

The investigation of emission characteristics and carbon deposition over motorcycle monolith catalytic converter using different fuels

Li-Wei Jia^a, Wen-Long Zhou^a, Mei-Qing Shen^{a,b,*}, Jun Wang^a, Man-Qun Lin^c

^aKey Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering & Technology, Tianjin University, Weijin Road 92#, Nankai district, Tianjin 300072, PR China

^bState Key Laboratory of Engine, Tianjin University, Tianjin 300072, PR China

^cTianjin Motorcycle Technical Center, Tianjin 300072, PR China

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Abstract

The effects of MTBE-blended gasoline and 10% (v/v) ethanol–gasoline blended fuel (E10) on HC, CO and NO_x conversions over catalytic converters were investigated. Two 4-stroke motorcycle engines outfitted with typical three-way catalytic converters were used and regulated emissions were measured according to ECE-40 test cycle. The results show that the influence of E10 on the catalytic conversion is less significant at grinding stages, compared with that of MTBE-blended gasoline, the catalytic conversion, however, decreases remarkably for E10 at the point of 10 000 km. The carbon deposition information in the direction of the radius of two used monolith exhaust catalytic converters was studied by SEM, EPMA, XPS, TG–DTA and FTIR after a 10 000 km test program. The results indicate that carbon deposition occurs first at the center of a converter, gradually extending to its edge. The carbonaceous species are in the form of C_xH_y if the vehicle is fueled with MTBE-blended gasoline, whereas the carbonaceous species are C_xH_yO for E10. The majority of the carbonaceous species are deposited on the precious metal (PM) sites. Further, aromatic rings, alkyl groups and their partial oxidation products are found in the carbonaceous deposit.

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1. Introduction

The emissions of pollutants from motorcycle engines into the atmosphere is a serious problem in China, because of its large number. The estimative number of motorcycle will range from

110 to 120 million in China alone (Yin et al., 2004). With the implementation of EURO motorcycle emission regulations in China, catalytic converters will have to be used to control the motorcycle emissions, and furthermore, the emission control system must be able to maintain a set of performance criteria to ensure the converter system function reliably over 10 000 km.

Currently, 10% (v/v) ethanol–gasoline blended fuel (E10) is combusted widely in China. The

*Corresponding author. Tel./fax: +86 22 27892301.

E-mail addresses: lwjia@tju.edu.cn (L.-W. Jia), mqshen@tju.edu.cn (M.-Q. Shen).

reasons are the facts that it is a major force in the effort to reduce petroleum consumption, harmful pollutants and exhaust emissions in the transportation sectors (He et al., 2003; Hsieh et al., 2002; Jia et al., 2005; Leong et al., 2002; Wu et al., 2004, Pouloupoulos et al., 2001).

However, few studies have been reported on the influence of E10 on HC, CO and NO_x conversions via motorcycle monolith catalytic converter and the formation of carbon deposition.

Carbon deposition is one of reasons leading to auto-exhaust catalyst deactivation (Jia et al., 2005; Shen et al., 2005; Harmsen et al., 2000; Corro et al., 2004). Therefore, it is important to understand the type of the species formed on the deposited carbon. In this study, two motorcycles catalytic converters were selected, which were used to control the emissions from motorcycles fueled with gasoline added with MTBE (common gasoline) or 10% (v/v) ethanol, since both fuels are widely used in China. The influence of E10 on performances of motorcycle catalytic converters reducing regulated pollutants were measured at 0 km (i.e. new tested motorcycle), 1000 km and 10 000 km of operations, respectively. When motorcycle had completed a 10 000 km of operations, the type of species and its quantity of the carbon deposition were characterized as a function of the relative location along the radius of used monolith exhaust catalytic converters using SEM, EPMA, XPS, TG–DTA. In addition, the functional groups of the components in coke residues were analyzed using FTIR, which allows us to determine the impact of the different types of fuel on carbon deposition on the surface of the catalysts. Moreover, according to deposited carbon amount along the axis of monolith converter, we can determine the exhaust flow distribution along the radial direction of the converters.

2. Experimental

2.1. Emission measurement of regulated pollutants

Common gasoline and E10 fuel adopted were purchased from China National Petroleum Corporation (CNPC). The compositions of these two test fuels are described in Table 1. Two new four-stroke motorcycles, HONDA CG125, were as chosen test units with common gasoline and E10 as fuels, respectively. In this experiment, the chassis dynamometer (AVL 20" Motorcycle) used is located in Tianjin Motorcycle Technical Center, China. The

Table 1
The compositions of test fuels

	Common gasoline	E10
Alkene	32.7 vol.%	29.4 vol.%
Benzene	2.3 vol.%	2.1 vol.%
Aromatic	24.5 vol.%	22.1 vol.%
Oxygen	2.5 wt.%	3.4 wt.%
MTBE	10.0 vol.%	0.0
Ethanol	0.0	10.0 vol.%

testings were performed on this chassis dynamometer according to ECE-40 test protocol. At each point of 0, 1000 and 10 000 km, two exhaust gases were sampled from the inlet and outlet of the catalytic converter with constant volume sampling (CVS, CUSSONS, P1800/P1500). Emissions of HC, CO and NO_x for one entire cycle were measured by a flame ionization detector (FID), a non-dispersive infrared analyzer (NDIR) and a chemiluminescent detector (CLD), respectively.

2.2. Investigation of carbon depositions

Two monolith catalytic converters were recovered from the above GC-125 motorcycles, which had completed a 10 000 km-road-testing program using common gasoline and E10 fuels, respectively. In Motorcycle Technical Center, PR China, this road aging was carried out according to GB/T4570-1995, which is the regulation of test protocol of durability for motorcycles and mopeds. A fresh one was intended as a reference. These converters with identical composition were made by GUILIN REECAT using a conventional wash coating technique. A slurry containing zirconia/ceria/bar-ya/ γ -alumina was washcoated on a metallic (Fe20-Cr5Al) monolithic substrate with the same amount of platinum group metal (PGM) (Pd:Pt = 3:1). The contents of washcoat and PGM were 15.0 wt.% and 0.6 vol.%, respectively, relative to the metallic monolithic substrate. Samples, center, transition-layer and edge sections, were obtained by dividing each monolith converter along the same radix with a hacksaw.

SEM, EPMA, TG–DTA, XPS and FTIR were applied for the characterization of coked catalysts. The surface morphology and corresponding elemental analysis were obtained by using a scanning electron microscope (SEM, Quanta 400) in conjunction with an electron probe micro-analyzer (EPMA, INCA). Carbon species were analyzed by X-ray

photoelectron spectroscopy (XPS, PHI-1600ESCA) equipped with a Mg anode (Mg K_{α} = 1253.6 eV) and operated at 15 kV and 250 W. The base pressure in the analysis chamber was controlled below 0.67 mPa. The analyzer pass energy was set at 25 eV. The carbon binding energy (BE) was referenced to the Au4f_{7/2} transition with a BE of 84.0 eV (samples were gold coated prior to analysis). Coked samples were also characterized with thermogravimetric analysis (TGA, Perkin-Elmer TGS-2). These experiments were performed under the conditions of 25–800 °C at the rate of 10 °C min⁻¹ and the air flow rate of 100 ml min⁻¹. The Fourier transform infrared spectroscopy measurements (FTIR) were carried out on a Spectrum GX infrared spectrophotometer, and the samples for the FTIR measurements were pressed into wafers.

3. Results and discussion

3.1. Emission of regulated pollutants

The results of regulated pollutant emissions from motorcycles using gasoline and E10 at 0, 1000 and 10000 km are presented in Table 2. At 0 km, HC, CO and NO_x conversions across the catalytic converter were 79.7%, 66.7% and 41.4%, respectively, if MTBE-blended gasoline was combusted by a 4-stroke motorcycle engine, whereas they were 76.7%, 64.4% and 42.0% for blended ethanol fuel. At the end of grinding stages (1000 km), regulated pollutant emission and corresponding catalysis conversions were improved for both gasoline and E10 fuels. We can conclude that the influence of E10 on the conversion efficiencies of catalytic converter is less significant at grinding stages, compared with MTBE-blended gasoline. When motorcycles had completed a 10000 km test program, catalysis conversions of HC, CO and NO_x from E10 fueled engine decreased remarkably to 19.4%, 19.4% and 15.6%, at the same time they were 69.6%, 45.9% and 39.4%, respectively, for MTBE-blended gasoline. It is obvious that ethanol-blended gasoline gives rise to more negative impact on conversion efficiencies of catalytic converter than MTBE-blended gasoline.

3.2. Analysis of carbon deposition

3.2.1. SEM and EPMA analysis

Figs. 1 and 2 show SEM images of the surface of the used catalyst samples from common gasoline

Table 2
Regulated emissions from motorcycles using common gasoline and E10 at 0, 1000 and 10000 km

	HC	CO	NO _x
<i>Common gasoline</i>			
0 km ^a			
A ^b (g km ⁻¹)	0.74	3.30	0.29
B ^b (g km ⁻¹)	0.15	1.10	0.17
CC ^{d,e} (%)	79.7	66.7	41.4
1000 km			
A ^a (g km ⁻¹)	0.69	3.14	0.28
B ^b (g km ⁻¹)	0.11	0.91	0.15
CC ^c (%)	84.1	71.0	46.4
10000 km			
A ^a (g km ⁻¹)	0.79	3.70	0.33
B ^b (g km ⁻¹)	0.24	2.00	0.20
CC ^c (%)	69.6	45.9	39.4
<i>E10</i>			
0 km			
A ^a (g km ⁻¹)	0.60	2.50	0.31
B ^b (g km ⁻¹)	0.14	0.89	0.18
CC ^c (%)	76.7	64.4	42.0
1000 km			
A ^a (g km ⁻¹)	0.56	2.43	0.29
B ^b (g km ⁻¹)	0.11	0.81	0.15
CC ^c (%)	80.3	66.7	48.2
10000 km			
A ^a (g km ⁻¹)	0.72	3.60	0.32
B ^b (g km ⁻¹)	0.58	2.90	0.27
CC ^c (%)	19.4	19.4	15.6

^a0 km means a new motorcycle.

^bGiven as “emission value from the inlet of the catalytic converter”.

^cGiven as “emission value from the outlet of the catalytic converter”.

^dCatalysis conversion (%) = [(A(inlet) - B(outlet)) / A(inlet)] × 100%.

^eStandard Deviation (SD): ±5%, N = 3.

and E10 fueled motorcycle engines, respectively. In both cases, spherical deposit was formed on the surface of the center sections, with some of them coalescing together. In the transition-layer sections, the deposit is in the form of flakes or floc where sintering happened to some extent. According to Figs. 1(c) and 2(c), it can be seen that there are a few spherules on catalyst edge surface. In sum, these indicate that the morphology of used catalysts underwent a transformation, during the aging progress, which is in a sharp contrast to that of the fresh catalyst sample (as Fig. 3).

The surface elemental analysis of the above samples was performed by EPMA technique.

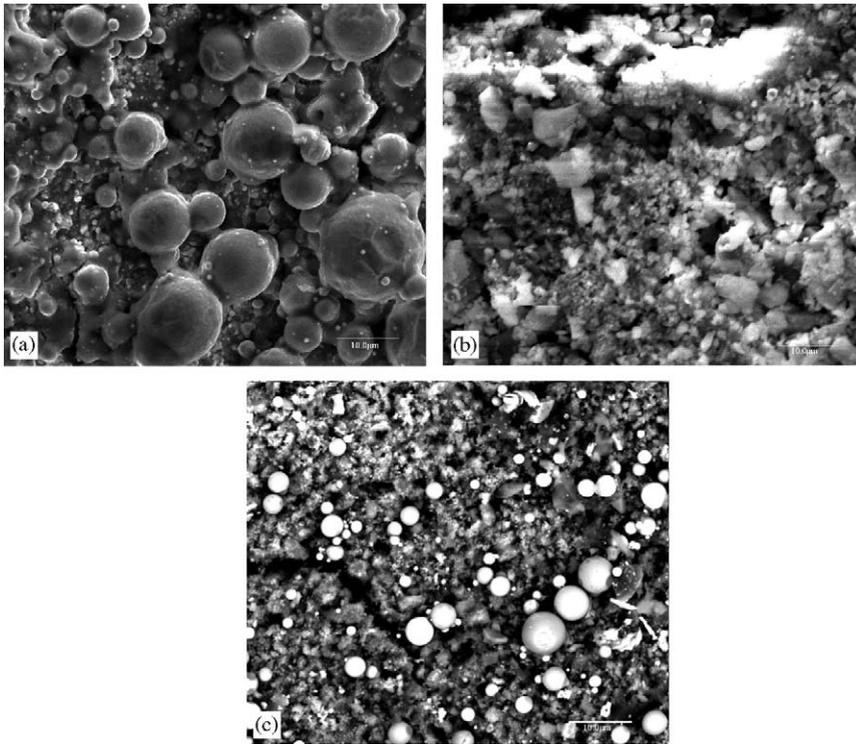


Fig. 1. SEM images of common gasoline fueled exhaust catalyst sample. (a) Center, (b) transition-layer, (c) edge.

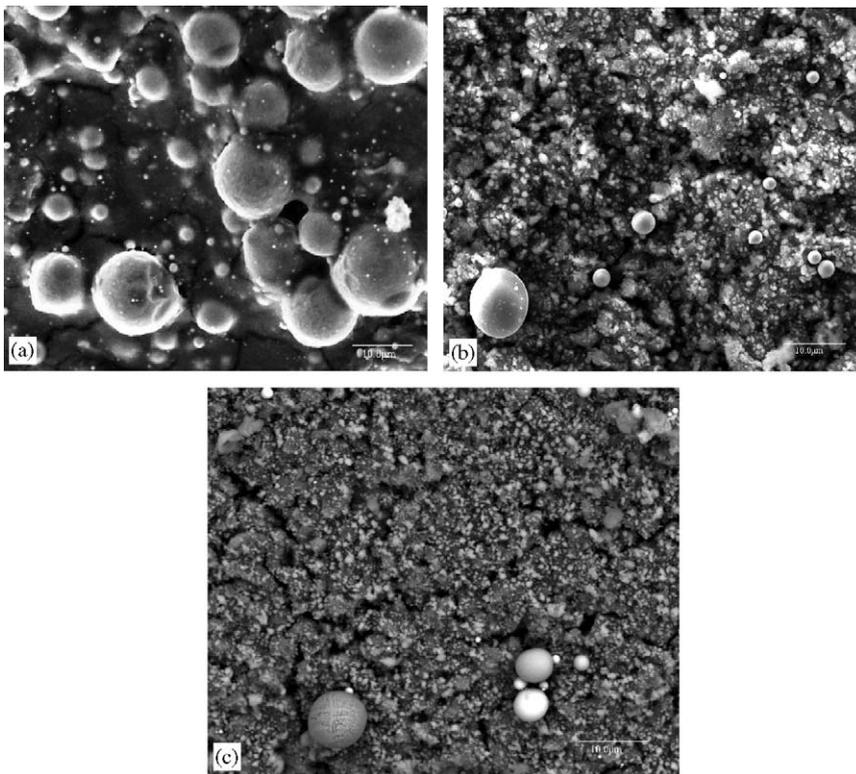


Fig. 2. SEM images of E10 fueled exhaust catalyst sample. (a) Center, (b) transition-layer, (c) edge.

Table 3 presents C/Al (carbon/aluminum) atom ratio at various locations on catalysts for both fuels. For the catalysts fueled with common gasoline, C/Al atom ratio of the center, transition-layer and edge surface sections were 7.21, 3.10 and 2.84, respectively. It is evident that the consequence of carbon deposition quantity is center > transition-layer > edge on radial positions of common gasoline fueled exhaust catalytic converter. From Table 3, we can also see that carbon deposition amount on E10 fueled converter radius has the similar tendency. Namely, the carbon deposition on catalytic converters was not distributed uniformly along radial directions. It can be explained by the fact that exhaust distributions were not uniform when emission gases went through catalytic converters in vent-pipes. By means of appropriate designs of catalytic converters may the radial uniformity of exhaust distributions be gained.

3.2.2. XPS analysis

In this study, all C1s binding energies were compared with the C1s BE value of the fresh

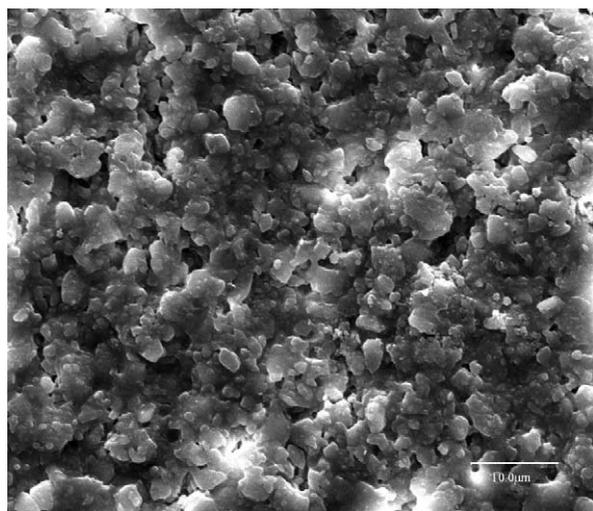


Fig. 3. SEM image of fresh catalyst.

Table 3
C/Al atom ratio on catalysts by EPMA

Sections	Gasoline	E10
Center	7.21	6.12
Transition-layer	3.10	2.72
Edge	2.84	1.74

catalyst surface at 284.6 eV. Based on the literature, the C1s XPS peaks at below 284.6 eV indicate the presence of C–C bonds, and the peaks above 284.6 eV can be attributed to C–O bonds (Effendi et al., 2003; Kvon et al., 1997; Hamoudi et al., 1999). The C1s XPS spectra of the used catalytic converter center, transition-layer and edge sections are shown in Fig. 4, where it can be seen that C1s binding energy of common gasoline fueled exhaust converter differed from that of E10. The C1s XPS peak of the former at center and edge section were observed at 283.7 and 283.6 eV, suggesting that species like C_xH_y were present on the surface of common gasoline fueled exhaust catalyst (Hughes, 1990; Paál et al., 1992; Wild et al., 1997). Whereas, it is abnormal that C1s peak of transition-layer was at about 285.0 eV. It is not distinct for this reason. For E10 fueled exhaust catalytic samples, the C1s BE of center, transition-layer and edge sections corresponded to 284.9, 284.7 and 285.2 eV, respectively, indicating that carbon deposition exists in the form of C_xH_yO on the surface of E10 fueled exhaust catalysts (Rodriguez et al., 2001). Thus, it can be seen that carbon species deposited on auto-exhaust catalyst are influenced by fuel types.

3.2.3. TGA analysis

The location of carbon deposition and its corresponding level were obtained by TGA (Fig. 5 and Table 4). From Fig. 5, it is evident that, for each coked sample, there are two peaks observed during the temperature ramp. A sharp peak appears at a lower temperature followed by a broad peak at a slightly higher temperature. According to previous literature (Mitsunobu et al., 1997; Li et al., 2000; Isarangura na ayuthaya et al., 2003; Pieck et al., 1989; Bond, 1997; Seo et al., 2004), the formation of carbon deposition on precious metal supported catalysts follows the following steps. Hydrogenolysis of hydrocarbons occurs at faces, edges and corners of the metallic sites, forming carbon deposition. Carbon deposition may diffuse through the bulk to reach the interfaces between the noble metal and the support. The C_xH_y species can be further polymerized and form deposit at the acid sites of the support. Furthermore, carbenium ions produced on precious metal sites are combusted at lower temperatures, whereas these sediments on the acid sites are burn-off at higher temperatures. Therefore, it can be concluded that lower temperature peaks in Fig. 5 are due to the coke deposited on platinum group metal particles and the

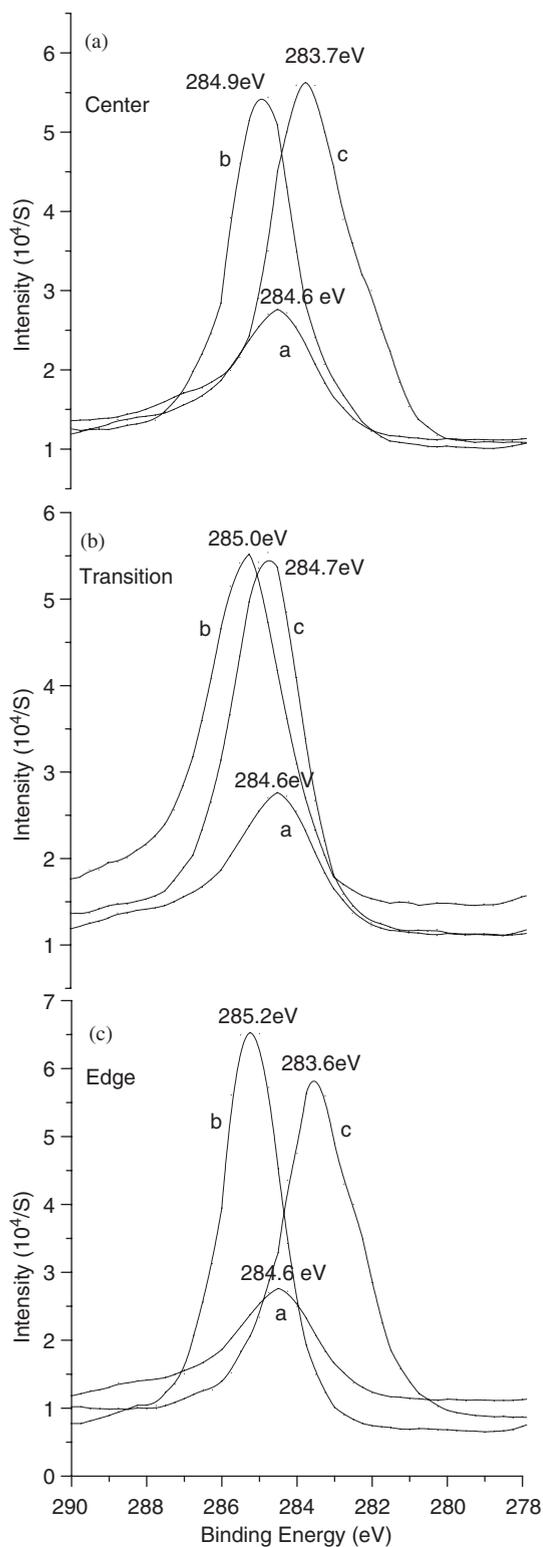


Fig. 4. XPS spectra of used catalysts. (a) Fresh catalyst, (b) E10 fueled exhaust catalyst sample (c) common gasoline fueled exhaust catalyst sample.

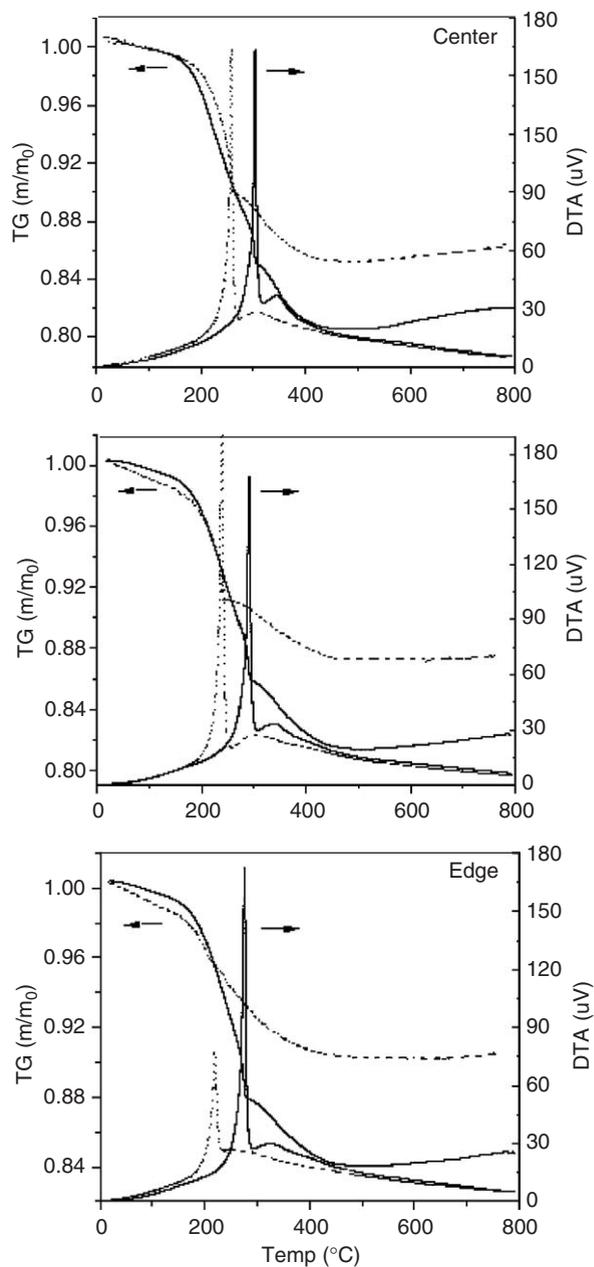


Fig. 5. TG–DTA curves of used catalysts. (...) Common gasoline fueled exhaust catalyst sample, (—) E10 fueled exhaust catalyst sample.

higher ones are the result of carbon formation on the acid sites within washcoat. In addition, the two peak temperatures of common gasoline fueled exhaust catalyst sample were lower than those of E10 fuel. Thus, it appears that the carbon deposit formed with the common gasoline fuel is easier to oxidize compared to that with E10 fuel.

Table 4
The percentage of carbon deposited at different locations

Sections	Total coke weight/sample weight (%)		Coke on precious metal/total coke (%)		Coke on acid sites/total coke (%)	
	Gasoline	E10	Gasoline	E10	Gasoline	E10
Center	15.0	19.9	70.0	77.9	30.0	22.1
Transition	12.6	17.8	73.0	83.7	27.0	16.3
Edge	9.9	15.9	55.6	80.5	44.4	19.5

Based on the TG/DTA results, the distribution of the carbon deposition within the catalyst was calculated as a percentage of the total carbon deposited and is shown in Table 4. It can be seen that, from center to edge sections, the total coke content decreased gradually on both gasoline and E10 fueled catalysts. This result is consistent with that of the above SEM–EPMA analyses. The main reason is the nonuniform distributions of exhaust over catalytic converters in pipes, too. From Table 4, the majority of the carbon species were deposited on the precious metal particles (corresponding to the low temperature peak in Fig. 5). Further, a higher level of carbon deposit was found on the precious metal sites of E10 fueled exhaust catalyst samples. Thus, the carbon deposition formed by the combustion of E10 fuel may result in a more negative impact on the catalytic activity of the converter, which is exactly what we found (Table 2).

There is a difference between total C deposition amount from TG–DTA and surface C from (EPMA). We think that it is attributed to the different characters of these two techniques. The former analyzes the total C deposited in the outside and the inside of washcoats, whereas only C on the surface of catalyst washcoat can be checked by EPMA.

3.2.4. FTIR analysis

The carbonaceous components were analyzed by using FTIR spectroscopy. Fig. 6 shows the FTIR spectra of the center sections of used gasoline and E10 fueled exhaust catalysts. For these two samples, the bands were found at similar positions. The band at 3470 cm^{-1} with very strong intensity indicates the presence of a large amount of –OH groups due to absorption of water vapor in air. The bands at 2963, 2878 and 1270 cm^{-1} are assigned to the characteristic vibration of –CH₂ and –CH groups (Jiang et al., 1993). The band at 1470 cm^{-1} is due to framework vibration absorption of the C=C bonds

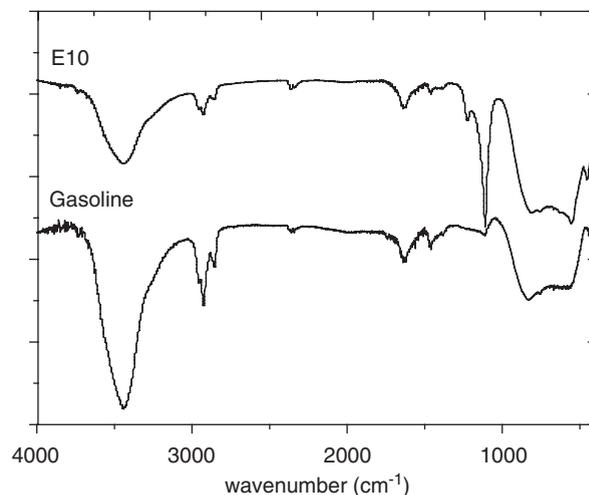


Fig. 6. FTIR spectra of used gasoline and E10 fueled exhaust catalysts.

in aromatic rings (Jiang et al., 2003). The bands at 1651 and 832 cm^{-1} are the results of the vibration of C=C bonds connecting aromatic rings in polycyclic aromatics (Jiang et al., 2003). The band at 1112 cm^{-1} is attributed to stretching vibration of C–O (Wang et al., 1987). Moreover, the strong band at 1112 cm^{-1} indicates the partial oxidation of coke on the surface of E10 fueled exhaust catalyst. This further confirms the result of XPS analysis. Hence, we can deduce that aromatic rings, alkyl groups and their partial oxides exist in the carbon deposition on used gasoline and E10 fueled exhaust catalysts.

4. Conclusions

From the above analysis, the main outcomes can be outlined as follows. When motorcycle equipped with catalytic converter had completed a 10 000 km-road-testing program, catalytic conversions of HC, CO and NO_x from E10 fueled engine decreased drastically, compared with MTBE-blended gasoline.

The quantity of carbon deposition, in the radial direction of the monolith exhaust catalytic converters, follows the following orders: center > transition-layer > edge after 10 000 km test program. Carbon species are C_xH_y and C_xH_yO , respectively, on the surface of gasoline and E10 fueled coked catalyst samples. The majority of total carbon is deposited on precious metal sites, and moreover carbon content on precious metal sites of E10 fueled exhaust catalyst is higher than that of common unleaded gasoline. FTIR confirms the presence of aromatic rings, alkyl groups and their partial oxidation products in carbon deposition.

According to above investigations, we can conclude that carbon deposition is one of the reasons for the main decrease of catalysis conversion for ethanol-blended fueled catalytic converter. To solve the carbon deposition problem, special catalytic converters must be designed for E10 fuel. For example, the element or materials such as some rare metals, alkaline-earth metals exhibiting carbon deposition resistance can be added into the catalyst (Borowiecki et al., 2004; Takeguchi et al., 2003). Additionally, from this study, exhaust distribution on the radial position of is not well-proportioned across some catalytic converters.

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References

- Bond, G.C., 1997. The role of carbon deposits in metal-catalysed reactions of hydrocarbons. *Applied Catalysis A: General* 149, 3–25.
- Borowiecki, T., Denis, A., Gac, W., Dziembaj, R., Piwowarska, Z., Drozdek, M., 2004. Oxidation–reduction of Ni/Al₂O₃ steam reforming catalysts promoted with Mo. *Applied Catalysis A: General* 274, 259–267.
- Corro, G., Fierro, J.L.G., Montiel, R., Bañuelos, F., 2004. Catalytic performance of Pt–Sn/γ-Al₂O₃ for particulates emission prevention. *Catalysis Communications* 5, 547–552.
- Effendi, A., Hellgardt, K., Zhang, Z.G., Yoshida, T., 2003. Characterisation of carbon deposits on Ni/SiO₂ in the reforming of CH₄–CO₂ using fixed- and fluidised-bed reactors. *Catalysis Communications* 4, 203–207.
- Hamoudi, S., Larachi, F., Adnot, A., Sayari, A., 1999. Characterization of Spent MnO₂/CeO₂ Wet Oxidation Catalyst by TPO–MS, XPS, and S-SIMS. *Journal of Catalysis* 185, 333.
- Harmsen, J.M.A., Hoebink, J.H.B.J., Schouten, J.C., 2000. Transient kinetic modeling of the ethylene and carbon monoxide oxidation over a commercial automotive exhaust gas catalyst. *Industrial & Engineering Chemistry Research* 39, 599–609.
- He, B.Q., Wang, J.X., Hao, J.M., Yan, X.G., Xiao, J.H., 2003. A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels. *Atmospheric Environment* 37, 949–957.
- Hsieh, W.D., Chen, R.H., Wu, T.L., Lin, T.H., 2002. Engine performance and pollutant emission of an SI engine using ethanol–gasoline blended fuels. *Atmospheric Environment* 36, 403–410.
- Hughes, R., 1990. *Deactivation of Catalysts*. Sci Press, Beijing, pp. 1–495.
- Isarangura na ayuthaya, S., Mongkolsiri, N., Praserttham, P., Silveston, P.L., 2003. Carbon deposits effects on the selective catalytic reduction of NO over zeolites using temperature programmed oxidation technique. *Applied catalysis B: Environmental* 43, 1–12.
- Jia, L.W., Shen, M.Q., Wang, Jun., Lin, M.Q., 2005. Influence of ethanol–gasoline blended fuel on emission characteristics from a four-stroke motorcycle engine. *Journal of Hazardous Materials A* 123, 29–34.
- Jia, L.W., Zhang, J., Shen, M.Q., Wang, J., Lin, M.Q., 2005. The influence of fuel type on carbon deposition over precious metal containing motorcycle catalysts. *Catalysis communications* 6, 757–761.
- Jiang, Y., Liang, J., Zhao, S., 1993. Properties of coke on ZnHZSM-5 and its effect on aromatization reaction. *Chinese Journal of Catalysis* 14, 134–137.
- Jiang, R.X., Xie, Z.K., Zhang, C.F., Chen, Q.L., 2003. Synthesis of 2,6-Diisopropylaniline by gas-phase amination on Mg–Al spinel-supported Pd–La catalyst. *Chinese Journal of Catalysis* 24, 489–493.
- Kvon, R.I., Boronin, A.I., Shaikhutdinov, Sh.K., Buyanov, R.A., 1997. *Applied Surface Science* 120, 239–242.
- Leong, S.T., Muttamara, S., Laortanakul, P., 2002. Applicability of gasoline containing ethanol as Thailand's alternative fuel to curb toxic VOC pollutants from automobile emission. *Atmospheric Environment* 36, 3495–3503.
- Li, C.L., Novaro, O., Muñoz, E., Boldú, J.L., Bokhimi, X., Wang, J.A., López, T., Gómez, R., 2000. Coke deactivation of Pd/H-mordenite catalysts used for C₅/C₆ hydroisomerization. *Applied Catalysis A: General* 199, 211–229.
- Mitsunobu, I., Tomohiko, T., Shigeo, G., 1997. Suppression of carbonaceous depositions on nickel catalyst for the carbon dioxide reforming of methane. *Applied Catalysis A: General* 177, 15–23.
- Paál, Z., Schlögl, R., Ertl, G., 1992. Photoelectron spectroscopy of polycrystalline platinum catalysts. *Journal of the Chemical Society, Faraday Transactions* 88, 1179–1184.
- Pieck, C.L., Verderone, R.J., Jablonski, E.L., Parera, J.M., 1989. Burning of coke on Pt–Re/Al₂O₃ catalyst activation energy and oxygen reaction order. *Applied Catalysis* 55, 1–10.
- Poulopoulos, S.G., Samaras, D.P., Philippopoulos, C.J., 2001. Regulated and unregulated emissions from an internal combustion engine operating on ethanol-containing fuels. *Atmospheric Environment* 35, 4399–4406.
- Rodriguez, N.M., Anderson, P.E., Wootsch, A., Wild, U., Schlögl, R., Paál, Z., 2001. XPS, EM, and Catalytic Studies of the Accumulation of Carbon on Pt Black. *Journal of Catalysis* 197, 365–377.

- Seo, J.W., Hernadi, K., Mikó, C., Forró, L., 2004. Behaviour of transition metals catalysts over laser-treated vanadium support surfaces in the decomposition of acetylene. *Applied Catalysis A: General* 260, 87–91.
- Shen, M.Q., Jia, L.W., Xu, Q.R., Wang, J., 2005. Influence of fuel types on the performance of auto-exhaust catalyst. *Chinese Journal of Catalysis* 26, 52.
- Takeguchi, T., Furukawa, S.N., Inoue, M., Eguchi, K., 2003. Autothermal reforming of methane over Ni catalysts supported over CaO–CeO₂–ZrO₂ solid solution. *Applied Catalysis A: General* 240, 223–233.
- Wang, Z.M., He, X.X., Sun, D.Q., 1987. *Utility Infrared Spectroscopy*. China Petrochemical Press, Beijing, pp. 2456–246.
- Wild, U., Pfänder, N., Schlögl, R., 1997. *Fresenius' Journal of Analytical Chemistry* 357, 420–425.
- Wu, C.W., Chen, R.H., Pu, J.Y., Lin, T.H., 2004. The influence of air–fuel ratio on engine performance and pollutant emission of an SI engine using ethanol–gasoline-blended fuels. *Atmospheric Environment* 38, 7093–7100.
- Yin, T., Zhao, J., He, W.J., Qiu, P.X., 2004. *Motorcycle Technology* 4, 25–26.