

Communication

Enhancing the Water Resistance of Mn-MOF-74 by Modification in Low Temperature NH₃-SCR

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Abstract: In this study, Mn-MOF-74 was successfully synthesized and further modified via two paths for enhanced water resistance. The structure and morphology of the modified samples were investigated by a series of characterization methods. The results of selective catalytic reduction (SCR) performance tests showed that polyethylene oxide-polypropylene-polyethylene oxide (P123)-modified Mn-MOF-74 exhibited outstanding NO conversion of up to 92.1% in the presence of 5 vol.% water at 250 °C, compared to 52% for Mn-MOF-74 under the same conditions. It was concluded that the water resistance of Mn-MOF-74 was significantly promoted after the introduction of P123 and that the unmodified P123-Mn-MOF-74 was proven to be a potential low-temperature SCR catalyst.

Keywords: Mn-MOF-74; modification; water resistance; NH₃-SCR performance

1. Introduction

As one of the major air pollutants, nitrogen oxides (NO_x) are considered to cause a series of environmental problems, such as acid rain, smog, and greenhouse effects [1]. The selective catalytic reduction (SCR) of NO_x with NH₃ (NH₃-SCR) is one of the most effective techniques for reducing NO_x from stationary resources caused by fossil fuel combustion (e.g., coal-burning power plants) [2]. In the past few years, considerable research work has been performed on the development of high efficiency catalysts for NH₃-SCR [3]. V₂O₅-WO₃-TiO₂ catalysts have been widely employed as commercial catalysts; nevertheless, the disadvantages of these catalysts are their high operating temperatures (300–400 °C) and the toxicity of vanadium [4]. Hence, it is of great importance to find a new type of catalyst which is able to effectively remove NO_x at low temperature since the catalyst is located behind the desulfurizer and electrostatic precipitator system to reduce the cost of NH₃-SCR. A series of transition metal oxides such as MnO_x, FeO_x, CoO_x, and CeO_x supported on different carriers have been studied to raise low temperature activity [2,5,6]. Notably, manganese-oxide-based catalysts have shown promising catalytic activity among the studied catalysts. However, the relatively lower specific surface area of traditional carriers might hinder the further application of manganese-oxide-based catalysts. Thus, it is especially important to find a carrier substitute with a large specific surface area.

Among the potential candidates, metal–organic frameworks (MOFs) have attracted significant attention due to their large specific surface area, low density, high chemical tenability, and controlled structure. It has been reported that a Ni-MOF activated at 220 °C achieved a NO conversion efficiency of over 92% for a large operating-temperature range of 275 to 440 °C [7]. MOF-74 is a potential support for the low-temperature NH₃-SCR process owing to its coordinatively unsaturated metal sites (CUSs),

highly dispersed and absolute exposed metal sites, large specific surface areas, and high porosity. According to our previous work [8], the Mn-MOF-74 catalyst has good catalytic performance for the low-temperature reaction of NH_3 -SCR, and we found the NO conversion to be nearly 99% at 220 °C. However, the NO conversion of Mn-MOF-74 was observed to drop by 44% after the adding of 5% water, which hinders the further application of these materials. It has been reported that the presence of water could reduce the capacity of gas adsorption significantly and destroy the crystal structure of MOF-74 [9]. It is therefore necessary to improve the water stability of the prepared MOF materials under the premise of maintaining good denitrification performance.

At present, two major strategies are being employed to raise the water-resistance of MOFs to expand their applications. The most effective strategy for preparing MOFs with water stability is to introduce strong coordination bonds [10]; another method is to install a hydrophobic moiety around the coordination sites or on the working surface of the crystal to prevent corrosion from water molecules [11–13]. It has been proven that the latter is an efficient way to enhance the water resistance of MOF materials. Wu and his co-authors enhanced the water resistance of IRMOF1 by adding water-repellent functional groups [12].

In this work, as-synthesized Mn-MOF-74 catalysts were modified via two methods to promote water resistance. One strategy used was to cover water-in-oil surfactants polyethylene oxide-polypropylene-polyethylene oxide (P123) or polyvinylpyrrolidone (PVP) on the surface of Mn-MOF-74 to increase the external surface hydrophobicity of MOFs, producing P123-Mn-MOF-74 and PVP-Mn-MOF-74. The other was to introduce hydrophobic groups ($-\text{CH}_3$) to the ligand of Mn-MOF-74 to synthesize Mn-MOF-74- CH_3 through a post-synthesis modification (PSM) method. In addition, the effects of these groups on crystal structure, morphology, and thermal stability were investigated by powder X-ray diffraction (PXRD), FT-IR, SEM, TEM, and thermogravimetry mass spectrometry (TG-MS), et al. In addition, NH_3 -SCR performances with low temperature and water resistance for the prepared catalysts were studied.

2. Results and Discussion

2.1. Characterization of MOFs

Figure 1 shows the PXRD patterns of Mn-MOF-74, P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74- CH_3 . As can be seen from this figure, the two strongest peaks at $2\theta = 6.5\text{--}7^\circ$ and $11.5\text{--}12^\circ$ of all the samples correspond to the crystal faces (2-10) and (300), respectively, which are characteristic diffraction peaks of MOF-74. The relative strength of the two diffraction peaks of P123-Mn-MOF-74 and PVP-Mn-MOF-74 accord with the standard pattern while the peak intensity of Mn-MOF-74- CH_3 at $2\theta = 11.5\text{--}12^\circ$ is higher than that at $2\theta = 6.5\text{--}7^\circ$. The patterns of $-\text{CH}_3$ -functionalized Mn-MOF-74 are inconsistent with the standard pattern, which was probably caused by the synthesis method. In other words, the harsher preparation conditions of Mn-MOF-74- CH_3 did have an influence on the structure of MOF-74, but the main crystal structure was maintained. In summary, the introduction of surfactants P123 and PVP and methyl had little effect on the crystal structure of MOF-74.

To further investigate the influence of modification on catalyst structure, FT-IR tests were carried out on Mn-MOF-74, P123/PVP-Mn-MOF-74, and Mn-MOF-74- CH_3 (the spectra are displayed in Figure S1). The peak at 1625 cm^{-1} can be assigned to $\nu(-\text{COO})$ of DHTP (2,5-dihydroxyterephthalic acid) [13]. The bands at 1558 cm^{-1} and 1400 cm^{-1} can be assigned to $\nu(\text{C}=\text{C})$, which belongs to the skeleton vibration of the benzene ring [14,15] of DHTP. The peak at 1245 cm^{-1} can be assigned to $\nu(\text{C}-\text{N})$ of DMF (N, N-Dimethyl formamide) [16,17], demonstrating that the solvent DMF exists on the catalysts' surface or in the channel of the catalysts. The bands at 888 cm^{-1} and 811 cm^{-1} can be attributed to a $\nu(\text{C}-\text{H})$ oscillatory vibration in and out of the plane of the benzene ring [18]. The peaks at 579 cm^{-1} and 473 cm^{-1} belong to the vibration absorption $\nu(\text{Mn}-\text{O})$ [19,20], which confirms the existence of a metal–ligand bond. Notably, as shown in Figure S1b, Mn-MOF-74- CH_3 has a weak absorption peak at 2960 cm^{-1} , which belongs to the stretching vibration absorption of $\nu(\text{C}-\text{H})$ in alkanes [19], proving that

-CH₃ had been introduced into the structure of Mn-MOF-74. According to the results of FT-IR and XRD, it can be concluded that the three catalysts were synthesized successfully.

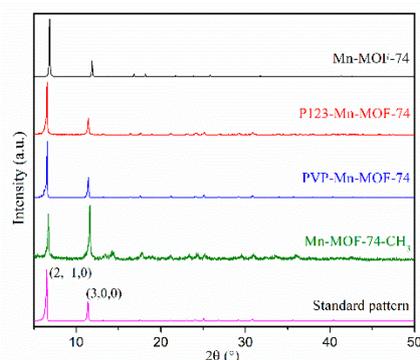


Figure 1. The powder X-ray diffraction (PXRD) patterns of Mn-MOF-74, polyethylene oxide-polypropylene-polyethylene oxide (P123)/polyvinylpyrrolidone (PVP)-Mn-MOF-74, and Mn-MOF-74-CH₃.

As can be seen from Figure S2, the four samples showed spherical particles. The morphology of Mn-MOF-74-CH₃ displayed almost no change except for there being a few tiny block crystals on the surface; the surfaces of P123-Mn-MOF-74 and PVP-Mn-MOF-74 were almost wrapped with a mass of tiny particles compared to Mn-MOF-74. The results suggest that the original spherical morphology of Mn-MOF-74 remained unchanged whether the water-in-oil surfactants P123 and PVP were introduced or ligand methyl functionalization was performed.

The edge of each sample was observed using TEM characterization techniques and the results are shown in Figure 2. It may be noted that there is no coating on the edges of Mn-MOF-74 and Mn-MOF-74-CH₃, while the edges of P123-Mn-MOF-74 and PVP-Mn-MOF-74 are obvious, which should be due to the coating of water-in-oil surfactants P123 and PVP, respectively. Compared with PVP-Mn-MOF-74, the P123-modified Mn-MOF-74 showed better surfactant dispersion and the particle size of the latter was more uniform. In summary, it can be speculated that the surfactants P123 and PVP were coated on the surface of the Mn-MOF-74 successfully.

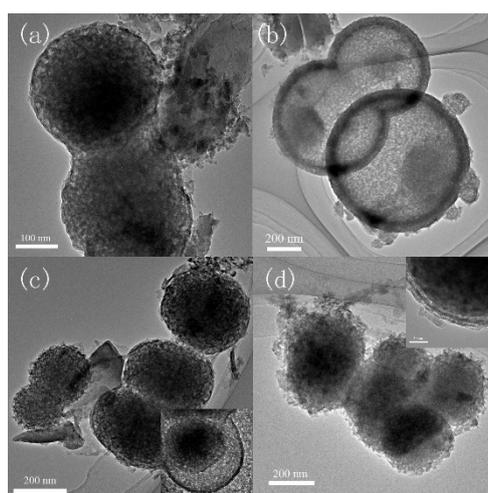


Figure 2. TEM images of (a) Mn-MOF-74, (b) P123-Mn-MOF-74, (c) PVP-Mn-MOF-74, and (d) Mn-MOF-74-CH₃. Illustration: edge of the related samples.

The prepared catalysts were analyzed by thermogravimetric analysis in air and under a nitrogen atmosphere and the results are shown in Figure S3a,b. Taking Mn-MOF-74-CH₃ as an example, the ion

fragments of decomposition products in the air atmosphere and N_2 atmosphere were detected by mass spectrometry, as shown in Figure S3c,d.

From Figure S3a, it can be observed that the weight loss of the three catalysts showed two significant stages under air conditions. In the first stage, the mass loss ratio of P123-Mn-MOF-74 can be seen to be about 20% near 235 °C, which can be attributed to the removal of $CHCl_3$, while that of PVP-Mn-MOF-74 and Mn-MOF-74- CH_3 are about 20% at 275 °C, which could be ascribed to methanol and $CHCl_3$ (as can be seen in Figure S3c), respectively. The second weight loss of all the samples is about 35% at about 320 °C, which is due to the total collapse of the skeleton structure. To sum up, it can be seen from the results that the three catalysts can maintain the integrity of the crystal structure when stored in air.

As shown in Figure S3b, there are three clear mass losses for the three catalysts in the N_2 atmosphere. The first stage is about 10% near 105 °C for the Mn-MOF-74- CH_3 sample, which can be attributed to the removal of $CHCl_3$ only (no water, methanol, or DMF ion fragmentations can be detected from the MS results shown in Figure S3d), suggesting that solvent molecules in the tunnel were almost discharged in the pre-preparation evacuation process. For P123-Mn-MOF-74 and PVP-Mn-MOF-74, it is known from the preparation method that the mass loss can be ascribed to the removal of $CHCl_3$ and methanol. The second stage is in the vicinity of 317 °C and is caused by the partial collapse of the skeleton structure from the MS results of Figure S3d. The third stage appears above 535 °C, suggesting the complete collapse of the MOF-74 skeleton structure. Combined with TG and MS results, the activation conditions of the samples should be set as N_2 atmosphere, 200 °C for 3 h, and a heating rate of 2 °C/min.

2.2. The Low-Temperature SCR Performance

Low-temperature SCR catalytic performance was tested to investigate the effects of the surfactants P123 and PVP and ligand methyl functionalization on the catalytic performance of Mn-MOF-74 at low temperature. As shown in Figure 3, Mn-MOF-74 performed well with regard to low-temperature NH_3 -SCR activity, but the water resistance still needs further study. As the temperature increased, the NO conversion of all the samples exhibited a rising trend; when the temperature rose to 280 °C, the NO conversion of Mn-MOF-74- CH_3 reached a maximum of 93.2%. The NO conversion of P123-Mn-MOF-74 and PVP-Mn-MOF-74 reached maxima of 92.1% and 71.8% at 265 °C and 250 °C, respectively, and then decreased with the continuous increase in temperature, which was caused by the collapse of the skeletal structure. Compared with the low-temperature SCR catalytic performance curve of Mn-MOF-74, the performance order was Mn-MOF-74 > Mn-MOF-74- CH_3 > P123-Mn-MOF-74 > PVP-Mn-MOF-74. The surfactants P123 and PVP and the methyl ligands existing in the pores may even have been partially covered in the metal active center, hindering the approaches of reactant molecules and thus depressing the SCR catalytic performance.

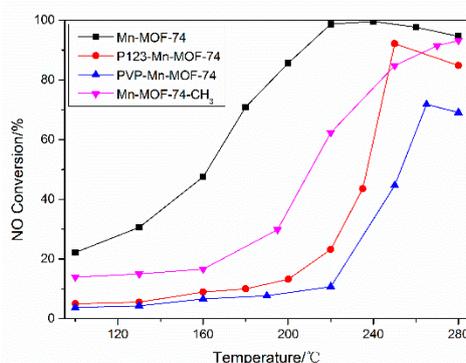


Figure 3. Low-temperature selective catalytic reduction (SCR) activities of P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74- CH_3 (gas flow rate: 100 mL/min; gas composition: NO 500 ppm, NH_3 500 ppm, O_2 5%, and Ar as balance gas).

2.3. Stability and Water Resistance Study

In this work, stability tests were carried out at temperatures corresponding to the maximum NO conversion of catalysts (MOF-74 240 °C, P123-Mn-MOF-74 250 °C, PVP-Mn-MOF-74 265 °C, and Mn-MOF-74-CH₃ 280 °C) for 12 h; the results are displayed in Figure 4. It was concluded that all the samples showed good stability at their own optimal temperature during the 12 h tests.

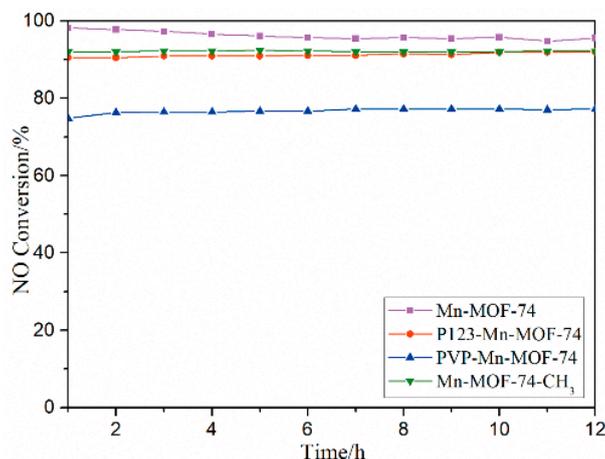


Figure 4. Stability test results of Mn-MOF-74, P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74-CH₃ under an SCR atmosphere at their own optimal conditions (gas flow rate: 100 mL/min; gas composition: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, H₂O (g) 5%, and Ar as balance gas).

To study the water resistance of the prepared samples, 5 vol.% H₂O was added into the feed gas and low-temperature catalytic activities were investigated (as shown in Figure 5). For a clearer explanation, the maximum NO conversion and the corresponding temperature, stability, and water resistance of Mn-MOF-74, P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74-CH₃ have been summarized in Table 1.

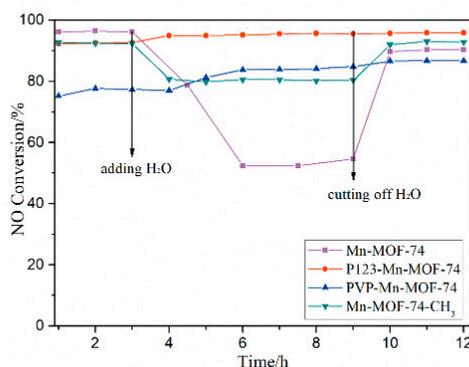


Figure 5. Stability test results of Mn-MOF-74, P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74-CH₃ under an SCR-H₂O atmosphere at their own optimal conditions (gas flow rate: 100 mL/min; gas composition: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, H₂O (g) 5%, and Ar as balance gas).

According to the results given in Figure 5 and Table 1, the NO conversion of Mn-MOF-74 decreased by 44% after adding H₂O. Combined with the SCR activity results, Mn-MOF-74 did show better catalytic activity, while the water resistance of it was very poor. The reason for this might have been that OH species of the dissolved H₂O were bonded to the exposed CUSs, thereby reducing the number of active sites and reducing the activity [21]. After modification, the NO conversion of 71.8% for PVP-Mn-MOF-74 and 81.2% for Mn-MOF-74-CH₃ can be observed to be higher than that of 55% for Mn-MOF-74 in the SCR-H₂O atmosphere, and then be recovered to the original level

when removing H₂O, suggesting that the water resistance of PVP-Mn-MOF-74 and Mn-MOF-74-CH₃ increased greatly. Notably, the NO conversion of P123-modified Mn-MOF-74 remained at 92.1% after the addition of 5 vol.% H₂O, which indicates that the introduction of P123 did enhance the water resistance of Mn-MOF-74.

Table 1. The effects of adding H₂O on the low-temperature SCR catalytic activities of Mn-MOF-74, P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74-CH₃.

Sample	Temperature (°C)	NO Conversion (%) (SCR)	Change in NO Conversion (%) (SCR and H ₂ O)
Mn-MOF-74	240	99.6	−44
P123-Mn-MOF-74	250	92.1	0
PVP-Mn-MOF-74	265	71.8	+4
Mn-MOF-74-CH ₃	280	93.2	−12

3. Materials and Methods

3.1. Materials

Manganese chloride (MnCl₂·4H₂O, purity ≥ 99%, Guangfu Fine Chemical Research Institute, Tianjin, China), 2,5-dihydroxyterephthalic acid (C₈O₆H₆, 98%, DHTP, Heowns Biochem LLC, Tianjin, China), (N, N-Dimethyl formamide (HCON(CH₃)₂, 99.5%, DMF, Jiangtian Chemical Technology Co., Ltd., Tianjin, China), ethanol (CH₃CH₂OH, ≥ 99.7%, Jiangtian Chemical Technology Co., Ltd., Tianjin, China), methanol (CH₃OH, ≥ 99.7%, Jiangtian Chemical Technology Co., Ltd., Tianjin, China), chloroform (CHCl₃, ≥ 99%, Jiangtian Chemical Technology Co., Ltd., Tianjin, China), polyvinylpyrrolidone ((C₆H₉NO)_n, Sigma-Aldrich, Shanghai, China), and polyethylene oxide-polypropylene-polyethylene oxide (PEO-PPO-PEP, Sigma-Aldrich, Shanghai, China) were used. The gas mixtures used in this work, including NO/Ar, NH₃/Ar, SO₂/Ar, and O₂/Ar, were supported by Beijing AP BAIF Gases Industry Co., Ltd. All the materials and gas mixtures were used without further processing unless noted.

3.2. Catalyst Preparation

According to the procedure described by Zhou et al. [22], Mn-MOF-74 was synthesized using a hydrothermal method. Briefly, 53 mL of DMF, 3.5 mL of ethanol, and 3.5 mL of H₂O were added to a 100 mL beaker and then the ligands DHTP was added into the above mixture. MnCl₂·4H₂O (0.4396 g, 2.22 mmol) was added into the solution, dispersed by ultrasound for 0.5 h, and then transferred to a Teflon-lined hydrothermal reactor. The hydrothermal reactor was placed in an oven at 135 °C for 24 h. The red-brown precipitates produced were cooled to room temperature, centrifuged, and washed three times with 60 mL of methanol. Finally, the product was dried and preserved for use.

The Mn-MOF-74 samples were pretreated for 3 h at a heating rate of 2 °C/min in a nitrogen atmosphere at 200 °C to remove the residual solvent. P123-Mn-MOF-74 and PVP-Mn-MOF-74 were synthesized by an impregnation method reported in the literature [23]. One gram of P123 or PVP was dissolved in solvent and then 0.2 g of pre-treated Mn-MOF-74 was added into the solution. The mixture was allowed to rest under static conditions at room temperature for 24 h, and then was washed with CHCl₃. The initial product was filtered and dried naturally.

Mn-MOF-74-CH₃ was synthesized by a post-synthesis modification method referred to in the synthesis method of CH₃-MOF-5 [24] but with some modification. Generally, a mixture of 15 mL CHCl₃ and 0.2 g pre-treated Mn-MOF-74 was placed in a Teflon-lined hydrothermal reactor and then placed in an oven at 65 °C for 12 h. The initial product was washed with CHCl₃ three times to remove unreacted species. The solids were dried at room temperature and stored in a desiccator for use.

3.3. Characterization

PXRD analysis was carried out to study the crystal phases. The instrument used in the PXRD tests was a D/MAX 2500 X-ray diffraction analyzer manufactured by RIGAKU. Analysis conditions were Cu target, scintillation counter tube (SC) detector, tube voltage 40 kV, tube current 200 mA, continuous scanning measurement, time constant 2, scan range 5–90°, and scan speed 5°/min. TG-MS was carried out under air conditions and a nitrogen atmosphere with a flow rate of 50 mL/min, and the temperature ranged from 30 °C to 700 °C with a heating rate of 10 °C/min.

In this study, the morphology of the catalysts was observed and analyzed using a Nanosem 430 scanning electron microscope manufactured by FEI. The instrument parameters were resolution 1 nm, acceleration voltage 0.1–30 kV, magnification 20–800,000, low vacuum, and low voltage deceleration mode. TEM was carried out on a Tecnai G2 F20 instrument made in America. The instrument parameters were accelerating voltage 200 kV, point resolution 0.248 nm, line resolution 0.102 nm, and magnification 1.05×10^6 times. FTIR was utilized to study the surface group of the catalysts on a Nicolet 6700 FTIR infrared spectrometer. The scans were taken 32 times and the scanning wave number was 400–4000 cm^{-1} with a resolution of 4 cm^{-1} .

3.4. Catalytic Activity

Low-temperature SCR catalytic performance of the as-prepared samples was tested in a fixed-bed reactor at atmosphere pressure. In a typical reaction test, 0.2 g of the samples and 0.4 g of quartz sand were loaded into the reactor tube. Before the activity test, the samples had to be pretreated under an N_2 atmosphere to remove the solvent and get activated. The pretreated conditions were as follows: 200 °C, 3 h, and heating rate 2 °C/min. After the pretreatment, the samples were tested for a temperature range of 80–280 °C under ambient conditions. The total flow rate of the feed gas was 100 mL/min, while the gas hourly space velocity (GHSV) was about 50,000 h^{-1} . The composition of the gas flow was as follows: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 5 vol.% H_2O (when used), and Ar as a balance gas.

The concentration of outlet NO and NO_2 were determined using KM9106 Quintox Kane International Limited, a flue gas analyzer. The concentrations of the products N_2 and N_2O were monitored by gas chromatography (Agilent GC-6820) at 30 °C when effluent gases passed through it. A 5 Å molecular sieve column and Porapak Q column were used, respectively. The calculation methods used were

$$X = \frac{[\text{NO}_x]_{in} - [\text{NO}_x]_{out}}{[\text{NO}_x]_{in}} \times 100\%$$

$$S = \frac{[\text{N}_2]_{out}}{[\text{N}_2]_{out} + [\text{N}_2\text{O}]_{out}} \times 100\%$$

In the formulas, X represents the conversion of NO_x , S represents the N_2 selectivity, $[\text{x}]$ represents the concentration of each gas, in represents the inlet gas, and out represents the outlet gas. In our work, the N_2 selectivity of our catalysts was 100%.

4. Conclusions

In this study, Mn-MOF-74 catalysts were modified by introducing surfactants P123 and PVP and by ligand methyl functionalization to enhance their water resistance. The structure and morphology of the samples were investigated by PXRD, FT-IR, SEM, TEM and TG-MA while low-temperature SCR performance was tested in a fix-bed reactor. It was concluded that the modified samples were successfully synthesized and that the water resistance of the samples was significantly enhanced after modification. Moreover, all the catalysts were able to remain stable for at least 12 h at their own optimal temperature in an SCR atmosphere. After the addition of 5% H_2O in the feed gas, the NO conversion of P123-Mn-MOF-74 remained at 92.1% at 250 °C while that of unmodified Mn-MOF-74 dropped by 44%. In summary, P123-Mn-MOF-74 has superior low temperature SCR activity, SCR stability, and

water resistance, and its NO conversion rate can be maintained above 90%, which proves it to be a potential low-temperature NH₃-SCR catalyst.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/12/1004/s1>, Figure S1: FT-IR spectra of P123/PVP-Mn-MOF-74 and Mn-MOF-74-CH₃ at (a) 4000~400 cm⁻¹ and (b) 4000~2500 cm⁻¹; Figure S2: SEM images of (a) Mn-MOF-74, (b) P123-Mn-MOF-74, (c) PVP-Mn-MOF-74, and (d) Mn-MOF-74-CH₃; Figure S3: TG curves of Mn-MOF-74, P123-Mn-MOF-74, PVP-Mn-MOF-74, and Mn-MOF-74-CH₃ under atmospheres of (a) air and (b) N₂. MS results of Mn-MOF-74-CH₃ under atmospheres of (c) air and (d) N₂.

Author Contributions: Conceptualization and methodology, S.W. and Q.G.; writing—original draft preparation, Q.W. and Y.N.; writing—review and editing, X.D. and Y.C.; supervision, H.J.; S.W., and Q.G. (these authors made equal contributions).

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Conflicts of Interest: The authors declare no conflict of interest.

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