Effects of H₂O and SO₂ on Selective Catalytic Reduction of NOx by NH₃

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Experiments have been investigated to study the effects of H_2O and SO_2 contents on NO_x reduction efficiency using ammonia (NH_3) as the reducing agent over the nanometer-class V-W/Ti catalyst under variable temperatures on a steady-flow reactor. The results show that the activity of selective catalytic reduction (SCR) is inhibited by H_2O content at low temperature, but higher NO conversion efficiency should be achieved at high temperature due to the reaction of NH_3 oxidized by O_2 to NO_x would be inhibited by H_2O content. The selective catalytic reduction activity will be promoted by SO_2 content in the range of 150-500 ºC, NO conversion efficiency can be improved to 98 % from 94 % by adding SO_2 content. The activity of selective catalytic reduction will be promoted at 150-240 ºC and 350-500 ºC when H_2O and SO_2 exist at the same time, but ammonium sulfates and other sulfates will be generated at low temperature. Additionally, following the ESC test, the positive influence to the NO_x conversion has been proved in the presence of H_2O and SO_2, but it has considerably negative effect to PM emission for the diesel engine.

Key Words: V_2O_5-WO_3/TiO_2 catalyst, Selective catalytic reduction, NH_3, H_2O, SO_2.

INTRODUCTION

The diesel engine is ideally suited as a mobile power source for its high efficiency and compacting design. Government agencies charged with cleaning and protecting the environment have identified emissions from diesel engines as an opportunity to reduce hydrocarbon, CO, NO_x and particulate emissions to the environment. Laws are in place or are proposed that progressively tighten emissions from diesel engines. Table-1 summarizes emission levels of the regulations of European union. Two test cycles are used to determine engine emissions, the European stationary cycle (ESC) and the European transient cycle (ETC). The European stationary cycle is a 16-mode test and the European transient cycle 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 Euro IV and Euro V regulations for heavy-duty diesel engines, both the NO_x and particulate emissions must be greatly reduced for today's state of the heavy-duty diesel engines. Euro V regulations, namely 2.0 g/kW h NO_x and 0.02 g/kW h particulate, cannot be achieved solely by engine management or improved engines, rather some sort of after treatment must be used. One solution is to use a particulate trap (DPF) to reduce soot emissions together with some sort of NO_x reducing after treatment preferably Urea-SCR. Comparing with DPF, the Urea-SCR systems have

TABLE-1
EMISSION STANDARDS OF EUROPEAN STATIONARY CYCLE AND EUROPEAN TRANSIENT CYCLE FOR HEAVY DUTY DIESEL ENGINES

Class		CO [g/(kW h)]	Hydro carbon [g/(kW h)]	NO_x [g/(kW h)]	Particulate matter [g/(kW h)]
III	ESC	2.1	0.66	5.0	0.10
	ETC	5.45	0.78	5.0	0.16
IV	ESC	1.5	0.46	3.5	0.02
	ETC	4.0	0.55	3.5	0.03
V	ESC	1.5	0.46	2.0	0.02
	ETC	4.0	0.55	2.0	0.03

been shown to be both very efficient and durable in vehicle applications[4-7], so the heavy-duty diesel engines manufacturers prefer Urea-SCR for reducing NO_x.

In the treatment of sulfur-containing exhaust gases, SO_2 is also fed to the SCR reactor; here it is partly oxidized to SO_3, which can react with water and unconverted ammonia to form sulfuric acid and ammonium sulfates. Accordingly, SO_2 oxidation represents a highly undesirable side reaction of the SCR process; 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[8-10].

The influence of H_2O and SO_2 in the feed gas flow to the NO conversion was studied 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.

EXPERIMENTAL

Selective catalytic reduction reaction: Urea will decomposes to ammonia and HNCO initially when exposed to hot exhaust gas. The HNCO reacts further with water (it is present in the exhaust gas as one of combustion products) to form ammonia (NH_3) and CO_2. The hydrolysis of HNCO could be presence homogeneously in the gas phase or catalyzed by a surface. In some cases, a dedicated hydrolysis catalyst is added to the system to promote the conversion of HNCO to NH_3 and CO_2. The basic chemical reactions of the urea-selective catalytic reduction process are as follows:

Urea decomposition:

$$\text{urea} \xrightarrow[\text{heat}]{\text{heat}} \begin{cases} \text{HNCO} + \text{NH}_3 \\ \xrightarrow[H_2O]{} \text{CO}_2 + \text{NH}_3 \end{cases} \tag{1}$$

NO_x reduction:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{2}$$
$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \tag{3}$$
$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \tag{4}$$
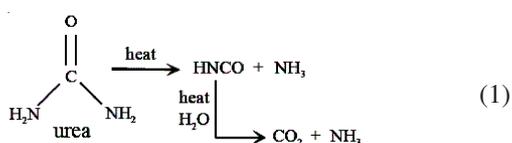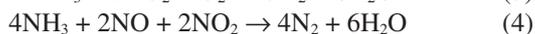
In addition, undesired reactions include formation of N_2O instead of N_2 and oxidation of NH_3. Also the exhaust include sulfur that is present in the diesel fuel and engine oil[11-14] and has negative effect to NO conversion efficiency and stability of the catalyst. So restrain oxidation of NH_3 and formulations of sulfur should be used to minimize their impacts and enhance the NO conversion efficiency.

$$4NH_3 + 5O_2 \rightarrow 4N_2O + 6H_2O \tag{5}$$
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{6}$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{7}$$
$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{8}$$
$$SO_3 + H_2O + NH_3 \rightarrow NH_4HSO_4 \tag{9}$$
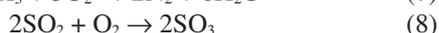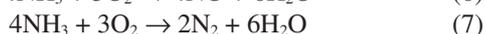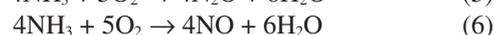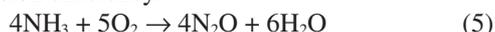
Test equipment and methodology: In order to investigate basic characteristics of the urea-SCR catalyst, NO_x reduction characteristics were measured using simulating gas test equipment. Fig. 1 shows the configuration of the simulating setup. The feed gas was consisted by NO (0-0.05 %), NH_3 (0.03-0.05 %), SO_2 (0-0.01 %), O_2 (5 %), vapourized water (0-3 %) and N_2 (balance). It corresponded to a typical exhaust gas but make up by standard gases. The catalyst temperature was controlled with the furnace which controlled by computer and capable of reaching temperatures up to *ca.* 750 ℃. 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 NH_3, which becomes the reducing agent and removes NO_x, while in the simulating gas tests this was simplified by directly using NH_3. The gas analysis was performed with a Five-Way-Gas Analyzer (AVL DiGas 4000 light).

One-inch samples (12.5 mm sides by 55 mm length) were used for the majority of the tests. The space velocity of 32000 h^{-1} was comparable to a mean value of the typical exhaust
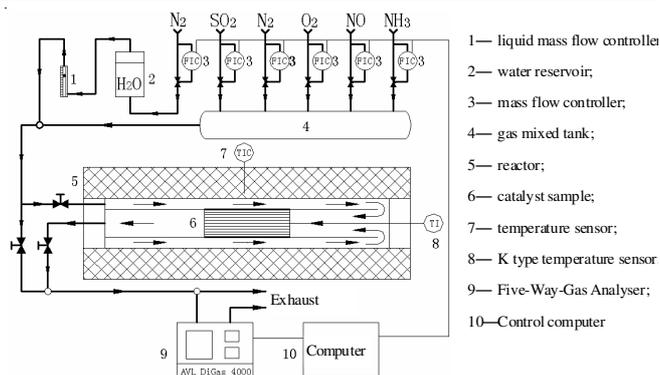
Fig. 1. Setup of simulating gas test

flow rates in vehicle. The examined samples were cut from the inner region of 5.66 inches diameter by 6 inches long catalyst to prevent variations of the wash-coat load. A 400/6 [cpsi/mil] substrate coated with a vanadium based wash-coat was used for all tests. 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. Table-2 shows specifications of the test engine and the urea-SCR system. The engine is based for one 12-liter class heavy duty diesel engine and for development installed the intercooler and VGT. 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-2 ENGINE CHARACTERISTICS	
Engine type	6 cyl. in line turbocharged inter cooled
Displacement	11.6 L
Injection system	Common rail
Calibration	Euro 3
Max. power	353 kW @ 2100 rpm
Max. torque	1970 Nm @ 1600 rpm

The urea dosage system was supplied by Bosch, it 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}.

RESULTS AND DISCUSSION

Results of simulating gas test

Influence of H_2O: Fig. 2 shows the influence of water concentration on conversion efficiency with a feed gas

composed of 0.05 % NO, 0.05 % NH₃ and 5 % O₂. It presents that water significantly influences the conversion efficiency of NO_x. The conversion decreases with H₂O at low temperature but is enhanced at high temperature. This indicates that the presence of water inhibits the catalyst activity and oxidation of NH₃ in the DeNO_x process.
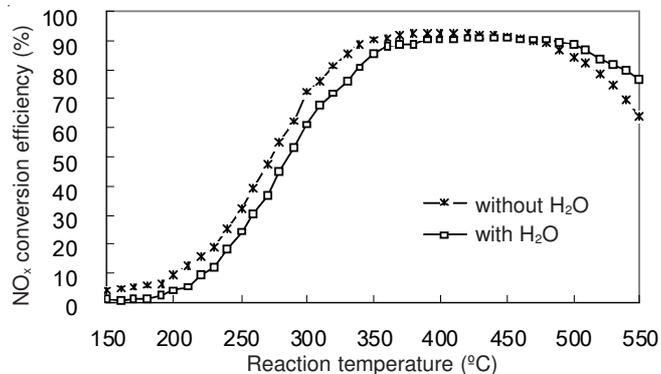
Fig. 2. NO_x conversion efficiency with and without H₂O

Fig. 3 shows the influence of water content on the oxidation of NH₃ to NO_x directly without NO content in the feed gas. It can be noted that the formation of NO_x is fecund for a dry feed, this suggest that gas oxidation of NH₃ to NO_x is inhibiting significantly in the presence of water and this results could explain logically about the phenomenon of NO_x conversion efficiency enhanced at high temperature in Fig. 2. Fortunately engine-generated exhaust gas usually contains more than 3 % water which inhibits the NO_x formation effectively, so oxidation of NH₃ is not serious with this catalyst.
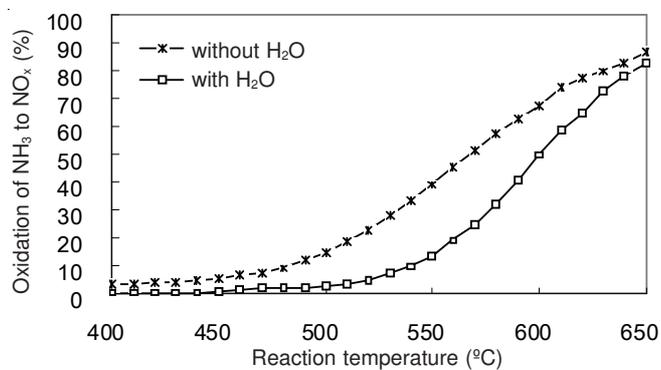
Fig. 3. Oxidation of NH₃ to NO_x with and without H₂O

Influence of SO₂: Fig. 4 shows the influence of SO₂ concentration on NH₃ oxidation with a feed gas composed of 0.01 % SO₂, 0.05 % NH₃, 5 % O₂ and no H₂O. The low and medium temperature performance of the SCR catalyst actually increases as a result of the sulfuric treatment and the maximum conversion efficiency rises from 94 to 98 % with SO₂. The high temperature performance is similar to that of without SO₂.

There are two possible explanations for this phenomenon. Firstly, SO₂ would be oxidized to SO₃ by O₂ in this case and SO₃ will enhance the oxidation of NO to NO₂, in which process SO₂ acts as catalyst. It is well known that NO₂ is a stronger oxidizing agent than oxygen, meanwhile NO₂ and NH₃ gives rise to an highly SCR chemistry at low temperature. On the other hand, it could increase the Bronsted acidity on the surface
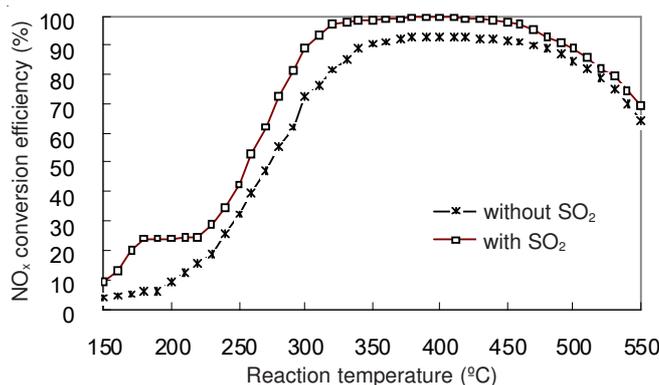
Fig. 4. NO_x conversion efficiency with and without SO₂

of catalyst due to the build-up of some sulfur species, consequently enhancing the NO_x conversion efficiency.

Influence of SO₂ and H₂O: Fig. 5 shows the influence of both SO₂ and H₂O contents on conversion efficiency of NO with a feed gas composed of 0.05 % NH₃, 3 % H₂O, 5 % O₂ and with 0.01 % SO₂ or without SO₂. The NO_x conversion efficiency with H₂O and SO₂ is higher than that with H₂O but without SO₂ at low temperature. It is similar when the temperature between 240 ºC and 320 ºC and it is enhanced between 320 ºC and 500 ºC. Ammonium sulfate would be generated by SO₃ and NH₃ in the presence of H₂O at low temperature, which was ascertained in the pipe after catalyst and destroy corrosively the polyethylene pipe during test. Ammonium sulfate will decrease the NO_x conversion efficiency, on the other hand. Ammonium sulfate would decompose into SO₃ and enhances the conversion of NO_x at higher temperature.
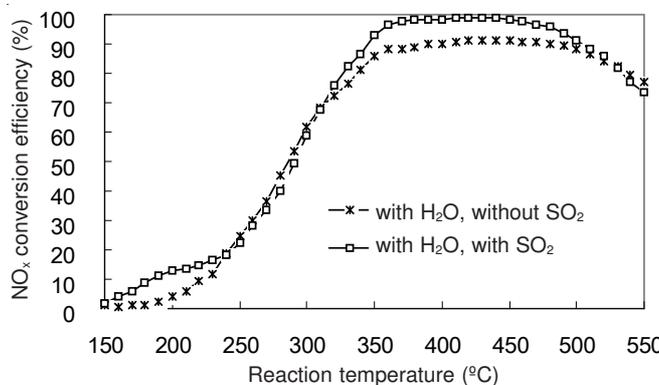
Fig. 5. NO_x conversion efficiency with and without SO₂ in the presence of H₂O

Result of engine testing: On-line test results with the calibrated urea dosage for steady-steady conditions during the European stationary cycle were shown as Fig. 6. The urea dosage system injects urea to exhaust proportionally according to the NO_x mass emissions dependent on the catalyst inlet temperature and exhaust flux. Fig. 6a and b show the consistence of exhaust temperature and gas flux on the 16 European stationary cycle conditions using different sulfur content fuel, the sulfur content of Euro III is 0.035 % and the sulfur content of Euro IV is 0.005 %. The exhaust temperature and space velocity using Euro IV fuel is almost same with using Euro III fuel, so we can consider that the NO_x concentration is equivalent before the catalyst. Fig. 6c shows the result of NO_x concentration after the catalyst under these conditions, it proves the positive

(a) Exhaust temperature

(b) Space velocity

(c) NOx concentration after SCR
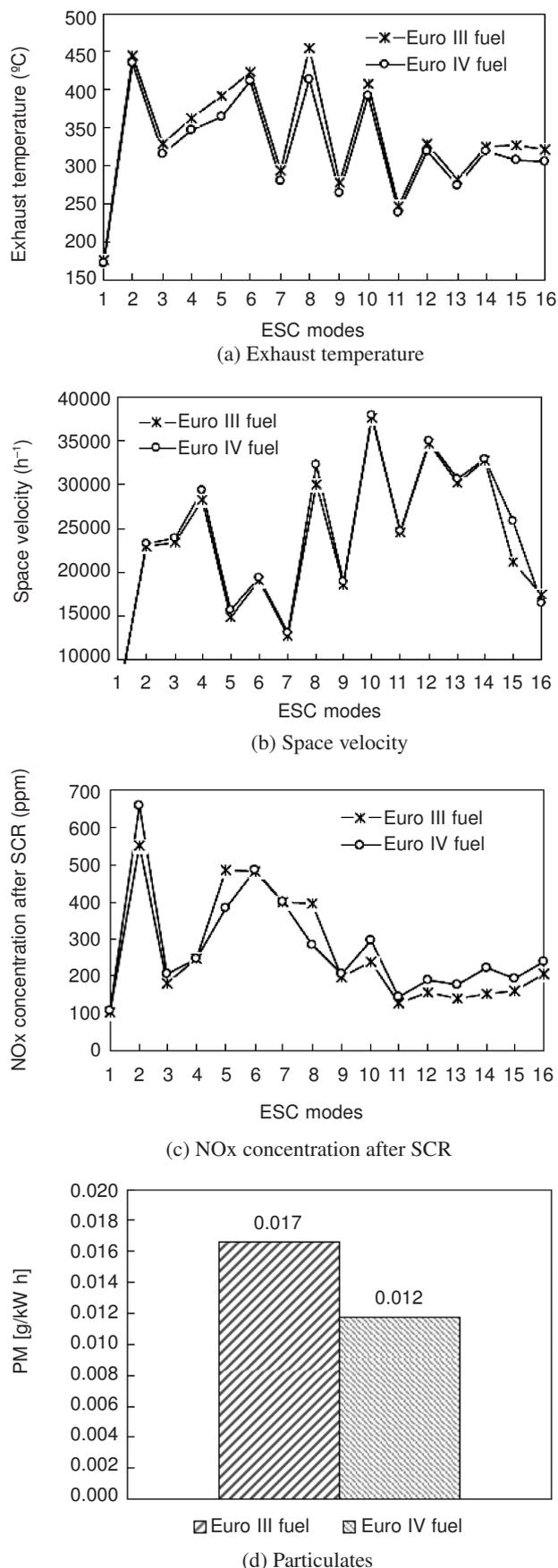
(d) Particulates

Fig. 6. Results of the diesel engine test over ESC with two level fuels

effect to NO_x conversion efficiency for the sulfur contents. But SO_2 content has negative effect considerably to particulate emissions as shown in Fig. 6d, it should be note that particulate emissions is 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.

Conclusion

Both SO_2 and H_2O have significantly influence to NO_x conversion efficiency under conditions of simulating gas test. The conversion efficiency will decreases in the presence of H_2O content at low temperature but it enhanced at high temperature. The conversion efficiency will be enhanced in 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 European stationary cycle test proves the influence to the NO_x 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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