Low-Temperature Performances for Monolithic V_2O_5 - WO_3 /TiO₂ Catalyst in the NH₃-SCR System

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(Received: 31 December 2012;

Accepted: 1 August 2013)

AJC-13876

According to the working characteristics of marine diesel engines, a SCR catalyst testing system was developed and catalytic activities of an extruded commercial monolithic V_2O_5 - WO_3 /TiO₂ catalyst at low temperatures were studied in this paper. Meanwhile, key parameters including catalytic temperature, space velocity, NH₃ consumption, excess O₂ and NO₂ concentration in the gas mixtures were also analyzed to enhance the low-temperature performances of marine SCR systems. It is found that desorption reaction of NH₃ absorbed on the catalyst surface may be responsible for a sharply increasing of NH₃ slip in a short time, which could also lead to the secondary pollution of NH₃ from the SCR system.

Key Words: NH₃-SCR, V_2O_5 - WO_3 /TiO₂, Experimental study, Catalyst activity, Low-temperature.

INTRODUCTION

Aiming to improve air quality and life conditions, limitations of NO_x emission from marine and automotive diesel engines are increasingly stringent¹. As one of the most effective means of reducing NO_x emission, SCR technology is being employed widely on the marine and automotive diesels. However, NO_x removal efficiencies (DeNO_x) in practical applications are limited by the low temperatures and complex components of diesel exhaust gases². Therefore, low-temperature performances of catalysts are becoming the major concerns for the applications and developments of SCR system.

V_2O_5 supported on TiO₂ (V_2O_5 /TiO₂), which is a commercial catalyst, exhibits excellent catalytic characterizations in the applications, but the activity at low temperature is poor in the SCR system. Peña *et al.*³ found that great numbers of Bronsted acidity exist on the V_2O_5 /TiO₂ catalyst surface at low temperatures and the surface area of SCR reactions is decreased, by which the activation of catalyst at low temperatures is inhibited, reducing the catalytic activity. Chae *et al.*⁴ studied the catalytic characterizations of V_2O_5 /Ti-PILC, V_2O_5 /TiO₂ and V_2O_5 /Al₂O₃. Catalytic activity is proved to be strongly dependent on the structure of vanadium on the catalyst surface and more activity sites present on the polymeric vanadium. Gao *et al.*⁵ found that NO₂ in the flow enhances the SCR activity at low temperatures and the optimum ratio of NO₂/NO_x for the SCR reaction is 0.5 over V_2O_5 - WO_3 -MnO₂/TiO₂ catalyst. In order to improve the catalytic activity at low temperatures, Qian *et al.*⁶, Yan *et al.*⁷, Jin-Hua *et al.*⁸, Choo *et al.*⁹, Casagrande

*et al.*¹⁰ separately introduced carbon nanotubes, CeO₂, La³⁺, Y³⁺, BaO and MoO₃ to the V_2O_5 /TiO₂ catalyst and tested their catalytic performances.

According to the working characteristics of marine diesel engines, a SCR catalyst testing system was built in this paper. And catalytic activities of a commercial V_2O_5 - WO_3 /TiO₂ catalyst at low temperatures, which is an extruded monolithic catalyst, were tested to improve the working performances of SCR system in the marine diesels. Before the studies, the monolithic catalysts were characterized by Brunauer-Emmett-Teller (BET) surface area analysis.

EXPERIMENTAL

Selective catalytic reduction (SCR) reaction: Selective catalytic reduction (SCR) reaction, which is a gas-solid heterogeneous catalytic reaction shown in Fig. 1, can reduce NO_x to N₂ and H₂O in the presence of O₂, reducing agent and catalyst at low temperatures^{1,2}. As an after-treatment technology of NO_x removal from exhaust gas, SCR systems have been built worldwide applications on the waste incinerator plant, power plant, gas turbine, automobile, ship *etc.* In practical applications, liquid ammonia, ammonia water and urea solution are often used as the reducing agents for SCR system, while hydrocarbons, ethanol, methyl ether *etc.* are also tested nowadays¹¹. In consideration of security and accessibility, urea solution is the most common reducing agent and urea can be decomposed to NH₃ and H₂O at low temperatures. Consequently, NH₃ adsorbed on the catalyst surface would take part in the reactions of SCR system, also called NH₃-SCR reaction and the reactions are as followings¹²:

Fig. 1. SCR reaction on the catalyst surface

Standard SCR reaction:

Fast SCR reaction:

Slow SCR reaction:

Selective catalytic oxidation (SCO) reaction of NH_3 :

In the SCR processes, many side reactions would be carried out, lowering the NO_x removal efficiencies. Therefore, selectivity of SCR reaction to N_2 is another limitation of the developments and applications of SCR system.

HEU-SCR system: SCR catalyst testing system called HEU-SCR system is shown in the Fig. 2. With HEU-SCR system, six gases including NO , NO_2 , NH_3 , SO_2 , O_2 and N_2 can be mixed together and heated up to 800°C . In order to simulate exactly actual conditions of marine SCR system, H_2O evaporating and urea solution introducing system were developed to get water vapor and urea solution. The components of NO , NO_2 , NO_x , NH_3 , O_2 , SO_2 and *etc.*, in the gas mixtures can be measured by the exhaust gas analysis system, which is made up of an infrared gas analyzer typed HARIBO EXSA-240CL and an electrochemical gas analyzer typed RBR ECOM-J2KN. With the two sets gas analyzers combined, measuring data can be reciprocally validated and measuring accuracy can be greatly improved.

Fig. 2. HEU-SCR testing system. 1-Mass flow-meter, 2-Bypass valve, 3-Dosing pump, 4-Water Evaporator, 5-Check valve, 6-Gas buffering and preheating tank, 7-Gas mixing tank, 8-Differential pressure flow-meter, 9-Steel mesh, 10-Catalyst, 11-Thermocouple, 12-Three-way valve

Testing sample: High-pressure gases, involving N_2 , O_2 , CO_2 , NO/N_2 , NO_2/N_2 , NH_3/N_2 and SO_2/N_2 , are used as gas sources and their flows are exactly controlled to form required reaction gases by the mass flow-meters. In this paper, an extruded commercial monolithic $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst, shown as in the Table-1, was tested at low temperatures. In order to get the reliable data, the catalyst samples were characterized by BET surface area analysis before the tests.

TABLE-1
MAIN PARAMETERS OF THE TESTING SAMPLE
OF $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ CATALYST

Type	Value
L × W × H	12 mm × 12 mm × 75 mm
Channel	9
Cell density	45cpsi
BET surface area	98.45 m ² /g
Total pore volume	1.89 × 10 ⁻¹ cm ³ /g
Average pore width	7.68 nm

RESULTS AND DISCUSSION

Influences of catalytic temperature and space velocity on the catalytic activity: Developments and applications of SCR system are limited by the low-temperature performances of catalysts, while exhaust gases discharged from marine diesel are at low temperatures, leading to reduce the NO_x removal efficiencies. In this paper, catalytic activities of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst were studied at low temperatures of $100\text{-}250^\circ\text{C}$. According to the combustion characteristics of marine diesel engines, most of NO_x in the exhaust gases are NO and NO_2 , of which NO is over 90 %¹. Therefore, the testing gas mixture contains 1150 ppm NO , 200 ppm NO_2 , 1400 ppm NH_3 and 7 % O_2 and N_2 is used as balance gas. The influences of catalytic temperature and space velocity on NO_x concentration in the flows are shown in the Fig. 3.

Fig. 3. Influences of catalytic temperature and space velocity on NO_x concentration in the exhaust gas; Reaction conditions: 1150ppm NO , 200 ppm NO_2 , 1400 ppm NH_3 , 7 % O_2 , balance gas N_2 , total flow rate 1000 mL/min

Fig. 3 shows that NO_x removal efficiency is decreased with increasing space velocity, leading to the decrease of catalytic reaction rate and the increase of NO_x concentration in the gas flow. The reactant diffusion rate containing reactant diffusion in the gas flow, between gas flow and microspores on the catalyst surface depends strongly on the space velocity

related to reaction time. It demonstrates that catalytic reaction rate is slightly affected by space velocity at low temperatures of $T < 150^\circ C$. Under the conditions, diffusion rate of reactant, involving NO , NO_2 , NH_3 , O_2 etc., is much larger than catalytic reaction rate and total SCR reaction rate is controlled by the intrinsic chemical reaction kinetics. While catalytic reaction rate is enhanced sharply with increasing the gas temperature at $T > 200^\circ C$ and exceeds gradually the diffusion rate, total reaction rate is limited by the reactant diffusion rate at the conditions. Consequently, NO_x removal efficiency is decreased and NO_x concentration is increased, with an increasing space velocity at $T > 200^\circ C$.

Influences of NH_3 on the catalytic activity: In practical applications, multiplex optimizations for SCR system are often carried out to maximize NO_x removal efficiency and minimize NH_3 slip. The influences of NH_3 consumption on the NO_x removal efficiency and NH_3 slip were analyzed on the monolithic V_2O_5 - WO_3 /TiO₂ catalyst at $250^\circ C$, which is shown in the Fig. 4.

Fig. 4. Influences of NH_3 consumption on the NO_x removal efficiency and NH_3 slip at $250^\circ C$; Reaction conditions: 1150 ppm NO , 200 ppm NO_2 , 7 % O_2 , balance gas N_2 , space velocity $6000\ h^{-1}$, total flow rate $1000\ mL/min$

It can be found that NO_x concentration in the flow is reduced rapidly with increasing NH_3 concentration up to 1350 ppm, while the increase rate is becoming reduced over 1350 ppm NH_3 and disappeared over 2000 ppm NH_3 . In the whole process, NH_3 slip continues to be increased and the increase rate is also enhanced sharply. Since total reaction rate is dependent on the standard and fast SCR reaction, consumption rate of NH_3 and NO_x would be close to be equimolar in the SCR processes. It is also proved that the total reaction rate is limited by the poor NH_3 concentration up to 1350 ppm and the NH_3 slip is increased slowly. When NH_3 concentration is over 1350 ppm and NH_3 in the flow is excess, NO_x concentration is becoming the controlling factor of SCR reaction. As acceptable excess NH_3 is found to promote SCR reaction, NO_x removal efficiency is slightly enhanced, but NH_3 slip is sharply increased to form the secondary pollution.

Influences of excess O_2 on the catalytic activity: According to the combustion characteristics of marine diesel engines, excess O_2 exists in the exhaust gas and takes part in reactions in the SCR system. Therefore, the influences effects

of excess O_2 on the NO_x removal efficiency and NH_3 slip were discussed on the monolithic V_2O_5 - WO_3 /TiO₂ catalyst at $250^\circ C$ (Fig. 5).

Fig. 5. Influences of excess O_2 on the NO_x removal efficiency and NH_3 slip at $250^\circ C$; reaction conditions: 1150 ppm NO , 200 ppm NO_2 , 1400 ppm NH_3 , balance gas N_2 , space velocity $6000\ h^{-1}$, total flow rate $1000\ mL/min$

It can be seen that NO_x concentration and NH_3 slip in the flow are both decreased gradually with increasing O_2 concentration up to 15 %, while NO_x removal efficiency is becoming constant over 15 % O_2 and NH_3 slip is disappeared from the flow. In the whole process, NO_x concentration and NH_3 slip in the flow are shown a similar reducing trend, while reducing rate of NH_3 slip nearly equals twice over NO_x concentration. Although acceptable excess O_2 is helpful to promote SCR reaction, NH_3 SCO reaction is also enhanced, leading to the increase of NH_3 consumption.

Influences of NO_2 on the catalytic activity: At low temperatures, fast SCR reaction rate is much larger than standard SCR reaction rate, which is widely used to optimize the low-temperature performances of SCR system. Therefore, the influences of NO_2 on the NO_x removal efficiency were tested on the monolithic V_2O_5 - WO_3 /TiO₂ catalyst at $250^\circ C$, which is shown in the Fig. 6.

Fig. 6. Influences of NO_2 on the NO_x removal efficiency at $250^\circ C$; reaction conditions: 1350 ppm NO_x , 1400 ppm NH_3 , 7 % O_2 , balance gas N_2 , space velocity $6000\ h^{-1}$, total flow rate $1000\ mL/min$

It is found that NO_x removal efficiency is enhanced with increasing NO_2/NO ratio up to 1 and an optimum efficiency-85 % is achieved at $\text{NO}_2/\text{NO} = 1$. As the increase of NO_2 concentration in the flow, total SCR reaction is becoming controlled by fast SCR reaction, which leads to an increasing total reaction rate. However, total SCR reaction is gradually dependent on slow SCR reaction with $\text{NO}_2/\text{NO} > 1$, decreasing sharply total reaction rate. Therefore, acceptable NO_2 is helpful to promote SCR reaction and optimum NO_2/NO ratio is 1.

Fig. 7. NO_x removal efficiency and NH_3 slip at 250 °C in the SCR process; reaction conditions: 1150 ppm NO , 200 ppm NO_2 , 1400 ppm NH_3 , 7 % O_2 , balance gas N_2 , space velocity 6000 h^{-1} , total flow rate 1000 mL/min

SCR reaction process analysis: In order to analyze the SCR process, SCR process shown in the Fig. 7 mainly contains three parts: NH_3 preparing process at $t < 10$ min, NH_3 supplying and reacting process at $10 \text{ min} \leq t \leq 57 \text{ min}$ and NH_3 disappearing process at $t > 57$ min. After NH_3 being introduced into the SCR reactor, SCR reaction is activated, resulting a decreasing NO_x concentration. Consequently, SCR reaction is in a quasi-equilibrium state and NH_3 slip is reached up to 100 ppm. Since SCR reaction is proved to react between gaseous NO_x and adsorbed NH_3 on the catalyst surface^{13,14}, great numbers of NH_3 would be adsorbed on the active sites of catalyst. While NH_3 is stopped introducing into the system, adsorbed NH_3 would be desorbed from the catalyst surface, NH_3 slip is sharply increased and NO_x removal efficiency is also enhanced at $58 \text{ min} \leq t \leq 1 \text{ h}$. However, NH_3 desorption is limited by the number of activity sites on the catalyst surface, both NH_3 slip and NO_x removal efficiency are becoming disappeared at $t > 1 \text{ h}$.

Obviously, reducing rate of NO_2 is found to be more than that of NO in the start-up process of SCR reaction ($10 \text{ min} \leq t \leq 15 \text{ min}$) at 250 °C (Fig. 8), while enhancing rate of NO_2 is found to be less than that of NO in the shut-up process of SCR reaction ($58 \text{ min} \leq t \leq 63 \text{ min}$). Meanwhile, NO_2 in the flow is nearly disappeared in stable reacting process ($25 \text{ min} \leq t \leq 58 \text{ min}$). It is indicated that standard SCR reaction would be promoted with an increasing temperature, but its rate is still lower than that of fast SCR reaction at 250 °C. Consequently, total SCR reaction rate can be enhanced by an increasing NO_2/NO ratio up to 1 at low temperatures over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst.

Conclusion

According to the working characteristics of marine diesel engines, catalytic activities of a commercial monolithic $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst at low temperatures were tested by the

Fig. 8. NO and NO_2 concentration at 250 °C in the SCR process; reaction conditions: 1150 ppm NO , 200 ppm NO_2 , 1400 ppm NH_3 , 7 % O_2 , balance gas N_2 , space velocity 6000 h^{-1} , total flow rate 1000 mL/min

HEU-SCR system and influences of key parameters on the low-temperature performances were also analyzed. Total SCR reaction is limited by the intrinsic chemical reaction kinetics at lower temperatures ($T < 150$ °C), while it is controlled by the reactant diffusion rate at higher temperatures ($T > 200$ °C). NO_x removal efficiency can be enhanced with an increasing NH_3 consumption, but NH_3 slip can also be increased. Since they are in a trade-offs raise, SCR applications can be developed by their optimization together. NO_x removal efficiency can be promoted by enhancing NO_2/NO ratio up to 1 at low temperatures, while it mainly depends on reaction time or called space velocity, at high temperatures. Acceptable excess O_2 is helpful to promote SCR reaction, but NH_3 SCO reaction can be also enhanced, leading to an increasing NH_3 consumption. After stopping introducing NH_3 into the SCR system, desorption reaction of NH_3 adsorbed on the activity sites of catalyst surface would be carried out, NO_x removal efficiency can be promoted in the flow. However, NH_3 secondary pollution would also be found in a short time.

ACKNOWLEDGEMENTS

The authors acknowledged the financial support of the National Natural Science Foundation of China (No. 51079035).

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