Short Communication

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Fast removal of pollutants from vehicle emissions during cold-start stage

https://doi.org/10.1515/chem-2018-0041
received November 26, 2017; accepted March 2, 2018.

Abstract: Recently, enormous research passion has been devoted to reduce air pollution caused by vehicle emissions. Effective vehicle emission control method is to convert exhaust pollutants by placing catalyst in the exhaust pipe. However, the major stumbling block is that a large portion of emission occurs in the initial 20–30 s during the engine cold-start stage, before catalyst can reach its operating temperature. To address the challenge, herein we developed a catalyst utilizing Pd and Rh as active components, Ce-Zr solid solution as assistant, γ-Al_2O_3 as coating and Fe-Cr-Al as supporter. The catalyst component was optimized (atom ratio of Ce:Zr is 6:4, mass ratio of Pd:Rh is 8:2, total weight of Pd and Rh is 1.2 g/L, pore density is 700 pores/inch^2) and high-frequency electrical heating technique was employed to decrease operating temperature from 400°C to 350°C and improve exhaust conversion efficiency by 78%.

Keywords: Vehicle exhaust; Emission control catalyst; High-frequency electrical heating; Engine cold-start stage.

1 Introduction

Hydrocarbons (HCs), nitrogen oxides (NO_x), carbon oxides (CO), which result from vehicle exhaust and industrial combustion of fossil fuels, are major air pollutants [1–2]. They contribute to a variety of harmful environmental effects, such as smog and acid rain [3–4], and threaten people's life [5]. It is reported that 90% of the pollutant in nine Chinese cities comes from vehicle exhaust, industrial manufacture, coal burning, and vehicle exhaust is the primary pollution source [6]. The reduction of vehicle exhaust has become one of the greatest challenges in environmental protection [7–12].

To date, scientists have developed several traditional vehicle exhaust control methods: electrical heating catalyst, second air injection system, exhaust gas recirculation and upstream catalyst [13–14], to simultaneously convert CO, HCs and NO_x into CO_2, H_2O and N_2, respectively. Among these methods, catalysts require 20–30 s to reach operating temperature (400°C), which causes the emission of 60–80% of HCs and CO [15]. Therefore, it is crucial to find a practical and effective method to shorten the time difference between engine cold-start and exhaust conversion.

Herein, we developed a catalyst utilizing Pd and Rh as active components, Ce-Zr solid solution as assistant, γ-Al_2O_3 as coating and Fe-Cr-Al as supporter, to decrease operating temperature and increase exhaust conversion efficiency. With the optimization of catalyst component and the employment of a high-frequency electrical heating method, the exhaust conversion efficiency was improved by 78%.

2 Experimental

2.1 Materials

Materials included $Pd(NO_3)_2$, $Rh(NO_3)_3$, HNO_3, $Ce_xZr_{(1-x)}O_2$, γ-Al_2O_3 (Sinopharm Chemical Reagent Co., Ltd, AR); $Al_2O_3{\cdot}H_2O$ (Jiangyan Chemicals Co., Ltd, AR); Fe-Cr-Al supporter (Corning Inc.); 10% C_3H_8/N_2, 5000 ppm NO/N_2, 5% CO/N_2 (Shanghai Pujiang Special Gas Industry Co., Ltd.).

Instruments included evaluation device, vacuum extraction unit (East China University of Science and Technology); induction heater (MacDZ-10/380, Shanghai OG Electrical Co., Ltd); thermal imager (Fluke Ti2, Fluke Corporation); NO_x analyzer (Model 42i-HL, Thermo Fisher

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Scientific); gas chromatography (9790, Fuli Analytical Instrument Co., Ltd); ball miller (QM-WX04, Nanjing University); drying oven (LC-223, Shanghai Environmental Equipment Corp.); muffle furnace (KS60-63-160, Shanghai Yifeng Co., Ltd).

2.2 Methods

2.2.1 Preparation

To prepare Pd slurry, $Pd(NO_3)_2$ solution (19.2 g, in concentration of 10%), $Al_2O_3{\cdot}H_2O$ (18.8 g), γ-Al_2O_3 (115.2 g) and Ce-Zr solid solution (28.8 g) were mixed in water (100 g) and stirred (800 rpm, 30 min). HNO_3 (7.4 g, in concentration of 65–68%) was slowly added to the solution until the pH reached 3–4. After adding 30.6 g water, the mixture was milled (1200 rpm, 2 h), in which the content of oxides and Pd in the slurry was 50% and 0.6%, respectively.

To prepare the Rh slurry, $Rh(NO_3)_3$ solution (9.6 g, in concentration of 10%), $Al_2O_3{\cdot}H_2O$ (9.4 g), γ-Al_2O_3 (57.6 g) and Ce-Zr solid solution (14.4 g) were mixed in water (50 g) and stirred (800 rpm, 30 min). HNO_3 (3.7 g) was slowly added to the solution until pH reached 3–4. After adding 15.3 g water, the mixture was milled (1200 rpm, 2 h), in which the content of the oxides and Rh was 50% and 0.6%, respectively.

Pd and Rh slurries were then mixed in a designed ratio to prepare the catalyst. Fe-Cr-Al supporter was cut into 2 cm × 2 cm × 2 cm cubes, washed with a cleaning agent, rinsed with water, annealed in air (750°C, 3 h), and then immersed in the mixed slurry (5 min, under vacuum). The slurry-supporter composite was dried (120°C, 24 h) and calcined (550°C, 3 h). The standard mass of the catalyst should be 810 ± 20 mg, and the content of oxides and metal should be ca. 100 g/L and 1.2 g/L, respectively. If mass was lower than the standard value, a second immersion was necessary. If higher, the catalyst should be discarded.

2.2.2 Instrumentation

The properties of obtained catalysts were evaluated using the instruments shown in Figure 1 (thermocouple was settled at the center of catalysts). A seal test on the pipeline joint was conducted using soap solution before the mix gas was pumped in. The exhaust gas during the engine cold-start stage is composed of CO (1%), C_3H_8 (1000 ppm), NO_x (1000 ppm), O_2 (determined based on the theoretical air-fuel ratio of 14.6), and N_2 (as a supplement), with a total gas flow of 1000 mL/(min·g).

Figure 1: Evaluation device.

In the normal evaluation, the reactor was heated to the setting temperature by an electric furnace (5 °C/min). The catalyst was rapidly heated *via* magnetic heating or *via* electrical heating. The reactants and products were taken after the reactor and remained at a settled temperature for 20 min. The concentration of NO and NO_2 was read out from NO_x analyser, and the concentration of other gases could be calculated from the gas chromatography.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and discussion

3.1 Catalyst Optimization

The simulation exhaust gas during the engine cold-start stage is composed of CO (1%), C_3H_8 (1000 ppm), NO_x (1000 ppm), O_2 (determined based on the theoretical air-fuel ratio of 14.6), and N_2 (as a supplement), with a total gas flow of 1000 mL/(min·g). The atom ratio of Ce:Zr, mass ratio of Pd:Rh, pore density of supporter and light-off temperature (where half of a component was transformed) was utilized to evaluate catalytic properties at low temperature (Figure 2).

Properties of catalysts with different atom ratios of Ce:Zr are depicted in Figure 2a and 2b. The light-off temperatures of CO, C_3H_8 and NO decrease initially and then increase when atom ratio of Ce:Zr increases from 4:6 to 8:2. The light-off temperatures of CO and C_3H_8 reach the lowest point at atom ratio of 6:4 while that of NO reaches its minimum at the atom ratio of 7:3. The results indicate that atom ratio of Ce:Zr should be around 6:4 for the catalyst with a low light-off temperature.

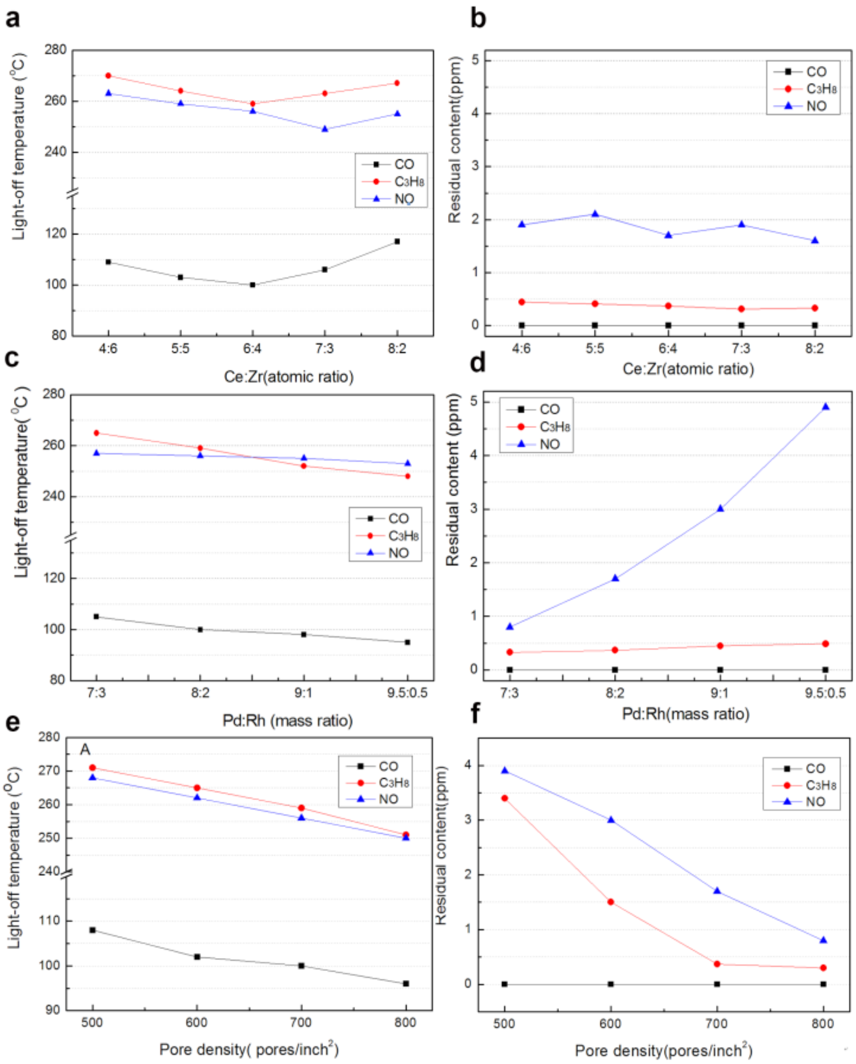

Figure 2: Effect of (a, b) Ce:Zr atom ratio, (c, d) Pd:Rh mass ratio, (e, f) pore density on light-off temperature and residual content.

Figure 2c and 2d indicate influence of the mass ratio of Pd:Rh on the catalytic properties while keeping the total weight of Pd and Rh at 1.2 g/L. The light-off temperatures of the catalysts for CO, C_3H_8 and NO decrease when Pd content increase. This is beneficial for catalytic effect at low temperature, but the excessive increase in Pd content will reduce Rh content of the catalyst and make the concentration of residual NO exceed the legal emission limit. Therefore, the mass ratio of Pd:Rh should be in the range of 8:2 to 9:1 to both lower the light-off temperature and residual gas concentration.

Figure 2e and 2f show the effect of pore density of supporter on the catalytic property in which the mass ratio of Pd:Rh is 8:2, atom ratio of Ce:Zr is 6:4, and total weight of Pd and Rh is 1.2 g/L. The light-off temperatures of catalysts and the concentration of residual gases decrease with the increase of pore density of supporter. The increased efficiency of exhaust conversion is attributed to the increase of contact surface area between catalyst and exhaust. However, if pore density increases excessively, pores will be too small and easily blocked by soot particles. The engine consequently cannot work stably due to the high emissions resistance in the exhaust pipe. Thus, an optimal supporter is a compromise between its pore density and its light-off temperature.

With these data in hand, we managed to determine the optimized catalyst component: atom ratio of Ce:Zr is 6:4, mass ratio of Pd:Rh is 8:2, total weight of Pd and Rh is 1.2 g/L, pore density is 700 pores/inch^2.

3.2 Transformation behaviour

We sought to probe the transformation behaviour of simulation exhaust gas over the optimized catalyst. Results were recorded in Table 1. The operating temperature is 350°C, lower than commercial emission control catalyst with an operating temperature of 400°C [13]. The residual concentration is CO (0 ppm), C_3H_8 (0.37 ppm), NO (1.7 ppm) and NO_2 (1.4 ppm), which meets the strict emission requirement.

Table 1: Residual concentration of simulated exhaust gases over optimized catalyst.

Time/min	t/°C	CO/ppm	C_3H_8/ppm	NO/ppm	NO_2/ppm
0	25	10000.00	1000.00	1000.00	0.00
40	100	10000.00	1000.00	870.21	14.01
	178	2.57	1022.74	642.07	7.11
	215	1.52	1015.85	698.02	11.01
	250	0.00	973.92	657.20	8.01
	300	0.00	98.04	410.30	6.10
177	350	0.00	0.37	1.70	1.40

3.3 Fast heating method

While the optimization of the catalyst can, to some extent, lower the light-off temperature, it is still necessary to shorten the time difference between engine cold-start and the time when catalyst reaches its operating temperature. Therefore, we took a step further to investigate two fast heating methods: magnetic heating and electrical heating.

Magnetic heating was first employed, and the catalyst could reach 350°C within 10 s (under the current of 20 A), but there was a large temperature difference between the outer (350°C) and center (185°C) of the catalyst, due to the magnetic shielding effect. Thus, we utilized high-frequency electrical heating method instead. The heating experiment was conducted with a gas flow (setting temperature of 350°C, current of 20 A, current frequency of 21.9 KHz and air flow rate of 6000 mL/min). Results indicate that both outer and center temperatures reach 350°C in 5 s with an even distribution.

The experiment of simulated exhaust gas over optimized catalyst with high-frequency electrical heating was conducted (Table 2). Compared with Table 1, conversion time (5 s *vs.* 2 h 57 min) and residual concentration of harmful nitrogen oxides, NO (0.9 ppm *vs.* 1.7 ppm) and NO_2 (1.2 ppm *vs.* 1.4 ppm), were significantly decreased, indicating that high-frequency electrical heating of catalyst could indeed improve exhaust conversion efficiency at engine cold-start stage. The residual concentration of NO is plotted to retention time (Figure 3), which shows that conversion efficiency increases by 78% compared with traditional techniques.

Table 2: Residual concentration of simulated exhaust gases over optimized catalyst with high-frequency electrical heating.

Time /s	t_{outer}/°C	t_{center}/°C	CO/ppm	C_3H_8/ppm	NO/ppm	NO_2/ppm
0	9	9	10000	1000	1001	0
1	228	227	—	—	763	9
3	349	347	—	—	131	11
5	350	350	0	0.56	0.9	1.2

t_{outer} – the outer temperature of catalyst, t_{center} – the center temperature of catalyst

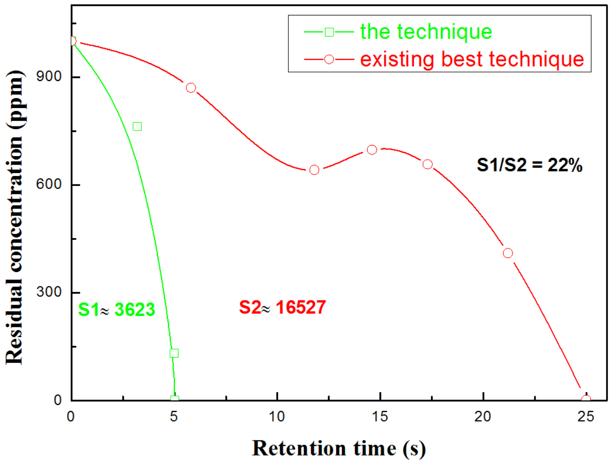

Figure 3: Comparison of NO removal effect between traditional and novel catalyst at engine cold-start stage.

4 Conclusions

To summarize, we developed a novel catalyst for fast removal of pollutants from engine cold-start stage. The catalyst was optimized to the following component: atom ratio of Ce:Zr is 6:4, mass ratio of Pd:Rh is 8:2, total weight of Pd and Rh is 1.2 g/L, pore density is 700 pores/inch^2 with Pd and Rh as active components, Ce-Zr solid solution as assistant, γ-Al_2O_3 as coating and Fe-Cr-Al as supporter. It is corroborated that modified catalyst starts to convert pollutants in 1 s, much faster than traditional catalyst which needs 20–30 s. Moreover, it can decrease operating temperature from 400°C to 350°C and improve exhaust conversion efficiency by 78% with the application of high-frequency electrical heating method. This novel catalyst is reliable and widely applicable, which provides a promising future in the advancement of exhaust conversion technique at engine cold-start stage.

Conflict of interest: Authors state no conflict of interest.

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