Adsorptive Separation of Ethanol Blended Gasoline on Zeolites

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Various types of zeolites were evaluated for the adsorptive separation of ethanol and gasoline in ethanol blended gasoline. Mixed solution of ethanol and n-heptane was used as a model fuel. Adsorption selectivities of zeolites for ethanol and n-heptane were measured by a pulse testing method at 80 °C. These properties were dependent on the framework structures, exchangeable cations and Si/Al atomic ratios of zeolites. The adsorption capacities of zeolites for ethanol and n-heptane were evaluated by a continuous flow adsorption testing method at 80 °C. Zeolites with the FAU type structure (Na-Y and H-Y) showed higher adsorption capacities compared to the other types of zeolites. Adsorption strength of ethanol on zeolites was evaluated by a temperature programmed desorption method. Ethanol molecules adsorbed on Na-Y and H-Y were desorbed by heat treatment at around 300 °C, but ethanol adsorbed on H-Y was partially dehydrated because of zeolite acidity.

Keywords
Ethanol blended gasoline, n-Heptane, Adsorptive separation, Zeolite, Temperature programmed desorption

1. Introduction

Reduction of the energy requirements of daily transportation systems is very important to achieve global environmental protection. The homogeneous charge compression ignition (HCCI) combustion engine is a significant advancement in the efficiency of energy utilization in automotive engines. The HCCI engine is achieves very lean fuel combustion by self-ignition without flame propagation due to the supply of a homogeneous air-fuel mixture. Generation of NOx is considerably suppressed under such lean-burn conditions, and no smoke is generated that is a problem with the direct injection engine. Therefore, the HCCI engine does not require any catalyst for removing NOx or particulate filter for removing smoke particles. The HCCI process operates at high efficiency because the combustion occurs at low temperature thus reducing heat loss and allowing very fast combustion. The HCCI engine has many advantages in terms of fuel consumption and control of exhaust gas. However, the technical difficulties of self-ignition combustion have hampered practical application of the HCCI engine. The engine ignition timing and combustion rate vary depending on the operating conditions and the fuel components. Misfires are likely to occur under low load conditions and knocking under high load conditions in both the normal and the HCCI engine. Consequently, the narrowness of the operating range becomes the limiting factor for practical engine operation.

Ethanol blended gasoline, e.g. E10 gasoline, has been introduced into the automotive fuel market of the United States of America, Brazil and other countries to reduce the emissions of carbon dioxide from fossil fuels through the combustion of ethanol derived from biomass. However, ethanol and gasoline have very different properties. For example, the octane number of normal gasoline is 89-100 and that of ethanol is 111. Whereas the theoretical air fuel ratio of normal gasoline is 14.7 and that of ethanol is 9.0. Therefore, fuel combustion efficiency and engine power generation will be improved by the separate combustion of ethanol and gasoline.

The dual fuel HCCI engine can be designed to combust both ethanol and gasoline. Good control of the dual fuel HCCI engine with self-ignition combustion avoiding knocking and misfiring can be achieved by separate supply of ethanol and gasoline. In fact, HCCI combustion can be controlled under the ideal state by the separate fuel supply method. However, actual vehicles will require separate fuel tanks for gasoline and ethanol, and the infrastructures for separate supply of gasoline and ethanol is not present today and will be hard to develop in the near future.

Therefore, the development of on-board fuel separation is desirable, to convert widely available ethanol blended gasoline into separate supplies of ethanol and gasoline.
gasoline. Extraction, distillation, absorption, adsorption and membrane separation\textsuperscript{8) are all potential separation methods. Adsorptive separation using zeolite, activated carbon or other porous materials as the adsorbent material is under consideration for vehicle installation\textsuperscript{9). In this study, adsorption and desorption characteristics of ethanol and gasoline components were investigated on zeolites with various framework structures, exchangeable cations and Si/Al atomic ratios.

2. Experimental

2.1. Materials

Commercially available zeolites listed in Table 1 were used as the adsorbents for the separation test in powder form as supplied by Tosoh Corp. (Na-A, Ca-A, H-Y, Na-Y, USY, H-mordenite and Na-mordenite) and Clariant Catalysts (Japan) K. K. (H-ZSM-5 and H-beta). Adsorbents were molded, crushed and sieved to obtain particle sizes within the range from 150 to 250 $\mu$m and were heated at 400 $^\circ$C for 2 h in air as a pretreatment. The water contents in the adsorbents after this pretreatment were 3-5 wt%.

2.2. Adsorption Test

The adsorption selectivities of various types of zeolites for ethanol and $n$-heptane were investigated by using a fixed-bed pulse reactor connected with a gas chromatograph (GC-8APF, Shimadzu Corp.) equipped with a flame ionized detector (FID). He was used as the carrier gas at a flow rate of 80 mL min\textsuperscript{-1}. The BX-10 column had 3 mm inner diameter and 3 m length (GL Sciences Inc.). The reactor contained 20 mg of adsorbent in a stainless reaction tube of $8 \text{ mm}$ inner diameter and the temperature was controlled at 80 $^\circ$C. The mixed solution consisted of equal weights of ethanol and $n$-heptane as a model fuel of ethanol blended gasoline. $2 \mu$L of the mixed solution was injected into the pulse reactor. The outlet gas was passed through the adsorbent bed and analyzed by the FID-GC. Adsorption ratio of ethanol was defined as the ratio of adsorbed ethanol to injected ethanol. Adsorption selectivity was evaluated by the adsorption ratio of ethanol and $n$-heptane at the first pulse.

The ethanol and $n$-heptane adsorption capacities of zeolites were measured by using a fixed-bed flow reactor under atmospheric pressure at 80 $^\circ$C. 1000 mg of adsorbent was placed into a stainless reaction tube of 8 mm inner diameter. The mixed ratio of ethanol and $n$-heptane in this test was adjusted to a weight ratio of 1 : 9. Flow rate of the mixed solution was controlled to 0.01 mL min\textsuperscript{-1}. The mixed solution was vaporized at 120 $^\circ$C before introduction into the reaction tube together with N\textsubscript{2} carrier gas (75 mL min\textsuperscript{-1}). The outlet gas of the reaction tube was analyzed by the FID-GC. The ethanol or $n$-heptane adsorption capacity of the adsorbents was determined by the breakthrough capacity, i.e. the uptake of ethanol or $n$-heptane at the moment of first detection of ethanol or $n$-heptane in the outlet gas.

2.3. Desorption Test

The adsorption strength of ethanol and $n$-heptane on each adsorbent was analyzed using a temperature programmed desorption apparatus (BEL-CAT, Bel Japan Inc.). About 100 mg of the fully ethanol or $n$-heptane adsorbed samples were put into a glass testing cell (8 mm of inner diameter) and the temperature was increased from 80 to 600 $^\circ$C. The temperature programmed rate was adjusted to 10 $^\circ$C min\textsuperscript{-1} in He carrier gas (50 mL min\textsuperscript{-1}). The desorbed gas species were analyzed by using a mass spectrometer (OmniSTAR, Pfeiffer Vacuum GmbH).

2.4. Repeated Tests

The reusability of adsorbent was confirmed by the change in adsorption capacity of fresh and regenerated adsorbent. The continuous adsorption test was carried out on fresh adsorbent until the breakthrough time at 80 $^\circ$C. The fully adsorbed adsorbent was heated at 400 $^\circ$C for 2 h in N\textsubscript{2} carrier gas (75 mL min\textsuperscript{-1}) to remove adsorbed species as a regeneration treatment. After the regeneration treatment, the continuous adsorption test was carried out again at 80 $^\circ$C. After reaching the breakthrough point, regeneration treatment was performed again. This adsorption and regeneration cycle was repeated for 3 times.

| Zeolite        | Framework type | Pore opening | Si/Al atomic ratio [-] |
|---------------|----------------|--------------|------------------------|
| Na-A          | LTA            | 8-MR         | 1                      |
| Ca-A          | LTA            | 8-MR         | 1                      |
| H-ZSM-5       | MFI            | 10-MR        | 90                     |
| H-beta (24)   | BEA            | 10-MR        | 24                     |
| H-beta (185)  | BEA            | 10-MR        | 185                    |
| H-Y           | FAU            | 12-MR        | 2.75                   |
| Na-Y          | FAU            | 12-MR        | 2.75                   |
| USY           | FAU            | 12-MR        | 375                    |
| H-mordenite   | MOR            | 12-MR        | 18                     |
| Na-mordenite  | MOR            | 12-MR        | 18                     |

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Table 2 Adsorption Ratio of Ethanol and n-Heptane on Various Zeolites Evaluated by the Pulse Method

| Zeolite      | Ethanol [wt%] | n-Heptane [wt%] |
|--------------|---------------|-----------------|
| Na-A         | 74.1          | 4.8             |
| Ca-A         | 91.5          | 3.2             |
| H-ZSM-5      | 97.2          | 80.9            |
| H-beta (24)  | 100.0         | 99.9            |
| H-beta (185) | 95.2          | 96.2            |
| H-Y          | 85.8          | 20.8            |
| Na-Y         | 99.3          | 33.2            |
| USY          | 10.0          | 100.0           |
| H-mordenite  | 96.2          | 38.3            |
| Na-mordenite | 98.2          | 30.0            |

The solution consisted of ethanol and n-heptane at 1:1 weight ratio.

3. Results and Discussion

3.1. Adsorption Selectivity by the Pulse Method

The ethanol and n-heptane adsorption selectivities of zeolites are summarized in Table 2. The zeolites tested in this study were classified into three types: LTA (Na-A and Ca-A); MOR (Na-mordenite and H-mordenite); and FAU (Na-Y and H-Y). Zeolites with low Si/Al atomic ratio adsorbed larger amounts of ethanol compared with n-heptane. These zeolites are promising adsorbents for the efficient separation of ethanol from ethanol blended gasoline. In contrast, the FAU type of zeolite, with high Si/Al atomic ratio (USY) adsorbed larger amounts of n-heptane compared with ethanol. The Na-Y and H-Y (FAU type) adsorbed ethanol selectively, whereas USY did not, probably because of its hydrophobic property. As E10 gasoline contains a large amount of gasoline compared to ethanol, USY was not suitable for separation of ethanol blended gasoline. Therefore, the adsorption selectivity of the zeolites was influenced by the hydrophilic and hydrophobic properties of zeolites controlled by their Si/Al atomic ratio.

BEA (H-beta) and MFI (H-ZSM-5) types of zeolites adsorbed both ethanol and n-heptane. These zeolites were unsuitable for separation of ethanol blended gasoline.

3.2. Adsorption Capacity by the Flow Method

The differences in the ethanol and n-heptane adsorption capacities of zeolites were investigated by a continuous adsorption test using a fixed-bed flow reactor. Figure 1 shows the breakthrough curves of n-heptane and ethanol on (A) Ca-A, (B) H-ZSM-5, (C) Na-Y and (D) USY. In the case of Ca-A, ethanol and n-heptane were not detected in the outlet gas during the first 165 min and 25 min, respectively (Fig. 1(A)). Therefore, the breakthrough points of ethanol and n-heptane on Ca-A were determined to be 165 min and 25 min, respectively. The adsorption capacities of the zeolites are summarized in Table 3. The ethanol and n-heptane adsorption capacities of Ca-A were calculated to be 250 mg g⁻¹ and 60 mg g⁻¹, respectively. Adsorption behavior of ethanol and n-heptane on H-ZSM-5 was similar to that on Ca-A with moderate ethanol adsorption capacity (Fig. 1(B)). Other zeolites including Na-A, H-beta (24), H-beta (185), H-mordenite and Na-mordenite also adsorbed ethanol preferentially in this flow adsorption test.

The breakthrough points of ethanol and n-heptane on Na-Y were 495 min and 0 min, respectively (Fig. 1(C)). Na-Y showed the highest adsorption capacity of ethanol (395 mg g⁻¹) among all zeolites tested in this study. The ethanol and n-heptane adsorption capacities of H-Y were 275 mg g⁻¹ and 50 mg g⁻¹, respectively. The ethanol selectivity of H-Y was slightly lower than that of Na-Y. On the other hand, the breakthrough points of ethanol and n-heptane on USY were 35 min and 50 min, respectively (Fig. 1(D)). The ethanol and n-heptane adsorption capacities of USY were 19 mg g⁻¹ and 207 mg g⁻¹, respectively, suggesting that n-heptane is preferentially adsorbed on USY. The results of the flow adsorption test on USY were in good agreement with the finding of the pulse method.

3.3. Desorption Behavior

After adsorption at around the breakthrough point of ethanol on Na-Y, the gas flow was changed to only nitrogen gas. Almost all n-heptane molecules adsorbed on Na-Y soon were desorbed ethanol molecules were partially desorbed slowly. Such desorption was allowed only weakly ethanol and n-heptane molecules were physically adsorbed only weakly on Na-Y.

About one-third of ethanol molecules adsorbed on Na-Y were desorbed after the gas flow was changed from the mixed gas to nitrogen. Temperature programmed desorption (TPD) profiles of ethanol from fully adsorbed Na-Y and H-Y at 80 °C are shown in Fig. 2. Almost all adsorbed ethanol on Na-Y was desorbed from 80 to 300 °C as shown in Fig. 2(A). Presumably the ethanol is adsorbed on Na-Y as the molecular form and is desorbed completely by heat treatment below 300 °C.

In contrast, desorption peaks of three components, n-heptane (very small), ethanol and ethylene (two peaks), were recorded in the TPD profiles of H-Y as shown in Fig. 2(B). Peak temperatures of the TPD profiles of n-heptane and ethanol were 130 °C and 150 °C, respectively, and two desorption peaks of ethylene were found at 240 °C and 380 °C. Ethoxide species derived from ethanol were detected on the Brønsted acid sites of H-Y at room temperature. Dehydration of ethanol adsorbed on the Brønsted acid sites of H-Y is known to occur at above 200 °C. The formation of ethylene observed by TPD as shown in Fig. 2(B) is probably derived from the ethanol strongly adsorbed on the acid sites of H-Y.

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Adsorption and desorption tests were repeated 3 times for the same Na-Y. The ethanol adsorption capacity of Na-Y was 395 mg g⁻¹ during the first cycle. After regeneration treatment, the ethanol adsorption capacity of Na-Y was 403 mg g⁻¹ during the second cycle and 402 mg g⁻¹ during the third cycle. Therefore, complete regeneration of Na-Y was achieved by heat treatment at 400 °C in N₂.

4. Conclusion

Various types of zeolites were evaluated for the adsorptive separation of ethanol and gasoline in ethanol blended gasoline. Zeolites with hydrophilic properties selectively adsorbed a large amount of ethanol. The ethanol adsorption capacity of Na-Y was the highest of all zeolites at 80 °C. The adsorbed ethanol on Na-Y could be removed by heat treatment at below 300 °C. The ethanol adsorption capacity of Na-Y was not changed after three adsorption-desorption cycles. Therefore, Na-Y was the most suitable zeolite for adsorptive separation of ethanol blended gasoline. H-Y also adsorbed ethanol selectively under the same conditions. However, TPD detected ethylene derived...
from the ethanol adsorbed on the acid sites of H-Y. Therefore, acid type zeolites were unsuitable for adsorptive separation of ethanol blended gasoline.

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Fig. 2 TPD Profiles of Ethanol (□), n-Heptane (●) and Ethylene (△) on (A) Na-Y and (B) H-Y.