Adsorption Characteristics of HCA(Hydrocarbon Adsorber) Catalysts for Hydrocarbon and NO$_x$ Removals under Cold-Start Engine Conditions

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Abstract—To meet the SULEV (Super Ultra Low Emission Vehicle) regulations, we have focused on the utilization of HCA (Hydrocarbon Adsorber) in order to adsorb the excess hydrocarbons emitted during a period of engine cold-start. As main recipes of HCA materials, many types of zeolite as well as a combination of alumina and precious metals were used. Representative physico-chemical factors of zeolite such as acidic and hydrophobic properties have been characterized and tried to find the optimum recipe of HCA materials. Among the acid properties of zeolites, the Si/Al ratio has been found to be the most important factor to achieve higher hydrocarbon adsorption capacity.

Key words: Automotive Catalyst, Hydrocarbon Adsorber, Adsorption Characteristic, Zeolite, Hydrocarbon

INTRODUCTION

A very important problem in the area of automobile emission control is how to resolve the problem of cold starting. Hydrocarbons from cold start emission emit more than 85% of total hydrocarbon emissions. In order to satisfy more stringent SULEV (Super Ultra Low Emission Vehicle) legislation, an increase of catalytic activity at cold start condition is quite necessary, and the research interest has been focused on the adsorption properties at cold-start conditions [Hirofumi et al., 1993; Naomi and Hiroshige, 1997; Robert et al., 1997]. The main research idea is to utilize a hydrocarbon adsorber (HCA) system which is combined with TWC in order to reduce NO$_x$ and hydrocarbon emission at a cold-start condition. To develop the optimized operating condition of HCA and TWC, many HCA recipes have been tried, and their physico-chemical properties have been characterized. Also, the adsorption characteristics of prepared HCA materials have been examined and the catalytic activities of an HCA and TWC combined system have been measured in a simulated flue gas and catalytic reactor system.

EXPERIMENTAL

1. Preparation of Catalysts

Zeolites as a major component of HCA material were prepared by ion exchanging steps proposed by Iwamoto and Yahiro. The final HCA material was prepared through conventional wet impregnation method [Yoon et al., 1997] to add precious metals (3 wt%) as Pd and Rh in the ratio of 9 : 1 refer to Paul and Todd [1999]. Those catalysts were calcined in air for four hours at 550 °C after drying for 2 hours at 150 °C. Additionally, in order to obtain extra function, base metal oxides such as Ba, Zr, Ce, La, etc. were added onto those samples in a similar manner [Ichikawa et al., 1999].

2. Catalytic Activity Test

To simulate the emission gases emitted from a gasoline engine, each reactant gas was passed through a mixing tank with enough mixing time. After that, those mixing gases were passed through a reactor which has a hydrocarbon adsorber and three-way catalysts in a dual bed form. To determine the change of emission concentration, an activity test was performed before and after the reactor passing. The simulated emission gas contents were: NO 450 ppm, CO 4,200 ppm, C$_3$H$_6$ 1,800 ppm, C$_3$H$_8$ 450 ppm, H$_2$ 1,400 ppm, CO$_2$ 3.0%, H$_2$O 10%, O$_2$ 1.6% and N$_2$ as a balance gas. An estimated Air/Fuel ratio (λ value) was approximately 1.0. Fig. 1 shows the activity testing apparatus that was used in this experiment.

RESULTS AND DISCUSSION

1. Effect of Si/Al Ratio

At first, the adsorption properties of ethylene on various kinds of ZSM-5 catalysts were examined [Oh et al., 2001] as shown in Fig. 2, depending upon the Si/Al ratio. In automobile emissions,
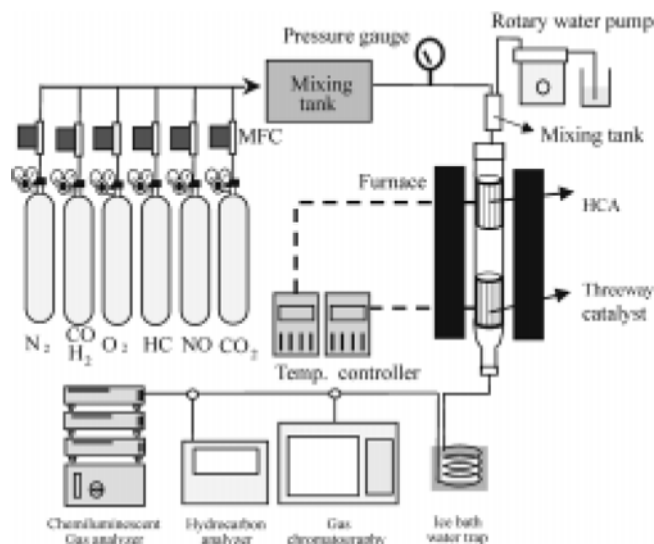

Fig. 1. A diagram of activity test apparatus.

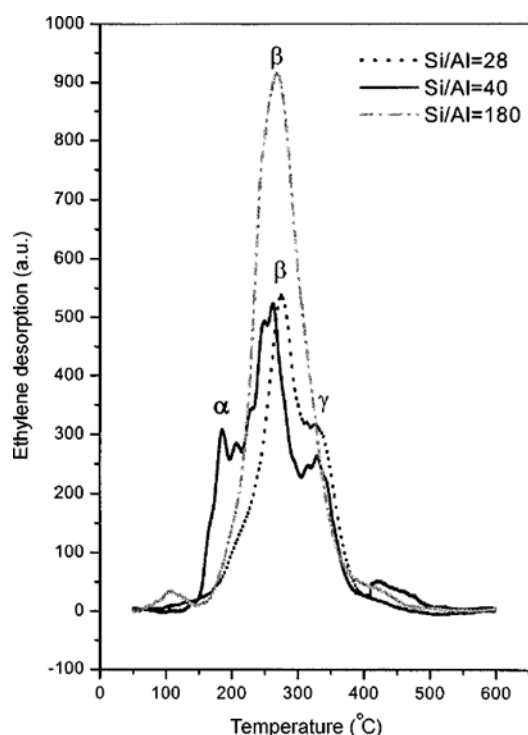[†]To whom correspondence should be addressed.
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Fig. 2. Ethylene adsorption amounts of HZSM-5 as a function of Si/Al ratio.

Table 1. Ethylene adsorption amount and BET surface area of ZSM-5 samples

Si/Al ratio	Pore volume (cc/g FTP)	Mean pore diameter (Å)	BET (m²/g)	Ethylene adsorption vol (cc)
28	0.006	5.32	375	0.135
40	0.008	5.31	394	0.139
180	0.011	5.14	395	0.192

ethene is as important as propene among hydrocarbon emissions. Therefore, we tested both gases as a probe hydrocarbon. Since we found that both gases showed similar adsorption behavior and amounts depending upon Si/Al ratio, we cited both data inter-mixed. As shown in Table 1, though the amounts of adsorption were similar in the case of 28 and 40 in Si/Al ratios, it was found that about 50% of adsorption amount increased when the Si/Al ratio was 180.

This could be interpreted that at higher range of Si/Al ratio, the hydrophobicity has jumped to a higher value, and therefore the selective adsorption of non-polar material, say, hydrocarbon, has been increased significantly. This result is coincides well with that by Engler et al. [1993] that at low Si/Al ratio of zeolite the polar materials, such as water, ammonia, alcohols as well as non polar materials such as hydrocarbon were well adsorbed without regard to polarity, but at high Si/Al ratio, by changing the surface property from hydrophilic to hydrophobic, an increased amount of hydrocarbon could be adsorbed selectively.

2. Effect of Hydrophobicity

In general, various kinds of experimental methods have been proposed for the determination of hydrophobicity quantitatively. Among them, the method of hydrophobic index calculation proposed by

Long [1997] was adopted for the present study. In this method, the hydrophobic index could be expressed as the weight loss of X_{HC}/X_{H_2O} in TGA curve. In the present study, we defined the hydrophobic index as the weight loss from room temperature up to 150 °C to the weight loss from 150 °C up to 400 °C in the thermogram curve for each sample as shown in Fig. 3. We tried to find a certain relationship between the hydrocarbon adsorption amounts and the measured values of hydrophobic index. Surprisingly, as shown in Fig. 4,
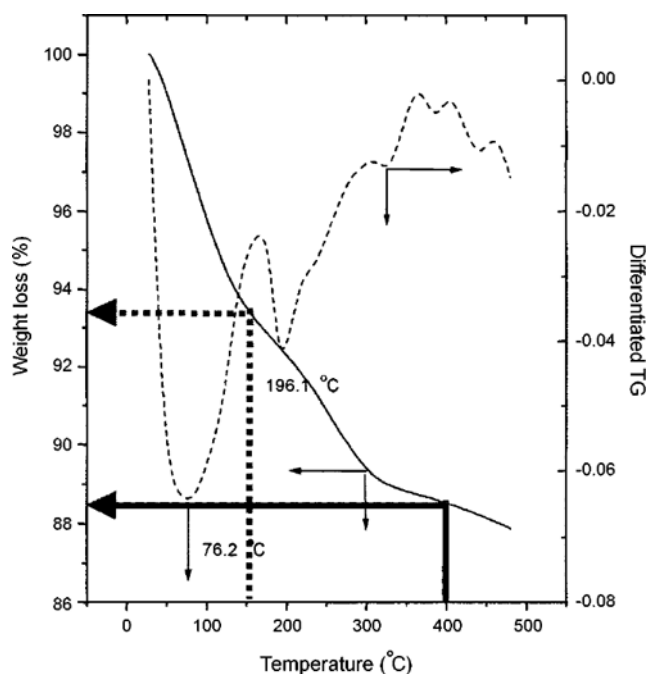

Fig. 3. DTG and TG curve of H-Mordernite (Si/Al=60, ← : water weight loss, ← : hydrocarbon weight loss).
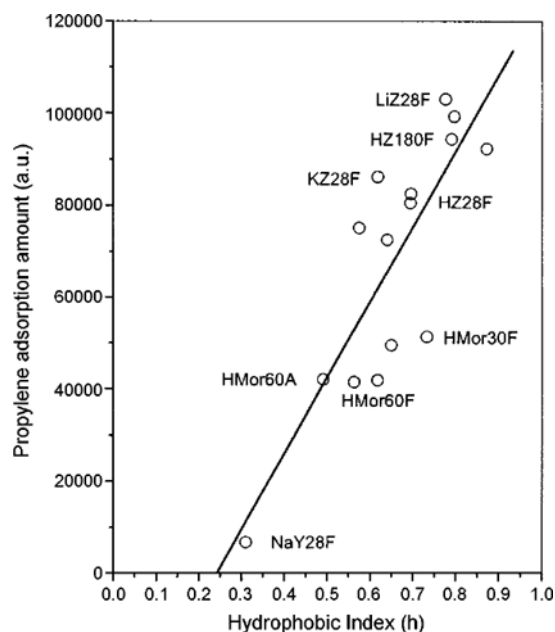

Fig. 4. Correlation of hydrophobicity and adsorption amount of ion exchanged zeolites [F=fresh, A=aged, Mor=mordernite and Z=ZSM5].

we were able to find a good linear relationship between the hydrophobic index (h) and the amount of adsorption for most of the zeolite samples we prepared. This result suggests that for the selection of zeolites to make an efficient hydrocarbon adsorber (HCA), the hydrophobic index is the most important factor to examine.

3. Effect of Surface Acidity

It has been understood that the ammonia temperature programmed desorption (TPD) method and amine titration method are effective characterization techniques for the determination of total surface acidity and acid strength distribution on catalyst surface [Hong et al., 1998]. As shown in Figs. 5 and 6, the acid amount and acid strength distribution have been measured for ZSM-5 catalysts, depending upon the Si/Al ratio.

As expected, increasing the value of Si/Al ratio, the total amount of acidity was reduced. From the ammonia TPD, it was found that strong acid sites at high temperature region were specially reduced as the Si/Al ratio increased. This phenomenon could also be confirmed from the acid strength distribution diagram that a large amount
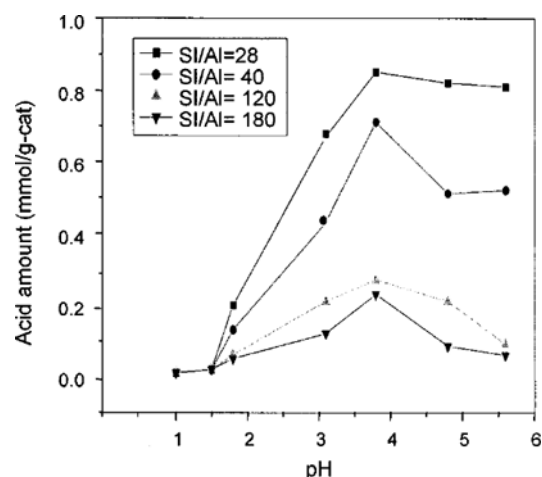
of acid sites stronger than PH=4 were reduced significantly with increasing the Si/Al ratio.

An important point is that, in spite of the reduction of total acidity at higher Si/Al ratio, the amount of hydrocarbon adsorption as described in Table 1 still shows a high value of adsorption. This means that between the two major factors governing the amount of hydrocarbon adsorption, the hydrophobic properties and acid amount, the effect of hydrophobicity is more dominant than acidity.

Depending upon alkali metals ion-exchanged in ZSM-5, minor change in the amounts of hydrocarbon adsorption could be monitored as shown in Fig. 7. This means that by changing some cations of zeolite to alkali-metals, we could obtain a minor improvement in the adsorption amount at a fixed Si/Al ratio. To verify the source of acidity increasement as well as adsorption amount for various ion-exchanged ZSM-5, we examined the change of acid sites by
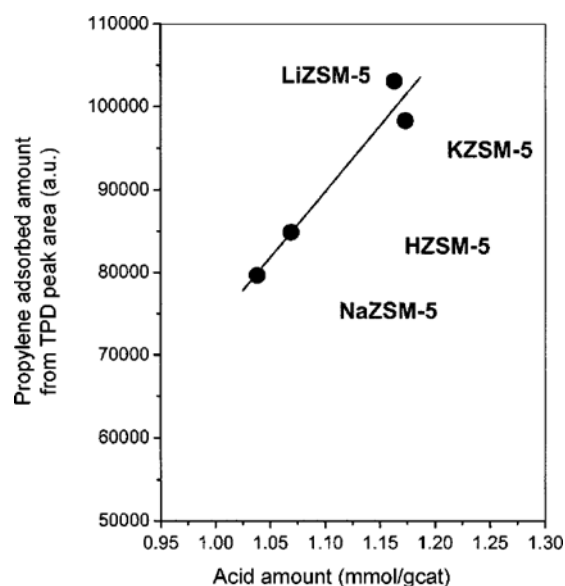

Fig. 5. Acid amounts of ZSM-5 as a function of Si/Al ratio.

Fig. 7. Correlation of acid amount and propylene adsorption amount on alkaline metal-exchanged ZSM-5 catalysts.

Fig. 6. Ammonia TPD patterns for ZSM-5 with different Si/Al ratios.
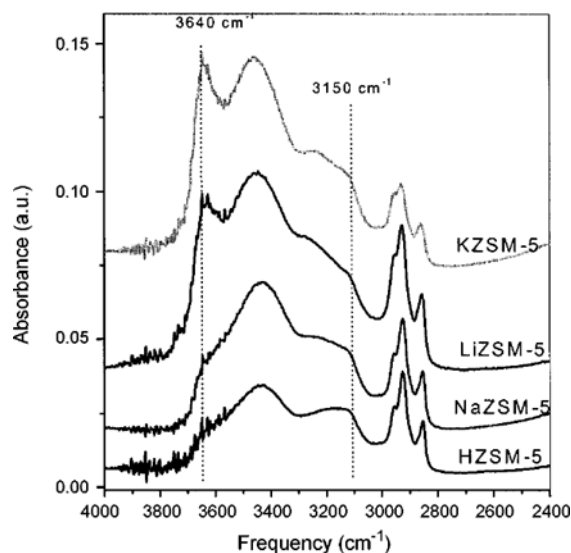

Fig. 8. FT-IR result of alkaline metal-exchanged ZSM-5 catalysts.

an ammonia adsorption experiment using in-situ IR. As a result, as shown in Fig. 8, in the case of either Li$^+$ or K$^+$-exchanged ZSM-5, it showed a new peak at 3,640 cm^{-1} which can be interpreted as a Brönsted acid site. However, there was no peak growth on H$^+$ and Na$^+$ ion exchanged ZSM-5. This result suggests that for specially selected ion exchanged ZSM-5 catalysts, some of the Lewis acid site could be transferred into Brönsted acid site so as to increase the amount of total acidity which results in the increase of hydrocarbon adsorption. This observation is supported by the Eisuke et al. [2000], that the main site of hydrocarbon adsorption is Brönsted acid site rather than Lewis acid site through a detrium labeling experiment. Therefore, it could be concluded that for a fixed Si/Al ratio, by changing the cations of zeolites to K$^+$ and Li$^+$ ions, we can obtain more improved hydrocarbon adsorption amounts. This principle can be applied to prepare HCA materials for the removal of excessively-emitted hydrocarbons during an engine cold-start period.

4. The Effects on Combination of HCA and TWC

To observe the combination effect of HCA with TWC, firstly the catalytic activity of TWC only was measured in a simulated flue gas and reactor system. And then, the combination effect was measured in the aspect of LOT$_{50}$, which is the temperature of reaction exhibiting the 50% conversion of hydrocarbon, together with the final conversion of NO$_x$, CO and hydrocarbon at reaction temperatures from 50 °C to 400 °C. Finally, in order to promote the thermal durability as well as improved catalytic activity, some base metal oxides were added on the surface of HCA materials and the catalytic activity was examined.

4-1. Catalytic Activity of TWC Only

For this study, two types of TWC were used: Pd-only catalyst and Pt/Rh catalyst. From comparative studies, it was observed that the Pd-only catalyst is superior to the conventional Pt/Rh catalyst in the aspect of the high temperature durability and the durability in sulfur poisoning. However, the conventional Pt/Rh catalyst showed a better catalytic activity in NO$_x$ reduction specially at low temper-
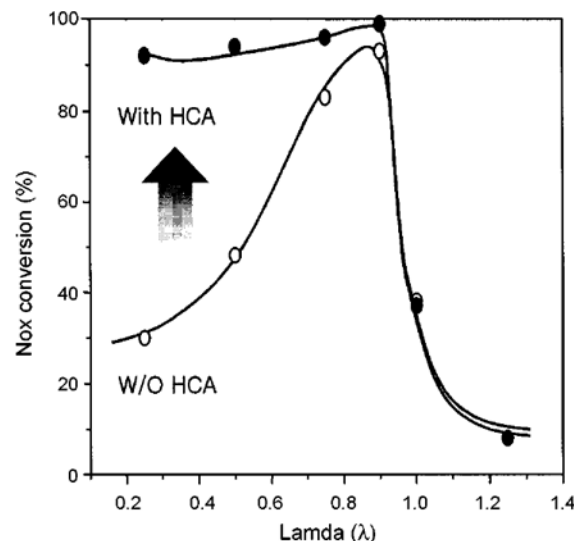

Fig. 9. NO$_x$ reduction over Pd-only catalyst with respect to Air/Fuel ratio on Pd-only catalyst (λ=Mole ratio of Air/Fuel).

ature region. The major problem of Pd-only catalyst in the deNO$_x$ activity is that this catalyst shows very poor low activity at fuel-rich region mainly due to the hydrocarbon poisoning. Since the Air/Fuel ratio (λ=1 at stoichiometric ratio) was perturbed around stoichiometric ratio, it is very important to monitor the removing efficiencies of NO$_x$, H/C and CO from fuel rich to fuel lean region [Chung et al., 1999]. Fig. 9 shows the de-NO$_x$ activity of Pd-only catalyst depending upon Air/Fuel ratio changes.

Specifically, the de-NO$_x$ activity at fuel rich region was very poor due to the poisoning of excess hydrocarbon. However, when the HCA was added, since the excess hydrocarbon was significantly adsorbed on HCA, the de-NO$_x$ activity at fuel rich region could be very much enhanced. This figure illustrates the advantage of HCA
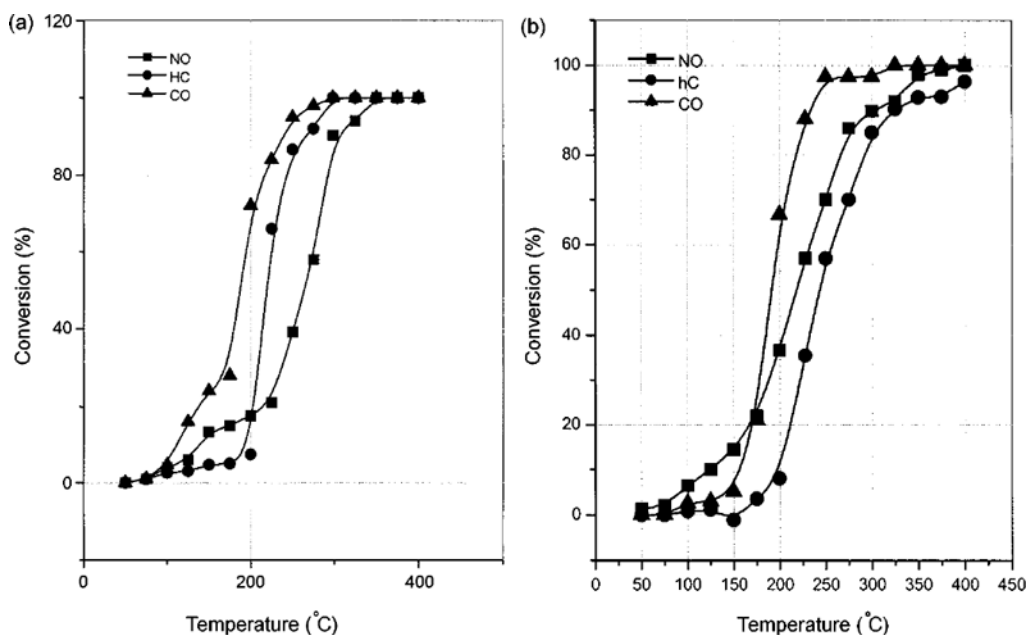

Fig. 10. NO, THC and CO removal efficiency of commercial Pd-only (a) and Pt/Rh (b) catalysts.

attachment on TWC system [Beck et al., 1997].

The results of catalytic activity measurements are shown in Fig. 10. Without regarding the types of catalyst, the behavior of CO conversion seems quite similar for the whole temperature range. However, in the case of NO and HC conversion, two types of catalyst show drastically different behaviors. Specially in the LOT$_{50}$ of hydrocarbon, while Pd-only catalyst exhibits at 220 °C, Pt/Rh catalyst shows at 243 °C, which is higher by 23 °C. Therefore, by considering the benefits of low LOT$_{50}$, Pd-only catalyst was selected for the combination study of TWC with HCA.

4-2. Combination Effect of Model HCAs and Pd-only TWC

Table 2 shows the various kinds of recipes for model HCAs that

Table 2. Hydrocarbon adsorber catalysts (HCA) compositions

Model	Catalyst composition
HCA I	PM 3 wt%+γ-Al$_2$O$_3$+LiZSM-5(120)
HCA II	PM 3 wt%+γ-Al$_2$O$_3$+LiZSM-5(120) +BMO(Ba etc.)
HCA III	PM 3 wt%+γ-Al$_2$O$_3$+Zeolite Y+MOR(120) +LiZSM-5(120)+BMO(Ba etc.)
HCA IV	PM 3 wt%+γ-Al$_2$O$_3$+HZSM-5(180)

were prepared on monolith wash-coated by γ-Al$_2$O$_3$, precious metals, base metal oxide (BMO), and Li$^+$ exchanged ZSM-5 (Si/Al=
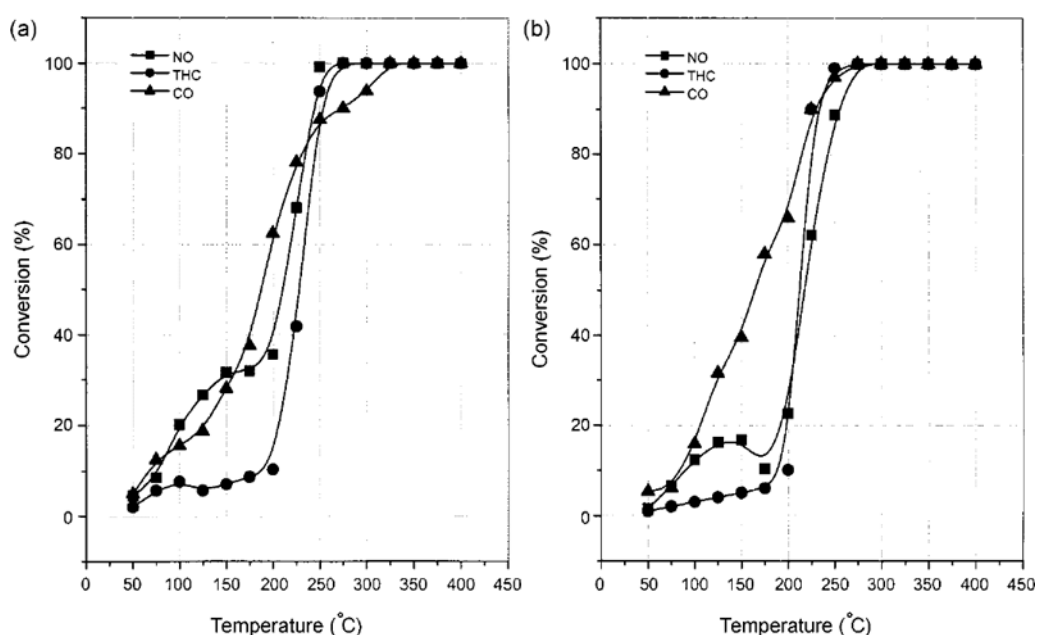

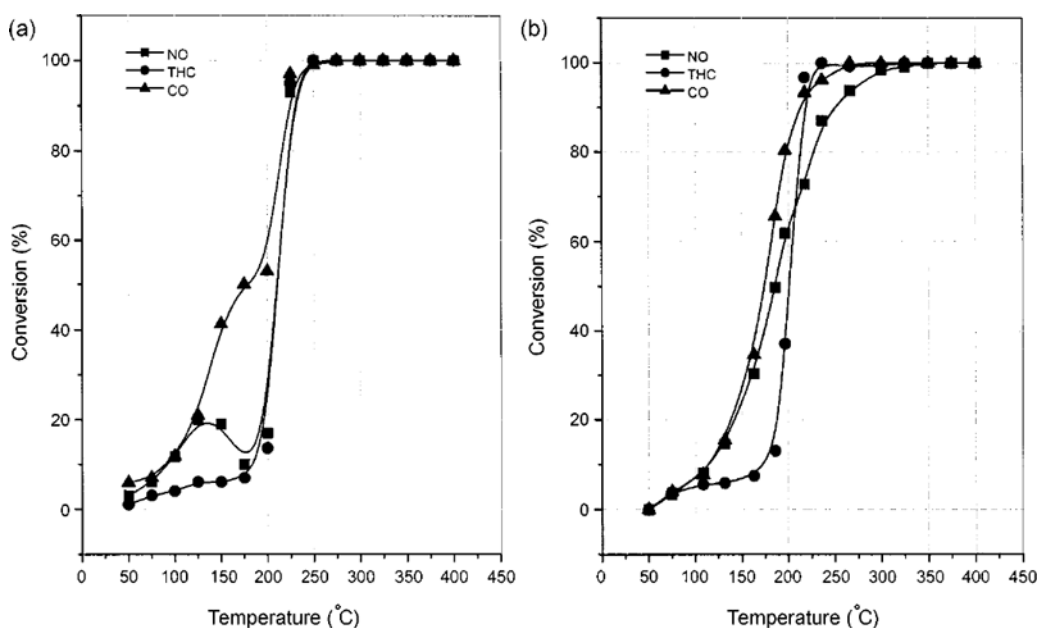Fig. 11. Combination effects of HCA I (a), HCA II (b) with Pd-only TWC.

Fig. 12. Combination effects of HCA III (a), HCA IV (b) with Pd-only TWC.

120, 180) based on the results of adsorption experiments mentioned above.

Figs. 11 and 12 show the activities of combined catalysts with Pd-only catalyst with prepared HCAs. In the case of HCA I, which was mixed with Pd-only catalyst, LOT$_{50}$ of hydrocarbon were impractically too high. HCA II was prepared by adding BMO. In this sample, La was specially added to prevent active site poisoning by excess hydrocarbon in rich condition together with promoted thermal stability. Ba addition was expected to increase NO$_x$ adsorption amount, and Zr and Ce addition might promote thermal stability and oxygen storage capacity (OSC) [Gallardo et al., 1998]. When BMOs were added, the LOT$_{50}$ of hydrocarbon was reduced by about 10 °C, and CO and NO$_x$ were reduced by 20 °C and 40 °C, respectively, when compared to those on Pd-only performance. In HCA III, zeolites, such as mordenite and Y-zeolite were added in HCA, hydrocarbon LOT$_{50}$ and CO LOT$_{50}$ were reduced by 10 °C, respectively, and NO$_x$ LOT$_{50}$ fell by 50 °C in contrast to Pd-only catalyst. However, those samples are not good enough to reduce LOT$_{50}$ of hydrocarbon significantly.

Finally, we investigated the combined effect of HCA prepared by ZSM-5 (Si/Al=180). As shown in Fig. 12, NO$_x$ LOT$_{50}$ was by 80 °C, CO LOT$_{50}$ was by 15 °C and hydrocarbon LOT$_{50}$ was by 20 °C less than Pd-only catalyst. It is surprising that the reduction of LOT$_{50}$ in NO$_x$ is much higher than LOT$_{50}$ in hydrocarbon. This effect probably comes from the prevention of hydrocarbon poisoning by uptaking the excess hydrocarbon through HCA. From these results, Si/Al ratio or hydrophobicity was a very important factor in selecting HCA. HCA materials using zeolite that have high Si/Al ratio and prepared by ion-exchanging method showed excellent reduction in LOT$_{50}$ in NO$_x$ by 80 °C. The main reason could be explained by its acid characteristics and hydrophobicity of zeolite.

CONCLUSION

At higher range of Si/Al ratio, the hydrophobicity has jumped to a higher value, and therefore, the selective adsorption of non-polar material such as hydrocarbon has been increased significantly. For specially selected ion exchanged ZSM-5 catalysts, some of the Lewis acid sites could be transferred into Brønsted acid sites so as to increase the amount of total acidity which results in the increase of hydrocarbon adsorption. Both hydrophobicity and total acidity affected the increase of hydrocarbon adsorption, but hydrophobicity is a more dominant factor than total acidity of catalyst.

If HCA is used with three way catalyst, it prevents Pd from poisoning by excess hydrocarbons, and in addition, it can induce better catalytic activity in NO$_x$ and CO conversion as well as lowering LOT$_{50}$ about 20-30 °C. BMO such as Ba, La, Zr and Ce etc was added to promote thermal durability, and it was found very helpful to promote catalytic activity in the low temperature region. Conse-

quently, those results are beneficial for the increase of catalytic activity at cold start conditions.

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