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***Article***

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# Influence of Steam and Sulfide on High Temperature Selective Catalytic Reduction

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**Abstract:** The influences of steam and sulfide on the efficiency of NOx reduction using ammonia ($NH_3$) over the nanometer-class V-W/Ti catalyst in conditions of high temperature is experimentally investigated using a steady-flow reactor. The results showed that selective catalytic reduction (SCR) is inhibited by $H_2O$ at low temperature, but higher NO conversion efficiency is achieved at high temperature since the reaction of $NH_3$ oxidized by $O_2$ to NOx is inhibited by $H_2O$. The activity of SCR is promoted by $SO_2$ in the temperature range of 200~500°C, the NO conversion efficiency was improved to 98% from 94% by adding $SO_2$. SCR would be improved at 350~500°C when $H_2O$ and $SO_2$ exist at the same time. Furthermore, the positive influence to the NOx conversion was proved in the presence of $H_2O$ and $SO_2$ as a result of the European Stationary Cycle test.

**Keywords:** High temperature; selective catalytic reduction; efficiency

## 1 Introduction

Diesel engines are widely used in medium and heavy trucks due to their high thermal efficiency, high power capabilities, low fuel consumption ratio and good durability. However, NOx and PM emissions from diesel engines can't be removed as gasoline engines with three-way catalytic converter. Thus, on the base of existing technology of internal purification, exploring advanced exhaust emissions after-treatment system is the key points to maintain diesel engines' survival and development. The European Stationary Cycle (ESC) and the European Transient Cycle (ETC) are used to determine engine emissions. The ESC is a 16-mode steady test, and the ETC is a transient engine dynamometer test consisting of an urban part, a rural part and a motorway part [1–3].

In order to comply with the CN V and CN VI regulations for heavy-duty diesel engines, both the NOx and particulate emissions must be greatly reduced for today's state of the heavy-duty diesel engines. CN V regulations, namely 2.0 g/kW·h NOx and 0.02 g/kW·h particulate, cannot be achieved by engine management or improved engines alone, rather some sort of after treatment must be used. Diesel particulate filter (DPF) to reduce soot emissions together with Urea-SCR to reduce NOx. The Urea-SCR systems have been shown to be both very efficient and durable in vehicle applications, so the heavy-duty diesel engines manufacturers prefer Urea-SCR for reducing NOx [4–7].

This study used certain vehicle diesel engine, chose lower speed and lower load working point, to analyze the influence of intake throttle valve on exhaust temperature before DOC, late post injection on temperature inside DOC and HC emission, injection quantity on DOC temperature rise behavior and engine specific fuel consumption. Experimental result showed that coupling intake throttle adjustment and late post injection can increase exhaust temperature after DOC significantly, to reach DPF active generation temperature [8–11].

In the treatment of sulfur-containing exhaust gases, $SO_2$ could be partly oxidized to $SO_3$ which can react with water and unconverted ammonia to form sulfuric acid and ammonium sulfates. Catalyst formulation and operating variables have to be designed in order to minimize its extent and, as a consequence, to avoid the risk of deposition of ammonium-sulfates or corrosion in the cold sections of equipment of the exhaust downstream from the reactor [12–15].

The influence of $H_2O$ and $SO_2$ in the feed gas flow to the NO conversion of SCR was experimental investigated in this paper, which was carried on the simulating gas test and stationary operation of the engine in order to make use of catalyst in the SCR process.

## 2 Experimental Apparatus and Methodology

### *2.1 Experimental Apparatus*

In order to investigate basic characteristics of the urea-SCR catalyst, NOx reduction characteristics were measured using simulating gas test equipment. Fig. 1 shows the configuration of the Setup of sample test. The feed gas was consisted by NO (0~0.05%), $NH_3$ (0.03%~0.05%), $SO_2$ (0~0.01%), $O_2$ (5%), vaporized water (0~3%) and $N_2$ (balance gas). It corresponded to a typical exhaust gas but make up of by standard gases. The catalyst temperature was controlled with the furnace which controlled by computer and capable of reaching temperatures up to 750°C. In the simulating gas tests, $NH_3$ was used as the model gas reducing agent. In the actual urea-SCR system, urea water injected in the exhaust pipe and decomposes to NH3, which becomes the reducing agent and removes NOx, while in the simulating gas tests this was simplified by directly using $NH_3$. The configuration of urea-SCR system and injection were shown in Fig. 2. The gas analysis was performed with a Five-Way-Gas Analyzer (AVL DiGas 4000 light).

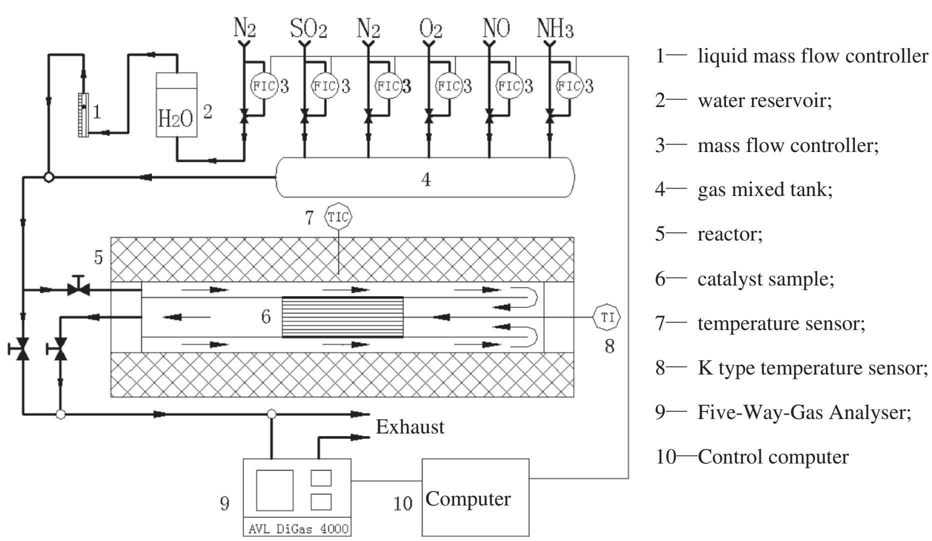
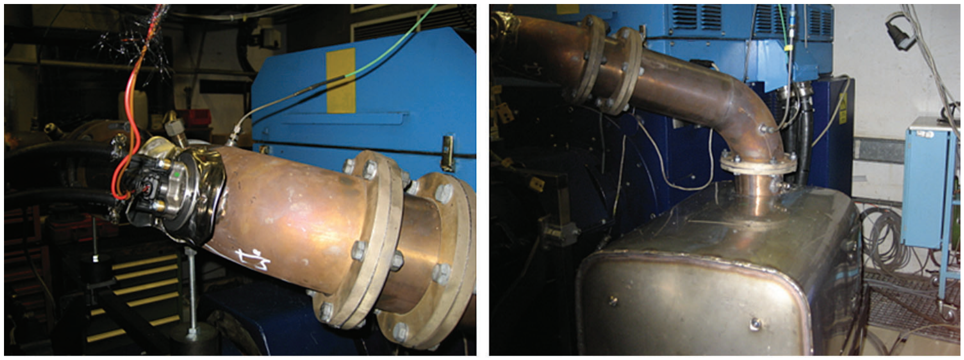



**Figure 1:** Setup of sample test



(a) (b)

**Figure 2:** Urea-SCR system (a) Urea injection system (b) SCR catalytic converter

Tab. 1 shows specifications of the test engine. Basically, the system consists of a dosage system for aqueous urea injection and a vanadium based SCR catalyst. This program used SCR catalysts without a special pre-catalyst for NO to $NO_2$ conversion and without a dedicated hydrolysis catalyst. A catalyst effective in oxidizing NO to $NO_2$ would also be effective in oxidizing $SO_2$ to $SO_3$. The fuel sulfur contents used in this study is about 0.035% and 0.005% corresponding to Euro III and Euro IV emission levels.

**Table 1:** Engine performance parameters

| Item | Parameter |
|---|---|
| Cylinders | 6 |
| Valves per cylinder | 4 |
| Bore/mm | 126 |
| Stroke/mm | 155 |
| Displacement/L | 11.6 |
| Standard Power/kW | 353 |
| Standard Speed/($r \cdot min^{-1}$) | 2100 |

### *2.2 Experimental Methodology*

Sample test was carried out firstly, one-inch sample of SCR Catalyst (12.5 mm sides by 55 mm length) was used for the majority of the tests, which was cut from the inner region of 5.66 inches diameter by 6 inches long catalyst to prevent variations of the wash-coat load. The space velocity of 32000 $h^{-1}$ was comparable to a mean value of the typical exhaust flow rates in vehicle. Fresh samples were used for every test to ensure the same baseline for every test run. Next, confirmatory test was carried out to verify the effectiveness of the urea-SCR system using the test engine.

The urea dosage system integrates a urea pump, filters, a dosage valve and a control unit in one box. Input signals to the control unit include engine speed, engine load and exhaust gas temperature downstream of the catalyst. The first two signals are obtained from the engine ECU via a CAN link. The SCR catalyst is making up by carrier and active vanadium oxide catalyst which coated onto 400 cells per square inch cordierite ceramic honeycombs. The SCR catalyst contains no precious metals. Six 5.66 inches diameter and 6 inches long honeycombs were used. The total catalyst volume was 30 $dm^3$ corresponding to a space velocities of 20000~45000 $h^{-1}$.

## 3 Results and Discussion

### *3.1 Results of Simulating Gas Test*

*3.1.1 Influence of Steam*

Fig. 3 shows the influence of water concentration on conversion efficiency with a feed gas composed of 0.05% NO, 0.05% NH3 and 5% $O_2$. It presents that water significantly influences the conversion efficiency of NOx. The conversion decreases with $H_2O$ at low temperature but is enhanced at high temperature. This indicates that the presence of water inhibits the catalyst activity and oxidation of $NH_3$ in the DeNOx process.

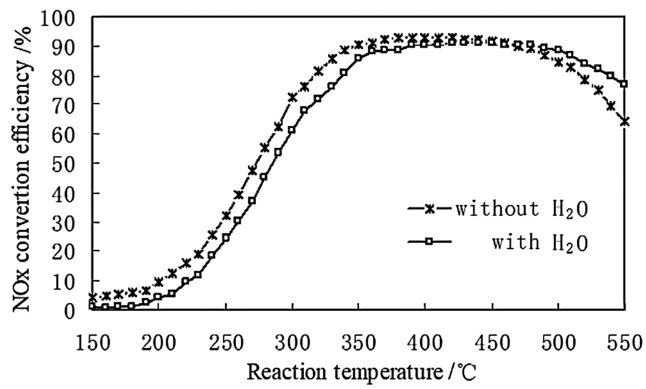



**Figure 3:** NOx conversion efficiency with and without $H_2O$

Fig. 4 shows the influence of water content on the oxidation of $NH_3$ to NOx directly without NO content in the feed gas. It can be noted that the formation of NOx is fecund for a dry feed, this suggest that gas Oxidation of $NH_3$ to NOx is inhibiting significantly in the presence of water, and this results could explain logically why the phenomenon of NOx conversion efficiency enhanced at high temperature in Fig. 3. Fortunately, engine-generated exhaust gas usually contains more than 3% water which inhibits the NOx formation very effectively, so oxidation of $NH_3$ is not serious with this catalyst.

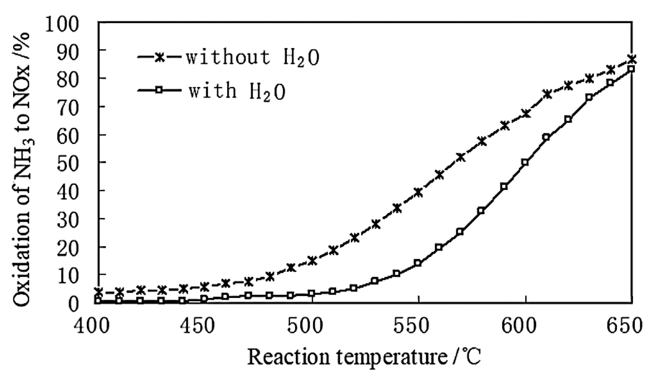



**Figure 4:** Oxidation of $NH_3$ to NOx with and without $H_2O$

*3.1.2 Influence of Sulfide*

Fig. 5 shows the influence of $SO_2$ concentration on NH3 oxidation with a feed gas composed of 0.01% $SO_2$, 0.05% NH3, 5% $O_2$ and no $H_2O$. Performance of the SCR catalyst at low and medium temperature actually increases as a result of the sulfuric treatment, and the maximum conversion efficiency rises from 94% to 98% with $SO_2$. The high temperature performance is similar to that of without $SO_2$.

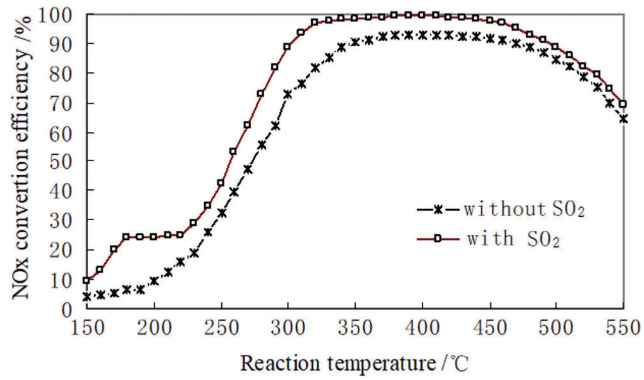



**Figure 5:** NOx conversion efficiency with and without $SO_2$

There are two possible explanations for this phenomenon. Firstly, $SO_2$ would be oxidized to $SO_3$ by $O_2$ in this case, and $SO_3$ will enhance the oxidation of NO to $NO_2$, in which process $SO_2$ acts function as catalyst. It is well known that $NO_2$ is a stronger oxidizing agent than oxygen, meanwhile $NO_2$ and $NH_3$ gives rise to an highly SCR chemistry at low temperature. On the other hand, it could increase the Bronzed acidity on the surface of catalyst due to the build-up of some sulfur species, consequently enhancing the NOx conversion efficiency.

*3.1.3 Influence of Steam and Sulfide*

Fig. 6 shows the influence of both $SO_2$ and $H_2O$ on conversion efficiency of NO with a feed gas composed of 0.05% $NH_3$, 3% $H_2O$, 5% $O_2$ and with 0.01% $SO_2$ or without $SO_2$. The NOx conversion efficiency with $H_2O$ and $SO_2$ is higher than that with $H_2O$ but without $SO_2$ at low temperature. It is similar when the temperature between 240°C and 320°C, and it is enhanced between 320°C and 500°C. Ammonium sulfate would be generated by $SO_3$ and $NH_3$ in the presence of $H_2O$ at low temperature, which was ascertained in the pipe after catalyst and destroy corrosively the polyethylene pipe during test. Ammonium sulfate will decrease the NOx conversion efficiency, on the other hand. Sulfate ammonia would decompose into $SO_3$ and enhances the conversion of NOx at higher temperature.

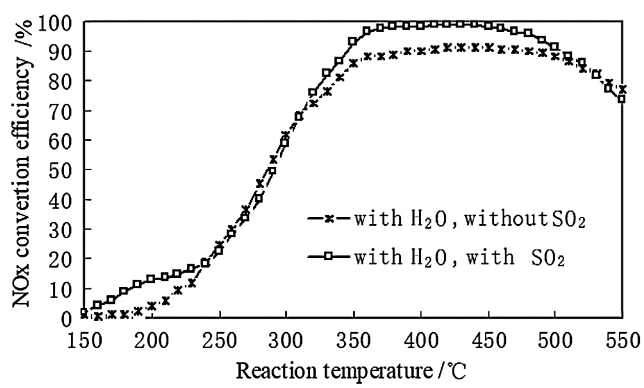



**Figure 6:** NOx conversion efficiency with and without $SO_2$ in the presence of $H_2O$

## ***3.2 Results of Engine Test***

Results of on-line test with the calibrated urea dosage for steady-steady conditions during the ESC were shown as Fig. 7. The urea dosage system injects urea to exhaust proportionally according to the NOx mass emissions dependent on the catalyst inlet temperature and exhaust flux. Figs. 7a and 7b show the consistence

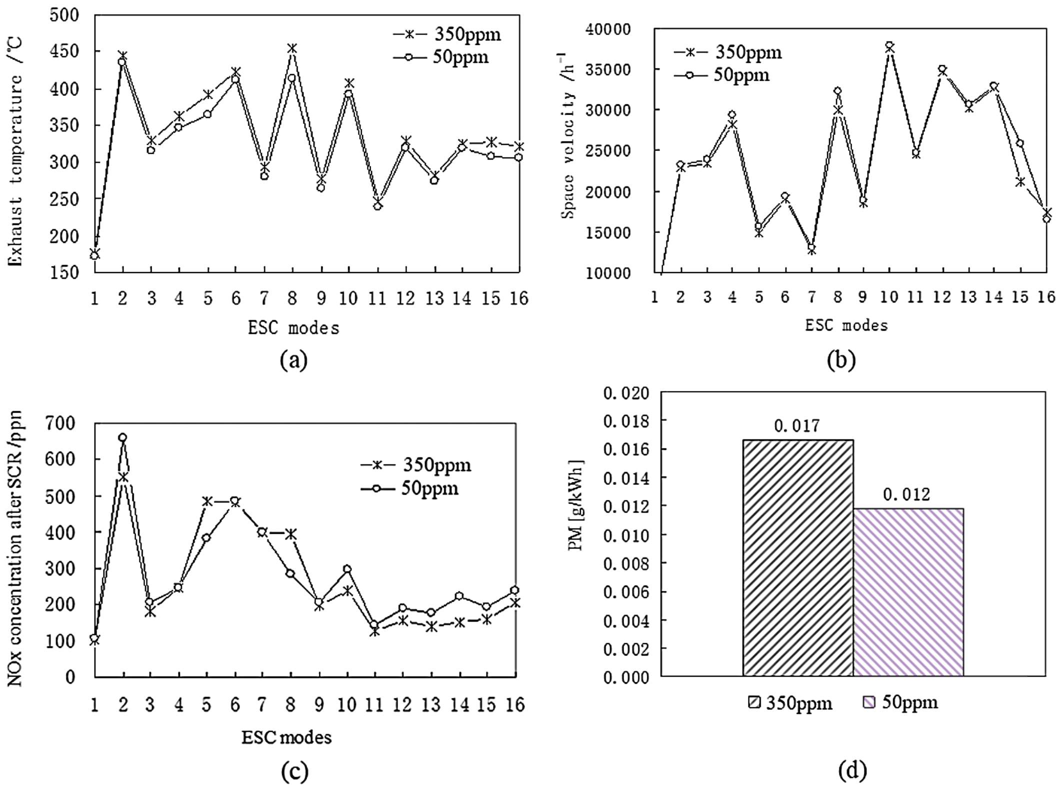



**Figure 7:** Results of the diesel engine test over ESC with two level fuels (a) Exhaust temperature, (b) Space Velocity, (c) NOx concentration after SCR, (d) Particulates

of exhaust temperature and gas flux on the 16 ESC conditions using different sulfur content fuel, the sulfur content of 0.035% and 0.005%. The exhaust temperature and space velocity using fuel with 0.005% is almost same with using fuel 0.035%, so we can consider that the NOx concentration is equivalent before the catalyst. Fig. 7c shows the result of NOx concentration after the catalyst under these conditions, it proves the positive effect to NOx conversion efficiency for the sulfur contents, but $SO_2$ content has negative effect considerably to particulate emissions as shown in Fig. 7d, it should be note that particulate emissions are increased more than 40% using fuel of 0.035% sulfur content fuel than that 0.005% sulfur content fuel. On the other hand, more ammonium sulfate will be generated and cover the catalyst using higher sulfur content fuel in a long term, so lower sulfur content fuel should be used for the engine with SCR system.

## 4 Conclusion

Both steam and sulfide have significantly influence on NOx conversion efficiency under conditions of simulating gas test. The conversion efficiency will decrease in the presence of $H_2O$ content at low temperature but it is enhanced at high temperature. The conversion efficiency will be enhanced in the presence of $SO_2$ content at low and medium temperature. The conversion decreases with both $H_2O$ and $SO_2$ at low temperature but it is enhanced at medium temperature. The engine ESC test proves the influence to the NOx conversion in the presence of both $SO_2$ and $H_2O$ contents by using 0.035% and 0.005% sulfur contents diesel fuels in turns. Higher sulfur content has positive effect, but it leads to increased significantly particulate emissions in the presence of $H_2O$.

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**Conflicts of Interest:** The authors declare that they have no conflicts of interest to report regarding the present study.

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