

Article

The Study of C₃H₆ Impact on Selective Catalytic Reduction by Ammonia (NH₃-SCR) Performance over Cu-SAPO-34 Catalysts

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Abstract: In present work, the catalytic performance of Cu-SAPO-34 catalysts with or without propylene during the NH₃-SCR process was conducted, and it was found that the de-NO_x activity decreased during low temperature ranges (<350 °C), but obviously improved within the range of high temperatures (>350 °C) in the presence of propylene. The XRD, BET, TG, NH₃-TPD, NO_x-TPD, in situ DRIFTS and gas-switch experiments were performed to explore the propylene effect on the structure and performance of Cu-SAPO-34 catalysts. The bulk characterization and TG results revealed that neither coke deposition nor the variation of structure and physical properties of catalysts were observed after C₃H₆ treatment. Generally speaking, at the low temperatures (<350 °C), active Cu²⁺ species could be occupied by propylene, which inhibited the adsorption and oxidation of NO_x species, confining the SCR reaction rate and causing the deactivation of Cu-SAPO-34 catalysts. However, with the increase of reaction temperatures, the occupied Cu²⁺ sites would be recovered and sequentially participate into the NH₃-SCR reaction. Additionally, C₃H₆-SCR reaction also showed the synergetic contribution to the improvement of NO_x conversion at high temperature (>350 °C).

Keywords: NH₃-SCR; C₃H₆ impact; Cu-SAPO-34; NO_x abatement; mechanism



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1. Introduction

Regardless of diesel or lean-burn gasoline engine exhaust, NO_x fouling has induced severe environmental problems [1–3] and the elimination of NO_x is still a big challenge under stringent emission regulations [4]. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is considered as the most potential de-NO_x technology for engine exhaust emission control [5,6]. In the past decades, V₂O₅-WO₃/TiO₂ SCR catalyst has been widely used in the commercial de-NO_x application [7,8]. However, the main drawbacks of these catalysts for mobile source domains are their insufficient low temperature SCR activity, poor thermal stability, and latent toxicity [9]. Compared with V₂O₅-WO₃/TiO₂, ZSM-5 and Beta zeolite-based catalysts, generally promoted by Cu or Fe ions, have been intensively studied for NO_x elimination [10,11] and they were considered as a potential substitute for vanadium-based catalysts due to their competitive activity and thermal stability [12]. However, their durability under hydrothermal aging condition is less than optimal [13–15]. In recent years, the Cu supported Chabazite catalyst (e.g., Cu-SAPO-34 or Cu-SSZ-13) has been reported as a leading candidate of the NH₃-SCR catalyst, owing to its high catalytic activity [16,17] and superior stability [18]. Furthermore, extensive researches have focused on the following topics, such as active Cu species. Especially based on the paper published by Xue et al., it was shown that four copper species in Cu/SAPO-34 samples were identified, including external surface copper oxide clusters, isolated Cu²⁺, nanosized copper oxide crystallites, and Cu⁺ species. It was indicated that the isolated Cu²⁺ species were responsible for the active sites for the NH₃-SCR reaction over the Cu/SAPO-34 catalyst (100–200 °C) [19,20], acidity [21], reaction intermediates [22],

reaction mechanism [23–26], formation and decomposition of the by-products N_2O [27–31], hydrothermal stability [32,33], and SO_x poisoning over Cu-SAPO-34 [34,35].

Although Cu-SAPO-34 has been widely reported in previous studies as a powerful potential application, another issue that needs to be addressed is the impact of hydrocarbons on SCR activity during cold startup or inactivation of upstream TWC catalysts, especially during the passive-SCR process [36], since the hydrocarbons in exhaust could slip and interact with downstream SCR catalyst. Even if the HCs-SCR could be a possible pathway for NO_x elimination, the hydrocarbons (e.g., C_3H_6) were still considered as poisons for NH_3 -SCR catalyst [37–39]. Li et al. illustrated that SCR performance of Fe-zeolites catalysts (Fe-BEA, Fe-ZSM-5, and Fe-MOR) was obviously inhibited in the presence of propylene [40,41]. The origin of C_3H_6 inhibition on activity over Cu-ZSM-5 and Fe-SZM-5 catalysts was the competitive adsorption of NH_3 and C_3H_6 on catalyst sites [42]. Meanwhile, another deactivation mechanism resulted from hydrocarbons was the blocking of active sites by carbonaceous species, which limited the overall SCR reaction rate [41]. Furthermore, Ma et al. stated that competitive adsorption of NO_x and C_3H_6 in the low temperature ranges and the coke formation on active sites during medium temperature ranges were critical for the deactivation of the Cu-SSZ-13 catalyst [36]. Conversely, Wang et al. reported that the improved NO_x removal efficiency resulted from the presence of hydrocarbons such as C_3H_6 in NH_3 -SCR gas stream for the commercial Cu-CHA catalyst in LNT-SCR configuration [43,44]. Meanwhile, Z. Gao et al. illustrated that the presence of CuO in Cu-SAPO-34 catalysts would accelerate the C_3H_6 oxidation process and improve the C_3H_6 conversions [45]. Furthermore, D. Yang et al. reported that Fe-SAPO-34 catalyst exhibited attractive C_3H_6 -SCR catalytic performance at 250–350 °C in the presence of 5% H_2O and 10% O_2 [46]. In a nutshell, the propylene impact on NH_3 -SCR performance during a different temperature range and the mechanism behind the catalyst's deactivation [47–51] is still controversial.

In the present work, the impact of C_3H_6 on NO conversion of Cu-SAPO-34 catalyst and the C_3H_6 influence mechanism were investigated at different temperature ranges. XRD, TG, gas-switch tests, and the temperature programmed desorption (TPD) of NH_3 (NO_x) with or without propylene were conducted to identify the influence of propylene on Bronsted acid sites, active sites, and reaction intermediates. Finally, in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) was employed to probe into the C_3H_6 effect mechanism on NH_3 -SCR performance.

2. Results

2.1. Structure and Physical Properties of Cu-SAPO-34 Catalysts

For XRD patterns of fresh Cu-SAPO-34 and HCs-Cu-SAPO-34 in the Figure 1, no significant change of CHA crystal structure was observed before and after propylene treatment and any detected crystal variation was not found through the above XRD patterns. Namely, it implied that the CHA structure of Cu-SAPO-34 barely changed after 1000 ppm, 6h C_3H_6 treatment at 300 °C.

The results of BET results of the fresh Cu-SAPO-34 and HCs-Cu-SAPO-34 were listed in Table 1. Compared to the fresh Cu-SAPO-34, the BET surface area of HCs-Cu-SAPO-34 still remained at 415 m^2/g , which was comparable with the fresh catalyst. It also suggested that the C_3H_6 treatment scarcely damaged the porous structure of catalysts.

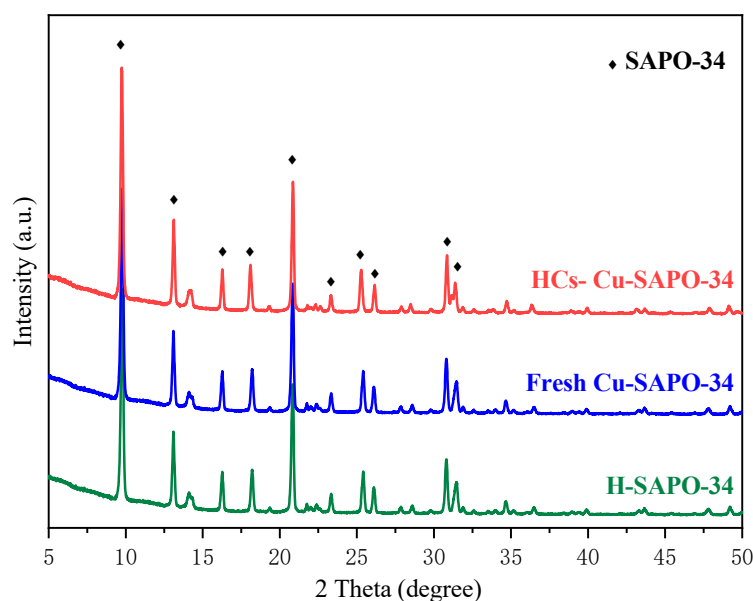


Figure 1. XRD patterns of H-SAPO-34, fresh Cu-SAPO-34, and HCs-Cu-SAPO-34.

Table 1. Comparison of BET surface area results of fresh Cu-SAPO-34 and HCs-Cu-SAPO-34.

Catalysts	Fresh Cu-SAPO-34	HCs-Cu-SAPO-34
BET specific surface area (m ² /g)	417	415

2.2. The TG Experiments

Figure 2a,b demonstrated the TG differential profiles and TG mass loss profiles of fresh Cu-SAPO-34 and HCs-Cu-SAPO-34 catalysts. As shown in the Figure 2a, two obvious mass losses were observed around 100 °C and 250 °C. Specifically, the main mass variation at 100 °C and the minor mass loss at 250 °C was deemed to derive from the dehydration process of adsorbed water on Cu-SAPO-34 samples [27]. Furthermore, it was calculated from Figure 2b that the H₂O mass losses were 13%, 5% for fresh Cu-SAPO-34, and 12%, 4% for HCs-Cu-SAPO-34, respectively. Importantly, no distinct mass loss was discovered at high temperature above 400 °C, which usually was considered as the essential temperature for coke removal on catalysts. Consequently, it indicated that the possibility of coke formation on Cu-SAPO-34 catalyst was small.

2.3. NH₃-SCR Activity of Cu-SAPO-34 Catalysts

For NO conversion in Figure 3a, the catalytic performance of fresh Cu-SAPO-34 catalyst presented a volcanic-type profile. After the propylene was introduced into the reaction system, the de-NO_x activity of Cu-SAPO-34 catalyst was obviously inhibited below 350 °C. However, the NO_x conversion was rapidly improved when temperatures were higher than 350 °C and C₃H₆ existed in the feed. The above results revealed that the propylene played an opposite role in NO_x removal during the low- and high-temperature ranges, implying that the influence of propylene on the NH₃-SCR reaction could be related to the reaction temperatures. Meanwhile, as shown in Figure 3b, the NH₃ conversion rate curve exhibited the same change pattern as the NO conversion in the low-temperature stage, but the NH₃ conversion kept increasing until 100% in the high-temperature stage. Simultaneously, it can be seen from the results in Figure 3c that the Cu-SAPO-34 catalysts shown excellent nitrogen selectivity with or without C₃H₆. Finally, the by-products NO₂ and N₂O were both less than 18 ppm.

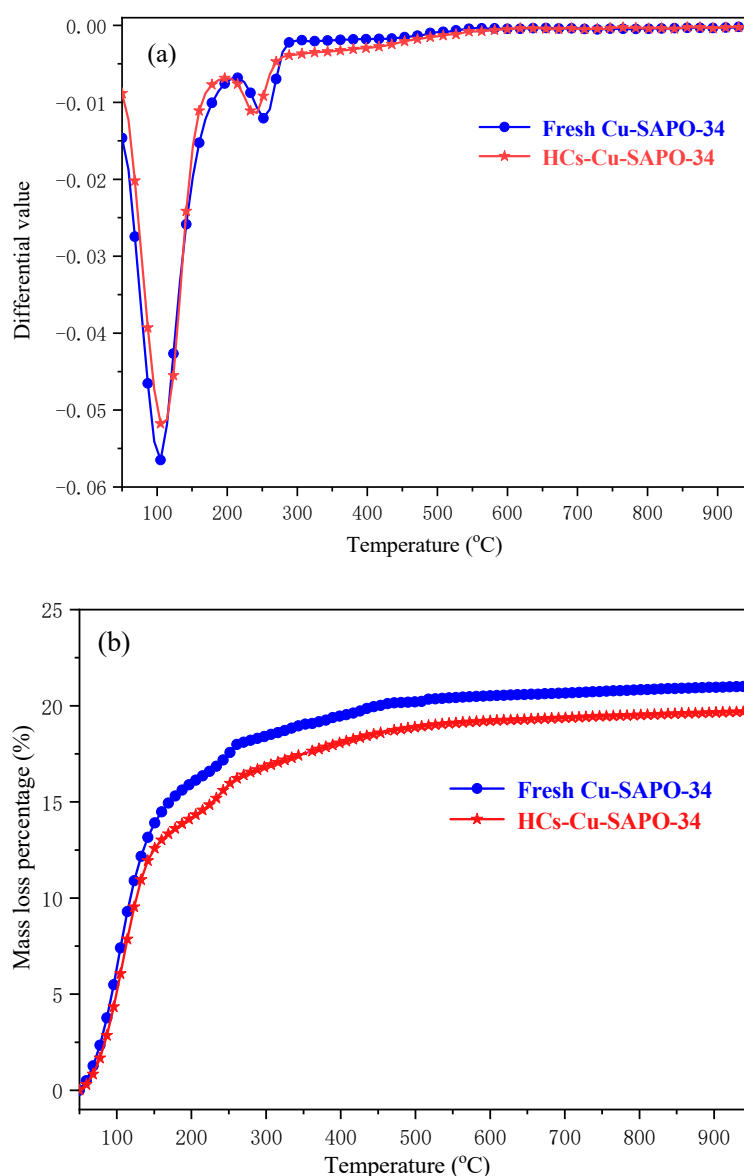


Figure 2. (a) the differential profiles and (b) mass loss profiles of fresh Cu-SAPO-34 and HCs-Cu-SAPO-34 samples.

Figure 4 displayed the results of long-term NH_3 -SCR activity changes with propylene over Cu-SAPO-34 catalyst through the gas-switch experiments. It was seen that the NO conversion achieved equilibrium after 50 min. Subsequently, propylene was introduced into the system with identical total flow rate for $100 \text{ mL} \cdot \text{min}^{-1}$. Then the C_3H_6 was cut off again at 150 min. Finally, the NH_3 -SCR reaction achieved stability after another 80 min. As shown in Figure 4, the NO conversion presented two types of trends at different temperatures after the propylene was introduced. The NO conversion sharply decreased at 200 °C and 300 °C, but distinctly increased under 400 °C and 500 °C. Specifically, the catalytic activity changed from 89.2% to 81.2% at 200 °C, 88% to 83% at 300 °C, but increased from 77.6% to 80.4% at 400 °C and 68% to 74.4% at 500 °C, respectively. It is worthy of mention that after propylene was removed from the infeed, the NO conversion could recover completely to the initial value at 400 °C and 500 °C. Nevertheless, de- NO_x activity could merely be regained to some extent at 200 °C and 300 °C.

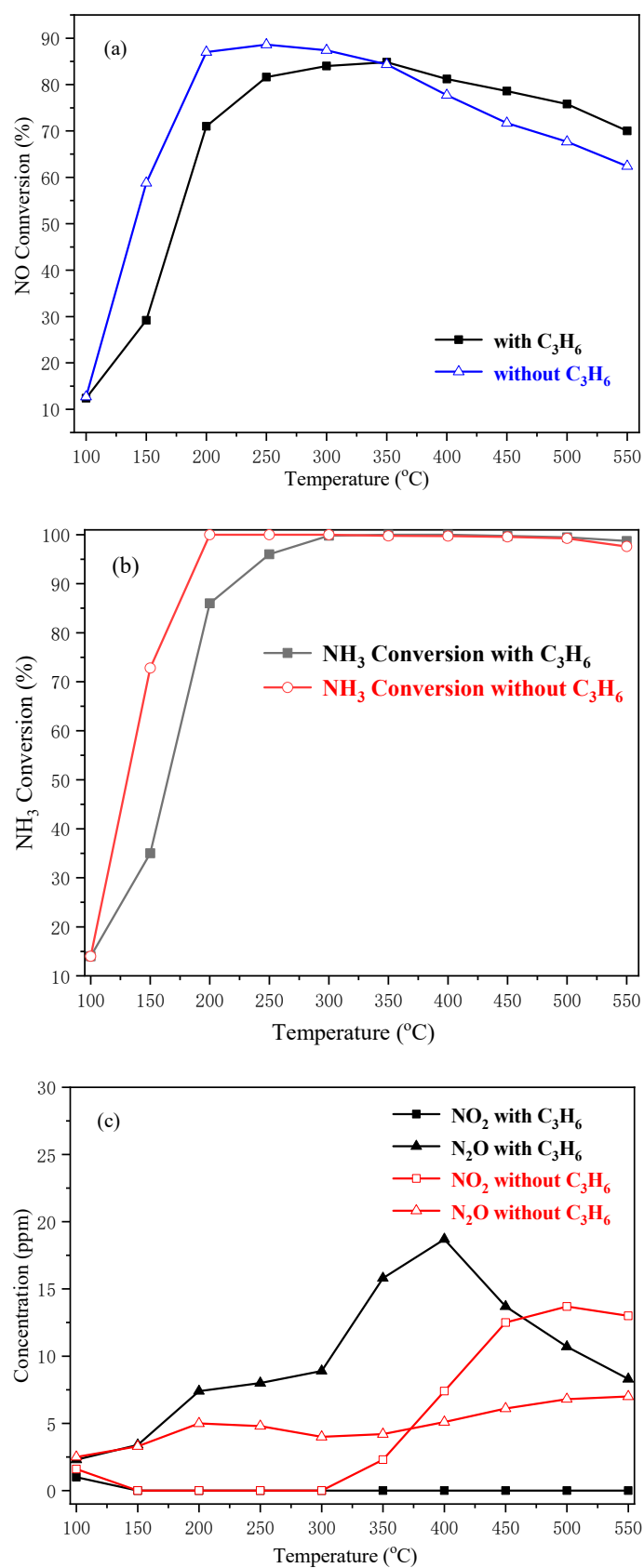


Figure 3. The SCR activities over Cu/SAPO-34 catalysts with or without C_3H_6 . (a) The NO conversion; (b) the NH_3 conversion; and (c) the concentrations of NO_2 and N_2O . Reaction condition: 500 ppm NO, 500 ppm NH_3 , 500 ppm C_3H_6 , 10% O_2 , with N_2 as balance gas. GHSV = 300,000 h^{-1} .

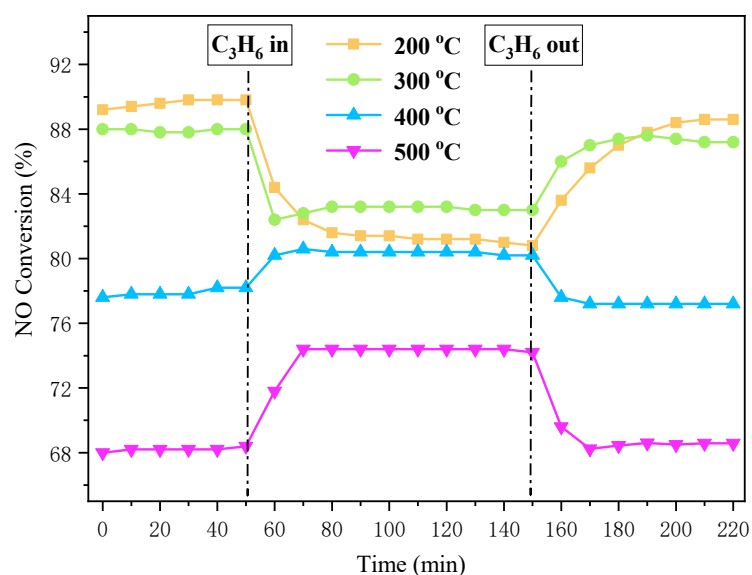


Figure 4. The gas-switch experiments of Cu-SAPO-34 with propylene at different temperatures, reaction condition: 0.1 g catalyst, 500 ppm NO, 500 ppm NH₃, 10% O₂ and N₂ as balance gas. GHSV = 300,000 h^{−1}.

2.4. The Adsorption Performance of Reactants

2.4.1. NH₃-TPD

Figure 5 displayed the NH₃-TPD profiles with or without propylene over H-SAPO-34 support at 100 °C. It was seen that three broad ammonia desorption peaks were detected over the whole temperature range for both NH₃-TPD curves. According to previous studies [25], the peak at low-temperature area around 150 °C was ascribed to NH₃ desorption from weak Brønsted acid sites at surface hydroxyl. The peaks around 246 °C and 335 °C were assigned to the moderate and strong structural Brønsted acid sites. Compared NH₃-TPD results without C₃H₆, only the peak at low temperature slightly decreased, while the peaks at moderate- and high-temperature ranges almost remained identical level when C₃H₆ existed in the gas composition. This meant that impact of C₃H₆ to NH₃ adsorption was mainly embodied in weak Brønsted acid sites, which could become inapparent with the increase of temperatures.

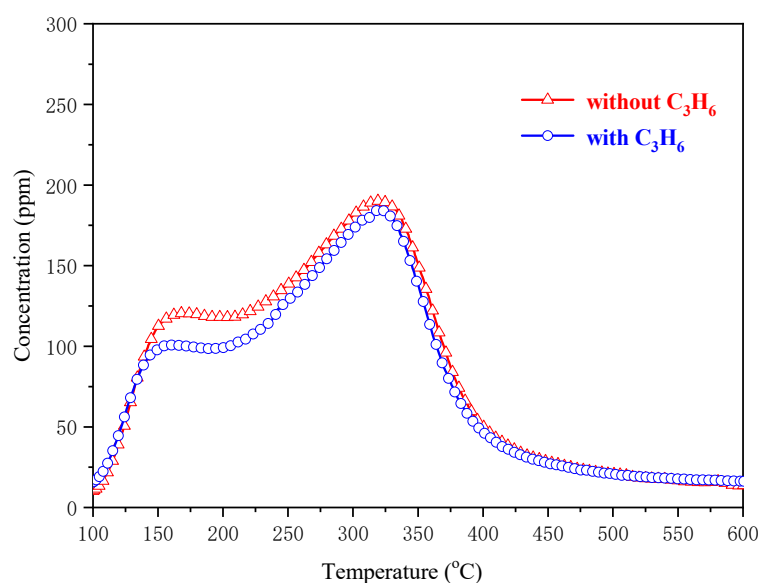


Figure 5. NH₃-TPD profiles over H-SAPO-34 support with or without C₃H₆.

Figure 6 presented the NH_3 -TPD profiles with or without propylene over the Cu-SAPO-34 catalyst at 100 °C. Specifically, four ammonia desorption peaks were observed over the range from 100 °C to 600 °C. The peak around 150 °C was ascribed to NH_3 desorption from weak Brønsted sites and Lewis acid sites related to Cu species. And the peak at medium temperature range around 246 °C was assigned to residual structural Brønsted acid sites. Additionally, peaks above 300 °C were considered as strong Brønsted acid sites and the new Lewis acid sites created by the Cu^{2+} species. Compared with results without C_3H_6 , the tendency of NH_3 -TPD test with C_3H_6 showed that just ammonia adsorption on weak acid site around 150 °C mildly decreased. And the propylene barely affected ammonia adsorption over medium and strong acid sites. Meanwhile, due to the huge difference of desorption amount, almost no C_3H_6 species was detected during the desorption process of the NH_3 -TPD test.

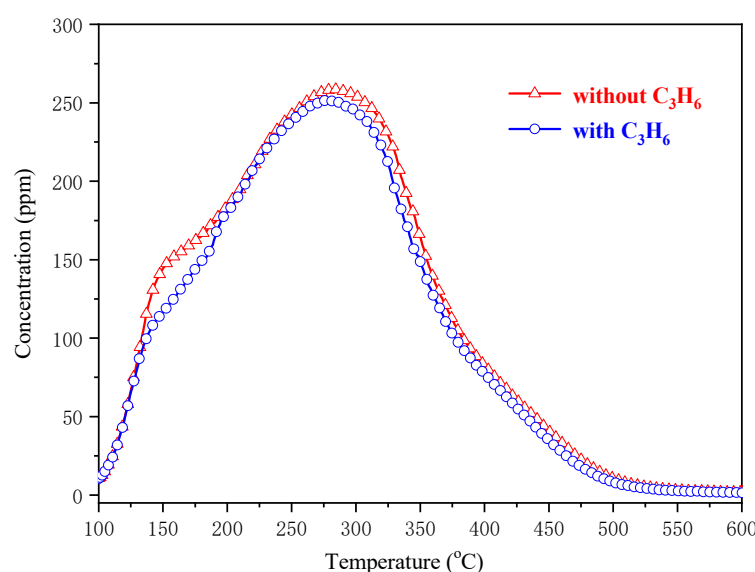


Figure 6. NH_3 -TPD profiles over Cu-SAPO-34 catalyst with or without C_3H_6 .

2.4.2. NO_x -TPD Experiments

Figure 7a,b exhibited the NO_x -TPD profiles over the Cu-SAPO-34 catalyst with or without propylene at 80 °C. For $\text{NO} + \text{O}_2$ adsorption behavior on the Cu-SAPO-34 catalyst, there was only one main NO_2 desorption peak and slight NO desorption peak around 250 °C, as shown in Figure 7a. Concretely, the NO_2 desorption species could be related to the decomposition of nitrates on the Cu-SAPO-34 catalyst. However, when C_3H_6 was introduced into the $\text{NO} + \text{O}_2$ adsorption process, all desorption peaks obviously shifted to the lower temperature around 150 °C and the desorption species mainly turned into NO . Only a slight amount of C_3H_6 and little N_2O were observed during the NO_x -TPD experiments. Accordingly, this implied that the adsorption and oxidation of NO_x on catalyst surface could apparently be weakened in the presence of C_3H_6 species, and the NO_x desorption peaks located around 150 °C were attributed to the weak adsorbed NO_x species on the catalyst's surface.

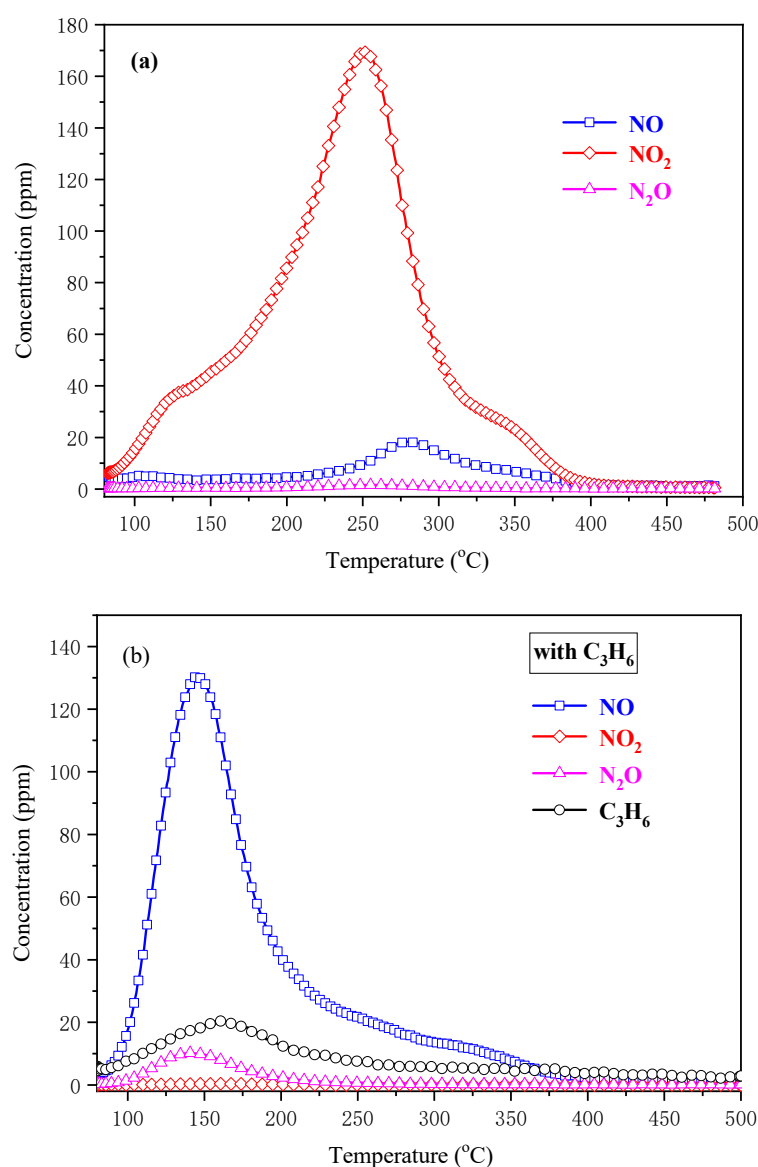


Figure 7. NO_x-TPD profiles over the Cu-SAPO-34 catalyst without C₃H₆ (a) and with C₃H₆ (b).

2.4.3. C₃H₆-TPD Experiments

Figure 8 shows the C₃H₆-TPD profiles after C₃H₆ adsorption saturation over H-SAPO-34 support and Cu-SAPO-34 catalyst at 100 °C. For C₃H₆ adsorptions on the H-SAPO-34 support, one main desorption peak at 220 °C was attributed to the weak adsorbed C₃H₆ species, yet the slight shoulder peak around 370 °C was assigned to the strong C₃H₆ adsorption species. Specifically, they were both related to C₃H₆ species adsorption on the Brønsted acid sites. Compared with the C₃H₆-TPD results over the H-SAPO-34 sample, two obvious desorption peaks were detected over the Cu-SAPO-34 catalyst. The larger C₃H₆ desorption peak around 370 °C should be ascribed to adsorption of C₃H₆ on Cu species, since only Cu species over the Cu-SAPO-34 catalyst could supply extra adsorption sites. Furthermore, it was suggested that the C₃H₆ adsorption strength on Cu species was stronger than that on the Brønsted acid sites, and the Cu²⁺ species played an important role in adsorption of HCs species, as shown in Figure 8.

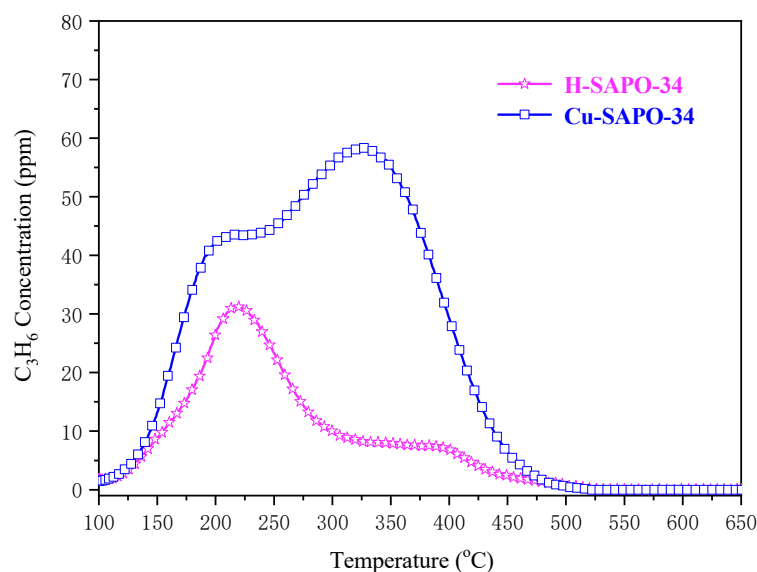


Figure 8. C_3H_6 -TPD profiles over H-SAPO-34 support and Cu-SAPO-34 catalyst.

2.5. The DRIFTS Experiments

2.5.1. Co-Adsorption of NH_3 and C_3H_6 Species

The DRIFTS spectra of NH_3 , C_3H_6 , and $NH_3+C_3H_6$ adsorption over the Cu-SAPO-34 catalysts at 200 °C are shown in Figure 9. For NH_3 adsorption over Cu-SAPO-34 reported previously [25], the doublet bands at 3624 cm^{-1} and 3590 cm^{-1} were assigned to the stretching model of bridged Brønsted OH groups $Al-(OH)-Si$, which was used to represent the Brønsted acid sites on the catalyst. Meanwhile, the bands at 885 cm^{-1} and 858 cm^{-1} were related to Lewis acid sites of copper cations. For C_3H_6 adsorption on the Cu-SAPO-34 catalysts, obvious IR adsorption peaks were only observed at 885 and 858 cm^{-1} , which could be related to the adsorption of C_3H_6 on copper species over Cu-SAPO-34. However, during the co-adsorption process of NH_3 and C_3H_6 , the peak intensity of 3624 cm^{-1} was almost consistent with the individual NH_3 adsorption test, which revealed that the ammonia adsorption on the Brønsted acid site was barely affected by the presence of C_3H_6 . Nevertheless, IR adsorption peaks strength at 885 cm^{-1} was relatively decreased in Figure 9b compared with the results of the NH_3 adsorption test. Based on the above results, it was concluded that the adsorption of NH_3 on the Brønsted acid sites of Cu-SAPO-34 catalysts would not be affected by the existence of propylene, while the ammonia adsorption on the Lewis acid sites was partially influenced by C_3H_6 .

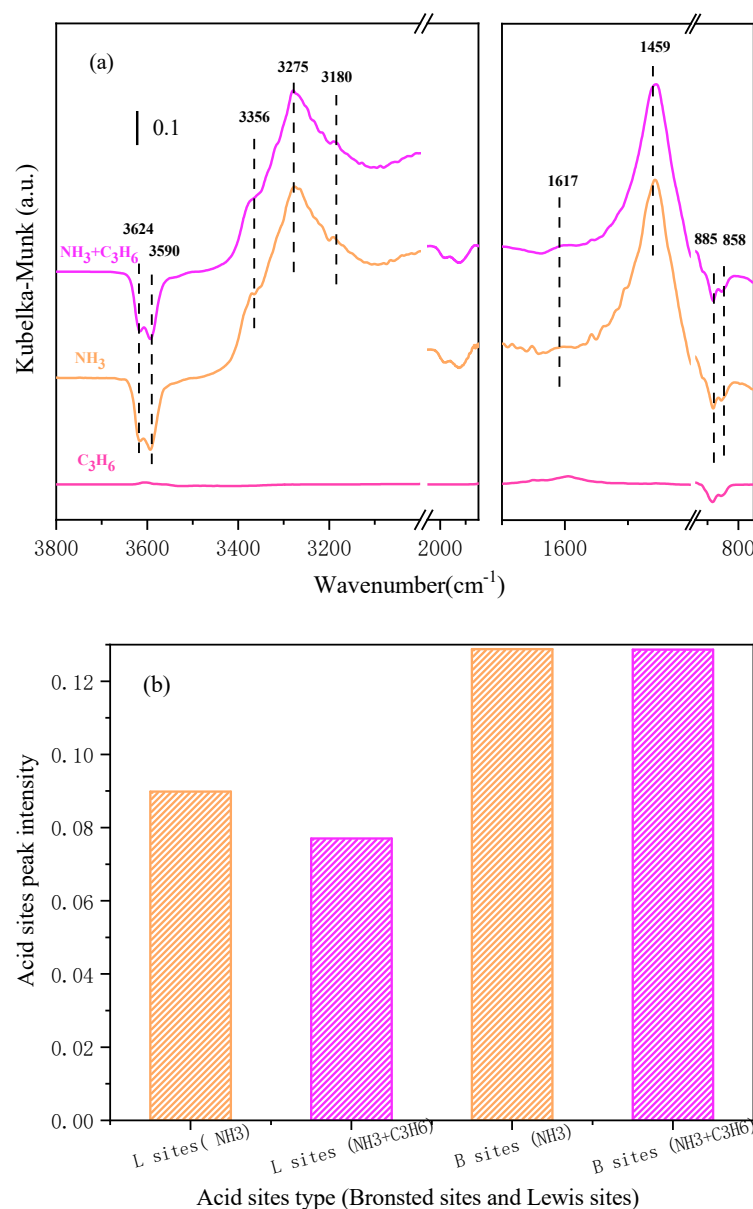


Figure 9. (a) IR characteristic peak spectra when NH₃, C₃H₆, and NH₃+C₃H₆ were, respectively, chemisorbed over Cu-SAPO-34 catalysts at 200 °C, (b) the change of peak intensity over the Lewis acid site (885 cm⁻¹) and the Brønsted acid sites (3624 cm⁻¹) with or without C₃H₆.

2.5.2. Co-Adsorption of NO and C₃H₆ Species

Figure 10 displayed the DRIFTS spectra of NO, C₃H₆, and NO + C₃H₆ adsorption over the Cu-SAPO-34 catalysts at 200 °C. When 500 ppm NO was introduced into the reaction cell at 200 °C, IR adsorption peak was scarcely observed, which suggested the NO species was hardly adsorbed on Cu-SAPO-34 catalyst, which was consistent with previous results of NO reaction orders of 1 [21]. For C₃H₆ adsorption over Cu-SAPO-34 at 200 °C, various IR bands of carbonaceous species appeared as shown in Figure 10. The IR bands at 1656 cm⁻¹ and 1591 cm⁻¹ were assigned to the C=O vibrations and C-H stretching vibrations of hydrocarbons, respectively. The band at 1430 cm⁻¹ was related to the surface carboxylate species. Nevertheless, when the NO and C₃H₆ were both present during the adsorption competition, the IR results were almost identical with C₃H₆ adsorption experiment results. Consequently, this illustrated that the adsorption strength of C₃H₆ was obviously stronger than NO on the Cu-SAPO-34, which could lead into the inhibition of nitrate/nitrite formation on the catalyst.

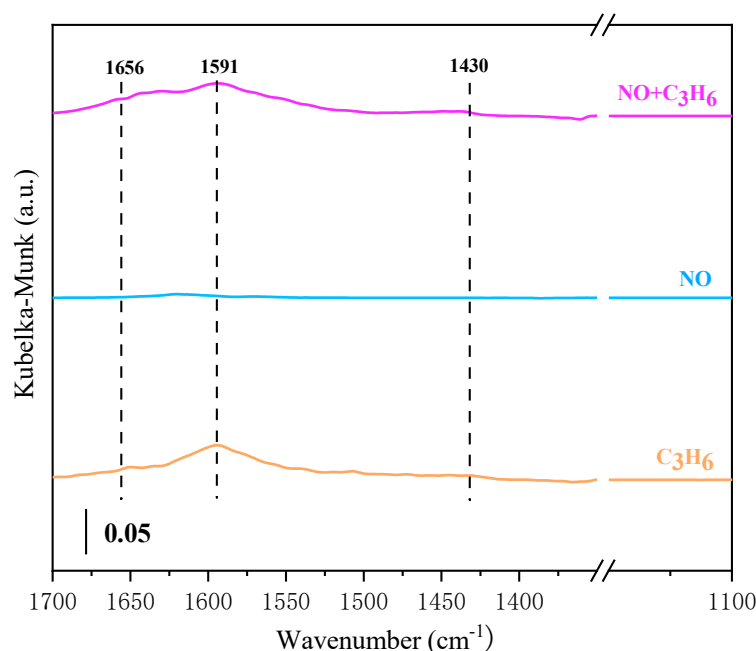


Figure 10. DRIFTS spectra of chemisorbed of NO, C₃H₆, and NO + C₃H₆ over the Cu-SAPO-34 catalysts at 200 °C.

2.5.3. The In Situ DRIFTS Experiments

The DRIFTS spectra of saturated NH₃ titration by NO + O₂ and NO + C₃H₆ + O₂ at 200 °C were shown in Figure 11a,b. After the Cu-SAPO-34 catalyst was purged by NH₃ until equilibrium, the NO + O₂ (Figure 11a) and NO + C₃H₆ + O₂ (Figure 11b) were introduced into the reaction cell. The spectra were recorded with the interval of 20 min until reaction equilibrium was attained. Herein, the doublet bands at 3624 cm^{−1} and 3590 cm^{−1} were ascribed to the Brønsted acid sites, while the bands at 885 cm^{−1} and 858 cm^{−1} were related to the Lewis acid sites of Cu²⁺ species on the Cu-SAPO-34. The peak intensity at 3624 cm^{−1} and 885 cm^{−1} in the present DRIFTS spectra were chosen as the representative of the Brønsted acid sites and Lewis acid sites to evaluate the behaviors of adsorbed ammonia species on the Cu-SAPO-34 catalyst. As shown in Figure 11a, the adsorbed ammonia species at 3624 cm^{−1} and 885 cm^{−1} had been consumed completely around 60 min. However, the pre-adsorbed NH₃ on the Lewis acid sites still distinctly existed after 60 min in the presence of C₃H₆ in Figure 11b. Consequently, it suggested that the consumption rate of adsorbed ammonia was apparently inhibited when the C₃H₆ existed in the mixture gas.

2.6. The Contribution of C₃H₆ to NH₃-SCR Performance

Figure 12a showed the SCR catalytic activity of NO_x removal with C₃H₆ over the Cu-SAPO-34 catalyst. Figure 12b displayed the NO_x conversion performance with a variation of the C₃H₆ concentration at 500 °C. As shown in Figure 12a, the NO_x conversion increased with an increase of reaction temperature. Concretely, the de-NO_x efficiency was very low when the temperature was below 300 °C, while NO_x conversion obviously improved up to 50% at 550 °C. Subsequently, in order to evaluate the effect of C₃H₆-SCR on the catalytic performance of NO_x, the NH₃-SCR reactions with different C₃H₆ concentration were performed at 500 °C. It was presented in Figure 12b that the NO_x conversion continuously increased with C₃H₆ concentration added from 100 ppm to 900 ppm. Accordingly, this implied that C₃H₆-SCR exhibited the evident contribution to the NO_x removal efficiency at high temperatures.

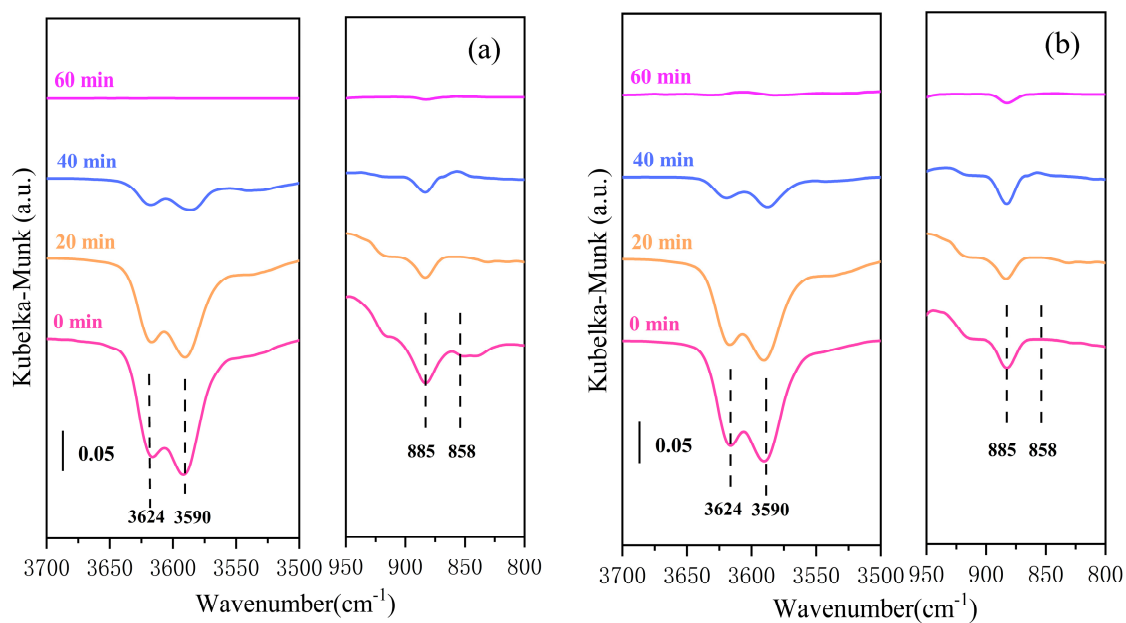


Figure 11. The DRIFTS spectra of saturated NH_3 titration by (a) $\text{NO} + \text{O}_2$, and (b) $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ over Cu-SAPO-34 at 200 °C.

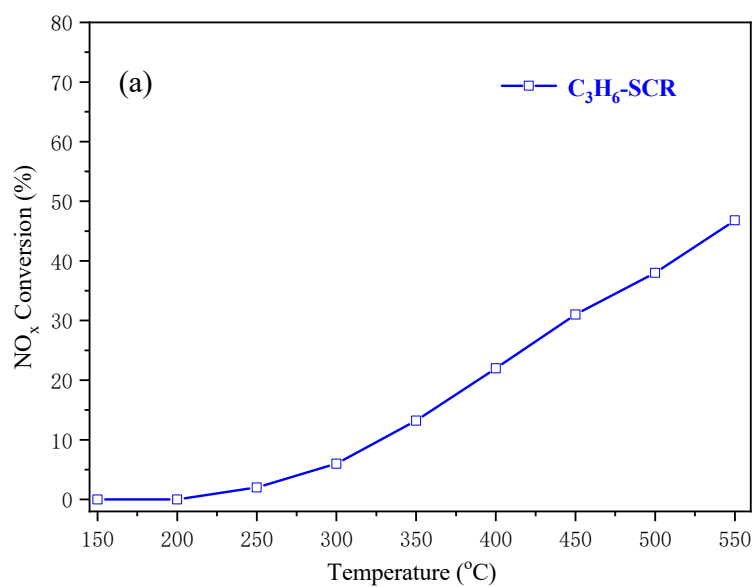


Figure 12. Cont.

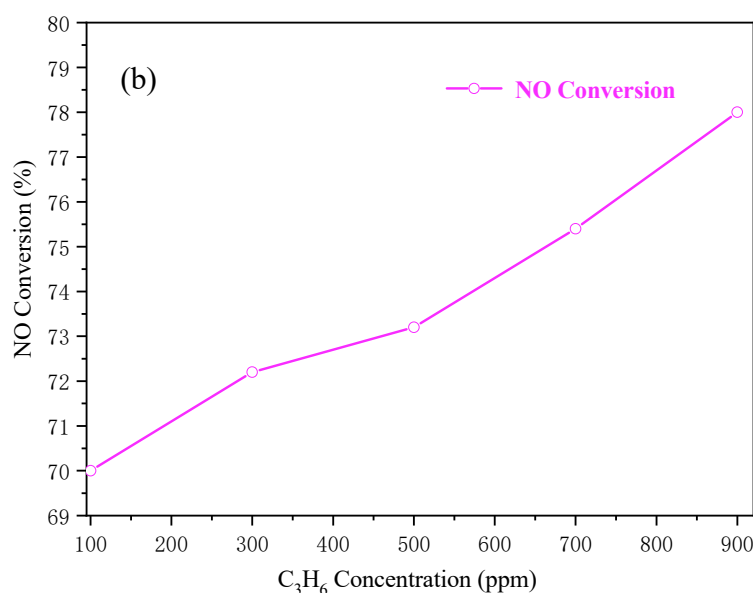


Figure 12. (a) The C₃H₆-SCR performance of Cu-SAPO-34 catalyst, reaction condition: 500 ppm NO, 500 ppm C₃H₆, 10% O₂, and N₂ as balance gas. GHSV = 36,000 h^{−1}. (b) The NO_x conversion as a function of C₃H₆ concentration at 500 °C. (C₃H₆ concentration = 100, 300, 500, 700, and 900 ppm).

3. Experiments

3.1. Catalyst Preparation

H-SAPO-34 was synthesized via the hydrothermal method with mole composition of 0.2 morpholine (MA): 0.1, Al₂O₃: 0.1, P₂O₅: 0.06, and SiO₂: 6.4 H₂O. The sources of Si, P, and Al were silica sol, 85% phosphoric acid and pseudoboehmite, respectively. Firstly, the pseudoboehmite and phosphoric acid were mixed with water. The mixture was fiercely stirred for 1 h. Secondly, the MA and silica sol were mingled well and dropwise added into the former mixture. Subsequently, the blend was sealed in 200 mL Teflon-lined stainless-steel pressure vessels and heated in an oven at 200 °C under autogenic pressure for 48 h. Finally, the H-SAPO-34 was obtained through centrifugal separation, washed, dried at 100 °C overnight, and calcined at 650 °C in air for 6 h.

The Cu-SAPO-34 catalyst was prepared by the ion-exchange method over H-SAPO-34 molecular sieve as following. Firstly, Cu-SAPO-34 was obtained by exchanging H-SAPO-34 in ammonium nitrate solution at 80 °C for 3 h. Additionally, NH₄-SAPO-34 was added into the copper sulfate solution then stirred at 70 °C for 4 h. The slurry was filtered, washed, and dried at 90–100 °C for 16 h. Lastly, the dried Cu-SAPO-34 was calcined at 500 °C for 5 h and denoted as fresh Cu-SAPO-34 catalyst. The Cu content of catalysts was 2.5% (wt. %), which was calculated on account of the ICP test result. Furthermore, after 1000 ppm C₃H₆ treatment at 300 °C for 6 h, the obtained Cu-SAPO-34 sample was called as HCs-Cu-SAPO-34.

3.2. Catalytic Performance Measurement

The SCR activity with or without C₃H₆ was tested in a quartz reactor (20 mm inner diameter), in which 0.1 g sample (60–80 mesh) was mixed with 0.9 g quartz (60–80 mesh) at atmospheric pressure. The sample was sealed in a reactor tube with quartz wool. The K-type thermocouple was inserted into the center of catalyst to control the temperature. A Fourier Transform Infrared (FTIR) spectrometer (MKS-2030, Andover, MA, United States) equipped with 5.11 m gas cell was used to measure the concentration of NH₃, NO, NO₂, N₂O, and C₃H₆. The flow rates in all experiments were controlled at 500 mL min^{−1}. After pretreated with 5% O₂/N₂ at 500 °C for 30 min, SCR tests were conducted with feed gas composition of 500 ppm NO, 500 ppm NH₃, 500 ppm C₃H₆ (when used), and 5% O₂.

The test temperature range was from 100 °C to 550 °C with an interval of 50 °C. The NO conversion and NH₃ conversion were calculated using the following equations:

$$\text{NO conversion}[\%] = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100[\%] \quad (1)$$

$$\text{NH}_3 \text{ conversion}[\%] = \frac{\text{NH}_3 \text{ inlet} - \text{NH}_3 \text{ outlet}}{\text{NH}_3 \text{ inlet}} \times 100[\%] \quad (2)$$

3.3. Catalyst Characterization

The XRD patterns were recorded using an X-ray diffraction (XRD, Bruker D8 Focus, Cu K α radiation, Karlsruhe, Germany). The XRD pattern was collected from 5° to 50° with the step size of 0.02°. The BET surface area (m²·g^{−1}) was determined from the linear portion of the BET plot by measuring the N₂ isotherm of the samples at 77 K using F-Sorb 3400 volumetric adsorption–desorption apparatus. Prior to the measurement, the zeolites were degassed at 150 °C under vacuum for 3 h.

Temperature programmed desorption (TPD, Tianjin, China) experiments were performed to evaluate the adsorption amount of NH₃ and NO_x in the presence or absence of C₃H₆. Prior to each of the following experiments, the catalysts were pretreated at 500 °C for 30 min in 5% O₂/N₂, then cooled to the test temperatures in N₂. At test temperatures, NH₃, NO_x, and C₃H₆ (when used) were introduced in 500 ppm NH₃/N₂ until the outlet concentration of NH₃ was stable. The catalysts were purged with N₂ to remove any weakly adsorbed NH₃. Finally, the catalysts were heated from test temperature to 600 °C at a ramp rate of 10 °C min^{−1}.

Thermo Gravimetric (TG) analysis was conducted on the STAR System TGA/DSC1 (Mettler, Zurich, Switzerland) to probe the mass variation during the temperature programming process. The sensitivity of the TG instruments is 0.1 µg, which ensures the veracity of the TG experiments. After the blank experiment, the samples were heated from 50 °C to 950 °C at a ramp rate of 10 °C min^{−1}.

3.4. In Situ DRIFTS Experiments

In situ Diffuse Reflectance Infrared Fourier transform spectra (in situ DRIFTS, Madison, Wisconsin, United States) were performed on Nicolet 6700 FTIR equipped with MCT detector at a resolution of 1 cm^{−1}. Four scans were operated for each spectrum. The total flow rate was 150 mL min^{−1}. Prior to each experiment, the samples were pretreated with 2% O₂/He at 500 °C for 30 min and the background spectra were collected under He gas at test temperature.

For the adsorption experiments, the NH₃ + C₃H₆ or NO + C₃H₆ were introduced into sample at 200 °C until the spectra were stable. And the spectra were collected after purged by He gas.

For the DRIFTS titration experiments of adsorbed NH₃, the 500 ppm NH₃ was firstly introduced into the catalyst at 200 °C until the spectra were stable. Then the catalyst was purged by He gas to eliminate the physically adsorbed NH₃. Finally, the sample was exposed to 500 ppm NO, 500 ppm C₃H₆ (when used), and 5% O₂ until equilibrium was attained.

4. Discussion

4.1. The Effect of C₃H₆ Treatment on Catalyst Structure

Although some researchers reported that the rapid deactivation during the SCR of NO_x with HCs (HCs-SCR) could result from coke formation, which could be due to the blocking of the pore, and reducing the pore volume and surface area of the catalyst [40]. However, based on the obtained results of BET, XRD, and TG of fresh and HCs treated Cu-*SAPO*-34 catalysts, it showed that the BET surface area of Cu-*SAPO*-34 was scarcely affected by 6 h C₃H₆ treatment on its microporous structure. Meanwhile, the CHA structure of Cu-*SAPO*-34 catalyst still remained intact after C₃H₆ treatment and no new crystalline

phase was detected as exhibited in Figure 1, which was consistent with previous results that the zeolite crystal structure did not change before and after propylene poisoning over Fe-zeolite catalyst [40]. Furthermore, according to the results of TG experiments in Figure 2, no obvious coke removal signals were observed except two mass loss peaks which could be assigned to the dehydration process at 100 °C and 250 °C, respectively. Consequently, it could be concluded that the physical properties of Cu-SAPO-34 catalysts were not affected by the long-term HCs treatment compared with the fresh catalysts, and the deactivation phenomenon caused by coke deposition would be less likely to appear on the Cu-SAPO-34 catalysts than other mesoporous molecular sieves.

4.2. The C₃H₆ Effect on the Adsorption Performance of NH₃, NO Species

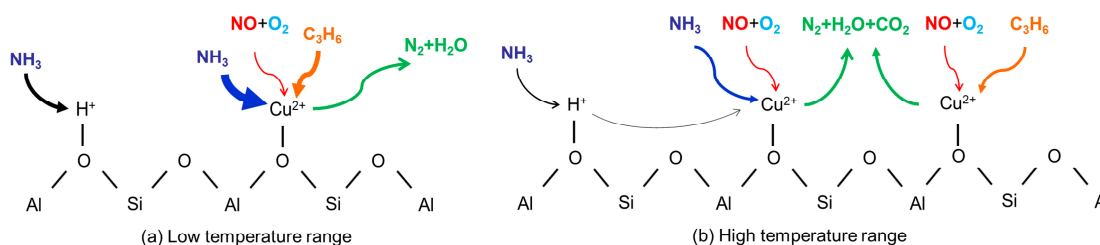
Based on the results of NH₃-TPD and NO_x-TPD with C₃H₆ in Figures 5–7 and C₃H₆-TPD in Figure 8, it was shown that the ammonia adsorption had not been obviously affected by C₃H₆ on the Brønsted acid sites, but competitive adsorption could occur between C₃H₆ and NH₃ on the Cu²⁺ sites. Although ammonia adsorption plays a dominant role in the adsorption process, the denitration performance at low temperature still could be reduced due to the reduction of ammonia adsorption capacity. In addition, the propylene adsorption site mainly ascribed to the copper divalent species, and the adsorption strength of propylene is stronger than that of nitrogen oxides. This could result in that nitrogen oxides cannot be oxidized on copper divalent at low temperature, on which the hydrocarbon SCR reaction was unable to be completed smoothly. Therefore, it would finally cause the decline of de-NO_x reaction activity at low temperature.

4.3. The C₃H₆ Effect on the SCR Performance over Cu-SAPO-34 Catalyst

Based on the obtained results and the published paper, it was shown that the isolated Cu²⁺ cations were proved as both of the active sites for NH₃-SCR reaction and C₃H₆-SCR reaction [45,52]. The standard NH₃-SCR utilizes NH₃ as a reductant to remove NO_x as follows: $4\text{NH}_3 + 4\text{NO} + \text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$. The main products are N₂ and H₂O, while the by-products are NO₂ and N₂O. Herein, at low temperatures (<350 °C), the standard NH₃-SCR is the dominant reaction, whether or not propylene exists, the amount of by-product remains below 15 ppm as shown in Figure 3c. Yet the conversion of C₃H₆-SCR is just under 10% at this time. It is concluded that the competitive adsorption of propylene could play an important role in reducing the probability of adsorbed NH₃ participating in NH₃-SCR reaction on the Cu²⁺ cations, without affecting the product distribution of the NH₃-SCR, while during high temperatures (>350 °C), it was known that the NH₃ oxidation and NH₃-SCR competed with each other during the SCR process. The NH₃ oxidation is one of the main causes of the decline of the NO conversion at high temperature [26]. But NO conversions are surging rather than falling with propylene at the present time, resulting from the increased activity of C₃H₆-SCR on the Cu²⁺ cations which compensates for the loss of de-NO_x efficiency due to the restraint of ammonia oxidation at high temperatures. In other words, C₃H₆-SCR shows the synergistic enhancement effect. Importantly, the amount of by-product still remains below 18 ppm, showing good nitrogen selectivity.

The mechanism of propylene effect on Selective Catalytic Reduction by Ammonia over Cu-SAPO-34 catalyst was shown in Scheme 1. For Scheme 1a, it was essentially shown that the sequence of adsorption strength on the Cu²⁺ sites of the catalysts during the low temperatures were as follows: ammonia > propylene > nitrogen oxides. Importantly, the presence of propylene not only affects the adsorption capacity of ammonia but also hinders the further oxidation of nitrogen oxides on the Cu²⁺ sites, while the above two aspects are of great significance for SCR reaction on the Cu-SAPO-34 catalyst. In short, the influence of propylene at low temperature is mainly reflected in the inhibition of the above adsorption or oxidation process, which ultimately reduces the performance of SCR reaction. For Scheme 1b, the possibility of competitive adsorption of propylene with ammonia and nitrogen oxides was weakened with the increase of reaction temperature. The C₃H₆-SCR under high temperature could synergistically improve the removal efficiency

of nitrogen oxides and inhibit the ammonia oxidation reaction which is unfavorable to the SCR reaction. In brief, the effect of propylene during high temperature is mainly embodied in the enhancement, which through restraining of the ammonia oxidation reaction and providing alternative de-NO_x reaction pathways, i.e., C₃H₆-SCR. These, finally, could give rise to the de-NO_x efficiency of the Cu-SAPO-34.



Scheme 1. The mechanism of propylene effect on NH₃-SCR over the Cu-SAPO-34 catalyst at low temperature range (a) and high temperature range (b).

5. Conclusions

The effect of propylene on NH₃-SCR of NO_x over the Cu-SAPO-34 catalysts has been systematically studied in the present work. Firstly, the XRD and BET results showed that the structure and physical properties of Cu-SAPO-34 were almost not influenced by the propylene treatment. Meanwhile, the TG results proved that coke deposition might not formed on the surface of Cu-SAPO-34 in spite of undergoing a long-term C₃H₆+O₂ treatment. Secondly, the adsorption intensity of C₃H₆ on Cu²⁺ species was stronger than that on the Brønsted sites, and the C₃H₆ mainly adsorbed on the Cu²⁺ sites of Cu-SAPO-34 catalyst. Furthermore, the oxidation state of Cu²⁺ species on the catalyst's surface could be affected by the propylene in the feed gas and it would also influence the adsorption performance of NO_x on Cu species and the formation ratio of nitrite/nitrate. Hence, the competitive effect of C₃H₆ on the adsorption amount and strength of ammonia could not be the dominating reason for the activity decrease of low temperate. Thirdly, the propylene effect on NH₃-SCR of NO_x over Cu-SAPO-34 catalyst could follow two different mechanisms with changes of reaction temperatures. Specifically, the activity decrease of NH₃-SCR with propylene over Cu-SAPO-34 at low temperatures (<350 °C) could result from occupation of the Cu²⁺ sites by C₃H₆ and inhibition to the proceeding of Cu²⁺-Cu⁺-Cu²⁺ redox cycle. Nevertheless, the activity of the occupied Cu species could be recovered and sequentially participate in the NH₃-SCR reaction with an increase of temperature. Meanwhile, the NO conversion efficiency was also benefited by the contribution of C₃H₆-SCR, which could restrain the ammonia oxidation reaction at high temperatures. Consequently, the propylene played a beneficial role in NH₃-SCR process over Cu-SAPO-34 at high temperatures (>350 °C) due to the synergetic contribution of C₃H₆-SCR reaction.

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