

## NO Adsorption on Zeolites and Active Carbon toward the Application for the Treatment of Highly Concentrated NO<sub>x</sub> in Industry

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### Abstract

The development of the economy and industry is accompanied by the emission of a large amount of exhaust gases such as NO, NO<sub>2</sub>, and N<sub>2</sub>O, which have a negative impact on the environment. In the study, the NO adsorption on zeolites and activated carbon was examined and compared. The adsorbents were also characterized using N<sub>2</sub> physical adsorption, NO temperature-programmed desorption, Scanning Electron Microscopy, and Energy-Dispersive Spectroscopy to expose specific surface area, adsorption ability, material morphology, and elemental content of the samples. The results showed that the NO adsorption efficiency on zeolite samples was superior to that of activated carbon due to the larger surface area and higher metal cation content, leading to their higher adsorption capacity due to the chemical adsorption at these metal cation sites. The modification of the adsorbent by adding Fe<sup>2+</sup> on Zeolite ZX5 has enhanced the active sites that are beneficial for the NO adsorption process, helping to improve the NO adsorption capacity compared to the original sample.

Keywords: activated carbon, adsorption, zeolite, NO, NO<sub>x</sub>.

### 1. Introduction

The era of industrialization and modernization has led to the rapid development of industries and population growth, contributing to economic development. However, along with these benefits, there are environmental consequences, especially air pollution, which harms human health and the living environment of animals and plants. Therefore, the problem of environmental pollution in general and air pollution in particular is one of the urgent global concerns today. Notable effects of NO<sub>x</sub> are the formation of acid rain, photochemical smog, ozone depletion, and fog [1, 2].

Recently, research efforts have been continuously carried out to meet the requirements of reducing NO<sub>x</sub> emissions with high efficiency in both mobile and stationary sources, in which post combustion treatment methods are widely applied. There are methods for treating NO<sub>x</sub> formed after combustion reactions, including adsorption, absorption, desorption, thermal, and chemical treatment. A combination of methods can be used to treat NO<sub>x</sub> thoroughly. Alternatively, the methods can be categorized into wet and dry processes based on the reaction environment. The dry method is further subdivided into those that employ a catalyst and those that do not [3]. In the non-catalytic process, the Selective Non-Catalytic Reduction (SNCR) method uses high temperatures (900-1000 °C) to reduce NO<sub>x</sub> in the presence of a reducing agent such as ammonia (NH<sub>3</sub>) or

urea (CO(NH<sub>2</sub>)<sub>2</sub>). This method is highly efficient but does not make sense thermodynamically and economically. For the catalytic process, it can be divided into four main directions: (1) Direct NO<sub>x</sub> decomposition; (2) Three Way Catalyst - TWC; (3) Selective reduction using hydrocarbon catalyst (HC - SCR); (4) Ammonia Selective Catalytic (NH<sub>3</sub> - SCR) [4, 5].

When the emission sources possess not too high NO<sub>x</sub> concentrations, such as the exhaust gases from vehicles and thermal power plants..., the NO<sub>x</sub> treatment method by selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) with NH<sub>3</sub> is still the optimal choice due to its high efficiency and reasonable cost. However, for factories with high NO<sub>x</sub> emissions, such as chemical fertilizer and explosives factories, selective catalytic reduction (SCR) will not be highly effective, causing a waste of NO<sub>x</sub> resources. Therefore, the adsorption method can be applied. The amount of adsorbed NO<sub>x</sub> can be recovered by the desorption at high temperatures afterward. The high recovered NO<sub>x</sub> concentration could be used for the nitric acid production process to serve many different needs in the industry. The adsorption process is carried out on an adsorption system using solid adsorbents. Exhaust fans collect the exhaust gas from the factory, which is then pushed by the fan system into the absorption columns with solid adsorbent materials. The adsorbed gas is then

desorbed by raising the temperature and using an inert gas flow to separate it from the adsorbent.

Solid materials selected as adsorbents must have outstanding characteristics such as a large specific surface area, capillaries suitable for the adsorbed substance, selective adsorption capacity, and easy desorption and reuse. Typical materials include activated carbon, zeolite, and MOF (Metal-organic Frameworks). Activated carbon is often activated under high temperatures in an anaerobic environment to create a porous structure, increasing the contact surface area for adsorption or chemical reactions [6]. In the study of Mei-Ling Fang *et al.* (2019), a mechanism for NO<sub>2</sub> adsorption onto activated carbon was proposed [7]: NO<sub>2</sub> can be directly adsorbed/desorbed by the “-C\*” functional group, forming an unstable -C(ONO) that tends to decompose and release a NO molecule and form a -C(O) group. The -C(O) functional group can bond with two NO<sub>2</sub> and temporarily form two -2C(ONO<sub>2</sub>) groups. Next, the C(ONO<sub>2</sub>) groups can react with the excess NO<sub>2</sub> molecule and form a more stable functional group -C(ONO<sub>3</sub>). On the other hand, two adjacent -C(NO<sub>2</sub>) groups can be combined and converted to a stable -C<sub>2</sub>(ONO<sub>2</sub>), and a NO molecule will escape from the AC surface. Finally, C<sub>2</sub>(ONO<sub>2</sub>) can be decomposed and form -C(O) and NO when the carbon is thermally regenerated. Here we use -C\* for active site on the carbon surface, and -C(O) for oxygenated carbon surface.

Therefore, zeolites have high adsorption and selectivity properties. Molecules that are significantly bigger than the pore size are pushed out and not adsorbed on zeolites [8, 9]. Zeolites are formed based on the basic MO<sub>4</sub> structural units of silica tetrahedra [SiO<sub>4</sub>]<sup>4-</sup> and alumina tetrahedra [AlO<sub>4</sub>]<sup>5-</sup> linked together through common oxygen vertices. The primary structural units are the same in all types of zeolites (The center is silicon or aluminum, and the vertex is oxygen). Each tetrahedron is linked to the remaining tetrahedrons through the oxygen atom at the vertex of each tetrahedron, forming -Si-O-Si or -Si-O-Al- bonds [10]. In the study of E. P. Hessou and colleagues (2018), an adsorption mechanism based on ion exchange interactions between NO<sub>x</sub> molecules and zeolite was proposed. NO is adsorbed through the primary interaction shown by the compensating cation Mn<sup>+</sup> bonded to nitrogen atoms. The interaction energy between NO and a proton in this zeolite structure is about -25 kJ/mol [7]. The NO<sub>2</sub> molecule has the exact mechanism as NO, adsorbing through nitrogen and a secondary interaction created by one of the two oxygen atoms with an energy level of -30 kJ/mol.

In this work, we aimed to compare the NO adsorption capacity of zeolite samples with that of the activated carbon sample. In addition, the pore size of the materials was determined by N<sub>2</sub> physical adsorption methods to evaluate their effects on the adsorption capacity. To improve the adsorption performance of

zeolites, Fe<sup>2+</sup>, which is considered to have good NO adsorption affinity in many studies [10], has been impregnated on zeolites.

## 2. Experiment

### 2.1. Materials

Zeolites were prepared previously in the laboratory. Different samples with the main composition of zeolite 13X mixed with different binders (boehmite or silica gel and other minor binders) to form different pellet shapes are symbolized as ZX5, 13X, ZX31 and ZX6. Activated carbon (AC) in pellet form was commercially purchased in Vietnam. Pictures of the samples are shown in Fig. 1.

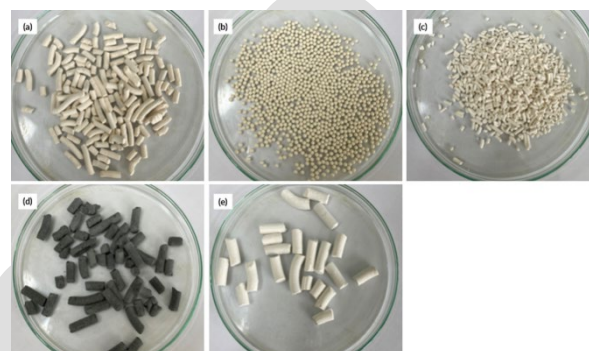


Fig. 1. Original shape of adsorbent materials: a) Zeolite ZX5 (zeolite 13X+ 15% boehmite, pellets, 4 mm diameter, 0.6 - 1.2 cm length, calcination temperature: 610 °C); b) Zeolite 13X (zeolite 13X, sphere, 2 mm diameter, calcination temperature 400 °C); c) Zeolite ZX31 (zeolite 13X + 25% boehmite, pillars, 2 mm diameter, 0.25 - 0.6 cm length, calcination temperature 550 °C); d) Activated carbon (pellets, 5 mm diameter, 0.7 - 1.2 cm length); e) Zeolite ZX6 (zeolite 13X + 15% silica gel, pellets, 6mm diameter, 0.9 - 2 cm length, calcination temperature: 610 °C)

Preparation of Fe<sup>2+</sup> impregnation sample on ZX5 (ZX5.Fe<sup>2+</sup>): Apparently, 0.2744 g of FeSO<sub>4</sub>·7H<sub>2</sub>O was dissolved in 50 mL of distilled water for 15 minutes. Then, 2.5 g of ZX5 was added to the above solution and stirred with a magnetic stirrer at 65-70 °C for 12 hours. This impregnation process was carried out under two conditions: maintaining stirring in an air environment or a flow of N<sub>2</sub> gas through the system. The sample was dried overnight (about 12 hours) at 90-100 °C in an air environment or a flow of N<sub>2</sub> gas. The composite samples in Air and N<sub>2</sub> were denoted Air/ZX5.Fe<sup>2+</sup>; N<sub>2</sub>/ZX5.Fe<sup>2+</sup>, respectively.

### 2.2. Characterization of the Materials

Emission Scanning Electron Microscope (SEM), Elemental mapping, and Energy-Dispersive Spectroscopy (EDS) measurement were performed on a JEOL JCM-7000 (Japan) integrated with an X-ray energy dispersive spectrometer (EDS) at the GeViCat Center, Hanoi University of Science and Technology. NO temperature programmed desorption (NO-TPD) was measured as follows: 0.15 (g) of a sample was put

directly into the analysis tube, which was then placed in the measuring device. First, the sample was pretreated by introducing an inert Helium gas flow at a rate of 30 mL/min from room temperature to 300 °C, the heating rate of 3 °C/min, and holding for 30 minutes to remove water and volatile substances in the sample. Then, the sample was cooled to 50 °C. After the sample had been surface cleaned and the sample temperature cooled to 50 °C, then 5% NO/He flow with a flow rate of 30 mL/min was introduced into the sample tube to carry out the NO adsorption process for 60 minutes. The samples were heated in a He gas stream at a 30 mL/min flow rate from 50 to 600 °C at a heating rate of 10 °C/min and held at 600 °C for 30 min. The gas stream from the device was passed through a mass spectrometer. The samples were measured on an AutoChem II 2920 V5.02 combined with a Cirrus 2-MKS spectrometer at the GeViCat Center, Hanoi University of Science and Technology. The N<sub>2</sub> adsorption-desorption (BET) method determined the materials' specific surface area. This method was performed on a Micromeritics Gemini VII 2390 (USA). The sample was vacuum treated at 150 °C for 1 hour and increased to 300 °C for 1 hour before measurement. The sample was then cooled to room temperature, pressure equilibrated with 99.999% N<sub>2</sub>, and weighed to re-determine the sample mass. The sample was introduced into the N<sub>2</sub> adsorption apparatus at -196 °C (77 K), with an N<sub>2</sub> gas flow rate of 25 mL/min.

### 2.3. Measurement of Adsorption Capacity

The sample was tested according to the scheme in Fig. 2. The initial sample was pretreated to remove water vapor and absorbed gases in the sample. Briefly, about 0.25 grams of adsorbent material was put it into the reaction column fixed by glass wool. Then, the sample was heated to 150 °C at a rate of 5 °C/min. Simultaneously, a 99.999% Ar was purged at a flow rate of 60 mL/min through the tube containing the adsorbent material to remove unwanted impurities in the material and maintain the system's temperature at 150 °C for 1 hour. After that, it was cooled down to room temperature.

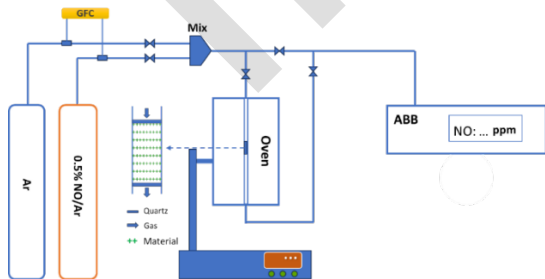


Fig. 2. Diagram of NO gas adsorption and desorption system

*Adsorption process:* 0.5% NO/Ar gas mixture was purged through the tube containing the treated material at a flow rate of 20.5 mL/min. The output gas (NO) was

detected by a UV-multi-gas sensor detector (ABB gas Analyzer models AO-2020, Limas 21HW, Mannheim, Germany), and the concentration values were displayed and recorded every 15 seconds until the gas concentration did not change.

*Desorption process:* the tested sample was heated to 200 °C at a rate of 5 °C/min under Ar flow at a 20.5 mL/min. The output gas (NO) was detected by a UV-multi-gas sensor detector (ABB gas Analyzer models AO-2020, Limas 21HW, Mannheim, Germany). NO concentration is measured and recorded every 15 seconds until the gas concentration does not change.

Adsorbed Quantity ( $A_{ads}$ ) was calculated as:

$$A_{ads} = \frac{Q_{out} \times S_{ads} \times 10^{-6}}{22,4 \times m}, \text{ mmol/g} \quad (1)$$

$$S_{ads} = \sum_0^t \left[ \frac{1}{2} \times (2C_{max} - (C_i + C_{i+1})) \times \Delta t \right] \quad (2)$$

Desorbed Quantity ( $A_{des}$ ) was calculated as:

$$A_{des} = \frac{Q_{out} \times S_{des} \times 10^{-6}}{22,4 \times m}, \text{ mmol/g} \quad (3)$$

$$S_{des} = \sum_0^t \left[ \frac{1}{2} \times (C_j + C_{j+1} - 2C_{min}) \times \Delta t \right] \quad (4)$$

where:

- $Q_{out}$  Flow rate (mL/min) of the 0.5% NO/Ar flow in the adsorption process and the Ar flow in the desorption process
- $S_{ads}$  Area formed by the vertical axis, horizontal axis, and adsorption process graph in adsorption process (ppm.min)
- $S_{des}$  Area formed by the vertical axis, horizontal axis, and desorption process graph in desorption process (ppm. min)
- $C_{max}$  Initial NO concentration (ppm)
- $C_{min}$  Final NO concentration of measurement (ppm)
- $C_i$  NO concentration at time  $i$  in the adsorption process (ppm)
- $C_j$  NO concentration at time  $j$  in the desorption process (ppm)
- $\Delta t$  Time between 2 measurements (minutes)
- $m$  Mass of catalyst (grams)

### 3. Results and Discussion

SEM images of adsorbents are presented in Fig. 3. The images show that the surface of the samples is uneven, in which the granular structures are interconnected to form large structures. These granular structures have heterogeneous sizes, shapes, and distributions. The 13X surface is smoother than the other samples, while the activated carbon (AC) sample shows a sizeable porous surface. The 13X sample also has smaller particles distributed on the surface. The ZX5 sample before and after  $\text{Fe}^{2+}$  impregnation ( $\text{N}_2/\text{ZX5.Fe}^{2+}$ ) does not have much change in shape and surface structure.

EPR spectrum for sample  $\text{ZX5.Fe}^{2+}$  was synthesized under two conditions, Air and  $\text{N}_2$ , denoted as  $\text{Air/ZX5.Fe}^{2+}$  and  $\text{N}_2/\text{ZX5.Fe}^{2+}$  was measured at room temperature in the measuring range 500 - 2500 G. A signal appears at  $B = 1570$  G. Substituting  $B$  into formula (5), the  $g$  factor can be calculated:

$$g = 0.7145 \times \frac{\nu}{B} = 0.7145 \times \frac{9400}{1570} = 4.28 \quad (5)$$

where:

- $g$  the electron's so-called  $g$ -factor
- $\nu$  microwave frequency (GHz)
- $B$  Magnetic field (Gauss)

The signal peak at  $g (=)$  equal to 4.28 is assigned to isolated  $\text{Fe}^{3+}$  ions located in octahedral/tetrahedral coordination sites with strong rhombohedral distortion, which have resonance lines at  $g (\approx)$  approximately to 4.26 and  $g (\approx)$  equal approximately to 2.0 [11]. Meanwhile,  $\text{Fe}^{2+}$  salt does not show a signal on EPR because it is a diamagnetic ion [12]. The  $\text{Fe}^{2+}$ -impregnated ZX5 sample synthesized in air conditions ( $\text{Air/ZX5.Fe}^{2+}$ ) shows a significant intensity peak at this position, indicating that there was a transformation from  $\text{Fe}^{2+}$  salt to  $\text{Fe}^{3+}$  during the synthesis process. At the same time, the  $\text{Fe}^{2+}$ -impregnated ZX5 sample synthesized in  $\text{N}_2$  conditions shows a much lower intensity peak than that of the above sample. Here, the synthesis in the absence of  $\text{O}_2$  helped to prevent the formation of  $\text{Fe}^{3+}$  better. Therefore, the sample synthesized under  $\text{N}_2$  conditions was chosen as the NO adsorbent.

Elemental mapping was applied to the zeolite samples to evaluate the elements' distribution on the material surface. The results in Fig. 4 show that the elements O, K, Na, Si, and Al, which are the main constituents of ZX5, were evenly distributed on the sample surface and in the shape of the grain structures. After impregnation with  $\text{Fe}^{2+}$ , the results showed that the appearance of the Fe element was evenly distributed on the surface. This result showed that the impregnation process successfully brought Fe to the ZX5 surface.

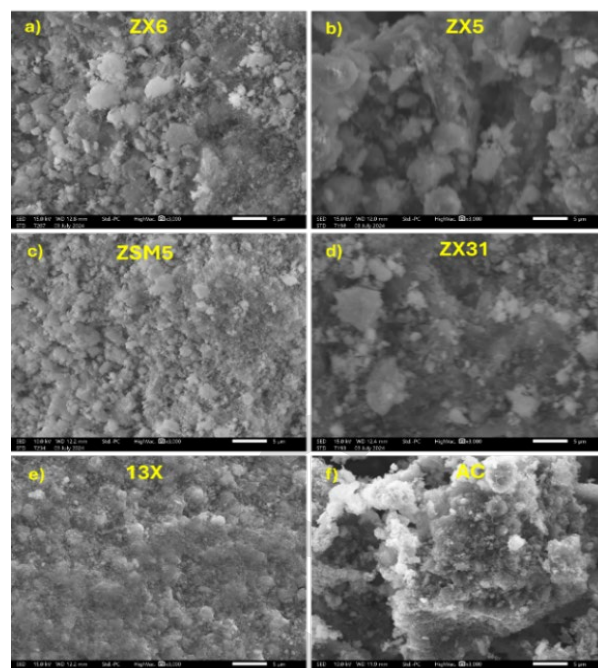


Fig. 3. SEM images of materials with different magnifications of 3000x a) ZX6; b) ZX5; c)  $\text{N}_2/\text{ZX5.Fe}^{2+}$ ; d) ZX31; e) 13X; f) AC

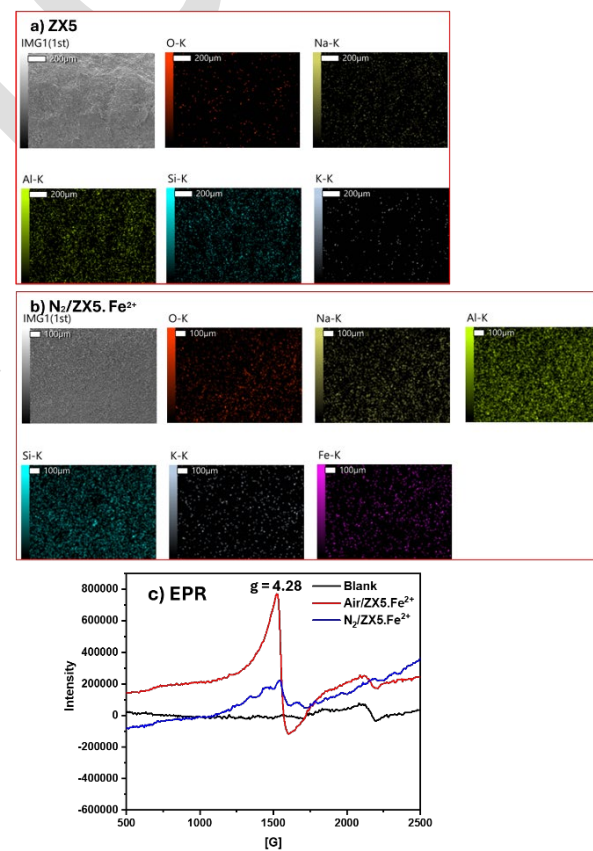


Fig. 4. Elemental mapping graphs of a) ZX5 and b)  $\text{N}_2/\text{ZX5.Fe}^{2+}$ , c) EPR of samples

Table 1. Element composition (from EDS) and surface area of the samples

Sample	Weight %		% Atom					Ratio Si/Al	$S_{BET}$ (m <sup>2</sup> /g)
	Fe	O	Si	Al	Na	K	Fe		
ZX6	0	55.6	15.2	18.5	9.9	-	-	0.8	60.8
13X	0	61.7	15.3	11.7	10.2	1.1	-	1.3	10.5
ZX31	0	54.8	12.6	27.3	6.8	0.3	-	0.3	150.7
ZX5	0	58.4	13.1	21.0	7.5	-	-	0.6	61.9
N <sub>2</sub> /ZX5.Fe <sup>2+</sup>	5.5	55.9	15.0	20.3	6.0	-	2.2	0.7	176.9
AC	0	-	-	-	-	-	-	-	18.0

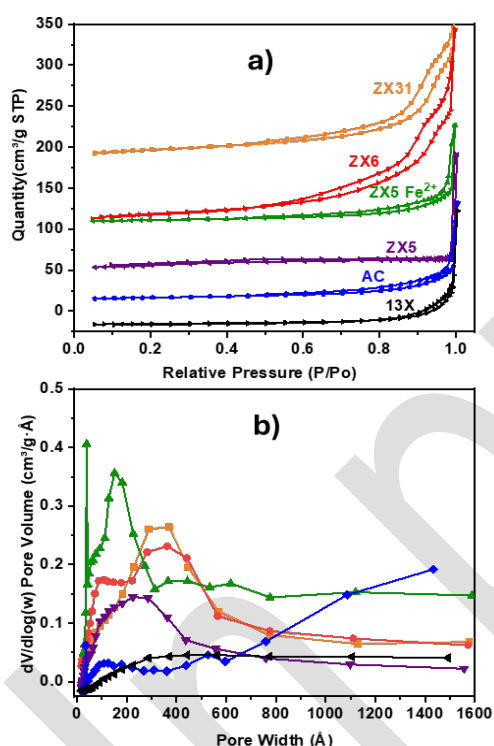


Fig. 5. a) N<sub>2</sub> adsorption-desorption isotherms and b) Pore size distribution

According to the Energy-Dispersive Spectroscopy (EDS) results from Table 1, the mass ratio of Fe impregnated on the ZX5 (N<sub>2</sub>/ZX5.Fe<sup>2+</sup>) sample is approximately the same as the theory. This shows that the previous impregnation process has achieved the desired ratio. The zeolite material samples have Si/Al ratios ranging from 0.3 - 1.30. ZX31 contains the highest Al content, which can be more acidic [13, 15]. Zeolites have TO<sub>4</sub> tetrahedra (SiO<sub>4</sub> or AlO<sub>4</sub><sup>-</sup>) linked by oxygen atoms to form the main structures; however, the presence of AlO<sub>4</sub><sup>-</sup> creates a negative charge in the structure and needs to be neutralized by exchangeable compensating cations (e.g., Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>). These cations are known to be able to change some properties of zeolite, especially for adsorption processes [16].

The N<sub>2</sub> adsorption-desorption isotherms and the pore distribution of the adsorbent material samples are shown in Fig. 5. Since the analysis system is limited to determining the average pore size and above, only the pore distribution from the average pore size and above is considered in this measurement. The results show that all materials exhibit type IV isotherms, which are typical of medium-pore materials (20 Å < d < 500 Å) [17].

From the shape of the hysteresis loop observed with the H<sub>2</sub> type hysteresis loop (0.6 < P/Po < 1) with the pore size concentrated at 200 Å and 500 Å, it shows that the material contains diverse types of pores and the pore diameter distribution is relatively large, with the capillaries having a bottleneck shape, narrow at the top and large at the bottom recorded on the samples: ZX31; ZX6; ZX5 and N<sub>2</sub>/ZX5.Fe<sup>2+</sup>. For AC, the hysteresis loop is narrower, belonging to the H<sub>3</sub> type (0.45 < P/Po < 1), which is typical for capillaries with a slit shape with uneven size and mainly concentrated in the range of 50-300 Å [17, 18]. In addition, there is the appearance of large capillary pores (>800 Å), possibly due to the adhesion of AC unit particles to these sites. Normally, powdered zeolites and powdered activated carbon (AC powder) have quite large specific surfaces. However, in this study, materials were pelletized with larger sizes, leading to a large decrease in specific surface area, as seen in Table 1. However, N<sub>2</sub>/ZX5.Fe<sup>2+</sup> possesses a significantly increased surface area compared to the original ZX5 sample. ZX5 sample has low mechanical strength, therefore during the impregnation of Fe<sup>2+</sup>, the sample surface was broken partly due to the stirring in an aqueous solution at 70 °C, and the partial dissolution of the binders and surface particles occurred, resulting in the decrease of particle size and the loosening of surface particles, thus leading to a significant increase in surface area, closer to the surface area of original zeolite (before making to the pellets). Besides, when Fe<sup>2+</sup> is impregnated on the ZX5 sample, no significant changes in capillary size and properties were recorded. In addition, the NO molecule size is only about 1.12 Å [19], so the used materials can fully adsorb NO.

Table 2. NO adsorption quantity was measured by the NO-TPD of the materials

Sample	Temperature at Maximum (°C)	NO adsorption quantity (mmol/g)	Total quantity (mmol/g)
ZX31	81	1.01	10.62
	436	9.61	
ZX5	83	2.05	7.54
	330	5.49	
N <sub>2</sub> /ZX5.Fe <sup>2+</sup>	82	2.02	8.25
	300		
	433	6.23	

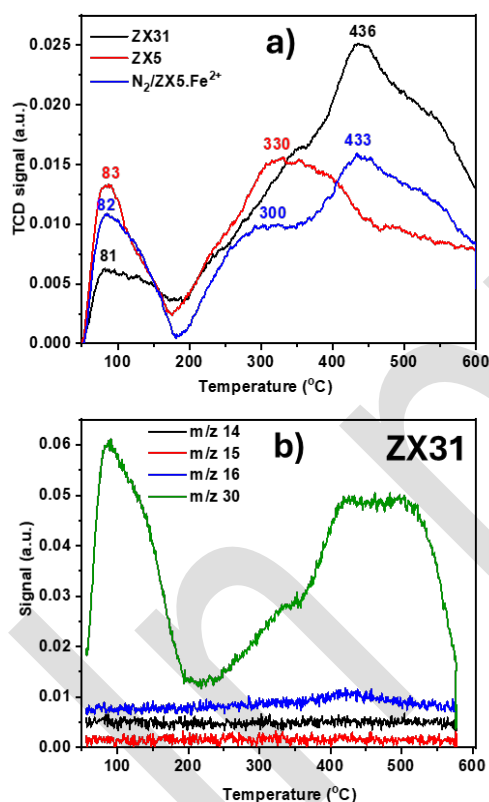


Fig. 6. a) NO-TPD profiles of ZX31; ZX5; N<sub>2</sub>/ZX5.Fe<sup>2+</sup> and b) Signal mass of ZX31

NO-TPD was performed on samples with large specific surfaces ZX31, ZX5, and N<sub>2</sub>/ZX5.Fe<sup>2+</sup>. The results shown in Fig. 6 a) and Table 2 show two NO desorption regions above and below 300 °C. The peaks below 300 °C are attributed to weak physical and chemical adsorption sites on the surface. The results show that all samples have small adsorption peaks at around 80-85 °C, in which the NO desorption capacity of the samples indicates that ZX31 exhibits the lowest

value, whereas N<sub>2</sub>/ZX5.Fe<sup>2+</sup> and ZX5 present nearly identical capacities. With the temperature range above 300 °C, the peaks are attributed to chemical adsorption sites formed by the thermal decomposition of nitrate and/or nitrite species generated by NO adsorption on the material, thanks to the ion exchange capacity at each AlO<sub>4</sub> tetrahedron in the zeolite framework. The adsorption mechanism based on the ion exchange interaction between NO<sub>x</sub> molecules and zeolites was proposed by E. P. Hessou *et al.* (2018) [7]. The results show that NO was absorbed on ZX5 at the lowest temperature (330 °C) and the smallest capacity among the analyzed samples.

Sample N<sub>2</sub>/ZX5.Fe<sup>2+</sup> desorbed NO at two peaks, 300 and 433 °C, the total desorption capacity was larger than that of ZX5, which showed that the presence of Fe<sup>2+</sup> improved the chemical adsorption capacity for ZX5. Besides, ZX31 also had a peak at 436 °C with the largest desorption capacity compared to the remaining samples, which could be due to the superior specific surface area leading to large adsorption centers and the ability of NO to contact those sites. In addition, the smallest Si/Al ratio of 0.31 showed that a large amount of Al led to a large enhancement of the active sites of the sample. In the study of L. Beco *et al.*, the multiple adsorptions of NO on Fe<sup>2+</sup> cations of Ferrierite were proposed. When a single NO molecule is adsorbed, a tetragonal pyramid is formed with four Fe-O bonds in the plane with the framework and one axial Fe-N bond. A cis tetrahedral complex is formed when a second NO molecule is adsorbed on the Fe<sup>2+</sup> cation. The tetrahedral complex contains a [Fe-(NO)<sub>2</sub>]<sup>+</sup> (dinitrosyl) particle, which carries only a single positive charge. Since such a particle compensates for only one Al/Si substitution, the resulting charge imbalance causes a high chemical reactivity of the Al framework sites. Therefore, a third NO molecule absorbs the activated oxygen atoms adjacent to the Al site [20].

Combined with the NO-TPD analysis of the ZX31 sample, the mass spectra of the desorbed gas flow were also recorded, which showed masses 14, 15, 16, and 30 m/z corresponding to N, O, and NO molecules. Fig. 6 b) shows that the significant increase in signal intensity only appears for the mass 30 m/z corresponding to NO at two different temperature regions, which is consistent with the NO-TPD results, proving that during the NO desorption process, only NO is released. The existence of NO chemical adsorption centers on the surface leads to the fact that NO is difficult to release and requires higher desorption temperatures.

Table 3. NO adsorption and desorption quantity measured by NO adsorption-desorption experiments in the microreactor setup

Sample	Quantity NO adsorption (mmol/g)	Quantity NO desorption (mmol/g)	% Retained NO
AC	0.052	0.014	73.07
13X	0.117	0.015	87.17
ZX5	0.234	0.010	92.72
ZX6	0.350	0.014	93.00
ZX31	1.130	0.017	99.50

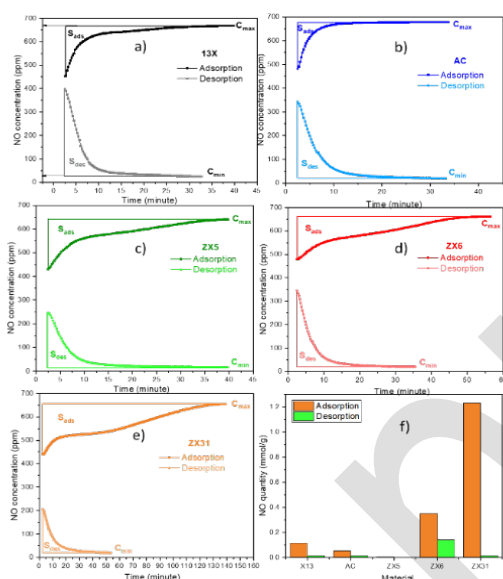


Fig. 7. NO adsorption and desorption curves of materials

The adsorption ability of all samples was also measured by using an adsorption experiment in a microreactor set, as shown in Fig. 2. The results are summarized in Fig. 7 and Table 3. The results show that the adsorption amount of the samples increases gradually, with AC exhibiting the lowest value, followed by 13X, ZX5, and ZX6, and reaching the highest in ZX31, which attained an adsorption capacity of 1.13 mmol/g. However, the desorption capacity of the samples at 200 °C was much smaller, accounting for only 1.5-27 % of the adsorption amount, showing that the absorbents adsorbed NO tightly and hardly released NO at low desorption temperatures. On the contrary, ZX5 has a lower adsorption ability than ZX31 but has a better desorption ability. This leads to the better reuse ability for NO adsorption processes of ZX5. Moreover, the results of the TPD-NO analysis without a physical adsorption removal stage showed that ZX5 has a better physical adsorption capacity than ZX31, while ZX31 has a better chemical adsorption capacity. Therefore, in this study, Fe<sup>2+</sup> was impregnated on ZX5 instead of ZX31 to

enhance the adsorption capacity, especially the chemical adsorption sites for the sample to a reasonable level (not too weak, not too strong).

Amongst the samples investigated, AC has low NO adsorption capacity but gives higher NO desorption efficiency than the others due to possessing a much lower surface area and bigger pore size. In particular, the existence of large capillary pores facilitates the easy release of NO molecules. In contrast, zeolite samples possess pores concentrated on smaller sizes (10-40nm), which is more suitable for the NO molecular size. Therefore, NO can adsorb easier. The NO release process also becomes more difficult due to the small pore size structure, making it difficult for NO gases to exit. Moreover, the existence of metal sites in zeolite may form the stable NO chemical adsorption

#### 4. Conclusion

In summary, the NO adsorption ability of the investigated samples increased progressively from AC, through 13X, ZX5, and ZX6, to the highest in ZX31. The zeolite samples have better adsorption capacity than activated carbon. Zeolite has a larger surface area and higher cation content, so it has a higher adsorption capacity due to the chemical adsorption on these sites. Zeolite ZX31 has the strongest adsorption capacity (1.13 mmol/g) among the investigated materials, but the affinity with NO is rather high, so the desorption ability at low temperatures (200 °C) is very small, leading to the difficulty to reuse. The modification of zeolite ZX5 with Fe<sup>2+</sup> has further enhanced the active sites that are beneficial for NO adsorption of ZX5, helping to improve the NO adsorption capacity compared to the original sample.

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