Pilot test of environment-friendly catalysts for the DeNO\textsubscript{x} of low-temperature flue gas from a coal-fired plant†‡

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Efficient, environment-friendly, and energy-saving low-temperature denitration (DeNO\textsubscript{x}) catalysts, applicable in practical flue gas, have a widespread market for use in small-scale boilers. A novel Ce-based low-temperature honeycomb catalyst was tested in a pilot-scale plant for DeNO\textsubscript{x} of flue gas from a coal-fired power plant. The pilot test results demonstrated the honeycomb catalyst’s ability to endure a high content of water vapor (H\textsubscript{2}O, 8–10 vol%) and low content of sulfur dioxide (SO\textsubscript{2}, ≤35 mg m\textsuperscript{-3}) in flue gas at temperatures as low as 100 °C. with >55% DeNO\textsubscript{x} efficiency over 3400 h and the catalyst showed no deactivation. Physicochemical properties of the catalyst were investigated by various characterization methods, such as Brunauer-Emmett-Teller analysis, X-ray diffraction analysis, inductively coupled plasma, temperature-programmed desorption of NH\textsubscript{3}, thermogravimetry, and Fourier-transform infrared spectroscopy. The results showed the effectiveness of the selective catalytic reduction unit in preventing the deposition of particulate matter in the flue gas, after being placed in the desulfurization and dust removal unit. However, a small amount of alkali metal and sulfate deposition were detected on the surface and micropores of the catalyst but did not significantly impact the catalyst performance. This catalyst thus has broad potential applicability in actual flue gas.

Introduction

The air quality in China improved significantly after implementation of the “Air Pollution Prevention Action Plan” between 2013 and 2017.\textsuperscript{1,2} During these 5 years, the annual average concentration of fine particulate matter (PM\textsubscript{2.5}), sulfur dioxide (SO\textsubscript{2}), and nitrogen dioxide (NO\textsubscript{2}) declined from 72 to 43 μg m\textsuperscript{-3}, from 40 to 18 μg m\textsuperscript{-3}, and from 44 to 31 μg m\textsuperscript{-3}, respectively. Furthermore, the “Three-Year Action Plan for the Blue Sky Defense War” clearly stated that by 2020, the PM\textsubscript{2.5} concentration and the total emissions of nitric oxides (NO\textsubscript{X}) must be reduced by more than 15% compared to those in 2015, which is an arduous environmental protection task.\textsuperscript{3} The results reported in the literature showed that secondary inorganic ions (sulfate, nitrate, and ammonium) comprised the majority of the PM\textsubscript{2.5} mass, accounting for 46% of the total.\textsuperscript{4} Furthermore, NO\textsubscript{X} contributes more than 40% of the inorganic components to PM\textsubscript{2.5} formation via conversion to a nitrate or nitric organic compound in air.\textsuperscript{5,6} In contrast, the formation of nitrate further promotes the increase in PM\textsubscript{2.5} concentration. Therefore, inability to effectively control NO\textsubscript{X} emission will inevitably intensify pressure regarding the reduction of atmospheric PM\textsubscript{2.5}.\textsuperscript{7}

Among the many fixed-source flue gas denitration (DeNO\textsubscript{x}) technologies, the NH\textsubscript{3}-selective catalytic reduction (NH\textsubscript{3}-SCR) technology is widely used in the purification of industrial fixed-source NO\textsubscript{X} because of its excellent efficiency, strong stability, and low cost.\textsuperscript{8,9} In the past few years, this technology has contributed greatly to the reduction of NO\textsubscript{X}.\textsuperscript{10} Furthermore, V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts are currently the most commonly used commercial SCR catalysts because of their high NO\textsubscript{X} removal efficiencies. To meet the requirements of high operating temperature (300–400 °C), the catalyst unit must be installed before desulfurization and dust removal to avoid reheating of the flue gas, during which the catalysts are prone to deactivation by particulate matter deposition and SO\textsubscript{2} poisoning. In contrast, the abandoned catalysts must be handled as hazardous waste, which implies increased environmental risks.\textsuperscript{11,12} It is generally difficult for...
industrial exhaust gas to meet the temperature requirements of high-temperature DeNO\textsubscript{x} catalysts; the increase in flue gas temperature will cause additional resource waste and higher costs. Hence, a low-temperature catalyst should be developed; the temperature of the catalytic process should be lower than 150 °C, where in the treatment process occurs after the desulfurization and dust removal and the toxic effect of dust and SO\textsubscript{2} is avoided. However, with the reduction in temperature, the presence of SO\textsubscript{2} and H\textsubscript{2}O in the flue gas will inevitably affect the catalysts, which should be avoided\textsuperscript{13–15} and the catalyst composition must not contain toxic components.

Thus far, extensive in-depth research has been conducted on low-temperature catalysts, including transition metals\textsuperscript{16–20} and precious metals.\textsuperscript{21,22} Many rare earth catalysts have shown good catalytic efficiencies at low temperatures, reflecting good application prospects. Most of the research on low-temperature DeNO\textsubscript{x} catalysts are focused on treatment of simulated flue gas by powder catalyst on laboratory scale. In real flue gas, many substances may have the potential to affect the catalytic process. Particularly, the impact of water vapor on the catalytic process should be considered. In most reported studies, water vapor content was less than 5%, which is much lower than that in real flue gas. Thus, some high-performance low-temperature laboratory-scale DeNO\textsubscript{x} catalysts were found to be inappropriate for industrial applications. Therefore, the industrial application of non-vanadium-based low-temperature DeNO\textsubscript{x} catalysts requires further investigation under practical flue gas conditions.

In our previous research, we found a rare earth catalyst with good DeNO\textsubscript{x} performance at low temperatures (100 °C) and H\textsubscript{2}O/SO\textsubscript{2} resistance.\textsuperscript{23} The honeycomb catalyst was prepared by coating the active component on the surface of a blank honeycomb cordierite using a coating method.\textsuperscript{24} Results of this research on honeycomb catalysts using a laboratory-scale pilot plant revealed the catalyst’s excellent DeNO\textsubscript{x} performance and H\textsubscript{2}O/SO\textsubscript{2} resistance at low temperatures (100–150 °C). However, air was used as the simulated flue gas of the carrier gas in this experiment.

In this study, a pilot test device was established, including a 125 MW generator in a thermal power plant. The DeNO\textsubscript{x} performance and stability of the shaped catalyst were studied under real flue gas conditions of 1000 m\textsuperscript{3} flow. The activity and stability of the catalyst in industrial practice were evaluated in a 3400 h experiment. Afterwards, both the fresh and used catalysts were analyzed using a variety of characterization methods to study the influence of practical coal-burning flue gas on the physicochemical properties of the catalyst’s active components. Study under practical flue gas conditions yielded more realistic and intuitive results on the applicability of the catalyst,\textsuperscript{25} establishing the practical significance of this study for future basic experiments and commercial promotion of low-temperature DeNO\textsubscript{x} catalysts.

### Materials and methods

#### Production of the honeycomb catalyst

The Ce-based honeycomb low-temperature DeNO\textsubscript{x} catalyst was prepared by coating the catalyst’s active component on the surface of a blank honeycomb cordierite. The details of this preparation have been presented in our previous paper.\textsuperscript{24}

#### Characterization

The crystal-phase structures of the samples were determined from the X-ray diffraction (XRD) spectra recorded in the 2θ range 10–90° using the Philips X’pert PRO diffractometer (Rigaku Corp., Tokyo, Japan). Cu Kα radiation was employed and the X-ray tube was operated at 40 kV and 30 mA.

The Brunauer–Emmett–Teller (BET) surface areas of the samples were determined by N\textsubscript{2} adsorption at ~196 °C on a Micromeritics ASAP-2460 (Micromeritics Instrument Corp., Norcross, USA) analyzer. The samples were activated for 3 h at 300 °C before the adsorption experiments.

Surface and cross-sectional scanning electron microscopy (SEM) images of the samples were obtained with a Sigma 300 scanning electron microscope (SEM, Carl Zeiss AG, Germany) operated at an accelerating voltage of 10 kV. The chemical compositions and elemental distributions of the samples were analyzed by X-ray energy-dispersive spectroscopy (EDS, FEI Talos F200, USA).

The deposited sulfate species of the samples were investigated by thermogravimetry (TG) measurements, carried out on an Exstar TG/DTA 7300 instrument (TG, Discover-550, USA) in air atmosphere at a heating rate of 10 °C min\textsuperscript{−1} from 30 °C to 1000 °C.

The acidity values of the samples were measured using the NH\textsubscript{3} temperature-programmed desorption (NH\textsubscript{3}-TPD) technique, performed in a Chemisorption Analyzer (micromeritics AutoChem II 2920, Micromeritics Instrument Corp., Norcross, USA). The amount of NH\textsubscript{3} desorbed was detected by a thermal conductivity detector. The samples were pretreated in He atmosphere at 500 °C for an hour. Subsequently, the samples were cooled to room temperature and then treated with the adsorbed gas (NH\textsubscript{3}) for an hour. Then, the samples were heated from 30 °C to 800 °C at a heating rate of 15 °C min\textsuperscript{−1} in He atmosphere.

Chemical compositions of the samples were determined using an Axios X-ray fluorescence (XRF) spectrometer (PANalytical X’pert, Axios, Netherlands) and inductively coupled plasma (ICP-OES730, Agilent, Japan).

Fourier-transform infrared (FT-IR) spectroscopy was performed using a Vertex 70 spectrometer (BRUKER, Germany) over a wavenumber range from 500 cm\textsuperscript{−1} to 4000 cm\textsuperscript{−1}; the spectra were obtained from 32 scans with a resolution of 4 cm\textsuperscript{−1}.

#### Evaluation of SCR catalyst

Fig. 1 schematically presents the pilot-scale test setup used for the coated low-temperature honeycomb SCR catalyst. The
The experimental device of the pilot test was placed after the semi-dry desulfurization and bag-type dust collection steps (the low-temperature and low-dust arrangement). Therefore, the flue gas had lower temperature, higher $H_2O$ concentration, and lower $SO_2$ concentration. The main components of flue gas are listed in Table 1.

A total of 16 catalyst module boxes were placed in the SCR unit perpendicular to the direction of the gas flow. In each catalyst module box, honeycomb catalysts were loaded in a 5 x 5 arrangement (Fig. 1). Liquid $NH_3$ was used as the reducing agent for the SCR reaction. The amount of liquid $NH_3$ was controlled by a flow meter. The change in flue gas composition was detected by an online monitoring system (SDL-SCS-900, China) and a smoke analyzer (Testo 350, Germany). The Municipal Environmental Protection Agency verified the monitoring instruments used herein to ensure credibility of the data obtained.

By studying the DeNO$_x$ efficiency of the catalyst under different process parameters, the effects of temperature, the $[NH_3/NO_x]$ ratio, the gaseous hourly space velocity (GHSV), and the NO$_x$ concentration on the DeNO$_x$ efficiency of the catalyst were investigated; the feasibility of the low-temperature DeNO$_x$ device was verified, and the optimum process parameters of the catalyst were determined. The reaction temperature was adjusted between 70 °C and 120 °C, while the initial $[NH_3/NO_x]$ ratio was adjusted between 0.8 and 1.2. The GHSV was varied between 1000 and 5000 h$^{-1}$, which was tuned by controlling the fan frequency. The NO$_x$ concentration of the flue gas was varied from 100 mg m$^{-3}$ to 500 mg m$^{-3}$.

To study the stability and DeNO$_x$ performance of the low-temperature catalyst, the experiment was planned to run continuously for 3000 h. The process parameters were set as follows: $[NH_3/NO_x] = 1$ and GHSV = 2000 h$^{-1}$. The reaction temperature was controlled at 100 °C, which reduced energy consumption.

### Results and discussion

**The structural and mechanical details of the catalyst**

The structure and mechanical details of the honeycomb catalyst are shown in Table 2.

**Investigation on the process parameters of the catalyst**

Laboratory investigation of the honeycomb catalyst under simulated flue gas revealed that the DeNO$_x$ of the catalyst increased from 70% to 90% when the reaction temperature was increased from 70 °C to 120 °C, with $[NH_3/NO_x] = 1$ and GHSV = 1667 h$^{-1}$. At the initial stage of the pilot test, the GHSV and $[NH_3/NO_x]$ ratio were set and the optimum operating conditions in laboratory were ensured. In addition, to reduce energy consumption, the operating temperature

### Table 1 Composition of flue gas from the coal-fired boiler

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$</td>
<td>10.5 vol%</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>$\leq$35 mg m$^{-3}$</td>
</tr>
<tr>
<td>$CO$</td>
<td>$\geq$70 mg m$^{-3}$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>10 vol%</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>14 vol%</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>$\leq$10 mg m$^{-3}$</td>
</tr>
</tbody>
</table>

### Table 2 Details of the honeycomb catalyst

<table>
<thead>
<tr>
<th>Aspects</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L \times W \times H$ (mm)</td>
<td>100 x 100 x 150</td>
</tr>
<tr>
<td>Wall thickness (mm)</td>
<td>Inner 0.30, Outer 0.90</td>
</tr>
<tr>
<td>Channels</td>
<td>53 x 53</td>
</tr>
<tr>
<td>Pore size (mm)</td>
<td>1.5 x 1.5</td>
</tr>
<tr>
<td>Aperture ratio (%)</td>
<td>63.20</td>
</tr>
<tr>
<td>Specific external surface (m$^2$ m$^{-3}$)</td>
<td>1685</td>
</tr>
<tr>
<td>Catalyst content (wt%)</td>
<td>16</td>
</tr>
<tr>
<td>Compressive strength (kN)</td>
<td>Axial 105, Radical 15</td>
</tr>
</tbody>
</table>
was set to 100 °C. After many tests, the DeNO\textsubscript{x} efficiency of the catalyst was found to be only ∼30% in the pilot, which was lower than the efficiency obtained in the laboratory. When using only air as the carrier gas instead of flue gas, the efficiency could reach 85% under the same conditions. The concentrations of SO\textsubscript{2} and particulate matter in the flue gas were low after desulfurization and dust removal; therefore, the associated toxicity was very low, which could not lead to such a drastic drop in DeNO\textsubscript{x} efficiency.

From literature reports, it is indicated that DeNO\textsubscript{x} efficiency of the low-temperature DeNO\textsubscript{x} catalyst will be significantly reduced in the presence of H\textsubscript{2}O.\textsuperscript{26,27} The water vapor content was as high as 14% in real flue gas. Therefore, in the laboratory, 13 vol% H\textsubscript{2}O was introduced into the simulated flue gas to investigate the effect of water vapor on catalyst activity, the DeNO\textsubscript{x} efficiency was reduced by ∼30%, and was maintained at above 50%. Therefore, to create a viable environment for improving the DeNO\textsubscript{x} efficiency of the catalysts and to achieve “White Smoke Elimination”, the H\textsubscript{2}O concentration in the flue gas was reduced from 14 vol% to 8–10 vol% by adding a H\textsubscript{2}O removal device. With decreasing H\textsubscript{2}O concentration, the DeNO\textsubscript{x} efficiency was increased from 30% to ∼65%.

Owing to the difference between the pilot tests conducted under real smoke conditions and laboratory-simulated smoke conditions, the optimal process conditions for the catalyst in the pilot test were investigated after adding the H\textsubscript{2}O removal device.

The effect of temperature on the DeNO\textsubscript{x} efficiency of the catalyst was investigated next (Fig. 2A). To reduce the energy waste caused by reheating of the flue gas, the effect of temperature on the catalytic activity was only examined at low temperatures. The experimental conditions were as follows: [NH\textsubscript{3}/NO\textsubscript{x}] ratio was 1, space velocity was ∼2000 h\textsuperscript{-1}, NO\textsubscript{x} concentration was ∼300 mg m\textsuperscript{-3}, and H\textsubscript{2}O concentration was 8–10 vol%. The effect of temperature on the DeNO\textsubscript{x} efficiency of the catalysts was very significant: the DeNO\textsubscript{x} efficiency of the catalysts increased from 32% to 86% with increase in flue gas temperature from 70 °C to 120 °C. When the flue gas temperature was 100 °C, the DeNO\textsubscript{x} efficiency of the catalyst was as high as 65%.

The DeNO\textsubscript{x} efficiency of the catalyst reaches 86% at 120 °C, which was a better level but slightly lower than the similar catalysts.\textsuperscript{16–20} The main reasons were relative low temperate, high H\textsubscript{2}O and the simultaneous existence of H\textsubscript{2}O and SO\textsubscript{2}. When the flue gas temperature was 100 °C, the DeNO\textsubscript{x} efficiency of the catalyst was as high as 65%. This is mainly due to the inhibitory effect of H\textsubscript{2}O on the catalyst activity under ultra-low temperature conditions. As the temperature decreases, the DeNO\textsubscript{x} efficiency decreases significantly. This also shows that in the practical application of low-temperature DeNO\textsubscript{x} catalysts, the effect of H\textsubscript{2}O on the activity of the catalyst at different temperatures should be considered to determine the best working conditions to further improve the DeNO\textsubscript{x} performance of the catalyst.

To investigate the DeNO\textsubscript{x} performance of the catalyst under more severe flue gas conditions and to reduce the energy consumption by flue gas reheating, the temperature was set to 100 °C for subsequent experiments.

![Fig. 2 Effects of different parameters on DeNO\textsubscript{x} efficiency of the catalyst in the pilot test: (A) [NH\textsubscript{3}/NO\textsubscript{x}] ratio, (B) GHSV, (C) temperature, and (D) NO\textsubscript{x} concentration.](image-url)
Fig. 2B shows the change in the DeNO\(_x\) efficiency of the catalysts as the [NH\(_3/\)NO\(_x\)] ratio was varied from 0.8 to 1.2. The experimental conditions were as follows: the space velocity was ~2000 h\(^{-1}\), NO\(_x\) concentration was ~300 mg m\(^{-3}\), and H\(_2\)O concentration was 8-10 vol%.

When the [NH\(_3/\)NO\(_x\)] ratio was increased from 0.8 to 1.0, the DeNO\(_x\) efficiency of the catalyst increased from 55% to 65%. When the [NH\(_3/\)NO\(_x\)] was increased further to 1.2, the DeNO\(_x\) efficiency remained almost unchanged. The DeNO\(_x\) efficiency was affected by many factors. When the [NH\(_3/\)NO\(_x\)] ratio reached 1, the amount of ammonia was already in an excessive state, and more ammonia was not effective to improve the DeNO\(_x\) efficiency. On the other hand, the excessive NH\(_3\) will cause secondary pollution and react with NO\(_x\) to produce NH\(_4\)NO\(_2\), which will have a toxic effect on the catalyst. To avoid secondary pollution caused by the introduction of excessive quantity of ammonia, the [NH\(_3/\)NO\(_x\)] ratio was set to 1.0 for subsequent experiments.

The GHSV directly affected the residence time of the flue gas on the catalyst surface, thus affecting the DeNO\(_x\) reaction process.\(^{28}\) During the experiment, the GHSV was changed from 1000 h\(^{-1}\) to 5000 h\(^{-1}\), keeping all other process parameters unchanged. Fig. 2C shows that the DeNO\(_x\) efficiency of the catalyst was increased and then decreased with increasing GHSV. The DeNO\(_x\) efficiency of the catalyst in the GHSV range from 1000 h\(^{-1}\) to 5000 h\(^{-1}\) was higher than 55%. The best efficiency achieved was ~65% at GHSV of 2000 h\(^{-1}\) in the pilot test. However, when the GHSV was 5000 h\(^{-1}\), the DeNO\(_x\) efficiency was only 43%. The flue gas contained harmful substances, such as particulate matter and SO\(_2\); therefore, although the gas–solid contact time was increased under low GHSV conditions, the particulate matter was deposited more favorably on the catalysts surface, blocking the microporous structure of the catalysts, and thus reducing the effective contact area of catalytic.\(^{30}\) Moreover, lower GHSV weakened the diffusion during the reaction.\(^{30}\)

Under high-GHSV conditions, the particulate matter deposition on the catalyst surface was not easy; however, the contact time between the flue gas and the catalyst was significantly shortened and it was difficult for the internal diffusion process to proceed fully. With increasing GHSV, the external diffusion process was insufficient, leading to reduced DeNO\(_x\) efficiency.\(^{31}\)

The NO\(_x\) content in the flue gas was different under different working conditions. Therefore, it was necessary to test the DeNO\(_x\) efficiency of the catalysts at different initial NO\(_x\) concentrations. Fig. 2D shows that the catalysts exhibited strong adaptability to the initial concentration of NO\(_x\), and the DeNO\(_x\) efficiency first increased and then remained stable with increasing initial concentration of NO\(_x\), within the experimental concentration range (100–500 mg m\(^{-3}\)).\(^{32}\) When the NO\(_x\) concentration exceeded 200 mg m\(^{-3}\), the DeNO\(_x\) efficiency was higher than 60%.

Comparing the experimental results obtained under real flue gas conditions and laboratory-simulated flue gas conditions revealed that the complex flue gas environment can inhibit and interfere with catalytic activity. Under real flue gas conditions, catalytic activity was reduced and the optimum operating point of the catalytic activity also shifts. The optimum flue gas temperature creates suitable reaction conditions for the catalyst and reduces energy consumption. When the practical smoke temperature was too low (<100 °C), the H\(_2\)O in the flue gas condensed and covered the active site of the catalyst, leading to competitive adsorption with NO\(_x\) and NH\(_3\). At the same time, H\(_2\)O reduced the catalyst’s oxidation performance.\(^{33}\) The pilot test results showed that appropriate GHSV effectively prevents the deposition of particulate matter in the flue gas and creates a good gas-solid contact for the DeNO\(_x\) process. Reasonable control of the amount of NH\(_3\) introduced effectively avoids secondary pollution caused by excessive NH\(_3\) and reduces the formation of (NH\(_4\))\(_2\)SO\(_4\) salt by the reaction between excessive NH\(_3\) and SO\(_2\) in flue gas to cover the active site of the catalyst.\(^{19}\)

**Catalytic evaluation**

To study the stability and DeNO\(_x\) performance of the low-temperature catalyst, the continuous experiment was planned to run for 3400 h. The process parameters were set as follows: [NH\(_3/\)NO\(_x\)] ratio = 1, H\(_2\)O concentration = 8–10 vol%, and GHSV = 2000 h\(^{-1}\). The reaction temperature was controlled at 100 °C, which could reduce the energy consumption.

Fig. 3A shows the NO\(_x\) concentrations at the inlet and outlet of the reactor and the DeNO\(_x\) efficiencies of the catalysts during the continuous operation of the SCR unit for 3400 h. During the first 1100 h, the NO concentrations at the inlet and outlet were 300 and 100 mg m\(^{-3}\), respectively, which met the discharge standard. However, the DeNO\(_x\) efficiency gradually decreased from 60% to 50% in 1100 h because of the increased water vapor content in the flue gas (Fig. 3B). In the experiment, the equipment was modified to reduce air leakage rate. Hence, the oxygen content dropped from 12% to 8%, close to the actual smoke level. At the same time, the water vapor content rose to 10%, leading to declined efficiency. After 1100 h, the NO concentration at the inlet was reduced to 200 mg m\(^{-3}\), which was the normal level for flue gas from coal-fired power plants. Under this condition, the catalyst ran stably for 2100 h. The DeNO\(_x\) efficiency was close to 60% and the outlet NO concentration was lower than 80 mg m\(^{-3}\). To verify the DeNO\(_x\) efficiency at low NO concentration, the NO concentration at the inlet was reduced to 55 mg m\(^{-3}\) and the reaction run for ~300 h. The NO concentration at the outlet was lower than 20 mg m\(^{-3}\), indicating the potential of this process to be used to achieve lower emission standards.

**Catalyst characterization**

The structure information of honeycomb catalyst.

Fig. 4 shows the digital photograph of the honeycomb catalyst (Fig. 4A, fully formed catalyst) and structural characterization results (Fig. 4B-E). In Fig. 4A, the left and right images show the honeycomb cordierite support and the
vacuum-coated Ce-based honeycomb catalyst, respectively. The relative surface area of the honeycomb catalyst was as high as 1685.4 m² m⁻³, providing more contact surface for the loading of the catalyst’s active component, thereby improving the efficiency of the low-temperature DeNOₓ catalyst. The XRD patterns (Fig. 4B) show a series of peaks at 29.2°, 33.3°, 47.7°, and 57.2°, attributable to the cubic CeO₂ crystallite (PDF#34-0394). No strong or sharp peaks associated with the oxides of Mn and Fe were observed in the XRD pattern, indicating the possibility of their presence in an amorphous form or highly dispersed on the catalyst’s surface. According to Machida et al., when Mn/(Mn + Ce) <0.5, only a broad peak of CeO₂ was observed, and when a third metal oxide was added, CeO₂ further increased the specific surface area of the catalyst. The BET results indicated that the catalyst exhibited a Langmuir type IV isotherm and a H3-type hysteresis loop at a relative pressure (p/p₀) >0.3, reflecting the mesoporous properties of the catalyst (Fig. 4C). The SEM images showed that the catalyst’s surface was composed of dense, clear, and uniformly distributed catalytic particles (Fig. 4D). The EDS characterization further confirmed that the main components of the catalyst were the environment-friendly metal elements Mn, Ce, Fe, and Al (Fig. 4E).

**Structural characteristics of used catalysts.**

The catalyst module boxes after 3400 h of operation (Fig. 5A) showed that the catalysts were not clogged. The catalyst module and entire pores were free of particulate matter, and
the strength of the catalyst carriers was not changed. Therefore, placing the SCR unit after the desulfurization and dust removal unit not only significantly reduced the influence of particulate matter and SO2 on the activity of the catalyst, but also extended its service life, thus reducing the DeNOx operating cost. However, the flue gas still contained low concentrations of particulate matter and SO2, whose influence on the catalysts could not be ignored.

To make the samples representative and comparative, the same position of different catalyst module boxes in the SCR unit was selected and the four groups at the front, middle, and back of the reactor were named the 1st sample, 6th sample, 11th sample, and 16th sample (Fig. 5B–E). After 3400 h of operation, different catalyst layers showed different degrees of color change. The surface color of the catalysts changed from dark black to off-white. The degree of color change of the catalyst in the SCR reaction unit decreased gradually from the inlet to the outlet (Fig. 5B and E). When the flue gas flowed through different layers of the catalyst, the catalyst placed in the front direction along the gas flow filtered out some of the particulate matter in the flue gas. Fig. 5F shows the photograph of the outer wall of the catalyst (shown in Fig. 5B), with the outer wall having significant H2O marks on its surface.

Fig. 5 Digital photographs of different samples: (A) the catalyst module boxes after 3400 h test; (B–E) 1st sample, 6th sample, 11th sample, and 16th sample; (F) outer wall of the 1st sample.

The test conditions were as follows: GHSV = 2000 h⁻¹, [NH3/NO] ratio = 1, temperature = 100 °C, and NOx concentration was ~200 mg m⁻³. The DeNOx efficiencies of the sixth, eleventh, and sixteenth layer catalysts remained almost unaffected, and were still stable at above 80%. However, the DeNOx efficiency of the first layer of catalyst was ~70%. The DeNOx efficiency of the catalyst was restored to about 81% in the laboratory by ultrasonic washing and calcination. This result indicated that the main reason for decreased activity of the first-layer catalysts was the formation of (NH4)2SO4 salt and the particulate matter deposition.

In future commercial applications, purging the deposited particulate matter and the heating process by using compressed air to regenerate the catalyst during the process must be considered. The test result indicated that the catalyst had good tolerance and high low-temperature DeNOx performance. It also had good prospects of practical application in the field of low-temperature DeNOx.

The surface morphologies of the samples were investigated by SEM observation. Fig. 6 shows some typical SEM images. After the 3400 h test, the catalyst particles coated on the surface of the carrier remained evenly distributed and no significant particle coverage was observed (Fig. 6A–D), indicating that the low-temperature and low-dust arrangement can effectively avoid blockage of catalyst pores.

The XRD characterization results are shown in Fig. 7. All samples showed diffraction peaks typical of the cubic fluorite structure of CeO2. The XRD patterns of the samples without intense peaks corresponding to Mn or Fe compounds indicated that these possibly existed in an amorphous or highly dispersed phase on the catalyst’s surface. Moreover, there were no visible sulfur or sulfate peaks indicating that these species were present as surface sulfuric acid or an amorphous sulfate, respectively.

The composition of the material before and after the catalytic reaction was characterized by XRF, and the main components are listed in Table 3. The contents of elements, such as K, Ca, Na, and S, had increased in different layers, especially in the 1st sample. Due to the small pore size of the catalysts, most of the particulate matter in the flue gas was deposited on the first layer of the catalyst. K, Na, and Ca as alkali metal elements was deposited on the catalyst surface.
and in the pores, but also covered the active sites of the catalyst. At the same time, Na and K decreased the quantity and stability of Brønsted acid sites, which in turn reduced the redox ability of the catalyst.\textsuperscript{38} The element S was mainly derived from SO\textsubscript{2} in the flue gas. SO\textsubscript{2} reacts with NH\textsubscript{3} and the alkali metal elements in the flue gas to form an active site of the sulfate-coated catalyst.\textsuperscript{39} This is also one of the main reasons for pore size blockage of the catalyst. The BET characterization results also confirmed the specific surface areas, pore diameters, and pore volumes of the used and fresh samples (Table 3). After 3400 h of operation, the specific surface area and pore volume of the 1st sample were reduced by 20.91 m\textsuperscript{2} g\textsuperscript{−1} and 0.08 cm\textsuperscript{3} g\textsuperscript{−1}, respectively, compared to those of the fresh catalyst. Due to the uneven distribution of the flue gas in the SCR unit, element S and alkali metals (such as Na and K) accumulated in the flue gas of the catalyst surface in the middle of the unit, causing blockage of the catalyst pores. However, compared to the high-temperature and high-dust arrangement, the low-temperature and low-dust arrangement can effectively reduce the harmful effects of particulate matter, SO\textsubscript{2}, and alkali metals in the flue gas on the catalysts.

The distribution of K, P, Na, and S on the cross-section of the honeycomb catalyst was further investigated by EDS mapping characterization. The first layer of catalyst was greatly affected after 3400 h of operation. Hence, the 1st sample and the fresh sample were selected for comparative analysis. The cross-section of the catalyst was characterized by the EDS mapping, and the distribution of the alkali metal plasma on the surface of the honeycomb catalyst was investigated. The results (Fig. 8A and B) showed that the alkali metal was not detected, indicating that the alkali metal plasma amount was small and was mainly deposited in the micropores of the catalyst, while the element S deposited on the surface of the honeycomb catalyst.\textsuperscript{40} Agglomeration was observed, indicating a small amount of sulfate deposition on the catalyst surface. Consistent with the SEM characterization results, the catalyst showed stable low-temperature DeNO\textsubscript{x} performance in actual flue gas, which further proves the superiority of the method.

**Fig. 6** Low-/high-magnitude SEM images of different samples: (A) 1st sample; (B) 6th sample; (C) 11th sample; (D) 16th sample.

**Fig. 7** XRD patterns of the different samples.
To investigate the amount and strength of acidic sites on the samples, TG and NH$_3$-TPD experiments were performed. The NH$_3$-TPD desorption amounts for fresh and used samples are shown in Fig. 9A. All the samples showed wide signals in the temperature range 100–475 °C and there were 2 acid sites. The desorption peak appeared at 100–325 °C, which is the analytical peak of the weak acid site. Compared to the fresh catalyst sample, the NH$_3$ desorption at the weak acid site of the catalyst decreased slightly after use. Ammonia adsorption at the weak acid site was conducive to the DeNO$_x$ reaction. However, the center of the desorption peak at 325–450 °C for the used catalyst was the analytical peak of the strong acid site. Compared to the fresh catalyst, the catalyst sample after the peak runs in the practical flue gas only appeared. Therefore, it can be inferred that SO$_4^{2-}$ formed in the reaction acts as a strong acid site for ammonia adsorption. Additionally, SO$_4^{2-}$ reacted with complex components in flue gas to form stable (NH$_4$)$_2$SO$_4$ and other substances, reducing the catalytic activity. Therefore, in the process of ammonia spraying, ammonia inflow must be reasonably controlled to reduce NH$_3$ escape and the formation of (NH$_4$)$_2$SO$_4$ salt. Since the deposited material decomposed at higher temperatures, the used catalyst still showed a signal at temperatures above 550 °C. Notably, the broad peak of the 1st sample in the high-temperature region (500–550 °C) may be because of the presence of a stronger acid site or because the first layer of catalyst directly faced the high-flow-rate flue gas. The peak appearing in the

### Table 3  Physicochemical properties of the different samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>SO$_3$ (wt%)</th>
<th>K$_2$O (wt%)</th>
<th>CaO (wt%)</th>
<th>Na$_2$O (wt%)</th>
<th>BET date</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>0.563</td>
<td>0.056</td>
<td>0.260</td>
<td>0.000</td>
<td>90.41</td>
<td>3.66</td>
<td>0.25</td>
</tr>
<tr>
<td>1st</td>
<td>5.818</td>
<td>0.322</td>
<td>3.711</td>
<td>2.321</td>
<td>69.50</td>
<td>3.53</td>
<td>0.17</td>
</tr>
<tr>
<td>6th</td>
<td>1.331</td>
<td>0.101</td>
<td>0.537</td>
<td>0.726</td>
<td>81.32</td>
<td>3.58</td>
<td>0.23</td>
</tr>
<tr>
<td>11th</td>
<td>1.090</td>
<td>0.087</td>
<td>0.494</td>
<td>0.324</td>
<td>85.31</td>
<td>3.58</td>
<td>0.24</td>
</tr>
<tr>
<td>16th</td>
<td>1.067</td>
<td>0.107</td>
<td>0.385</td>
<td>0.327</td>
<td>83.33</td>
<td>3.58</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Fig. 8  EDS mapping of (A) the fresh sample and (B) the 1st sample.

Fig. 9  (A) NH$_3$-TPD and (B) TG results of different samples.
temperature range 550–600 °C may be because of decomposition of the sample. The catalyst’s 1st sample had been eroded by prolonged exposure to the complex components in the flue gas, which caused its active component to be unstable and decompose at high temperatures.

Further analysis by TG characterization confirmed that the strong acid site indicated by the NH3-TPD analysis (Fig. 9A) was SO4$^{2-}$. Fig. 9B shows that the 6th, 11th, and 16th samples had slight weight losses compared to the fresh catalyst sample, but the overall trend was consistent. The weight loss below 200 °C was because of the evaporation of H2O from the catalyst surface and the degradation of substances, such as the chemicals incorporated in the molding catalyst coating process. In particular, the weight losses in the two stages of 300–600 °C and 650–800 °C were more obvious in the 1st sample of the catalyst. The range from 300 °C to 500 °C was mainly attributed to the decomposition of (NH4)2SO4 on the catalyst surface, which was formed by the element S in the flue gas at the reaction temperature. At the same time, the element S penetrated the pores of the catalyst to the inside. Metal sulfides decompose at temperatures between 500 °C and 600 °C. Combined with the results of the NH3-TPD analysis (Fig. 9A), the weight loss in the temperature range 650–800 °C was attributed to the decomposition of the catalyst or the metallic sulfates formed.

From the previous analysis results, it was found that change in the middle portion of the catalyst after the reaction was relatively obvious, and the samples of the first and sixteenth layers and fresh catalysts were selected for comparison. The FT-IR spectra of the catalyst before and after the reaction (Fig. 10) show that the characteristic peak at 3423 cm$^{-1}$, which was attributed to the O–H bending vibration in H2O, was stronger after 3000 h of reaction, indicating that the catalyst adsorbed more H2O after the reaction. Fig. 10(a) shows peaks at 1747, 1638, and 1563 cm$^{-1}$ after reaction, attributed to symmetrical bending vibration of Bronsted acid site NH$_4$$^+$, the gaseous or weakly adsorbed NO$_3$, and the adsorbed NH$_3$, respectively. The catalysts at different positions after the reaction showed characteristic peaks of NO$_3^-$ at 1385 cm$^{-1}$ and 1030 cm$^{-1}$, indicating that NO$_2$ in the flue gas reacted with other components of the flue gas to form nitrates. The vibration peak of SO$_4^{2-}$ appeared at 1139 cm$^{-1}$. These results confirmed the aforementioned characteristic catalyst structure and the formation of sulfate on the catalyst surface. Fig. 10(b) also reflects that the disappearance of the acidic sites at the middle portion of the catalyst may be the cause of the decreased activity of the catalyst.

**Conclusion**

Results of the 3400 h pilot-scale test of the modified Ce-based honeycomb catalyst for NO$_x$ removal of the flue gas from a coal-fired boiler in thermal power plants showed that the honeycomb catalyst can endure low SO$_2$ (<3.5 mg m$^{-3}$) and high H2O (8–10 vol%) contents, and work stably with adjustable DeNO$_x$ efficiency (60–70%) with a [NH$_3$/NO$_x$] ratio of 1.0 at low temperatures of 100–110 °C. At the same time, the low-temperature and low-dust arrangement reduced the process modification and operation cost. Addition of a H$_2$O removal device contributed to the national “elimination of white smoke” requirements, and provided a reference for the transformation of the DeNO$_x$ of low-temperature flue gas with high H$_2$O content. Physicochemical properties of the used catalyst sample, cut from different positions of the SCR unit, further revealed that the deposition of a small amount of (NH$_4$)$_2$SO$_4$ and alkali metal formed during the reaction had little effect on the catalytic activity. However, the effect of H$_2$O on the catalyst performance was significant at low temperatures, but the effect was reversible and increased temperature reduced the inhibition of catalyst performance by H$_2$O.

**Author contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was financially supported by National High Technology Research and Development Program of China (No. 2015AA03A401).

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