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REACTION BEHAVIOR OF C_6H_6 IN THE THREE-WAY CATALYTIC CONVERTER EQUIPPED A GASOLINE ENGINE

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ABSTRACT: The reaction behavior of C_6H_6 was investigated in a tubular-flow reactor containing a three-way catalyst. Experiments were performed to investigate the effects of coexistence gas components, temperature, gas flow rate and operating age of catalytic converter. The components of C_6H_6, H_2, CO, H_2O, HC, O_2 and N_2 were selected from the gasoline engine exhaust gas. The experimental results show that the oxidation of C_6H_6 was enhanced by the presence of O_2 and CO, while the presences of H_2, HC and H_2O have suppressive effect on the oxidation of C_6H_6 than O_2 and CO. The results reveal that catalyst has lower catalytic oxidation activity for C_6H_6 oxidation at lower temperature, and has higher catalytic oxidation activity for C_6H_6 than CH_4, C_2H_6 and C_3H_8, and decomposition of C_6H_6 via catalyst was similar to the decompositions of C_2H_4 and C_3H_6. The operating age of catalytic converter has lower effect on the oxidation of C_6H_6 with an increase in the operating time of catalytic converter from 0 to 80,000km.

Keywords: C_6H_6, Catalytic Converter, Coexistence Gas, Temperature, Operating Age

1. INTRODUCTION

Volatile chlorinated hydrocarbons such as chloroform, trichloroethylene, aromatic compounds such as benzene, xylene etc. 18 substance are in the substance on the hazardous air pollutants list defined as atmospheric pollutants with long term toxicity. 18 substances is also a substance in hazardous air pollutants list, high detection rates in our living environments, especially in the indoor air. Carcinogenic substance has been demonstrated to 18 types of being measured in benzene only. Benzene was also given priority initiatives substance of atmospheric organic harmful substances in Environment Agency, a revision of the Clean Air Act air quality guideline value less than 3μg/m^3[1]. Automobile exhaust gas, petroleum industry and various combustion systems etc. are the major C_6H_6 emission sources. C_6H_6 is estimated to about 83% in automotive-related source of C_6H_6 [2]. For building measures to prevent air pollution caused by C_6H_6, there is a need to clarify the discharge mechanism from the Automobile. Most modern gasoline engines equipped with three-way catalytic converters that simultaneously convert NOx, CO and HC into non-polluting forms by means of precious metal-based heterogeneous catalyst. However, gasoline engine exhaust contains up 150 different hydrocarbons, except for NOx and CO[3]. Among these, the reactivity of C_6H_6 on the three-way catalytic converter is different with the other components. The three-way catalytic converter varies extremely with the change of driving mode of the automobile, and the operating age of catalytic converter has been pointed out to potentially result in higher pollutant emissions.

The experiments reported here were designed to investigate the reaction behavior of C_6H_6 in the three-way catalytic converter equipped a gasoline engine under different operating conditions. The effect of degradation of the catalytic converter on the C_6H_6 emission is also discussed.

2. EXPERIMENTS

The experimental apparatus is shown in Fig.1, and the reaction tube is shown in Fig.2. The reaction tube consisted of a preheating zone and a reaction zone. To achieve as near isothermal conditions as possible, the temperature of reaction tube was controlled by an electric furnace. The reaction tube was 18mm of inside diameter and 1300mm long. The preheating zone occupied 750 mm of the length and main reaction zone was 250mm in length. The reaction tube housed a commercial catalyst of 17mm outside diameter and 150mm in length used in an automobile. A rapid cooling zone, 10mm inside diameter and 300mm long, below the main reaction zone, was used to halt the reaction at the outlet of the reactor as rapidly as possible. The gas mixture was made up from seven streams (C_6H_6, CO, H_2, HC, H_2O, O_2 and N_2) supplied by calibrated mass controllers. The experiments were carried out for various flow rates of individual stream, using individual control valves so as to keep the concentration at the inlet of the reactor at the stated level. Measurements of C_6H_6, CO, H_2, HC and O_2 concentration were then performed after the temperature of the reaction zone stabilized. The experiments were carried out for the various gas compositions, flow rate and reaction temperature. C_6H_6 and HC were measured using

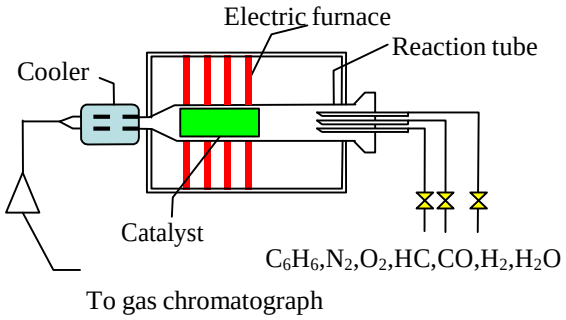

Fig.1 Experimental apparatus

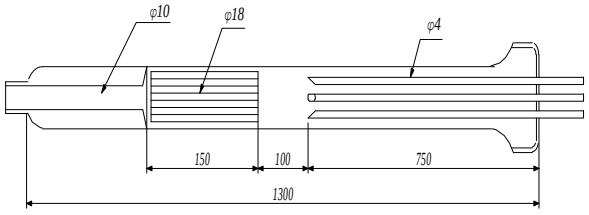

Fig.2 Details of reaction tube

Table 1 Experimental conditions

Gas component and concentration							
C_6H_6: 30ppm, O_2: 0.5%, HC: 1800ppm, CO: 0.2%, H_2: 2.0%							
No.	N_2	C_6H_6	O_2	CO	H_2	H_2O	HC
1	O	O	O				
2	O	O	O	O			
3	O	O	O		O		
4	O	O	O			O	
5	O	O	O				O
6	O	O	O	O	O	O	O
gas flow rate: 10-24(ℓ/min), reaction temperature: 300-700℃, catalyst: 0km, 40000km, 80000km							

aflame ionization detector (FID) gas chromatograph (G2500, Hitachi). The concentrations of O_2, CO, H_2 were measured using a thermal conductivity detector (TCD) gas chromatograph (G5000, Hitachi). The activity of the catalytic converter is expected to be greatly dependent on the operating age. In order to elucidate the operating age with respect to C_6H_6 emission, three three-way catalytic converters were employed in these experiments. The catalytic converters tested are the same type in the composition and water was injected in a manner to pass gas into the distilled water in the reaction tube inlet.

3. RESULTS AND DISCUSSION

3.1 Effects of O_2, H_2, CO, H_2O and HC on the Oxidation of C_6H_6

Initial experiments were carried out with the $C_6H_6/O_2/N_2$ gas system in the absence and presences of H_2, CO and H_2O. The reactions were investigated as the function of gas flow rate (Fig.3). The decomposition of C_6H_6 is 100% in the range from 10

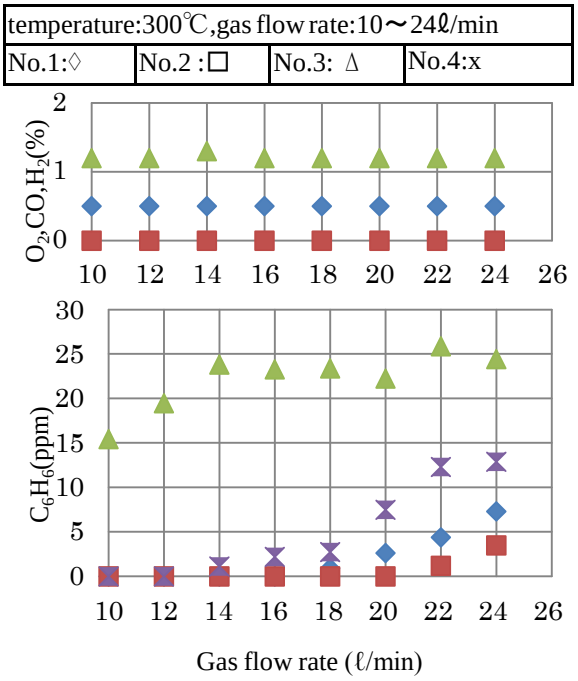

Fig. 3 Effects of O_2, CO, H_2 and H_2O on the oxidation of C_6H_6

ℓ/min to 16ℓ/min and the concentration of C_6H_6 increases from 0ppm to 7ppm as the gas flow rate is increased from 16ℓ/min to 24ℓ/min in the $C_6H_6/O_2/N_2$ gas system. The variation of C_6H_6 concentration in the presence of CO is similar to that shown in $C_6H_6/O_2/N_2$ gas system, however, the emission of C_6H_6 is observed at 22ℓ/min and maximum concentration of C_6H_6 of 4ppm is much lower than that for the $C_6H_6/O_2/N_2$ gas system. In the gas system of H_2O presence, the concentration of C_6H_6 increases from 0ppm to 3ppm with the increase in the gas flow rate from 10ℓ/min to 18ℓ/min, while the concentration of C_6H_6 increase sharply from 3ppm to 13ppm in the range of gas flow rate of 18ℓ/min ～ 24ℓ/min. For the $C_6H_6/H_2/O_2/N_2$ gas system, as the gas flow rate is increased from 10ℓ/min to 14ℓ/min, the concentration of C_6H_6 increases from 15ppm to 24ppm. Above 14ℓ/min, the concentration of C_6H_6 maintains nearly a same valve. In these experimentations, CO was decomposed completely and the concentration of H_2O was not measured.

Fig.4 shows the variation in Paraffin (CH_4, C_2H_6, C_3H_8), olefin (C_2H_4, C_3H_6) hydrocarbon concentrations and benzene (C_6H_6) concentration at the outlet of converter with respect to gas flow rate. The variation in concentrations of CH_4, C_2H_6 and

C_3H_8 show the similar tendency for the change of the gas flow rate, and show the lower decomposition rate at any gas flow rate. the variation in concentrations of C_2H_4, C_3H_6 and C_6H_6 also show the similar tendency for the change of the gas flow rate, however, the concentrations of C_2H_4, C_3H_6 and C_6H_6 show higher decrease in the range of lower gas flow rate.

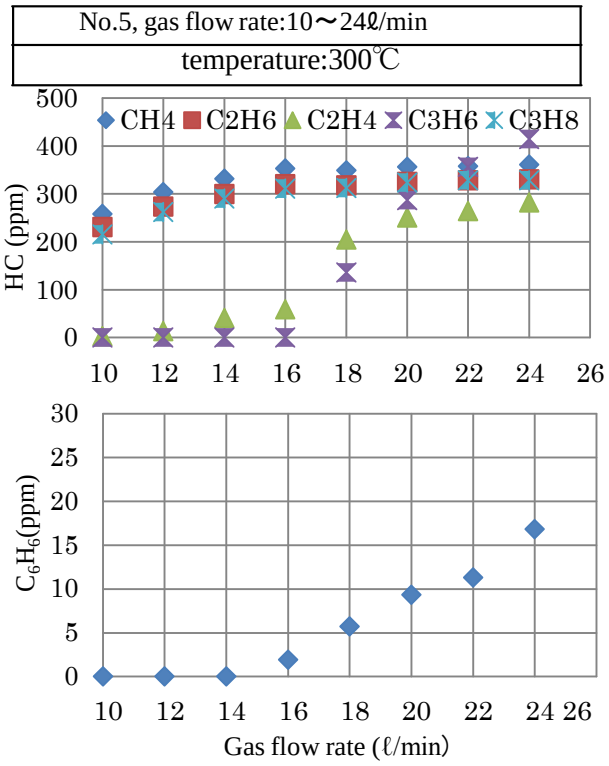

Fig. 4 Effect of HC on the oxidation of C_6H_6

Comparison of the effects of O_2, CO, H_2O, H_2 and HC on the decomposition of C_6H_6 shows that at 300℃, addition O_2, CO, H_2O, H_2 or HC to C_6H_6/N_2 gas system can strongly influence the C_6H_6 decomposition. These also evident that by contrast H_2O, H_2 and HC, O_2 and CO have significant accelerating effect respectively on the decomposition of C_6H_6.

Fig.5 shows effect of coexistence of CO, H_2O, H_2 and HC with $C_6H_6/O_2/N_2$ gas system on the decomposition of C_6H_6. When increasing the gas flow rate from 10ℓ/min to 18ℓ/min, the concentration of C_6H_6 increases from 15ppm to 25ppm. Above 18ℓ/min, the concentration of C_6H_6 maintains nearly a same valve. These results resemble with the variation of C_6H_6 concentration in the $C_6H_6/H_2/O_2/N_2$ gas system, show that the inhibition of H_2 for C_6H_6 degradation is greater than the coexistence of other gas.

3.2 Effect of Temperature on the Oxidation of C_6H_6

Fig.6 shows effect of temperature on the C_6H_6 oxidation in the $C_6H_6/CO/H_2/H_2O/HC/N_2$ gas system. Car exhaust gas temperature will vary with changes in the running speed of the car. Usually, under normal pressure, gasoline catalyst performs

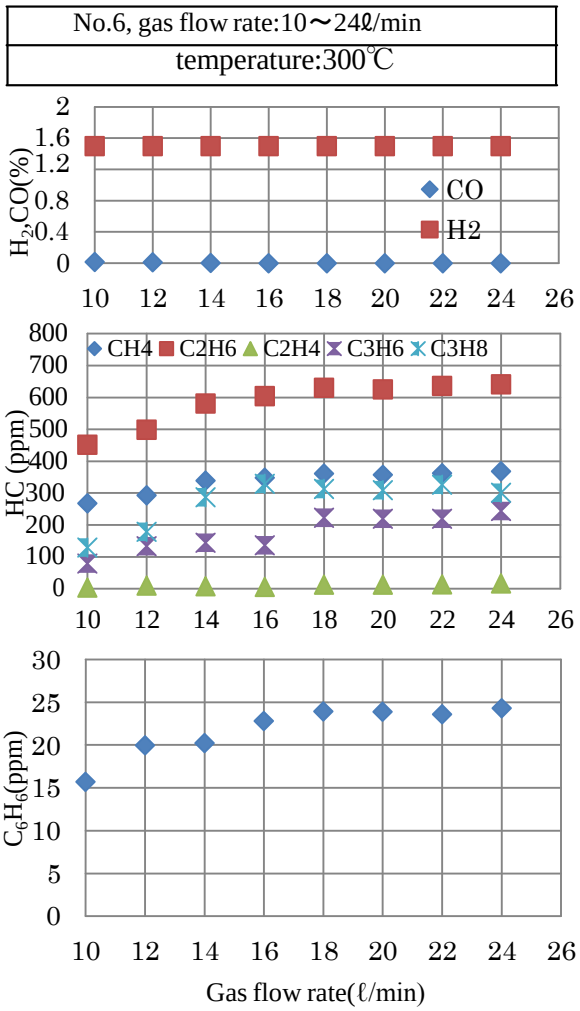

Fig. 5 Effect of coexistent gas on the C_6H_6 oxidation

oxidation and reduction reactions in a range of 300℃ ～ 600℃[4]. In this experiment, the initial gas rate is 24ℓ/min. As shown in Fig.6, C_6H_6 is about 20ppm at the temperature less than 500℃, and maintained a constant concentration substantially, as the catalyst temperature rises from 500℃ to 700 ℃, C_6H_6 concentration is reduced to about 11ppm.

Comparing the results in Figure 5, these results indicate that the decomposition of C_6H_6 in the catalyst is influenced by temperature, and there is a temperature range, in which the C_6H_6 decomposition is enhanced. When increasing the temperature from 500 ℃ to 700 ℃, the concentrations of CH_4, C_2H_6 and C_3H_8 were impaired, while the concentrations of C_3H_6, C_2H_4 were increased conversely. These experimental results differ from the experimental results shown in

Fig.5. When the gas in the reactor is externally heated, the gas volume is expands, and the reaction time of the gas component is shorten. These results indicate that the temperature direct influence the decomposition process of each component in the catalyst by the change reaction time and catalytic activity. The results also reveal that there is a certain range of the temperature, at which the catalysts have higher catalytic activity for C_6H_6 oxidation.

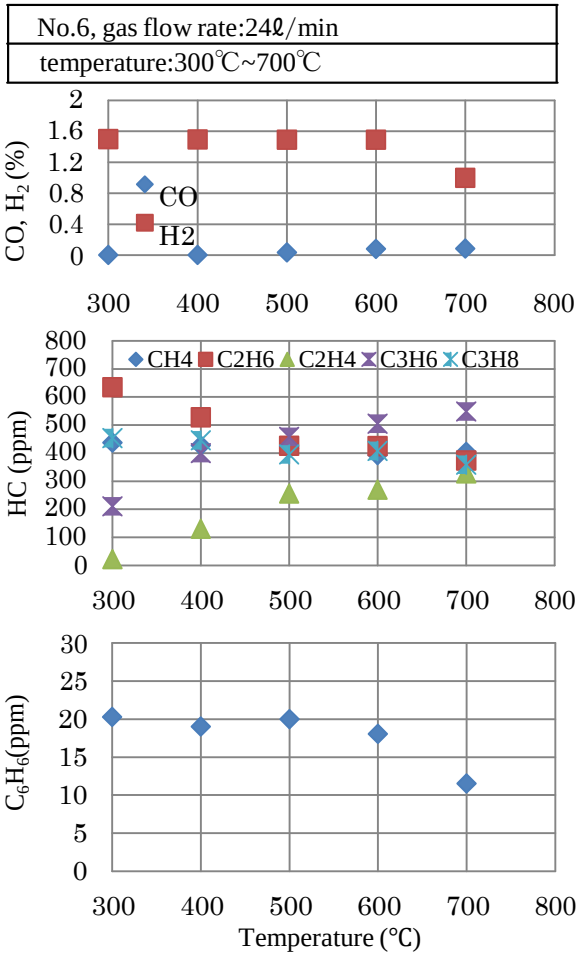

Fig. 6 Effect of temperature on the C_6H_6 oxidation

3.3 Effect of Catalyst Degradation on the Oxidation of C_6H_6

It is believed that the performance of the automotive catalyst to decline with an increase in the mileage of the car. Besides mechanical destruction, wear, alteration, catalyst degradation is also advanced by the alteration and dissipation of the active substance, and adsorption of toxic substance.

Fig.7 is the results of the experiment with three catalyst taken from used gasoline car. The mileages of the automobiles are 0km, 40000km and 80000km

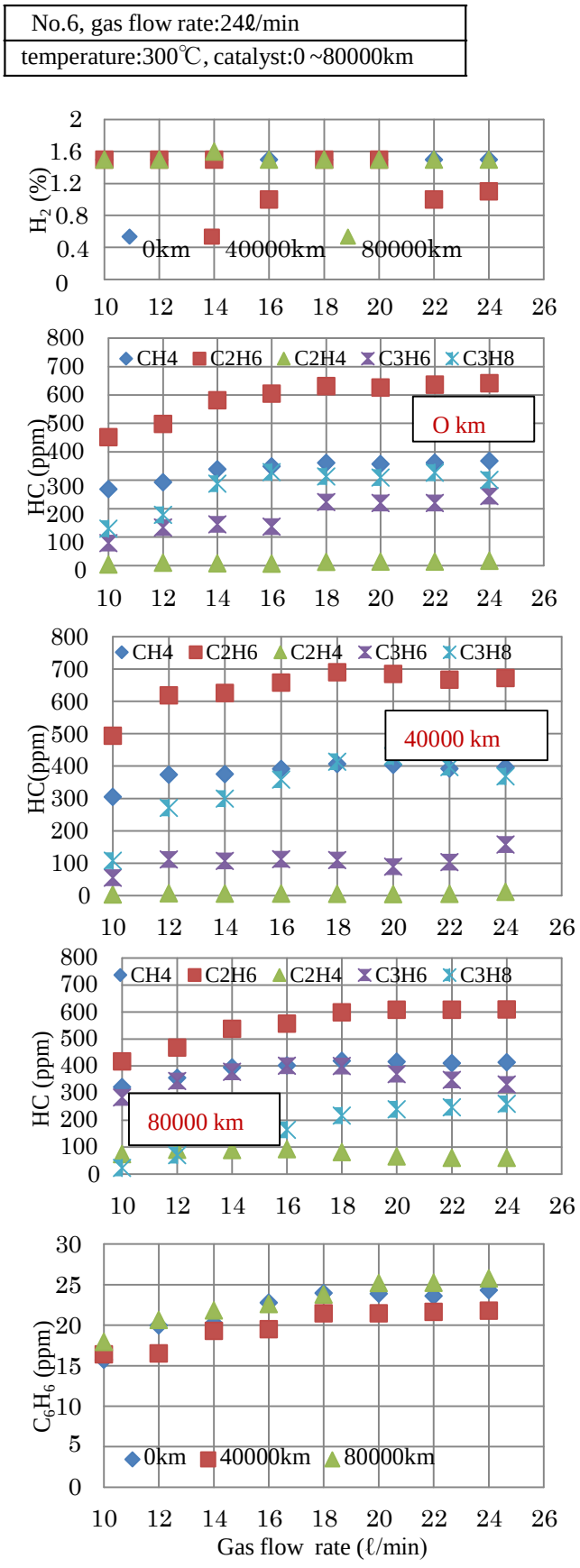

Fig. 7 Effect of catalytic degradation on the C6H6 oxidation

respectively. As shown in Fig.7, C_6H_6 concentrations are hardly affected by the increase in the mileage from 0km to 80000km. There is no significant difference on the concentration of H_2, and CO concentration was not detected. However, the effect of mileage on the CH_4, C_2H_6, C_3H_8 concentration is small in the range of the mileage, and concentrations of C_2H_4, C_3H_6 significantly increase with the increasing in the mileage from 0km to 80000km. These results indicate that the effect of degradation of the catalyst with increasing mileage of the car on the decomposition of the gas components depend on the components.

4. CONCLUSION

The effects of the gasoline engine operating conditions on the C_6H_6 emission have been investigated with respect to gas flow rate, coexistence gas components and temperature in a tubular-flow reactor containing a three-way catalyst. The comparisons of the effects of coexistence gas components and gas flow rate on the C_6H_6 decomposition have clarified that the oxidation of C_6H_6 is effected by the presence of coexistence gas component, and C_6H_6 oxidation is enhanced by the presences of O_2 and CO, while the presences of H_2, HC and H_2O have suppressive effect on the oxidation of C_6H_6 than O_2 and CO. The results also reveal that there is a certain range of the temperature, at which the catalysts have higher catalytic activity for C_6H_6 oxidation. The effect of catalyst degradation on the oxidation of C_6H_6 has also investigated. It was found that in the range of the mileage from 0km to 80000km, the degradation of catalyst has lower effect on the decomposition of C_6H_6.

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