsorption catalytic reaction.

5 Conclusion

The samples of multicomponent modified MIL-101 (Fe) catalyst were prepared by microwave hydrothermal method. The results show that the best catalyst is $\text{NH}_2\text{-Cu}$ (5%) - Co (1%)-MIL-101 (Fe). When the reaction temperature is $200\text{ }^\circ\text{C}$ and the initial concentration of NO_x is 1640 mg/m^3 , the NO_x removal rate can reach 86%, which is 1.5 times higher than that before modification, and the nitrogen removal performance is significantly improved at high concentration. The continuous service time of the modified catalyst is prolonged, and it has excellent anti-interference performance. The characterization results showed that the

modification of amino group was mainly to increase the specific surface area of the catalyst and enhance its adsorption capacity. The doping of metal elements increased the number of active sites and improved the adsorption capacity of NO, which was consistent with the experimental results. Mechanism analysis also shows that adsorption is the speed control step of SCR denitration process.

The project was supported by the National Basic Research Program of China(2018YFB060420103)

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