

A Comparison of Hydrothermal Aging, SO₂ and Propene Poisoning Effects on NH₃-SCR over Cu-ZSM-5 and Cu-SAPO-34 Catalysts

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Abstract

This study was aimed to investigate the effects of hydrothermal aging, propene and SO₂ poisoning on the ammonia-selective catalytic reduction (NH₃-SCR) performance of both Cu-SAPO-34 and Cu-ZSM-5. The catalytic activities of fresh, aged and poisoned samples were tested in ammonia-selective catalytic reduction (NH₃-SCR) of NO_x conditions. The XRD, TG and N₂-desorption results showed that the structures of the Cu-SAPO-34 and Cu-ZSM-5 remained intact after 750°C hydrothermally aged, SO₂ and propene poisoned. After hydrothermal aging at 750°C for 12 h, the NO reduction performance of Cu-ZSM-5 was significantly reduced at lower temperatures, while that of Cu-SAPO-34 was less affected. Moreover, Cu-SAPO-34 catalyst showed high NO conversion with SO₂ or propene compared to Cu-ZSM-5. However, Cu-ZSM-5 showed a larger drop in catalytic activity with SO₂ or propene compared to Cu-SAPO-34 catalyst. The H₂-TPR results showed that Cu²⁺ ions could be reduced to Cu⁺ and Cu⁰ for Cu-ZSM-5, while no significant transformation of copper species was observed for Cu-SAPO-34. Meanwhile, the UV-vis DRS results showed that CuO species were formed in Cu-ZSM-5, while little changes were observed for the Cu-SAPO-34. Cu-SAPO-34 showed high sulfur and hydrocarbon poison resistance compared to Cu-ZSM-5. In summary, Cu-SAPO-34 with small-pore zeolite showed higher hydrothermal stability and better hydrocarbon and sulfur poison resistant than Cu-ZSM-5 with medium-pore.

Keywords

Hydrothermal Aging, Propene and SO₂ Poisoning, Ammonia-Selective

1. Introduction

Various catalyst technologies such TWC, NSR and SCR have been developed to remove pollutants from engine exhaust [1] [2]. Nitrogen oxide (NO_x) generated by the combustion of fossil fuel, both in transportation and industrial process, is a major air pollutants and specially those working with diesel engine are the main source of NO_x emission [2] [3]. The selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) has become one of the most effective ways to reduce NO_x pollution from diesel exhaust [3] [4] [5]. In a typical after-treatment system of diesel engines, DOC and DPF are used to remove unburned HC, CO and PM upstream of the SCR catalyst. High thermal stability is required for NH₃-SCR because soot removal from DPF occurs at high temperature [6]. According to previous studies [1] [5], various catalysts have been developed for NH₃-SCR, and it has been demonstrated that zeolite-based metal catalysts are the best candidates. Among the transition metal exchanged zeolite, copper exchanged zeolite, NH₃-SCR catalyst, has been recognized to be the most promising due to its excellent low-temperature deNO_x activity [7].

Efforts on several studies have been devoted to Copper ion-exchanged ZSM-5 in order to investigate NH₃-SCR performance [6] [8]. The results demonstrated that Cu-ZSM-5 catalyst has high activity and better stability at high temperatures [9]. However, it is limited by its relatively low activity in the presence of water vapor and by dealumination at high temperatures [10] [11]. The results showed that the catalytic activity was lost as a result of Cu-ion migration, while the zeolite framework remained less affected [12] [13] [14] [15]. Malin *et al.* [16] reported that the hydrothermal stability of Cu-ZSM-5 deNO_x catalysts could be affected by the choice of synthesis condition for the parent ZSM-5. It is also demonstrated that in accordance with theoretical predictions, suggesting that the copper-ions coordinate differently depending on the aluminium distribution of the zeolite [17].

Recently, Cu/CHA catalysts have received widespread attention as ammonia-selective catalytic reduction (NH₃-SCR) on catalysts with excellent activity and N₂ selectivity [18]. Under a real-world application, Cu-SSZ-13 catalysts suffer from two major degradation mechanisms: sulfur poisoning and hydrothermal aging, which are responsible for the change in the nature of active sites [19]. Briend *et al.* [20] reported that the structure and acidity of SAPO-34 rapidly and irreversibly deteriorated when exposed to moisture at low temperature after the template was removed, this became a major drawback for its practical application. The application of transition metal exchanging the zeolite catalysts also led to catalyst deactivation due to sulfur and hydrocarbon poisoning, which are detrimental to the performance of NH₃-SCR system [21]. The main focus hereby

were the effects of sulfur and hydrocarbon poisoning on the NH₃-SCR system over Cu-ZSM-5 and Cu-SAPO-34 catalysts. During cold start condition and the time when the upstream oxidation catalysts are not active, the inhibition of zeolite catalytic activity in the presence of propene occurs [9] [22] [23] [24]. Lei *et al.* [25] [26] reported the mechanism of propene poisoning on Cu-CHA, and the results demonstrated that the competitive adsorption process between NO_x and propene contributed to the deactivation of the catalysts. Until now, the cause of catalytic performance inhibition of both Cu-ZSM-5 and Cu-SAPO-34 in the presence of sulfur and hydrocarbon has remained on the debate [27] [28]. Meanwhile, the discrepancies between Cu-ZSM-5 and Cu-SAPO-34 upon the hydrothermal aging in the whole testing temperature range still have not been clear. The aims of this study is to investigate the impacts of hydrothermal aging, SO₂ and propene poisoning on Cu-SAPO-34 and Cu-ZSM-5 catalysts. A series of analytical techniques, including XRD, BET, TG, UV-vis-DRS, H₂-TPR and NH₃-TPD were herein used to characterize the structure, acidity, and evaluate the Cu site changes during the hydrothermal treatment.

2. Experimental

2.1. Catalysts Preparation

H-SAPO-34 was prepared by a hydrothermal method. The mixture solution of Orthophosphoric acid (H₃PO₄, 85 wt%), morpholine (MOR, 99 wt%), aluminium (boehmite, 75 wt%) and silica (silica sol, 30 wt%) was stirred for 5 h at a temperature of 38 °C. The mixture was put in autoclave at 200 °C for 48 h under autogenous pressure for crystallization process. The product was filtered, washed, dried at 110 °C overnight and the dried product was calcined in the air at 550 °C for 4 h. H-SAPO-34 was ion-exchanged with NH₄⁺ ion by using NH₄NO₃ (95 wt%). Then, the solid was filtered, washed with deionized water and the obtained sample NH₄⁺-SAPO-34 was dried at 110 °C overnight before the ammonium-exchange process was repeated for a total of two exchanges. The Cu-SAPO-34 zeolite was also prepared via wet ion exchange method by using an aqueous solution of copper sulfate (2%) [29] [30]. The mixture of copper sulfate aqueous solution (0.1M) and the NH₄⁺-SAPO-34 was magnetically stirred for 12 h at 70 °C. The product was washed with deionized water and dried at 110 °C overnight. After the product was dried, it was calcined in the air at 550 °C for 4 h.

The Cu/ZSM-5 catalyst was prepared using a commercial H-ZSM-5 (SiO₂/Al₂O₃ = 25) by the improved incipient wetness impregnation method, as previously reported [31]. It was performed by mixing the H-ZSM-5 powders with the required amount of Cu (NO₃)₂ solution at ambient temperature. The mixture was stirred and then ultrasonically treated for 1 h. The prepared sample was dried at 100 °C for 12 h, calcined at 500 °C for 2 h. After calcination, certain amount of water was added to the as-prepared powders, and then all these were mixed to form some well-proportioned slurries. A cordierite (cylinder, diameter: 11 mm, length: 22 mm, bulk: 2.1 cm³, 400 cell·cm⁻²) was coated by dipping it into the

slurries [32].

2.2. NH₃-SCR Activity Evaluation

The monolithic SCR catalyst was used to evaluate the catalytic activity. Firstly, a certain amount of powder was added into deionized water to form slurry until the channel was filled with liquid. And then, the cordierite (cylinder, diameter: 11 mm, bulk: 2.1 cm³, length: 22 mm, 400 cell·cm⁻²), was put in the as-prepared slurry until the channel was filled with liquid. The immersion times and concentration of slurry were controlled strictly, in order to deposit a similar amount of catalyst powder on each cordierite. Finally, the activity of the monolithic SCR catalysts was tested in fixed-flow reactor (VDRT-200SCR) produced by Quzhou Vodo instrument Co. Ltd., China. The temperature was varied from 225°C to 550°C. The reaction gas mixture was typical: 1000 ppm NO, 1100 ppm NH₃, 5% O₂, 10% water vapor and N₂ as the carrier gas. The water vapor was generated by passing N₂ through a heated gas-wash bottle containing deionized water. The total flow rate was 1000 L·min⁻¹ and thus a GHSV was obtained 30,000 h⁻¹. The NO gas concentration in an outlet stream was monitored by an exhaust analyzer. An NH₃ trap containing phosphoric acid solution was installed before the input of the exhaust analyzer to avoid errors caused by the reduction of NH₃. The NO conversion of catalyst was evaluated as follows [33].

$$[\text{NO}] = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) \times 100 / [\text{NO}]_{\text{in}}$$

The interactions between propene or SO₂ and NO_x on the catalyst surface were investigated [34]. At a steady state, a gas mixture containing 50 ppm SO₂ or 50 ppm propene, 1000 ppm NO, 1100 ppm NH₃, 5% O₂, 10% water vapor and N₂ was introduced into the reactor [35]. The total flow rate was 1000 L·min⁻¹ and thus a GHSV was obtained 30,000 h⁻¹.

The hydrothermal aging was performed in a simulated diesel engine exhaust gas composed of 10% H₂O in air with a flow rate of 1000 cm³/min for 12 h at 650°C, 700°C and 750°C, respectively.

2.3. Catalyst Characterization

X-ray diffraction measurements were conducted on multi-sample Philips X'Pert diffractometer with a Cu K α detector, and the diffraction angle ranged from 5° to 50° at a scanning speed of 5°/min. The surface area and N₂ physisorption isotherm (77.3 K) were determined using Micrometrics ASAP 2020M surface area and porosity analyzer from the linear portion of the BET plot by measuring the N₂ isotherm of the samples. A UV-vis-DRS absorbance spectrum was obtained at a room temperature on a Shimadzu spectrophotometer. The temperature-programmed desorption of hydrogen (H₂-TPR) was conducted on Micrometrics AutoChem 2920II chemisorption analyzer. After being pre-treated in Ar at 550°C for 1 h, the sample was cooled down to 40°C. Finally, the sample was heated to 1000°C in a flow of 10% H₂/Ar at a ramp rate of 10°C/min. The liquid nitrogen cold trap was used to remove the interference of H₂O. The tempera-

ture-programed desorption of ammonia (NH_3 -TPD) was also carried out on Micrometrics AutoChem 2920II chemisorption analyzer. 50 mg of the sample was first pre-treated in Ar at 550 °C for 1 h to remove the impurities, and then cooled down to 100 °C. The sample was saturated with 3000 ppm NH_3/Ar at 100 °C for 45 min. After that, the sample was purged with Ar for 1 h to remove the physical adsorption NH_3 and then heated in Ar from 100 °C to 600 °C at ramp rate of 10 °C/min. The outlet NH_3 was monitored by the thermal conductivity detector. Thermal analysis was performed in a TGA/DSC system. The samples were heated in the flowing 20/min Air as protective gas from 50 °C to 700 °C at ramp rate of 10 °C/min [36]. 50 ppm of SO_2 or propene was introduced into the reactor for 1 h, then the weight signals were recorded.

3. Results and Discussions

3.1. Activity Test

NH_3 -SCR performance of Cu-SAPO-34 and Cu-ZSM-5, along with their hydrothermal aged catalysts, were examined between 200 °C and 550 °C. As shown in **Figure 1**, an excellent NO reduction activity was obtained from fresh Cu-ZSM-5 and Cu-SAPO-34 catalysts. While the fresh Cu-ZSM-5 catalyst presents an inferior NO conversion in the range of lower and higher temperatures, it exhibits a superior NO conversion between 250 °C and 350 °C. After hydrothermal aged at 650 °C for 12 h, the catalytic activities of Cu-SAPO-34 catalyst is well maintained and only seen a slight decrease at lower temperatures (<250 °C) and higher temperatures (>500 °C). However, with further increasing the aging temperature to 750 °C, as presented in **Figure 1(a)**, shows a slight decline of NO conversion, corresponding to a 10% reduction in the catalytic activity of Cu-SAPO-34 aged (750 °C) compared with the fresh catalyst. **Figure 1(b)** shows that, after aging at 650 °C for 12 h, the catalytic activities of Cu-ZSM-5 catalyst are maintained at higher temperature (>400 °C) and significantly dropping at temperatures < 400 °C. After increasing the aging temperature to 700 °C, the catalytic activities of Cu-ZSM-5 almost remain the same, at the temperature > 450 °C and then they further decrease at temperature < 450 °C. Interestingly, with further increasing the aging temperature to 750 °C, the NO conversions are well-maintained at temperatures > 500 °C, and further dropping at temperature < 500 °C. For instance, the NO conversion of Cu-ZSM-5 aged (750 °C) drop from 90% to 20% at 500 °C and 200 °C, respectively. Following the hydrothermal treatment at 750 °C for 12 h, a slight loss of NO_x reduction activity is observed in Cu-SAPO-34 at low and high temperatures, and a total loss is observed for Cu-ZSM-5 in a part (temperature < 500 °C) as shown in **Figure 1**. Ja *et al.* [1] found similar results, they reported that the total loss of activity of Cu-ZSM-5, in part, could be detected owing to the increased N_2O formation following hydrothermal aging.

During an operation of diesel engine, the catalyst is exposed to a hydrocarbon coking and a hostile environmental where SO_2 is an important contaminant generated by burning sulfurous species in fuels [9]. **Figure 1(c)** and **Figure 1(d)**

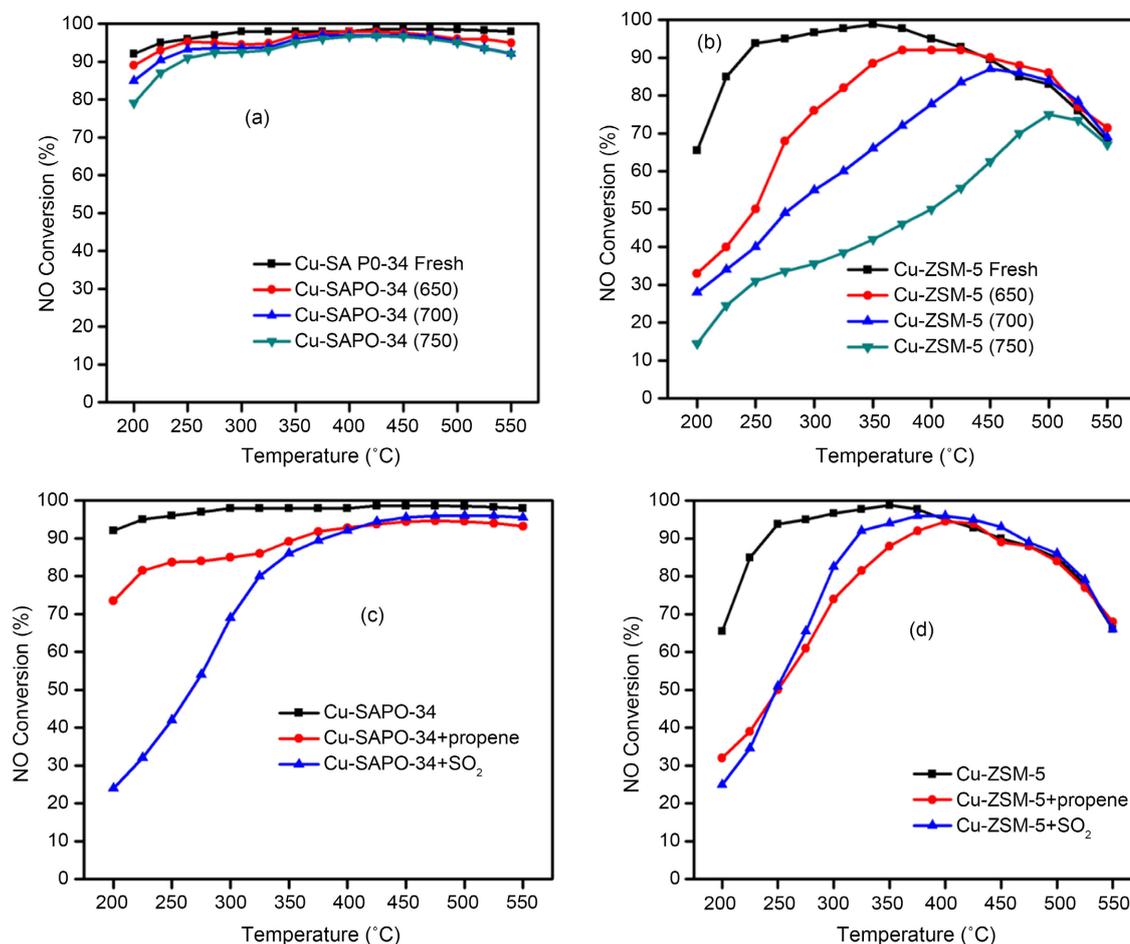


Figure 1. NH_3 -SCR performance of the fresh, aged and poisoned: (a) Cu-SAPO-34; (b) Cu-ZSM-5; (c) Poisoned Cu-SAPO-34; (d) Poisoned Cu-ZSM-5 catalysts.

show the NO conversion with propene or SO_2 over Cu-ZSM-5 and Cu-SAPO-34 catalysts. After propene and SO_2 poisoning, the Cu-SAPO-34 show that the NO conversions are well-maintained at a temperature above 350°C , but the NO conversion of Cu-SAPO-4 with propene slightly decreases, and that of Cu-SAPO-34 with SO_2 significantly decreases at temperature below 350°C . However, the NO conversion of Cu-ZSM-5 in the presence of propene or SO_2 is maintained at temperature above 350°C and then dramatically dropping at a temperature below 350°C .

3.2. XRD and BET

In order to better understand the changes in the NO_x reduction activity induced by hydrothermal aging, the changes in the morphology and the structure of the zeolites catalysts were examined by using XRD and N_2 -desorption techniques. The XRD patterns show that the fresh Cu-ZSM-5 has MFI structure and the fresh SAPO-34 has the typical CHA structure as shown in **Figure 2**. After hydrothermal aging, no detectable CuO crystallites are observed in any of two catalysts [37], probably due to the proper dispersion of the Cu species or the CuO

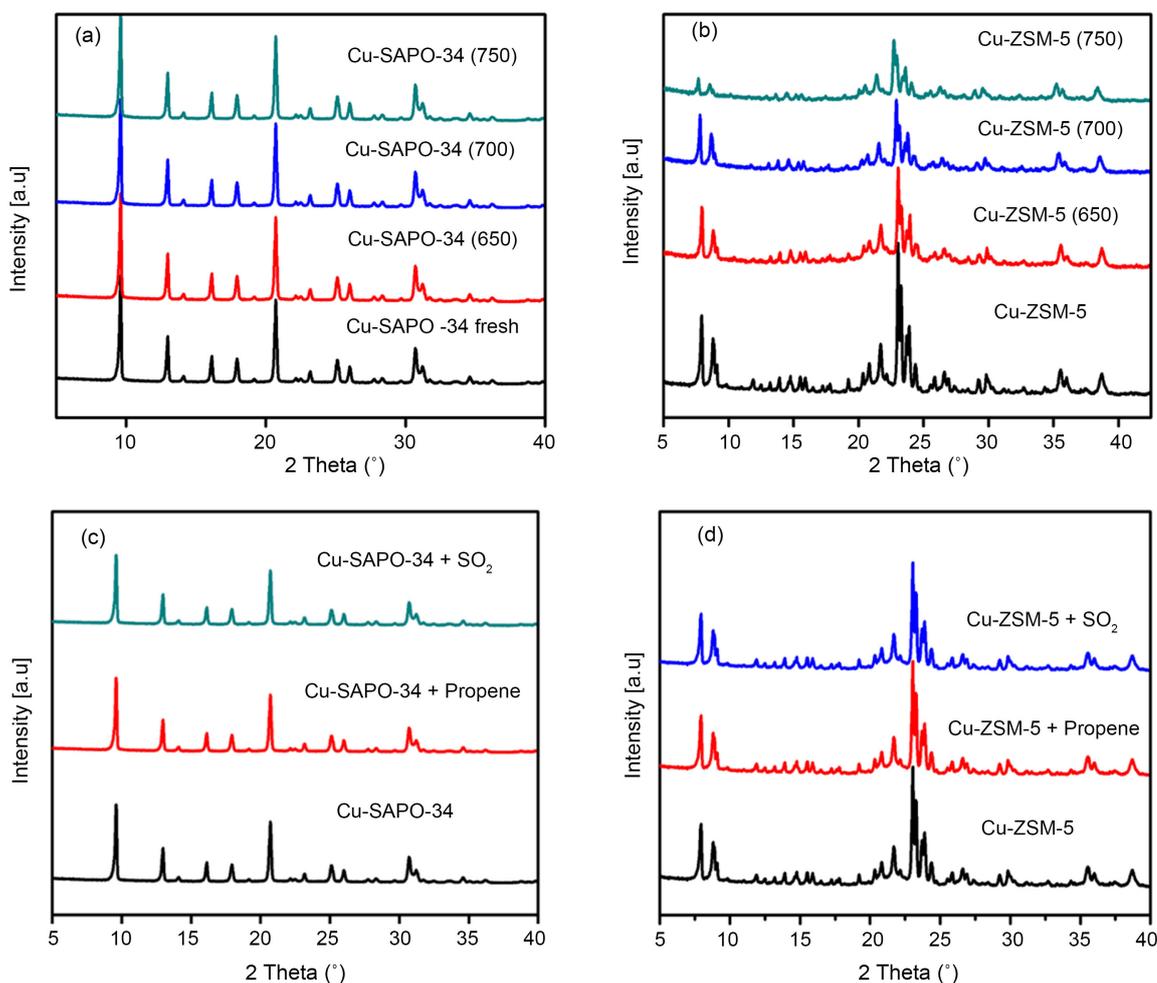


Figure 2. XRD patterns of the fresh, aged and poisoned: (a) Cu-SAPO-34, (b) Cu-ZSM-5, (c) poisoned Cu-SAPO-34 and (d) poisoned Cu-ZSM-5 catalysts.

particles are too small to be detected. In addition, the XRD patterns of fresh and aged samples show no changes for Cu-SAPO-34, which indicates that the zeolite structure remains largely intact during the hydrothermal aging [1] [37]. However, little changes are observed for Cu-ZSM-5, suggesting that its structure also remains less affected during the hydrothermal aging [38]. Based on the relative crystallinity, the BET surface area and micropore volume results show that the hydrothermal have no significant effect on the crystal structure or textural properties of Cu-SAPO34 catalyst.

Even for the Cu-SAPO-34-750 sample, its relative crystallinity remained almost 95%. Compared with Cu-ZSM-5, the surface area and micropore volume of Cu-ZSM-5 Aging (750 °C) drop from 342 to 280 $\text{m}^2\cdot\text{g}^{-1}$ and 0.16 to 0.08 $\text{cm}^3\cdot\text{g}^{-1}$, respectively (Table 1). These results in good agreement with the early report, which indicates that the Cu-ZSM-5 catalyst displays good hydrothermal stability, however, it is remarkable that Cu-SAPO-34 displays a better hydrothermal stability. After propene and SO_2 poisoning, the physical properties were investigated by using the XRD, and the results are shown in Figure 1(c) and Figure 1(d).

Table 1. Physicochemical properties of CU-SAPO-34 and Cu-ZSM-5 before and after hydrothermal aging at 750 °C.

| Samples | S _{BET} (m ² ·g ⁻¹) | Micropore volume (cm ³ ·g ⁻¹) |
|------------------|---|--|
| Cu-SAPO-34 | 633 | 0.2866 |
| Cu-SAPO-34 (650) | 633 | 0.2864 |
| Cu-SAPO-34 (700) | 632 | 0.2830 |
| Cu-SAPO-34 (750) | 330 | 0.2812 |
| Cu-ZSM-5 | 342 | 0.16 |
| Cu-ZSM-5 (650) | 335 | 0.13 |
| Cu-ZSM-5 (700) | 319 | 0.11 |
| Cu-ZSM-5 (750) | 280 | 0.08 |

For Cu-ZSM-5 catalysts, the results show that all the XRD patterns and their intensities are well-preserved after SO₂ and propene poisoning. Similar results are obtained between Cu-SAPO-34 catalyst and its propene or SO₂ poisoning form. These results confirm that the crystalline structure of the sample is well-preserved after hydrothermal treatment, propene and SO₂ poisoning.

3.3. H₂-TPR

H₂-TPR experiments were performed to examine the effects of hydrothermal aging on the nature of Cu species [37]. **Figure 3** represents the H₂-TPR profiles of the fresh and aged catalysts. According to the literature, the H₂-TPR spectra collected over fresh and aged Cu-ZSM-5 zeolites could be divided into two groups based on the reducibility of copper species. According to the early report [37] [39], it was suggested that Cu²⁺ is reduced to Cu⁺ at ~ 200 °C, while Cu⁺ ions is reduced to Cu⁰ at 250 °C - 350 °C for Cu-ZSM-5 catalysts. The hydrogen reduction peaks of Cu-ZSM-5 and Cu-ZSM-5 (650) were similar. Increasing the temperature of hydrothermal aging to 750 °C, significant differences in the H₂-TPR patterns were observed over the Cu-ZSM-5 as shown in **Figure 3(b)**. The peak at ~200 °C tends to disappear with a further increase of the hydrothermal aging temperatures, indicating the migration of copper species might have taken place and that a much more stable copper species was formed during the high temperature hydrothermal treatment [4]. In addition, the peak assigned to the reduction of Cu⁺ to Cu⁰ at 250 °C - 350 °C gradually increased with the increase of the hydrothermal aging temperature. Thus, the amount of isolated Cu²⁺ ions in the structure of Cu-ZSM-5 catalyst decreases while the CuO increases after the hydrothermal treatment, which could be attributed to the transformation of isolated Cu²⁺ ions to CuO species. However, the H₂ consumption profiles of Cu-SAPO-34 catalysts could be divided into three peaks (A, B and C) based on the reducibility of Cu ions. According to the reviewed literature, peak A appearing at (200 °C - 300 °C) represents the reduction of isolated Cu²⁺ ions to Cu⁺ ions, peak B appearing at (500 °C - 600 °C) could be assigned to the reduction of CuO to

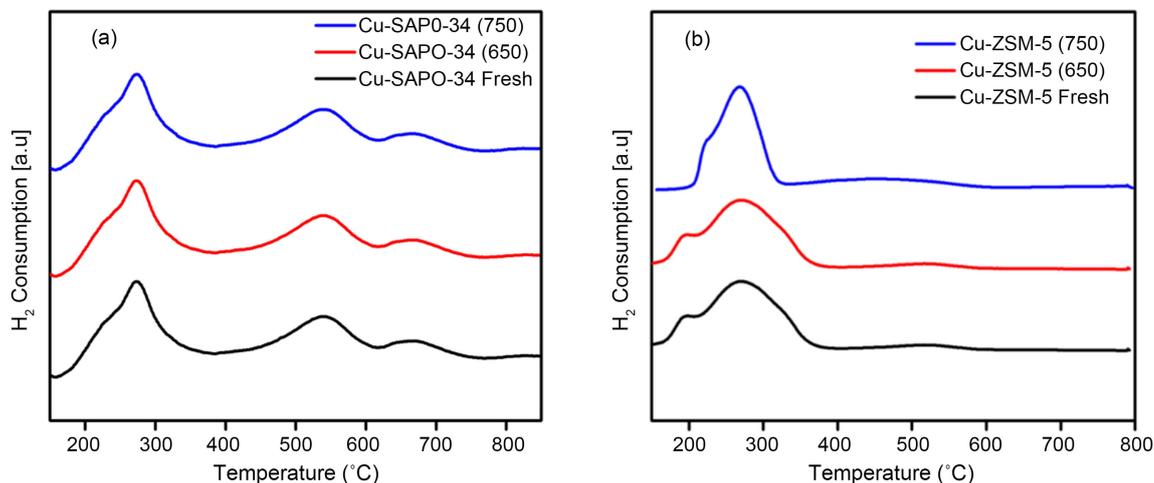


Figure 3. H₂-TPR profiles of the fresh and aged: (a) Cu-SAPO-34 and (b) Cu-ZSM-5 catalysts.

Cu⁰ and peak C appearing at high temperature (600°C - 700°C) being attributed to the reduction of Cu⁺ ions to Cu⁰ [1] [3] [9] [24] [30]. **Figure 3(a)** shows that the reduction peaks are still present and are almost maintained after hydrothermal aging of Cu-SAPO-34 at 650°C, 700°C and 750°C for 12 h. Moreover, the H₂ consumed are quite similar to both fresh and aged samples, suggesting relatively small changes in the distribution of Copper species in their zeolite structures [1].

3.4. UV-Vis-DRS

The UV-vis spectra of fresh and aged Cu-SAPO-34 and Cu-ZSM-5 catalysts are shown in **Figure 4**. As can be seen, fresh Cu-SAPO-34 and Cu-ZSM-5 exhibited two bands at ~200 and ~210 nm, and at ~800 and 700 nm, respectively. The band located at lower wavelengths can be assigned to a charge transfer (CT) band, while the band at higher wavelengths was attributed to the d-d transitions of isolated Cu²⁺ ions in distorted octahedral surrounding by oxygen in CuO particles [40] [41]. After the hydrothermal aging of Cu-SAPO-34 at 650°C for 12 h, the band ascribed to the isolated Cu/Cu²⁺ ions remained unchanged in its intensity, and its position was slightly shifted to 215 nm due to a strong interaction between copper species and the SAPO-34 support. Up to the aging temperature of 750°C, that band related to the CuO species gradually disappeared, while the band related to the isolated Cu/Cu²⁺ ions remained high in its intensity. These changes confirm that, during the hydrothermal process of Cu-SAPO-34 catalyst, the copper oxide species on the external surface could disperse as copper ions and migrate to the exchanged sites, rather than sintering to even larger particles on the external surface [41]. In the order hand, the hydrothermal treatment may enhance the performance of NH₃-SCR over Cu-SAPO-34. As for the Cu-ZSM-5, both bands ascribed to isolated Cu/Cu²⁺ ions and the CuO species significantly changed after the hydrothermal treatment at 650°C during 12 h. The band at 210 nm shows a significant decrease in its intensity, while that of high wavelength shows a significant increase in intensity. This phenomenon becomes more significant with the temperature increase of hydrothermal aging to 700°C for 12 h.

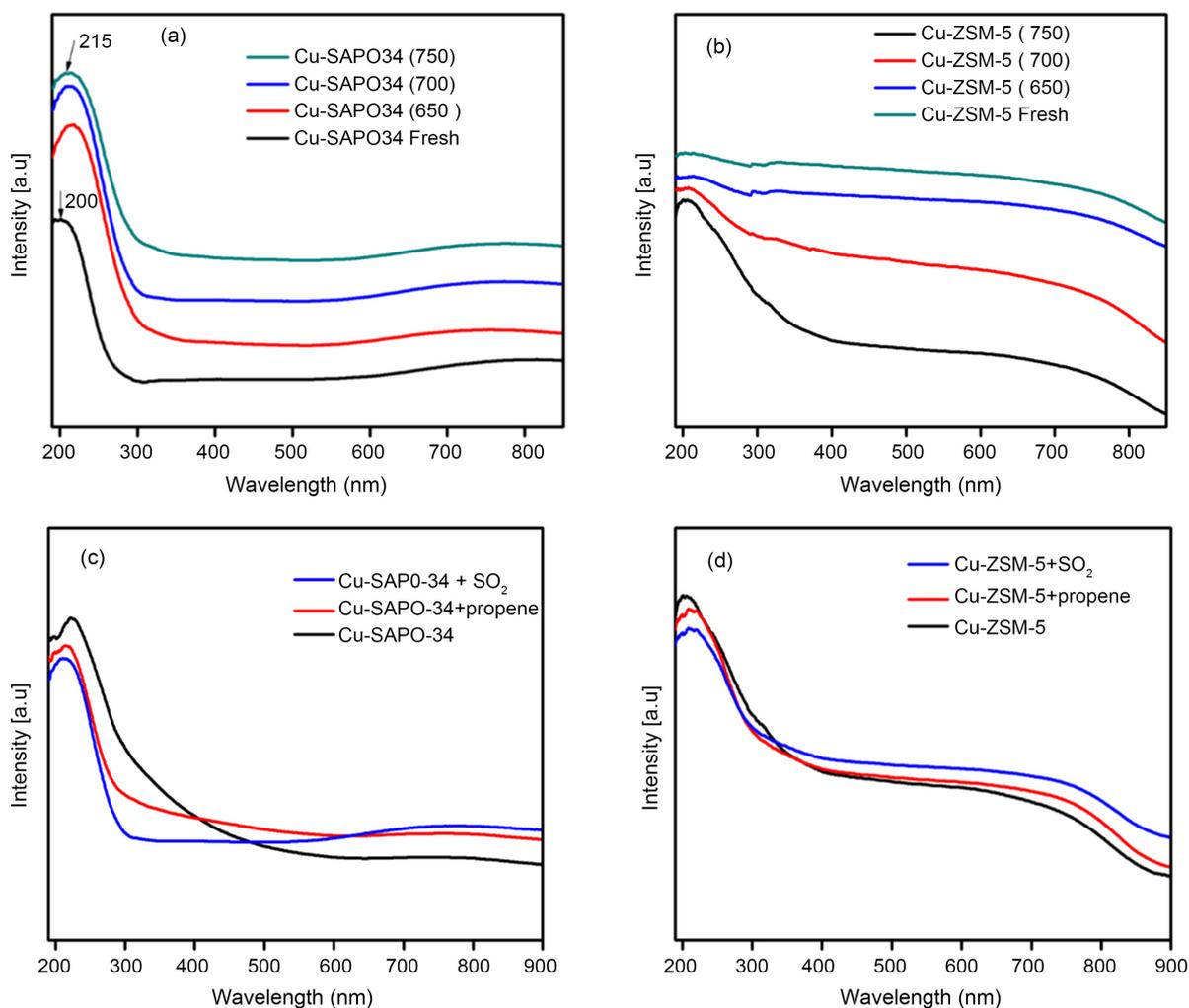


Figure 4. UV-vis-DRS profiles of the fresh, aged and poisoned: (a) Cu-SAPO-34; (b) Cu-ZSM-5; (c) poisoned Cu-SAPO-34; (d) poisoned Cu-ZSM-5 catalysts.

Interestingly, further increase of temperature was marked at 750°C for 12 h, the band related to isolated Cu/Cu²⁺ ions tends to disappear, while that band attributed to CuO species becomes larger. These changes during hydrothermal aging of Cu-ZSM-5 catalyst confirm that, the copper ions are transformed to copper oxide species, which migrate to the external surface. After propene or SO₂ poisoning, it is observed that the bands centered at 200 - 250 nm decrease in the intensity, while those bands centered at 600 - 800 nm increase. These results demonstrated an effect on Cu²⁺ sites upon propene and SO₂ addition, leading to the reduction in the number of isolated Cu²⁺ ions and the formation of Cu_xO_y clusters.

3.5. NH₃-TPD

NH₃-TPD is used to determine the strength and the amount of different acid sites [38]. In order to probe the effect of hydrothermal aging on the acidity of Cu-SAPO-34 and Cu-ZSM-5, NH₃-TPD measurement is performed on the fresh

and hydrothermally aged catalysts as shown in **Figure 5**. Both fresh Cu-SAPO-34 and Cu-ZSM-5 catalysts show three NH₃ desorption peaks. Furthermore, a low-temperature peak at around 170 °C and 180 °C was attributed to the weakly adsorbed NH₃ on the weak Lewis acid sites, a medium-temperature peak at 230 °C and 270 °C due to the NH₃ adsorbed on the strong Lewis acid sites was created by the isolated Cu²⁺ ions at around 280 °C and a high-temperature desorption peak at 390 °C and 360 °C was assigned to the NH₃ desorption from the Brønsted acid sites, respectively [33] [38] [41].

The acid amounts of the fresh and hydrothermally aged catalysts obtained by deconvolution of the NH₃-TPD curves are shown in **Table 2**. After the hydrothermal treatment at 650 °C for 2 h, all of the acid sites were reduced as compared with the fresh catalyst due to the destruction of the MFI structure and the loss of isolated Cu²⁺ ions. Following the hydrothermal aging at 750 °C, the desorption peaks of ammonia ligands bound to copper cations and the chemical desorption peaks on strong acid sites decreased for Cu-ZSM-5 catalysts. Taking into account the above results, it was obvious that the hydrothermal treatment of Cu-ZSM-5 catalyst would result in a drop in the ammonia ligands bound to copper cations. A similar result was found by Lei *et al.* [4], and they demonstrated that it might be mainly caused by the migration of copper species and the result in a decrease in the Lewis and Brønsted acidity. However, after hydrothermal treatment of Cu-SAPO-34, all of the acid sites were similar compared to their fresh counterpart. Therefore, the hydrothermal aging showed a slight effect on the isolated Cu²⁺ ions for the Cu-SAPO-34 catalyst. For instance, the 750 °C aging treatment reduces the strong Lewis acidity in the Cu-ZSM-5 catalyst from 0.23 to 0.11 mmol/g, yet the decline in the Cu-SAPO-34 (750) catalyst is negligible. These results indicated that the isolated Cu²⁺ ions were better preserved in the Cu-SAPO-34 (750) catalyst, which is also in good agreement with the UV and H₂-TPR results. In addition, it is widely accepted that the transformation of Cu²⁺ ions to CuO occurs during the hydrothermal process, and the formation of CuO may result in the collapse of zeolite structure of Cu-ZSM-5. Meanwhile, the hydrothermal treatment of Cu-SAPO-34 catalyst improves its NH₃-SCR performance.

Table 2. The adsorbed NH₃ content over the fresh and hydrothermal aged catalysts.

| Samples | A (mmol/g) | B (mmol/g) | C (mmol/g) | Total amount (mmol/g) |
|------------------|---------------|---------------|---------------|--------------------------|
| Cu-SAPO-34 | 0.39 | 0.33 | 0.24 | 0.96 |
| Cu-SAPO-34 (650) | 0.38 | 0.31 | 0.23 | 0.92 |
| Cu-SAPO-34 (750) | 0.36 | 0.31 | 0.21 | 0.88 |
| Cu-ZSM-5 | 0.28 | 0.23 | 0.17 | 0.68 |
| Cu-ZSM-5 (650) | 0.22 | 0.19 | 0.15 | 0.56 |
| Cu-ZSM-5 (750) | 0.15 | 0.11 | 0.08 | 0.36 |

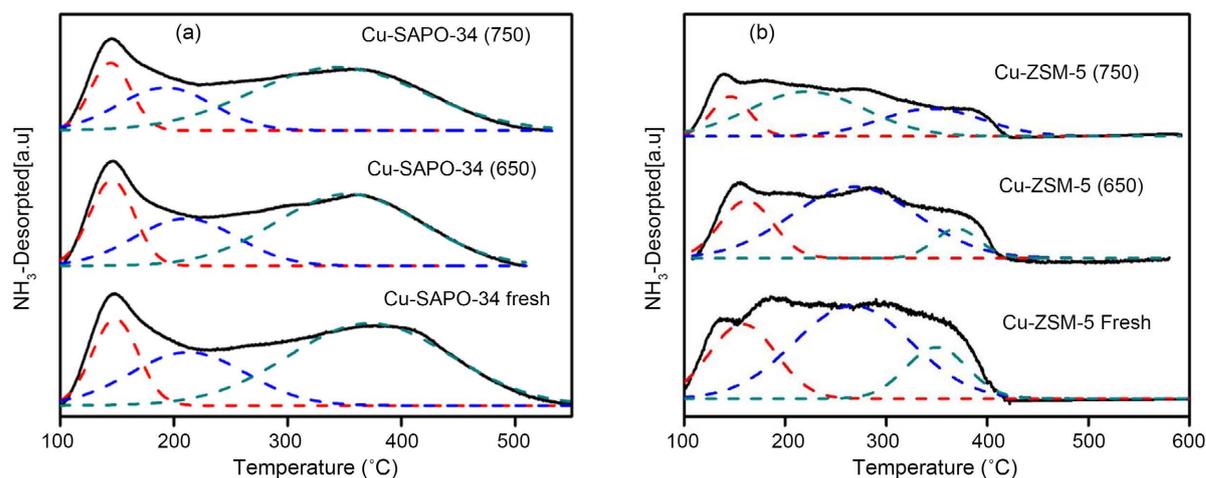


Figure 5. NH₃-TPD profiles of the fresh and aged: (a) Cu-SAPO-34 and (b) Cu-ZSM-5 catalysts.

3.6. Resistance to Propene and Sulfur Dioxide

The standard SCR reaction activities were performed over the monolith-supported Cu-ZSM-5 and Cu-SAPO-34 samples from 200°C - 550°C. According to the above-given results, it has been proved that the catalytic activity is maintained at higher temperature and significantly dropping at a temperature between 200°C and 300°C after propene and SO₂ exposing. Similar results were reported by Li Zhang *et al.* [42], in which the SO₂ significantly decreases the catalytic activity at low temperature (130°C - 300°C). Wenkang *et al.* [43] also reported that a significant decrease of the activity was detected for the poisoned catalyst at 130°C - 350°C and more pronounced degradation was found in the mid-temperature range (250°C - 350°C). In order to further investigate the effects of sulfur and hydrocarbon poisoning on the catalytic activities, Cu-ZSM-5 and Cu-SAPO-34 catalysts were exposed to propene and SO₂. The effects of SO₂ and the propene on Cu-ZSM-5 and Cu-SAPO-34 at various temperatures 250°C, 350°C and 450°C are shown in **Figure 6**. The results show that at 450°C, NO conversion decreases from 98% to 97% and from 90% to 85% for Cu-SAPO-34 and Cu-ZSM-5 catalysts, respectively. After a removal of SO₂, the activity almost recovered to the same value as it was at the beginning, at higher temperatures as shown in **Figure 6(a)** and **Figure 6(b)**. In addition, at 350°C, NO conversion decreases from 96% to 88% and from 94% to 73% for Cu-SAPO-34 and Cu-ZSM-5 catalysts, respectively, while at 250°C with significant decreases from 92% to 70% and 93% to 65%. Meanwhile, the catalytic activity could recover to some extent at 250°C and 350°C. **Figure 6(c)** and **Figure 6(d)** show the results of propene effect on the catalytic activities of Cu-SAPO-34 and Cu-ZSM-5 catalysts, respectively. The results show that the NO conversions at 250°C, 350°C and 450°C decrease were in existence when the Cu-SAPO-34 and Cu-ZSM-5 were exposed to propene. The NO conversion of Cu-SAPO-34 catalyst decreases from 98% to 97% at 450°C, 96% to 93% at 350°C and 93% to 80% at 250°C, respectively. Thus, the catalytic activity of Cu-SAPO-34 in the presence of propene at 350°C and 450°C exhibits a slight change compared with that of 250°C. However, the

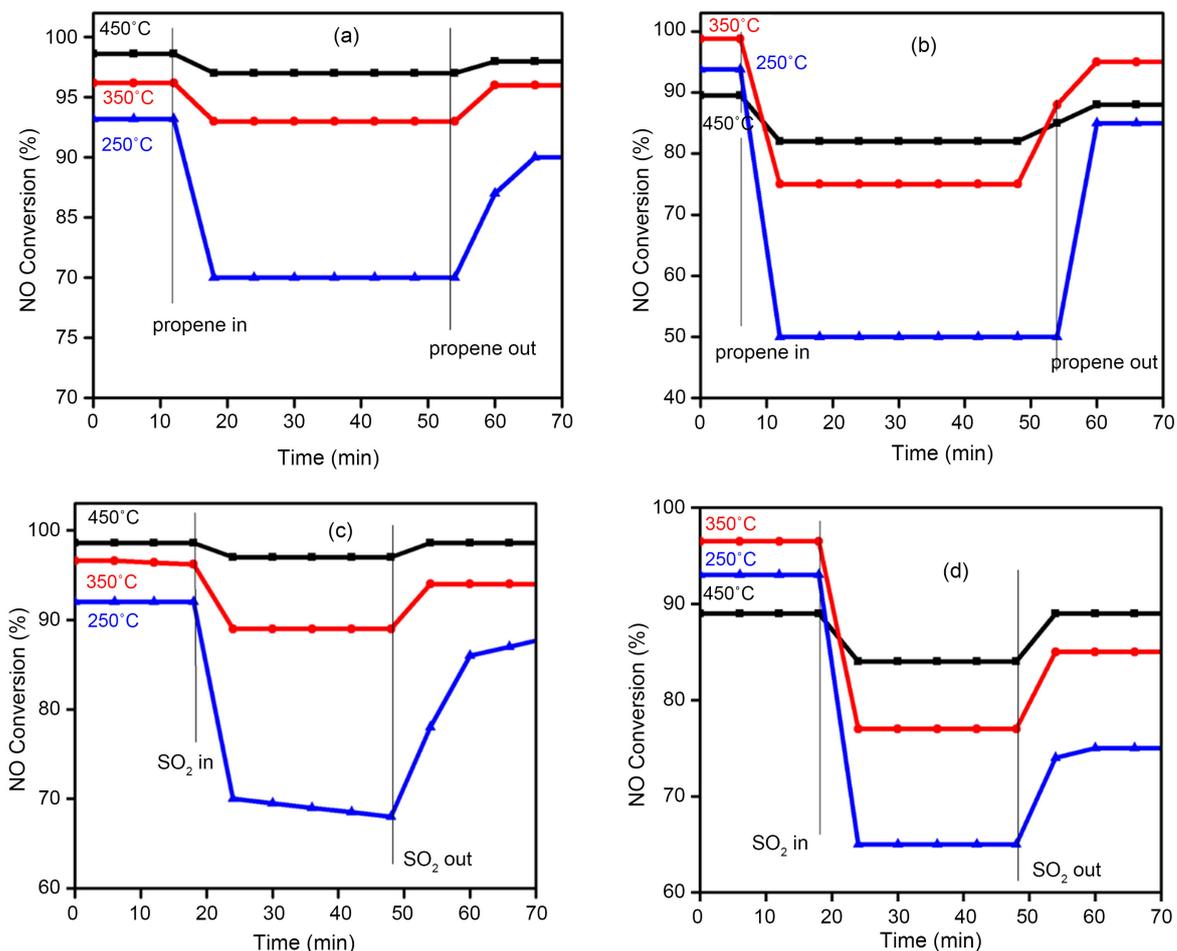


Figure 6. The deactivation at various temperature of: (a) Cu-SAPO-34 with propene; (b) Cu-ZSM-34 with propene; (c) Cu-SAPO-34 with SO₂; ZSM-5 with SO₂ catalysts. Reaction conditions: 1.25 g catalyst, 50 ppm SO₂ or 50 ppm propene, 1000 ppm NO, 1100 ppm NH₃, 5% O₂, 10% water vapor and N₂.

NO conversion of ZSM-5 decreases from 89% to 82% at 450°C, 98% to 75% at 350°C and 93% to 50% at 250°C, respectively. After an injection of propene into Cu-ZSM-5 catalyst, the results show that the catalytic activity drops by propene at 350°C and 450°C. However, the catalytic activity of Cu-ZSM-5 significantly decreases at low temperature (250°C). After the propene was removal, the catalytic activity could recover to some extent at 250°C, 350°C and 450°C.

3.7. TG

TG was conducted to further investigate the changes in the zeolite structure after being exposed to the propene or SO₂ at 250°C as shown in **Figure 7**. The results show a slight drop and a significant drop in TG curves at a temperature below 200°C for Cu-SAPO-34 and Cu-ZSM-5 catalysts, respectively, which were attributed to the weight loss. Similar results were found by Qing *et al.* [9], the weight loss was attributed to the removal of deposited carbonaceous on the catalyst. It was obvious that coke formation in Cu-ZSM-5 was larger than in Cu-SAPO-34 catalyst.

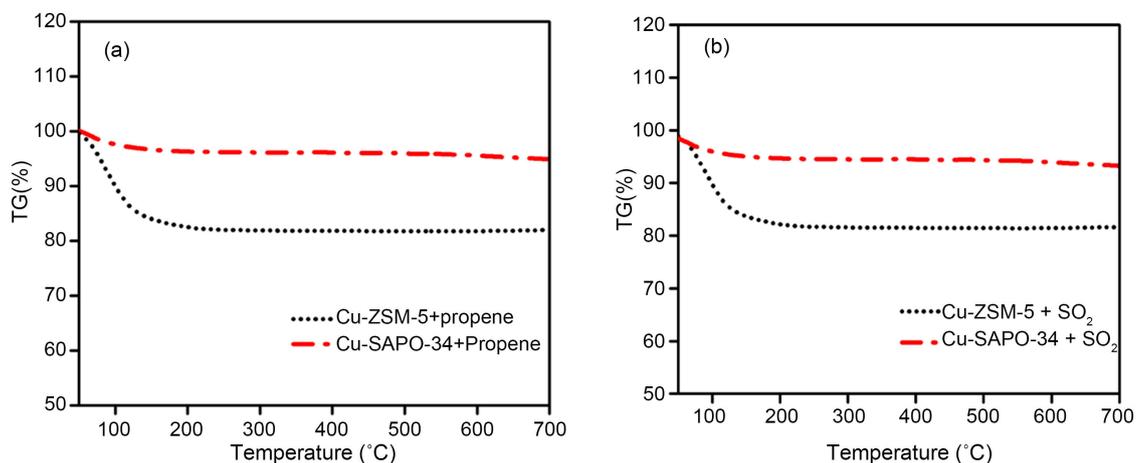


Figure 7. TG curves of poisoned: (a) Cu-SAPO-34 and (b) Cu-ZSM-5 catalysts.

3.8. The Effect of Hydrothermal Aging, Propene and SO₂ on the NH₃-SCR Performance of Cu-SAPO-34 and Cu-ZSM-5 Catalysts

This study was conducted in order to assess the behaviors of Cu-SAPO-34 and ZSM-5 catalysts after hydrothermal aging. Concretely, we tested the catalytic activity of both commercial Cu-SAPO-34 and Cu-ZSM-5 catalysts aged at 650 °C, 700 °C and 750 °C for 12 h, and compared the changes in their microstructure properties, acidity and copper species. The activity test results indicated that Cu-SAPO-34 was much more robust than Cu-ZSM-5 at the temperatures < 450 °C and was resistant to harsh hydrothermal treatment. Cu-SAPO-34 (700) and Cu-SAPO-34 (750) showed a slight decrease in activity at low and high temperatures, while Cu-ZSM-5 (700) and Cu-ZSM-5 (750) showed very low NO conversion at the temperatures < 450 °C. Lei *et al.* [41] reported that after hydrothermal treatment at 700 °C for 48 h, the Cu-exchanged SAPO-34 showed no deterioration in SCR activity, and no essential changes in the structure were observed. However, the SCR activity of the aged Cu-SAPO-34 was found to be improved. We speculated that the slight decrease in activity of Cu-SAPO-34 could be explained by the differences in hydrothermal aging treatment operating conditions. In addition, Ja *et al.* [1] reported that after hydrothermal treatment at 800 °C for 16 h, Cu-ZSM-5 was found losing its NH₃-SCR activity. Following the hydrothermal aging at 750 °C for 12 h, significant differences in the H₂-TPR and UV patterns were observed for Cu-ZSM-5 catalysts. Considering these observed changes, it seems like some Cu²⁺ ions in aged Cu-ZSM-5 are still located in ion exchange position within the zeolite, which are responsible for the high NO_x reduction activity at higher temperatures. Recently, Ja *et al.* [7] reported that the new Cu/AlO_x structures that form upon hydrothermal aging and which exhibit strong interactions between Al ions and paramagnetic Cu are, at least partially, responsible for the maintenance of higher temperature NH₃-SCR activity. The NH₃-TPD results described above show that the total acidity in Cu-ZSM-5 catalyst significant decreases with the temperature increase of hydrothermal treatment, while that of Cu-SAPO-34 catalyst show a slight change. Following the

hydrothermal aging of Cu-ZSM-5 at 750 °C for 12 h, dramatic decreases in the Brønsted acidity and strong Lewis acidity created by Cu²⁺ ions are also observed, while a small change is observed in Cu-SAPO-34.

Additionally, the Cu-ZSM-5 and the Cu-SAPO-34 catalysts have shown distinct responses to propene and sulfur dioxide poisoning. The NO conversions of Cu-ZSM-5 and Cu-SAPO-34 catalysts are affected after exposed to propene and SO₂. The above results show that after an injection of propene into Cu-ZSM-5 and Cu-SAPO-34 catalysts, the catalytic activity of the Cu-ZSM-5 catalyst significantly drops at low temperature compared to the Cu-SAPO-34 catalysts. The catalytic activity of Cu-ZSM-5 significantly decreases at temperature below 250 °C compared to Cu-SAPO-34 catalyst. However, at high temperature the catalytic activities of both Cu-ZSM-5 and Cu-SAPO-34 catalysts show a slight changes after SO₂ addition. After the propene and the SO₂ removal, the catalytic activities of Cu-ZSM-5 and Cu-SAPO-34 catalysts could recover to some extent at 250 °C, 350 °C and 450 °C, and 250 °C, respectively. However, the catalytic activity of Cu-SAPO-34 catalyst almost recovered to the same value as it was at the beginning, at higher temperatures. These XRD results confirm that the crystalline structures of the Cu-ZSM-5 and the Cu-SAPO-34 catalysts are well-preserved after propene and SO₂ poisoning. Nevertheless, the TG results show a weight loss which could be attributed to the removal of deposited carbonaceous on the catalyst, however, the coke formation in Cu-ZSM-5 was larger than in Cu-SAPO-34 catalyst. Furthermore, the UV-vis-DRS results demonstrated an effect on Cu²⁺ sites upon propene and SO₂ addition, leading to the reduction in the number of isolated Cu²⁺ ions and the formation of Cu_xO_y clusters.

Therefore, the Cu-ZSM-5 catalyst, without sufficient amounts of Brønsted acid sites, exhibits a poor NH₃-SCR performance because the Brønsted acid sites in Cu-CHA catalysts which act as reservoir providing some reactive NH₃ molecules to Cu sites play a beneficial role in NH₃-SCR reaction. We can conclude that the actively isolated Cu²⁺ ions content, the distribution of Cu species and the zeolite acidity, which are related to the catalytic activity and hydrothermal durability of both Cu-SAPO-34 as well as ZSM-5 catalysts are all found to be influenced by the hydrothermal treatment.

4. Conclusion

The effects of propene, SO₂ and hydrothermal aging on the physical materials and chemical properties, and the catalytic activity of Cu-SAPO-34 as well as the Cu-ZSM-5 catalysts for NO_x removal were studied in this report. It has been shown that after hydrothermal treatment at 750 °C for 12 h, Cu-ZSM-5 exhibited a significant influence on the microstructures of the support, copper species and acidity, which led to different NH₃-SCR activities. After hydrothermal treatment at 750 °C for 12 h, the Cu-SAPO-34 showed no significant changes in the structure, this was consistent with the slight decrease in catalytic activity. Meanwhile, Cu-SAPO-34 showed better hydrocarbon and sulfur resistance than the

Cu-ZSM-5 catalyst. When the redox behavior of Cu species was investigated using UV and H₂-TPR, it was found that the copper oxide species on the external surface could disperse as copper ions and migrate to the exchanged sites in Cu-SAPO-34, while Cu²⁺ could be reduced to Cu⁺ and Cu⁰. In summary, the Cu-SAPO-34 catalyst exhibits a better deNO_x catalytic performance and hydrothermal stability than Cu-ZSM-5 catalyst, which makes it an attractive candidate for diesel exhaust purification.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Kwak, J.H., Tran, D., Burton, S.D., Szanyi, J., Lee, J.H. and Peden, C.H.F. (2012) Effects of Hydrothermal Aging on NH₃-SCR Reaction over Cu/Zeolites. *Journal of Catalysis*, **287**, 203-209. <https://doi.org/10.1016/j.jcat.2011.12.025>
- [2] Doi, Y., Haneda, M. and Ozawa, M. (2014) Direct Decomposition of NO on Ba Catalysts Supported on Rare Earth Oxides. *Journal of Molecular Catalysis A: Chemical*, **383-384**, 70-76. <https://doi.org/10.1016/j.molcata.2013.11.033>
- [3] Ma, L., Cheng, Y., Cavataio, G., McCabe, R.W., Fu, L. and Li, J. (2013) Characterization of Commercial Cu-SSZ-13 and Cu-SAPO-34 Catalysts with Hydrothermal Treatment for NH₃-SCR of NO_x in Diesel Exhaust. *Chemical Engineering Journal*, **225**, 323-330. <https://doi.org/10.1016/j.cej.2013.03.078>
- [4] Franco, R.M., Moliner, M., Franch, C., Kustov, A. and Corma, A. (2012) Rational Direct Synthesis Methodology of Very Active and Hydrothermally Stable Cu-SAPO-34 Molecular Sieves for the SCR of NO_x. *Applied Catalysis B: Environmental*, **127**, 273-280. <https://doi.org/10.1016/j.apcatb.2012.08.034>
- [5] Gabrielsson, L.T. (2004) Urea-SCR in Automotive Applications. *Topics in Catalysis*, **28**, 177-184. <https://doi.org/10.1023/B:TOCA.0000024348.34477.4c>
- [6] Wang, D., Jangjou, Y., Liu, Y., Sharma, M.K., Luo, J., Li, J., Kamasamudram, K. and Epling, W.S. (2015) A Comparison of Hydrothermal Aging Effects on NH₃-SCR of NO_x over Cu-SSZ-13 and Cu-SAPO-34 Catalysts. *Applied Catalysis B: Environmental*, **165**, 438-445. <https://doi.org/10.1016/j.apcatb.2014.10.020>
- [7] Kwak, J.H., Zhu, H., Lee, J.H., Peden, C.H.F. and Szanyi, J. (2012) Two Different Cationic Positions in Cu-SSZ-13? *Chemical Communications*, **48**, 4758-4760. <https://doi.org/10.1039/c2cc31184d>
- [8] Iwamoto, M., Furukawa, H., Mine, Y., Uemura, F., Mikuriya, S.-I. and Kagawa, S. (1986) Copper (II) Ion-Exchanged ZSM-5 Zeolite as Highly Active Catalysts for

- Direct and Continuous Decomposition of Nitrogen Oxide. *Journal of the Chemical Society, Chemical Communications*, No. 16, 1272-1273.
<https://doi.org/10.1039/c39860001272>
- [9] Ye, Q., Wang, L. and Yang, R.T. (2012) Activity, Propene Poisoning Resistance and Hydrothermal Stability of Copper Exchanged Chabazite-Like Zeolite Catalysts for SCR of NO with Ammonia in Comparison to Cu/ZSM-5. *Applied Catalysis A: General*, **427-428**, 24-34. <https://doi.org/10.1016/j.apcata.2012.03.026>
- [10] Gomez, S.A., Campero, A., Martinez-Hernandez, A. and Fuentes, G.A. (2000) Changes in Cu²⁺ Environment upon Wet Deactivation of Cu-ZSM-5 DeNO_x Catalyst. *Applied Catalysis A: General*, **197**, 157-164.
[https://doi.org/10.1016/S0926-860X\(99\)00546-3](https://doi.org/10.1016/S0926-860X(99)00546-3)
- [11] Kucherov, A.V., Hubbard, C.P. and Shelef, M. (1995) Rearrangement of Cationic Sites in CuH-ZSM-5 and Reactivity Loss upon High Temperature Calcination and Steam Aging. *Journal of Catalysis*, **157**, 603-610.
<https://doi.org/10.1006/jcat.1995.1325>
- [12] Tanabe, T., Iijima, T., Koiwai, A., Mizuno, J., Yokota, K. and Isogai, A. (1995) ESR Study of the Deactivation of Cu-ZSM-5 in a Net Oxidizing Atmosphere. *Applied Catalysis B: Environmental*, **6**, 145-153.
[https://doi.org/10.1016/0926-3373\(95\)00012-7](https://doi.org/10.1016/0926-3373(95)00012-7)
- [13] Rokosz, M.J., Kucherov, A.V., Jen, H.W. and Shelef, M. (1997) Spectroscopic Studies of the Stability of the Zeolite deNO_x Catalysts. *Catalysis Today*, **35**, 65-73.
[https://doi.org/10.1016/S0920-5861\(96\)00144-7](https://doi.org/10.1016/S0920-5861(96)00144-7)
- [14] Kucherov, A.V., Gerlock, J.L., Jen, H.W. and Shelef, M. (1995) *In situ* ESR Monitoring of CuH-ZSM-5 up 500°C in Flowing Dry Mixtures of NO (NO₂), C₃H₆ (C₂H₅OH), and an Excess O₂. *Journal of Catalysis*, **152**, 63-69.
<https://doi.org/10.1006/jcat.1995.1060>
- [15] Zhang, Y. and Stephanopoulos, M.F. (1996) Hydrothermal Stability of Cerium Modified Cu-ZSM-5 Catalyst for Nitric Oxide Decomposition. *Journal of Catalysis*, **164**, 131-145. <https://doi.org/10.1006/jcat.1996.0369>
- [16] Breggrund, M., Ingelsten, H.H., Skoglundh, M. and Palmqvist, A.E.C. (2009) Influence of Synthesis for ZSM-5 on the Hydrothermal Stability of Cu-ZSM-5. *Catalysis Letters*, **130**, 79-85. <https://doi.org/10.1007/s10562-009-9890-5>
- [17] Gabova, V., Dedeeek, J. and Cejka, J. (2003) Control of Al Distribution in ZSM-5 by Condition of Zeolite Synthesis. *Chemical Communications*, No. 10, 1196-1197.
<https://doi.org/10.1039/b301634j>
- [18] Wang, J., Fan, D., Yu, T., Wang, J., Hao, T., Hu, X. and Shen, M. (2015) Improvement of Low-Temperature Hydrothermal Stability of Cu/SAPO-34 Catalysts by Cu²⁺ Species. *Journal of Catalysis*, **322**, 84-90.
<https://doi.org/10.1016/j.jcat.2014.11.010>
- [19] Luo, J., Wang, D., Kumar, A., Li, J., Kamasamudram, K., Currier, N. and Yezerets, A. (2016) Identification of Two Types of Cu Sites in Cu-SSZ-13 and Their Unique Responses to Hydrothermal Aging and Sulfur Poisoning. *Catalysis Today*, **267**, 3-9.
<https://doi.org/10.1016/j.cattod.2015.12.002>
- [20] Briend, M., Vomscheid, R., Peltre, M.J., Man, P.P. and Barthomeuf, D. (1995) Influence of the Choice of the Template on the Short- and Long-Term Stability of SAPO-34 Zeolite. *Journal of Physical Chemistry*, **99**, 8270-8276.
<https://doi.org/10.1016/j.cattod.2015.12.002>
- [21] Sultana, A., Nanba, T., Sasaki, M., Haneda, M., Suzuki, K. and Hamada, H. (2011) Selective Catalytic Reduction of NO_x with NH₃ over Different Copper Exchanged Z

- eilites in the Presence of Decane. *Catalysis Today*, **164**, 495-499.
<https://doi.org/10.1016/j.cattod.2010.11.036>
- [22] Tukur, N.M. and Al-Khattaf, S. (2005) Catalytic Cracking of *n*-Dodecane and Alkyl Benzenes over FCC Zeolite Catalysts. Time and Stream and Reactant Converter Models. *Chemical Engineering and Processing*, **44**, 1257-1268.
<https://doi.org/10.1016/j.cep.2005.02.009>
- [23] He, C., Wang, Y., Cheng, Y., Lambert, C.K. and Yang, R.T. (2009) Activity, Stability and Hydrocarbon Deactivation of Fe/Beta Catalyst for SCR of NO with Ammonia. *Applied Catalysis B: General*, **368**, 121-126.
<https://doi.org/10.1016/j.apcata.2009.08.020>
- [24] Luo, J.Y., Oh, H., Henry, C. and Epling, W. (2012) Effect of C₃H₆ on Selective Catalytic Reduction of NO_x by NH₃ over a Cu/Zeolite Catalyst: A Mechanistic Study. *Applied Catalysis B: Environmental*, **123-124**, 296-305.
<https://doi.org/10.1016/j.apcatb.2012.04.038>
- [25] Ma, L., Su, W., Li, Z., Li, J., Fu, L. and Hao, J. (2015) Mechanism of Propene Poisoning on Cu-SSZ-13 Catalysts for SCR of NO_x with NH₃. *Catalysis Today*, **245**, 16-21. <https://doi.org/10.1016/j.cattod.2014.05.027>
- [26] Selleri, T., Nova, I., Tronconi, E., Weibel, M. and Schmeißer, V. (2017) Modelling Inhibition Effect of Short-Chain Hydrocarbons on a Small-Pore Cu-Zeolite NH₃-SCR Catalysts. *Topics in Catalysis*, **60**, 214-219.
<https://doi.org/10.1007/s11244-016-0600-4>
- [27] Wang, D., Li, Z. and Song, C. (2021) The Enhanced Catalytic Activity of Cu/SAPO-34 by Ion Exchange Method for Selective Catalytic Reduction of Nitric Oxide. *Materials Research Express*, **8**, Article 025507.
<https://doi.org/10.1088/2053-1591/abe6d3>
- [28] Zhang, Q., Li, Z., Cui, J., Ma, Y., *et al.* (2023) Efficiency of Temperature on Ce and La Doping Cu Modified IM-5 Catalyst in DeNO_x Performance and SO₂/H₂O Resistance. *Research on Chemical Intermediates*, **49**, 4997-5013.
<https://doi.org/10.1007/s11164-023-05127-y>
- [29] Ma, J., Si, Z., Weng, D., Wu, X. and Ma, Y. (2015) Potassium Poisoning on Cu-SAPO-34 Catalyst for Selective Catalytic Reduction of NO_x with Ammonia. *Chemical Engineering Journal*, **267**, 191-200.
<https://doi.org/10.1016/j.cej.2014.11.020>
- [30] Wang, J., Huang, Y., Yu, T., Zhu, S., Shen, M., Li, W. and Wang, J. (2014) The Migration of Cu Species over Cu-SAPO-34 and Its Effect on NH₃ Oxidation at High Temperature. *Catalysis Science & Technology*, **4**, 3004-3012.
<https://doi.org/10.1039/C4CY00451E>
- [31] Cao, Y., Zou, S., Yang, Z., Xu, H., Lin, T., Gong, M. and Chen, Y. (2015) Promotional Effect of Ce on Cu-SAPO-34 Monolith Catalyst for Selective Catalytic Reduction of NO_x Ammonia. *Journal of Molecular Catalysis A: Chemical*, **398**, 304-311.
<https://doi.org/10.1016/j.molcata.2014.12.020>
- [32] Pang, L., Fan, C., Shao, L., Song, K., Yi, J., Cai, X., Wang, J., Kang, M. and Li, T. (2014) The Ce Doping Cu/ZSM-5 as a New Superior Catalyst to Remove NO from Diesel Engine Exhaust. *Chemical Engineering Journal*, **253**, 394-401.
<https://doi.org/10.1016/j.cej.2014.05.090>
- [33] Zhang, T., Liu, J., Wang, D.X., Zhao, Z., Wei, Y.C., Cheng, K., Jiang, G.Y. and Duan, A.J. (2014) Selective Catalytic Reduction of NO with NH₃ over HZSM-5-Supported Fe-Cu Nanocomposite Catalysts: The Fe-Cu Bimetallic Effect. *Applied Catalysis B: Environmental*, **148-149**, 520-531.

- <https://doi.org/10.1016/j.apcatb.2013.11.006>
- [34] Zhang, L., Wang, D., Liu, Y., Kamassamudram, K., Li, J. and Epling, W. (2014) SO₂ Poisoning Impact on the NH₃-SCR Reaction over a Commercial Cu-SAPO-34 SCR Catalyst. *Applied Catalysis B: Environmental*, **156-157**, 371-377. <https://doi.org/10.1016/j.apcatb.2014.03.030>
- [35] Heo, I., Lee, Y., Nam, I.-S., Choung, J.W., Lee, J.-H. and Kim, H.-J. (2011) Effect of Hydrocarbon Slip on NO Removal Activity of Cu-ZSM-5, Fe-ZSM-5 and V₂O₅/TiO₂ Catalysts by NH₃. *Microporous and Mesoporous Materials*, **141**, 8-15. <https://doi.org/10.1016/j.micromeso.2010.02.005>
- [36] Ma, L., Li, J., Cheng, Y., Lambert, C.K. and Fu, L. (2012) Propene Poisoning on Three Typical Fe-Zeolites for SCR of NO_x with NH₃: From Mechanism Study to Coating Modified Architecture. *Environmental Science & Technology*, **46**, 1747-1754. <https://doi.org/10.1021/es203070g>
- [37] Yan, J.Y., Sachtler, W.M.H. and Kung, H.H. (1997) Effect of Cu Loading Addition of Modifiers on the Stability of Cu/ZSM-5 in Lean NO_x Reduction Catalysis. *Catalysis Today*, **33**, 279-290. [https://doi.org/10.1016/S0920-5861\(96\)00100-9](https://doi.org/10.1016/S0920-5861(96)00100-9)
- [38] Zhang, T., Shi, J., Liu, J., Wang, D., Zhao, Z., Cheng, K. and Li, J. (2016) Enhanced Hydrothermal Stability of Cu-ZSM-5 Catalyst via Surface Modification in the Selective Catalytic Reduction of NO with NH₃. *Applied Surface Science*, **375**, 186-195. <https://doi.org/10.1016/j.apsusc.2016.03.049>
- [39] Yan, J.Y., Lei, G.-D., Sachtler, W.M.H. and Kung, H.H. (1996) Deactivation of Cu-ZSM-5 Catalyst for Lean NO_x Reduction: Characterization of Changes of Cu State and Zeolite Support. *Journal of Catalysis*, **161**, 43-54. <https://doi.org/10.1006/jcat.1996.0160>
- [40] Dang, T.T.H., Zubowa, H.L., Bentrup, U., Richter, M. and Martin, A. (2009) Microwave-Assisted Synthesis and Characterization of Cu-Containing ALPO₄-5 and SAPO-5. *Microporous and Mesoporous Materials*, **123**, 209-220. <https://doi.org/10.1016/j.micromeso.2009.04.003>
- [41] Wang, L., Gaudet, J.R., Li, W. and Weng, D. (2013) Migration of Cu Species in Cu/SAPO-34 during Hydrothermal Aging. *Journal of Catalysis*, **306**, 68-77. <https://doi.org/10.1016/j.jcat.2013.06.010>
- [42] Su, W., Li, Z., Zhang, Y., Meng, C. and Li, J. (2017) Identification of Sulfate Species and Their Influence on SCR Performance of Cu/CHA Catalyst. *Catalysis Science & Technology*, **7**, 1523-1528. <https://doi.org/10.1039/C7CY00302A>
- [43] Zhang, D. and Yang, R.T. (2017) NH₃-SCR of NO over One-Pot Cu-SAPO-34 Catalyst: Performance Enhancement by Doping Fe and MnCe and Insight into N₂O Formation. *Applied Catalysis A: General*, **543**, 247-256. <https://doi.org/10.1016/j.apcata.2017.06.021>