AMMONIA ADSORPTION PERFORMANCE AND APPLICATION OF SSZ-13 ZEOLITE CATALYST AFTER ACID-BASE TREATMENT

Hongling YE[1]*, Lin WANG[2], Pengfei WANG[3]

A series of Cu/SSZ-13 SCR catalysts were prepared by acid-base treatment of SSZ-13 zeolite. The SCR reactivity, selectivity, ammonia adsorption performance and physical and chemical properties of different catalysts were studied. The results showed that the CHA structure of SSZ-13 was not destroyed after treatment with nitric acid, oxalic acid and phosphoric acid. The BET surface area of the catalyst was increased after acid-base treatment. Through comparative study, the nitric acid treatment can increase the B-acid sites of the catalyst then improve the ammonia adsorption performance of the catalyst. Meanwhile, the SCR reaction efficiency of SSZ-13 catalysts after treatment is unchanged, the selectivity of SSZ-13 catalysts after treatment is higher than the Cu/SSZ-13 comparison sample, and the ammonia adsorption capacity of SSZ-13 catalysts after treatment is optimal. The nitric acid-treated Cu/SSZ-13 is amplified and applied in the actual engine. The emission reduction effect is obvious, which is suitable for industrialization.

Keywords: SCR, SSZ-13, Ammonia adsorption, Diesel engine

1. Introduction

China has gradually tightened regulations on pollutant emission of heavy-duty diesel engines. The "Heavy-Duty Diesel Vehicle Pollutant Emission Limits and Measurement Methods (China Phase VI)" requires ammonia leakage of engines to be less than 10 ppm under the World Harmonized Steady-State Cycle (WHSC) and the World Harmonized Transient Cycle (WHTC), which puts forward higher requirements for ammonia storage of catalysts in Selective Catalytic Reduction (SCR) system [1]. At present, the commonly used SCR catalysts for diesel vehicles are vanadium-based catalysts. These catalysts have a narrow temperature window, poor low-temperature activity, and are toxic. However, given their mature technology and low cost, they are still the mainstream catalysts for National V heavy-duty vehicles [2-4]. National VI SCR catalysts need to possess good high temperature resistance, mainly using small-pore zeolites (SSZ-13, SAPO-34, Beta, ZSM-5, etc.) as direct carriers. Where, SSZ-13 zeolite catalysts have the advantages of good ammonia storage characteristics, wide NO_x temperature window, good low temperature activity, and strong resistance to high temperature aging [5-8]. Even after the application of SSZ-

[1] Bengbu University, Bengbu 233000, Anhui, China. e-mail: 4437506@qq.com
[2] Bengbu University, Bengbu 233000, Anhui, China.
[3] Bengbu University, Bengbu 233000, Anhui, China.

13 zeolite catalyst, serious ammonia leakage still exists under some severe working conditions, so the rear end of SCR still needs to be added with ammonia slip catalysts (ASC) to convert the leaked ammonia gas into nitrogen gas [9].

Methods to reduce ammonia emissions mainly include increasing ASC, modifying urea injection model or parameters, and SCR catalyst modification, etc. [9]. Most researchers solve the problem of ammonia gas escape by directly adding ASC, but ASC requires addition of precious metals, so the cost is high. Although there are some studies on ASCs with no or low precious metals, no mature cases of industrialization have been found. By modifying the urea injection model, it is possible to reduce the ammonia leakage amount, but reduced urea injection amount will also lower the NO_x conversion efficiency. If this method is used on the premise of guaranteeing NO_x conversion efficiency, there is a theoretical upper limit of ammonia leakage value, so excessive reduction of ammonia escape is impossible [10]. Acid treatment can enhance the ammonia adsorption capacity of zeolites [11-14]. The application of acid-treated SSZ-13 as SCR catalyst is expected to solve the problem of ammonia leakage without adding ASC, and the modification process is simple with low cost.

In this paper, according to the chemical properties of ammonia gas, a simple, low-cost and industrialized catalyst modification method is proposed for the Cu/SSZ-13 catalyst most commonly used in China VI diesel engines, which can improve the acid site of the catalyst without affecting the denitration performance and hydrothermal aging resistance of the catalyst itself.

2. Experimental Research

2.1 Catalyst Preparation

The main reagents include copper nitrate $Cu(NO3)_2$ (analytical grade, from Tianjin City Guang Fu Tech. Development Co., Ltd.), SSZ-13 (from a domestic zeolite manufacturer), phosphoric acid (85%, from Tianjin City Guang Fu Tech. Development Co., Ltd.), nitric acid (65 %~68%, from Aladdin), oxalic acid (analytical pure, from Tianjin City Guang Fu Tech. Development Co., Ltd.), sodium hydroxide (analytical pure, from Tianjin City Guang Fu Tech. Development Co., Ltd.).

For carrier pretreatment, 5g SSZ-13 zeolite was added to 60 mL prepared acid-base (phosphoric acid/nitric acid/oxalic acid/sodium hydroxide) solution with 5% mass fraction, soaked in ultrasonic for 10 min and filtered. The zeolite samples were repeatedly washed with deionized water to neutrality, dried at 110°C for 5 h, calcined at 550°C for 5h, and labeled with SSZ-13 (P/N/C/NaOH).

0.36g copper nitrate was dissolved in 80 mL deionized water. After the dissolution was over, 4.85g SSZ-13 (P/N/C/NaOH) was added, evaporated to dryness in a water bath at 80°C, dried at 110 °C for 5 h, and calcined at 550°C for 5 h to prepare Cu/SSZ-13 (P/N/C/NaOH), as shown in Table 1.

Coated catalyst preparation: Referring to the SCR catalyst engineering method of a domestic enterprise, the self-made catalyst was subjected to engineering amplification to implement engine test research of the overall sample.

Table 1

Labels and names of different samples

No.	Sample name	Cu content/% (w)	Processing time (h)	Acid (base) concentration and type
1#	Cu/SSZ-13	3	0	
2#	Cu/SSZ-13(P)	3	2	5% phosphoric acid
3#	Cu/ SSZ-13(N)	3	2	5% nitric acid
4#	Cu/SSZ-13(C)	3	2	5% oxalic acid
5#	Cu/SSZ-13(Na)	3	2	5% sodium hydroxide

2.2 Catalyst Characterization

The physical adsorption of the catalyst was carried out using the ASAP 2010 adsorption analyzer from Micromeritics Instrument Corp, and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) test method.

The NH_3 chemisorption performance of the catalyst was measured using an AutoChem II 2920 chemisorption instrument from Micromeritics Instrument Corp, the pretreatment temperature was 400°C, and ammonia gas adsorption started after the temperature was lowered to 120°C, which lasted 30 min to eliminate the effect of physical adsorption. The signal was received by the Thermal Conductivity Detector (TCD) with the temperature increased to 800°C at a rate of 10 °C/min.

The crystal morphology of the catalysts was analyzed using a D8 ADVANCE X-ray diffractometer, the scanning angle 2θ ranged from 5° to 50°, the scanning speed was 4°/min, and the step size was 0.02°.

The surface morphology of the catalysts was examined using a Shimadzu SS-50 scanning electron microscope from Shimadzu Corporation, Japan, with a magnification of 20~200,000, a secondary electron image resolution of 3.5 nm, and an accelerating voltage of 0.5~30 kV.

2.3 Catalyst Testing System

The performance test of the SCR catalyst powder samples was carried out in the self-made reaction device shown in Fig. 1, and the reaction temperature was 100~600°C. The exhaust gas components were analyzed using a Nicolet iS 10 Fourier transform infrared spectrometer from Thermo Scientific, the United States. The composition of the simulated flue gas is as follows: NH_3 concentration 500 ppm, NO concentration 500 ppm, O_2 volume fraction 5%, with N_2 as balance gas. Space velocity was 30,000 h^{-1}, and the total gas flow was 1,000 mL/min.

The ammonia adsorption saturation test was carried out under simulated flue gas conditions. The Cu/SSZ-13 zeolite catalysts prepared by different acid-base treatments were subjected to ammonia adsorption under the reaction

atmosphere at 25°C. In order to complete the adsorption test as soon as possible, the space velocity was adjusted to 120,000 h^{-1}. After the reaction atmosphere was introduced, the valve was rotated to turn the gas path in the direction of the catalyst bed after the reaction atmosphere was balanced. The total gas flow was 1,000 mL/min, and one point was recorded once every 3 min.

The hydrothermal aging test conditions were as follows: temperature 650°C, water vapor content 10%, air as balance gas, 24 h aging duration, and space velocity at 30,000 h^{-1}. The catalytic reactions equations are as follows.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad \text{standard reaction} \quad (1)$$

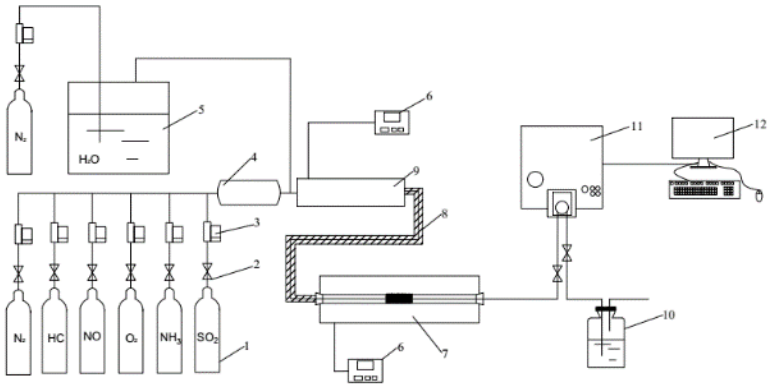
$$4NH_3 + 2NO + 2O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$

$$NO_2 + NO + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad \text{rapid reaction} \quad (3)$$

The catalyst conversion efficiency and selectivity are calculated according to the following formula:

$$x_{NO} = \frac{n_{NO_{in}} - n_{NO_{out}}}{n_{NO_{in}}} \times 100\% \quad (4)$$

$$s_{N_2} = \frac{n_{NH_{3in}} - n_{NH_{3out}} + n_{NO_{in}} - n_{NO_{out}} - n_{NO_{2out}} - 2n_{N_2O_{out}}}{n_{NH_{3in}} - n_{NH_{3out}} + n_{NO_{in}} - n_{NO_{out}}} \times 100\% \quad (5)$$



1. Gas; 2. Pressure reducing valve; 3. Mass flow meter; 4. Gas mixer; 5. Steam generator; 6. Temperature controller; 7. Reactor; 8. Heating belt; 9. Preheater; 10. Exhaust gas treatment device; 11. Infrared analyzer; 12. Computer

Fig. 1 Catalyst activity evaluation system

2.4 Engine Bench Test System

HFC4DAI-2D type four-cylinder in-line diesel engine from Anhui Jianghuai Automobile Group Corp., Ltd. was selected as the test object. The test engine parameters are shown in Table 2.

Table 2

Test engine parameters

Parameter	Value	Parameter	Value
Displacement /L	2.771	Rated speed /r·min^{-1}	3200
Maximum output power /kW	88	Maximum torque /N·m	285

3. Results and discussion

3.1 Effect of Acid-Base Treatment on Reaction Efficiency

The NO conversion efficiencies of Cu/SSZ-13 zeolite catalysts with different acid and base treatments are shown in Fig. 2. The untreated Cu/SSZ-13 samples and the Cu/SSZ-13(N) samples prepared after nitric acid treatment have similar activity window with NO conversion efficiency in NH_3-SCR (the temperature range where NO conversion efficiency exceeds 80%). Other acid-base treated samples including Cu/SSZ-13(P), Cu/SSZ-13(C) and Cu/SSZ-13(Na) show varying degrees of reduction in NO conversion efficiency, and Cu/SSZ-13 (Na) has the most reduction in conversion efficiency, with no obvious temperature window. The T_{50} of the Cu/SSZ-13 catalyst (the temperature at which the NO conversion efficiency reaches 50%) is 155℃, T_{90} (the temperature at which the NO conversion efficiency reaches 90%) is 185℃, and the T_{50} of the Cu/SSZ-13(N) catalyst is 160℃, T_{90} is 190℃. The overall conversion efficiency of the samples prepared after nitric acid treatment is not much different from that of the original sample.

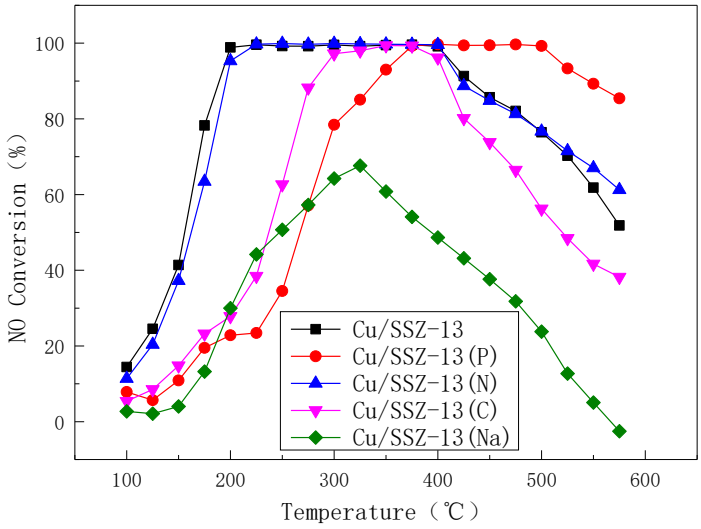


Fig. 2 NO conversion efficiency of Cu/SSZ-13 zeolite catalysts with different acid-base treatments

The N_2 conversion efficiencies of Cu/SSZ-13 zeolite catalysts with different acid-base treatments are shown in Fig. 3: when the temperature is below

400°C, the N_2 selectivity of Cu/SSZ-13(P) is mostly smaller than 95%, the conversion efficiency at 325°C and 400°C is lower than 85%, and the N_2 selectivity of Cu/SSZ-13(Na), Cu/SSZ-13(C), Cu/SSZ-13(N) and Cu/SSZ-13 catalysts are above 95%. The N_2 selectivity of the three acid-treated samples is improved compared with that of Cu/SSZ-13. When the temperature exceeds 400°C, the N_2 selectivity of Cu/SSZ-13(Na) and Cu/SSZ-13 (C) presents an obvious downward trend. The N_2 selectivity of Cu/SSZ-13(N) remains above 95% in the whole temperature range, which is superior to that of untreated Cu/SSZ-13 catalyst.

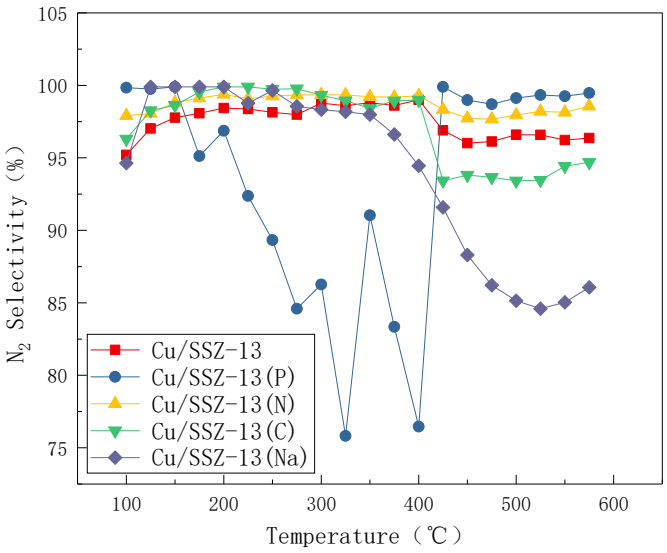


Fig. 3 N_2 selectivity of Cu/SSZ-13 zeolite catalysts with different acid-bases treatments

3.2 Effect of Acid-Base Treatment on Ammonia Adsorption Performance

3.2.1 Ammonia adsorption capacity at room temperature

Under the reaction atmosphere, the room temperature ammonia adsorption capacity of Cu/SSZ-13 zeolite catalysts with different acid-alkali treatments is shown in Fig. 4. The volume concentration of NH_3 in the reaction atmosphere is 500 ppm. The reaction gas was transferred to the catalyst bed for adsorption test after 20 min. In the ammonia adsorption process of Cu/SSZ-13(Na) samples, the NH_3 outlet concentration increases the fastest, indicating that its NH_3 adsorption saturation rate is the highest, and the adsorption is basically saturated at 90 min. The room temperature ammonia adsorption capacity of all samples Cu/SSZ-13(P), Cu/SSZ-13(N), and Cu/SSZ-13(C) is improved after different acid treatments, indicating that acid treatment can significantly improve NH_3 adsorption capacity of SSZ-13 zeolite. The test results in Section 3.1 of this paper show that the SCR

reaction activity is not significantly improved, indicating that acid treatment can improve ammonia adsorption capacity of the catalyst, but the improvement of the SCR reaction efficiency requires the synergistic effect of multiple factors. After 120 min, the volume fraction of NH_3 in the outlet gas of the Cu/SSZ-13(N) sample was only 430 ppm, and it would take a long time before the adsorption saturation, indicating that the Cu/SSZ-13(N) sample had the optimal ammonia adsorption capacity.

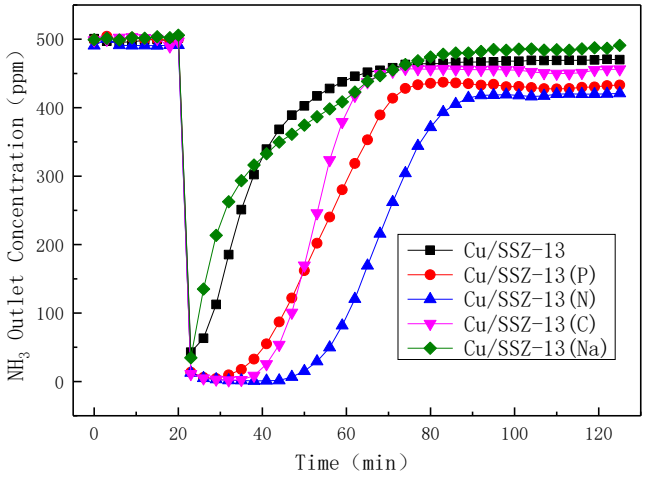


Fig. 4 Room temperature ammonia adsorption capacity of Cu/SSZ-13 zeolite catalysts with different acid-base treatments

3.2.2 NH_3 temperature programmed desorption

The total desorption peak area in NH_3 Temperature Programmed Desorption (TPD) represents the adsorption capacity of NH_3. After acid treatment, Cu/SSZ-13(P), Cu/SSZ-13(N), Cu/SSZ-13(C) have significantly larger peak area than Cu/SSZ-13 and Cu/SSZ-13(Na), as shown in Fig. 5. This is consistent with the findings of ammonia adsorption experiment under the reaction gas condition at room temperature.

The Cu/SSZ-13 catalyst has three main desorption peaks [15-17]: the desorption peak at 232°C is attributed to the weak adsorption of ammonia gas, mainly the desorption of ammonia gas adsorbed on the L acid site. The desorption peak at 401°C is attributed to the desorption of NH_3 adsorbed by active Cu^{2+}. The desorption peak at 530℃ is attributed to the desorption of NH_3 adsorbed on the acid site of the strong acid site B.

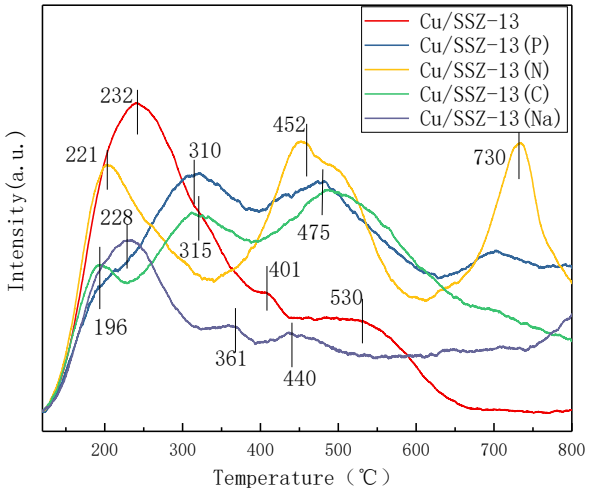


Fig. 5 NH_3-TPD results of Cu/SSZ-13 zeolite catalysts with different acid-alkali treatments

The low-temperature desorption peaks (100-240℃) of the zeolite samples Cu/SSZ-13(P), Cu/SSZ-13(N), and Cu/SSZ-13(C) prepared after acid treatment are significantly reduced. In the process of acid treatment, both skeleton aluminum and non-framework aluminum fell off to different degrees. Non-skeleton aluminum mainly concerns L acid site, and the reduction of extra-skeleton aluminum leads to a corresponding decrease in L acidity [18]. Therefore, all the desorption peaks of L acid in the three acid-treated samples shift to the low temperature section, as shown in Fig. 6. The medium and high temperature desorption peaks of Cu/SSZ-13(P) and Cu/SSZ-13(C) shift to about 310°C in the low temperature section, and the high temperature desorption peaks shift to 475°C in the low temperature section, but the overall peak intensity increases and the strong acid site is weakened but increased, so the ammonia adsorption capacity is still strong. The acid site weakening of Cu/SSZ-13(P) also relates to the incomplete decomposition of phosphoric acid, which is a result of phosphate attachment. During the acid treatment, a certain amount of H^+ was mixed into the framework or the amorphous silicon-alumina compound. H^+ itself can provide strong acid sites, so there are more strong acid sites after acid treatment. The strong acid peaks of Cu/SSZ-13(N) merged into one peak at around 452℃, where the peak intensity was the strongest. A stronger peak appeared at 730℃. In the ammonia adsorption test of Cu/SSZ-13(N) at room temperature, the gas adsorption capacity was also the strongest.

Compared with Cu/SSZ-13 sample, all the peaks of the Cu/SSZ-13(Na) sample shifted to the low temperature section, with B acid and L acid sites

reduced to varying degrees, demonstrating small peak area and weak ammonia adsorption capacity.

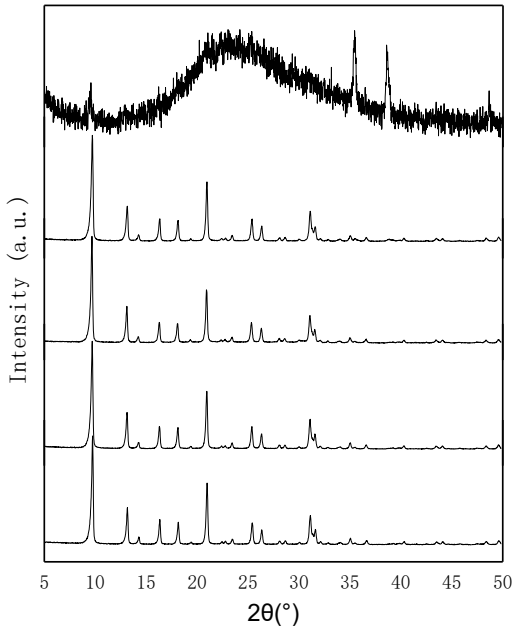


Fig. 6 XRD patterns of Cu/SSZ-13 zeolite catalysts with different acid-base treatments

3.3 Effect of Acid-Base Treatment on Crystal Structure

All the acid-treated zeolite catalysts exhibited characteristic peaks of SSZ-13, indicating that the acid treatment with a mass fraction of 5% would not destroy the zeolite framework structure. After the treatment with phosphoric acid, oxalic acid and nitric acid, the characteristic peak intensity of the zeolite decreased slightly, indicating that acid treatment reduces the zeolite crystallinity, a result of the removal of Al in the framework during acid treatment [19]. The zeolite catalyst prepared after NaOH treatment failed to display the characteristic peaks of SSZ-13, indicating that NaOH treatment destroys the SSZ-13 structure. Cu/SSZ-13(Na) is an amorphous Si-Al chemical compound, which is formed because strong alkali treatment leads to zeolite desiliconization, while the silicon molecule is located at the core position of the SSZ-13 framework structure. After desiliconization, the framework is difficult to reform, resulting in the destruction of the cage [20]. The acid site change of Cu/SSZ-13(Na) sample in NH_3-TPD results is also related to the structural damage.

3.4 Effect of Acid-Base Treatment on Physical Structure

The specific surface area changes of different samples are shown in Table 3. The specific surface area and total pore volume of Cu/SSZ-13(P) treated with phosphoric acid decrease. The main reason is that phosphoric acid cannot be

completely decomposed by heating, so that the generated phosphate is attached to the catalyst surface, causing some pores to be blocked. The specific surface area of nitric acid-treated Cu/SSZ-13(N) increases slightly, while the total pore volume and pore diameter are basically the same as those of the Cu/SSZ-13 sample. The specific surface area of oxalic acid-treated Cu/SSZ-13(C) increases, which is because new pores are formed during the oxalic acid decomposition, resulting in changes in pore volume and pore size. After nitric acid and oxalic acid treatment, the specific surface area of all the catalysts increases, because there may be some non-framework aluminum in the process of zeolite synthesis, and some non-framework aluminum may block the pores [21], while acid treatment can remove this part of non-framework aluminum, thus slightly increasing the specific surface area. The specific surface area of sodium hydroxide-treated Cu/SSZ-13(Na) decreases, with the total pore volume and pore size changed greatly.

Table 3

Results of specific surface area

Sample name	Specific surface area/$m^2 \cdot g^{-1}$	Total pore volume/$cm^3 \cdot g^{-1}$	Pore size/nm
Cu/SSZ-13	568.58	0.31	24.09
Cu/SSZ-13(P)	488.20	0.26	27.70
Cu/ SSZ-13(N)	572.57	0.30	24.23
Cu/SSZ-13(C)	617.58	0.29	23.72
Cu/SSZ-13(Na)	73.48	0.11	4.91

The adsorption and desorption isotherms of the original sample and the acid-treated sample SSZ-13 zeolite are shown in Fig. 7. P/PO>0.4, there is no obvious hysteresis loop, which is a typical I-type curve, indicating that the pore size distribution of the acid-treated zeolite is not greatly changed, and it is still the microporous structure. The adsorption and desorption curve of the sample treated with sodium hydroxide changes obviously. It can be determined that the sample pore structure is destroyed and the skeleton collapses, which is consistent with X-Ray Diffraction (XRD) results.

The pore sizes of Cu/SSZ-13, Cu/SSZ-13(P), Cu/SSZ-13(N), and Cu/SSZ-13(C) are shown in Fig. 8, which are all concentrated around 0.38 nm and display the same pore size distribution as SSZ-13 zeolites, indicating that the above-mentioned four samples have similar structures and are dominated by micropore structures. There were no 0.38 nm pores in the pore size distribution results of Cu/SSZ-13(Na), which can also indicate that its microporous structure is destroyed.

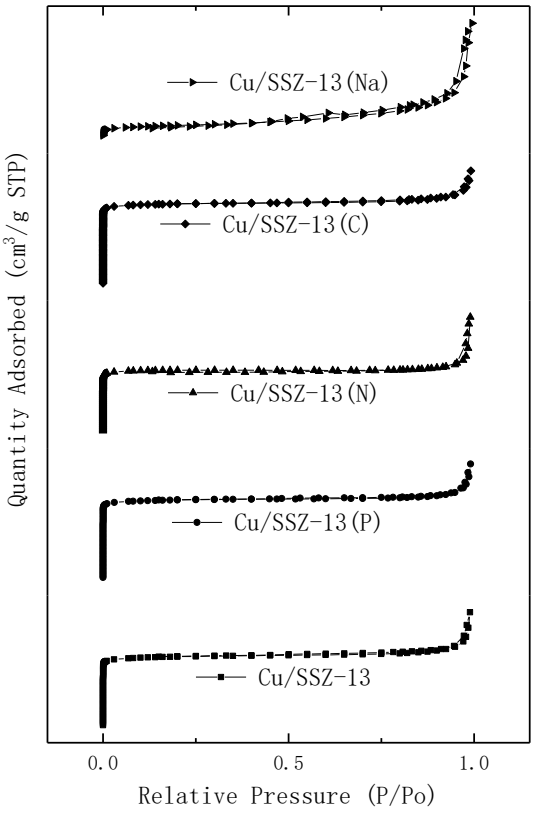


Fig. 7 Adsorption and desorption isothermal curves of Cu/SSZ-13 zeolite catalysts with different acid and base treatments

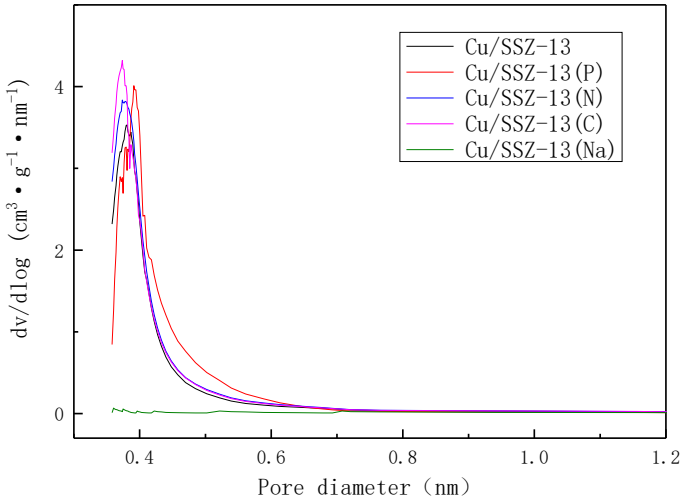


Fig. 8 Pore size distribution of Cu/SSZ-13 zeolite catalysts with different acid and alkali treatments

3.5 Effect of Acid-Base Treatment on Surface Morphology

The surface morphologies of Cu/SSZ-13, Cu/SSZ-13(N), and Cu/SSZ-13(C) samples are shown in Fig. 9.

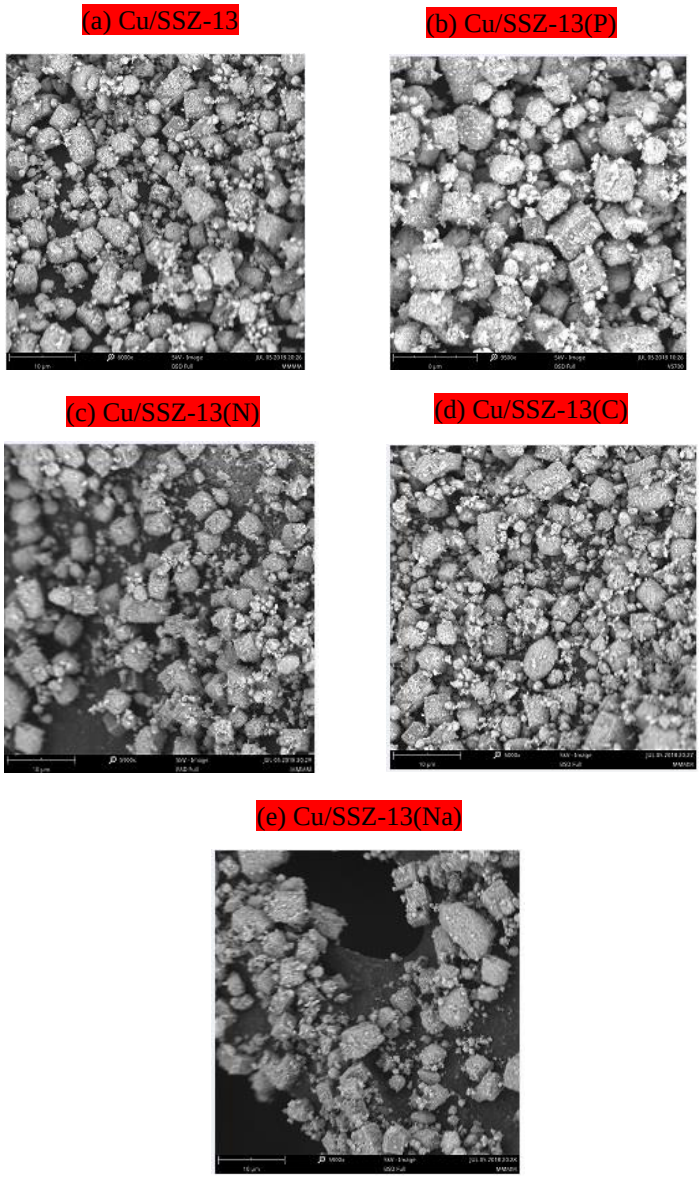


Fig. 9. Surface morphologies of Cu/SSZ-13 zeolite catalysts with different acid-base treatments

Small particles of SSZ-13 can be observed, and Cu/SSZ-13 (P) sample has obvious surface agglomeration with larger particles, which is caused by the incomplete decomposition of phosphoric acid. It is consistent with the detection result of the specific surface area. The surface morphology of the sample Cu/SSZ-13(Na) changes after NaOH treatment, and small particles of SSZ-13 can be seen. According to XRD and specific surface area detection results, this is related to the structural change of the Cu/SSZ-13(Na) sample.

3.6 Effect of Acid-Base Treatment on Hydrothermal Stability

The NOx conversion efficiencies of different samples after hydrothermal aging are shown in Fig. 10. Cu/SSZ-13, Cu/SSZ-13(P), Cu/SSZ-13(N), Cu/SSZ-13(C) have small catalyst activity changes after hydrothermal aging. From the results of XRD, it can be seen that the cage structure of the sample SSZ-13 has not changed, so the aged sample has similar NOx conversion rate as fresh sample [22-23]. Where, NOx conversion efficiency of Cu/SSZ-13(N) aged sample at low temperature section (100~200 ℃) is close to that of the Cu/SSZ-13 aged sample, while its high temperature activity is already higher compared to Cu/SSZ-13 aged sample. The nitric acid-treated Cu/SSZ-13(N) aged sample shows the least obvious decrease in activity and the best NOx conversion efficiency.

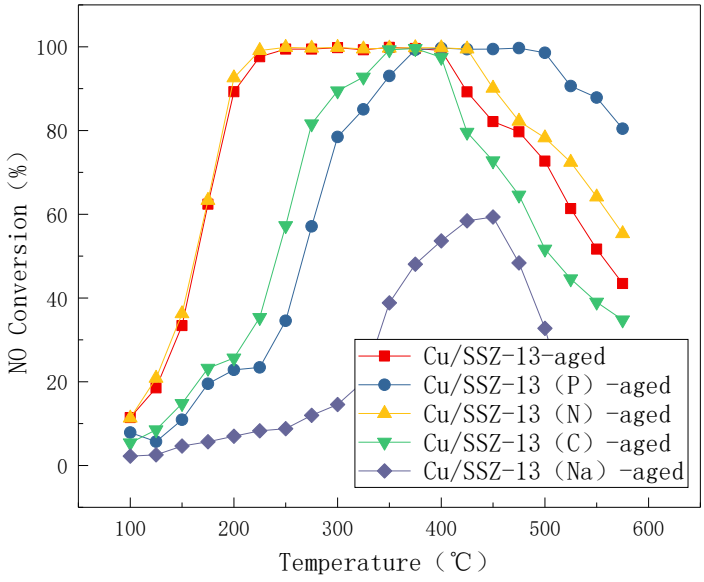


Fig. 10 NO_x conversion efficiency of different samples after hydrothermal aging

3.7 Bench Verification

The self-made Cu/SSZ-13(N) coated catalyst overall samples were selected to compare with foreign SCR catalyst samples and tested under European Steady-State Cycle(ESC) and European Transient Cycle(ETC), with the results shown in Table 4. The original National V SCR catalyst of the engine meets the requirements of National V. After replacement with foreign zeolite catalysts and self-made Cu/SSZ-13(N) catalysts, the NOx emissions under ESC and ETC cycles were significantly reduced, and the Cu/SSZ-13(N)-coated catalysts exhibited more obvious emission reduction effects.

Table 4

Test data of catalyst on engine bench

Sample	Cycle	NO_x emission /mg·kWh^{-1}	NH_3 peak-value leak/ppm	NH_3 average peak/ppm
The original National V SCR catalyst	ESC	1 127.1		
	ETC	1 987.2	138.3	16.2
Foreign SCR zeolite catalyst	ESC	272.1		
	ETC	402.9	78.1	5.6
Cu/SSZ-13(N) coated catalyst	ESC	238.2		
	ETC	382.8	60.3	4.2

4. Conclusion

a. After modification by treatment with 5% concentration of phosphoric acid, oxalic acid and nitric acid, the physical structure of Cu/SSZ-13 catalyst was well maintained, and the specific surface area was improved to some extent, indicating that acid treatment could dissolve non-framework aluminum and improve the physical properties of zeolites. Where, because the nitric acid treatment increases the strong acid site of the catalyst, the adsorption of ammonia gas is firmer, and the adsorption capacity of ammonia gas is significantly improved. After modification by alkali treatment, the crystal structure of Cu/SSZ-13 was destroyed, the microporous structure disappeared, and the ammonia adsorption capacity decreased, indicating that 5% NaOH treatment was not ideal for improving the ammonia adsorption performance of SSZ-13 catalyst.

b. The ammonia adsorption capacity of the SSZ-13 zeolite catalyst was enhanced after phosphoric acid treatment and oxalic acid treatment, but the SCR performance was reduced to varying degrees. There is no corresponding relationship between ammonia adsorption capacity and SCR reaction efficiency. Where, the Cu/SSZ-13(N) catalyst was optimal after nitric acid treatment, with the strongest ammonia adsorption capacity, SCR activity similar to that of Cu/SSZ-13, and better selectivity. SCR efficiency in the high temperature section after hydrothermal aging is higher compared with the conventional Cu/SSZ-13 catalyst. The temperature points at which the NO conversion efficiency reaches 50% and

90% are 160°C and 190°C, respectively, and further industrial research is recommended.

c. The Cu/SSZ-13(N) coated catalyst can significantly improve the pollutant emission level under both ESC cycle and ETC cycle. The Cu/SSZ-13(N)-coated catalyst has a simple preparation process and strong ammonia storage. The urea injection amount can be appropriately increased at low temperature to improve the low-temperature activity of the SCR system.

R E F E R E N C E S

[1] Guan B, Zhan R, Lin H, et al. Review of State of the Art Technologies of Selective Catalytic Reduction of NOx from Diesel Engine Exhaust. Applied Thermal Engineering, 2014, 66(1-2): 395-414.

[2] Praveena V, Martin L J M. A Review on Various After Treatment Techniques to Reduce NOx Emissions in a CI Engine. Journal of the Energy Institute, 2018, 91(5): 704-720.

[3] Yang B, Shen Y S, Shen S B, et al. Regeneration of the Deactivated TiO2-ZrO2-CeO2/ATS Catalyst for NH3-SCR of NOx in Glass Furnace. Journal of Rare Earths, 2013, 31(2): 130-136.

[4] Zhao X, Huang L, Li H R, et al. Highly Dispersed V2O5/TiO2 Modified with Transition Metals (Cu, Fe, Mn, Co) as Efficient Catalysts for the Selective Reduction of NO with NH3. Chinese Journal of Catalysis, 2015, 36(11): 1886-1899.

[5] Li Shuzhen, Zhang Xiaoge, Zhang Changming, et al. Fe-modified in-Situ Cu/SSZ-13 Catalyst for Denitrification of Diesel Vehicle Exhaust. Acta Scientiae Circumstantiae, 2020,40(1): 119-127.

[6] Han L N, Zhao X G, Yu H F, et al. Preparation of SSZ-13 Zeolites and Their NH3-Selective Catalytic Reduction Activity. Microporous and Mesoporous Materials,2018, 261(1): 126-136.

[7] Wang J, Shao L, Wang C, et al. Controllable Preparation of Various Crystal Size and Nature of Intra-Crystalline Diffusion in Cu/SSZ-13 NH3-SCR Catalysts. Journal of Catalysis, 2018, 367: 221-228.

[8] Gao F, Szanyi J, et al. On the Hydrothermal Stability of Cu/SSZ-13 SCR Catalysts. Applied Catalysis A: General, 2018, 560(25): 185-194.

[9] Wang Hao. Experimental Research on Structural Optimization and Emission Performance of SCR Aftertreatment System for Heavy-Duty Diesel Engines. Hefei University of Technology, 2021.

[10] Wang Guoyang. SCR System Modeling and Control Strategy Optimization of Heavy-Duty Diesel Vehicles. Shandong University, 2020.

[11] Yao Zhisong, Wu Xuehua, Xu Tianyu, et al. Oxalic Acid Modification of Nay Zeolite and Its Characterization. China Oils and Fats, 2021, 46(4): 148-152.

[12] Chu Ge, Liu Tonghui, Zhang Doudou, et al. Impact of Acidity and Pore Structure of Y-Type Zeolites on Isobutane/Butene Alkylation Reaction. Acta Petrolei Sinica(Petroleum Processing Section), 2021, 37(6): 1357-1365.

[13] Luo Yongna, Wang Yinye, Xiao Yanhua, et al. Study on the Adsorption of Ammonia in Indoor Air by X-Type Small-Grain Zeolites under Different Modification Conditions. Journal of Safety and Environment, 2013, 13(1): 54-57.

[14] Yao Keru, Shao Gaosong, Li Jianhua, et al. Study on HX Zeolite Modification and Its Ammonia Adsorption Performance. Journal of the Armed Police Academy, 2015, 31(10): 5-8.

[15] Luo J Y, Kamasamudram K, Currier N, et al. NH3-TPD Methodology for Quantifying Hydrothermal Aging of Cu/SSZ-13 SCR Catalysts. Chemical Engineering Science, 2018, 190(23): 60-67.
[16] Zhao Z C, Yu R, Zhao R R, et al. Cu-Exchanged Al-Rich SSZ-13 Zeolite from Organotemplate-Free Synthesis as NH3-SCR Catalyst: Effects of Na+ Ions on the Activity and Hydrothermal Stability. Applied Catalysis B: Environmental, 2017, 217(15): 421-428.
[17] Xie K P, Leistner K, Wijayantia K, et al. Influence of Phosphorus on Cu-SSZ-13 for Selective Catalytic Reduction of NOx by Ammonia. Catalysis Today, 2017, 297(15): 46-52.
[18] Zhang Chuanchuan, Wang Qingfa. Influence of Acid Treatment on the Selective Ring Opening of Dcalin over Beta Zeolite. Chemical Industry and Engineering, 2017, 34(2): 16-20.
[19] Lv Jiangjiang, Huang Xingliang, Zhao Leilei, et al. Effects of Acid-Base Treatment on Physicochemical Properties and Reactivity of ZSM-5 Zeolites. Journal of Fuel Chemistry and Technology, 2016, 44(6): 732-737.
[20] Gao F, Washton N M, Wang Y L, et al. Effects of Si/Al Ratio on Cu/SSZ-13 NH3-SCR Catalysts: Implications for the Active Cu Species and the Roles of Brønsted Acidity. Journal of Catalysis, 2015, 331: 25-38.
[21] Chang Wei. Effects of Different Modification Methods on the Structure and Acidity of Y-type Zeolites. Chemical Engineering Design Communications, 2018, 44(3): 108.
[22] Xie K P, Woo J, Bernin D, et al. Insights into Hydrothermal Aging of Phosphorus-Poisoned Cu-SSZ-13 for NH3-SCR. Applied Catalysis B: Environmental, 2019, 241: 205-216.
[23] Leistner K, Mihai O, Wijayanti K, et al. Comparison of Cu/BEA, Cu/SSZ-13 and Cu/SAPO-34 for Ammonia-SCR Reactions. Catalysis Today, 2015, 258: 49-55.