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Insight into the origin of sulfur tolerance of Ag/Al_2O_3 in the H_2 - C_3H_6 -SCR of NOx



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ABSTRACT

The sulfur tolerance of Ag/Al₂O₃ catalysts in H₂-assisted C₃H₆-SCR was investigated by UV–vis, TPR, TPSR, DRIFTS-MS, and DFT calculations. Ag/Al₂O₃ with higher silver loadings exhibited better deNOx performance and sulfur tolerance, especially the 4% Ag/Al₂O₃ catalyst. UV–vis and H₂-TPR revealed that highly dispersed Ag⁺ cations were predominant on 2% Ag/Al₂O₃, while more metallic Ag clusters with large sizes were present on the 4% Ag/Al₂O₃. After exposure to SO₂, large amounts of sulfates were adsorbed on the Ag sites and Al sites of the Ag/Al₂O₃ surface. The sulfates were reduced to H₂S and SO₂ in a reducing atmosphere, while they showed little decomposition under real SCR reaction conditions. DRIFTS-MS experiments showed that sulfate species transferred rapidly between Ag sites and Al sites on the Ag/Al₂O₃ catalysts with higher amounts of Ag clusters. DFT calculations revealed that Ag₁ cations show stronger affinity for sulfate species than Ag clusters, thus resulting in blockage by sulfates at the Ag-O-Al interface. Such blocking by sulfates suppressed the activation of C₃H₆ as well as the formation of -NCO species, and thus severely inhibited the deNOx performance of 2% Ag/Al₂O₃. In contrast, the rapid mobility of sulfate species on 4% Ag/Al₂O₃ made more active sites available for the formation of key intermediates of HC-SCR, finally contributing to its excellent sulfur tolerance.

1. Introduction

NOx emission reduction for diesel engines is an important task for environmental protection. For this application, selective catalytic reduction of NOx utilizing on-board diesel or its additives as reductants (HC-SCR) exhibits unique advantages for NOx removal compared to the commercial application of NH₃-SCR [1–4]. Among the catalysts employed for the HC-SCR process, alumina-supported silver (Ag/Al₂O₃) is one of the most promising catalysts [4–14]. Moreover, a small amount of hydrogen addition significantly enhances the low-temperature activity of Ag/Al₂O₃ in HC-SCR, which is beneficial for its practical application [15–24].

As diesel engine exhaust contains a certain amount of SO₂, development of catalysts with high sulfur resistance is important for their practical application [1,2,25–27]. Therefore, several researchers have investigated the SO₂ poisoning mechanism of Ag/Al₂O₃ during HC-SCR [28–35]. Generally, the deactivation induced by SO₂ is mainly due to

the generation of thermodynamically stable sulfate species, which reduce the active sites available for NOx reduction [29,31,32,35]. Meunier et al. [29] found that pretreatment of 1.2% Ag/Al₂O₃ with SO₂ (100 ppm) resulted in rapid and permanent deactivation for C₃H₆-SCR, due to the formation of two sulfate species interacting with Al₂O₃ and silver species, respectively. In contrast, Houel et al. [34] found that sulfur-poisoned 4 wt% Ag/Al₂O₃ could be regenerated in n-octane-SCR at 600 °C. During C₃H₆-SCR at 500 °C, similarly, Park et al. reported that the deNOx performance of 2 wt% Ag/Al₂O₃ was completely recovered after the removal of SO₂ [31]. Over an 8 wt% Ag/Al₂O₃ catalyst, interestingly, the addition of SO₂ improved the NOx reduction due to the formation of active Ag₂SO₄. Furthermore, the sulfur resistance of Ag/Al₂O₃ is closely related to the nature of the reductant, and oxygenated hydrocarbons were found to be more advantageous for achieving high SO₂ tolerance [32].

Compared with Ag/Al₂O₃, Ag/TiO₂-Al₂O₃ catalysts synthesized by a sol-gel method exhibited superior deNOx activity and SO₂ resistance

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due to a lower rate of sulfate accumulation [36]. Similarly, Umbarkar et al. [33] found that magnesia doping decreased the total acidity of Ag/Al_2O_3 and thus prevented the formation of sulfates, finally contributing to excellent low-temperature catalytic performance and sulfur resistance. Meanwhile, it was reported that H_2 addition improved the SO_2 tolerance of Ag/Al_2O_3 by cleaning off the sulfates adsorbed on silver-containing sites [28,32].

The results mentioned above show that the deactivation of Ag/ Al₂O₃ induced by SO₂ is related to the catalyst formulation, gas mixture composition, and reaction temperature [32,33,36,37]. Under real conditions of HC-SCR, the sulfate species were hard to decompose or reduce [29,31,34], while the activity of Ag/Al₂O₃ was completely regenerated once SO_2 was removed [31]. Hence, not only the decomposition and/or reduction behavior of sulfates, but also other factors govern the SO₂ tolerance of Ag/Al₂O₃, which have not yet been fully clarified. To this aim, Ag/Al2O3 catalysts were prepared and carefully characterized, and the behaviors of sulfates on the surface of Ag/Al₂O₃ were investigated by TPSR, DRIFTS-MS, and DFT calculations. It was found that sulfate species transferred rapidly at the Ag-O-Al interface of Ag/Al₂O₃ catalysts with greater proportions of Ag clusters, which showed excellent sulfur resistance during H₂-C₃H₆-SCR. This investigation provides a clue for the development of Ag/Al₂O₃ catalysts with excellent sulfur tolerance in HC-SCR.

2. Materials and methods

2.1. Materials and catalytic performance studies

Ag/Al₂O₃ catalysts were prepared by an impregnation method, as reported in our previous works [7,38]. After impregnation, these samples were further calcined in flowing air at 600 °C for 3 h. A sample with x wt% silver loading is hereafter named x% Ag/Al₂O₃. For comparison, an Al₂O₃ sample without silver loading was prepared via the same process. In the SO₂ poisoning studies, the samples (2 g) were poisoned in a SO₂-containing gas flow (50 ppm SO₂ + 10% O₂, 1000 mL/min) at 400 °C for 12 h [35], and thus described as x% Ag/Al₂O₃-S.

To study the influence of the nature of the silver species on the sulfur tolerance of Ag/Al₂O₃ catalysts, a 2% Ag/Al₂O₃ sample was synthesized and calcined in air at 900 °C for 3 h, and thereafter named 2%Ag/Al₂O₃-900 [38]. In addition, another 2% Ag/Al₂O₃ sample was synthesized and calcined at 600 °C, with Al₂O₃ pre-calcined at 900 °C as the precursor, and thereafter named 2%Ag/(Al₂O₃-900). The Al₂O₃ sample pre-calcined at 900 °C is named Al₂O₃-900.

The catalytic measurements were carried out in a fixed-bed reactor with inner diameter of 7 mm as reported in our previous works [7,38]. The gas flow (1000 mL/min) consisted of 800 ppm NO, 1714 ppm C_3H_6 , 1% H_2 , 10% O_2 , and 3% H_2O , with N_2 balance. 300 mg catalyst samples (20–40 mesh) were used, thus corresponding to a GHSV of 100 000 h⁻¹. The reactants and products (NO, NO₂, NH₃, N₂O, and C_3H_6) were monitored by a FTIR spectrometer (Nicolet is10). The NOx and C_3H_6 conversions and N_2 yield were calculated by the following equations:

$$NOx \quad conversion = \left(1 - \frac{[NO_x]_{out}}{[NO_x]_{in}}\right) \times 100\%$$
(1)

$$C_{3}H_{6}$$
 conversion = $\left(1 - \frac{[C_{3}H_{6}]_{out}}{[C_{3}H_{6}]_{in}}\right) \times 100\%$ (2)

$$N_{2} \quad yield = \left(\frac{[NO_{x}]_{in} - [NO_{x}]_{out} - [NH_{3}]_{out} - 2^{*}[N_{2}O]_{out}}{[NO_{x}]_{in}}\right) \times 100\%$$
(3)

where $NOx = NO + NO_2$

2.2. Catalyst characterization

BET analysis and X-ray powder diffraction (XRD) measurements

were carried out according to our previous works [7,38]. UV-vis measurements were carried out in absorption mode with alumina as reference (Shimadzu, UV3600Plus, Japan). H₂-TPR experiments were carried out on a chemical adsorption instrument (AutoChem II 2920, Micromeritics) equipped with a TCD detector. Before each experiment, the samples (100 mg) were pretreated in 20% O_2/N_2 at 350 °C for 30 min, and subsequently cooled down to 50 °C. The TPR experiments were then performed in 10% H₂/Ar at a rate of 10 °C/min.

TPSR experiments were performed on the Micromeritics AutoChem 2920 apparatus using a MS detector (Cirrus 2, MKS). The poisoned samples (150 mg) were pretreated in Helium at 300 °C for 60 min and then cooled to 50 °C. Then the samples were further heated up (20 °C/min) in a flow of 10%H₂/Ar and 1%H₂/10%O₂/Ar (30 mL/min), respectively.

The amounts of residual sulfates adsorbed on the Ag/Al₂O₃ catalysts after catalytic test were analyzed by ion chromatography. The samples were diluted with ultrapure water to 25 mL and then extracted by sonication for 30 min. The solution was then analyzed using Wayee IC-6200 ion chromatography equipped with a TSKgel Super IC-CR cationic analytical column.

2.3. In situ DRIFTS studies

In situ DRIFTS experiments were performed on a FT-IR spectrometer (Nexus 670, Thermo Nicolet) equipped with an MCT/A detector. The samples were pretreated at 350 °C for 30 min in $10\%O_2/N_2$ (300 mL/min) and cooled to the desired temperature to collect spectra for reference [7,38]. The concentration of SO₂ in the outlet was monitored by a mass spectrometer (InProcess Instruments, GAM 200).

2.4. DFT calculations

DFT calculations were performed using the Materials Studio (MS) Modeling CASTEP package from Accelrys (Materials Studio 7.0, 2013). Based on previous works [7,11,39,40], the dehydrated (100) and (110) surfaces of γ -Al₂O₃ were modeled. For the Ag ion, AgO units adsorbed on the Al₂O₃ (100) and (110) surfaces were established and relaxed (Fig. S1). For the Ag_n cluster, Ag₃ units adsorbed on the Al₂O₃ (100) and (110) surfaces were established and relaxed (Fig. S2) according to our previous work [11]. Detailed information about the DFT calculations has been provided in the supplementary materials.

The adsorption energies of sulfate (SO₄^{2–}) on the Ag/Al₂O₃ surface were calculated as follows:

 $E_{ad} = E_{adsorbate + surface} - (E_{surface} + E_{adsorbate})$, where E_{ad} indicates the adsorption stability of sulfate on the surface of Ag/Al₂O₃.

3. Results

3.1. DeNOx performance and sulfur tolerance

The deNOx performance of fresh and poisoned Ag/Al₂O₃ samples was examined in H₂-C₃H₆-SCR (Fig. 1). Except for 1% Ag/Al₂O₃, other fresh samples obtained ~100% NOx conversion at ~320 to ~500 °C. Notably, the Ag/Al₂O₃ samples with higher silver loading exhibited better low-temperature deNOx performance, especially 4% Ag/Al₂O₃. Furthermore, as the silver loading increased, the light-off temperature of C₃H₆ conversion gradually decreased, consistent with the change in NOx conversion (Fig. S3). In our previous works, it was found that increasing the silver loading of Ag/Al₂O₃ usually resulted in a decrease in water tolerance due to the formation of large metallic silver species [7,38]. In the present work, the 4% Ag/Al₂O₃ catalyst showed excellent deNOx performance, possibly due to the lower concentration of water vapor (3%), which showed a significant effect on NOx reduction in HC-SCR [14]. In addition, the 2% Ag/Al₂O₃-900 and 2% Ag/(Al₂O₃-900) samples exhibited worse water tolerance than that of 2% Ag/Al₂O₃ (not shown), consistent with our previous work [38]. Meanwhile, it was



Fig. 1. NOx conversions on the Ag/Al₂O₃ (A) and Ag/Al₂O₃-S (B) during the H₂-C₃H₆-SCR. Feed composition: 800 ppm NO, 1714 ppm C₃H₆, 1% H₂, 10% O₂, 3% H₂O, N₂ balance. GHSV: 100 000 h^{-1} .

found that the addition of a low amount of H₂ (2000 ppm) also significantly improved the deNOx performance of Ag/Al₂O₃ in C₃H₆-SCR [38]. On the poisoned Ag/Al₂O₃ samples, the deNOx performance of all samples was suppressed to some extent (Fig. 1B), particularly for those with low silver loadings. For example, the NOx conversion decreased from 100% to 61% over 2% Ag/Al₂O₃ after SO₂ poisoning. In contrast, 4% Ag/Al₂O₃-S exhibited excellent deNOx performance, achieving > 95% NOx conversion in the range of ~ 300 – ~ 500 °C.

To further investigate the sulfur tolerance of the Ag/Al₂O₃ catalysts, step-response experiments were performed at 400 °C (Fig. 2). In this case, the 1% Ag/Al₂O₃ sample was not measured due to its poor deNOx performance. In the initial stage under SO₂-free conditions, all samples achieved 100% NOx conversion. After the introduction of SO₂, the deNOx performance of 2% Ag/Al₂O₃ catalyst was severely suppressed and the NOx conversion decreased to ~30% after 4 h of SO₂ exposure. Such suppression was also observed over 3% Ag/Al₂O₃, which achieved NOx conversion of ~75% after SO₂ exposure. In contrast, 4% Ag/Al₂O₃ exhibited excellent sulfur tolerance and achieved ~93% NOx conversion even after 30 h of SO₂ exposure (Fig. S5). Notably, the C₃H₆ conversion exhibited a similar trend as the NOx reduction (Fig. S4), revealing the crucial role of C₃H₆ activation in NOx reduction.

Meanwhile, the sulfur tolerance of Ag/Al₂O₃ catalysts has been investigated in the H_2 -C₃ H_6 -SCR at a high GHSV of 300 000 h⁻¹ at various temperatures (Fig. S6). At 300 °C, the 2% Ag/Al₂O₃ and 3% Ag/Al₂O₃ were almost completely deactivated in the presence of SO₂ with



Fig. 2. The effect of SO₂ on the NOx conversion over Ag/Al₂O₃ catalysts with different silver loadings (A) and 2%Ag/Al₂O₃ calcined at different temperatures (B) during the H₂-C₃H₆-SCR at 400 °C. Feed composition: 800 ppm NO, 1714 ppm C₃H₆, 1% H₂, 10% O₂, 3% H₂O, 20 ppm SO₂ (when added), N₂ balance. GHSV: 100 000 h⁻¹.

NOx conversions of less than 5%. Under the same reaction conditions, although the NOx conversion of 4% Ag/Al₂O₃ decreased from 80% to 23%, this sample was still the best among these catalysts. At 400 °C, the decrease in NOx conversion for 2% Ag/Al₂O₃ was 69% (from 94% to 25%) after exposure to SO₂, while the corresponding values for 3% Ag/ Al₂O₃ and 4% Ag/Al₂O₃ were 25% (from 87% to 62%) and 15% (from 83% to 68%), respectively. At 500 °C, the NOx conversion of 2% Ag/ Al₂O₃ and 3% Ag/Al₂O₃ decreased by 41% and 13% after exposure to SO₂, respectively. In contrast, the addition of SO₂ increased the NOx conversion of 4% Ag/Al₂O₃ from 47% to 59% at 500 °C. Similar phenomenon has also been found in the work of Angelidis et al [30], in which this enhancement was attributed to the suppression on direct combustion of reductant. Obviously, the sulfur tolerance of these catalysts enhanced as the reaction temperature increased. From overall view, the Ag/Al₂O₃ samples with higher silver loading exhibited better sulfur tolerance at various temperatures.

Interestingly, the 2% Ag/Al₂O₃-900 and 2% Ag/(Al₂O₃-900) samples also exhibited excellent sulfur tolerance in the above step-response experiments, obtaining NOx conversion of 80% and 85% in the presence of SO₂, respectively (Fig. 2B). The N₂ yield and C₃H₆ conversion exhibited the same trend as the NOx conversion (Fig. S7). Hence, both the silver loading and the state of silver species affected the sulfur tolerance of Ag/Al₂O₃. Considering the difference in sulfur tolerance



Fig. 3. UV–vis spectra of fresh and SO_2 poisoned 2% Ag/Al_2O_3 and 4% $Ag/Al_2O_3.$

shown by Ag/Al_2O_3 with 2 and 4 wt% silver loadings, the following investigation focused on these samples.

3.2. Structural properties of Ag/Al₂O₃

BET analysis (Table S1) showed that the specific surface areas of Ag/Al₂O₃ catalysts calcined at 600 °C are similar to that of the pure Al₂O₃ (237 m²/g). However, calcination at 900 °C caused a decrease in BET surface area of Al₂O₃-900 (163 m²/g), 2% Ag/Al₂O₃-900 (167 m²/g), and 2% Ag/(Al₂O₃-900) (152 m²/g). XRD measurements revealed that only the γ -Al₂O₃ phase existed in the Al₂O₃ and Ag/Al₂O₃ catalysts calcined at 600 °C (Fig. S8). In contrast, the δ -Al₂O₃ phase was also detected for the samples calcined at high temperature, together with the presence of γ -Al₂O₃ phase. Therefore, calcination at 900 °C induced the phase transition of γ -Al₂O₃ to δ -Al₂O₃, which further led to the reduction of surface area [38,41]. Furthermore, XRD measurements did not detect any crystal phase of silver species on any of the samples.

Fig. 3 exhibits the UV–vis spectra of fresh and SO₂-poisoned Ag/ Al₂O₃ samples. To eliminate interference from the absorption of the support, the spectrum of pure Al₂O₃ was subtracted from the spectra of the Ag/Al₂O₃ samples. For these samples, five adsorption peaks at 230, 260, 290, 350, and 450 nm were observed. According to previous literature [42,43], the peaks located at 230 and 260 nm are commonly attributed to dispersed Ag cations (Ag⁺) and oxidized Ag clusters (Ag_n δ^+), respectively. In addition, the peaks at 290 and 350 nm are generally due to small metallic Ag clusters (Ag_n°), and the broad peak at 450 nm is attributed to metallic Ag clusters with large sizes [43–45].

In order to quantitatively compare different silver species, the spectra of Ag/Al_2O_3 catalysts were fitted and deconvoluted to constituent peaks (Fig. S9 and Table S2) [38,42]. Over the fresh samples, dispersed Ag^+ species were predominant, along with some metallic Ag clusters (Ag_n°) of different sizes. Notably, the amount of large metallic Ag clusters on 4% Ag/Al_2O_3 (22%) was significantly higher than on 2% Ag/Al_2O_3 (6.6%). The spectrum of Ag/Al_2O_3 calcined at 900 °C is shown in Fig. S9. Compared with 2% Ag/Al_2O_3 (6.6%), there are more metallic Ag clusters with large sizes on 2% Ag/Al_2O_3 -900 (35%) and 2% $Ag/(Al_2O_3-900)$ (21%). On the poisoned samples, the peaks at 350 and 450 nm almost disappeared, while the intensities of bands with lower wavelengths (260 and 290 nm) increased. This result revealed that SO₂ poisoning induced the transition of metallic silver species to



Fig. 4. H₂-TPR profiles of the Al₂O₃ and Ag/Al₂O₃ catalysts.

oxidized ones via the following reaction [29]:

$$2Ag + SO_2 + O_2 \rightarrow Ag_2SO_4 \tag{4}$$

H₂-TPR profiles showed that a minuscule H₂ consumption between 250 and 300 °C occurred on the pure Al₂O₃ (Fig. 4), which may be caused by the baseline [46]. Only a strong H₂ consumption peak centered at ~270 °C was observed over for 2% Ag/Al₂O₃. This peak also appeared for 4% Ag/Al2O3, accompanied by a low-temperature shoulder at ~100 - ~200 °C. Clearly, both Ag/Al₂O₃ samples contain reducible species (Ag₂O and/or Ag⁺), while those on 4% Ag/Al₂O₃ can be reduced at lower temperatures [45-47]. Quantitative data on the H₂ consumption of Ag/Al₂O₃ samples are provided in Table S3. The reduction degree is calculated based on the stoichiometry, such that reduction of 1 mol Ag⁺ requires 1/2 mol H₂ [46]. The reduction degrees for 2% Ag/Al₂O₃ and 4% Ag/Al₂O₃ are 64.8% and 46.4%, respectively, indicating that the proportion of non-reducible metallic silver on 4% Ag/Al₂O₃ is higher than on 2% Ag/Al₂O₃. Besides, there are also two H₂ consumption peaks observed on 2% Ag/Al2O3-900 and 2% Ag/(Al2O3-900), the reduction degrees for which are 55.9% and 56.6%, respectively (Fig. S10). Obviously, the proportions of non-reducible metallic silver on these two samples are also higher than on 2% Ag/Al₂O₃. The results of H2-TPR were consistent with the UV-vis results, further confirming that there were more metallic Ag clusters with large sizes on 4% Ag/Al₂O₃, 2% Ag/Al₂O₃-900, and 2% Ag/(Al₂O₃-900) than 2% Ag/ Al_2O_3 .

To further investigate the adsorption of sulfate species on these samples, TPSR experiments were performed in different atmospheres (Fig. 5). In a reducing atmosphere of 10% H₂/Ar, H₂S (m/z = 34) and SO₂ (m/z = 64) were detected over all poisoned samples (Fig. 5A). On the Al₂O₃-S sample, SO₂ appeared at temperatures above 500 °C, while the signal of H₂S emerged at 550–750 °C. Notably, two peaks of SO₂ centered at ~550 °C and ~650 °C were observed, the latter of which emerged simultaneously with the signal of H₂S. The peak at ~550 °C can be attributed to direct desorption of weakly adsorbed SO₂, and the peak at ~650 °C is assigned to the reduction of sulfates. Over the poisoned Ag/Al₂O₃, it should be noted that H₂S and SO₂ appeared simultaneously at temperatures above 400 °C.

To quantitatively investigate the formation of the above species, all spectra in Fig. 5A were integrated, with the results shown in Table S4. The SO₂ profile of Al_2O_3 -S was fitted and deconvoluted into constituent peaks (Fig. S11), which were further integrated. For these samples, the



Fig. 5. TPSR spectra of SO₂ poisoned Al₂O₃ and Ag/Al₂O₃ in a flow of 10% H₂/ Ar (A) and 1%H₂/10%O₂/Ar (B). Before measurement, the samples were pretreated in a flow of He at 300 °C for 30 min.

amount of desorbed species could be arranged in descending order as follows: 2% Ag/Al₂O₃-S > 4% Ag/Al₂O₃-S > Al₂O₃-S. Notably, the proportion of the desorbed amounts of these species was almost the same over all samples, approximately equal to 0.15: 1 (SO₂/H₂S), revealing the same mechanism for sulfate reduction on all samples.

The TPSR measurements were also performed in a flow of 1%H₂/10%O₂/Ar, which is closer to practical reaction conditions. In this situation, however, only SO₂ (m/z = 64) was detected over all samples, giving a strong peak centered at ~950 °C with almost the same intensity in all cases. The absence of H₂S confirmed that decomposition of sulfates rather than reduction took place during this process. It should be noted that the desorption of sulfur species was much less than that obtained in the reducing atmosphere, revealing that the sulfates showed little decomposition under real reaction conditions. In addition, a weak peak at ~250 - ~400 °C was observed over 2% Ag/Al₂O₃-S, the occurrence of which possibly explained the improvement of deNOx performance at 200 ~ 400 °C on this sample (Fig. 1B).

3.3. In situ DRIFTS studies of sulfate species

3.3.1. Sulfate formation and its influence on C_3H_6 oxidation and nitrate formation

In-situ DRIFTS experiment was performed to investigate the adsorption of sulfates on the Ag/Al₂O₃ catalysts during SO₂ poisoning



Fig. 6. In situ DRIFTS spectra of adsorbed species over Al_2O_3 and Ag/Al_2O_3 in steady states in a flow of $SO_2 + O_2$ at 400 °C for 5 h. Feed composition: SO_2 50 ppm, O_2 10%, N_2 balance.

(Fig. 6). In this case, two peaks at 1365 and $1345 \,\mathrm{cm}^{-1}$ emerged on the pure Al₂O₃, indicating the formation of sulfates adsorbed on the Al sites (Al-sulfates) [28,35]. Over Ag/Al₂O₃ catalysts, the Al-sulfate species were also produced and exhibited much stronger intensity during the above process. Meanwhile, another two bands at 1316 and 1270 cm⁻¹ were observed, suggesting the appearance of sulfates adsorbed on the Ag sites (Ag-sulfates) [32,48].

To further compare the adsorption of sulfate species, the above spectra (Fig. 6) were fitted and deconvoluted into constituent peaks (Fig. S12A) [28]. As shown in Fig. S12B, the amounts of sulfates adsorbed on different samples can be arranged as follows: Al_2O_3 (3.6 a.u.) < 4% Ag/Al_2O_3 (55.8 a.u.) < 2% Ag/Al_2O_3 (71.3 a.u.), which is consistent with the TPSR results. It is generally recognized that SO₂ reacts with O₂ to form ad-SO₄²⁻, which is further adsorbed on the Ag/Al₂O₃ surface [28,29]. Hence, it could be speculated that the pure Al₂O₃ was inefficient for the oxidation of SO₂ to produce ad-SO₄²⁻, most of which further migrated to the Al sites [28,35]. The smaller amount of sulfate species on 4% Ag/Al₂O₃ may be due to the decrease in acidity of Al₂O₃ with increasing silver loading [49], and/or the decrease in the sites for sulfates adsorption stemmed from the coverage of Al₂O₃ by silver species.

Generally, the activation of hydrocarbons is the initial step of HC-SCR over Ag/Al₂O₃ catalysts [1–4]. Hence, the partial oxidation of C₃H₆ was investigated on the fresh and poisoned Ag/Al₂O₃ samples (Fig. S13). During this process, large amounts of enolic species (1633, 1406, and 1336 cm⁻¹) and acetate (1576 and 1460 cm⁻¹) were produced on the fresh samples, particularly at temperatures below 350 °C [7,50,51]. On 2% Ag/Al₂O₃-S, the formation of enolic species was severely suppressed at temperatures below 350 °C, while acetate was hardly affected except at the temperature of 200 °C. In contrast, a considerable amount of enolic species was yielded on the 4% Ag/Al₂O₃-S at temperatures above 250 °C, while the formation of acetate was slightly enhanced. Furthermore, a weak negative peak at 1365 cm⁻¹ attributed to the overlay of sulfates was also observed on the poisoned samples (Fig. S13B and D).

The influence of sulfates on the formation of nitrates was also investigated for these samples (Fig. S14). After exposure to a flow of $H_2 + NO + O_2$, several strong characteristic peaks (1614, 1582, 1560,



Fig. 7. In situ DRIFTS spectra of adsorbed species over Ag/Al_2O_3 after exposure to a flow of $H_2 + NO + C_3H_6 + SO_2 + O_2$ at 400 °C for 3 h. Before measurement, these samples were pre-exposed to a flow of $H_2 + NO + C_3H_6 + O_2$ at 400 °C for 1 h. Feed composition: 800 ppm NO, 1714 ppm C_3H_6 , 1% H_2 , 10% O_2 , 20 ppm SO₂ (when added), N_2 balance.

1550, 1530, 1300, and 1245 cm⁻¹) were observed on the fresh samples due to monodentate nitrates (1560, 1550, 1530, and 1245 cm⁻¹), bidentate nitrates (1582 and 1300 cm⁻¹), and bridging nitrates (1614 cm⁻¹), respectively [7,38,52]. On the poisoned samples, however, the formation of nitrates was severely suppressed. It is generally recognized that nitrates mainly adsorb on the surface of alumina [1,2], on which sulfates also accumulated seriously during the process of SO₂ poisoning (Fig. 6). Hence, the adsorption of sulfate species reduced the adsorption sites on the Ag/Al₂O₃ available for the formation of nitrates [29,35].

3.3.2. The influence of sulfates on H_2 -C₃H₆-SCR over Ag/Al₂O₃

The effect of SO₂ on H₂-C₃H₆-SCR over Ag/Al₂O₃ catalysts was further investigated (Fig. 7). In this case, several intermediates emerged on the Ag/Al₂O₃ surface, including nitrates (1540, 1300, and 1245 cm⁻¹), acetate (1570 and 1460 cm⁻¹), formate (2997, 2905, and 1591 cm⁻¹), and –NCO species (2232 cm⁻¹) [1,2,7]. Among them, the –NCO species is generally recognized as an important intermediate for NOx reduction in HC-SCR [1,2,53,54]. The enolic species was not observed under the current conditions, probably due to its higher reactivity at high temperature (400 °C) [7].

After introducing SO₂ into the gas feed for 3 h, strong peaks due to sulfate species (1365, 1345, 1316, and 1270 cm⁻¹) were observed over both samples. Notably, the intensities of sulfate species were almost the same over these catalysts under the current conditions. Over 2% Ag/Al₂O₃, formate (2997, 2905, and 1591 cm⁻¹) and nitrate (1540 cm⁻¹) were severely suppressed by SO₂ addition, while the intensity of acetate was increased. Notably,–NCO species (2232 cm⁻¹) almost completely disappeared after SO₂ addition, suggesting the severe suppression of the deNOx performance. On 4% Ag/Al₂O₃, although the formation the nitrate was serevely inhibited, the –NCO species were hardly affected by SO₂ addition, indicating that this sample exhibited excellent sulfur tolerance, which is consistent with the results in Fig. 2.

The formation of nitrates was severely suppressed by sulfates over both 2%Ag/Al₂O₃ and 4%Ag/Al₂O₃ catalysts, while these samples showed quite different sulfur tolerance in the H₂-C₃H₆-SCR. Therefore, the suppression of the formation of nitrates could not be the key factor in the deactivation of Ag/Al₂O₃. In contrast, sulfates exhibited different influences on the activation of C_3H_6 on these samples (Fig. 7 and Fig. S13). Though formate shows low reactivity toward NOx reduction during HC-SCR [7,51], it can serve as a monitor for the activation of C_3H_6 . The oxidation of C_3H_6 on 2% Ag/Al₂O₃ was severely suppressed by SO₂ addition, while it was hardly affected on 4% Ag/Al₂O₃. Hence, it was speculated that the inhibition of C_3H_6 activation was more likely to be responsible for the suppression of NOx reduction.

3.3.3. The reduction/desorption of sulfates on Ag/Al_2O_3

Although large amounts of sulfates were produced on both samples in the above experiments, they showed markedly different influences on the deNOx performance of these catalysts (Fig. 7). To highlight this issue, step-response DRIFTS-MS experiments were performed in different atmospheres (Fig. 8). Specifically, after the formation of sulfates in the above experiment (Fig. 7), the samples were further sequentially exposed to N₂, 1%H₂/N₂, and 1%H₂/10%O₂/N₂. During this process, the dynamic changes of adsorbed species were measured by in situ DRIFTS (Fig. 8A and C), and the SO₂ in the effluent gas was detected by mass spectrometry (m/e = 64) simultaneously (Fig. 8B and D). Furthermore, the corresponding integrated areas of the peaks due to Alsulfates (1365 and 1345 cm⁻¹) and Ag-sulfates (1316 and 1270 cm⁻¹) were calculated and shown in Fig. 8B and D.

In the first stage of N₂ purging, the amount of Al-sulfates increased slowly, accompanied by a decrease of Ag-sulfates over both samples, indicating that the sulfates adsorbed on Ag sites slowly transferred to Al sites. When switching to 1% H₂/N₂, the sulfate species on 2% Ag/Al₂O₃ decreased very slowly. On 4% Ag/Al₂O₃, in contrast, the Ag-sulfates decreased rapidly in the initial 5 min, accompanied by a slow decrease in the next 25 min (Fig. 8D), and the Al-sulfates rapidly increased in the first minute. Furthermore, a rapid release of SO₂ (*m*/*e* = 64) was detected in the effluent gas within the initial 5 min. In the reducing atmosphere, the sulfates adsorbed on Ag sites rapidly transferred to Al sites over 4% Ag/Al₂O₃, while this was hardly observed on 2% Ag/Al₂O₃.

When switching to a flow of $1\%H_2/10\%O_2/N_2$, which is closer to practical reaction conditions, the sulfates on Al sites rapidly migrated to Ag sites, accompanied with release of SO₂ in the gas phase. Notably, such migration was much more remarkable on 4% Ag/Al₂O₃ than 2%



Fig. 8. Dynamic change in the DRIFTS spectra of adsorbed species on $2\% \text{ Ag/Al}_2O_3$ (A) and $4\% \text{ Ag/Al}_2O_3$ (C) at 400°C during the gas mixture switching from H₂/NO/C₃H₆/O₂/SO₂ (-30 - 0 min) to N₂ (0-30 min), H₂/N₂ (30-60 min), and H₂/O₂/N₂ (60-90 min), continuously. Before measurement, the samples were pre-exposed to a flow of H₂/C₃H₆/NO/SO₂/O₂ at 400°C for 3 h. The integrated areas of the peaks (1270 and 1316 cm⁻¹) due to Ag-sulfates and the peaks (1345 and 1365 cm⁻¹) due to Al-sulfates over 2%Ag/Al₂O₃ (B) and 4%Ag/Al₂O₃ (D), together with MS signal of SO₂ (*m*/*e* = 64). The feed composition was the same as Fig. 7.

Ag/Al₂O₃. In fact, the amount of SO₂ released in the gas phase from 4% Ag/Al₂O₃ was almost three times that from 2% Ag/Al₂O₃, indicating that more active sites are released for NOx reduction. Clearly, the sulfates on 4% Ag/Al₂O₃ were more mobile between Ag sites and Al sites, and were also more easily decomposed and released from the surface. As the sulfur tolerance of 4%Ag/Al₂O₃ was significantly different with the change of reaction temperature, the mobility of sulfate species on this catalyst was further investigated at 300 °C and 500 °C (Fig. S15). In this experiment, the mobility of sulfate species between Ag sites and Al sites was slower at 300 °C if compared with that at 500 °C. This result further confirmed the critical effect of mobility of sulfate species on the sulfur tolerance of Ag/Al₂O₃ catalysts. At 300 °C, notably, the amount of sulfate species adsorbed on the 4% Ag/Al₂O₃ was smaller than that at 400 °C and 500 °C. This may be attributed to the competitive adsorption of oxygenated hydrocarbons at lower temperature [35].

To further investigate the mobility of sulfate species, similar experiments were performed on the $2\% \text{ Ag/Al}_2\text{O}_3$ -900 and $2\% \text{ Ag/(Al}_2\text{O}_3$ -900) samples. After exposure to $\text{H}_2/\text{SO}_2/\text{O}_2$ at 400 °C for 3 h, large

amounts of sulfate species adsorbed on these samples (Fig. S16). The amounts of Al-sulfate on 2% Ag/Al₂O₃-900 and 2% Ag/(Al₂O₃-900) were lower than that on 2% Ag/Al₂O₃, possibly due to the lower BET surface area of the former samples. Afterwards these samples were further sequentially exposed to N₂, 1%H₂/N₂, and 1%H₂/10%O₂/N₂ as described above (Fig. 9 and Fig. S17). On the 2% Ag/Al₂O₃ sample calcined at 600 °C, the sulfates transferred slowly during the above process, accompanied by a low release of SO₂ (Fig. S17). On the 2% Ag/Al₂O₃-900 and 2% Ag/(Al₂O₃-900) samples, in contrast, the Ag-sulfates rapidly transferred to Al sites in the reducing atmosphere, and then quickly migrated to Ag sites after switching to a flow of H₂/O₂/N₂ (Fig. 9). Obviously, the mobility of sulfates on 2% Ag/Al₂O₃-900 and 2% Ag/(Al₂O₃-900) was also greater than that on 2% Ag/Al₂O₃.

3.4. DFT calculations of sulfate adsorption energy

The in-situ DRIFTS experiments showed that the mobility and desorption of sulfates on 4% Ag/Al₂O₃ was much greater than on 2% Ag/

G. Xu et al.



Fig. 9. Dynamic change in the DRIFTS spectra of adsorbed species on the 2%Ag/Al₂O₃-900 (A) and 2%Ag/(Al₂O₃-900) (B) at 400 °C during the gas mixture switching from H₂/SO₂/O₂/N₂ (-30 – 0 min) to N₂ (0–30 min), H₂/N₂ (30–60 min), and H₂/O₂/N₂ (60–90 min), continuously. Before measurement, the samples were pre-exposed to a flow of H₂+SO₂+O₂ at 400 °C for 3 h (Fig. S16).

Al₂O₃. Hence, the adsorption energies of sulfates on the surface of Ag/ Al₂O₃ were calculated. UV–vis and H₂-TPR measurements confirmed that dispersed Ag⁺ cations were predominant on 2% Ag/Al₂O₃, while more Ag clusters were present on 4% Ag/Al₂O₃. As a result, Ag₁ cations and Ag₃ clusters supported on the Al₂O₃ (110) and (100) surface were established and relaxed, which are hereafter described as Ag₁-Al₂O₃ and Ag₃-Al₂O₃ (Fig. S1 and S2), corresponding to 2% Ag/Al₂O₃ and 4% Ag/Al₂O₃, respectively [11,55]. The structures of sulfates adsorbed on the Ag and Al sites of the above models were established and relaxed (Fig. S18 and S19).

The DFT calculations showed that the adsorption energies of sulfates are negative, indicating a strong affinity between the sulfates and the catalyst surface (Table 1). Over the Ag_1 - Al_2O_3 sample, the adsorption energies of sulfates adsorbed on the Ag_1 sites of (110) and (100) surfaces were 12% and 28% less negative than those on the corresponding Al sites, respectively. Similarly, the adsorption energies of sulfates on the Ag_3 clusters of (110) and (100) surfaces were significantly less negative than those on the Al sites over the Ag_3 - Al_2O_3 sample. On both samples, the adsorption energies of sulfates adsorbed on the Ag sites were less negative than those on the Al sites, indicating that desorption of sulfates from the Ag sites was easier than that from Al sites. Furthermore, the adsorption energy of sulfates on the Ag_3 clusters was less negative than for those adsorbed on the Ag_1 cation, especially on the (100) surface. This result revealed that desorption of sulfates from the Ag_3 clusters was more efficient than that from Ag_1 cations.

The above results show that the adsorption energies of sulfates can be arranged as follows: $|Ag_3| < |Ag_1| < |A||$ sites, consistent with Doronkin's work [56], in which the SO₂ resistance of Ag/Al₂O₃ in H₂-NH₃-SCR was investigated. In that work, the authors calculated the adsorption energies of SOx species on the surfaces of bulk silver, Al₂O₃, and a single-atom Ag site, and found that SOx species bind weaklier to the bulk silver surface than to Al₂O₃ and the single-atom Ag site. Notably, the adsorption energy of SO₄²⁻ on the Ag (111) surface (-2.65 eV) in that work is consistent with the adsorption energy of sulfates on the Ag₃ clusters of the (110) surface (-2.43 eV). Therefore, the calculations of the adsorption energies of sulfates in the present work are believed to be reliable.

Table 1

DFT-calculated adsorption energies of sulfates on different sites of Ag/Al_2O_3.

Site	adsorption energy (eV)	
	Ag/Al ₂ O ₃ (110)	Ag/Al ₂ O ₃ (100)
(Ag ₁ -Al ₂ O ₃)-Al	-3.04	-3.58
(Ag ₁ -Al ₂ O ₃)-Ag ₁	-2.69 (-12%)	-2.56 (-28%)
(Ag ₃ -Al ₂ O ₃)-Al	-2.77	-2.80
(Ag ₃ -Al ₂ O ₃)-Ag ₃	-2.43 (-12%)	-1.63 (-42%)

4. Discussion

It is generally recognized that the HC-SCR reaction starts with the activation of HCs to yield reactive oxygenated hydrocarbons such as enolic species and acetates [1,2]. As for H2-C3H6-SCR over Ag/Al2O3 catalyst, the activation of reductant involves the activation of C-C bonds and/or C-H bonds, the occurrence of which require O species adsorbed on silver species and/or the electrons provided by silver species [42]. Hence, the activation of C_3H_6 primarily occurs at the Ag sites of the Ag/Al₂O₃ catalyst. The above reactive oxygenated hydrocarbons further react with NO + O_2 and/or nitrate (adsorbed on the Al sites adjacent to the Ag sites) to produce the -NCO species, which is also anchored at the Ag sites or the interface between Ag sites and Al₂O₃ support [53,54,57,58]. Then the -NCO species reacts either directly with NO + O2 and/or nitrate to produce N2 or with water vapor to produce NH₃, which further reacts with NO + O_2 and/or nitrate to produce N₂ [53,54]. Clearly, the Ag sites and the interface between Ag sites and Al sites (denoted as Ag-O-Al interface) is critical for NOx reduction in HC-SCR over Ag/Al₂O₃ [53,54,57].

On Ag/Al₂O₃ catalysts, the formation of sulfates starts with the oxidation of SO₂ on Ag sites, followed by further migration to Al sites [28,35]. UV-vis analysis revealed that adsorption of sulfates induced the transition of metallic silver to oxidized silver on Ag/Al₂O₃. In a reducing atmosphere, H₂ facilitated the reduction of oxidized silver species, providing a driving force for the migration of sulfates from Ag sites to Al sites and the desorption of sulfates to yield SO₂ (Fig. 8). The sulfates adsorbed on the Al sites were further reduced to yield H₂S and SO₂ (Fig. 5A). In a similar reducing atmosphere, Shimizu et al. [32] also observed a migration of sulfates from Ag sites to Al sites and desorption of SO₂ during H₂-C₃H₈-SCR over Ag/Al₂O₃. In that case, it was proposed that H₂ cleaned off the sulfates adsorbed on the Ag sites, and thus enhanced the sulfur tolerance of Ag/Al_2O_3 . In the atmosphere of $1\%H_2/$ 10%O₂/N₂, which is closer to practical reaction conditions, however, the sulfates cannot actually be reduced to H_2S and SO_2 (Fig. 5B). In contrast, the Al-sulfates rapidly migrated to the Ag sites where they were further decomposed to produce SO₂. Hence, a cyclic pathway of sulfate formation and desorption between Ag sites and Al sites was observed on the surface of Ag/Al₂O₃.

DFT calculations revealed that the adsorption energies of sulfates on different sites of Ag/Al_2O_3 can be arranged as follows: $|Ag_3| < |Ag_1| < |Al|$ sites. Therefore, desorption of sulfates from Ag_3 clusters was more efficient than from Ag_1 cations, while the desorption of sulfates from Al sites was inefficient. UV–vis analysis showed that there were more metallic Ag clusters with large sizes present on 4% Ag/Al_2O_3 compared to 2% Ag/Al_2O_3. Hence, it is reasonable that the desorption of sulfates on 4% Ag/Al_2O_3 surface was more rapid than that on 2% Ag/Al_2O_3. The H₂-TPR experiment revealed that the silver species

on 4% Ag/Al₂O₃ were more easily reduced at lower temperatures than those on 2% Ag/Al₂O₃. Hence, the migration of sulfates from Ag sites to Al sites in a reducing atmosphere on 4% Ag/Al₂O₃ was also more rapid than that on 2% Ag/Al₂O₃. In the flow of 1%H₂/10%O₂/N₂, the rapid migration of sulfates from Al sites to Ag sites on 4% Ag/Al₂O₃ could be attributed to the great difference in adsorption energies of sulfates on Ag clusters and Al₂O₃ surface. In contrast, the Ag⁺ showed strong affinity for sulfate species, resulting in the blockage by sulfates on the 2% Ag/Al₂O₃.

To further investigate the mobility of sulfate species, 2% Ag/Al₂O₃ catalysts were synthesized and calcined at higher temperature. Calcination at 900 °C induced the phase transition of γ -Al₂O₃ to δ -Al₂O₃, which further led to the reduction of surface area for 2% Ag/Al₂O₃-900 and 2% Ag/(Al₂O₃-900). Besides, the formation of δ -Al₂O₃ further induced the aggregation of dispersed Ag⁺ cations to produce large Ag clusters. Hence, the amounts of large Ag clusters on these two samples were significantly greater than that on 2% Ag/Al₂O₃ calcined at 600 °C (Table S2). The DRIFTS-MS experiment shows that the mobility of sulfate species on the samples calcined at high temperature was greater than that on 2% Ag/Al₂O₃ (Fig. 9), further confirming that the mobility of sulfur species was closely related to the state of silver species.

The deNOx performance of 2%Ag/Al₂O₃ was severely suppressed after exposure to SO₂ for 3 h (Fig. 2), while the 4%Ag/Al₂O₃ catalyst maintained high NOx conversion even after 30 h of SO₂ exposure (Fig. S5). The results of ion chromatography show that after exposure to 20 ppm SO₂ for 10 h (Fig. 2), the amount of SO₂ deposited on the 2%Ag/Al₂O₃, 3%Ag/Al₂O₃, and 4%Ag/Al₂O₃ were 7.79 \times 10⁻⁵ mol/g, 9.50×10^{-5} mol/g, and 8.96×10^{-5} mol/g, respectively. This indicates that the amounts of sulfates adsorbed on these catalysts were approximately equal, consistent with the DRIFTS results (Fig. 7). On the 4%Ag/Al₂O₃, the amount of sulfate species adsorbed at 300 °C was even smaller than those at 400 °C and 500 °C (Fig. S15), while this sample exhibited poorer sulfur tolerance at 300 °C. Considering the above results, the amount of sulfate species adsorbed on the surface cannot reasonably explain the different sulfur tolerance of these Ag/Al₂O₃ catalysts. Hence, there are other factors governing the sulfur tolerance of Ag/Al₂O₃ catalysts.

As mentioned above, the H2-C3H6-SCR reaction starts with the activation of C₃H₆ to yield reactive oxygenated hydrocarbons such as enolic species and acetates, which primarily occurs at the Ag sites and the Ag-O-Al interface [7,42]. The adsorption of sulfate species on the Ag/Al₂O₃ catalysts induces the formation of Ag-sulfates and/or Ag₂SO₄ species. In particular, Ag⁺ cations show strong affinity for sulfate species, resulting in the blockage of sulfates on the 2%Ag/Al₂O₃. The formation of Ag-sulfates and/or Ag₂SO₄ species may affect the electrondonating ability of silver species, and thus inhibits the activation of C_3H_6 to produce enolic species on the 2%Ag/Al_2O_3 (Fig. S13). Furthermore, the strong adsorption of sulfate species may hinder the reaction between C₃H₆ and O species on the Ag sites due to a strong steric effect. Afterward, these effects induced by sulfates may further hinder the reaction between enolic species and $NO + O_2$ (and/or nitrate) to produce -NCO species, finally resulting in the suppression on the deNOx performance of 2% Ag/Al₂O₃ catalyst (Fig. 7). Besides, the formation of nitrates was severely suppressed due to competitive adsorption of sulfates on Al₂O₃ surface (Fig. S14). However, the adsorption of nitrates on the Al sites far from Ag sites showed little effect on the reduction of NOx as the reaction primarily occurred at the Ag sites and Ag-O-Al interface [53,54,57,58].

On the Ag/Al₂O₃ catalysts with large amounts of Ag clusters (4% Ag/Al₂O₃, 2% Ag/Al₂O₃-900, and 2% Ag/(Al₂O₃-900)), the sulfates were more mobile between Ag sites and Al sites, and were also more easily decomposed and released from the surface. The rapid mobility of sulfate species at the Ag-O-Al interface provided an opportunity for the reaction between C_3H_6 , NO, and O species at the Ag sites. Hence, the above suppression induced by sulfates was weakened due to the rapid

mobility of sulfate species at the Ag-O-Al interface. Over these samples, as a result, more active sites were available for the formation of enolic species, acetates, and -NCO species, which have been observed in Fig. S13 and Fig. 7. Hence, the rapid mobility of sulfate species showed an important effect on the sulfur tolerance of Ag/Al₂O₃ catalysts. At 300 °C, the slow mobility of sulfates induced a poor sulfur tolerance of 4% Ag/Al₂O₃, which in turn confirmed the critical effect of mobility of sulfates on the sulfur tolerance of Ag/Al₂O₃. As mentioned above, the sulfate species transferred rapidly between Ag clusters and Al₂O₃ surface due to the weak affinity of Ag clusters for sulfates. Therefore, increasing the number of Ag clusters on the Ag/Al₂O₃ catalysts helps to enhance the mobility of sulfates at the Ag-O-Al interface, and thus improved the sulfur tolerance of these catalysts.

5. Conclusion

The sulfur tolerance of Ag/Al_2O_3 in the H_2 - C_3H_6 -SCR is governed by the mobility of sulfate species, which is closely related to the state of silver species. Highly dispersed Ag⁺ predominates on 2% Ag/Al₂O₃, while more metallic Ag clusters with large sizes are present on 4% Ag/ Al₂O₃. High temperature calcination promoted the transformation of γ -Al₂O₃ into δ -Al₂O₃, which induced the aggregation of dispersed Ag⁺ cations to produce large Ag clusters on 2% Ag/Al₂O₃-900 and 2% Ag/ (Al₂O₃-900). DFT calculations reveals that Ag₁ cations show strong affinity for sulfate species, resulting in blockage by sulfates at the Ag-O-Al interface on 2% Ag/Al₂O₃. Such blocking by sulfates suppressed the activation of C_3H_6 and the formation of -NCO species as well as its further transformation, thus severely inhibiting the deNOx performance of 2% Ag/Al₂O₃. In contrast, the weak affinity of Ag clusters for sulfates led the rapid migration of sulfates between Ag clusters and Al sites. The rapid migration of sulfates at the Ag-O-Al interface had little effect on the formation of enolic species and -NCO species, and thus contributed to the excellent sulfur tolerance observed for 4% Ag/Al₂O₃, 2% Ag/ Al₂O₃-900, and 2% Ag/(Al₂O₃-900). Hence, developing Ag/Al₂O₃ catalysts with more Ag clusters is crucial to improve the sulfur tolerance of HC-SCR.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.11.050.

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