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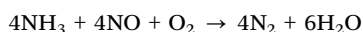
Impact of hydrothermal aging on SO₂-deactivation of Cu–CHA catalysts for NH₃-SCR

Shivangi Singh,^{*ab} Ton V. W. Janssens^{ib} and Henrik Grönbeck^{ib} ^{*a}

SO₂ poisoning and hydrothermal aging are two major deactivation mechanisms limiting the long-term performance of Cu–CHA catalysts for NH₃-SCR of NO_x. SO₂ deactivates Cu sites and water exposure at high temperatures leads to loss of Brønsted acid sites and structural degradation. We study how the mechanism of SO₂-deactivation is affected by hydrothermal aging using activity measurements, NH₃-TPD, and NO-temperature-programmed reaction. NH₃-TPD measures the number of Brønsted acid sites, whereas the NO-temperature-programmed reaction probes the amount of [Cu₂(NH₃)₄O₂]²⁺ species, which is a key intermediate in the SCR-reaction. Exposure to SO₂ results in a 60–70% loss of activity for both fresh and hydrothermally aged catalysts, indicating that the mechanism of sulfur-induced deactivation is largely independent of prior hydrothermal aging. Furthermore, hydrothermal aging prior to SO₂ exposure reduces the possibility of catalyst regeneration, primarily due to irreversible hydrothermal deactivation.

1. Introduction

Selective catalytic reduction of NO_x using ammonia as a reducing agent (NH₃-SCR) is the leading technology for NO_x control under oxygen rich conditions.^{1,2} Cu-exchanged small-pore chabazite (CHA) zeolites have shown favorable low-temperature activity and N₂ selectivity for NH₃-SCR.^{2–4} Cu–CHA has, therefore, become a key component in diesel exhaust aftertreatment systems to meet increasingly stringent NO_x emission regulations. The global, so-called, standard NH₃-SCR reaction is:



The NH₃-SCR reaction cycle involves alternating oxidation and reduction of the Cu-sites. The Cu-sites are oxidized from Cu^I to Cu^{II} during O₂ adsorption and reduced back to Cu^I during the coupling of NO and NH₃. The Cu ions are solvated by NH₃ below ~300 °C and the reaction proceeds *via* mobile [Cu(NH₃)₂]⁺ complexes.^{5–11} The mobility of [Cu(NH₃)₂]⁺ facilitates the formation of [Cu(NH₃)₂]⁺ pairs, which are required for O₂ adsorption and the formation of [Cu₂(NH₃)₄O₂]²⁺ peroxo-complexes.^{12–16} A detailed (atomistic) reaction path for NH₃-SCR has been suggested based on density functional theory (DFT) calculations^{17–19} and DFT-based micro-kinetic modeling.²⁰ In these models, NO adsorbs on [Cu₂(NH₃)₄O₂]²⁺ and reacts with

NH₃ forming H₂NNO and [Cu₂(NH₃)₄OOH]²⁺.^{17,20} The OH groups on the Cu-sites react with NO forming HONO species. These H₂NNO and HONO intermediates decompose over Brønsted acid sites to form N₂ and H₂O, the final products of the NH₃-SCR reaction. Thus, the reaction mechanism relies on both Cu and Brønsted acid sites to form N₂ and H₂O.^{17,20}

A drawback of Cu–CHA based catalysts is their sensitivity to sulfur containing species, which are formed during the combustion of sulfur-containing fuels. SO₂ and H₂SO₄ are the main sulfur containing species reaching the catalyst during low-temperature operation²¹ and are known to suppress the activity of the NH₃-SCR catalysts below 300 °C, while the activity at higher temperature is less affected.^{22–28} *In situ* XANES measurements have revealed that SO₂ predominantly interacts with [Cu₂(NH₃)₄O₂]²⁺ peroxo complexes and other Cu^{II} species.²⁹ The reaction between SO₂ and Cu^{II} species leads to a partial reduction of Cu^{II} to Cu^I and the formation of Cu^{II}-sulfated compounds, which are not reducible by NO/NH₃.³⁰ Based on these observations, a two-step mechanism has been proposed where a single SO₂ molecule reacts with two [Cu₂(NH₃)₄O₂]²⁺ complexes to form two [Cu(NH₃)₂]⁺, framework-bound Cu^I (fw-Cu^I) and a sulfate like Cu^{II}SO₄ species.³⁰

The interaction of SO₂ with [Cu₂(NH₃)₄O₂]²⁺ hinders NO from reacting with [Cu₂(NH₃)₄O₂]²⁺, which leads to a loss of NH₃-SCR activity at low temperatures.³¹ However, heating Cu–CHA to 450–550 °C releases some SO₂ and recovers most of the initial activity,^{26,28–30,32–34} which makes this type of SO₂-deactivation largely reversible. A DFT study has suggested an alternative mechanism for the reversible deactivation,³⁵ namely, the formation of bulky ammonium

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sulfate species, $(\text{NH}_4)\text{HSO}_4$, which restricts the inter-cage diffusion of $[\text{Cu}(\text{NH}_3)_2]^+$ and thereby hinders the O_2 adsorption.

The performance of Cu-CHA catalysts in diesel exhaust systems is reduced not only by the presence of SO_2 in the exhaust gas, but also by hydrothermal aging, which results in degradation of the zeolite structure. This type of degradation is most severe at temperatures above 600°C in the presence of water, a condition encountered during regeneration of the diesel particulate filter, which is placed upstream of the SCR-catalyst in the aftertreatment system. Hydrothermal aging is due to displacement of the Al atoms in the zeolite framework. In the absence of Cu, hydrothermal aging leads to loss of Brønsted acid sites and formation of extra-framework $\text{Al}(\text{OH})_3(\text{H}_2\text{O})$ species.^{36,37} For Al-sites balanced by Cu, hydrothermal aging may lead to the formation of Cu-aluminate species,^{38,39} which are inactive for the NH_3 -SCR.^{40,41} DFT calculations have shown that the formation of framework-bound Cu-aluminate species is thermodynamically favored over the formation of mobile $\text{Al}(\text{OH})_3\cdot\text{H}_2\text{O}$ species in Cu-CHA.³⁷ Besides the loss of Brønsted acid sites, temperatures above 800°C may change the Cu speciation in the catalyst. X-ray absorption near-edge spectroscopy (XANES) studies have shown that the amount of $[\text{Cu}(\text{NH}_3)_2]^+$ complexes decreases as a consequence of hydrothermal aging. The loss of $[\text{Cu}(\text{NH}_3)_2]^+$ complexes leads to a reduction of the formation of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ species, which results in lower NH_3 -SCR activity.⁴²

As both SO_2 deactivation and hydrothermal aging occur during the application of Cu-CHA, the lifetime of the catalyst is determined by their combined effects. Hydrothermal aging of Cu-CHA catalysts typically leads to a lower uptake of SO_2 as compared to that of fresh catalysts. This decrease has been attributed to the transformation of ZCuOH sites into Z_2Cu during hydrothermal aging at 650°C , where Z represents an Al-site.⁴³ Z_2Cu is less susceptible to sulfur poisoning than ZCuOH .⁴³ Under more severe hydrothermal aging conditions (800 – 850°C), the formation of CuO can occur, which, when exposed to SO_2 at 200°C , forms Cu-sulfate species, leading to a loss of active Cu-species.²⁶ As Cu-sulfates decompose only above 700°C ,⁴⁴ Cu bound to sulfate species cannot be regenerated at typical NH_3 -SCR operating temperatures of 550°C .⁴⁵

We have performed a mechanistic study to investigate how the mechanism of SO_2 -deactivation is affected by hydrothermal aging. We focus on sulfur deactivation by SO_2 , as it is expected

to be the most abundant species under NH_3 -SCR conditions. Moreover, SO_2 exposure to $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ under SCR conditions is shown to form an SO_3 -like intermediate,³⁰ which subsequently reacts to form $\text{SO}_4(\text{NH}_4)_2$ and $\text{HSO}_4(\text{NH}_4)$ that would be the products when Cu-CHA is exposed to H_2SO_4 .³⁵ As the SO_2 uptake occurs primarily through SO_2 reaction with the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes,^{29,30} we have studied this pathway by promoting the formation of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes in both fresh and hydrothermally aged Cu-CHA catalysts. The impact of hydrothermal aging conditions is controlled by varying the aging duration and aging temperature. The effects of SO_2 exposure on NH_3 -SCR activity, the formation and reactivity of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes, and SO_2 uptake are evaluated for both fresh and hydrothermally aged catalysts. In addition, the possibility to regenerate the catalyst is studied by repeating the measurements after heating the catalyst so as to remove adsorbed SO_2 under conditions representative of practical NH_3 -SCR operation.

2. Methods

2.1. Catalyst information and experimental scheme

In this study, we have used a Cu-CHA catalyst (a Si/Al ratio of 6.7) containing 3.2 wt% Cu. The catalyst was prepared by impregnation of the parent H-CHA material with an appropriate amount of Cu-nitrate solution, followed by calcination at 600°C for 2 h. Catalyst samples of 50 mg (sieve fraction 150 – $300\ \mu\text{m}$) were loaded in a U-tube quartz reactor (6 mm inner diameter) to measure the activity, NH_3 adsorption capacity by NH_3 -TPD, and reactivity of NO with the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex. The measurements investigated different aging conditions for four samples of the same catalyst material. The procedure of the measurements for each sample is shown in Fig. 1.

Part A represents the activity measurement and characterization of fresh samples. The activity was measured at 175°C with 500 ppm NO, 600 ppm NH_3 , 10% O_2 , and 5% H_2O in N_2 . The total flow was $13.5\ \text{NL h}^{-1}$, corresponding to a gas hourly space velocity (GHSV) of $270\ \text{NL g}^{-1}\ \text{cat h}$ or $405\ 000\ \text{h}^{-1}$ on a dry catalyst volume basis (density of dry acidic chabazite is $1.50\ \text{g cm}^{-3}$). The activity measurement was followed by

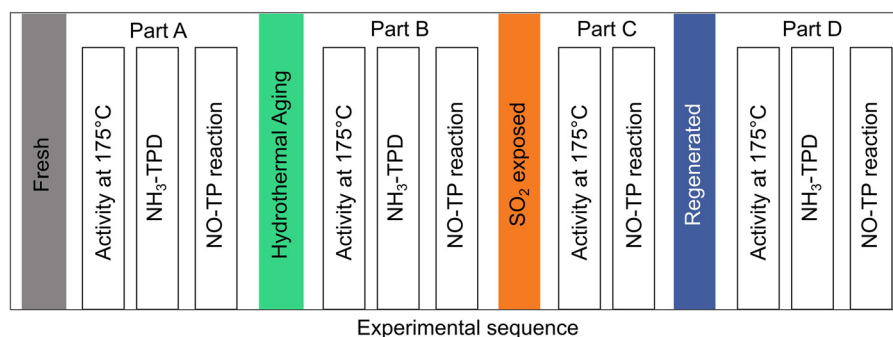


Fig. 1 Experimental scheme for the measurements.

NH₃-TPD. The NH₃-TPD was performed by exposing the sample to 1500 ppm NH₃ for 1 h at 100 °C, at a total gas flow of 11.4 NL h⁻¹ after which the temperature was decreased to 80 °C. The TPD was performed at a heating rate of 3 °C min⁻¹ to 550 °C, at a total flow of 11.4 NL h⁻¹ of N₂. After the TPD treatment, the catalyst was found to contain [Cu₂(NH₃)₄O₂]²⁺ species. The [Cu₂(NH₃)₄O₂]²⁺ species was prepared by first heating the catalyst to 550 °C in 10% O₂, followed by cooling down to 200 °C. The catalyst was then reduced in 800 ppm NO and 960 ppm NH₃, resulting in the formation of [Cu(NH₃)₂]⁺ complexes.³¹ The reduced catalyst was subsequently oxidized in 10% O₂/N₂, leading to the formation of the [Cu₂(NH₃)₄O₂]²⁺ peroxo species. The amount of [Cu₂(NH₃)₄O₂]²⁺ species, which is a measure of the amount of reducible Cu in the catalyst, was probed by exposure of the sample to 680 ppm NO during a temperature ramp from 50 to 300 °C (NO-TP reaction) at a total gas flow of 12 NL h⁻¹. After part A, the samples were hydrothermally aged for 2 h at 650 °C, 10 h at 650 °C, or 10 h at 800 °C. The hydrothermal aging was performed in 10% H₂O and 10% O₂. In part B, activity, NH₃-TPD, and NO titration measurements were performed. After the NH₃ and NO titrations, the sample was exposed to 100 ppm SO₂ and 10% O₂/N₂ at 200 °C for 45 minutes at a flow of 12 NL h⁻¹ (see the SI). The NH₃-SCR activity and NO-TP reaction activity were measured (part C in Fig. 1) after the SO₂ uptake. After part C, the sample was regenerated at 550 °C in the presence of 10% O₂, after which the activity, NH₃-TPD, and NO titration were measured again (part D).

As a reference, a measurement of SO₂ deactivation without hydrothermal aging was also done, by omitting the hydrothermal aging step (part B) in the procedure described above. A detailed account of the experimental steps is provided in the SI.

The NH₃-SCR activity was determined by evaluating the rate constant of the NH₃-SCR reaction based on the conversion of

NO_x (sum of NO and NO₂ concentrations), under the assumptions of plug-flow conditions and that the NH₃-SCR reaction is the first order in NO and zeroth order in NH₃.^{46–48} The rate constant k is then given as:

$$k = -\frac{F \ln(1 - X_{\text{NO}})}{W} \quad (1)$$

where F is the molar flow (mmol h⁻¹), W is the amount of catalyst (mg) and X_{NO} is the conversion of NO_x.

3. Results

3.1. Impact of SO₂ on the activity of hydrothermally aged Cu-CHA

To determine the effect of hydrothermal aging on SO₂ deactivation, we measured first-order rate constants at 175 °C for the fresh catalyst, after hydrothermal aging, after subsequent SO₂ exposure, and after regeneration at 550 °C, which are shown in Fig. 2(a). Without hydrothermal aging, the catalyst shows a pronounced decrease in rate constant after SO₂ exposure, demonstrating significant deactivation by SO₂. After regeneration at 550 °C, the activity is restored to 91% of the initial activity. This result is in full agreement with the literature, showing that the deactivation by SO₂ is mainly reversible, but leads to some irreversible deactivation.^{22,23,49,50}

A similar trend is observed for SO₂ deactivation and regeneration of the hydrothermally aged catalysts. The activity is reduced upon hydrothermal aging and subsequent SO₂ exposure results in a further reduction of the activity. Regeneration largely restores the activity back to the level after hydrothermal aging. This indicates that the deactivation introduced by hydrothermal aging is irreversible, whereas the SO₂ deactivation is largely reversible.

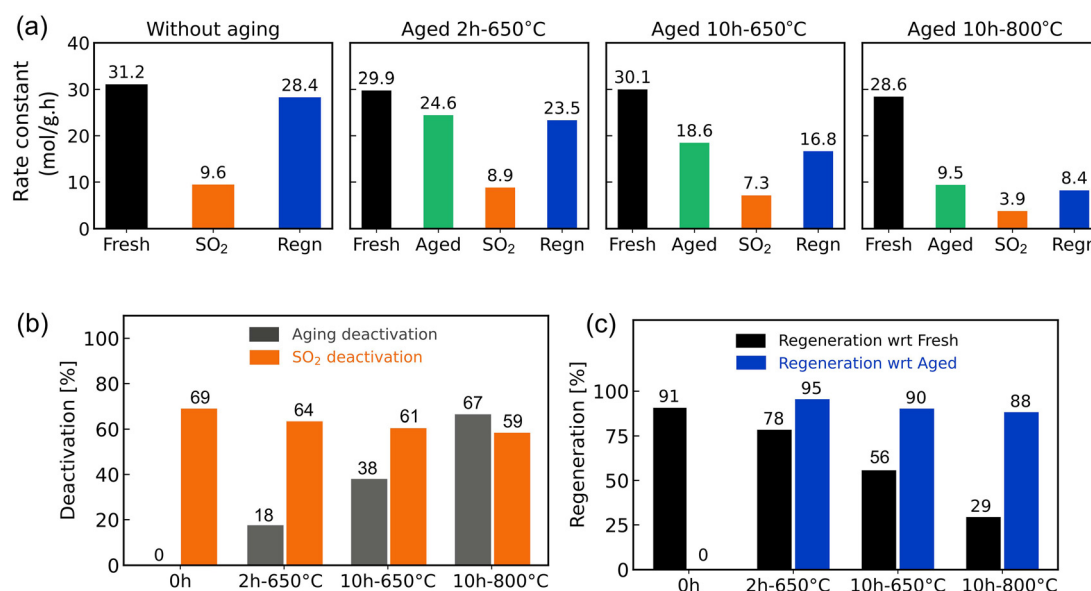


Fig. 2 (a) Rate constants of fresh, hydrothermally aged, SO₂ exposed, and regenerated catalysts. (b) Deactivation in % by hydrothermal aging and SO₂ exposure. (c) Regeneration with respect to fresh and aged catalysts under the four aging conditions: 0 h, 2 h at 650 °C, 10 h at 650 °C, and 10 h at 800 °C.

A more quantitative analysis of the deactivation on the hydrothermally aged catalysts is shown in Fig. 2(b). The deactivation by hydrothermal aging is evaluated as $(1 - k_{\text{aged}}/k_{\text{fresh}})$. The deactivation is 18% and 38% when the catalyst was aged at 650 °C for 2 and 10 h, respectively. Increasing the aging temperature to 800 °C for 10 h results in a deactivation of 67%. The results show that deactivation becomes more severe with increasing aging duration and temperature.

The effect of hydrothermal aging on SO₂ deactivation is also shown in Fig. 2(b). The deactivation for the catalyst without aging was evaluated as $(1 - k_{\text{SO}_2}/k_{\text{fresh}})$. The extent of deactivation by SO₂ was for the other catalysts evaluated as $(1 - k_{\text{SO}_2}/k_{\text{aged}})$. The catalyst without aging has a 69% deactivation upon SO₂ exposure. The deactivation is slightly reduced to 64%, 61%, and 59% when the catalyst is aged at 650 °C for 2 h, 650 °C for 10 h, and 800 °C for 10 h prior to SO₂ exposure, respectively. The results indicate that SO₂ deactivation is only marginally affected by hydrothermal aging.

Fig. 2(c) shows the regeneration of the samples, calculated as $k_{\text{reg}}/k_{\text{fresh}}$. The possibility to regenerate the catalyst decreases with increasing aging prior to SO₂ exposure (black bars). The catalyst without aging recovered approximately 91% of its initial activity after regeneration, whereas the catalyst-regeneration decreased to 78%, 56%, and 29% for catalysts aged prior to SO₂ at 650 °C for 2 h, 650 °C for 10 h, and 800 °C for 10 h, respectively. A large part of the activity of the SO₂-deactivated catalysts is possible to regenerate (blue bars). The catalysts are regenerated to 95%, 90% and 88% for SO₂ exposure of catalysts aged at 650 °C for 2 h, 650 °C for 10 h, and 800 °C for 10 h. The trend observed for the regenerated catalysts can be attributed mainly to the effects of hydrothermal aging. The influence of SO₂ appears to be largely independent of deactivation caused by hydrothermal aging.

Hydrothermal aging is related a loss of Brønsted acid sites.^{37,51} In contrast, the deactivation by SO₂ involves a reaction of SO₂ with the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes.³⁴ To further understand the impact of hydrothermal aging on SO₂ deactivation, we use NH₃-TPD to observe the changes in Brønsted acid sites and temperature-programmed reaction of NO, to monitor the ability to form the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes. Fig. 3 compares the NH₃-TPD profiles of the fresh and hydrothermally aged catalysts and the SO₂-exposed aged catalyst after regeneration at 550 °C. The fresh catalysts (a) show a peak at around 430 °C, which is associated with NH₃ adsorbed on Brønsted acid sites and another peak at around 280 °C, which corresponds to NH₃ on Lewis acid sites or ligand-NH₃ on the Cu-complexes^{11,52–54} (black lines in Fig. 3). The integrated peak areas are reported in the SI. Hydrothermal aging (b–d) results in a significant loss of NH₃ desorbing at 430 °C, consistent with a loss of Brønsted acid sites due to transformation of ZCuOH sites into Z₂ Cu and dealumination. Furthermore, the low-temperature peak increases and shifts to around 210 °C. Interestingly, the NH₃-desorption curves after exposure to SO₂ at 200 °C and subsequent regeneration at 550 °C (regenerated) are identical to those obtained before SO₂ exposure (aged). This indicates that the SO₂ exposure and regeneration does not

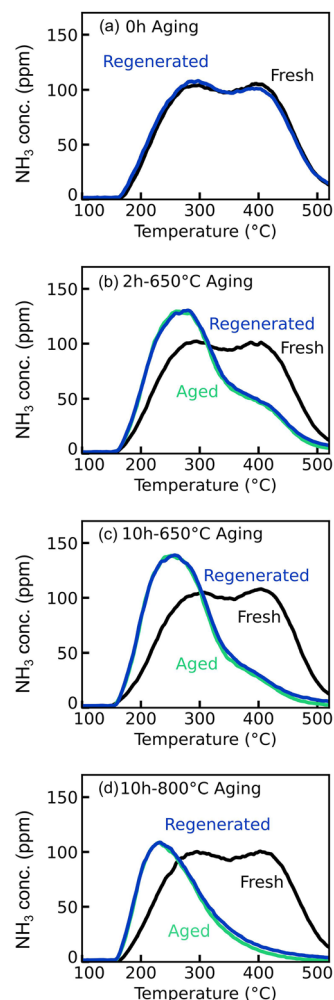


Fig. 3 NH₃-TPD profiles of the fresh catalyst (black), the hydrothermally aged catalyst (green), and the SO₂-exposed aged catalyst after regeneration at 550 °C (blue) under the four aging conditions: 0 h (a), 2 h at 650 °C (b), 10 h at 650 °C (c), and 10 h at 800 °C (d).

affect the amount and type of adsorption sites for NH₃. Consequently, all changes observed in NH₃-TPD are due to hydrothermal aging.

To investigate the formation of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes, NO-TP reaction measurements were performed on the catalysts subjected to the different aging conditions (Fig. 4). These experiments provide information on how hydrothermal aging and subsequent SO₂ exposure affect the formation of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$. The reaction of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes with NO results in a consumption of NO in the range of 100–200 °C, resulting in a decrease in NO concentration at the reactor outlet, typically with a minimum around 120–135 °C. To assess the effect of hydrothermal aging on the impact of SO₂, the data for the fresh catalyst are included as a reference. The consumption of NO is related to the amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ species such that high NO consumption corresponds to a high amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ species.

Fig. 4(a) shows the NO consumption for the reference catalyst without aging. The NO consumption takes place at 120 °C. After exposure of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex to SO₂,

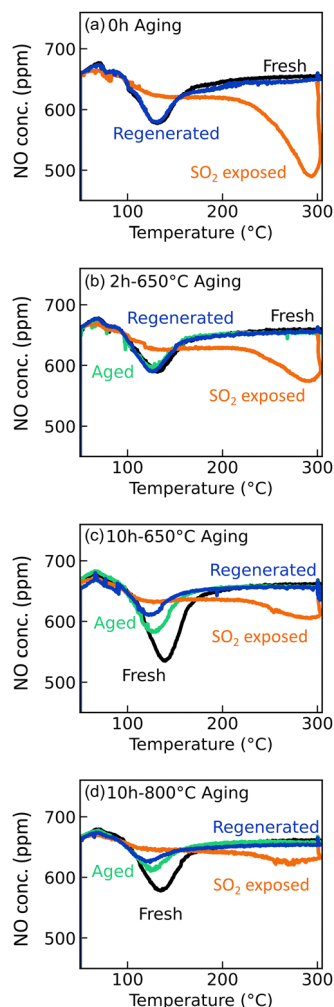


Fig. 4 NO-TP reaction for fresh, aged, SO_2 -exposed aged, and regenerated catalysts under four aging conditions: 0 h (a), 2 h at 650 °C (b), 10 h at 650 °C (c), and 10 h at 800 °C (d).

the NO consumption peak shifts to 290 °C. This shift indicates that SO_2 exposure reduces the reactivity of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ peroxy complexes towards NO at low temperatures, and that a higher temperature is needed for the reaction to proceed. This observation is in agreement with earlier observations.³¹ After regeneration by heating to 550 °C, the NO consumption around 120 °C is restored. This agrees well with the observed impact on the trend in NH_3 -SCR activity after exposure to SO_2 and regeneration. Furthermore, it indicates that the loss of activity at 175 °C in the presence of NO is due to a reduced reactivity of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex in the presence of SO_2 , most probably due to the formation of some Cu-sulfate species.³⁰

Fig. 4(b) shows the NO-TP reaction for aging at 650 °C for 2 hours before SO_2 exposure. The fresh and aged catalysts show similar NO consumption profiles, suggesting that the amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes is not affected by 2 h hours of aging. The effect of hydrothermal aging prior to SO_2 exposure (orange curve) is a lower NO consumption, indicating a lower amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes. This is consistent with the lower activity of the aged and SO_2 exposed catalysts

compared to the fresh catalyst as shown in Fig. 2(b). After regeneration, the catalyst shows a NO consumption similar to that of the fresh and aged catalysts, indicating that most of the catalysts can be regenerated.

Fig. 4(c) and (d) shows the NO-TP reaction for 10 hours aging at 650 °C and 800 °C before SO_2 exposure, respectively. The aged catalyst shows a lower $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex formation in both the cases compared to the fresh catalyst. This suggests that with increased aging duration and temperature, the ability to form $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ is reduced along with the loss of Brønsted acid sites. The SO_2 exposed aged catalyst (10 h at 650 °C and 800 °C) shows the same trend, with a delayed reaction of NO with the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex to 300 °C. However, the consumption of NO is significantly lower in these cases, which may indicate a further reduction of the reactivity of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes. In these cases, the regeneration at 550 °C does not result in a complete restoration of the NO consumption of the aged catalysts, indicating that SO_2 exposure also affects the ability to form $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes.

The uptake of SO_2 is also influenced by hydrothermal aging. Fig. 5 shows the SO_2 uptake profiles measured during the SO_2 exposure to the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex over fresh and hydrothermally aged catalysts. The measured SO_2 uptake for the fresh catalyst is 202 $\mu\text{mol g}^{-1}$. Hydrothermal aging leads to progressively lower SO_2 uptakes of 151, 126, and 104 $\mu\text{mol g}^{-1}$ after aging for 2 h at 650 °C, 10 h at 650 °C, and 10 h at 800 °C, respectively. We note that the Cu-content in the catalyst is 3.2 wt%, which corresponds to 504 $\mu\text{mol g}^{-1}$. Thus, the SO_2 uptake values correspond to a SO_2/Cu ratio of 0.40 for the fresh catalyst, and 0.30 (2 h at 650 °C), 0.25 (10 h at 650 °C), and 0.21 (10 h at 800 °C). As the SO_2 uptake proceeds *via* a reaction with the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex,^{29,30} the lower SO_2 uptake in the aged catalysts is a consequence of the lower concentration of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex in the hydrothermally aged catalysts.

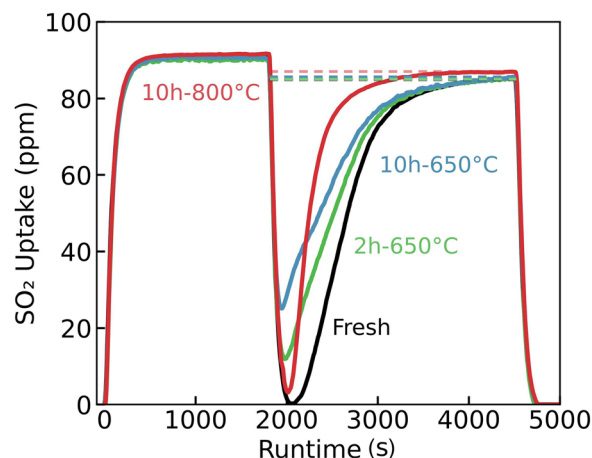


Fig. 5 SO_2 uptake for fresh, aged, SO_2 exposed aged, and regenerated catalysts under four aging conditions: 0 h, 2 h at 650 °C, 10 h at 650 °C, and 10 h at 800 °C. The baselines for the integration of the SO_2 uptake are indicated by dashed lines.

4. Discussion

Our results show that the deactivation by SO_2 in fresh and hydrothermally aged catalysts follows the same pattern and is related to the ability to form the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ peroxo complexes. In our measurements, we have adopted a procedure to maximize the amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ in the catalyst before exposure to SO_2 , as the main pathway for SO_2 uptake is the reaction with $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$. Even though such a procedure does not represent the actual conditions in an exhaust after-treatment system, it links the impact of hydrothermal aging on the SO_2 deactivation to the formation of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes before and after hydrothermal aging. The measurement monitors the ability of the catalyst to form the Cu-ions that are available for the SCR-reaction. To form the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes, the catalyst is exposed to NO and NH_3 , and therefore, ammonia will be present in the catalyst when exposed to SO_2 . The presence of NH_3 is important, as the impact of SO_2 is enhanced in the presence of ammonia.^{26,33,55,56}

The data in Fig. 2 show that the hydrothermally aged catalysts have a decreased activity by about 60% upon SO_2 exposure with respect to the activity before SO_2 exposure. This is a lower value than for the fresh catalyst, which has a decrease by 70%. Furthermore, the deactivation by SO_2 seems to decrease somewhat with increasingly severe hydrothermal aging conditions. The similar impact of hydrothermal aging is a consequence of the fact that both the rate of the NH_3 -SCR reaction at 175 °C and the deactivation by SO_2 depend on the formation of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes.^{29–31,34,57} Hydrothermal aging results in a lower amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex, as indicated by the decrease in NO consumption around 120 °C in Fig. 4, in good agreement with a slower oxidation half cycle in the NH_3 -SCR cycle.⁵⁸

Hydrothermal aging can also lead to the formation of “occluded” CuO_x nanoclusters that become trapped within the zeolite cages.⁵⁴ These CuO_x species are catalytically poor and reduce the amount of framework-exchangeable Cu sites available for the formation of the active $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complex. The lower amount of the $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes then leads to the lower NH_3 -SCR activity, a reduced consumption of NO around 120 °C (Fig. 4), and a lower uptake of SO_2 (Fig. 5).

From a comparison of the SO_2 uptake data and deactivation, we observe that the 60–70% deactivation by SO_2 corresponds to SO_2/Cu ratios in the range of 0.2–0.4. This means that, in the deactivated state, only a small fraction of Cu actually interacts with SO_2 . Furthermore, at such low SO_2/Cu ratios, it is not possible to accumulate larger amounts of ammonium sulfate. A similar SO_2/Cu ratio has been observed earlier and indicates a high SO_2 sensitivity of Cu-CHA catalysts.^{23,34,50,59} This strong effect of SO_2 is consistent with a SO_2 -deactivation mechanism, in which a single SO_2 molecule can affect two $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ complexes.³⁰

The NH_3 -TPD data in Fig. 3 show that an exposure to SO_2 followed by a regeneration step at 550 °C does not affect the adsorption of NH_3 . This indicates that the interaction of SO_2

with hydrothermally aged catalysts does not further change the structure of the catalyst. This agrees with the conclusion that deactivation by SO_2 and hydrothermal aging are rather independent. Hydrothermal aging results in structural changes, and relocation of Cu in the catalyst. These changes result in a lower amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$, and the corresponding loss of NH_3 -SCR activity and SO_2 uptake. On the molecular level, however, the interaction of SO_2 with the catalyst remains unchanged.

5. Conclusions

We have studied the impact of hydrothermal aging on SO_2 deactivation on Cu-CHA using activity measurement, NH_3 -temperature-programmed desorption (NH_3 -TPD), NO-temperature-programmed reduction (NO-TPR), and SO_2 uptake measurements. For both fresh and hydrothermally aged catalysts, exposure to SO_2 causes a 60–70% loss in activity. Subsequent regeneration by heating to 550 °C in 10% O_2/N_2 restores roughly 90% of the activity of the aged catalyst. Therefore, the mechanism of SO_2 deactivation is independent of hydrothermal aging. The SO_2 deactivation occurs at SO_2/Cu ratios of 0.2–0.4, indicating that SO_2 affects more than one Cu-ion. The impact of hydrothermal aging on the deactivation by SO_2 is determined by the amount of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ that can be formed. The SO_2 -exposed aged catalysts form less $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ compared to only the SO_2 -exposed catalyst and the formation of $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ decreases with increased aging duration and temperature. At a molecular level, the reaction between SO_2 and $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$ is not affected by hydrothermal aging. All structural changes in the catalyst are due to hydrothermal aging, and a cycle of SO_2 exposure and regeneration does not change the adsorption of ammonia. Moreover, aging prior to SO_2 exposure reduces the regeneration ability of the catalyst mainly due to irreversible deactivation caused by hydrothermal aging, along with an additional 5–10% irreversible loss associated with SO_2 exposure. Our results indicate that modeling the combined effects of hydrothermal aging and SO_2 poisoning can be done by first describing how hydrothermal aging affects the ability to form the Cu-peroxo complex, and then incorporating the effects of SO_2 .

Author contributions

Shivangi Singh: investigation and writing – original draft. Ton V. W. Janssens: supervision, writing – review and editing, and funding acquisition. Henrik Grönbeck: supervision, writing – review and editing, and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information (SI): the detailed experimental procedure for measurements of activity, NH_3 -TPD and NO-TP

reactions and SO₂ uptake measurements. See DOI: <https://doi.org/10.1039/d6cp02296k>.

Numerical data for all figures are available at <https://doi.org/10.5281/zenodo.18805340>.

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