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Short Communication

High-efficiency reduction of NO_x emission from diesel exhaust using a $CeWO_x$ catalyst

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ABSTRACT

A $CeWO_x$ catalyst was washcoated on cylindrical cordierite honeycomb for the tests under practical conditions. The catalyst exhibited outstanding NH_3-SCR performance. A European steady-state cycle (ESC) test showed that the NH_3-SCR system based on the $CeWO_x$ catalyst could make the NO_x emission from diesel engine completely meet the Euro V limit without the help of any other after-treatment device.

1. Introduction

Nitrogen oxides (NO_x) from mobile source exhaust are major pollutants in urban atmosphere, causing acid rain, photochemical smog, and possibly resulting in the serious haze pollution as that occurring in China now. Three-way catalysts have already been successfully adopted for the simultaneous abatement of NO_x, CO, and unburned hydrocarbons from gasoline powered vehicles. However, the emission of NO_x and particulate matters (PM) remains a major problem for diesel powered vehicles to meet the more and more restrictive emission standards [1,2].

Due to the trade-off relationship between NO_x and PM in diesel engine exhaust, it is difficult for the conventional engine modification technology to simultaneously reduce both of them. Usually, high combustion efficiency will result in low PM and high NO_x emission. Therefore, for the purpose of energy saving, great efforts have been made to reduce NO_x emissions under lean burn conditions from the diesel engine exhaust over the past years [1–4].

Selective catalytic reduction of NO_x with NH_3/urea (NH_3/urea-SCR) is considered to be one of the most promising after-treatment technologies for NO_x abatement from diesel engines. Various catalysts have been reported to be effective for NH_3/urea-SCR, including vanadium-based catalysts [5], Fe-, Cu-, Ce-exchanged zeolite materials [4,6–21], and various vanadium-free oxide catalysts [22–28]. The toxicity of active vanadium species, together with the low stability at high temperatures, has restrained the wide application of vanadium-based catalysts, while the activities of vanadium-free oxide catalysts are often insufficient and mainly tested using simulating gas in laboratory. The zeolite materials promoted by Fe or Cu metal ions also have some problems in their practical applications, such as the insufficient low-temperature activity of Fe-ZSM-5 [4], the lack of high hydrothermal stability of Cu-ZSM-5 [4], and the high synthesis cost of Cu-SSZ-13 [9].

In our previous study, we have successfully developed a series of active Ce-based oxide catalysts, including the Ce-Ti, Ce-W-Ti, and Ce-W catalyst systems [29–33]. Among these catalysts, powder $CeWO_x$ catalyst showed nearly 100% NO_x conversion from 250 °C to 425 °C under an extremely high GHSV of 500,000 h^{-1}, which is a promising candidate for the potential application in diesel engine exhaust treatment [33]. The poisoning resistance and stability of this catalyst were further tested in this study. The $CeWO_x$ catalyst showed high resistance to the poisoning impact of alkali/alkaline earth metals and presented very good stability (see the Electronic Supplementary Information for the details of the tests). Furthermore, the catalytic performance of NO_x abatement from diesel exhaust was tested on engine benches, which can supply more information for the industrial applications of the $CeWO_x$ catalyst.

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2. Experimental

2.1. Catalyst synthesis

The $CeWO_x$ catalyst, with a Ce/W molar ratio of 1.0, was prepared by a homogeneous precipitation method using urea as precipitator. The detailed preparation procedures have been described in our previous study [33]. Cylindrical cordierite honeycomb (300 cpsi) was washcoated by $CeWO_x$ catalyst slurry. After drying at 100 °C and subsequent calcination at 500 °C for 3 h in air condition, the $CeWO_x$ washcoated honeycomb catalyst with a loading amount of *ca.* 120 g/L was obtained. Certain (16 or 24) blocks of cylindrical washcoated honeycomb catalysts (11 cm in diameter × 10.5 cm in length, *ca.* 1 L in volume) were encapsulated into a catalytic converter for engine bench tests.

2.2. Catalytic activity tests

The SCR activity measurements were carried out in laboratory in a fixed-bed quartz flow reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO (or 250 ppm NO and 250 ppm NO_2), 500 ppm NH_3, 5 vol.% O_2, N_2 balance. The effluent gas, including NO, NH_3, NO_2, and N_2O, was continuously analyzed by an online NEXUS 670-FTIR spectrometer equipped with a gas cell with 0.2 L volume.

A preliminary engine bench test was carried out to investigate the influence of reaction temperature and space velocity on the NO_x conversion over $CeWO_x$ catalyst under practical conditions. The total volume of the catalyst used in the test was 16 L. A SINOTRUK diesel engine (WD615.96, Displacement 9.726 L, Output/Speed 276 kw/2200 rpm) was used. Another engine bench test of the European steady-state cycle (ESC) was carried out using a SINOTRUK diesel engine (D10.34, Displacement 9.726 L, Output/Speed 250 kw/1900 rpm) and 24 L of $CeWO_x$ washcoated honeycomb catalyst. The exhaust gas was analyzed online by an AVL AMA 4000 analyzer bench. More details of the test on the flow stream of the exhaust, speed and torque, and pressure build-up and GHSV can be found in the Electronic Supplementary Information. The diesel fuels for both of the tests were met the Chinese IV standard.

3. Results and discussion

3.1. NH_3-SCR activity of the washcoated honeycomb catalyst

The washcoated honeycomb catalyst was tested using a cylinder sample with the volume of 1.5 mL. Different GHSVs were obtained by changing the total flow rate of feeding gas. The washcoated honeycomb catalyst showed over 90% NO_x conversion in a wide temperature range from 200 °C to 450 °C under a GHSV of 10,000 h^{-1} (Fig. 1). With the increase of GHSV, the low temperature NO_x conversion decreased to a certain extent especially at temperatures below 250 °C. However, it still exhibited more than 80% NO_x conversion from 250 °C to 450 °C under a relatively high GHSV of 40,000 h^{-1}. When NO_2 was added to the feeding gas with a NO_2:NO ratio of 1:1, near 100% NO_x conversion was obtained even in a broad temperature range from 200 °C to 450 °C due to the "fast SCR" effect. The "fast SCR" effect is a common phenomenon for NH_3-SCR catalysts, and this positive effect could remarkably enhance the NO_x conversion at low temperatures through the occurrence of following reaction: $2NH_3 + NO + NO_2 \rightarrow 2\,N_2 + 3H_2O$.

We further tested the NH_3-SCR activity under practical conditions on an engine bench using a SINOTRUK WD615.96 diesel engine and a catalytic converter with 16 L $CeWO_x$ washcoated honeycomb catalyst. The test temperature was varied by changing the operation points of the engine; thus, the GHSV and original NO_x concentration were changed simultaneously. The feed of urea was controlled with a NH_3/NO_x molar ratio of 0.95, and the data were recorded under steady-state conditions.

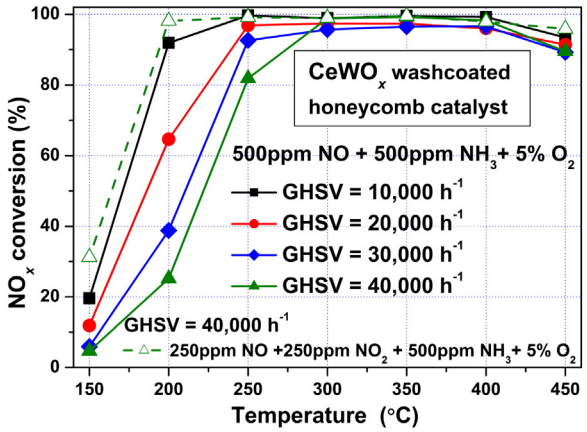

Fig. 1. NO_x conversions over $CeWO_x$ washcoated honeycomb catalyst. Reaction conditions: 500 ppm NO (or 250 ppm NO and 250 ppm NO_2), 500 ppm NH_3, $[O_2] = 5$ vol.%, and N_2 balance. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

Fig. 2 shows the original NO_x concentration (the number marked on the columns, in ppm) and NO_x conversion under different temperature and GHSV conditions during the engine bench test. The original NO_x concentration was in a range of 478–940 ppm. Under relatively high GHSVs of 35,000–45,000 h^{-1}, over 50% and 80% NO_x conversions could be obtained above 300 °C and 400 °C, respectively, indicating that the $CeWO_x$ catalyst is a promising catalyst for the removal of NO_x from diesel engine exhaust. As we have shown in Fig. 1, the "fast SCR" effect could significantly enhance the low temperature NO_x conversion of the catalyst. Therefore, if an upstream DOC was used, the low temperature NO_x conversion over the $CeWO_x$ catalyst could be promoted by the increase of NO_2 proportion in NO_x.

3.2. ESC test

The ESC test of the $CeWO_x$ catalyst was carried out using a SINOTRUK D10.34 diesel engine and 24 L washcoated honeycomb catalyst. The urea dosing strategy during the ESC test was developed based on closed-loop control. The inlet temperature and the GHSV at each test mode were shown in Fig. 3. The GHSV was mainly between 15,000 and 45,000 h^{-1}, which is in the effective range of $CeWO_x$ catalyst. The exhaust temperature was mainly between 350 °C and 500 °C. The

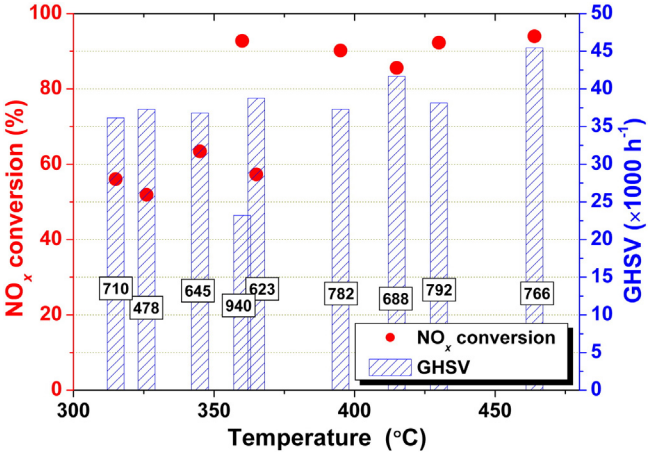

Fig. 2. An engine bench test result showing the influence of temperature and space velocity on the NO_x conversion of $CeWO_x$ catalyst under practical conditions. The number marked on the columns is the original NO_x concentration (in ppm). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

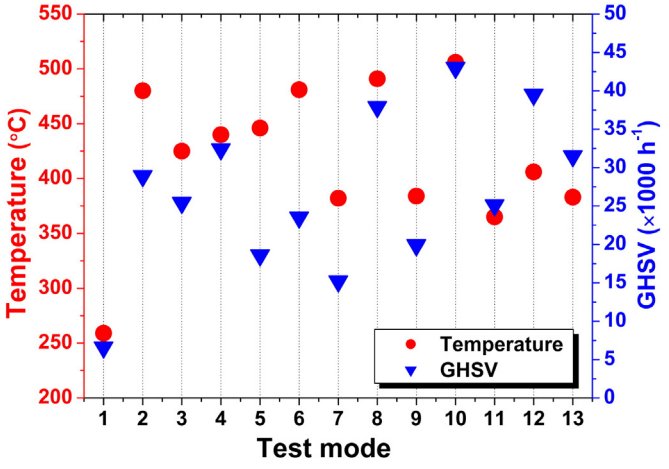

Fig. 3. The inlet temperature and GHSV at each mode point of the ESC test. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

temperature of the catalytic converter was lower than the exhaust temperature for about 20 °C–30 °C due to the heat lose in the connecting exhaust pipe.

Before the test of $CeWO_x$ catalyst, original ESC tested PM emission of the engine was adjusted by engine modification to be 0.015 g/(kW · h), which is lower than the Euro V limit value of 0.02 g/(kW · h). In addition, the original CO and HC emission were 0.30 and 0.18 g/(kW · h), respectively, both lower than the Euro V limit values (1.5 g/(kW · h) for CO and 0.46 g/(kW · h) for HC).

The NO_x concentrations during the ESC test of the $CeWO_x$ catalyst were shown in Fig. 4. At mode 1, due to the special operation condition of engine, the original NO_x concentration was obviously lower than those at other mode points. Considering the low NO_x concentration together with low temperature, no urea was injected at this mode, and the NO_x was not reduced. The original NO_x concentrations at mode 2–13 were in a range of 430–1273 ppm. After NH_3-SCR treatment, the NO_x concentrations were significantly reduced to 95–358 ppm, with the corresponding NO_x conversions of 68%–85%. The original weighted average NO_x emission of the engine during the ESC test was 8.76 g/(kW · h), while the weighted average NO_x emission after NH_3-SCR treatment was only 1.90 g/(kW · h), which is lower than the Euro V limit value of 2.0 g/(kW · h). Accordingly, during the whole ESC test process, the weighted average NO_x conversion was *ca.* 78%.

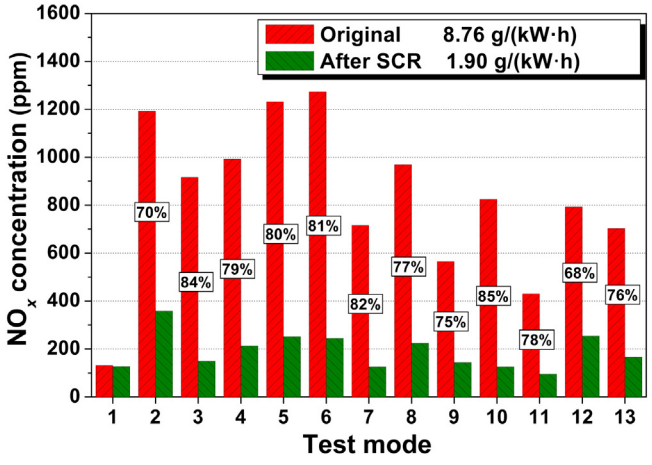

Fig. 4. The original and treated NO_x concentration at each mode point of the ESC test. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

4. Conclusions

Both laboratory and engine bench tests showed that a $CeWO_x$ catalyst could reduce the NO_x emission efficiently under high space velocities. In an ESC test using a SINOTRUK D10.34 diesel engine (Displacement 9.726 L) and an NH_3-SCR system with 24 L washcoated honeycomb $CeWO_x$ catalyst together with the closed-loop control of urea dosing, the NO_x emission was reduced from 8.76 g/(kW · h) to 1.90 g/(kW · h). Without the help of any upstream DOC, the NO_x emission from the diesel engine could completely meet the Euro V limit, indicating that this $CeWO_x$ is a very efficient catalyst for the removal of NO_x from diesel vehicles.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.10.032.

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