A Study of HCA and TWC Hybrid System for Reducing Cold-Start Emission

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ABSTRACT– In line with the Super Ultra Low Emission Vehicle (SULEV) regulation, the main idea in this study has been focused on the utilization of hydrocarbon adsorber (HCA) 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 the combination of alumina and precious metals were used. Representative physico-chemical factors of zeolite such as acidic and hydrophobic properties were characterized. The optimum recipe of HCA materials was also determined. Among the acid properties of zeolites, the Si/Al ratio was found to be the most important factor to get higher hydrocarbon adsorption capacity.

KEY WORDS: HCA, Zeolite, SULEV, Hybrid system

1. INTRODUCTION

One of the very important problems in automobile emission control is how to resolve the problem of cold start [1, 2]. Hydrocarbons from cold start emission emit more than 85% of total hydrocarbon emission. Emission regulations are met today by using three-way catalysts (TWC), which reduce exhaust emissions through catalytic reaction [3]. However, these systems are inactive during cold start and warm-up of an engine, as they require a temperature level typically around 300 ℃ for sufficient conversion. In order to satisfy the stringent Super Ultra Low Emission Vehicle (SULEV) legislation, the increase of catalytic activity at cold start condition is quite necessary. The research interest has been focused on the adsorption properties at cold-start conditions. The concept of using a hydrocarbon adsorber (HCA) to reduce the amount of cold-start hydrocarbons emitted from vehicles is well known [4, 5, 6].

Although the HCA technique is quite effective, tighter emission regulations may not be sufficiently met by simply using configuration with HCA. Therefore much research effort has utilized the HCA system in combination with TWC in order to reduce NOx and hydrocarbon emission at cold-start condition. To develop the optimized operating condition of HCA and TWC, many of the HCA recipes have been tried, and their physico-chemical properties have been characterized. The adsorption characteristics of prepared HCA materials have also been examined. Furthermore, the catalytic activities of HCA and TWC combined system have been measured in a simulated flue gas and catalytic reactor system.

2. EXPERIMENTAL

2.1. Preparation of Catalysts

Zeolite, as a major component of HCA material, was prepared by ion exchanging steps proposed by Iwamoto and Yahiro. The final HCA material was prepared through conventional wet impregnation method, and the precious metals (3wt%) Pd and Rh were added in the ratio of 9:1. The catalysts were calcined in air for four hours at 550□ after drying for 2 hours at 150 ℃.

2.2. Catalytic Activity Test

To simulate the emission gases emitted from gasoline engine, each reactant gas was passed through a mixing tank with enough mixing time. The mixing gases were then passed through the reactor having the hydrocarbon adsorber and three-way catalysts in a dual bed form. To determine the change of emission concentration, the activity test was performed before and after the gases were passed through the reactor. The simulated emission gas contents were: NO 450 ppm, CO 4200 ppm, C_3H_6 1800 ppm, C_3H_8 450 ppm, H_2 1400 ppm, CO_2 3.0%, H_2O 10%, O_2 1.6%, and N_2 as a balance gas. The estimated Air/Fuel ratio (λ value) was approximately 1.0.

2.3. Characterization

Various temperature programmed desorption measurements were carried out on a conventional TPD system equipped with a thermal conductivity detector (TCD) cell. The catalysts were exposed to He gas at 350 ℃ for 2 h in order to remove water and impurities on the surface. After pretreatment, the samples were exposed to adsorbate for 1h. Finally, the programmed heating at a rate of 10°C/min was started and the samples were then heated to 650°C. The amount of the desorbed gas was continuously monitored with a TCD cell.

3. RESULTS AND DISCUSSION

3.1. Effect of Si/Al Ratio

At first, the adsorption properties of ethylene on various kinds of ZSM-5 catalysts were examined depending upon the Si/Al ratio (Figure 1). In automobile emissions, ethene is as important as propene among hydrocarbon emissions. Therefore, both gases were tested as probe hydrocarbon. Since both gases showed similar adsorption behavior and amounts depending upon Si/Al ratio, the data for both were cited inter-mixed.

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 was jumped into higher value; therefore, the selective adsorption of non-polar material such as hydrocarbon was increased significantly. This result coincides with that of Engler et al. [5], which shows that at low Si/Al ratio of zeolite the polar materials like water, ammonia, and alcohols as well as non-polar materials such as hydrocarbon were well adsorbed regardless of polarity. But at high Si/Al ratio, by changing the surface property from hydrophilic to hydrophobic, the increased amount of hydrocarbon could be adsorbed selectively.

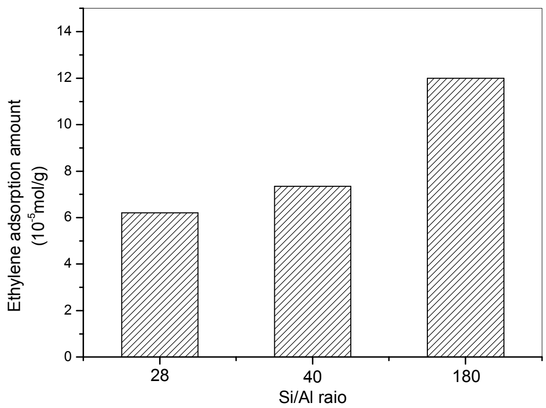


Figure 1. Ethylene adsorption amounts of HZSM-5 as a function of Si/Al ratio.

3.2. Effect of Hydrophobicity

In general, various kinds of experimental methods have been proposed for the quantitative determination of hydrophobicity. Among them, the method of hydrophobic index calculation proposed by Long was adopted for this study. In this method, the hydrophobic index could be expressed as the weight loss of X_{HC}/X_{H2O} in thermogravimetric analysis (TGA) curve. In this study, the hydrophobic index was defined 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 (Figure 2) for each sample. The relationship between the hydrocarbon adsorption amounts and the measured values of hydrophobic index was examined. Surprisingly, as shown in Figure 3, a linear relationship between the hydrophobic index (h) and the amount of adsorption was observed for most zeolite samples. This result suggests that for the selection of zeolites to make an efficient HCA, the hydrophobic index is the most important factor to examine.

3.3. Effect of Surface Acidity

The ammonia temperature programmed desorption (TPD) method and amine titration method are known to be effective characterization techniques for the determination of total surface acidity and acid strength distribution on catalyst surface. As shown in Figure 4 and 5, the acid amount and acid strength distribution had been measured for ZSM-5 catalysts, depending upon the Si/Al ratio. As expected, upon 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. These phenomena could also be confirmed from the acid strength distribution diagram that large amount of acid sites stronger than pH 4 was 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, which are the hydrophobic properties and acid amount, the effect of hydrophobicity is more dominant than acidity.

Table 1. Ethylene adsorption amount of ZSM-5.

Si/Al ratio	Ethylene adorption vol. (ml)
28	0.135
40	0.139
180	0.192

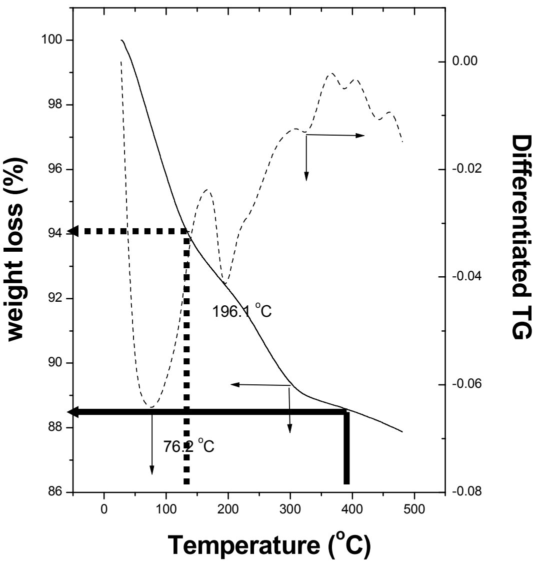


Figure 2. DTG and TG curve of H-Mordernite (Si/Al=60, ⟵: water weight loss, ◂┈┈: hydrocarbon weight loss).

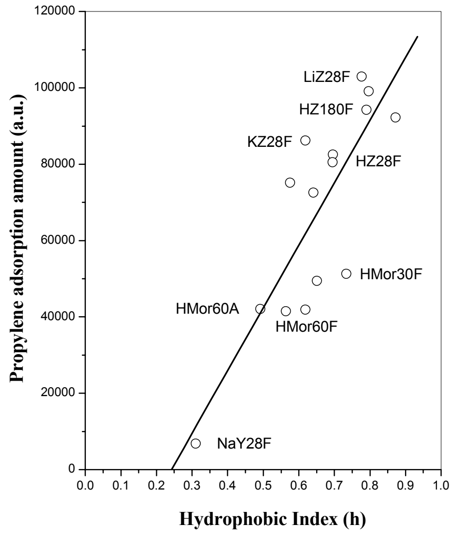


Figure 3. Correlation of hydrophobicity and adsorption amount of ion exchanged zeolites [F=fresh, A=aged, Mor=mordernite and Z=ZSM5]

Depending upon alkali metals ion-exchanged in ZSM-5, minor changes in the amount of hydrocarbon adsorption could be monitored (Figure 6). This means that by changing some cations of zeolite to alkali-metals, a minor improvement in the adsorption amount could be obtained at a fixed Si/Al ratio.

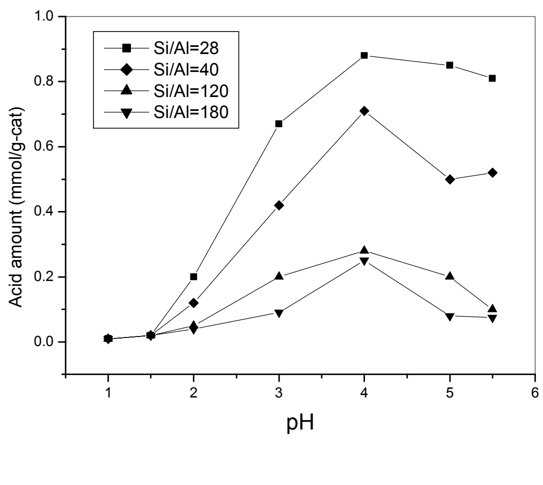


Figure 4. Acid amounts of ZSM-5 as a function of Si/Al ratio.

To verify the source of acidity increase as well as adsorption amount for various ion-exchanged ZSM-5, the change of acid sites was examined through an ammonia adsorption experiment using in-situ IR. As a result, in the case of either Li^+ or K^+-exchanged ZSM-5, a new peak was observed at 3640cm^{-1} (Figure 7), 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 Lewis acid sites could be transferred into Brönsted acid site so as to increase the amount of total acidity, which in turn results in the increase of hydrocarbon adsorption.

Therefore, for a fixed Si/Al ratio, by changing the cations of zeolites to K^+ and Li^+ ions, more improved hydrocarbon adsorption amounts could be obtained. This principle could be applied to prepare HCA materials for the removal of excessibly emitted hydrocarbons during an engine cold-start period.

3.4. The Effects on Combination of HCA and TWC

To observe the combination effect of HCA with TWC, the catalytic activity of TWC was measured in a simulated flue gas and reactor system. The combination effect was measured in the aspect of light-off temperature $(LOT)_{50}$, which is the temperature of the reaction exhibiting the 50% conversion of hydrocarbon, together with the final conversion of NO, CO, and hydrocarbon at reaction temperatures from 50°C to 400°C. Finally, in order to promote 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.

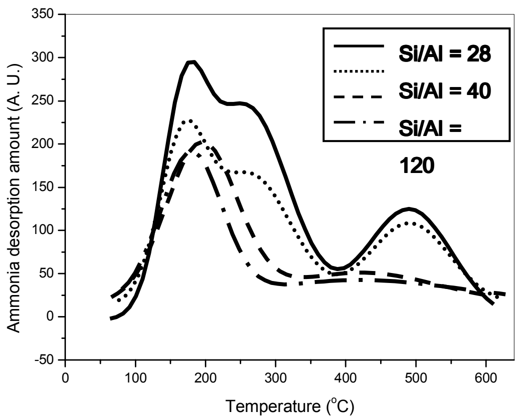


Figure 5. Ammonia TPD patterns for ZSM-5 with different Si/Al ratios.

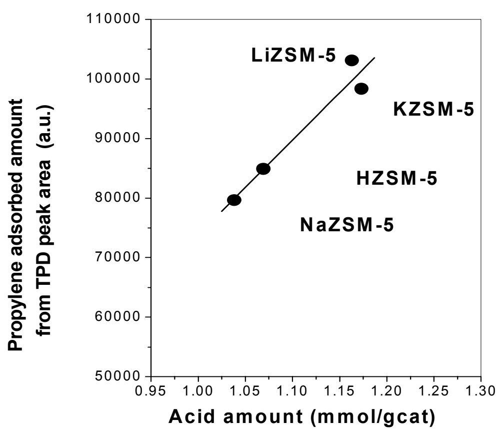
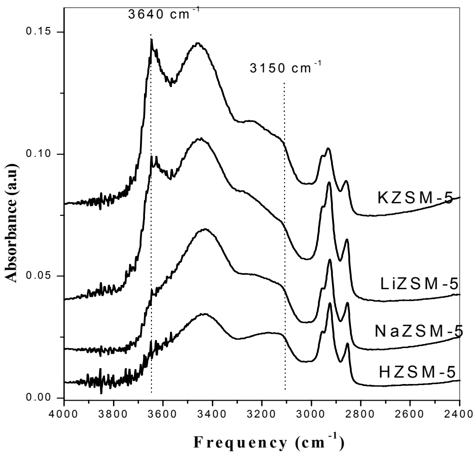


Figure 6. Correlation of acid amount and propylene adsorption amount on alkaline metal-exchanged ZSM-5 catalysts.



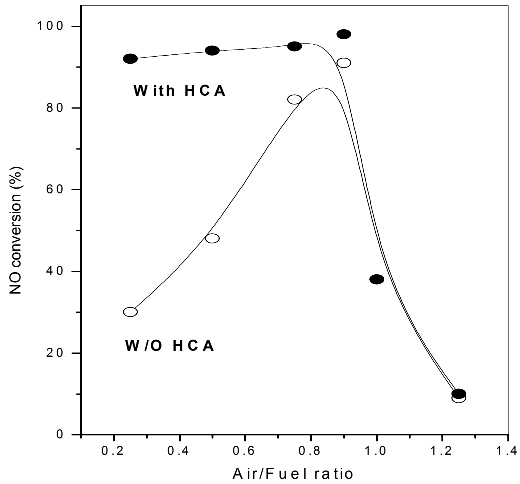
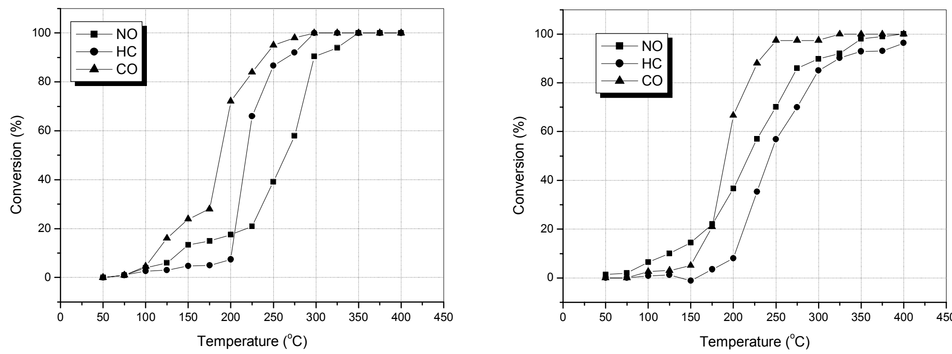


Figure 7. FT-IR result of alkaline metal-exchanged ZSM-5 catalysts.

Figure 8. NO_x reduction over Pd-only catalyst with respect to Air/Fuel ratio on Pd-only catalyst.



(a) (b)

Figure 9. NO, THC and CO removal efficiency of commercial Pd-only(a) and Pt/Rh(b) catalysts.

4. CONCLUSION

(1) At higher range of Si/Al ratio, the hydrophobicity has been jumped into higher value. Therefore, the selective adsorption of non-polar material such as hydrocarbon has been increased significantly.

(2) For specially selected ion exchanged ZSM-5 catalysts, some Lewis acid sites could be transferred into Brönsted acid site so as to increase the amount of total acidity, resulting in the increase of hydrocarbon adsorption.

(3) If hydrocarbon adsorption catalyst is used with three-way catalyst, it could prevent Pd from poisoning by hydrocarbon. In addition, it could make better NO and CO conversion catalytic activity as well as lowering LOT_{50} about 20-30°C. It is beneficial to the increase of catalytic activity at cold start condition.

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