journal of environmental sciences 106 (2021) 182–193

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Research on ammonia emissions characteristics from light-duty gasoline vehicles

Yingshuai Liu[1,2], *Yunshan Ge*[2], *Jianwei Tan*[2,*], *Haili Wang*[1], *Yan Ding*[3]

[1] *Weifang University of Science and Technology, Weifang 262700, China*
[2] *National Lab of Auto Performance and Emission Test, School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100081, China*
[3] *Vehicle Emission Control Center, Ministry of Environmental Protection, Beijing 100012, China*

ARTICLE INFO

Article history:
Received 21 August 2020
Revised 17 January 2021
Accepted 18 January 2021
Available online 5 February 2021

Keywords:
Ammonia emissions
Light-duty gasoline vehicles
Three-way catalytic converter
Ambient temperature
Air-fuel ratio

ABSTRACT

In this study, ammonia emissions characteristics of typical light-duty gasoline vehicles were obtained through laboratory vehicle bench test and combined with New European Driving Cycle (NEDC) condition and Worldwide Harmonized Light Vehicles Test Cycle (WLTC) condition. The influence of ambient temperature on ammonia emissions is mainly concentrated in the cold start stage. The influence of ambient temperature on ammonia emission is shown that the ammonia emissions of light-duty gasoline vehicles under ambient temperature conditions (14 and 23°C) are lower than those under low ambient temperature conditions (−7°C) and high ambient temperature conditions (35 and 40°C). The influence of TWC on ammonia emission is shown that ammonia is a by-product of the catalytic reduction reaction of conventional gas pollutants in the exhaust gas in the TWC. Under NEDC operating conditions and WLTC operating conditions, ammonia emissions after the catalyst are 45 times and 72 times that before the catalyst, respectively. In terms of ammonia emissions control strategy research, Pd/Rh combination can reduce NH_3 formation more effectively than catalyst with a single Pd formula. Precise control of the engine's air-fuel ratio and combination with the optimized matched precious metal ratio TWC can effectively reduce ammonia emissions.

Introduction

With the rapid development of urbanization, industrialization, and motorization over the past few decades, China's air pollution problem has become increasingly prominent. In 2012, only 40.9% of 325 prefecture-level and above cities were able to meet the standards based on the revised ambient air quality standards. From December 8 to 10, 2015, severe pollution occurred in Beijing, and the concentration of fine particulate matter increased nearly tenfold within 12 hours. According to the 2018 China Motor Vehicle Environmental Management Annual Report released by the Ministry of Ecology and Environment, mobile sources in 12 cities accounted for more than 20% of local emissions, and emissions from mobile sources in six cities, including Beijing, Shanghai, Hangzhou, Ji-

* Corresponding author.
E-mail: tanjianwei@bit.edu.cn (Jianwei Tan).

https://doi.org/10.1016/j.jes.2021.01.021
1001-0742/

nan, Guangzhou, and Shenzhen, have become the top source of fine particulate matter. At the same time, a large number of studies at home and abroad have shown that ammonia emissions had a significant effect on the formation of secondary particles, and controlling ammonia emissions could significantly reduce the concentration of fine particles. Ammonia contributed 30% to the mass concentration of inorganic secondary aerosols. Also, ammonium sulfate is more specific in summer and ammonium nitrate is more prominent in winter, and it is pointed out that any measures to control fine particulate matter should consider its precursors, including ammonia emission control (Behera and Sharma, 2010). A 50% reduction in ammonia emissions resulted in a 24% decrease in fine particulate concentrations in Northwest Europe, mainly as a result of the ammonium nitrate decrease, and that the effect was more pronounced in winter (Backes et al., 2016). Controlling ammonia emissions in winter can reduce the concentration of fine particulate matter better than controlling sulfur oxides and nitrogen oxides. The cost of cutting ammonia can be lower than 8000 USD per ton, and many current technologies can meet this condition (Robert and Peter, 2017). Ammonia in the atmosphere was the main controlling reason for the formation of secondary particles in the other three seasons except for summer. Although agricultural ammonia emissions are dominant in all anthropogenic ammonia emissions, motor vehicle ammonia emissions in urban areas and winter account for a large proportion (Peng et al., 2000). In Charlotte, North Carolina, and Fresno, California, the proportion of ammonia emissions from motor vehicles in winter reached 73% and 70%, respectively (William et al., 2003).

Motor vehicles mainly include gasoline vehicles and diesel vehicles, gasoline owners are light vehicles, while diesel vehicles are mainly heavy vehicles. In response to stringent emission regulations, gasoline vehicles are equipped with TWC converters to control CO, HC, and NO_x emissions in the exhaust, while diesel vehicles are generally equipped with particulate filters and selective catalytic reduction (SCR) to control particulate and NO_x emissions in the exhaust for better fuel economy. Ammonia emissions from diesel vehicles are mainly caused by ammonia escape from SCR injection of urea, while ammonia emissions from light-duty gasoline vehicles include ammonia directly generated by fuel combustion and ammonia by-products produced by ternary catalysts in the catalytic reaction process to eliminate conventional gas pollutants (CO, HC, and NO_x), mainly the latter (Czerwinski et al., 2010).

Ammonia was present in engine exhaust and increased with the increase of engine load (Baum et al., 2001). Ammonia emissions from gasoline vehicles were not mainly generated by fuel combustion, and the TWC commonly used in light-duty gasoline vehicles produced much more ammonia as a by-product in the catalytic reaction process than the ammonia generated by fuel combustion. Foreign researchers measured ammonia emissions from gasoline vehicle exhaust and found that vehicles equipped with TWC had much higher ammonia emissions than those without TWC (Behera et al., 2013). With the widespread use of TWC converters, the ammonia emitted by cars increased from 2% to 15% in the air area of the whole south bank (Carslaw and Rhys-Tyler, 2013). Vehicles meeting more stringent emission standards emit more ammonia, and a large amount of secondary pollutant ammonia is produced after TWC reaches the ignition temperature (Durbin et al., 2002). Research by Heeb et al. (2006a, 2008) produced similar results. Suarez-bertoa et al. (2014) conducted ammonia emission tests on 9 vehicles meeting Euro V and Euro VI under NEDC conditions. The results showed that the emission levels of these vehicles were similar to those tested more than a decade ago, and the ammonia emission levels of vehicles meeting Euro VI were the highest, reaching 62 and 70 g/km at 22 and −7°C, respectively. However, by raising emission standards and adopting hybrid technology, NH_3 emissions could be reduced (Carslaw and Rhys-Tyler, 2013). This conclusion is consistent with the monitoring data of Kean et al. (2009) in the San Francisco Bay Area of the United States. Aging TWC is more likely to produce NH_3 (Huai et al., 2003). However, ammonia emissions of two light plug-in hybrid and conventional hybrid gasoline vehicles meeting the requirements of Euro V were not significantly different from that of the corresponding conventional vehicles (Suarez-Bertoa and Astorga, 2016).

The following reactions may occur in the ternary catalytic converters Vartuli, 1974; Mordecai et al., 1972; Gandhi et al., 1974), as shown in Eqs. (1)–((3):

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{1}$$

$$2NO + 2CO + 3H_2 \rightarrow 2CO_2 + 2NH_3 \tag{2}$$

$$NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{3}$$

In TWC, in addition to catalytic reactions such as the oxidation of CO and HC and reduction of NO_x, NO_x also reacts with H_2 generated by the reaction of CO and H_2O to produce a by-product of NH_3. Thus, it can be seen that CO and NO_x are precursors to the formation of NH_3. Also, the sulfur content of the fuel will poison the TWC converters and affect the production of ammonia and the conversion of nitric oxide (Wang et al., 2017a). NH_3 concentration after the TWC converter was much higher than the NH_3 concentration before the TWC converter, and the concentration before and after the catalytic converter could differ by two orders of magnitude (Heeb et al., 2006a). Ammonia concentration after the installation of TWC converters was significantly higher than that before the installation of TWC converters, which further confirmed that TWC converters were the main cause of ammonia production. At the same time, ammonia emission corresponding to more radical driving in the test condition was also significantly higher (Vanderlei and João, 2017).

Thus, although the TWC converter can effectively reduce conventional gas pollutants such as CO, HC, and NO_x, it is easy to generate the by-product NH_3 in the catalytic reaction process.

The research on the actual ammonia emissions of light-duty gasoline vehicles has not yet started. This study will focus on the ambient temperature, the influence of TWC converters, noble metal ratio, and air-fuel ratio on the ammonia emissions of light-duty gasoline vehicles. The ammonia emission characteristics of typical light-duty gasoline vehicles were obtained through laboratory bench test and combined with NEDC and WLTC working conditions.

1. Materials and methods

1.1. *Test equipment*

Taking into account the good performance of Fourier transform infrared (FTIR) spectrometer and the need for the measurement of multiple pollutants in the test (Li et al., 2020), this method is mainly selected for automobile ammonia emission testing in the world. To facilitate the comparison of test data, the Fourier infrared spectrometer is selected in this study. Fourier infrared spectrometer (MEXA-6000FT, HORIBA, Japan) measures the NH_3 emission in the exhaust of motor vehicles, and the measurement result is the ammonia emission before treatment. The main parameters of the instrument are range (0–1000) $\times$ 10^{-6}, linearity $\pm$1% full range, zero point noise 0.5%–2.0% full range (FS), zero drift $\pm$1% of full scale within 8 hr, minimum detection limit 0.4 $\times$ 10^{-6}, sampling flow rate 0.1–10 L/min, response time $<$ 5 sec, heating pipe temperature 130°C/205°C, heating module temperature 130°C, warm-up time $<$ 2 hr, and response time $<$ 2 sec.

The specific parameters of the test gasoline in this study are shown in Table 1.

The constant volume sampling (CVS) (CVS-7400T, Horiba, Japan) system produced used in this study contains multiple venturi tubes, which can provide a flow test range of 6–30 m^3/min, and the actual flow value during the test is measured by a flow meter. Also, the system can use a Teflon airbag to collect diluted exhaust and background air (referring to fresh air used to dilute the exhaust). The measurement error of the non-dispersive infrared spectrometer (MEXA-7400LE, Horiba, Japan) analyzer used in this study is less than or equal to $\pm$1.0% of the full scale or $\pm$2.0% of the reading, and the repeatability error does not exceed $\pm$0.5% of the reading. In this study, the electric dynamometer (ECDM-48L-4WD, MAHA, Germany) was used as the chassis dynamometer in the light-duty gasoline vehicles emission measurement system (Roy et al., 2016).

Table 1 – Specific parameters of the test gasoline.

Parameters	Value	Test method
Sulfur content ($\times$ 10^{-6})	10	GB 17930-2016
Calorific value (MJ/kg)	46	GB 384-1988
Octane number	92	GB 17930-2016
Density at 20°C (kg/m^3)	750	GB17930-2016
Kinematic viscosity at 20 °C (mm^2/sec)	0.76	GB 17930-2016
Carbon content	85.9%	SH/T 0656-1998
Hydrogen content	13.4%	SH/T 0656-1998
Oxygen content	<0.2%	ASTM D5622-95
Ash	0.01%	GB 17930-2016

1.2. *Experiment testing system*

The sampling, analysis, detection, and analysis system of conventional pollutants and ammonia emissions used in this study is shown in Fig. 1, which mainly includes constant volume sampling (CVS) system for diluting exhaust gas, chassis dynamometer, conventional pollutant analyzer, ammonia analyzer, etc. During the test, the driver performs driving operations through the prompts of the driving assistance system. The driving assistance system displays the speed of the driving cycle (including the allowable deviation zone), shift information, and time on the screen to guide the driver to control the vehicle in real-time (Tyagi and Ranjan, 2015; Wang et al., 2018).

The ammonia emission sampling point in the test should be as close as possible to the exhaust end to minimize the impact of ammonia absorption due to water vapor condensation.

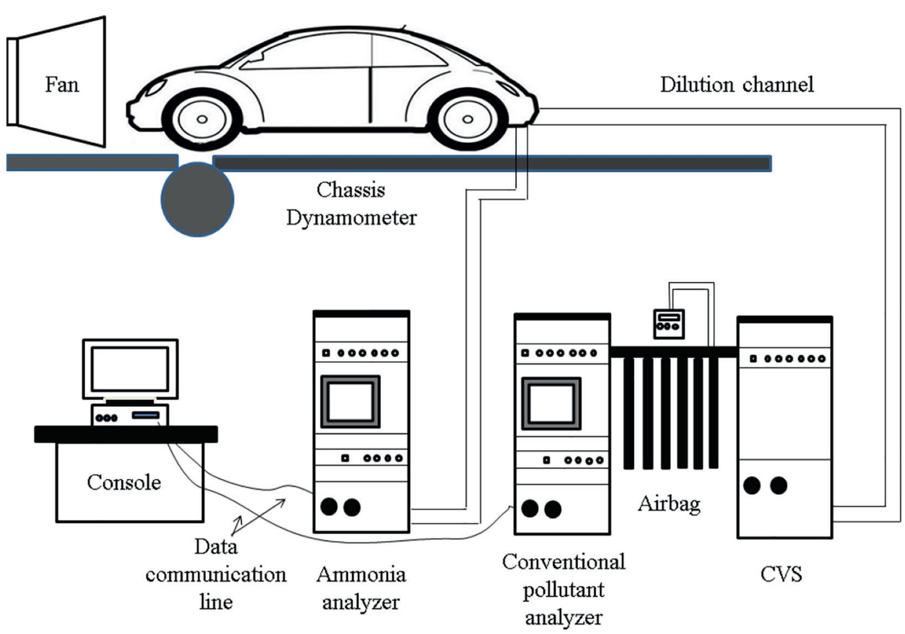

Fig. 1 – Schematic diagram of conventional pollutant and ammonia emission detection system. CVS: constant volume sampling.

To avoid the loss of ammonia adsorption, dissolution, and reaction in the sampling tube as far as possible, and to sample and analyze NH_3 more accurately, the sampling point in the test process is close to the exhaust outlet of the vehicle.

1.3. *Test cycle*

The NEDC was adopted in China's light-duty vehicle emission certification cycle before and after the China V emission regulations. Until the China VI emission regulations, its emission certification cycle was changed to the WLTC. NEDC has been used for a long time in China, Europe, and many other countries in the world. Its total cycle test duration is 1180 sec, corresponding to a total mileage of 11.007 km, and the average speed of the whole cycle is 33.6 km/hr. The total NEDC includes urban driving cycle (UDC) and extra urban driving cycle (EUDC). Among them, UDC represents low speed and low engine load operation of the vehicle, while EUDC represents high speed and load status of the vehicle.

The WLTC was not adopted until the China VI emission standards promulgated by China in 2016 (Roy et al., 2017). Its components include a low-speed section (Low), medium-speed section (Medium), high-speed section (High), and ultra-high-speed section (Extra high). The duration of each section is 589, 433, 455, and 323 sec. Compared with the NEDC, the acceleration and deceleration transient changes are more and more intense, and the steady-state driving state such as constant speed is significantly reduced, during which the maximum driving speed reaches 131.3 km/hr.

Also, from the perspective of idling time and its proportion, WLTC is relatively low in terms of idling time and proportion compared to NEDC conditions, which are 242 sec and 13.4% and 280 sec and 23.7% respectively. Further comparative analysis can find that NEDC operating conditions are relatively simple, easy to repeat, and easy to follow, but obviously, it cannot accurately reflect the instantaneous change of actual road driving. In comparison, WLTC operating conditions cover a larger range of engine speed and load, and high load and high-speed conditions are also reflected, even including extreme driving behavior considerations, which can better reflect actual road driving conditions (Huang et al., 2017).

1.4. *Experiment data processing method*

The error analysis adopts the standard deviation formula (Eq. (4)):

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2} \quad (4)$$

where σ is the standard deviation; N is the total number of samples; i is the serial number of samples; X_i is the value of the i sample; and μ is the arithmetic mean.

The exhausting volume formula (Eq. (5)):

$$Q_{VF} = \frac{1000R_{FC}\rho_g R_{CWF}}{0.866Y_{HC}\rho_{HC} + 0.429Y_{CO}\rho_{CO} + 0.273Y_{CO_2}\rho_{CO_2}} \quad (5)$$

where Q_{VF} (L/sec) represents the exhausting volume; R_{CWF} (87.98%) is the carbon quality percentage in the gasoline; ρ (g/m^3) represent the mass percentage; Y ($\times 10^{-6}$) is the exhaust volume percentage; And the gas standard density, for example, the volume percentages of HC, CO, and CO_2 are 0.866, 0.429 and 0.273, respectively. The diesel density ρ_g is 0.725 kg/L.

1.5. *Experimental scheme*

The exhaust gas discharged from the motor vehicle first passes through the primary filter at the entrance of the sampling pipe to remove the particulates therein, and then the sample gas enters the analyzer after passing through the sampling pump, sampling pipeline, and secondary heating filter. In the test, the tip of the sampling head has zero gas (N_2) and calibration gas (NH_3) injection functions to verify the accuracy of the entire test system. During the sample gas collection process, the temperature of the parts in contact with the sample gas is maintained at about 130°C, and all pipelines are insulated, so the ammonia loss is caused by the condensation of water vapor into the water to dissolve NH_3 can be avoided to the greatest extent.

Conventional pollutants in the exhaust emissions of light-duty gasoline vehicles mainly include carbon monoxide (CO), total hydrocarbons (THC), and nitrogen oxides (NO_x). Also, the exhaust includes a large amount of carbon dioxide (CO_2). After the exhaust gas emitted by light-duty gasoline vehicles flows out of the exhaust pipe, it first enters the full-flow constant volume dilution sampling system (CVS) for dilution. The CVS system fully mixes the exhaust gas and fresh air in the dilution pipeline to dilute and cool the exhaust gas with a higher concentration and temperature. In addition to protecting the test module from high-temperature damage, it also adjusts the exhaust gas concentration to the higher accuracy of the analyzer test module. Test range, to ensure the accuracy and accuracy of test results. Relying on multiple venturi tubes, CVS can ensure that the total flow of exhaust gas and fresh air remains constant (Huang et al., 2018). To avoid the influence of conventional pollutants such as CO and NO_x contained in the background gas on the measurement, these components need to be excluded. Also, the system contains a heat exchanger to ensure that the exhaust gas temperature after dilution does not exceed the legal limit. The diluted exhaust gas enters the conventional pollutant test equipment for real-time measurement, to obtain the real-time concentration of various pollutants in the exhaust gas emitted by light-duty vehicles. The (MEXA-7400LE, Horiba, Japan) analyzer used for CO and CO_2 testing is non-dispersive infrared (NDIR), the THC testing method is flame ionization detector (FID), and the NO_x testing method is chemiluminescence (CLD). Calibration is required before each test to reduce test errors. The electric dynamometer (ECDM-48L-4WD, MAHA, Germany) has a dual-axis design and is suitable for testing front and rear wheel drives. Vehicles can also test four-wheel-drive vehicles. Simulating the driving process of a motor vehicle on an actual road on a chassis dynamometer needs to fully consider the resistance of the vehicle during driving, which mainly includes rolling resistance, air resistance, acceleration resistance, and ramp resistance caused by ramps.

During the vehicle test, the driver drives the vehicle on the chassis dynamometer based on the speed, time, and gear indicated by the system. The time deviation is controlled within plus or minus 1 sec, and the vehicle speed deviation is not more than 2 km/hr.

Table 2 – Different temperature test schemes.

Vehicle number	Engine type	Displacement (L)	Emission standards	Test conditions	Test temperature (°C)
#1	Multi-point EFI	1.5	China VI	WLTC	-7, 14, 23, 35, 40
#2	Direct injection	1.4	China V	NEDC	-7, 25

2. Results and discussion

2.1. *Influence of ambient temperature on ammonia emissions*

The influence of ambient temperature on emissions is quantitatively analyzed by studying the characteristics of conventional pollutants and ammonia emissions of two light-duty gasoline vehicles at different ambient temperatures. The influence of ambient temperature on ammonia emissions is mainly concentrated in the cold start stage. The specific test plan is shown in Table 2.

The results of the WLTC test of #1 are shown in Fig. 2. The ammonia emissions at the ambient temperature of 14 and 23°C are 0.3 and 1.3 mg/km, respectively, which are far smaller than those at low ambient temperature −7°C and high ambient temperature 35 and 40°C. The ammonia emission is the highest at 40°C, reaching 26.9 mg/km; the ammonia emission factor at −7°C is 7.0 mg/km. It can be seen that at a high ambient temperature of 40°C and a low ambient temperature of −7°C, the ammonia emissions are 20 times and 5 times that of 23°C, respectively. The main reason for the large ammonia emissions at a high ambient temperature of 40°C is that the ambient temperature deviates from the laboratory emission certification ambient temperature. The calibration engineer has less experience in calibrating the air-fuel ratio at this ambient temperature, and there is a certain test error. At a low ambient temperature, the engine can ensure reliable ignition by enriching the mixture, which will also cause the CO in the exhaust to raise and increase the ammonia emissions. Therefore, the CO concentration in the exhaust gas shows a similar change pattern to that of ammonia emissions. CO emissions at ambient temperature are lower than those at high and low ambient temperatures, while NO_x emissions have no obvious rules (Choi et al., 2009; Durbin et al., 2002).

The #2 was subjected to low ambient temperature (−7°C) and ambient temperature (25°C) NEDC working condition emission test respectively. The ammonia emissions in low ambient temperature are 6.7 and 1.1 mg/km, respectively. The ammonia emissions in low ambient temperature are more than 6 times that in ambient temperature, which is close to the result of #1. Fig. 3 shows the pollutant emission and engine transient data at two ambient temperatures. It can be seen from the figure that the peak value of ammonia emission in low ambient temperature is higher than that in ambient temperature. It is because the water temperature of the engine is different at two ambient temperatures, it is necessary to calibrate and enrich the mixture to make the water temperature rise rapidly, resulting in different CO emission concentrations in the exhaust gas. CO emission at low ambient temperature is much higher than that at ambient temper-

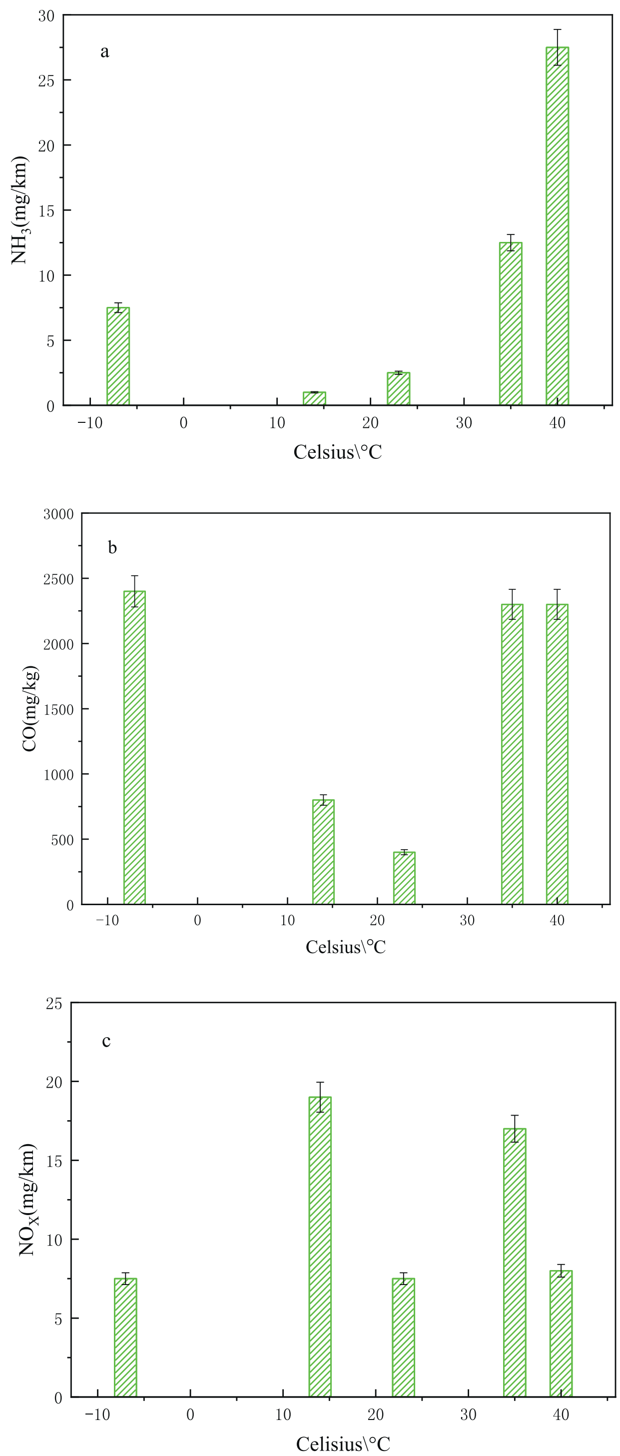

Fig. 2 – (a) Ammonia, (b) CO, and (c) NO_x emission results at different ambient temperatures.

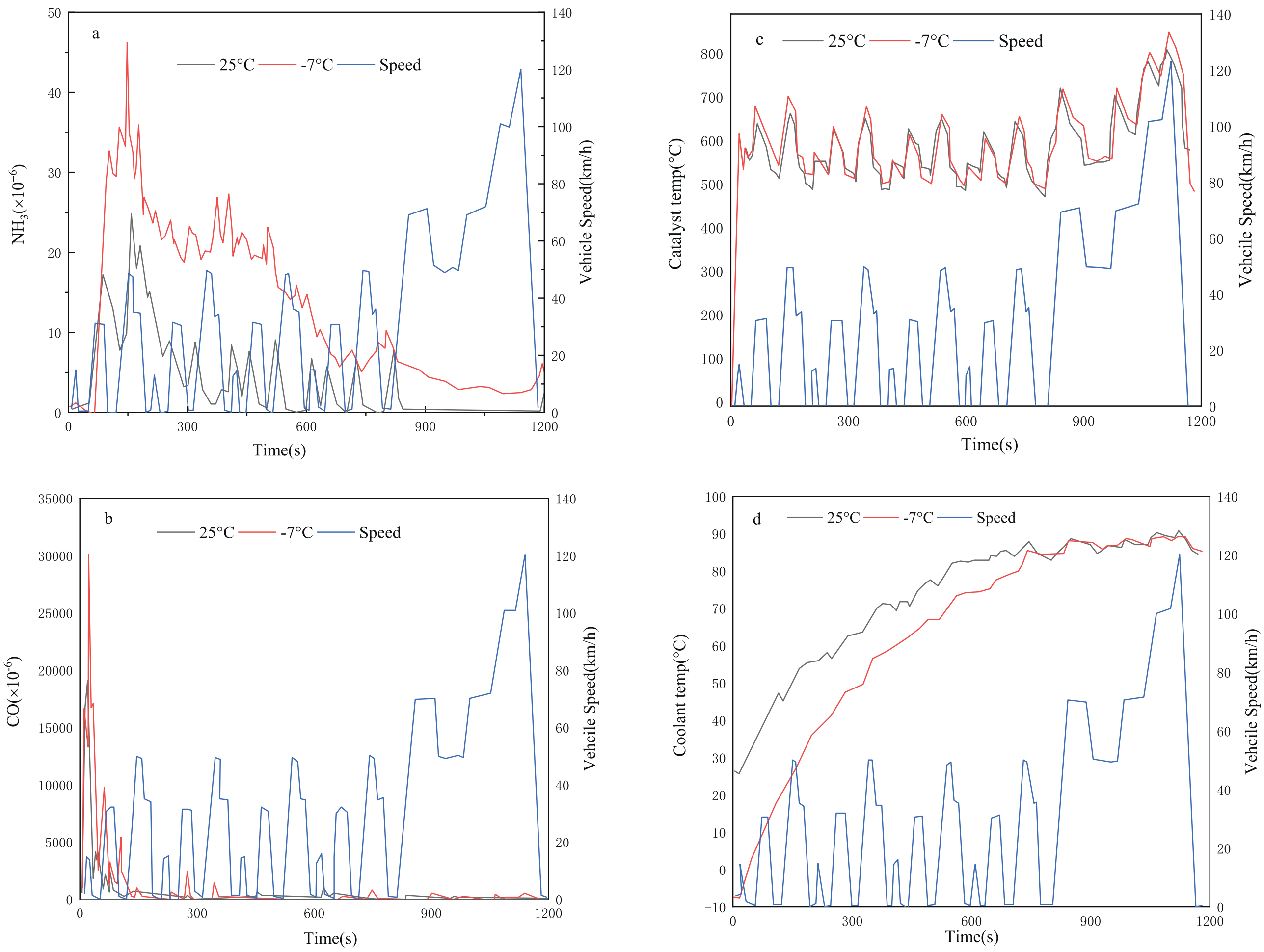

Fig. 3 – (a) Ammonia emissions, (b) CO emissions, (c) TWC temperature, and (d) engine coolant temperature (temp) at two ambient temperatures.

ature. Simultaneously, the peak value of ammonia emission at low ambient temperature is higher than that at ambient temperature. However, the corresponding time of ammonia emission peak at the two ambient temperature is the same, mainly because the time when the catalyst reaches the ammonia generation window exhaust gas temperature (500°C) is the same under the two ambient temperature (Cao et al., 2015).

2.2. *Influence of the TWC on ammonia emission*

The influence of the TWC on the production of ammonia emissions was studied by measuring the ammonia emission concentration before and after the TWC. Test vehicle TWC before and after ammonia emissions are shown in Table 3. Two non-direct-injection light-duty gasoline vehicles that meet the China V emission standards and have a displacement of 1.6 and 1.5 L respectively were installed with sampling pipes before and after the TWC to measure the ammonia emission concentration before and after the TWC. The vehicles were marked as #3 and #4 respectively. #3 was subjected to the hot car test under NEDC and WLTC conditions, and #4

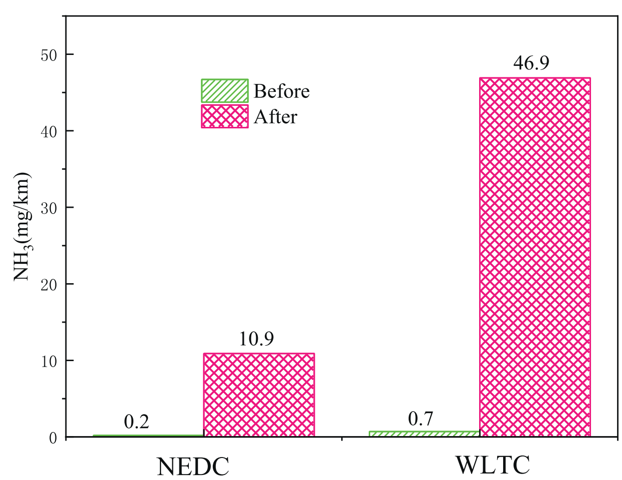

Fig. 4 – Ammonia emissions (#3) before and after TWC under different operating conditions. NEDC: New European driving cycle; WLTC: worldwide harmonized light vehicles test cycle.

Table 3 – Test vehicle TWC before and after ammonia emissions.

Vehicle number	Test conditions	Measuring position	Ave ($\times 10^{-6}$)	Max ($\times 10^{-6}$)	NH_3 (mg/km)
#3	NEDC	Catalysts before	0.41	19.89	0.24
		Catalysts after	21.75	300.80	10.93
	WLTC	Catalysts before	1.87	23.72	0.65
		Catalysts after	70.77	318.30	46.94
#4	WLTC	Catalysts before	0.00	0.51	0.00
		Catalysts after	3.02	62.31	2.97

NEDC: New European driving cycle; WLTC: worldwide harmonized light vehicles test cycle; Ave: average; Max: maximum.

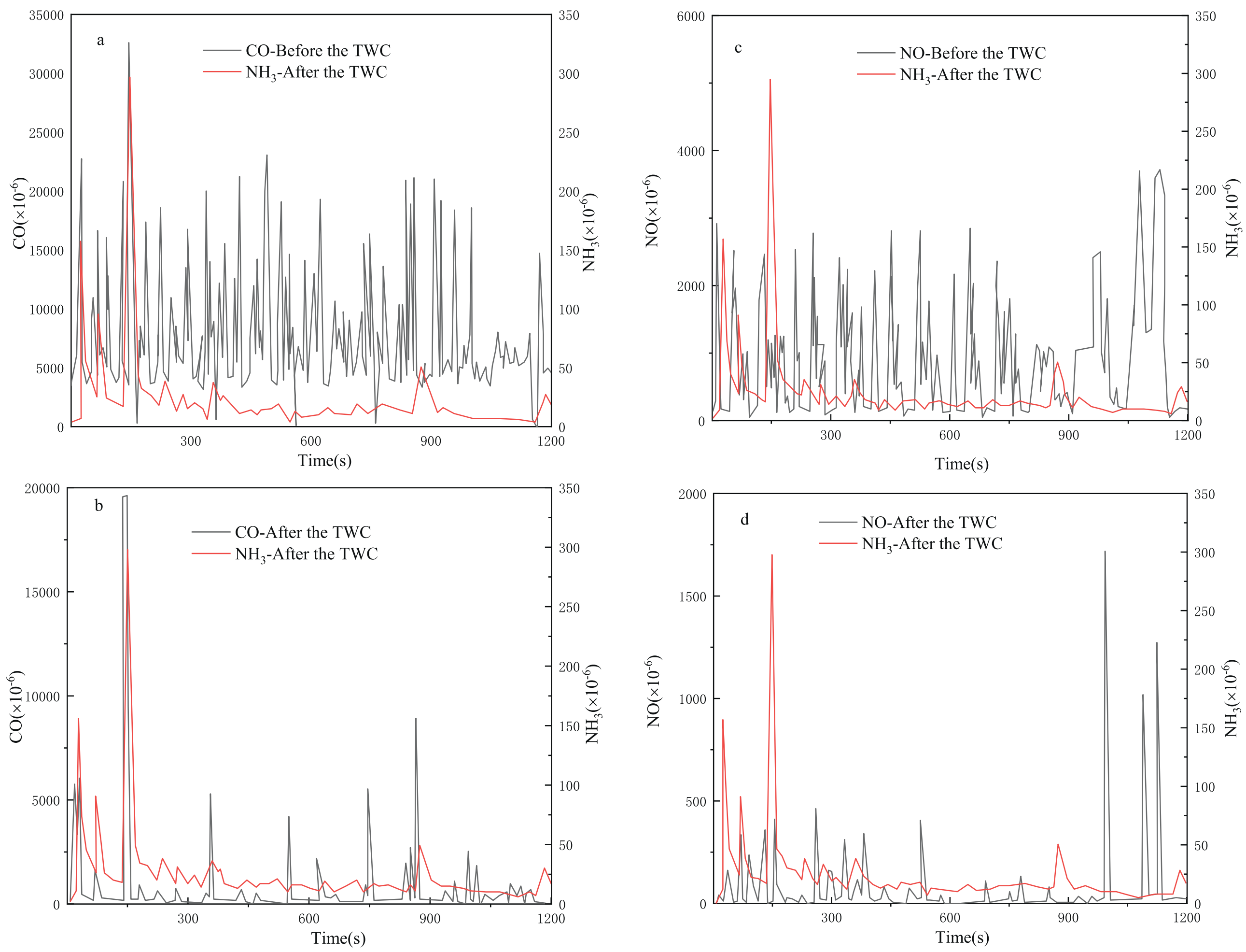

Fig. 5 – (a) CO emissions before the TWC and NH_3 after the TWC, (b) CO and NH_3 emissions after the TWC, (c) NO emissions before the TWC and NH_3 after the catalyst, and (d) NO and NH_3 emissions after the TWC of #3.

was only subjected to the hot car test under WLTC conditions (Choi et al., 2019; Chong et al., 2018).

Fig. 4 shows the results of #3 ammonia emissions before and after the TWC under different working conditions. It can be seen from the figure that the ammonia emissions before the TWC is close to zero under the two working conditions, and the ammonia emission after the TWC is much higher than that before the TWC. Under NEDC working conditions, the ammonia emission after the TWC is 45 times the ammonia emission before the TWC, while the ammonia emission after the TWC under WLTC condition is 72 times the ammonia emission before the TWC. The main reason is that under the action of the noble metal catalyst, CO and water in the exhaust gas react with water gas to generate hydrogen at high temperature, and then hydrogen and NO further generate ammonia under the action of TWC. Therefore, the ammonia emission before the TWC is 0, while the ammonia emission after the TWC increases rapidly. This is consistent with the conclusion of foreign research (Qu et al., 2015; Liu and Frey, 2015).

Fig. 5 show the comparison of CO and NO emissions and ammonia emissions before and after the TWC of #3 under the NEDC condition. It can be seen from the figure that the CO and no emissions in the exhaust after the TWC are far less than those in the front exhaust of the TWC. There is a good cor-

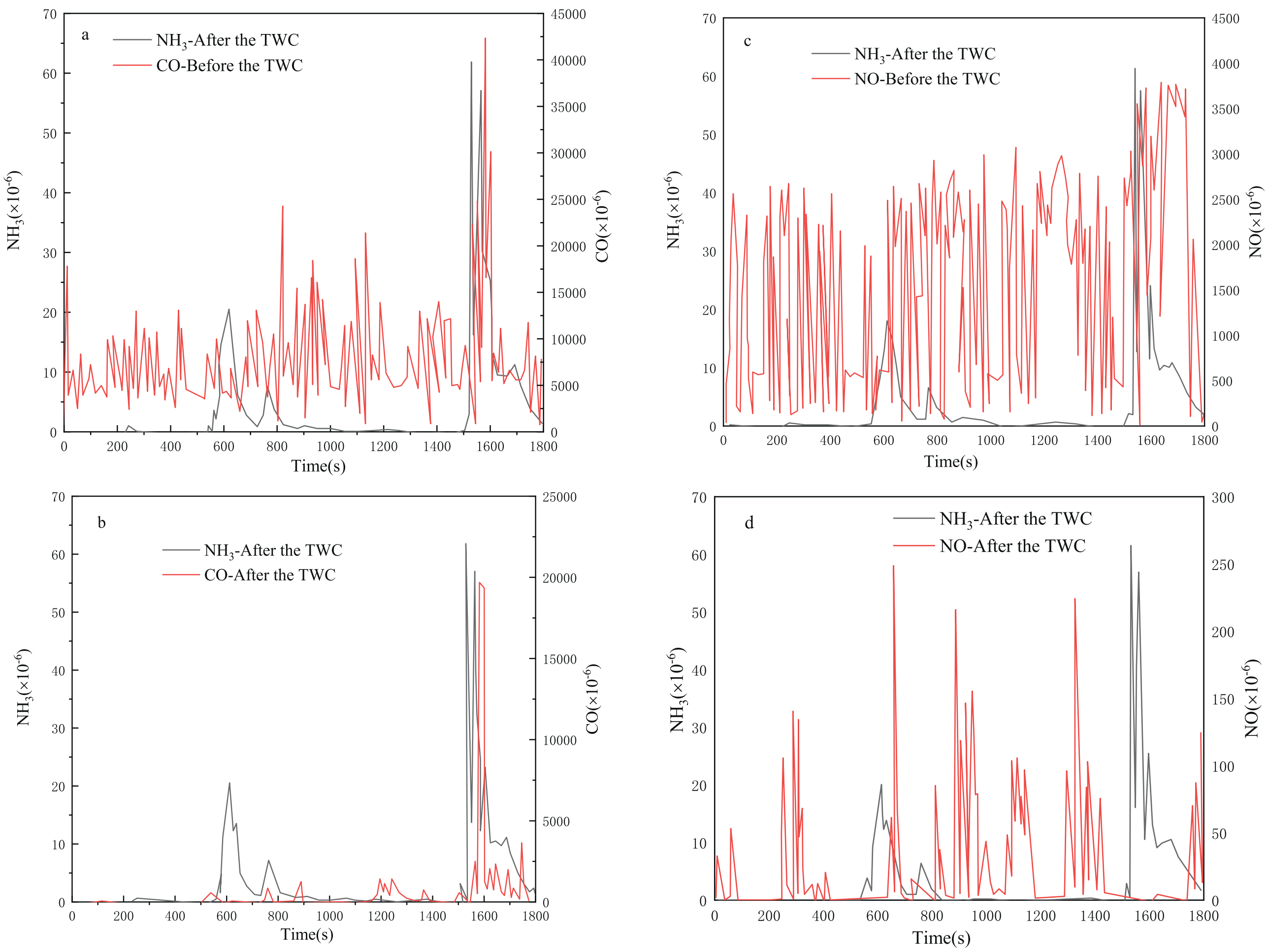

Fig. 6 – (a) CO emissions before the TWC and NH_3 after the TWC, (b) CO and NH_3 emissions after the TWC, (c) NO emissions before the TWC and NH_3 after the catalyst, (d) NO and NH_3 emissions after the TWC of #4.

responding relationship between the CO peak value and the ammonia peak value in the front of the TWC, while the CO emission peak after the TWC is slightly earlier than the NH_3 emission peak because CO affects the generation of hydrogen and then affects the ammonia emissions, and the chemical reaction of ammonia needs a certain duration (Carla et al., 2009; Coelho et al., 2009).

Fig. 6 shows the relationship between the ammonia emissions after the TWC and the CO and NO emissions before and after the TWC under the WLTC condition of the #4 in the warm state. The difference between the #4 and the #3 is that the CO and NO in the exhaust after the TWC of the #4 are relatively small in the hot state of the car, so the NH_3 emission is lower under low-speed conditions; in the ultra-high-speed stage, the CO emission increases, which leads to the increase of NH_3 emission. Combining vehicles #3 and #4 shows that ammonia emissions are mainly produced by the reaction of CO and NO in the exhaust gas in the TWC instead of combustion in the engine cylinder. Also, ammonia emissions have a good correlation with CO in the exhaust gas (Li et al., 2013; Myung et al., 2009).

2.3. *Ammonia emission reduction measures*

2.3.1. *Influence of precious metal content in TWC on ammonia emission*

As ammonia is produced under the action of noble metal catalysts in TWC, the ratio and content of catalysts may have an impact on ammonia emissions. In this study, four TWCs with different noble metal content were set up to study their influence on ammonia in the laboratory sample evaluation device. The parameters of the four matching ratios are shown in Fig. 7.

It can be seen from Fig. 7 that only noble metal Pd leads to the highest production of NH_3. In comparison, the combination of Pd and Rh can significantly reduce the production of NH_3, and the reduced NH_3 production varies from 22.2% to 29.8% relative to the single Pd benchmark. It can also be seen from the data that a parallel comparison of the combination of the two catalysts shows that changing the ratio of Pd and Rh has a small difference in the effect of reducing ammonia, both of which are about a quarter. Excessive palladium or rhodium may increase ammonia emissions.

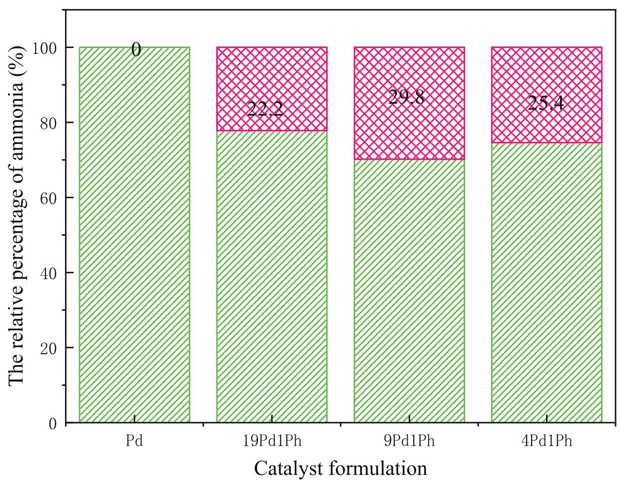

Fig. 7 – Four kinds of catalysts of precious metals.

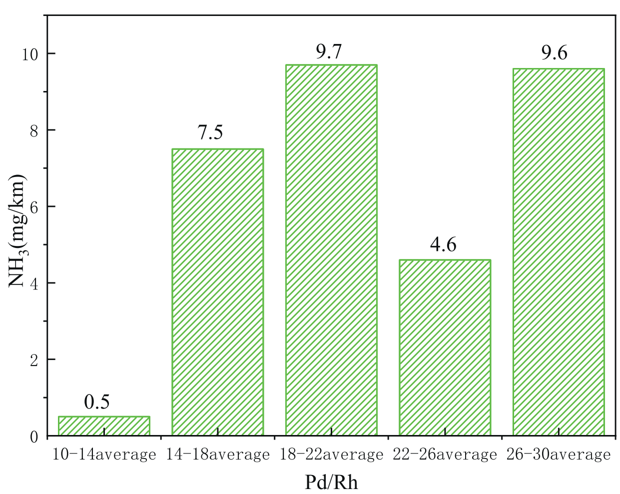

Fig. 8 – Ammonia emission results of different Pd/Rh ratios. 10–14 average, 14–18 average, 18–22 average, 22–26 average, and 26–30 average are the ratio of palladium and rhodium.

2.3.2. *Experiment on the ammonia emission of different TWCs with a precious metal ratio*

All test vehicles only contain palladium and rhodium in the TWC, so according to the proportion of palladium and rhodium from small to large, the models are divided into 5 categories, as 10–14 average, 14–18 average, 18–22 average, 22–26 average and 26–30 average. The relationship between the proportion of palladium and rhodium and ammonia emission is shown in the figure below.

As can be seen from Fig. 8, except that the mean ammonia emission is only 0.5 mg/km when the Pd/Rh ratio is between 10 and 14, the ammonia emission is relatively high and there is no obvious change rule with the change of Pd/Rh ratio.

2.3.3. *Influence of air-fuel ratio on ammonia emission*

In a non-direct injection gasoline vehicle with a displacement of 2.4 L, its influence on ammonia emission was studied by changing the fuel injection pulse width of the engine and then changing the air-fuel ratio. Vehicle parameters are vehicle type ZN1035UCN5, displacement of 2.4 L, emission standards China V, oil supply way multi-point EFI (MPI), Fuel type gasoline, and Load moment of inertia 1360 kg.

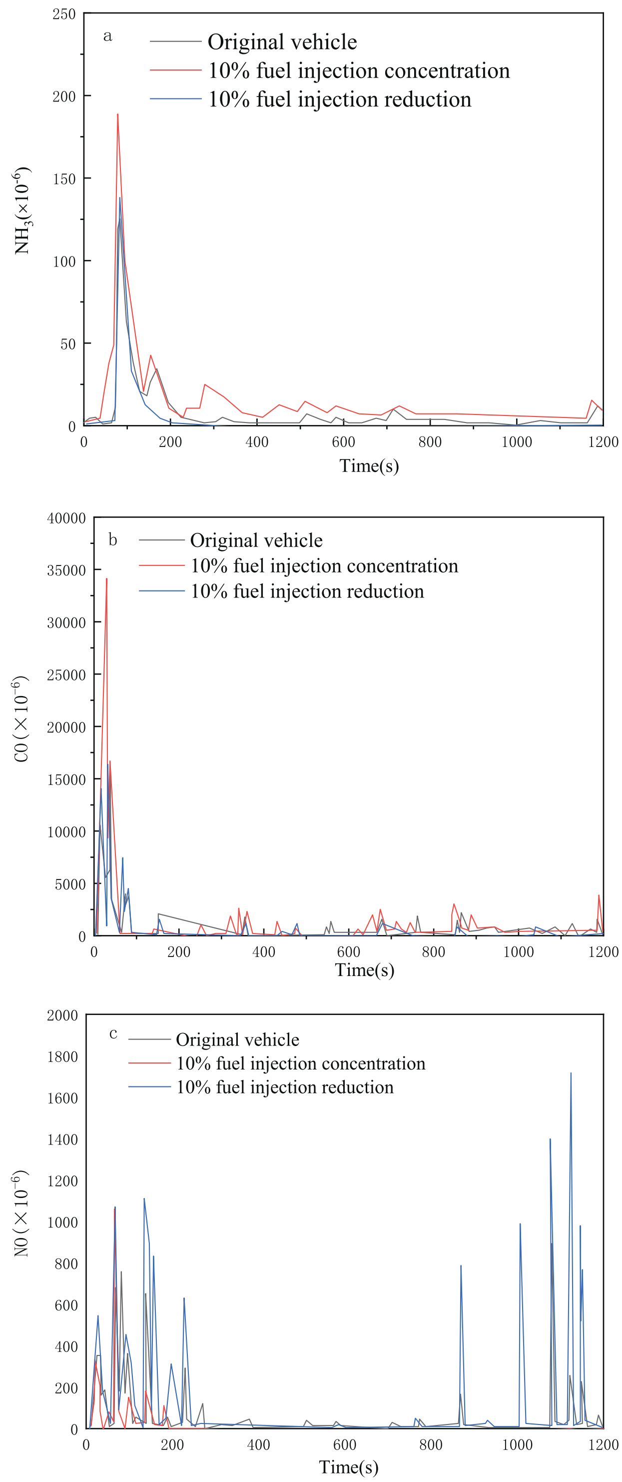

Fig. 9 – (a) Ammonia, (b) CO and (c) NO emissions under different fuel injection quantities.

The original vehicle calibration, 10% fuel injection concentration calibration, and 10% fuel injection reduction calibration tests were carried out respectively. After each calibration modification, the vehicle pretreatment test was carried out before the test began after the vehicle ran more than 100 km on the chassis dynamometer, to ensure the accuracy of the test results. At least two parallel tests were carried out in each calibration state.

Fig. 9 shows the comparison of transient emission data of NH_3, CO, and NO_x under three conditions of different oil injection volumes. Under the mixed gas concentration condition, there is no excess oxygen in the combustion chamber, which inhibits NO_x emission from the exhaust. Therefore, CO will increase in turn with the mixed gas concentration and NO_x will decrease in turn, while ammonia emission is generated in the concentrated mixture area, and ammonia emissions will increase gradually with the increase of mixture.

By reducing the mixture can reduce the exhaust ammonia emissions, but if the air-fuel ratio is too thin, will increase the proportion of NO_x generation, so the engine needs to work in a slightly diluted mixture area, and the increased NO_x emissions in the exhaust can be eliminated through the TWC.

Compared with Pd and Rh mixed catalytic converters, the ammonia emission of single Pd catalytic converters is increased. Actual vehicle statistics and laboratory sample test data show that the ammonia emission concentration is low when the proportion of Rh in Pd/Rh mixed catalyst is between 7%−10%.

Therefore, ammonia emission can be effectively reduced by increasing Rh in the catalyst with appropriate proportion content.

3. Comparative analyses with relevant studies

In this study, we compared and analyzed the ammonia emission factor of vehicles in line with the China VI standards in this paper with previous studies on relevant aspects (Suarez-Bertoa and Astorga, 2016a; Livingston et al., 2009; Heeb et al., 2006a, 2006b, 2008; Huai et al., 2003; Durbin et al., 2002; Bielaczyc et al., 2012, 2015; Woodburn et al., 2013; Suarez-Bertoa et al., 2014; Suarez-Bertoa and Astorga, 2016b; Smith and Black, 1980; Harvey et al., 1983; Wang et al., 2017a, 2017b), and the results are shown in Fig. 10.

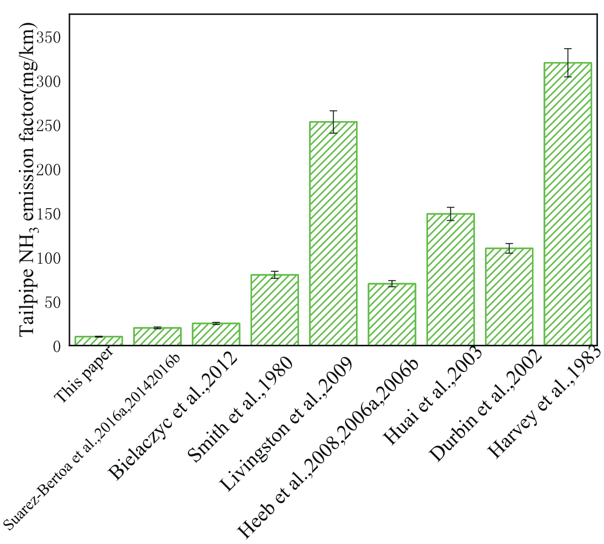

Fig. 10 – Result comparison between this study and other publications.

It can be seen from Fig. 10 that the ammonia emission factor of the light-duty gasoline vehicle in this study is lower than that of the predecessors. Compared with the gasoline vehicles satisfying Euro V tested by Bielaczyc et al. (2012), the gasoline vehicles conforming to The China VI standard have lower ammonia emissions. Also, many previous studies have been conducted under NEDC test conditions. Compared with WLTC, the NEDC operating condition has a large fluctuation in vehicle speed and a small idle speed, without any special regularity. In theory, this property could reduce ammonia emissions.

4. Conclusions

This paper mainly studies the impact of test environment temperature and TWC on the ammonia emission of ignition engine vehicles. The main conclusions are as follows:

(1) The influence of ambient temperature on ammonia emissions is mainly concentrated in the cold start stage. The ammonia emissions of light-duty gasoline vehicles under ambient temperature conditions (14 and 23°C) are less than those under low ambient temperature conditions (−7°C) and high ambient temperature conditions (35 and 40°C). Among them, high ambient temperature 40°C and low ambient temperature −7°C ammonia emissions are 20 times and 5 times that of 23°C ammonia emissions.

(2) Ammonia is a by-product of the catalytic reduction reaction of conventional gas pollutants in the exhaust gas in the TWC. When the catalyst reaches the exhaust gas temperature of about 500°C, the ammonia emissions increase greatly, and the ammonia emissions concentration after the TWC much higher than before the TWC. Under NEDC operating conditions and WLTC operating conditions, ammonia emissions after the TWC are 45 times and 72 times that before the TWC, respectively.

(3) Pd/Rh combination can reduce NH_3 formation more effectively than catalyst with a single Pd formula. However, changing the ratio of Pd and Rh does not have an obvious effect on reducing ammonia emission. Excessive palladium or rhodium may be detrimental to ammonia control.

(4) Precise control of the engine's air-fuel ratio and combination with the optimized matched precious metal ratio TWC can effectively reduce ammonia emissions, which is also the reason why ammonia emissions continue to decrease with the stricter emission control standards, the technological progress of the engine and the precise matching of TWC.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 51508304 and 41275133). The authors are grateful to the China Environmental Monitoring Center and Vehicle Emission Control Center for their cooperation.

REFERENCES

Backes, A.M., Aulinger, A., Bieser, J., Matthias, V., Quante, M., 2016. Ammonia emissions in Europe, part II: how ammonia emission abatement strategies affect secondary aerosols. Atmos. Environ. 126, 153–161.

Baum, M.M., Kiyomiya, E.S., Kumar, S., Lappas, A.M., Kapinus, V.A., Lord, H.C., 2001. Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. Direct on-road ammonia measurements. Environ. Sci. Technol. 35, 3735–3741.

Behera, S.N., Sharma, M., 2010. Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment. Sci. Total Environ. 408, 3569–3575.

Behera, S.N., Sharma, M., Aneja, V.P., Balasubramanian, R., 2013. Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. Environ. Sci. Pollut. Control Ser. 20, 8092–8131.

Bielaczyc, P., Szczotka, A., Swiatek, A., Woodburn, J., 2012. A comparison of ammonia emission factors from light-duty vehicles operating on gasoline, liquefied petroleum gas (LPG) and compressed natural gas (CNG). SAE Int. J. Fuels Lubr. 5, 2012-01–1095 2012-01–1095.

Bielaczyc, P., Szczotka, A., Woodburn, J., 2015. Regulated and unregulated exhaust emissions from CNG fueled vehicles in light of Euro 6 regulations and the New WLTP/GTR 15 test procedure. SAE Int. J. Engines 8, 2015-01–1061 2015-01–1061.

Cao, X., Yao, Z., Shen, X., Ye, Y., Jiang, X., 2015. On-road emission characteristics of VOCs from light-duty gasoline vehicles in Beijing, China. Atmos. Environ. 124, 146–155.

Carla, S., Marc, R., Tiago, F., 2009. Analysis and simulation of 'low-cost' strategies to reduce fuel consumption and emissions in conventional gasoline light-duty vehicles. Energy Convers. Manag. 50, 215–222.

Carslaw, D., Rhys-Tyler, G., 2013. New insights from comprehensive on-road measurements of NOx, NO_2 and NH_3 from vehicle emission remote sensing in London, UK. Atmos. Environ. 81, 339–347.

Choi, H.W., Frey, H.C., 2009. Light-duty gasoline vehicle emission factors at high transient and constant speeds for short road segments. Transport. Res. Part D Transport. Environ. 14, 610–614.

Choi, Y.Y., Lee, J.T., Jang, J.W., Park, S.W., 2019. Effects of fuel-injection systems on particle emission characteristics of gasoline vehicles. Atmos. Environ. 217 116941.1-116941.7.

Chong, H.S., Park, Y.H., Kwon, S., Hong, Y.D., 2018. Analysis of real driving gaseous emissions from light-duty diesel vehicles. Transport. Res. 65, 485–499.

Coelho, M.C., Frey, H.C., Rouphail, N.M., Zhai, H., Pelkmans, L., 2009. Assessing methods for comparing emissions from gasoline and diesel light-duty vehicles based on microscale measurements. Transport. Res. Part D Transport Environ. 14, 91–99.

Czerwinski, J., Heeb, N., Zimmerli, Y., Forss, A.M., Hilfiker, T., Bach, C., 2010. Unregulated emissions with TWC, gasoline and CNG. SAE paper 2010-01-1286.

Durbin, T.D., Wilson, R.D., Norbeck, J.M., 2002. Estimates of the emission rates of ammonia from light-duty vehicles using standard chassis dynamometer test cycles. Atmos. Environ. 9, 1475–1482.

Gandhi, H.S., Shelef, M., 1974. Ammonia formation in the catalytic reduction of nitric oxide. III. The role of water gas shift, reduction by hydrocarbons, and steam reforming. Ind. Eng. Chem. Prod. Res. Dev. 13, 73–80.

Harvey, C., Garbe, R., Baines, T., Somers, J., Hellman, K.H., Carey, P.M., 1983. A Study of the Potential Impact of Some Unregulated Motor Vehicle Emissions. SAE Technical Papers, 830987.

Heeb, N.V., Forss, A.M., Bruehlmann, S., Luescher, R., Saxer, C.J., Hug, P., 2006a. Three-way catalyst-induced formation of ammonia-velocity- and acceleration-dependent emission factors. Atmos. Environ. 31, 5986–5997.

Heeb, N., Saxer, C.J., Forss, A.M., Brühlmann, 2006b. Correlation of hydrogen, ammonia and nitrogen monoxide (nitric oxide) emissions of gasoline-fueled euro-3 passenger cars at transient driving. Atmos. Environ. 40, 3750–3763.

Heeb, N.V., Saxer, C.J., Forss, A.M., Brühlmann., S., 2008. Trends of NO-, NO_2-, and NH_3-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars. Atmos. Environ. 10, 2543–2554.

Huai, T., Durbin, T.D., Miller, J.W., Pisano, J.T., Norbeck, J.M., 2003. Investigation of NH_3 emissions from New technology vehicles as a function of vehicle operating conditions. Environ. Sci. Technol. 37, 4841–4847.

Huang, C., Tao, S., Lou, S., Hu, Q., Wang, H., Wang, Q., et al., 2017. Evaluation of emission factors for light-duty gasoline vehicles based on chassis dynamometer and tunnel studies in Shanghai, China. Atmos. Environ. 169, 193–203.

Kean, A.J., Littlejohn, D., Ban-Weiss, G.A., Harley, R.A., Kirchstetter, T.W., Lunden, M.M., 2009. Trends in on-road vehicle emissions of ammonia. Atmos. Environ. 8, 1565–1570.

Li, S., Lang, J., Zhou, Y., Liang, X., Chen, D., Wei, P., 2020. Trends in ammonia emissions from light-duty gasoline vehicles in China, 1999-2017. Sci. Total Environ. 700 134359.1-134359.9.

Li, T., Chen, X., Yan, Z., 2013. Comparison of fine particles emissions of light-duty gasoline vehicles from chassis dynamometer tests and on-road measurements. Atmos. Environ. 68, 82–91.

Liu, B., Frey, H.C., 2015. Variability in light-duty gasoline vehicle emission factors from trip-based real-world measurements. Environ. Sci. Technol. 49 (20), 12525–12534.

Livingston, C., Rieger, P., Winer, A., 2009. Ammonia emissions from a representative fleet of light and medium-duty vehicles in the California south coast air basin. Atmos. Environ. 43, 3326–3333.

Mordecai, S., Gandhi, H.S., 1972. Ammonia formation in catalytic reduction of nitric oxide by molecular hydrogen. II. Noble metal catalysts. Ind. Eng. Chem. Prod. Res. Dev. 11, 393–396.

Myung, C.L., Lee, H., Choi, K., Lee, Y.J., Park, S., 2009. Effects of gasoline, diesel, LPG, and low-carbon fuels and various certification modes on nanoparticle emission characteristics in light-duty vehicles. Inter. J. Automotive Technol. 10, 537–544.

Peng, Y.D., Yang, M.Z., Shen, L.X., 2000. Beijing ammonia source emission and its impact on the formation of secondary particles. Environ. Sci. 21, 101–103.

Qu, L., Li, M.L., Chen, D., Lu, K.B., Jin, T.S., Xu, X.H., 2015. Multivariate analysis between driving condition and vehicle emission for light-duty gasoline vehicles during rush hours. Atmos. Environ. 110, 103–110.

Robert, W.P., Peter, J.A., 2017. Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the Eastern United States. Environ. Sci. Technol. 41, 380–386.

Roy, A., Choi., Y, 2017. Effect of ambient temperature on species lumping for total organic gases in gasoline exhaust emissions. Atmos. Environ. 152, 240–245.

Roy, A.A., Sonntag, D., Cook, R., Yanca, C., Schenk, C., Choi, Y., 2016. Effect of ambient temperature on total organic gas speciation profiles from light-duty gasoline vehicle exhaust. Environ. Sci. Technol. 50, 6565–6573.

Smith, L., Black, F., 1980. Characterization of Exhaust Emissions From Passenger Cars Equipped With Three-Way Catalyst Control Systems. SAE Technical Papers, 800822.

Suarez-Bertoa, R., Zardini, A., Astorga, C., 2014. Ammonia exhaust

emissions from spark ignition vehicles over the new European driving cycle. Atmos. Environ. 43–53.
Suarez-Bertoa, R., Astorga, C., 2016a. Unregulated emissions from light-duty hybrid electric vehicles. Atmos. Environ. 136, 134–143.
Suarez-Bertoa, R., Astorga, C., 2016b. Isocyanic acid and ammonia in vehicle emissions. Transport. Res. Transport Environ. 49, 259–270.
Tyagi, R.K., Ranjan, R., 2015. Effect of heating the catalytic converter on emission characteristic of gasoline automotive vehicles. Int. J. Ambient Energy 36, 235–241.
Vanderlei, B., João, V., 2017. Ammonia emissions from a light-duty vehicle. Transport. Res. Part D Transport. Environ. 53–61.
Vartuli, J.C., Gonzalez, R.D., 1974. Ammonia formation in the catalytic reduction of nitric oxide by hydrocarbons: I. Promotional effects of hydrogen. J. Catal. 3, 470–481.
Wang, X., Ge, Y., Gong, H., Yang, Z., Tan, J., Hao, L., et al., 2018. Ammonia emissions from China-6 compliant gasoline vehicles tested over the WLTC. Atmos. Environ. 199, 136–142.
Wang, C., Xia, W., Zhao, Y., 2017a. New insight into hydroxyl-mediated NH_3 formation on the Rh-CeO_2 catalyst surface during catalytic reduction of NO by CO. Chin. J. Catal. 38, 1399–1405.
Wang, C., Zheng, T., Lu, J., Wu, X., Hochstadt, H., Zhao, Y., 2017b. Three-way catalytic reactions on Rh-based catalyst: effect of Rh/ceria interfaces. Appl. Catal. A Gen. 544, 30–39.
William, B., Viney, P.A., Paul, A.R., 2003. Evaluation and improvement of ammonia emissions inventories. Atmos. Environ. 37, 3873–3883.
Woodburn, J., Bielaczyc, P., Szczotka, A., 2013. Chassis Dynamometer Testing of Ammonia Emissions From Light-duty SI Vehicles in the Context of Emissions of Reactive Nitrogen Compounds. SAE Technical Papers, 2013-01-1346.