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Article

Selective catalytic reduction of NO_x by NH_3 for heavy-duty diesel vehicles

Fudong Liu [a], Wenpo Shan [a], Dawei Pan [b], Tengying Li [b], Hong He [a,]*

[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] China National Heavy Duty Truck Group Jinan Rubber and Plastic Co., Ltd., Jinan 250031, Shandong, China

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ABSTRACT

A catalyst production line with a production capacity of 6000 catalyst monoliths per month for the selective catalytic reduction of NO_x by NH_3 (NH_3-SCR) for NO_x abatement in diesel vehicle exhaust was set up based on a detailed laboratory study of the catalyst formulation and washcoating technology for V_2O_5-WO_3/TiO_2 catalyst. The catalyst produced by this line was tested on a bench scale diesel engine. The V_2O_5-WO_3/TiO_2 powder catalyst prepared in the laboratory and production line both achieved >80% NO_x conversion at 200–450 °C and a GHSV of 50000 h^{-1}. The washcoated catalyst used a large cordierite support and gave >80% NO_x conversion at 250–450 °C and GHSVs of 10000–30000 h^{-1}. The engine bench tests showed that after treatment by the catalyst, the NO_x emission met the European steady-state cycle (ESC) and European transient cycle (ETC) limits of the China IV standard. The production line can also be used for the production of vanadium-free NH_3-SCR catalysts to meet the required replacement of the present vanadium-based NH_3-SCR catalyst in the future.

1. Introduction

Diesel engines are competitive because of their high fuel efficiency and power output. However, the removal of NO_x from diesel engine exhaust is a major challenge in environmental catalysis and air pollution control [1,2]. According to the China vehicle emission control annual report (2012) [3], diesel vehicles, which are only 17% of total vehicles, contribute 67.4% of the total NO_x emission from vehicles. Heavy-duty trucks, which are only 5% of total vehicles, are the main contributor to the NO_x emission (48.6%).

The selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is one of the most promising technologies for NO_x abatement in diesel exhaust [4]. To meet more stringent NO_x emission control regulations, many automobile and engine manufacturers in developed countries have developed the industrial application of NH_3-SCR technology and used it in commercial vehicles. The NH_3-SCR technology will also be used by some Chinese companies, e.g., China National Heavy Duty Truck Group (SINOTRUK), Weichai Power Co., Ltd. (WEICHAI), and Shanghai Diesel Engine Co., Ltd., to meet the China IV (Euro IV) standard. The key issue in this technology is the development and industrial production of the NH_3-SCR catalyst.

Vanadium-based NH_3-SCR catalysts, especially WO_3 or MoO_3 promoted V_2O_5/TiO_2, have been widely used for the removal of NO_x from stationary sources since the 1970s. These catalysts have also been introduced for use in diesel vehicles [4–6]. However, the toxicity of vanadium species together with the

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* Corresponding author. Tel/Fax: +86-10-62849123; E-mail: honghe@rcees.ac.cn

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narrow operation temperature window has limited the practical application of vanadium-based catalysts. Accordingly, some transition metal exchanged zeolites, e.g., Fe-ZSM-5 [7–9], Cu-SSZ-13 [10–13], and Cu-SAPO-34 [14–16], and vanadium-free oxide catalysts, e.g., Ce-based [17–24], Fe-based [25–27], and Cu-based [28] oxides, have been studied as potential substitutes of vanadium-based catalysts for diesel vehicles. However, the quality of the diesel fuel in China is still relatively low, and the sulfur content in the diesel fuel is often rather high. Therefore, the vanadium-based catalyst with its excellent sulfur poisoning resistance is still the preferred choice for NO_x abatement from diesel vehicles in China at present.

2. Experimental

2.1. *Catalyst preparation*

The V_2O_5-WO_3/TiO_2 catalyst with 4.5 wt% V_2O_5 and 10 wt% WO_3 was prepared by the conventional impregnation method using NH_4VO_3, $(NH_4)_{10}W_{12}O_{41}\cdot xH_2O$, and $H_2C_2O_4\cdot 2H_2O$ as precursors and anatase TiO_2 as the support. In a typical procedure, 12.48 g $C_2H_2O_4\cdot 2H_2O$, 5.79 g NH_4VO_3, and 10.94 g $H_{40}N_{10}O_{41}W_{12}\cdot xH_2O$ were dissolved in 300 mL distilled water. Anatase TiO_2 powder (100 g) was then added into the solution. After continuous stirring for 1 h, excess water was removed in a rotary evaporator. The sample was dried at 100 °C overnight and then calcined at 550 °C for 3 h. A catalyst slurry was prepared by mixing the catalyst powder and an adhesive agent in distilled water. A cylindrical cordierite honeycomb (300 mesh) was washcoated with the catalyst slurry. After drying at 100 °C and subsequent calcination at 550 °C for 3 h, the washcoated honeycomb catalyst was obtained. The powder catalyst manufacturing section of the production line in SINOTRUK was built by simulating the laboratory preparation. The washcoated honeycomb catalyst was produced by an automatic washcoating device using a large cordierite honeycomb (ϕ 285.75 mm × 152.4 mm).

2.2. *Activity measurement and engine bench tests*

SCR activity measurements were carried out in the laboratory in a fixed-bed quartz tube flow reactor at atmospheric pressure. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH_3, 5 vol% O_2, balance N_2, and 500 mL/min total flow rate. During the test, 0.6 mL powder catalyst or 1–3 mL washcoated honeycomb catalyst were used, which gave GHSV of 50000 or 10000–30000 h^{-1}, respectively. The effluent gas containing NO, NH_3, NO_2, and N_2O was continuously analyzed by an online Nicolet Nexus 670-FTIR spectrometer equipped with a 0.2 L gas cell. The NO_x conversion was calculated as $(1 - ([NO]+[NO_2])_{out}/([NO]+[NO_2])_{in}) \times 100\%$.

Engine bench tests for the European steady-state cycle (ESC) and European transient cycle (ETC) were carried out using a SINOTRUK diesel engine (D10.34, Displacement 9.726 L, Output/Speed 250 kW/1900 r/min) and a catalytic converter containing 20 L V_2O_5-WO_3/TiO_2 washcoated honeycomb catalyst.

3. Results and discussion

3.1. *Catalyst activity measurements in laboratory*

In a preliminary study on the NH_3-SCR catalysts, several oxides, e.g., Al_2O_3, SiO_2, ZrO_2, and TiO_2, were used as the support for V_2O_5 loading. TiO_2 was finally chosen as the support due to its exceptional sulfur poisoning resistance [29,30]. WO_3 and MoO_3 are often used as promoters for a V_2O_5/TiO_2 catalyst. V_2O_5-MoO_3/TiO_2 catalyst is suitable for stationary application due to its high resistance to As poisoning, while V_2O_5-WO_3/TiO_2 catalyst is more suitable for mobile application due to its higher activity and wider operation temperature window.

Based on the investigations in our laboratory, the final catalyst formulation for industrial production was determined as 4.5 wt% V_2O_5 and 10 wt% WO_3 supported on anatase TiO_2. The activity measurement showed that the V_2O_5-WO_3/TiO_2 catalyst gave >80% NO_x conversion in the relatively wide temperature range of 200–450 °C at a GHSV of 50000 h^{-1} (Fig. 1).

A V_2O_5-WO_3/TiO_2 monolith catalyst is often obtained by extrusion or washcoating technology. The extruded monolith SCR catalyst comprises the active V_2O_5-WO_3/TiO_2 mass, but it is mechanically weak and its cell density is very low. A high cell density V_2O_5-WO_3/TiO_2 catalyst with an excellent mechanical property can be obtained by washcoating the V_2O_5-WO_3/TiO_2 powder onto a cordierite honeycomb, which is highly suitable for mobile applications. Therefore, the washcoating technology for the V_2O_5-WO_3/TiO_2 catalyst was systemically investigated in our laboratory. The effects of one-step and two-step washcoating procedures on the catalyst properties were compared, and the influence of silicasol, aluminasol, and several surfactants on slurry viscosity, solid content, catalyst loading, coating stability, and catalytic activity was investigated. From this study, an optimum washcoating process was developed for the industrial production line. The washcoated honeycomb catalyst was tested in the laboratory, and the results showed that >80% NO_x conversion was obtained at 200–450 °C and a GHSV of 10000 h^{-1} (Fig. 2). This washcoated honeycomb catalyst could main-

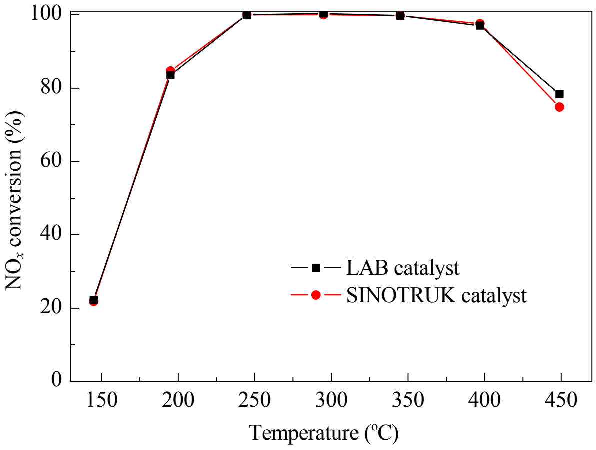

Fig. 1. NO_x conversion over V_2O_5-WO_3/TiO_2 powder catalysts prepared in the laboratory (LAB catalyst) and in the SINOTRUK production line (SINOTRUK catalyst). Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol%, N_2 balance, and GHSV = 50000 h^{-1}.

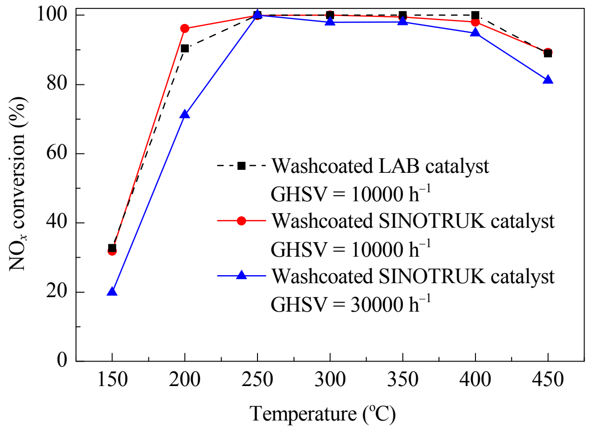

Fig. 2. NO$_x$ conversion over V_2O_5-WO_3/TiO_2 washcoated catalysts prepared in laboratory and SINOTRUK (loading amount = 120 g/L). Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol%, N_2 balance.

tain >80% NO$_x$ conversion at 200–450 °C after calcination at 600 °C for 8 h, that is, it has good thermal stability. However, after calcination at 650 °C for 8 h, the NH_3-SCR activity decreased and there was a smaller operation temperature window, indicating that above 650 °C the catalyst suffered some changes in microstructure, e.g., the phase transformation of TiO_2 and the loss of surface area. In a future study, the thermal stability of this catalyst would be further improved by tuning the catalyst compositions or changing the physical-chemical properties of the catalyst support. At the moment, this washcoated honeycomb catalyst does not need to be coupled with the diesel particulate filter (DPF) in the diesel engine, thus a high temperature heat shock from the regeneration of the DPF is not a critical problem for this catalyst. The typical exhaust temperature from diesel engines is lower than 500 °C, and this washcoated V_2O_5-WO_3/TiO_2 honeycomb catalyst can maintain satisfactory deNO$_x$ efficiency and meet the needs of long-term use.

3.2. *Industrial production line and product tests*

Based on the above study on the V_2O_5-WO_3/TiO_2 powder and monolith catalyst preparation, an industrial production line was set up and optimized in SINOTRUK. The production line consists of powder catalyst preparation, catalyst milling, slurry preparation, honeycomb pretreatment, washcoating, monolith drying, and monolith calcination. Some important parameters in the powder catalyst preparation, catalyst slurry preparation, honeycomb pretreatment, and washcoating were investigated and optimized. The flow chart of the production line is shown in Fig. 3. It is composed of two sections, namely, powder catalyst preparation and monolith catalyst preparation. The powder V_2O_5-WO_3/TiO_2 catalyst prepared by this production line in SINOTRUK showed similar NH_3-SCR activity to the sample prepared in the laboratory (Fig. 1), indicating that in the scaled up production process of this powder catalyst, its physicochemical properties and deNO$_x$ efficiency were effectively and precisely controlled. Cordierite honeycombs with a large size (ϕ 285.75 mm × 152.4 mm) were used for the washcoating, and the V_2O_5-WO_3/TiO_2 loading on the honeycomb was well controlled at 120 g/L, which met the needs of the practical application. As shown in Fig. 2, the washcoated V_2O_5-WO_3/TiO_2 monolith catalyst from SINOTRUK exhibited similar NH_3-SCR activity to the washcoated catalyst from the laboratory at a GHSV of 10000 h^{-1}. Even under a high GHSV of 30000 h^{-1}, the monolith catalyst from the production line achieved >80% NO$_x$ conversion at 250–450 °C, which fulfilled the deNO$_x$ demand for the diesel engines under high load operation conditions.

3.3. *Engine bench tests*

To evaluate the catalyst from the production line in SINOTRUK under more industrial conditions, engine bench tests were carried out for the V_2O_5-WO_3/TiO_2 monolith catalyst, and the catalytic performance was compared with a commercial vanadium-based NH_3-SCR catalyst from a well known company. The inlet temperature and GHSV at each mode during the ESC test are shown in Fig. 4. Except for mode 1, the GHSVs of the other modes were between 15000 and 45000 h^{-1}, and the exhaust temperatures were between 320 and 500 °C, which were in the effective range of the V_2O_5-WO_3/TiO_2 catalyst.

The NO$_x$ concentrations during the ESC tests of the SINOTRUK and commercial V_2O_5-WO_3/TiO_2 NH_3-SCR catalysts

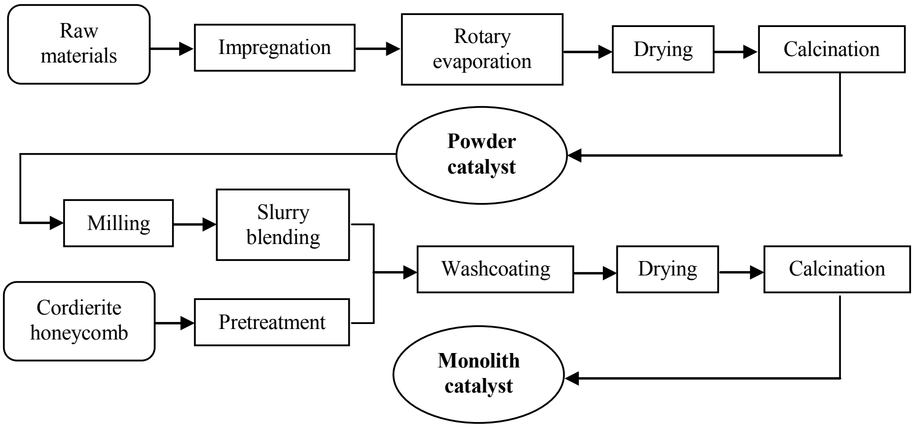

Fig. 3. Flow chart of the powder catalyst production and catalyst washcoating process.

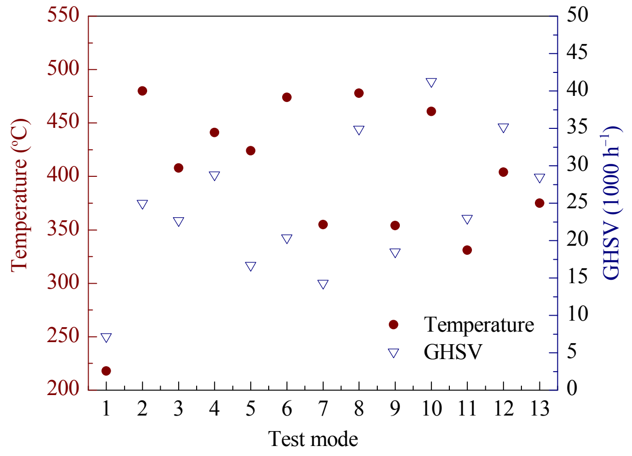

Fig. 4. Inlet temperature and GHSV at each mode point for the ESC test of the V_2O_5-WO_3/TiO_2 catalyst produced from SINOTRUK.

Table 1
ESC test results of the SINOTRUK and commercial V_2O_5-WO_3/TiO_2 NH_3-SCR catalysts.

Catalyst	PM (g/(kW·h))	THC (g/(kW·h))	CO (g/(kW·h))	NO_x (g/(kW·h))
Original	0.016	0.03	0.40	9.38
SINOTRUK	0.020	0.05	0.44	2.56
Commercial	0.013	0.04	0.38	2.90
China IV limit	0.020	0.46	1.50	3.50
China V limit	0.020	0.46	1.50	2.00

are shown in Fig. 5. At mode 1, due to the low speed and zero torque, the original NO_x concentration was lower than those at the other mode points. Except for mode 1, the NO_x concentrations in the other modes were all clearly decreased by the NH_3-SCR treatment. The original NO_x concentrations in modes 2–13 were in the range of 598–1480 ppm. The mass average NO_x conversion over the SINOTRUK catalyst was 73%, while that over the commercial catalyst was 69%. After NH_3-SCR treatment, the NO_x concentration was significantly reduced to 95–358 ppm, with corresponding NO_x conversions of 68%–85%. The original mass average NO_x emission from the diesel engine during the ESC test was 9.38 g/(kW·h), while the mass average NO_x emissions after the NH_3-SCR treatment by the SINOTRUK catalyst and commercial catalyst were 2.56 and 2.90 g/(kW·h), respectively. As shown in Table 1, both NO_x emissions after the NH_3-SCR treatment met the China IV (Euro IV) ESC limit of 3.5 g/(kW·h), but neither met the China V (Euro V) ESC limit of 2.0 g/(kW·h). At the same time, the particulate matter (PM), total hydrocarbon (THC), CO, and NH_3 slip values were all lower than the China IV (Euro IV) ESC limit values. In addition, the PM concentration during the ESC test with the SINOTRUK catalyst was slightly increased; this might be due to the relatively high V_2O_5 loading of this catalyst, which facilitated the oxidation of SO_2 to SO_3 and enhanced the production of $(NH_4)_2SO_4$ particles by combination with NH_3. This point will be confirmed in a future study by the reduction of the V_2O_5 loading of the catalyst through an improved preparation method. In another ETC bench test, the original mass average NO_x emission of the engine during the ETC test was 9.34 g/(kW·h), while the mass average NO_x emissions after NH_3-SCR treatment by the SINOTRUK catalyst and commercial catalyst were 2.38 and 2.41 g/(kW·h), respectively. Both NO_x emissions after the NH_3-SCR treatment met the China IV (Euro IV) ETC limit of 3.5 g/(kW·h). In conclusion, the NH_3-SCR performance of the V_2O_5-WO_3/TiO_2 catalyst product from the SINOTRUK production line met both the ESC and ETC limits of China IV (Euro IV). Under the same test conditions, the V_2O_5-WO_3/TiO_2 catalyst prepared by SINOTRUK showed higher catalytic performance than the commercial one.

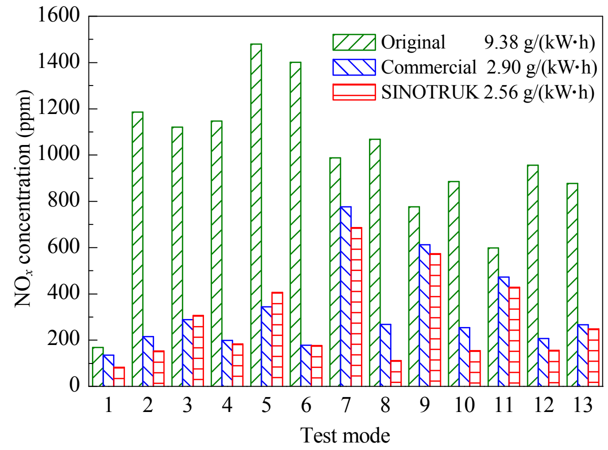

Fig. 5. ESC test results of the SINOTRUK and commercial V_2O_5-WO_3/TiO_2 NH_3-SCR catalysts for NO_x abatement from diesel engine exhaust.

Due to the high sulfur content in the diesel fuel in China today, the product from the SINOTRUK NH_3-SCR catalyst production line is only the V_2O_5-WO_3/TiO_2 catalyst at present. However, this catalyst still has some problems, such as the toxicity of vanadium species and a low sublimation temperature. Although the usage of vanadium-based NH_3-SCR catalysts is still permitted in China now, these catalysts will be removed from the market for mobile application in the next few years with the stricter environmental protection demands. Therefore, efforts should be made for the development and industrial application of environmentally benign NH_3-SCR catalysts for controlling NO_x emissions from diesel engines. In our previous studies, we developed several easily prepared Ce-based [17,18] and Fe-based [25] oxide catalysts and a Cu-SSZ-13 [13] small pore zeolite catalyst with excellent NH_3-SCR performance. The Ce-WO_x catalyst has already been studied for industrial application. The engine bench test showed that the NH_3-SCR system based on this $CeWO_x$ catalyst can get the NO_x emission from diesel engines to meet the China V (Euro V) ESC limit without the help of an after-treatment device. We are also working on the large-scale production of the Cu-SSZ-13 and Cu-SAPO-34 NH_3-SCR catalysts with excellent hydrothermal stability and HC poisoning resistance. When the quality of the diesel fuel in China becomes much improved, it would just need some modifications for the SINOTRUK NH_3-SCR catalyst production line to produce washcoated vanadium-free and environmentally benign catalysts with higher deNO_x efficiency based on large-size cordierite honeycombs.

Graphical Abstract

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Selective catalytic reduction of NO_x by NH_3 for heavy-duty diesel vehicles

Fudong Liu, Wenpo Shan, Dawei Pan, Tengying Li, Hong He*
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences;
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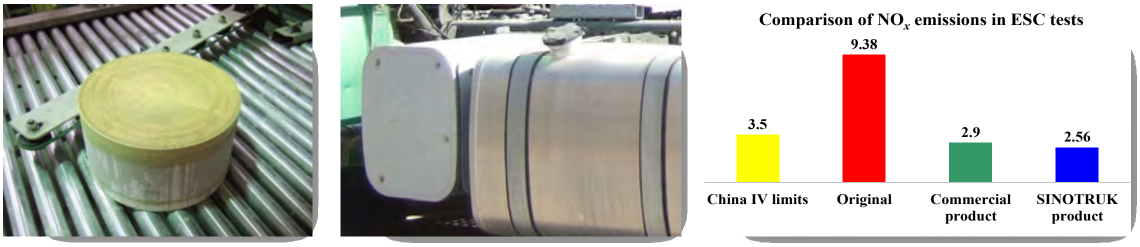

NH_3-SCR catalysts manufactured by SINOTRUK efficiently reduced NO_x emission from diesel engines to meet the China IV standard.

4. Conclusions

The industrial production of a NH_3-SCR catalyst for diesel vehicle application in China was achieved by the optimization of a V_2O_5-WO_3/TiO_2 catalyst and the washcoating technology. A NH_3-SCR catalyst production line with a production amount of 6000 catalyst monoliths per month was set up in SINOTRUK for NO_x abatement from diesel vehicles. Cordierite honeycombs with a large size were used for the washcoating. Engine bench tests showed that the NO_x emissions after the NH_3-SCR treatment by the V_2O_5-WO_3/TiO_2 catalyst from SINOTRUK met the China IV (Euro IV) ESC and ETC limits. When the diesel fuel in the future reaches the quality requirements, just some modifications are needed for this NH_3-SCR catalyst production line to produce environmentally-benign vanadium-free catalysts to meet more stringent emission regulations for diesel engines.

Acknowledgments

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NH_3选择性还原NO_x技术在重型柴油车尾气净化中的应用

刘福东[a], 单文坡[a], 潘大伟[b], 李腾英[b], 贺 泓[a,*]
[a]中国科学院生态环境研究中心, 北京100085
[b]中国重汽集团济南橡塑件有限公司, 山东济南250031

摘要: 基于实验室对柴油车用V_2O_5-WO_3/TiO_2催化剂配方以及涂覆成型技术的大量研究, 设计了一条产量为6000只/月的NH_3选择性催化还原NO_x (NH_3-SCR)催化剂中试生产线, 并对生产的催化剂产品进行了发动机台架测试. 结果表明, 实验室制备的V_2O_5-WO_3/TiO_2粉体催化剂和生产线产品, 在空速为50000 h^{-1}和200–450 °C条件下NO_x转化率均可达80%以上; 采用大尺寸堇青石载体涂覆后制备的V_2O_5-WO_3/TiO_2整体催化剂经实验室小样测试, 在空速为10000–30000 h^{-1}和250–450 °C条件下NO_x转化率也为80%以上. 发动机台架测试结果表明, 该催化剂产品可使重型柴油机NO_x排放达到国IV标准中欧洲稳态循环(ESC)和欧洲瞬态循环(ETC)排放限值的要求. 该生产线经适当调整后也可用于生产非钒基NH_3-SCR整体催化剂, 以满足未来钒基NH_3-SCR催化剂更新换代的需求.

关键词: 柴油车尾气; 氮氧化物; 选择性催化还原; 钒基催化剂; 工业化生产

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*通讯联系人. 电话/传真: (010)62849123; 电子信箱: honghe@rcees.ac.cn
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1. 前言

柴油车由于具有燃油经济性好和动力性强的特点而日益受到重视, 但其尾气中NO_x的消除仍然是环境催化和环保领域一个亟待解决的问题[1,2]. 根据我国环境保护部发布的2012年《中国机动车污染防治年报》[3], 柴油车仅占我国汽车保有量的17%, 但排放的NO_x却占汽车排放总量的67.4%; 尤其是以柴油为燃料的重型载货汽车虽然只占我国汽车保有量的5%, 但其NO_x排放量却占汽车排放总量的48.6%.

NH_3选择性催化还原NO_x (NH_3-SCR)被认为是最有希望全面应用于柴油车尾气NO_x净化的技术之一[4]. 为了满足日益严格的NO_x排放法规, 国外众多汽车及发动机生产企业已经大力开展了NH_3-SCR系统的应用化研究及产业化. 中国重汽(SINOTRUK)、潍柴、上柴等国内企业都将采用NH_3-SCR技术路线进行尾气后处理, 以满足“国IV标准”的要求. NH_3-SCR技术广泛应用于柴油车尾气NO_x去除已经是大势所趋, 该技术的关键是NH_3-SCR催化剂的研发.

自20世纪70年代以来, 钒基NH_3-SCR催化剂在以燃煤电厂为代表的固定源烟气脱硝中得到了广泛应用, 并被引入到柴油车尾气NO_x催化净化领域[4–6]. 针对钒基NH_3-SCR催化剂操作温度窗口较窄并具有生物毒性等缺点, 研究者们开发了Fe-ZSM-5[7–9], Cu-SSZ-13[10–13]和Cu-SAPO-34[14–16]等系列过渡金属交换的分子筛催化剂以及Ce基[17–24]、Fe基[25–27]和Cu基[28]等无钒金属氧化物催化剂, 以期替代钒基催化剂在柴油车上的使用. 但目前我国普遍存在燃油质量偏低、车用柴油含硫量不能满足标准需求的问题, 钒基催化剂由于其优异的抗硫中毒能力仍然是现阶段重型柴油车用NH_3-SCR催化剂的首选.

2. 实验部分

2.1. 催化剂制备

采用浸渍法制备以TiO_2为载体, V_2O_5和WO_3负载量分别为4.5和10 wt%的V_2O_5-WO_3/TiO_2催化剂. 将12.48 g $C_2H_2O_4\cdot 2H_2O$, 5.79 g NH_4VO_3 和 10.94 g $H_{40}N_{10}O_{41}W_{12}\cdot xH_2O$溶于300 mL去离子水中, 加入100 g TiO_2粉末载体, 充分搅拌1 h以上, 然后将混合浆液进行旋转蒸发至水分充分挥发, 并在100 °C空气气氛下干燥过夜, 最后在550 °C空气气氛下焙烧3 h.

将所制粉体催化剂、去离子水及适当的粘结剂按一定比例混合, 搅拌均匀即制得催化剂涂敷浆液. 将堇青石蜂窝陶瓷载体(300目)切割打磨成圆柱体后, 浸没于涂层浆液中进行涂敷. 经100 °C干燥后, 在550 °C下焙烧3 h, 即得整体催化剂.

中国重汽集团中试生产线粉体催化剂制备工段主要模拟实验室催化剂制备过程进行设计建设. 催化剂采用大尺寸堇青石蜂窝陶瓷载体进行全自动涂覆成型, 载体规格为ϕ285.75 mm × 152.4 mm.

2.2. 催化剂评价及发动机台架测试

催化剂稳态活性评价实验在实验室自行搭建的多气路固定床连续评价系统上进行, 催化剂固定于石英管反应器中央, 采用电阻炉对反应管进行加热. NH_3-SCR反应条件如下：500 ppm NO, 500 ppm NH_3, 5 vol% O_2, N_2为平衡气体, 气体总流量为500 mL/min. 粉体催化剂用量为0.6 mL, 折合反应空速GHSV为50000 h^{-1}；整体催化剂用量为1–3 mL, 折合GHSV为10000–30000 h^{-1}. 在催化剂活性评价过程中, NO, NH_3, N_2O和NO_2的浓度均由配有2 m光程气体池的傅里叶变换红外光谱仪(Nicolet Nexus 670)测得. NH_3-SCR反应中的NO_x转化率计算如下：NO_x转化率 = $(1 – ([NO]+[NO_2])_{out}/([NO]+[NO_2])_{in}) \times 100\%$.

使用一台中国重汽 D10.34柴油发动机(排量即发动机各缸工作容积的总和为9.726 L, 最大输出功率250 kW, 额定转速1900 r/min)和装有20 L V_2O_5-WO_3/TiO_2整体催化剂的催化转化器进行了欧洲稳态循环(ESC)和欧洲瞬态循环(ETC)测试实验.

3. 结果与讨论

3.1. 实验室小试

在早期筛选NH_3-SCR催化剂的过程中, 人们尝试了以Al_2O_3, SiO_2, ZrO_2和TiO_2等诸多氧化物作为V_2O_5的载体, 并最终选择了具有优异抗SO_2中毒能力的锐钛矿TiO_2[29,30]. WO_3和MoO_3通常被用作V_2O_5/TiO_2催化剂的助剂, 其中V_2O_5-MoO_3/TiO_2催化剂具有较好的抗As中毒能力, 在固定源脱硝应用中具有一定的优势；比较而言, V_2O_5-WO_3/TiO_2催化剂具有更高的催化活性和更宽的温度窗口, 因此在柴油车尾气NO_x净化的应用中更有优势.

在进行了大量的筛选和测试工作后, 最终确定了可实际工业化应用的V基NH_3-SCR催化剂原料配比, 以TiO_2为载体, 负载4.5 wt% V_2O_5和10 wt% WO_3. 实验室条件下所制备的V_2O_5-WO_3/TiO_2粉体催化剂在空速为50000 h^{-1}条件下, 在200–450 °C的较宽温度范围内NO_x转化率可达80%以上, 结果如图1所示.

V_2O_5-WO_3/TiO_2整体催化剂的制备通常有挤压成型和涂覆成型两种方式. 挤压成型技术制备的催化剂主要由V_2O_5-WO_3/TiO_2活性组分构成, 机械强度较低, 可实现的孔密度非常有限；而涂覆成型技术通过使用高机械强度的堇青石载体, 可制备出具有很高孔密度且不易破碎的V_2O_5-WO_3/TiO_2整体催化剂, 非常适合应用于柴油车尾气净化. 因此, 采用实验室小试的方法, 全面开展了催化剂涂覆成型技术工艺研究, 对比了一步涂覆和两步涂覆的差别, 考察了硅溶胶、铝溶胶以及多种表面活性剂对浆液粘度、固形物含量、催化剂粉末涂覆量、涂层强度以及SCR活性的影响, 最终成功开发出可满足工业化应用要求且可操作性强的涂覆成型工艺配方. 涂覆后制备的V_2O_5-WO_3/TiO_2整体催化剂经小样测试, 在空速为10000 h^{-1}的条件下, 可在200–450 °C范围内实现80%以上的NO_x转化率, 结果如图2所示. 需要特别指出的是, 该催化剂经过600 °C焙烧8 h后, 在200–450 °C范围内NO_x转化率仍保持80%以上, 稳定性良好；但经过650 °C焙烧8 h后, 催化剂活性则明显降低, 操作温度窗口变窄. 这表明在650 °C以上该催化剂可能发生了微观结构变化, 如TiO_2晶型转变以及比表面积降低等, 后续可以通过进一步调变催化剂组成或改变载体性质以提高催化剂的稳定性. 现阶段, 该催化剂不需与柴油颗粒物过滤器(DPF)联用, 也就不存在DPF再生时产生的高温热冲击, 而柴油机的排气温度也通常低于500 °C, 因此在典型的柴油机排温工作条件下, 该催化剂能够保持良好的NO_x净化效率, 并满足长期工作的需要.

3.2. 催化剂生产线建设及活性评价

基于上述对V_2O_5-WO_3/TiO_2粉体催化剂和催化剂涂覆成型技术的研究, 在中国重汽集团开展了中试生产线建设与调试工作. 所建NH_3-SCR催化剂生产线主要包括粉体催化剂制备、催化剂研磨、催化剂调浆、载体预处理、催化剂涂覆、整体催化剂干燥与焙烧等工序；所进行的调试工作主要包括粉体催化剂制备参数, 调浆设备试运行与改进, 催化剂浆液粒度、粘度和固形物含量的精确控制, 催化剂载体水洗时间、干燥时间与含水率精确控制以及催化剂涂覆过程中浆液喷射量、喷射时间、吹扫强度、吹扫时间的精确控制等, 结合实验室模拟测试结果的反馈, 最终确定了一整套切实可行的粉体催化剂生产与整体催化剂涂覆成型工艺(见图3). 利用该生产线粉体催化剂制备单元以工业原材料生产的V_2O_5-WO_3/TiO_2催化剂, 在相同的反应条件下其催化活性与实验室样品极为接近(见图1), 证明在V_2O_5-WO_3/TiO_2粉末催化剂放大生产过程中, 其理化性质及NO_x净化活性可以得到有效且精确的控制, 有利于下一步开展催化剂涂覆成型研究. 整体催化剂涂覆单元可使大尺寸堇青石蜂窝陶瓷载体上的涂覆量控制达到120 g/L左右, 满足实际应用需求；如图2所示, 涂覆后的V_2O_5-WO_3/TiO_2整体催化剂在相同空速条件下与实验室涂覆制备的样品NH_3-SCR活性基本相同, 重现性极佳,

且在较高空速条件 (30000 h^{-1}) 下, 该生产线制备的样品仍能在250–450 °C的较宽温度范围内实现80%以上的NO_x净化效率, 可满足柴油机高负荷运转时的NO_x净化要求.

3.3. 发动机台架测试结果

为了更好地评价所建生产线催化剂产品的NH_3-SCR活性, 在更接近真实使用条件的发动机台架上测试了中国重汽集团生产的V_2O_5-WO_3/TiO_2整体催化剂, 并且与国外某知名催化剂公司的商用钒基催化剂产品的性能进行了对比. 图4为ESC测试时各工况点的柴油发动机排气温度和反应空速. 可以看出, 测试过程中, 除工况1以外, 反应空速主要在10000–45000 h^{-1}; 发动机排气温度主要在320–500 °C, 处于V_2O_5-WO_3/TiO_2催化剂的活性温度范围.

图5为中国重汽SCR催化剂生产线产品和商用V_2O_5-WO_3/TiO_2催化剂进行ESC测试时各工况下的NO_x浓度, 同时给出了发动机的原始排放浓度. 在工况1条件下, 由于发动机处于低转速、零扭矩状态, NO_x初始浓度明显低于其他工况. 除工况1外, 其他工况条件下的NO_x浓度经过催化剂处理后均显著降低. 工况2–13条件下的NO_x原始排放浓度在598–1480 ppm. ESC测试过程中, 中国重汽SCR催化剂的NO_x加权平均去除率为73%, 而商用催化剂产品的NO_x加权平均去除率为69%. 发动机ESC测试的NO_x原始排放量为9.38 g/(kW·h), 而经过基于中国重汽催化剂产品和商用催化剂的NH_3-SCR系统处理后, NO_x排放量分别降至2.56和2.90 g/(kW·h), 均可达到国IV排放标准(3.5 g/(kW·h))的要求, 但尚不能满足国V排放标准(2.0 g/(kW·h)) (见表1). 同时, 测试的颗粒物(PM)、总碳氢化合物(THC)、CO以及NH_3泄漏指标也均可达到国IV标准. 中国重汽SCR催化剂测试时PM浓度略有升高, 推测可能与该催化剂含钒量较高、对尾气中SO_2氧化作用较强进而与NH_3结合生成部分$(NH_4)_2SO_4$颗粒物有关, 可在后续研究中予以确认, 并可尝试通过改进制备方法以降低催化剂中钒氧化物的含量. 在另外进行的ETC测试中, NO_x原始排放量为9.34 g/(kW·h), 经过基于中国重汽催化剂产品和商用催化剂的NH_3-SCR系统处理后, NO_x排放量分别降至2.38和2.41 g/(kW·h), 均可达到国IV排放标准. 综上所述, 中国重汽SCR催化剂生产线生产的V_2O_5-WO_3/TiO_2的NH_3-SCR催化性能在满足国IV标准ESC和ETC排放限值方面均略优于国外商用催化剂, 可与国产重型柴油车进行配套使用.

由于我国目前车用柴油含硫量普遍偏高, 中国重汽集团SCR催化剂生产线主要以生产V_2O_5-WO_3/TiO_2催化剂产品为主. 由于钒基催化剂存在活性组分V_2O_5高温易升华且具有生物毒性等问题, 尽管我国目前还允许钒基催化剂的生产和使用, 但随着环境保护要求的不断提高和科学技术的全面进步, 全面淘汰钒基催化剂也只是时间问题. 因此, 非常有必要开展非钒基NH_3-SCR催化剂的开发和工业化应用研究, 为满足更为严苛的柴油车尾气排放标准提供技术储备. 我们前期已经开发了多种制备方法简单、催化性能较钒基催化剂更为优异的Ce基[17,18]和Fe基[25]氧化物催化剂以及Cu-SSZ-13小孔分子筛催化剂[13]. 其中, 性能优异的$CeWO_x$催化剂已经进行了实用化研究, 基于该催化剂体系的催化转化器可使国产重型柴油发动机的NO_x排放量降至1.90 g/(kW·h), 满足国V排放标准中的ESC排放限值; 针对水热稳定性高、抗HC中毒性能良好的Cu-SSZ-13和Cu-SAPO-34小孔分子筛催化剂体系, 目前也正在进行合成规模的扩大化研究, 预期将取得重要进展. 在我国, 待燃油品质等外在条件成熟以后, 只需对该SCR催化剂生产工艺的粉体催化剂制备环节进行相关调整, 即可用于生产基于大尺寸堇青石蜂窝陶瓷载体的涂覆型非钒基NH_3-SCR整体催化剂, NO_x净化效率更高, 且环境友好.

4. 结论

为了实现柴油车用NH_3-SCR催化剂的工业化生产, 通过大量的实验室研究确定了V_2O_5-WO_3/TiO_2催化剂的最优配方及其涂覆成型工艺技术, 并在中国重汽集团建成了一条产量为6000只/月的NH_3-SCR催化剂中试生产线. 该生产线利用国产大尺寸堇青石蜂窝陶瓷为载体进行涂覆, 所生产的V_2O_5-WO_3/TiO_2整体催化剂经发动机台架测试, NO_x排放可达国IV标准中的ESC和ETC排放限值要求. 一旦燃油品质等外在条件成熟, 该生产线经过相关调整后即可用于生产替代型、环境友好的非钒基NH_3-SCR整体催化剂, 以满足未来更为严格的柴油车排放法规.

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