The dual effects of ammonium bisulfate on the selective catalytic reduction of NO with NH₃ over Fe₂O₃-WO₃ catalyst confined in MCM-41

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Keywords:
NH₃-SCR
Ammonium bisulfate
Metal sulfate
Fe₂O₃-WO₃ catalyst
Sulfur-resistant

HIGHLIGHTS

- The dual effects of ABS on NH₃-SCR performance of Fe₂O₃-WO₃/MCM-41 is observed and illustrated for the first time.
- The formation of surface metal sulfates sustainably promotes the catalytic performance.
- Nearly 90% of sulfates in ABS are immobilized after NH₄⁺ consumption.
- Both the acidity and redox properties of catalyst are greatly improved after metal sulfates formation.

ABSTRACT

Ammonium bisulfate (ABS) has long been considered as a main poisoning material in the selective catalytic reduction by NH₃ (NH₃-SCR) due to the inevitable coverage of sticky ABS on catalytic active sites in sulfur-containing atmospheres, which severely hinders the achievement of stable and highly active NH₃-SCR catalysts. In the present study, we report a novel observation of the dual effects of ABS on the NH₃-SCR reaction. That is, ABS inhibits the NH₃-SCR performance of Fe₂O₃-WO₃/MCM-41 catalyst at low temperatures (50–200 °C) but shows apparent and sustainable reaction promotion when the temperature surpasses 250 °C. X-ray photoelectron spectroscopy (XPS) and NO probing adsorption confirmed that when ABS is deposited on the catalyst surface, a partial interaction between ABS and the Fe₂O₃-WO₃ component occurs, resulting in blocking of the active sites and an obvious loss of catalytic activity. With increasing reaction temperature, the ammonium in ABS can be facilely consumed by NO/O₂, thus inducing the disintegration of poisoning species. The sulfate group transforms into metal sulfate and survives at high temperatures. Importantly, owing to the strong inductive effect of sulfate species, both the acidity and redox properties of the catalyst are greatly improved, which contributes to the enhanced activity. The results of the present study expand our knowledge of the role of ABS in the NH₃-SCR reaction and will be useful for designing high-performing NH₃-SCR catalysts.
1. Introduction

Nitric oxides (NOx), a major kind of air pollutant originated from burning fossil fuel, have gained much attention due to the increasingly harmful impacts on the environment and human health [1–3]. For years, the most effective technology for NO emission control has been selective catalytic reduction by NH3 (NH3-SCR) [4]. Although the V2O5-WO3/TiO2 catalyst has been used commercially for decades, its low N2 selectivity at high temperature, narrow reaction temperature window and toxicity of vanadia are still not satisfactory [5]. Therefore, the development of new catalysts with high activity at low temperature is urgently demanded. By far, there are numerous examples of transition metal and rare earth (e.g. Mn, Fe, Ti, Cu, Ce and Sm) oxide catalysts exhibit excellent activity between 80 and 300 °C under ideal reaction conditions [6–8]. Nevertheless, due to the presence of SO2 in flue gas, these catalysts are exceptionally susceptible to deactivation at low-temperature operation. The mixture of SO2 with NH3 and H2O could easily produce NH4HSO4 (ammonium bisulfate, ABS) with the assistance of the NH3-SCR catalyst, which barricades the active sites from reactants adsorbing onto the catalyst surface, thus deactivates the NH3-SCR catalysts [9]. Thus, the deposition of ABS is always regarded as the main poisoning factor when the catalysts are operated in flue gas with SO2 at low temperature.

In recent years, the increasing attention has been devoted to understand the behavior of ABS on the catalyst surface to alleviate the poisoning effect for developing novel sulfur-resistant NH3-SCR catalysts. Zhu et al. found that the ABS could react with gaseous NO and its decomposition was promoted by activated carbon (AC) due to the reducible property of carbon [10]. A recent study by Chen et al. showed that decomposition of deposited ABS could be promoted by intercalating NH4+ into the layer structure of MoO3 [11]. Wang et al. reported that the V2O5-WO3/TiO2 catalyst deactivated by in situ deposited ABS could be rapidly recovered by the reaction between NH4+ and a NO/NO2/O2 mixture [12]. Moreover, the pore structure of the catalyst is also shown to have a significant impact on the thermal behavior of ABS [13]. In our previous study, we have reported that the decomposition temperature of ABS could be simply tailored by adjusting the pore size of the support. The model catalyst with larger pores certainly showed superior sulfur resistance to that of the catalyst with smaller pores, which confirmed that the effect of pore expansion could accelerate ABS decomposition [14,15]. The studies shown above provide various effective strategies to promote the decomposition and reactivity of ABS thus alleviating the deactivation effects. On the other hand, the sulfation of metal components, which usually occurs simultaneously with the formation of ABS, also needs to be considered. It reported that the sulfation of ceria-based catalysts prevents the redox cycle of Ce3+ and Ce4+, thus playing a negative role in the NH3-SCR reaction [16]. However, there are also reports showing the metal oxide sulfation can enhance the Brunsted acidity of the catalyst, which in turn promotes NO reduction efficiency to a large extent [17–19]. The seemingly controversial phenomenon reminds us that the sulfation of metal components may not always be a disadvantage, and the unique properties of metal sulfates might be utilized in sulfur-resistant catalyst development.

It is well acknowledged that the ABS deposition is unavoidable at low temperatures and causes deactivation of NH3-SCR catalyst, thus the interaction between ABS and the catalyst has become a primary question that needs to be addressed. Ye et al. reported that after the deposition of ABS on the V2O5/TiO2 catalyst surface, HSO4- transformed into bidentate SO42-, and an increase in ABS deposition led to formation of the (NH4)2SO4/Fe2O3, which diversely affected the ABS decomposition and reactivity behaviors [20]. Unfortunately, this kind of interaction strongly affects NH3-SCR performance but has yet been illustrated so far. Thus, in this work, ABS is intentionally deposited on an environment friendly Fe2O3-WO3/MCM-41 catalyst to investigate the effect of ABS on NH3-SCR performance [21]. Because of that in our previous report, Fe2O3 supported mesoporous silica catalyst exhibits good stability in presence of SO2 due to its ABS decomposition promotion effect [14]. However, the deficiency in surface acidity makes the catalyst activity is not that promising. As a typical kind of acid oxide, WO3 is widely used as a promoter in NH3-SCR, which could provide high thermal stability and sufficient acidity. Hence, WO3 is added to compensate the weak acidity of FeOx and construct FeOx-WO3/MCM-41 catalyst. Interestingly, the dual effects of ABS on deNOx efficiency, in which ABS slightly inhibited the catalyst performance at temperatures lower than 250 °C, but largely promoted the reaction above 250 °C, are discovered for the first time. The real-time behavior of ABS on the catalyst is evaluated by temperature-programmed surface reaction (TPSR) and inductively coupled plasma (ICP) analysis. The fresh and used catalysts are characterized by X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of ammonia (NH3-TPD), temperature-programmed reduction by hydrogen (H2-TPR), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric (TG) analysis to illustrate how ABS interacts with catalysts. Finally, the reaction mechanisms of fresh and used samples are studied by in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS). The results of this work might provide new insights on the regeneration of ABS deactivated NH3-SCR catalysts, which will benefit the development of long-lived catalysts for practical applications.

2. Experiments

2.1. Sample preparation

MCM-41 was purchased from the supplier and calcined at 750 °C for 5 h before use. Fe2O3-WO3 oxides supported on MCM-41 were synthesized by a conventional wetness impregnation method. In a typical preparation, calculated amounts of Fe(NO3)3·9H2O (0.257 g) and (NH4)2WO4·4H2O (0.052 g, nFe:nW = 3:1) were dissolved in 30 ml distilled water. MCM-41 (0.5 g) was added, and the mixture was stirred for 5 h before use. Fe2O3-WO3 oxides supported on MCM-41 were synthesized by a conventional wetness impregnation method. In a typical preparation, 10 wt% ABS was dissolved in 20 ml deionized water and treated by ultrasonic for 2 h, then the solution was filtered, liquid phase is kept for ICP tests. The concentrations of various cations in leached solutions were measured by Ion Chromatography (IC, DIONEX ICS-1100AR, Thermo Fisher scientific, India). The system
consisted of one IC pump, an injection valve, column heater, an ion-exchange analytical column (AS19), and a guard column (AG19). Samples were loaded onto a 100 μL sample loop with a syringe. All columns, tubing, and fittings were made of poly-ether-ether-ketone. During the IC measurement, 25 mM KOH eluent, 0.38 ml/min flow rate, and 24 mA applied current were maintained.

H₂-TPR was carried out in a quartz U-tube reactor connected to a thermal conductivity detector (TCD) with a H₂/Ar mixture (7% H₂ by volume) as a reductant. 20 mg of each sample is used for measurements. Before introducing the sample to the H₂/Ar stream, the sample was pretreated in N₂ stream at 200 °C for 1 h. The H₂ consumption profile was collected from room temperature to 900 °C at a rate of 10 °C/min. The acidic properties of the catalysts were determined from NH₃-TPD by using a Micromeritics Autochem II 2920 instrument. Sample was pretreated by helium (25 ml/min) at 200 °C for 1 h, then cooled to 100 °C and exposed to 10% NH₃/He (25 ml/min) for 4 h. Thereafter, the sample was purged with helium at 100 °C for 1 h. All NH₃-TPD tests were carried out by increasing the temperature from 100 to 800 °C at a rate of 10 °C/min. The signal of released NH₃ was analyzed by a TCD. TPSR was carried out with an activity test system. Briefly, 100 mg sample was placed in a quartz tube and heated to 450 °C at a heating rate of 2 °C/min with blow of 100 ml/min 500 ppm NO/Ar flow. In situ DRIFTS was performed on a Nicolet Nexus 5700 FT-IR spectrometer equipped with a highly sensitive mercury cadmium telluride detector with 32 scans at a resolution of 4 cm⁻¹, and a diffuse reflectance reaction cell (HARRICK) equipped with KBr window was used. The sample was pretreated in a flowing N₂ stream at 400 °C for 1 h to eliminate physisorbed water and other impurities, and the sample background was collected at various target temperatures during the cooling process. For the experiments of NH₃ or NO + O₂ adsorption–desorption, the reaction cell with sample was saturated with NH₃/N₂ (1% NH₃ by volume) or NO/N₂ + O₂/N₂ (500 ppm NO and 5% O₂ by volume) for steady state at room temperature, then the sample was purged by N₂ for 30 min and the spectra were recorded at target temperatures. The decomposition behaviors of various samples were measured by TG-DTA (Thermogravimetry-differential thermal analysis). The measurement was carried out in flowing of nitrogen atmosphere (60 ml/min) on a NETZSCH STA-449-F5 and the heating rate is set at 5 °C/min. The reference curve for DTA was generated from measurements of an empty crucible.

2.3. Catalytic activity test

The NH₃-SCR performance of the catalysts was evaluated in a fixed-bed quartz reactor (8 mm internal diameter). The feed stream is fixed with 500 ppm NO, 500 ppm NH₃, 5% O₂, and Ar in balance with a gas flow of 200 ml/min (Weight hourly space velocity, WHSV, was 60000 ml·g⁻¹·h⁻¹). Gas hourly space velocity, GHSV, was approximately 30000 h⁻¹ because the density of the sample varied). The catalyst (200 mg) was sieved to 40–60 mesh. Before the test, the sample...
was pretreated in a purified Ar stream at 150 °C for 1 h to avoiding surface impurities. Then, the mixed gases were switched on, and the activity data were collected at every target temperature after stabilizing for 30 min in the range of 50–400 °C. The concentration of effluent gases was continuously analyzed on an IS10 FT-IR spectrometer equipped with a 2 m path-length gas cell (2 L volume). The NO conversion and N₂ selectivity were calculated based on the following equations:

\[
\text{NO conversion(\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%
\]  

(1)

\[
N_2 \text{ selectivity(\%)} = \frac{[\text{N}_2]_{\text{out}} - [\text{N}_2]_{\text{in}} + [\text{NH}_3]_{\text{out}} - [\text{NH}_3]_{\text{in}} - [\text{NO}]_{\text{out}} - 2[N_2O]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100\%
\]  

(2)

3. Results and discussion

3.1. Reaction features of fresh and ABS-deposited FeW/MCM-41 in NH₃-SCR

The influence of ABS deposition on the catalytic performance of FeW/MCM-41 in NH₃-SCR is displayed in Fig. 1. In general, the fresh FeW/MCM-41 catalyst shows poor NO conversion efficiency, particularly at low temperatures. It is clear from Fig. 1a that no activity is detected for FeW/MCM-41 until 200 °C and the NO conversion reaches a saturated value at 78% when the reaction temperature rises to 350 °C. The absence of a consecutive activity increment at high temperatures is assumed to be related to the competitive oxidation of ammonia from oxygen, which reduces the availability of NH₃ for NO reduction [22]. This conclusion is supported by the decreasing N₂ selectivity at high temperatures (Fig. 1b).

After ABS deposition, the reaction characteristic of the catalyst is not greatly changed. The activity of ABS/FeW/MCM-41 increases from 200 °C, and a plateau is observed at 350 °C, which is the same as that of FeW/MCM-41. Nevertheless, by comparing the detailed NO conversions between the two samples, differences can be clearly discriminated. It is found that at reaction temperature lower than 250 °C, the efficiency of ABS-deposited sample is obviously restrained, demonstrating the apparent inhibition effect caused by ABS deposition. This finding conforms to the general impact of ABS on NH₃-SCR catalysts [23]. However, the activity order is reversed when the reaction temperature surpasses 250 °C. The activity of the ABS-deposited sample reveals a NO conversion much higher than that of the fresh sample, with almost 100% NO conversion achieved in the range of 350–400 °C. This phenomenon is peculiar and has yet been reported. This also allows us to utilize the poisoning species (ABS) to promote NH₃-SCR performance. Intuitively, by considering the limited thermal stability of ABS at elevated temperatures [24], we expect unique temperature-dependent reaction behavior that can be related to composition/structure modification of ABS/FeW/MCM-41 during the reaction. To simply confirm this hypothesis, another round of activity test was performed, and the used catalyst was denoted as ABS/FeW/MCM-41-U. For ABS/FeW/MCM-41-U, the reaction curve at temperatures higher than 250 °C essentially overlaps with that of ABS/FeW/MCM-41. Combining the stability test at 350 °C in Fig. 1c, the results both suggest that the promotion effect is sustainable. Moreover, the used catalyst exhibits promising sulfur resistance (Fig. S1). The activity profile in the low-temperature range (50–250 °C) is no longer the same as that of ABS/FeW/MCM-41, implying that composition or structural variation of the catalyst indeed occurred.

The above results clearly show that deposition of ABS on the catalyst surface, which is usually considered detrimental to NH₃-SCR application, may not always be negative to the reaction. For FeW/MCM-41, a distinct dual effect is exhibited. That is, ABS degrades the catalyst performance at low temperatures but largely enhances the NO conversion at higher temperatures. Additionally, the repeated activity test suggests that modification of the catalyst composition or structure occurs around the breakpoint of 250 °C. To obtain more details about the changes of catalysts and the nature of the interaction between ABS and the active component, a series of characterizations was carried out.

3.2. The dispersion of surface species

Table 1 summarizes the textual properties of various FeW/MCM-41 catalysts. The pore sizes are comparable for different samples. However, the surface area and pore volume are largely changed. For pristine MCM-41, the surface area and pore volume are 1025 m²/g and 0.93 m³/g, respectively. After the introduction of FeW oxides, the parameters decrease to 845 m²/g and 0.69 m³/g, and decreases of the surface area and pore volume are observed when ABS is deposited. These results suggest that most ABS and active components are inserted into the pore channels of MCM-41 resulting in the decrease in surface area and pore volume.

The X-ray diffraction (XRD) patterns of fresh and ABS-deposited FeW/MCM-41 samples are shown in Fig. S2. Only a broad peak related to amorphous SiO₂ can be observed [25], demonstrating well dispersion of the guest species (Fe₂O₃-WO₃ and ABS) on MCM-41. This result is further supported by the transmission electron microscopy (TEM) images (Fig. S2), since no bulk particles are found on the surface of mesoporous silica framework for both fresh and used samples. These results collectively indicate that the deviation of catalytic performance cannot be attributed to variation in surface dispersion of active components.

3.3. The chemical states of surface species

To explore the chemical states of surface species, XPS characterization was performed, and the results are shown in Fig. 2. For FeW/MCM-41, the binding energies at 35.9 eV and 38.0 eV are characteristic of W species in the +6 oxidation state [26,27]. For Fe species, the signal at 711.8 eV and 725.7 eV, indicates the presence of Fe³⁺ [28]. After ABS deposition, perturbation of Fe and W signals is observed, demonstrating that certain chemical interactions between ABS and FeW components. In particular, important information can be distilled by examining the peak shifts. The W 4f signals deviates approximately 0.3 eV to the lower binding energy after ABS deposition, suggesting an increased electron cloud density of W atoms upon interaction with ABS. Thus, it is deduced that W⁶⁺ is dominantly bonded with NH₄⁺ which exhibits an electron donation effect. This conclusion is reasonable because WO₃ is well known as an acidic oxide and can easily bond with NH₄⁺ [29]. The Fe 2p signal shifts to a higher binding energy suggesting Fe species mainly interact with sulfate group due to the apparent electron inductive effect of the S = O covalent bond. This finding is consistent with literature report indicating that when Fe species are sulfated, an obvious shift in the Fe XPS spectra to higher binding energy is observed [19].

Table 1  The textual properties of MCM-41 and various catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SBET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>1025</td>
<td>0.93</td>
<td>2.85</td>
</tr>
<tr>
<td>FeW/MCM-41</td>
<td>845</td>
<td>0.69</td>
<td>2.74</td>
</tr>
<tr>
<td>ABS/FeW/MCM-41</td>
<td>634</td>
<td>0.54</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Table 1 summarizes the textual properties of various FeW/MCM-41 catalysts.
reaction (ABS/FeW/MCM-41-U), it is shown that the W 4f peak shifts back to a high binding energy, even higher than that of pristine FeW/MCM-41. Considering the strong electron inductive effect of sulfate group, we suppose that the NH4+ connected to WO3 is replaced by SO42− after the NH3-SCR reaction, which may be due to NH4+ consumption. Further evidence for this conclusion can be found from the TPSR and FT-IR results described in the following sections.

### 3.4. Evolution of ABS during the reaction

To disclose the ABS evolution during the reaction, the TPSR of ABS/FeW/MCM-41 with NO + O2 was carried out, and the result is present in Fig. 3. After initial saturated adsorption, the level of NO becomes constant (500 ppm). The outlet NO concentration starts to decrease only when the temperature exceeds 200 °C, which also suggests that the NH4+ in ABS is unreactive at low temperatures. The largest NO consumption occurs at approximately 300 °C. Since the adsorption of NO + O2 is saturated, the decrease in NO concentration above 200 °C reflects the chemical reaction between deposited ammonium ions and NO/O2 [10,30]. Moreover, the recovery of NO concentration to the saturated value (500 ppm) near 400 °C suggests that most of the ammonium ions are consumed during the reaction. On the other hand, it is clear from Fig. 3 that no obvious SO2 evolves, implying that the sulfates are thermostable on the catalyst surface during the reaction.

FT-IR is sensitive to variations of sulfate and ammonium ions on the catalyst surface and is thus a suitable tool to explore the surface species. Fig. 4a is the FT-IR spectra of various catalysts. Typically, bands at 1047 cm−1, 958 cm−1 and 795 cm−1 are observed and attributed to vibrations of silica framework from MCM-41 [31,32]. After ABS deposition, the NH4+ signal (1434 cm−1) appears [33]. For the reacted catalyst, this band is still present, but the intensity is much weaker, implying that ammonium ions on the catalyst surface are largely consumed, which supports the TPSR result.

It is noted that the signals of sulfate-containing species are masked by the Si-O vibrations from MCM-41 [14,31,34]. To discriminate the signals, differential IR spectra obtained by subtracting the spectrum of FeW/MCM-41 are depicted and displayed in Fig. 4b. In the differential spectra, the difference between ammonium ions (1436 cm−1) in ABS/FeW/MCM-41 and ABS/FeW/MCM-41-U can still be observed. Moreover, the signals attributed to sulfate species appear. The bands at 960 cm−1 and 1096 cm−1 represent the asymmetrical stretching of S=O, and the band at 1174 cm−1 is attributed to the symmetrical stretching of the S=O bond [12,20]. An additional band at 1040 cm−1 can be assigned to the v3 vibration of bidentate SO42− [35]. The intensity of these bands of two samples is comparable, suggesting that most sulfur-containing species are preserved on the catalyst surface, most likely in the form of metal sulfates by considering its relatively high thermal stability [19]. Apart from FT-IR, XPS spectra of N 1s and S 2p in Fig. S4 also reveal the same conclusion.

The possible transformation of ABS to metal sulfates is further verified by thermal analysis by taking advantage of the distinctly different thermal stabilities of ABS and metal sulfates. Fig. 5 shows the TG profiles of the three catalysts. For FeW/MCM-41, the major weight loss that occurred at step 1 (40–200 °C) is attributed to the release of physically adsorbed H2O on the catalyst surface. For ABS/FeW/MCM-41, three weight loss steps can be detected. The signal attributed to adsorbed H2O is enhanced, indicating the presence of ABS can promote water adsorption on catalyst surface. The process of ABS decomposition is represented by a notable weight loss in step 2 (200–450 °C). In addition, the obvious weight loss in step 3 (450–800 °C) is attributed to the decomposition of metal sulfates [36,37], indicating partial reaction between deposited ABS and metal oxide during the heating process [38,39]. The remarkable weight loss of ABS/FeW/MCM-1-U in step 2 is much less than that of ABS/FeW/MCM-41, which further supports the consumption of ammonium ions during the NH3-SCR reaction process. Furthermore, the signal represents weight loss of metal sulfates in the stream of 500 ppm NO and 5% O2.

From the TG results, we recognize that most sulfate groups are bonded with ammonium ions (in the form of ABS) in pristine ABS/FeW/
MCM-41, then they evolve as metal sulfates after a cycle of the NH3-SCR reaction. Nevertheless, the key information regarding the quantitative aspect of the various sulfate species (ABS and metal sulfates) is still under discover. To elucidate the variation in the surface species during ABS evolution, the ABS/FeW/MCM-41 sample was treated at designated temperatures (200, 300 and 400 °C), and a leaching process in distilled water was performed to obtain solutions containing soluble surface species. The extent of metal sulfation can be estimated from the solution by measuring the soluble metal ions. Fig. 6 shows the result of the detected concentration of Fe$^{3+}$. The solution from pristine ABS/FeW/MCM-41 contains minor Fe$^{3+}$ species (4.57 mg/L), verifying the partial chemical interaction between the deposited ABS and Fe$_2$O$_3$-WO$_3$ components. The concentration of Fe$^{3+}$ reaches 6.68 mg/L for the sample treated at 200 °C. This value is close to the data for pristine ABS/FeW/MCM-41, implying that the majority of deposited ABS is stable enough at this temperature and that the formation of metal sulfate does not vastly occur. For the sample treated at 300 °C, it is reasonable to deduce that the sulfate species are largely combined with iron oxides, resulting in a drastic increase in the Fe$^{3+}$ concentration to 18.6 mg/L. The residual sulfate species in deposited ABS can continually react with metal oxide at the 400 °C, finally leading to 23.1 mg/L Fe$^{3+}$ in the solution. In addition to the concentration of Fe$^{3+}$, the concentration of SO$_4^{2−}$ in solutions is also analyzed and results are depicted in Fig. 6. The SO$_4^{2−}$ from the samples treated below 300 °C showed nearly identical values and only a small decrease was observed for the sample treated at 400 °C, indicating the negligible loss of sulfates from the catalyst during the heating process. From the leaching results, we can quantitatively conclude that 90% of sulfates in ABS/FeW/MCM-41 remain as metal sulfates on the catalyst surface after a cycle of activity testing.

Base on the characterizations shown above, the existence states and evolution of ABS on the FeW/MCM-41 surface under reaction conditions are clarified. As shown in Scheme 1, when ABS is deposited, it shows a strong chemical interaction with the active Fe$_2$O$_3$-WO$_3$ component. The ammonium ions are partially bonded with WO$_3$ and sulfate groups are connected with Fe$_2$O$_3$ species. Due to the combined effects of physical coverage and chemical interaction, the adsorption properties of FeW/MCM-41 are greatly restrained, leading to obvious activity loss. However, when the reaction temperature increases to 200 °C, the chemical reaction between the deposited ammonium ions with NO + O$_2$ begins. With the depletion of ammonium ions, the WO$_3$ component is liberated and promotes the chemical interaction between WO$_3$ and SO$_4^{2−}$, which induces a significant shift of the W 4f signal to a higher binding energy. From the TG results, we know that in comparison with ABS, the metal sulfates are more thermally stable. Hence, most of the sulfate groups can be stored on the catalyst surface in the form of metal sulfates after one cycle of reaction.

The inhibitory effect on the catalytic performance of the FeW/MCM-41 catalyst at low temperatures can be well explained by the coverage of ABS on the FeW components that remarkably reduce the exposed
active sites to reactants (Fig. S5) and the inertness of NH₄⁺ in ABS. However, the promotion effect at high temperatures is still not well understood. Thus, the acid and redox properties of the catalyst are characterized.

3.5. Surface acidity of catalysts (NH₃-TPD and NH₃-DRIFTS)

Fig. 7a displays the NH₃-TPD profiles of FeW/MCM-41 and ABS/FeW/MCM-41-U. For FeW/MCM-41, three well resolved peaks at 173 °C, 350 °C and 469 °C are detected, demonstrating the simultaneous possession of weak, medium and strong acid sites on the catalyst surface [21,40]. Moreover, the comparable intensity of the three peaks suggests that these different acid sites are evenly distributed. After ABS deposition and a cycle activity test, the intensity of the desorption peak shows an obvious increase, revealing that the amount of NH₃ adsorption on the ABS/FeW/MCM-41-U catalyst is significantly increased. In particular, in comparison with the signals at low and medium temperatures, the desorption peak at 433 °C, typical of a strong acid, exhibits a sharp increase. The signal at temperatures above 600 °C, is abnormal, which is attributed to the evolution of SO₂ caused by metal sulfate decomposition, which has been proven by the TG results. From the results above, it is obvious that the presence of metal sulfates derived from the interaction between the deposited ABS and metal oxide components can significantly enhance the catalyst acidity. The improved surface acid property of ABS/FeW/MCM-41-U catalyst should mostly account for the promoted NH₃-SCR activity at high temperatures.

To ascertain the nature of the acid sites on the catalyst surface, the DRIFT spectra of NH₃ adsorption are shown in Fig. 7b. The bands at 1638 cm⁻¹ and 1478 cm⁻¹ correspond to NH₃ adsorbed on Brønsted acid sites [41], while the bands at 1610 cm⁻¹ and 1276 cm⁻¹ are attributed to NH₃ adsorbed on Lewis acid sites [42,43]. The strongest peak observed at 1478 cm⁻¹ suggests that both catalysts are dominated by Brønsted acid sites. Correlating with the NH₃-TPD results, it is supposed that the strong acid sites are represented by Brønsted acid. Importantly, the distinct increase in both Brønsted and Lewis acid sites...
on ABS/FeW/MCM-41-U compared to those on FeW/MCM-41 is shown. According to previous studies, the increase in Brønsted acid sites is thought to originate from the generation of metal sulfates, while the increase in Lewis acid sites may result from the electron-withdrawing effect of sulfates, making the metal atoms more affable to lone pair electrons in gaseous NH₃ [44]. The obtained results indicate that there are still both Lewis and Brønsted acid sites on the surfaces of fresh and used samples. Furthermore, the strength of NH₃ chemisorption on the acid sites of ABS/FeW/MCM-41-U sample is reinforced as well, as evidenced by the in situ DRIFT results shown in Fig. S6. It is clear that the NH₃ molecules can still adsorb on the ABS/FeW/MCM-41-U surface at temperatures higher than 400 °C. On the other hand, for FeW/MCM-41, the NH₃ completely desorbs from the acid sites at approximately 250 °C. The stable adsorption of NH₃ at high temperatures is believed to be conducive to continuous and effective reduction of NO.

3.6. Redox properties of catalysts (H₂-TPR, NH₃ and NO oxidation, NO + O₂ DRIFTS)

H₂-TPR characterization was performed to obtain the redox profiles of the catalysts, and the results are given in Fig. S7. Unfortunately, the reduction profile of ABS/FeW/MCM-41-U is dominated by H₂ consumption at 507 °C from sulfate species [17], which covers the signal from the active component. To avoid this issue, NO and NH₃ oxidation tests were performed to evaluate the redox properties of the catalysts, and the results are depicted in Fig. 8. For FeW/MCM-41, negligible NO oxidation (< 1%) is observed over the whole test range (50–400 °C), suggesting the poor efficiency of FeW/MCM-41 in converting NO to NO₂. This explains the poor NH₃-SCR performance at low temperatures, since the absence of NO₂ could not promote the reaction via ‘fast SCR’ pathway. Additionally, the poor redox property is reflected by the inferior NH₃ oxidation performance at low temperatures. Compared to FeW/MCM-41, ABS/FeW/MCM-41-U achieves better NO and NH₃ oxidation performances, demonstrating that the redox properties of FeW/MCM-41 can be enhanced by ABS deposition and a subsequent NH₃-SCR reaction [45].

The improved redox property of ABS/FeW/MCM-41-U can be further evidenced by the enhanced adsorption of NO + O₂ on catalyst surface. Fig. 9 shows the DRIFT spectra of NO₂ adsorption over FeW/MCM-41 and ABS/FeW/MCM-41-U catalysts. For FeW/MCM-41, when NO + O₂ mixed gases are introduced, several bands appear in the range of 1200–1800 cm⁻¹. The bands at 1675 and 1607 cm⁻¹ can be attributed to cis-HNO₂ and NO₂ species [46,47], and the bands at 1625 and 1575 cm⁻¹ are assigned to different vibration modes of the bridging bidentate nitrate [40,48,49]. In comparison, the signal is obviously enhanced for ABS/FeW/MCM-41-U. Moreover, the configurations of absorbed species are more complex than those of FeW/MCM-41 catalyst. New bands at 1740 and 1287 cm⁻¹ assigned to N₂O₄ and nitro compounds are present. These phenomena might originate from the inductive effect of the S=O bond in the formed metal sulfate resulting in a much stronger affinity and leading to an enhancement of the electrophilicity of iron and tungsten species that provide more adsorption sites for NO + O₂ [50].

3.7. Reaction mechanism of NH₃-SCR over fresh and ABS deposited catalysts

To determine whether the formation of surface sulfate species on the catalysts alters the SCR reaction pathway, a transient reaction was performed by in situ DRIFT. For FeW/MCM-41, after NH₃ adsorption for 1 h at 250 °C, the weak peak at 1451 cm⁻¹ assigned to the NH₄⁺ species appears (Fig. 10a). When NO + O₂ is introduced, NH₄⁺ species are consumed, accompanied by the gradual augmentation of the signal attributed to gaseous NO vibrations (1600 and 1628 cm⁻¹). Subsequently, NH₃ was injected into the catalyst with pre-adsorbed NO + O₂, and the resulting spectra are shown in Fig. 10b. After the adsorption of NO + O₂, bands assigned to various vibration modes of nitrates at 1577, 1524 and 1349 cm⁻¹ emerge [46,51]. However, along with the appearance of the NH₄⁺ vibration bands, the intensity of nitrate bands is hardly affected, indicating that the chemisorbed nitrate species is
inert to gaseous ammonia or surface ammonium species. Therefore, it can be deduced that the SCR reaction simply proceeded via the Eley-Rideal (E-R) mechanism over the FeW/MCM-41 catalyst.

As for the ABS/FeW/MCM-41-U catalyst, the spectra of NH3 introduced into the catalyst with NO + O2 pre-adsorption are illustrated in Fig. 10c. No infrared bands attributed to nitrate species are detected, implying that although nitrate species are abundant at low temperatures, they are not stable enough to stay on the catalyst surface at 250 °C. Since the absorbed nitrates are inert, the absence of nitrates on ABS/FeW/MCM-41-U at 250 °C is expected to provide more adsorption sites for NH3, which promotes the activation of ammonia and enhances the NO removal efficiency. After NH3 injection, only the IR band at 1451 cm\(^{-1}\) assigned to NH\(_4^+\) appears. Fig. 10d shows the in situ DRIFT experiment of the reaction between NO + O2 and pre-adsorbed NH3 species. After NH3 adsorption, an intense band ascribed to ionic NH\(_4^+\) at 1451 cm\(^{-1}\) shows up, suggesting that only NH3 adsorbed on Brønsted acid sites is stable enough on the catalyst surface, similar to the result of the FeW/MCM-41 sample. The subsequent introduction of NO + O2 results in an evident diminishing of the NH\(_4^+\) IR band and no appearance of nitrate species bands. The above results reveal that after the formation of metal sulfates, the NH\(_3\)-SCR reaction pathway is not changed, and thus, the reaction can proceed more effectively because many more NH3 species are adsorbed and activated on ABS/FeW/MCM-41, which improves the NO reduction efficiency.

Lastly, we would like to present a short discussion on the possible modulation of the breakpoint of the dual effect for improved low-temperature performance. In view of the abundant acidity and suitable redox properties made by sulfate groups, it is reasonable to expect that if we could accelerate the release of NH3 in ABS, it would be possible to shift the promotion effect to ideal lower temperatures.

4. Conclusion

In summary, we initiated this research by intentionally depositing ABS on an environmental friendly NH3-SCR catalyst (Fe\(_2\)O\(_3\)-WO\(_3\)/MCM-41). The dual effects of ABS on the catalytic performance over FeW/MCM-41 are shown and the reason for that unique behavior is explored. At low temperatures, the NH\(_4^+\) is not reactive and ABS mainly serves as a physical blocking layer on catalyst surface, preventing the adsorption and activation of reactants. Nevertheless, the case is changed when reaction temperature elevates. The deposited ABS is disintegrated by NO/O2 consuming ammonium ions at reaction temperature higher than 200 °C. As such, the blocking effect of ABS is removed and more importantly, the sulfate species can be preserved on catalyst surface in the form of the metal sulfates. The immobilization of the residual sulfate after NH\(_4^+\) consumption provides sufficient strong acid sites for NH3 adsorption. Apart from acidity, the ABS/FeW/MCM-41-U also reveals improved NO oxidation ability, thus prompts activity enhancement via the “fast NH\(_3\)-SCR” pathway. Moreover, the reacted catalyst shows negligible adsorption of inactive surface nitrates at high temperatures, giving out more adsorption sites for NH3. In terms of the simply E-R
mechanism over FeW/MCM-41 catalyst, the enhanced surface acidity and improved ability to produce NO₂ ensure the reaction goes through more effectively over ABS/Fe/W/MCM-41-U sample. This work precisely illustrates the impact of ABS on NH₃-SCR performance, which inspires a new strategy to the regeneration of ABS deactivated NH₃-SCR catalyst and benefit the development of long-lived catalysts for the practical applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


