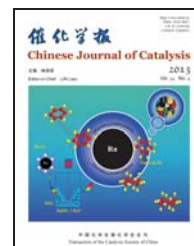available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Communication

A novel diesel oxidation catalyst with low SO₂ oxidation activity and capable of meeting Euro V emission standards

CHEN Yongdong [a],*, WANG Lei [b], GUAN Xiaoxu [a], TANG Shuihua [a], GONG Maochu [c], CHEN Yaoqiang [c],#

[a] *State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, Sichuan, China*
[b] *Sichuan Zhongzi Exhaust Purge Co., Ltd., Chengdu 610225, Sichuan, China*
[c] *Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China*

A B S T R A C T

A diesel oxidation catalyst was prepared from several high performance materials: the new rare earth oxygen storage compound $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3, the composite oxide $Ti_{0.9}Zr_{0.1}O_2$ and chromium-modified β molecular sieve. These component materials were characterized and used to prepare a Pt-based catalyst designed to reduce diesel engine exhaust emissions. The results of low temperature N_2 adsorption-desorption and oxygen storage capacity tests demonstrated that $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3 exhibits a large specific surface area and excellent oxygen storage capacity, and that $Ti_{0.9}Zr_{0.1}O_2$ exhibits superior textural properties. Evaluations of catalytic activity showed that the catalyst prepared from these materials has reduced capacity for the oxidation of SO_2 but high catalytic activity towards the oxidation of hydrocarbons (HC) and CO, and is also able to convert the exhaust soluble organic fraction at temperatures as low as 140 °C. Tests using a domestic YC4F-type diesel engine found that exhaust treated by the catalyst prepared in this research is capable of meeting the HC and CO emission requirements of the Euro V standard.

The significant progress in diesel engine technology to date has resulted in rapid development of the diesel vehicle industry. Diesel vehicles have become increasingly popular, partly because of their superior fuel economy, but also because they are durable and provide excellent performance. Diesel engine exhaust, however, contains a number of toxic or otherwise harmful compounds, including particulate matter (PM), nitrous oxides (NO$_x$), hydrocarbons (HC), CO and SO₂. There may be as many as 14 different harmful compounds in the PM exhaust fraction and carcinogenic pollutants can also be formed from atmospheric photochemical reactions in which NO$_x$ can be converted to surface O₃ and peroxides. In addition, NO$_x$ contributes to the formation of acid rain, while HC and CO are both potential health hazards. As a result of these harmful exhaust components, as the number of diesel vehicles continues to increase, the associated increase in exhaust emissions has become a threat to the health of both humans and the environment [1,2].

There are two general approaches to the reduction of harmful diesel emissions: in-engine and out-of-engine treatments. The out-of-engine treatments have thus far been favoured, because they are typically more convenient and less costly, and include diesel oxidation catalysts (DOCs), diesel particulate filtration (DPF), NO_x selective catalytic reduction (SCR) and four-way catalysts (FWCs). These technologies can be used together or singly depending on the composition of the diesel exhaust and the regulatory requirements which must be satisfied [3]. DOCs are primarily used to remove HC, CO and the soluble organic fraction (SOF) of the PM [4]. These same catalysts, however, can oxidize SO_2 contained in the exhaust to SO_3, which will subsequently react with moisture to produce either sulfurous or sulfuric acid, which in turn will deactivate the catalyst and thus increase PM emissions [5,6]. Because the quality of the diesel fuel available in China is generally poor [7,8], such that 87% of these fuels have SO_2 concentrations in excess of 0.035%, the exhaust of diesel engines operating in China will typically have levels of SO_2. As a result, DOCs used in China must be both highly active and highly selective, with high catalytic activities for the destruction of CO, HC and SOF, but low activity in terms of SO_2 oxidation.

At present, DOC technology is most advanced in Europe, the United States and Japan, and research and development concerning this technology is primarily performed by a small number of multi-national corporations, including Engelhard in the United States, Johnson Matthey in the United Kingdom, Umicore in Belgium and BASF in Germany. In a typical DOC, a precious metal such as Pt or Pd is the active component and is loaded on the surface of a support material. The particular active component and support material employed in making the catalyst, as well as the working conditions of the engine, the sulfur content of the fuel and the rate of exhaust flow are the main factors which influence the efficiency of the DOC.

Initially, DOC technology was based on the use of Pt loaded on an alumina support. As emissions regulations became more stringent, however, both oxidation activity towards the SOF at low temperatures and reduced oxidation of SO_2 became necessary aspects of DOC technology, and cerium-based catalysts which enabled the low temperature oxidation of the SOF became common, along with composite supports made from materials such as SiO_2, TiO_2 and ZrO_2, because these substances exhibit low SO_2 adsorption. In addition, DOCs incorporating molecular sieves were developed, to improve the oxidation of HC, CO and the SOF under cold start conditions. Considering all the above developments in catalyst composition, as well as other improvements in the preparation processes, the current state of DOC technology has become quite complex [9–11].

In the study reported herein, a new type of high-performance diesel oxidation catalyst was prepared and its performance investigated using a domestic IV YC4F-type diesel engine. The results show that treatment by the new catalyst allows the engine exhaust to meet the HC and CO emission requirements of the Euro V standards. In addition, the catalyst exhibits high oxidation activity towards the SOF and low oxidation activity with regard to SO_2.

High performance DOCs developed in recent years have been primarily based on three components [12,13]: ceria-based materials, Pt-loaded sulfur-tolerant supports and molecular sieves. The oxygen storage material investigated in this work, $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3 (3:1 mass ratio of $Ce_{0.75}Zr_{0.25}O_2$ to Al_2O_3), was prepared using a co-precipitation technique. In this method, zirconyl carbonate is first dissolved in an appropriate quantity of concentrated nitric acid, following which aqueous solutions of $Ce(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ are added in the appropriate stoichiometric ratios. Subsequently, H_2O_2 is added and the solution is stirred for 30 min, after which the reaction product is removed from solution by co-precipitation resulting from the addition of an ammonia/ammonium carbonate solution. Following co-precipitation, the solution is subjected to sequential heat treatment, stirring, washing and filtration. The precipitate is dried at 70 °C for 24 h and then calcined at 600 °C for 5 h to produce the final product. The composite support material $Ti_{0.9}Zr_{0.1}O_2$ is also prepared using essentially the same co-precipitation method as above. Zirconyl carbonate is dissolved in an appropriate quantity of concentrated nitric acid and an aqueous solution of titanyl sulfate is mixed in, after which the solution is co-precipitated with ammonia/ammonium carbonate solution. After co-precipitation, the solution obtained is subjected to heat treatment, stirring, washing and filtration, and the precipitate is dried at 70 °C for 24 h and then calcined at 550 °C for 5 h to obtain the composite oxide. Lastly, the Cr-modified β molecular sieves are prepared by equivalent-volume impregnation, involving the impregnation of β-molecular sieves (Si/Al = 25) with the necessary quantity of chromium nitrate solution. The resulting product is dried at 110 °C for 6 h and calcined at 550 °C for 5 h to obtain Cr-β molecular sieve powder (1 wt% Cr).

Nitrogen adsorption testing using a QUADRASORB SI automated surface area and pore size analyser (Quantachrome Instruments, USA) was employed to characterize the textures of the synthesized materials. In addition, an oxygen storage capacity (OSC) measurement device was used to determine the OSC of the materials at 200 °C. The results of both series of tests are presented in Table 1, where it can be seen that $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3 exhibits a large specific surface area and excellent low temperature OSC, a capability which facilitates the removal of the SOF [14].

According to some reports, both TiO_2 and ZrO_2 have only limited capacities for SO_2 adsorption [15,16], and therefore using composite oxides composed of Ti and Zr-based materials as DOC support materials is anticipated to inhibit the adsorption of SO_2 by the catalyst and accordingly reduce the oxidation of SO_2 over the Pt component, increasing the catalyst's resistance to the deleterious effects of sulfur in diesel fuel. Both TiO_2 and ZrO_2, however, have relatively low specific surface areas, and thus are not suitable for application as support ma-

Table 1
Textural properties and OSC of catalyst samples.

| Sample	A_{BET}/(m²/g)	V_p/(ml/g)	OSC (μmol/g)
$Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3	169	0.39	400
$Ti_{0.9}Zr_{0.1}O_2$	94	0.33	—
Cr-β molecular sieves	424	0.46	—
β molecular sieves	429	0.46	—

terials in their natural form [17]. In contrast, the specific surface area of $Ti_{0.9}Zr_{0.1}O_2$, the composite oxide prepared in this work, is measured at 94 m^2/g, suggesting that it is a viable candidate for use an acidic support for Pt. As well, the combination of Pt with $Ti_{0.9}Zr_{0.1}O_2$, when used for the removal of HC and CO, has been shown to simultaneously exhibit both excellent catalytic activity and sulfur resistance [8]. β molecular sieves are primarily used for the adsorption of HC at low temperatures, which improves catalytic efficiency during diesel engine cold starts. As the data in Table 1 show, the surface area and pore volume of the Cr-modified sieves are essentially unchanged by the modification process. Previous studies have demonstrated that the surface acidity of β molecular sieves is enhanced after the sieves are modified by the addition of Cr [18,19]. Because increased acidity in these materials tends to inhibit SO_2 adsorption, the modification of β molecular sieves by Cr addition tends to result in reduced SO_2 oxidation by the DOC. Therefore, the above three materials are all well suited to form the components of an oxidation catalyst meant for purifying diesel exhaust.

The catalyst investigated in this work was prepared by an equivalent-volume impregnation method. $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3 and $Ti_{0.9}Zr_{0.1}O_2$ were impregnated with aqueous solutions of H_2PtCl_6, after which they were dried and calcined at 550 °C for 5 h to obtain catalytic material in the form of a powder. This powder was then mixed with the Cr-β molecular sieves, added to an appropriate quantity of water, and made into a slurry by ball-milling of the aqueous dispersion. Cordierite honeycomb ceramic substrates (400 cpsi, Corning, USA) were immersed in this slurry then withdrawn, following which excess slurry on the substrates was removed using a stream of compressed air. The substrates were subsequently dried and calcined at 550 °C for 5 h to produce the finished catalyst test specimens. The measured Pt, $Ti_{0.9}Zr_{0.1}O_2$, $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3 and Cr-modified β molecular sieve contents in the final catalyst samples were 1, 72.6, 36.3, and 12.1 g/L, respectively. Artificially aged catalyst specimens were obtained by placing freshly prepared catalyst samples in a tube furnace and heat treating the material at 750 °C for 30 h in a N_2 atmosphere containing 0.02% SO_2, 10% O_2 and 10% H_2O.

Catalytic activity was measured using a continuous flow micro-reactor. A mixture of CO (0.112%), C_2H_4 (0.056%), NO (0.07%), SO_2 (0.02%), CO_2 (6%), O_2 (10%) and H_2O (10%), with the balance being N_2, at a space velocity of 30000 h^{-1}, was used to simulate the exhaust output of a diesel vehicle. The temperature of diesel exhaust is normally in the range of 200 to 400 °C, and the oxidation of SO_2 to SO_3 is constrained by thermodynamic effects, such that the oxidation reaction rate generally decreases above 450 °C [20]. For this reason, an infrared analyser was used to follow the conversion of SO_2 at 350 °C to evaluate the inhibition of the oxidation reaction, because a low SO_2 conversion rate is correlated with increased inhibition of the catalytic oxidation process. Variations in CO concentration over the course of the catalytic reaction were evaluated with an FGA-4100 automobile exhaust gas analyser (Foshan Analytical Instrument Co., Ltd.), while a GC-2001 gas chromatograph incorporating a Porapak T column and a flame ionization detec-

tor was employed to measure changes in HC concentration. The results of the catalytic activity trials are listed in Fig. 1 and Table 2, in which T_{50} is the light-off temperature (the temperature at which 50% conversion is achieved), T_{90} is the total conversion temperature (at 90% conversion) and $\Delta T_1 = T_{90} - T_{50}$.

Prior studies of domestic IV YC4F-type diesel engines with DOC have shown that the SOF primarily originates from engine lubricating oil, as well as from small amounts of unburned diesel fuel [21]. In many studies, lubricating oil is accordingly used as a substitute for the SOF, and the catalytic and oxidative processes in the DOC are simulated by thermogravimetry-differential thermal analysis (TG-DTA) [14,22]. In our work, diesel lubricating oil uniformly distributed on the catalyst powder was also used to simulate the SOF, applying an oil to catalyst mass ratio of 1:10, and the TG-DTA method was employed to determine the extent of SOF conversion. TG-DTA analyses were performed using a HCT-2 thermogravimetric analyser (Beijing Scientific Instrument Factory, China), under air at a flow velocity of 40 ml/min and at a heating rate of 10 °C/min. The TG-DTA plots obtained for the catalytic oxidation of SOF on both fresh and aged catalysts are shown in Fig. 2, while the catalytic activity results calculated from these plots are presented in Table 3, where T_i is the temperature at which SOF conversion begins, T_m is the temperature at which the highest rate of mass loss is observed, T_f is the temperature at which the reaction ends and $\Delta T_2 = T_f - T_i$. The exothermic peak
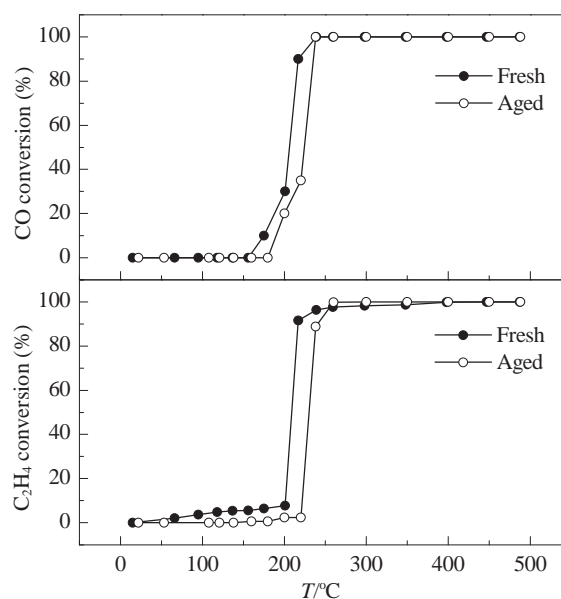
Fig. 1. Catalytic activity of fresh and aged catalyst. Conditions: NO 0.07%, C_2H_4 0.056%, CO 0.112%, SO_2 0.02%, CO_2 6%, O_2 12%, H_2O 10%, balance N_2, catalyst 140 g/L, GHSV = 30000 h^{-1}.

Table 2
Catalytic activity towards C_2H_4, CO, and SO_2.

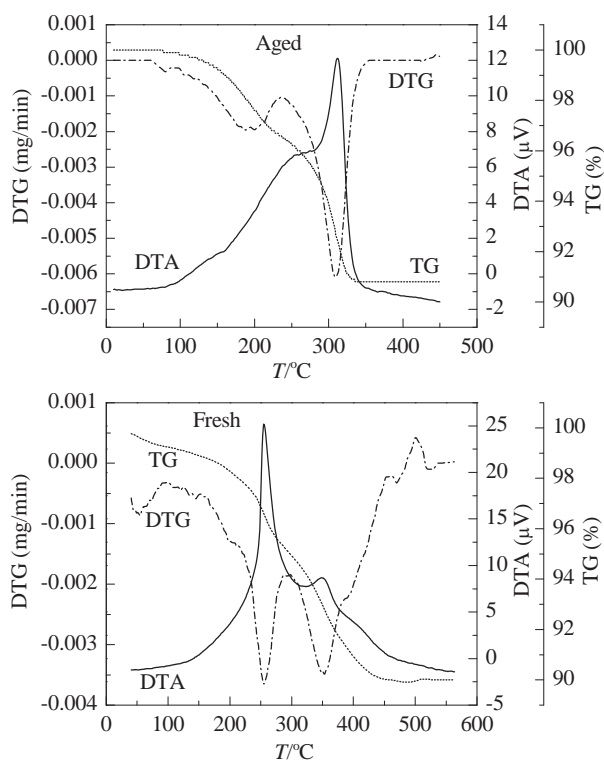| Catalyst	CO			C_2H_4			SO_2 conversion at 350 °C (%)
	T_{50} (°C)	T_{90} (°C)	ΔT_1[a] (°C)	T_{50} (°C)	T_{90} (°C)	ΔT_1 (°C)	
Fresh	192	203	11	203	224	21	22.5
Aged	224	235	11	229	241	12	13.2

[a] $\Delta T_1 = T_{90} - T_{50}$.

Fig. 2. TG-DTG-DTA curves for simulated SOF combustion over fresh and aged catalyst.

Table 3
TG-DTG-DTA data for the conversion of SOF.

Sample	T_i/°C	T_m/°C	T_f/°C	ΔT_2 [a]/°C	A ($\mu V \cdot °C/(mg_{oil} \cdot mg_{sample})$)
Blank	288	335	650	362	63.7
Fresh	140	265	550	410	265.1
Aged	180	303	446	266	231.0

[a] $\Delta T_2 = T_f - T_i$.

area (in units of $\mu V \cdot °C$) is determined in each case by integration of the DTA curve. The relative exothermic peak area [$\mu V \cdot °C/mg_{oil}$] is obtained by dividing the peak area by the mass of lubricating oil applied to the catalyst, and this value is further divided by the total mass of the test sample to give the standardized exothermic peak area, A $\mu V \cdot °C/(mg_{oil} \cdot mg_{sample})$. According to research by Zhang et al. [14], a large standardized exothermic peak area is associated with a reduced probability that the lubricating oil will be volatilised, meaning that catalytic combustion is more likely and the overall catalytic effect is greater.

The durability of DOCs is another important factor used to evaluate their performance. According to research by Andersson et al. [23], treating a catalyst by hydrothermal aging at 670 °C for 15 h, followed by heating at 250 °C for 15 h in 0.005% SO_2, simulates an aged catalyst which has been used in a diesel vehicle with exhaust gas containing 0.001% S over a distance of 160000 km. These aging conditioning can therefore be reasonably applied as suitable parameters when evaluating DOCs in the laboratory. However, because the diesel fuel commonly used in China typically has very high sulfur content, more demanding ageing conditions are appropriate and so, in this

work, catalysts were evaluated using a N_2 atmosphere containing 0.02% SO_2, 10% O_2 and 10% H_2O at 750 °C for 30 h.

The activities of both the aged and unaged catalyst are summarized in Fig. 1 and Table 2. The T_{50} values of the fresh catalyst with regard to the oxidation of CO and C_2H_4 are 192 and 203 °C, respectively, and its T_{90} values are 203 and 224 °C. These results demonstrate that the catalyst exhibits high activity at relatively low temperatures, such that its activity will increase rapidly after engine ignition, allowing complete conversion of the exhaust.

In the case of the aged catalyst, the T_{50} values for CO and C_2H_4 are 224 and 229 °C, and the T_{90} values are 235 and 241 °C, respectively. Compared with the fresh catalyst, these values indicate relatively little increase in either T_{90} or T_{50}, and thus complete conversion can still be rapidly achieved after ignition. These results indicate that the catalyst possesses both high catalytic activity and excellent aging resistance.

The conversion of SO_2 to SO_3 over the catalyst at 350 °C was also investigated, and the results show that these conversions are 22.5% for the fresh material and 13.2% for the aged catalyst.

As noted above, DOCs can also be used to remove the SOF in the exhaust of diesel vehicles, and the results concerning the catalytic conversion of the SOF over fresh and aged catalyst are presented in Table 3. The standardized exothermic peak areas in this table show the catalyst exhibits greatly improved activity for the catalytic combustion of the SOF at significantly decreased temperatures. The data show that the catalyst may begin to convert SOF at temperatures as low as 140 °C and also that the catalyst exhibits generally high performance.

The test results obtained using the diesel oxidation catalyst in a domestic IV YC4F-type diesel engine are presented in Table 4. Comparison of these data with the Euro V emission standard shows that 99% CO conversion is achieved, resulting in a CO level approximately 1000 times lower than the Euro V emission standard, and almost 100% conversion of C_2H_4 is achieved, equal to a level about 100 times lower than the Euro V standard.

The excellent catalytic properties exhibited by this catalyst are closely associated with the higher specific surface of the support material and the outstanding oxygen storage performance of the ceria-zirconia alumina material. As a result, the oxidation catalyst prepared in this study possesses both high activity and high selectivity, and its application in diesel engines will allow exhaust emissions of vehicles in China to meet higher standards.

Table 4
Diesel engine emission results with and without DOC, compared with Euro V emission standards.

Test	Emissions (g/kWh)	
	CO	HC
Euro IV emission standards	0.5	0.23
Emissions without DOC	0.74	0.20
Emissions with DOC	0.004	0.002
Conversion with DOC (%)	99%	~100%

Test conditions: domestic IV YC4F-type diesel engine, emissions 2.659 L, ESC-13 operation mode cycle.

Graphical Abstract

A novel diesel oxidation catalyst with low SO₂ oxidation activity and capable of meeting Euro V emission standards

CHEN Yongdong *, WANG Lei, GUAN Xiaoxu, TANG Shuihua, GONG Maochu, CHEN Yaoqiang *
Southwest Petroleum University; Sichuan Zhongzi Exhaust Purge Co., Ltd.; Sichuan University

A high performance diesel oxidation catalyst was prepared which demonstrated the ability to meet the Euro V standard for HC and CO exhaust emission content requirements.
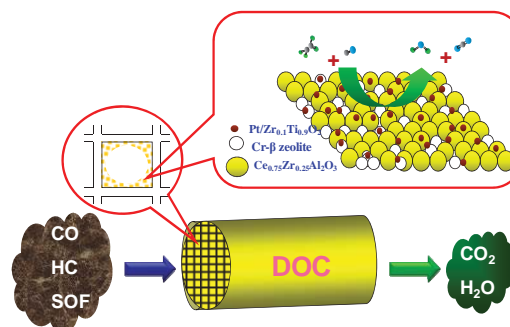
References

[1] Nejar N, Makkee M, Illán-Gómez M J. *Appl Catal B*, 2007, 75: 11
[2] Chin J Y, Batterman S A, Northrop W F, Bohac S V, Assanis D N. *Energy Fuels*, 2012, 26: 6737
[3] Johnson T V. *SAE*, 2010-01-0301
[4] Uchisawa J, Obuchi A, Nanba T, Hara S, Caravella A, Tango T, Murakami T, Nakagawa H, Kogawa T, Abe A. *Ind Eng Chem Res*, 2012, 51: 719
[5] Wiebengac M H, Kima C H. *Catal Today*, 2012, 184: 197
[6] Zhong F L, Zhong Y J, Xiao Y H, Cai G H, Zheng Y, Wei K M. *Chin J Catal* (钟富兰, 钟喻娇, 肖益鸿, 蔡国辉, 郑勇, 魏可镁. 催化学报), 2011, 32: 1469
[7] Zhang K S, Hu J N, Gao S Z, Liu Y G, Huang X J, Bao X F. *Energy Policy*, 2010, 38: 2934
[8] Yang Zh Zh, Chen Y D, Zhao M, Zhou J F, Gong M Ch, Chen Y Q. *Chin J Catal* (杨铮铮, 陈永东, 赵明, 周菊发, 龚茂初, 陈耀强. 催化学报), 2012, 33: 819
[9] Votsmeier M, Schutze F, Malmberg S, Gieshoff J, Lox E, Kreuzer T. US Patent 7 737 081. 2010
[10] Sampara C S, Bissett E J, Assanis D. *Chem Eng Sci*, 2008, 63: 5179
[11] Kim Y S, Lim S J, Kim Y H. *Res Chem Intermed*, 2012, 38: 947
[12] Yavuz B O, Voss K E, Deeba M, Adomaitis J R, Farrauto R J. US Patent 2005/0 201 916. 2005
[13] Wei X Y, Roth S A. US Patent 2012/0 124 975. 2012
[14] Zhang Z L, Zhang Y X, Mu Z G, Yu P F, Ni X Z, Wang S L, Zheng L S. *Appl Catal B*, 2007, 76: 335
[15] Ueno H, Furutani T, Aono T N N, Goshima H, Kasahara K. *SAE*, 980195
[16] Chen Y X, Jiang Y, Li W Z, Jin R C, Tang S Z, Hu W B. *Catal Today*, 1999, 50: 39
[17] Peng L C, Zhuang J P, Lin L. *J Nat Gas Chem*, 2012, 21: 138
[18] Liu P, Wang Jun, Wei R P, Ren X Q, Zhang X G. *Catal Lett*, 2008, 126: 346
[19] Voss K E, Dettling J C, Roth S, Kakwani R, Lui Y K, Gorel A, Rice G W. US Patent 2003/0 108 465. 2003
[20] Ball D J, Stack R G. *SAE*, 902110
[21] Durán A, Carmona M, Monteagudo J M. *Chemosphere*, 2004, 56: 20
[22] Farrauto R J, Voss K E. *Appl Catal B*, 1996, 10: 29
[23] Andersson J, Antonsson M, Eurenius L, Olsson E, Skoglundh M. *Appl Catal B*, 2007, 72: 71

一种具有低SO₂氧化活性并满足欧V排放标准的柴油车氧化型催化剂

陈永东ᵃ,*，王　磊ᵇ，关小旭ᵃ，唐水花ᵃ，龚茂初ᶜ，陈耀强ᶜ,#

ᵃ西南石油大学油气藏地质及开发工程国家重点实验室, 四川成都610500
ᵇ四川中自尾气净化有限公司, 四川成都610225
ᶜ四川大学绿色化学与技术教育部重点实验室, 四川成都610064

摘要: 制备了具有高性能的稀土储氧材料Ce₀.₇₅Zr₀.₂₅O₂-Al₂O₃, Ti₀.₉Zr₀.₁O₂复合材料和Cr改性的β分子筛(Cr-β分子筛), 并以此制备了单Pt型柴油车尾气净化氧化型催化剂. 低温N₂吸附-脱附、储氧量测试结果表明, Ce₀.₇₅Zr₀.₂₅O₂-Al₂O₃样品具有较大的比表面积和优异的储氧性能, Ti₀.₉Zr₀.₁O₂复合材料也具有优越的织构性能. 催化剂对HC和CO具有较高的催化活性, 可使SOF在140 ℃开始转化, 且具有较低的SO₂氧化活性. 在YC4F国Ⅳ柴油机的测试结果表明, 经该催化剂处理后的尾气排放能够满足欧Ⅴ排放标准对HC和CO排放要求.
关键词: 储氧材料; 钛; 锆; 复合氧化物; 铬改性分子筛; 氧化型催化剂

柴油机技术的巨大进步推动了柴油车行业的迅猛发展, 尤其在石油资源短缺的今天, 柴油车以其经济性、耐久性和优异动力性能而越来越受到人们的青睐. 然而柴油车尾气中含有颗粒物(PM), NO_x, 烃类(HC), CO和SO_2, 其中PM中含有14种高致癌污染物; NO_x经大气光化学反应后将产生地表O_3和过氧化物, 同样为致癌物, 它本身还是产生酸雨的物质之一; HC和CO均为致病物质. 随着柴油车保有量的逐年增加, 对人类健康和环境造成巨大危害[1,2].

净化柴油尾气可采用机内净化和机外净化两种方式. 其中机外净化技术因具有使用便捷和成本低等特点而备受关注. 柴油车尾气机外净化技术包括柴油车氧化型催化剂(DOC), 颗粒物捕获器(DPF), NO_x选择性催化还原(SCR)和四效催化剂(FWC). 各技术依据柴油车尾气中污染物的组成和环境要求可联合使用, 也可单独使用[3]. DOC主要是用于去除柴油车尾气中的HC, CO和PM中的可溶性有机物(SOF)[4].

然而, 柴油车尾气中含有SO_2, 它在催化剂的作用下会氧化形成SO_3, 后者极易与水生成亚硫酸或硫酸乃至硫酸盐, 从而导致催化剂中毒和增加颗粒物的排放[5,6]. 尤其是我国油品质量差[7,8], 目前87%的柴油中S含量超过0.035%, 导致柴油车尾气中的SO_2浓度偏高, 因此适用于中国柴油车尾气净化的DOC必须具有高活性和高选择性, 即对CO, HC和SOF高的活性, 同时对SO_2的氧化活性低.

目前, 欧美、日本等一些发达国家的DOC技术最为成熟, 主要研发集中在Engelhard, Johnson Matthey, Umicore和BASF等少数几家跨国公司. DOC一般以Pt或Pd等贵金属为活性组分, 并负载于载体表面上. 影响DOC催化效率的因素主要有: 催化剂的活性物种、载体材料、发动机工况、燃油的含硫量、排气流速等. DOC早期为Pt/Al_2O_3, 随着排放标准的提高, 要求DOC具有SOF的低温氧化活性, 同时对SO_2具有低的氧化性能, 发展了对SOF具有低温活性的Ce基催化剂组分, 对SO_2具有低吸附性能的含SiO_2, TiO_2和ZrO_2的复合载体和提高HC, CO和SOF冷启动转化性能的分子筛组分, 构成了目前DOC催化剂的基础, 其成分和制备技术已变得相当复杂[9~11].

本文报道了一种高性能柴油车氧化型催化剂及其在YC4F国IV柴油机上的试验结果. 结果表明, 处理后的汽车尾气满足欧V排放标准对HC, CO排放的要求, 且具有高的SOF氧化活性和低的SO_2氧化活性.

目前效果较好的DOC主要由三部分组成[12,13]: Ce基催化剂、耐硫载体负载的Pt催化剂以及分子筛组分. 因此, 本文采用共沉淀法制备$Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3储氧材料(其中$Ce_{0.75}Zr_{0.25}O_2$与Al_2O_3质量比为3:1), 首先将计量的碳酸氧锆溶解于适量浓硝酸中, 再将一定量的$Ce(NO_3)_3 \cdot 6H_2O$和$Al(NO_3)_3 \cdot 9H_2O$的盐溶液, 按计量混合均匀, 加入H_2O_2搅拌30 min, 以氨水-碳酸铵混合溶液为沉淀剂, 采用并流法进行共沉淀, 沉淀完毕后加热搅拌、洗涤、抽滤, 于70 °C干燥24 h, 600 °C焙烧5 h, 得到样品. 将计量的碳酸氧锆溶解于适量浓硝酸中, 再与一定量硫酸氧钛溶液混合均匀, 以氨水-碳酸铵混合溶液为沉淀剂, 采用并流法进行共沉淀, 沉淀完毕后加热搅拌、洗涤、抽滤, 于70 °C干燥24 h, 550 °C焙烧5 h, 制得$Ti_{0.9}Zr_{0.1}O_2$复合氧化物载体. 采用等体积浸渍法制备了Cr修饰的β分子筛, 用一定量的硝酸铬溶液浸渍β分子筛(Si/Al = 25), 于110 °C干燥6 h, 550 °C焙烧5 h, 即制得Cr-β分子筛粉末(其中含Cr 1%).

在美国康塔公司的QUADRASORB SI型N_2自动吸附仪表征材料的织构性质, 用储氧量(OSC)测定装置于200 °C测定储氧材料的储氧量, 结果见表1. 由表可知, 所制$Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3样品具有较大的比表面积和优异的低温储氧性能, 有利于去除SOF[14]. 研究发现, TiO_2和ZrO_2对SO_2的吸附能力较小[15,16]. 因此, 用Ti-Zr复合氧化物作载体可抑制SO_2的吸附, 进而抑制Pt对SO_2的氧化, 以提高催化剂的耐硫性能; 而单独的TiO_2和ZrO_2的比表面积都较小, 不适合用于作载体[17], 本文制备的$Ti_{0.9}Zr_{0.1}O_2$复合材料的比表面积可达94 m^2/g, 适合用于作为负载Pt的酸性载体; 所制Pt/$Ti_{0.9}Zr_{0.1}O_2$催化剂用于去除HC和CO, 具有优异的催化活性和耐硫性能[8]. β分子筛主要用于低温下吸附HC, 从而有利于提高柴油车冷启动时的催化剂效率. 由表1可见, 经Cr修饰后, β分子筛比表面积和孔容几乎没有减少, 且表面酸性增强[18,19], 因而有利于抑制SO_2的吸附, 起到抑制SO_2氧化的目的. 因此, 以上3种材料适合用于作柴油车尾气净化氧化型催化剂的组分.

采用等孔体积浸渍法制备Pt基催化剂. 使用一定量的H_2PtCl_6水溶液分别浸渍到$Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3和$Ti_{0.9}Zr_{0.1}O_2$载体上, 经干燥, 550 °C焙烧5 h得到催化剂粉

末；再和一定量的Cr-β分子筛混合并加入适量的水，球磨制成浆料，取400 cpsi的堇青石蜂窝陶瓷基体(美国Corning公司)浸入浆液，取出后用压缩空气吹出多余的浆液，经干燥，550 ℃焙烧5 h, 得到新鲜催化剂. 该催化剂中 Pt 含量为 1 g/L, $Ti_{0.9}Zr_{0.1}O_2$ 含量为 72.6g/L, $Ce_{0.75}Zr_{0.25}O_2$-Al_2O_3含量为36.3g/L, Cr修饰的β分子筛含量为12.1g/L. 将新鲜催化剂置于管式炉中，在0.02%SO_2-10%O_2-10%H_2O-N_2平衡气的气氛下，于750 ℃老化30 h, 得到老化催化剂.

在连续流动微型反应器中进行催化剂活性测试. 模拟柴油车尾气的组成为：0.112%CO-0.056%C_2H_4-0.07%NO-0.02%SO_2-6%CO_2-10%O_2-10%H_2O-N_2平衡气，反应空速控制在30000 h^{-1}. 由于柴油车尾气温度一般200~400 ℃, 且SO_2氧化成SO_3受到热力学的限制，在高于450 ℃时反应活性一般会降低[20]. 因此，本文用红外分析仪(北京均方理化科技研究所)检测350 ℃时SO_2转化率来评价催化剂抑制SO_2氧化的能力，SO_2转化率越低，催化剂抑制SO_2氧化能力越强；反之亦然. 用FGA-4100型汽车排气分析仪(佛分环保仪器检测设备制造有限公司)检测CO随反应变化的浓度；GC-2001 II型色谱仪(上海市计算技术研究所, Porapak T色谱柱, 氢火焰(FID)检测)测量HC随反应变化的浓度. 其活性测试结果见图1和表2. 其中T_{50}为起燃温度(转化50%时的温度), T_{90}为完全转化温度(转化90%时温度), $\triangle T_1$= T_{90}-T_{50}. 柴油车氧化型催化剂经封装后，在YC4F国4柴油机上检测.

研究表明，SOF主要源于柴油中的润滑油和少量未燃烧的柴油成分[21]. 因此，很多研究者用润滑油替代SOF, 采用TG-DTA联用法模拟催化剂催化氧化SOF的过程[14,22]. 本文将柴油车润滑油代替SOF均匀地负载到催化剂粉末上，使润滑油与催化剂粉末样品质量之比为1:10, 采用TG-DTA法在HCT-2型热重分析仪(北京恒久科学仪器厂)上进行测定，空气流气氛(40 ml/min), 升温速率10 ℃/min. 根据TG-DTA曲线，得出SOF转化率变化规律，结果如图2所示，其活性测试结果见表3. T_i为开始转化温度，T_m为失重最快点温度，T_f为反应终止温度，$\triangle T_2$=T_f-T_i. DTA曲线放热峰面积(μV·℃)除以催化剂中润滑油的质量为相对放热峰面积(μV·℃/(mg lube)); 再除以测试样品的总质量，即为标准放热峰面积

(A)(μV·℃/(mg sample)/(mg lube)). Zhang等[14]的研究表明，标准放热峰面积越大，表明润滑油挥发掉的几率越少，发生催化燃烧的几率越大，催化剂的催化效果越好.

新鲜和老化催化剂样品的活性见图1. 由图1和表2可知，新鲜催化剂对CO和C_2H_4的T_{50}分别为192和203 ℃, T_{90}分别为203和224 ℃, 相应的$\triangle T_1$分别为11和21 ℃, 表明催化剂具有较高的低温活性，起燃后其活性快速上升，尾气迅速完全转化. 耐久性是评价DOC的一个重要指标，Andersson等[23]的研究表明，催化剂在经过670 ℃水热老化15 h后，再通入0.005% SO_2于250 ℃水热老化15 h所得的催化剂，与行驶了160000 km, 尾气中含0.001% S的车辆老化催化剂相似度较高，可以作为合适的实验室DOC老化条件. 然而，中国柴油S含量很高，老化条件应更加苛刻. 因此，本文的老化条件是：0.02%SO_2-10%O_2-10%H_2O-N_2平衡气，于750 ℃老化30 h, 然后测定催化剂的活性. 测试结果如图1所示. 可以看出，经老化后，催化剂对CO和C_2H_4的T_{50}分别为224和229 ℃, T_{90}分别为235和241 ℃, 相应的ΔT_1分别为11和12 ℃, 比老化前有所升高，但幅度不大，仍能在起燃后迅速达到完全转化. 这表明催化剂不仅具有高的催化活性，而且具有优异的抗老化性能. 同时还考察了催化剂老化前后350 ℃时SO_2氧化成SO_3的转化率. 测试结果表明，催化剂老化前后对SO_2的转化率分别仅为22.5%和13.2%. DOC的另一个作用是除去柴油车尾气中的SOF, 新鲜和老化催化剂催化氧化SOF反应活性列于表3. 可以看出，加入催化剂后，SOF的燃烧活性大幅度提高，开始转化温度大幅度提前，新鲜催化剂可使SOF在140 ℃开始转化，表现出优异的催化性能.

所制备的柴油车氧化型催化剂在YC4F国IV柴油机上的检测结果如表4所列，并与欧V排放标准进行了比较. 结果表明，对CO的转化率达到99%, 排放值仅为欧V排放标准的5‰左右；对C_2H_4的转化率接近100%, 排放值仅为欧V排放标准的1%左右，表现出优异的催化性能. 这与该催化剂所用的载体材料具有较高的比表面积和Ce-Zr-Al复合氧化物优异的储氧性能密切相关. 由此可见，本文制备的氧化型催化剂具有高活性和高选择性，它的应用将有助于推动我国柴油车尾气排放向更高标准靠近.