Adsorption and conversion of various hydrocarbons on monolithic hydrocarbon adsorber

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Abstract

Adsorption and conversion of various hydrocarbons on monolithic hydrocarbon adsorbers were studied using a new experimental model, temperature-programmed adsorption (TPA). In this study, methyl alcohol, acetone, acetaldehyde, 2,2,4-trimethylpentane, n-octane, and toluene were chosen as model hydrocarbons for cold start of a vehicle. The effect of the hydrocarbon components and oxygen concentration on the TPA curve was investigated. Depending on the presence of O2, the adsorbed and desorbed amounts of the hydrocarbons were decreased, while the conversion efficiency of the hydrocarbons was increased. In the case of hydrocarbons containing oxygen, the thermal decomposition appeared to be in the order methanol, acetaldehyde, and acetone.

Keywords: TPA; Adsorption; Conversion; H-ZSM-5; Cold start; Hydrocarbon

1. Introduction

Technologies have been developed to reduce hydrocarbon emissions during cold starts. One of the technologies, the hydrocarbon adsorber [1–7], has been most attractive to automotive makers because it has the advantage with respect to cost and performance. Hydrocarbons in a cold start are dependent on the condition of the vehicle, fuel, and driver. About 100 hydrocarbon species are present in the exhaust during a cold start. They consist of about 10% methane, about 30% alkenes such as ethylene or propene, about 30% alkanes such as pentane or hexane, about 20% aromatics such as toluene or xylene, and about 10% other species [8]. Therefore, a hydrocarbon adsorber should be designed to have good selectivity for the hydrocarbons. In order to remove the adsorbed hydrocarbons effectively, the hydrocarbon adsorber needs to have an additional function, catalytic conversion of hydrocarbons.

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Until now, experimental tests using vehicle and engine dynamometers have been employed in order to select a hydrocarbon adsorber with higher hydrocarbon trapping as well as conversion efficiency. Very recently, a new model, temperature-programmed adsorption (TPA), has been proposed by Kim et al. [9], which is very effective in saving cost and time to select an excellent adsorber. The model has the advantage of analyzing the adsorption, desorption, and conversion of hydrocarbons simultaneously. The main feature of TPA in an adsorber system is shown in Fig. 1. This feature can be represented by concentration and time or concentration and temperature. The feature represents TPA behavior of hydrocarbons on adsorbers (or adsorbents) in the presence of O2 supply gas. As shown in Fig. 1, the concentrations are represented as relative values, which means ratios of outlet concentration (Cout) to inlet concentration (Cin). Generally, three parts such as adsorption, desorption, and reaction appear in the curves. The range below the value of 1 at lower temperatures is the adsorption-predominant part (0 − ts). The range above the value of 1 at medium temperatures is the desorption-predominant part (ts − tf). The range below the value of 1 at higher temperatures means the reaction-predominant part (tf − 0).
The adsorbed amount can be calculated using the mass balance equation [10,11]

\[ q_{i,a} = \frac{F C_{i,\text{in}}}{w} \left[ t_s - \int_{0}^{t_s} \frac{C_{i,\text{out}}}{C_{i,\text{in}}} \, dt \right] \]

(1)

where \( q_{i,a} \) is the adsorbed amounts of species \( i \), \( F \) is the volume flow rate, \( C_{i,\text{in}} \) is the inlet concentration of species \( i \), \( C_{i,\text{out}} \) is the exit concentration of species \( i \), \( w \) is the mass of adsorber, and \( t_s \) is the saturation time.

The desorbed amount can be also calculated by using the mass balance equation

\[ q_{i,d} = \frac{F C_{i,\text{in}}}{w} \left[ \int_{t_f}^{t_s} \left( \frac{C_{i,\text{out}}}{C_{i,\text{in}}} - 1 \right) \, dt \right] \]

(2)

where \( q_{i,d} \) is the desorbed amounts of species \( i \) and \( t_f \) is the end time of desorption.

In this study, methyl alcohol, acetone, acetaldehyde, 2,2,4-trimethylpentane, \( n \)-octane, and toluene are chosen as the model hydrocarbons of cold start. The effects of the hydrocarbon components and the oxygen concentration on the TPA behavior are investigated.

2. Experimental

2.1. Adsorber and hydrocarbon

The monolithic hydrocarbon adsorber used in this study was obtained by coating a washcoat onto the cordierite honeycomb ceramic substrate (cell density of 62 cells/cm\(^2\) (400 cells/in\(^2\)), wall thickness of 0.165 mm, 19 mm \((D) \times 30\) mm \((L)\)). The washcoat consisted of H-ZSM-5, \( \gamma \)-Al\(_2\)O\(_3\), and base metals (Ce and Zr). The adsorber containing the adsorbent \((\text{Si}/\text{Al} = 150)\) was impregnated with Pd and Rh \((\text{Pd}/\text{Rh} = 10/1)\), and it was named HA #1. \( \text{PdCl}_2 \) and \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) were used as the precursors of Pd and Rh to impregnate the coat with precious metals (PMs). After metal impregnation, all samples were dried at 150 °C for 5 h and calcined at 600 °C for 4 h. The loaded amounts of the washcoat and PM were 140 and 4.5 g/l, respectively. The physical and metal dispersion of HA #1 are listed in Table 1. The washcoat thickness \((W_t)\) and the hydraulic diameter \((D_h)\) of the adsorber were measured by SEM (Phillip 505) with an EDS detector. For the adsorption studies, methyl alcohol (Aldrich, 99%), acetone (Aldrich, 99%), acetaldehyde (Aldrich, 99%), 2,2,4-trimethylpentane (Aldrich, 99.8%), \( n \)-octane (Aldrich, 99%), and toluene (Aldrich, 99.95%) were used as received.

2.2. TPA experiments

The TPA experiments were evaluated using a fixed-bed quartz reactor mounted in an electric furnace. For all experiments, the dimensions of a sample were fixed at 20 \((D) \times 30\) mm \((L)\). Before the experiment, the sample was oxidized at 400 °C for 1 h in air flow (1 l/min). Subsequently, the reactor was purged with \( \text{N}_2 \) (1 l/min) at 400 °C for 1 h and cooled to 30 °C in \( \text{N}_2 \) flow (1 l/min). For TPA analysis, the sample was heated from 30 to 250 °C in the flow of 1000 ppm hydrocarbon/\( \text{N}_2 \) mixture (1 l/min) with a ramping rate of 1 °C/min. In addition, \( \text{O}_2 \) was supplied with a concentration of 0.8 or 1.8% to evaluate the conversion of hydrocarbon. The concentrations of hydrocarbon at the inlet and the outlet of the reactor were measured using FTIR (Nicolet) with a gas cell, Infrared Analysis Company, and a mercury–calcium–telluride (MCT) detector that was cooled by liquid nitrogen. The measurement was carried out with 16 scans and a resolution of 2 cm\(^{-1}\). The concentrations were also checked using GC (HP5890plus) with an FID (flame ionization detector) and an HP plot column.

2.3. Chemisorption

The chemisorption for CO was carried out at 30 °C to evaluate the metal dispersion on the adsorber. The amount of CO adsorbed irreversibly on the metal surface was determined by subtracting the second isotherm from the first isotherm. Metal dispersion was calculated using extrapolation and assuming 1:1 stoichiometry for Pd:CO and Rh:CO. After the experiment, we obtained 19.7% metal dispersion for the adsorber. The apparatus and procedure for the chemisorption experiments are well described in earlier papers [12,13].
3. Results and discussion

Fig. 2 shows TPA curves of 2,2,4-trimethylpentane, toluene, and n-octane on HA #1. In all cases, the inlet concentration of the hydrocarbons and flow rate were kept constant at 1000 ppm and 1 l/min in nitrogen gas. Fig. 2 is represented according to temperature and relative concentration. The relative concentration means the ratio of outlet concentration ($C_{\text{out}}$) to inlet concentration ($C_{\text{in}}$). A value of 1 stands for full saturation of hydrocarbon on the adsorber. A value over 1 represents the sum of supplied hydrocarbon and desorbed hydrocarbon from the adsorber. Adsorbed or desorbed amounts of n-octane, 2,2,4-trimethylpentane, and toluene obtained using Eqs. (1) and (2) are listed in Table 2. Desorption start temperature ($T_s$) and reaction start temperature ($T_f$) were also presented in Table 2. From Fig. 2 and Table 2, the order of breakthrough, adsorbed amount, and desorption start temperature appears to be n-octane, 2,2,4-trimethylpentane, and toluene. This result may be due to the difference in adsorption affinity of the hydrocarbons on the adsorber.

In this study, the ratio of the desorbed amount to the adsorbed amount was employed in order to check the desorbed extent of the hydrocarbons from the adsorber. In the case of n-octane, the ratio was around 1. However, the ratios for 2,2,4trimethylpentane and toluene appeared to be below 1, although the gas flow did not contain O2. Furthermore, 2,2,4-trimethylpentane had a relative concentration below 1 at temperatures over 208°C. For toluene, relative concentrations below 1 appeared at temperatures over 148°C. These results may be attributed to the oxidation of the hydrocarbons and the adsorbed oxygen over the surface of the adsorber during the pretreatment.

Fig. 3 shows FTIR spectra for gases collected at 30 and 230°C during the TPA experiment for 2,2,4-trimethylpentane on HA #1 in the nitrogen atmosphere. As shown in Fig. 3, the main peak of 2,2,4-trimethylpentane between 2800 and 3100 cm$^{-1}$ is almost unchanged regardless of the temperature. However, as the temperature increases, new peaks such as CO, CO$_2$, and H$_2$O appear. It is reasonable that this oxidation reaction plays a key role in reducing the relative concentration of 2,2,4-trimethylpentane at higher temperatures.

Fig. 4 shows TPA curves of acetone, methanol, and acetaldehyde on HA #1. The inlet concentration and the flow rate were the same as in Fig. 2. Although oxygen was not supplied, the relative values of three hydrocarbons moved to 0 with increased the temperature. The order of thermal decomposition appeared to be methanol, acetaldehyde, and acetone.

The results of Figs. 2 and 4 imply that the thermal decomposition of methanol, acetaldehyde, and acetone may be

![Fig. 2. TPA curves of 2,2,4-trimethylpentane, toluene, and n-octane on HA #1.](image)

![Fig. 3. FTIR spectra of 2,2,4-trimethylpentane on HA #1 at 30 and 230°C.](image)

![Fig. 4. TPA curves of acetone, methanol, and acetaldehyde on HA #1.](image)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>$\text{AA}^a$ (mmol/g)</th>
<th>$\text{DA}^b$ (mmol/g)</th>
<th>$\text{DA}/\text{AA}$</th>
<th>$T_s$ (°C)</th>
<th>$T_f$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Octane</td>
<td>0.0638</td>
<td>0.0641</td>
<td>1.005</td>
<td>47</td>
<td>–</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>0.0739</td>
<td>0.0731</td>
<td>0.989</td>
<td>53</td>
<td>208</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.1149</td>
<td>0.0862</td>
<td>0.750</td>
<td>57</td>
<td>148</td>
</tr>
</tbody>
</table>

$^a$ Adsorbed amount.
$^b$ Desorbed amount.
Fig. 5. FTIR spectra of acetaldehyde on HA #1 at 30 and 230 °C.

Fig. 6. TPA curves of 2,2,4-trimethylpentane on HA #1 with respect to O₂ concentration.

Fig. 7. TPA curves of toluene on HA #1 with respect to O₂ concentration.

Table 3
Adsorbed and desorbed amounts for TPA of 2,2,4-trimethylpentane and toluene on HA #1 according to O₂ concentration

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>O₂</th>
<th>AA a (%)</th>
<th>DA b (mmol/g)</th>
<th>DA/AA</th>
<th>Ts (°C)</th>
<th>Tf (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>0.8</td>
<td>0.0437</td>
<td>0.0431</td>
<td>0.986</td>
<td>43</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.0345</td>
<td>0.0335</td>
<td>0.971</td>
<td>41</td>
<td>128</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.8</td>
<td>0.1131</td>
<td>0.0728</td>
<td>0.644</td>
<td>55</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.1126</td>
<td>0.0698</td>
<td>0.620</td>
<td>55</td>
<td>107</td>
</tr>
</tbody>
</table>

a Adsorbed amount.

b Desorbed amount.

more affected by the oxygen in the structure of the molecules than the oxygen adsorbed on the HA #1 during pretreatment.

FTIR spectra of acetaldehyde on HA #1 at 30 and 230 °C in nitrogen are shown in Fig. 5. As the temperature increased, the main peaks of acetaldehyde between 2600 and 2900 cm⁻¹ almost disappeared and new peaks such as CO, CO₂, and H₂O appeared. From this FTIR result, it can be found that acetaldehyde is partially converted to CO, CO₂, and H₂O during thermal decomposition. This is consistent with TPA results.

TPA curves for 2,2,4-trimethylpentane and toluene on HA #1 according to different O₂ concentrations are shown in Figs. 6 and 7. From Figs. 6 and 7, according to the increase of O₂ concentration, the hydrocarbons were quickly emitted and the conversion efficiency was advanced. The adsorbed or desorbed amounts, the desorption start temperature (Tₛ), and the reaction start temperature (Tᵣ) obtained from Figs. 6 and 7 are presented in Table 3.

In comparison of Tables 2 and 3, both 2,2,4-trimethylpentane and toluene have the same pattern for all parameters. However, the reduction pattern of the parameters is different. According to the increase of O₂ concentration, the adsorbed amount for toluene is changed little while the adsorbed amount for 2,2,4-trimethylpentane is sharply reduced. It can be stated that toluene has higher adsorption affinity than 2,2,4-trimethylpentane. This result agrees well with the previous paper [13], in which the adsorbed amount of toluene is higher than that of 2,2,4-trimethylpentane under the same conditions of adsorber and adsorption temperature.

For conversion efficiency, toluene was found to be higher than 2,2,4-trimethylpentane.

4. Conclusion

Adsorption and conversion of various hydrocarbons on monolithic hydrocarbon adsorbers are studied using a new experimental model, temperature-programmed adsorption (TPA). In this study, methyl alcohol, acetone, acetaldehyde, 2,2,4-trimethylpentane, n-octane, and toluene are chosen as model hydrocarbons for cold start of a vehicle. The effect of the hydrocarbon components and the oxygen concentration on the TPA curve was studied. According to the presence of O₂, the adsorption and desorption amount were decreased, while the conversion efficiency of the hydrocarbons was increased. FTIR spectra confirmed that the hydrocarbons used in this study were partially converted to CO, CO₂, and H₂O. The conversion of the hydrocarbons, which had oxygen in the structure of the molecules, occurred even in the nitrogen atmosphere. This implies that the thermal decomposition of methanol, acetaldehyde, and acetone may be more affected by the oxygen in the structure of the molecules than the
oxygen adsorbed on the HA #1 during pretreatment. The order of thermal decomposition appeared to be methanol, acetaldehyde, and acetone.

References