Pilot-Scale Study on Medium-Low Temperature SCR Catalyst for Denitrification of Coke Oven Flue Gas

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Medium-low temperature SCR (MLT SCR) denitrification technology has become widely adopted in industrial coking plants, leading to a significant demand for flue gas purification. In this study, a V/Ti-based MLT SCR catalyst with a high $DeNO_x$ efficiency (>90%) and resistance to SO_2, designed to reduce NO_x at a temperature of 220°C under simulated flue gas conditions, was prepared in plate-type. It was well characterized using SEM, TEM, EDS, and BET analyses before pilot-scale testing with coke oven flue gas. The anti-spalling performance of the plate-type MLT SCR catalyst complies with the industrial standard for plate-type catalysts, with a maximum allowable weight loss of less than 1.0 grams under sandblasting tests. The pilot-scale test of coke oven flue gas demonstrated excellent $DeNO_x$ efficiency (>97%) at 207~210°C, irrespective of normal operational conditions or post-maintenance startup. Despite the flue gas containing a small amount of SO_2 (30 ppm), the successful long-term (3-day) continuous pilot operation tests of the MLT SCR catalyst for denitrification certify the stability of the catalyst, indicating that the catalyst's surface was not affected by NH_4HSO_4. This stability provides reassurance about the long-term performance of the catalyst.

Keywords: Coke oven flue gas, Pilot-scale test, Medium-low temperature SCR catalyst, $DeNO_x$

1. INTRODUCTION

The coke oven process is a critical step in ironmaking, providing fuel and a reducing agent for the iron ore reduction process in the blast furnace. The selective catalytic reduction of nitrogen oxides (NO_x) with NH_3 (NH_3-SCR) technology is extensively employed to manage NO_x emissions in coke oven flue gas[1]. NH_3-SCR catalysts, such as V_2O_5-WO_3(MoO_3)/TiO_2, are widely used in industrial applications[2, 3]. The catalyst functions optimally at temperatures between 300°C and 400°C. However, the flue gas temperature of the coke oven typically falls below this range, around 180 to 230°C. Consequently, the gas must be heated before entering the SCR denitrification tower to reach the high temperatures (~300°C) required for conventional SCR catalysts. This heating process, unfortunately, results in a significant increase in energy consumption. However, the use of SCR catalysts with high $DeNO_x$ efficiency at low and medium-low temperatures can avoid the need for flue gas reheating, leading to a substantial reduction in energy consumption. This not only leads to significant energy saving and carbon reduction benefits but also reduces the overall complexity and cost of the process.

Owing to coke oven flue gas commonly contains sulfur dioxide (SO_2) and moisture. When the SCR catalysts come into contact with the flue gas, SO_2 is readily oxidized to SO_3. The resulting SO_3 then reacts with NH_3 and water (H_2O) to form ammonium bisulfate (NH_4HSO_4), causing significant pore blockage in the SCR catalyst at lower temperatures[4]. Therefore, there are a variety of low- and medium-low temperature SCR catalysts have been developed and studied for the efficient decomposition and reaction of NH_4HSO_4 on the catalyst surface to promote the SO_2 resistance[5], including vanadium/titanium-based (V/Ti-based)[6-8], Mn-based oxides[9], CeO_2-based[10], and zeolite-based[11] SCR catalysts. Among these, the V_2O_5-MoO_3/TiO_2 SCR catalyst was developed to enhance low-temperature activity and expand the operating temperature window to 160 to 400°C[8]. It also demonstrates acceptable resistance to SO_2 and H_2O at low temperatures. Mn-based oxides are extensively researched as low-temperature SCR catalysts because of their multiple oxidation states and superior redox ability. These properties facilitate the SCR process and enhance the "Fast SCR" reaction at low temperatures[12]. However, it is essential to note that the Mn-based catalysts are significantly hindered by poisoning from H_2O and SO_2. CeO_2-based SCR catalysts are valued for their high oxygen storage capacity, strong metal interactions, and unique redox properties, which enhance the SCR reaction at low temperatures[10]. Despite these benefits, sulfate formation and low-temperature SCR performance of the CeO_2-based SCR catalyst pose limitations for industrial applications.

In this study, we developed a V/Ti-based medium-low temperature (MLT) SCR catalyst and investigated its physicochemical characteristics. Additionally, we prepared the plate-type MLT SCR catalyst and conducted a pilot-scale investigation of medium-low temperature NH₃-SCR technology for treating coke oven flue gas. Self-design pilot equipment was installed beside the coke oven plant with a maximum gas flow capacity of 240 Nm³/hr. We systematically examined the effects of operation conditions, temperature, and flow rate on the DeNO$_x$ efficiency of the SCR pilot reactor. The research findings offer robust technical support for the denitrification of coke oven flue gas, with the potential to inspire significant advancements in the field.

2. EXPERIMENTAL METHOD

2.1 Preparation of the Plate-Type MLT SCR Catalyst

A V/Ti-based MLT SCR catalyst was synthesized by impregnating the active vanadium and other promoters onto anatase (TiO₂) support, followed by calcination at 500°C for 4 hours, resulting in the catalyst in powder form. In the subsequent stage, the catalyst powder was mixed with binders, kneaded, and coated onto SUS 304 stainless steel mesh. The coated mesh was then pressed into a zig-zag shape to form 15 × 15 cm plates, which were calcined at 500°C to complete the preparation of the plate-type MLT SCR catalyst.

2.2 Characterization

The surface area and pore volume of the catalyst were measured by N₂ adsorption at 77 K using the BET method and the BJH method, respectively (Micromeritics Instrument Corp., USA). The morphology and chemical composition of the catalyst was characterized using a transmission electron microscope (TEM) (FEI Tecnai F20 G2 S-TWIN, USA) and scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) operated at 15 kV (1540 XB Crossbeam, Zeiss, Germany). A sandblasting test was conducted on a 10 × 10 cm plate-type catalyst sample at a 12-degree angle using glass beads (50-105 μm) at 2.0 kg/cm² pressure. Each side of the sample was sandblasted for 15 seconds and weighed before and after the process.

2.2 Catalytic Evaluation

The activity and durability of the MLT SCR catalyst were evaluated using a quartz fixed-bed reactor system (CATA 4000, Best Instrument Co., Ltd, Japan) at atmospheric pressure. The plate-type sample was prepared into a granular type which was then packed into the middle of the reactor (i.d. 25 mm) containing 4.9 ml catalyst of 14-18 mesh. The reaction temperature was monitored by a thermocouple located at the bed of the catalyst. The feed gas mixture contained 200 ppm NO, 200 ppm NH₃,

3 vol.% O₂, 1000 ppm SO₂ (when used), 14 vol.% H₂O (when used), and N₂ as the balance gas with a total flow rate of 2,250 mL/min, corresponding to a gas hourly space velocity (GHSV) of 27,751 h⁻¹. The concentration of NO for the gases before and after passing through the catalyst bed was analyzed using a gas analyzer. The denitrification (DeNO$_x$) efficiency was calculated using the following equation

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

2.3 Pilot-Scale Test and the Evaluation of SCR Catalyst Activity

A self-designed SCR pilot plant has been constructed and tested at CSC (China Steel Corporation). It is set up beside the #1 coke oven plant as shown in Fig.1(a), which has dimensions of 2.3 × 2.2 × 3.05 m and was designed to a maximum gas flow of 240 m³/h. The schematic diagram in Fig.1(b) illustrates the pilot-scale equipment composed of a heater, a catalyst bed, and a draught fan. A total of four plate-type SCR catalyst modules were filled in the catalyst bed, each measuring 15 × 15 × 15 cm and with a total volume of 0.0135 m³. The SCR reaction utilized 10% ammonia-water solution as a reducing agent, which was mixed with the flue gas upstream.
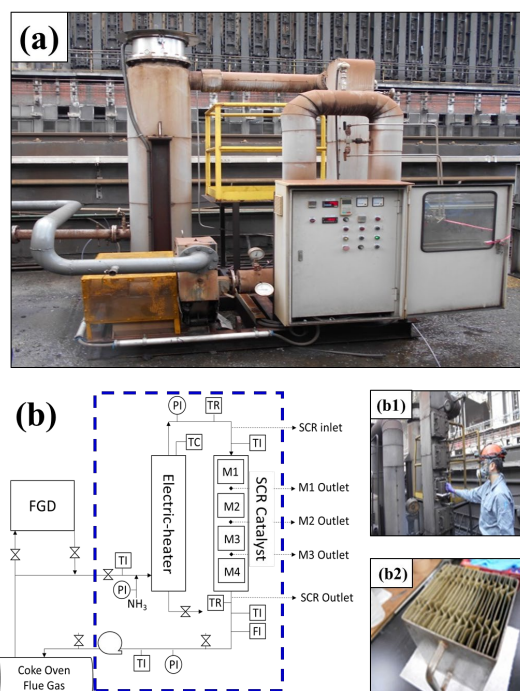

Fig.1. (a) Picture of the self-designed SCR pilot plant；(b) schematic diagram of pilot-scale test for the plate-type MLT SCR catalyst；dashed square referred to the SCR pilot, and picture of SCR catalyst modules (b1) containing 25 pieces of 15 × 15 cm plate-type MLT SCR catalyst per module (b2).

During the pilot-scale test, different flue gas conditions (e.g., temperature, flow rate) are applied. The tests are performed at 170, 210, 234, 252, 268, 285, and 290°C, respectively. The flow rates from 40 Nm^3/h to 160 Nm^3/h are tuned by fan frequency. Additionally, the heater was employed to elevate the flue gas temperature, ensuring it reached the catalyst reaction temperature. A portable flue gas analyzer (PG-300, Horiba, Japan) was used to analyze the composition of the flue gas both before and after the SCR reactor.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Plate-type MLT SCR Catalyst

We used SEM to observe the morphology of the catalyst. As shown in Fig.2(a), the MLT SCR catalyst predominantly exhibits a granular structure, with small particles aggregating into larger ones. Furthermore, TEM analysis in Fig.2(b) reveals that these small catalyst particles are formed by the aggregation of 10-20 nm crystalline TiO_2 nanoparticles. Additionally, EDS was employed to examine the distribution of different elements within the catalyst as shown in Fig.2(c) and Fig.2(d). Elemental mapping confirms that the active component, V_2O_5, is uniformly distributed on the TiO_2 support.

The denitrification reaction primarily occurs on the catalyst's surface, so its specific surface area directly impacts its denitrification activity. Therefore, we conducted an assessment of the BET-specific surface area and BJH pore characteristics of the MLT SCR catalyst. For the TiO_2 support without the active component, the specific surface area and pore volume are 92.2 m^2/g and 0.28 cm^3/g, respectively. After adding the active component (including V_2O_5 and other promotors), these values decrease to 74.1 m^2/g and 0.27 cm^3/g, respectively. This reduction occurs because V_2O_5 tends to aggregate on the TiO_2 support surface during the sintering process, thereby reducing the specific surface area and pore volume of the support[13].

To avoid the pressure drop associated with a granule-type SCR catalyst in actual coke oven flue gas application, we prepared plate-type MLT SCR catalysts by incorporating clay and glass fibers as binders to enhance their strength. To evaluate the anti-spalling performance
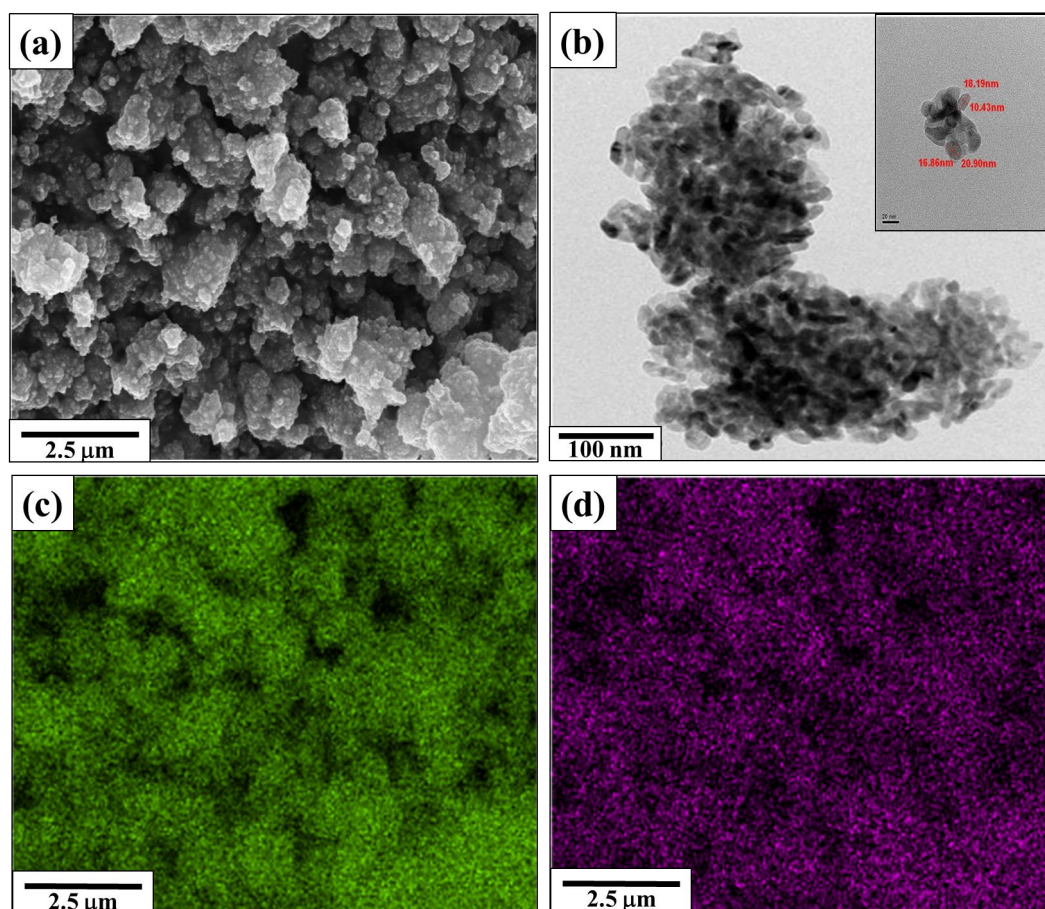

Fig.2.   SEM micrograph (a), TEM micrographs (b), and EDS mapping of Ti kα1 (c) and V kα1 (d) of the MLT SCR catalyst.

of the plate-type catalyst, we conducted a sandblasting test. The results indicated that 10 × 10 cm samples subjected to sandblasting exhibited a weight loss of 0.12 to 0.23 grams per sample. This outcome complies with the industrial standard for plate-type catalysts, which specifies a maximum allowable weight loss of less than 1.0 grams under sandblasting conditions.

3.2 Activity of the SCR Catalyst

We tested the DeNO$_x$ activity of the MLT SCR catalyst under simulated flue gas at various reaction temperatures using laboratory catalyst reaction equipment. As shown in Fig.3(a), the DeNO$_x$ efficiency of the catalyst is 67.9% at 180°C. The efficiency increases with temperature, reaching a peak of 96.5% at 250°C. However, the DeNO$_x$ efficiency decreases to 86.5% once the temperature reaches 300°C. This decline at higher temperatures is likely due to the catalyst causing direct oxidation of NH$_3$ to NO, thereby reducing the overall DeNO$_x$ efficiency.

Additionally, we investigated the impact of high H$_2$O (14%) and high SO$_2$ content (1,000 ppm), as well as the simultaneous presence of both high moisture and high sulfur content, on the DeNO$_x$ performance of the MLT SCR catalyst at 220°C. In Fig.3(b), the catalyst's DeNO$_x$ efficiency was initially ≥99% in the absence of H$_2$O or SO$_2$. However, the introduction of H$_2$O (14%) led to a decrease in DeNO$_x$ efficiency to 93%. This decrease can be attributed to competitive adsorption between H$_2$O and NH$_3$, resulting in a reduction in active sites on the catalyst[14]. Moreover, the introduction of SO$_2$ (1,000 ppm) caused a slight decrease in DeNO$_x$ efficiency to 98.3%. This reduction is primarily due to SO$_2$ competing with NO for adsorption on the catalyst surface in the absence of H$_2$O, leading to a minor decline in catalytic activity[15]. The combined introduction of H$_2$O (14%) and SO$_2$ (1000 ppm) resulted in a drop in DeNO$_x$ efficiency to 89.7%. This significant reduction is likely due to the combined effects of H$_2$O competing with NH$_3$ for active sites and SO$_2$ competing with NO for adsorption, leading to a more pronounced decrease in the number of available active sites for the DeNO$_x$ reaction.

Additionally, we observed the long-term effects of high H$_2$O and high SO$_2$ environments on the DeNO$_x$ efficiency of the MLT SCR catalyst. The DeNO$_x$ efficiency of the catalyst decreases from 99.5% to 80% as exposure time to high H$_2$O and high SO$_2$ conditions is extended from 1 hour to 32 hours. The primary reason for this decline is the formation of (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$ on the catalyst surface, reducing its catalytic activity[15]. Notably, commercially available MLT SCR catalysts currently used in China also gradually decrease DeNO$_x$ efficiency under the same laboratory test conditions. These commercial catalysts have an operational

lifespan of 3 years in actual field applications. Therefore, our MLT SCR catalyst is anticipated to meet the standards for the lifespan of field applications.
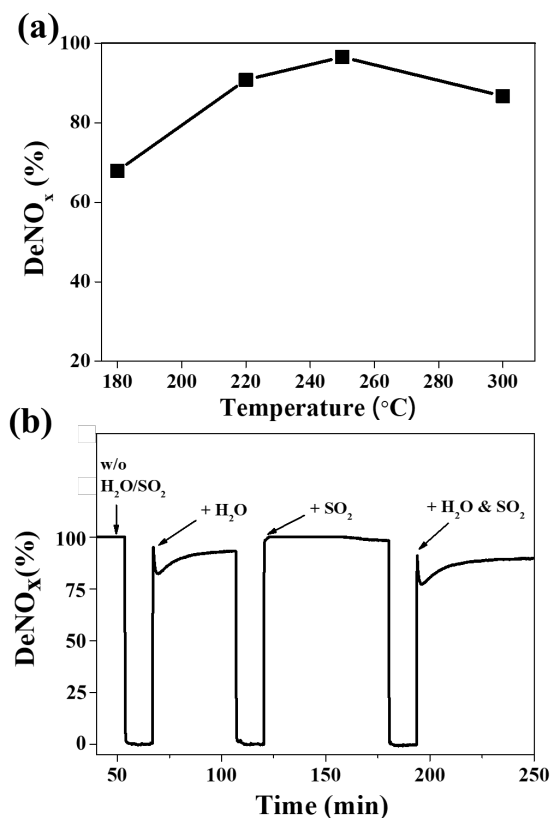

Fig.3. The activity tests of the granule-type MLT SCR catalyst in simulated flue gas; (a) effect of temperature and (b) effect of H$_2$O and SO$_2$ on the DeNO$_x$ efficiency of the catalyst at 200 ppm NO, 3% O$_2$, NH$_3$/NO=1, GHSV of 27,751 h^{-1}.

3.3 Results of Pilot-scale Test

The flue gas originating from the coke oven is comprised of 18% CO$_2$, 8% H$_2$O, 8.5% O$_2$, 0.2% CO, 15-30 ppm of SO$_2$, and 60-250 ppm of NO$_x$, all calculated on a dry basis. It is crucial to recognize the significant variation in NO concentration within coke oven flue gas under different operational conditions and the presence of certain amounts of SO$_2$, as these factors have the potential to attenuate the DeNO$_x$ efficiency of the MLT SCR catalyst. Therefore, during the pilot-scale test, we measured NO concentrations at the inlet flue gas of the SCR pilot and the outlet flue gas of each of the four SCR catalyst modules under various coking oven operating conditions, gas flow rates, and temperatures. As shown in Fig.4(a), under normal coking oven operation, the fuel gas was from the BFG (blast furnace gas), LDG (Linz-Donawitz converter gas), and COG (coke oven gas)

mixture, with a calorific value of 1050 Kcal/Nm³. The inlet gas flow rate to the SCR pilot was 40 m³/h, and the recorded maximal inlet NO concentration was 60 ppm at 210°C. As the flue gas passed through pilot catalyst modules 1 to 4 (GHSV 3,000~12,000 h⁻¹), the outlet NO concentrations were reduced to 17, 12, 1.3, and 0.9 ppm, respectively. The DeNO$_x$ efficiencies for the 1 to 4 modules are 71.6%, 80%, 97.8%, and 98.5%, respectively. In addition, we also investigated the DeNO$_x$ efficiency of the MLT SCR catalyst following the annual maintenance startup of the coke oven. During the initial stage of the coking process, COG was used as fuel gas to increase the gas calorific value to 4200 Kcal/Nm³. As shown in Fig.4(a), the highest recorded inlet NO concentration was 236 ppm at 207°C, with an inlet gas flow rate of 60 m³/h, caused by high NH$_3$ content in COG leading to thermal NO$_x$ formation. As the flue gas passed through pilot catalyst modules 1 to 4 (GHSV 4,500~18,000 h⁻¹), the NO concentrations at the outlets were reduced to 48, 24, 20, and 6 ppm, respectively. The DeNO$_x$ efficiencies for the 1 to 4 modules are 80%, 90%, 92%, and 97%, respectively. It indicates that, whether the coking process is in regular operation or during the annual maintenance startup period, the DeNO$_x$ efficiency increases with the number of pilot catalyst modules the flue gas passes through. Flue gas passing through the four pilot catalyst modules (at a GHSV of 3000-4500 h⁻¹ and a temperature of 207-210°C) consistently achieves over 97% DeNO$_x$ efficiency.

We also examined the impact of increasing the flue gas linear velocity to 2 m/s (flow rate 160 m³/h) on the DeNOx efficiency of the MLT SCR catalyst at a temperature of 193°C. The results indicated that the NO concentration at the SCR inlet was 75 ppm, which decreased to 28 ppm after passing through the four SCR catalyst modules. This corresponded to a GHSV of 11,850 h⁻¹, with a catalytic DeNO$_x$ efficiency of 63%. The findings strongly suggest that higher space velocities significantly reduce the DeNO$_x$ efficiency due to the reduced contact time between the flue gas and the catalyst.

The impact of flue gas temperature on the DeNO$_x$ efficiency of the MLT SCR catalyst was also examined in the study. As shown in Fig.4(b), when the SCR inlet flue gas temperatures were increased to 170°C, 210°C, 234°C, 252°C, 268°C, 285°C, and 290°C, with a GHSV of 3,185-3,500 h⁻¹, the DeNO$_x$ efficiencies after passing through the four SCR catalyst modules were 86.5%, 97%, 97.8%, 98.7%, 98.6%, 88.0%, and 66.4%, respectively. It indicates that the optimal temperature for the MLT SCR catalyst is between 210-268°C in the pilot-scale test, achieving DeNO$_x$ efficiencies of over 95%, consistent with the laboratory-simulated flue gas DeNO$_x$ test results.

The composition of coking oven flue gas contains a small amount of SO$_2$, less than 30 ppm. It is known that
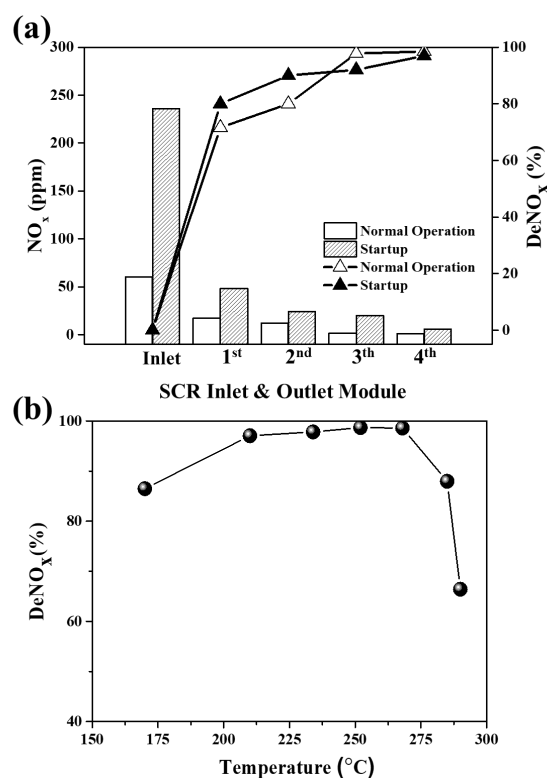

Fig.4. DeNO$_x$ efficiency of the plate-type MLT SCR catalyst at the pilot plant: (a) effect of SCR catalyst modules on DeNO$_x$ efficiency under different operating conditions, and (b) effect of temperature on the DeNO$_x$ efficiency at the outlet of the 4th SCR catalyst module with a GHSV of 3,185-3,500 h⁻¹.

SO$_2$ can be oxidized to SO$_3$ through the SCR catalyst reaction and then react with ammonia to form NH$_4$HSO$_4$, which can poison and deactivate the SCR catalyst. Therefore, we conducted long-term (3-day) continuous operation tests of the MLT SCR catalyst for denitrification to clarify the impact of flue gas components on catalyst poisoning. During the 3-day continuous operation tests, we carefully monitored the SCR operating conditions, maintaining a temperature of 215°C, with GHSV ranging from 3,500 to 4,500 h⁻¹, and a consistent NH$_3$/NO ratio of 1. Throughout this period, we conscientiously recorded the SCR inlet and outlet NO concentrations. Despite the frequent variations in coking oven operation, we observed that the fluctuating SCR inlet NO concentrations corresponded with changes in the SCR outlet NO concentrations. The highest recorded inlet NO concentration was 64 ppm; however, after passing through the four SCR catalyst modules, the outlet NO concentrations consistently remained low at 0.4-0.5 ppm, demonstrating DeNO$_x$ efficiencies exceeding 99%. These findings suggest that the catalytic DeNO$_x$ activity remained largely unaffected during the 3-day test period.

4. CONCLUSIONS

We successfully fabricated plate-type MLT SCR catalysts, which exhibited outstanding resistance to spalling with a weight loss of less than 1.0 grams. The results from the SCR pilot study on coking processes indicate that the catalyst maintains excellent $DeNO_x$ efficiency, achieving over 97% within a gas hourly space velocity (GHSV) range of 3,000-4,500 h^{-1} and a temperature range of 207-210°C, irrespective of normal operational conditions or post-maintenance startup. The catalyst demonstrated good stability throughout a 3-day operating period in long-term performance tests. These findings underscore the effectiveness of the medium-low temperature NH_3-SCR technology in treating coke oven gas, highlighting its potential for significant energy savings and carbon reduction benefits.

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