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Adsorption Isotherms of CO and VOCs on Hydrocarbon Adsorbers of Honeycomb Shape

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Three hydrocarbon adsorbers of honeycomb shape were prepared using a slurry coating method according to the cell density and geometric surface area of a ceramic substrate. Adsorption isotherms of CO and two VOCs (2,2,4-trimethylpentane and toluene) on three adsorbers were measured using a volumetric adsorption apparatus. The isotherms of CO were measured at 303.15 K, and equilibrium experiments for two VOCs were carried out at 303.15 K, 323.15 K, and 343.15 K. The amount of CO adsorbed and metal dispersion was increased with the increase of geometric surface area. The amount of toluene adsorbed was higher than that of 2,2,4-trimethylpentane for all samples. The increase of geometric surface area led to an increase in the amount adsorbed. The equilibrium data of two VOCs were correlated by the Langmuir and the Langmuir−Freundlich isotherms. The latter isotherm predicted equilibrium data better than the former isotherm.

Introduction

To meet more stringent emission regulations, hydrocarbon emissions during the cold start period of an engine must be reduced drastically. Until now, several technologies such as close-coupled catalyst[1] and hydrocarbon adsorber[2] have been developed. The hydrocarbon adsorber has adsorbing materials such as zeolite or other adsorbent materials to effectively adsorb hydrocarbons at lower temperatures and precious metals to convert hydrocarbons into CO_2 and H_2O at higher temperatures. The performance for adsorption and conversion of adsorber can be advanced by the increase of cell density and geometric surface area.[3]

We proposed previously a new model,[4] temperature programmed adsorption (TPA), to choose an adsorber with high efficiency for adsorption and conversion. The model can evaluate simultaneously the adsorption capacity and the conversion of hydrocarbons as a function of temperature during cold start. To understand fully the TPA behavior on an adsorber, thermodynamic data of adsorption of hydrocarbons on the adsorber are needed. Metal dispersion is also required to predict the conversion. Metal dispersion is measured commonly using H_2 and CO adsorption or temperature programmed reduction (TPR).[5]

The components of hydrocarbons generated from an engine during cold start are dependent on fuels, vehicles, and driving conditions. However, regardless of these conditions, 2,2,4-trimethylpentane and toluene, which compose about 10% of hydrocarbons, are the main emissions.[6]

In this paper, the adsorption capacity of CO and two VOCs, 2,2,4-trimethylpentane and toluene, on three monolithic adsorbers was measured as a function of cell density and geometric surface area (GSA) using a volumetric adsorption apparatus. For CO, adsorption isotherms were measured at 303.15 K and pressures up to 50 kPa. For the two vapors, the equilibrium experiments were carried out at different temperatures of 303.15 K, 323.15 K, and 343.15 K and pressures up to 3 kPa. Adsorption data of each vapor were fitted to the Langmuir and the Langmuir−Freundlich equations. [7]

Table 1. Properties of Three Adsorbers: HA #1, HA #2, and HA #3

	HA #1	HA #2	HA #2
t/mm	0.206	0.143	0.088
t_w/mm	0.041	0.034	0.025
D_h/mm	1.064	0.887	0.757
OFA/%	70.2	74.2	80.3
GSA/$m^2 \cdot m^{-3}$	26.4	33.4	42.4
bulk density/$kg \cdot m^{-3}$	650	560	460
cell density/CPSM	6.2×10^5	9.3×10^5	1.4×10^6

Experimental Section

Adsorbers and Adsorbate. Three monolithic adsorbers were prepared by coating the wash coat onto three honeycomb ceramic substrates. The cell densities of the substrates were 6.2×10^5 CPSM (cell/m^2), 9.3×10^5 CPSM, and 1.4×10^6 CPSM. The dimension of the samples was identical to 0.019 m (D) × 0.03 m (L). The wash coat consisted of γ-Al_2O_3 (80%) and ZSM5 zeolite (20%) (a Si/Al ratio of 150/1). Solutions of $PdCl_2$ and $RhCl_3 \cdot 3H_2O$ were added into the slurry of the washcoat. The precious metal (Pd:Rh) ratio was 14:1. The loading amount of the washcoat and precious metals used in the three samples was 120 g/L and 5.3 g/L. The samples were dried at 423.15 K overnight and calcined at 823.15 K for 4 h. The adsorbers of 62, 93, and 140 cpsc were named as HA #1, HA #2, and HA #3. Table 1 shows the properties of the three adsorbers. The wall thickness of the substrates (t) and the wash coat thickness of the adsorbers (t_w) were measured by a SEM (Phillip 505) with an EDS detector. According to the

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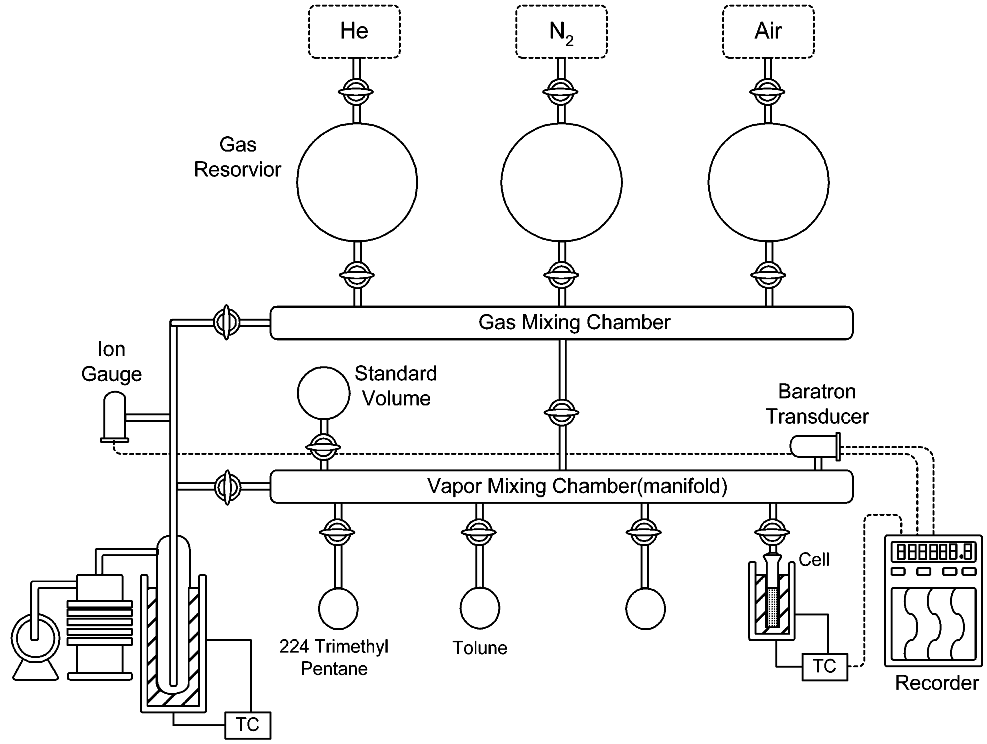

Figure 1. Adsorption equilibrium apparatus.

increase of cell density and the decrease of the wall thickness of the substrate (t), the GSA and OFA (open frontal area) of the adosorbers are increased, and the bulk density, hydraulic diameter (D_h), and wash coat thickness (t_w) are decreased.

In this study, CO (99.999%), 2,2,4-trimethylpentane (Aldrich, 99.8%), and toluene (Aldrich, 99.95%) are used as adsorbates without any pretreatments.

Adsorption Apparatus and Procedure. A schematic diagram of the adsorption apparatus is shown in Figure 1. It is based on the static volumetric method. The amount of vapor supplied to the adsorption cell is determined by *PVT* measurements. The pressure in the manifold and adsorption cell was measured using a Baratron absolute pressure transducer (MKS type 690A13TRA) with a signal conditioner (MKS type 270D). Its reading pressure is 0 to 101.33 kPa. The temperature of the adsorption cell was controlled using a water bath (Jeiotec, MC-11) that could maintain a constant temperature within ±0.04 K. The principal part of the apparatus is a pressure transducer, manifold, and adsorption cell.

The adsorption of CO was carried out to evaluate the metals dispersion on an adsorber. For CO adsorption, before conducting the experiment, the sample in the adsorption cell was reduced under 101.33 kPa of 10% H_2/He at 673 K for 2 h by using the electric heater installed outside the adsorption cell. After that, it was evacuated to the high vacuum of 10^{-6} kPa using a turbomolecular pump (Varian, V70) and a rotary pump at 673 K and kept for 1 h, and then it was cooled to ambient temperature. The adsorption temperature of 303.15 K was controlled by the water bath. The adsorption experiment was carried out at pressures of 10 kPa and 50 kPa of CO. On finishing the first adsorption test, it was evacuated at the adsorption temperature and held for 1 h. The second adsorption experiment was then conducted. To calculate the metal dispersion, the amount of CO adsorbed irreversibly was determined by subtracting the second isotherm from the first isotherm. The detail of the procedure was described elsewhere.[8]

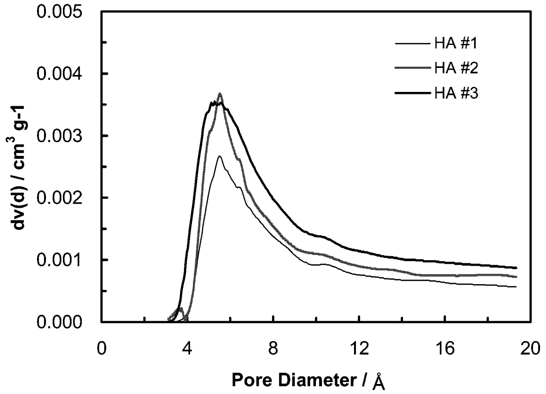

Figure 2. Pore size distribution of HA #1, HA #2, and HA #3.

Table 2. BET Surface Area, Micropore Volume, and Metal Dispersion of Three Adsorbers: HA #1, HA #2, and HA #3

	HA #1	HA #2	HA #3
BET surface area/$m^2 \cdot g^{-1}$	48.8	54.3	71.3
micropore volume/$cm^3 \cdot g^{-1}$	0.0192	0.0204	0.0275
metal dispersion/%	18.1	21.3	23.5

The adsorption experiments of the two VOCs (2,2,4-trimethylpentane and toluene) on the adsorbers were carried out in the same apparatus used for the CO adsorption. The adsorption temperature used was 303.15 K, 323.15 K, and 343.15 K. The detailed procedure of a static volumetric adsorption was described in an earlier paper.[9]

Results and Discussion

BET Surface Area and Pore Volume. Micropore distributions (<20 Å) of the three adsorbers are shown in Figure 2. The micropore distribution was obtained by N_2 isotherms and a method of Horvath and Kawazoe (HK).

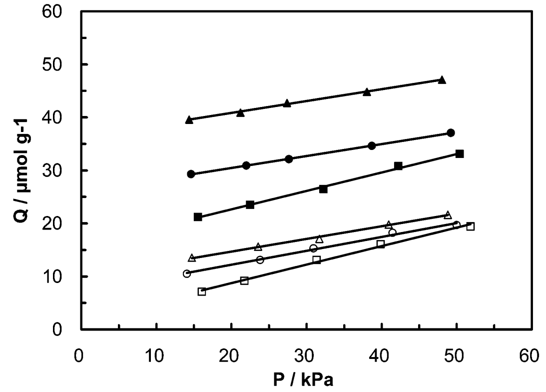

Figure 3. Adsorption isotherms of CO on HA #1, HA #2, and HA #3 at 303.15 K. (HA #1: ■ (1st), □ (2nd). HA #2: ● (1st), ○ (2nd). HA #3: ▲ (1st), △ (2nd).)

Table 3. Equilibrium Data of 2,2,4-Trimethylpentane and Toluene on HA #1 at 303.15 K, 323.15 K, and 343.15 K

303.15 K		323.15 K		343.15 K	
P/kPa	Q/mol·kg^{-1}	P/kPa	Q/mol·kg^{-1}	P/kPa	Q/mol·kg^{-1}
		2,2,4-Trimethylpentane			
0.053	0.038	0.092	0.034	0.039	0.015
0.118	0.057	0.237	0.051	0.125	0.024
0.204	0.074	0.421	0.069	0.250	0.033
0.355	0.098	0.658	0.087	0.487	0.045
0.566	0.122	0.947	0.103	0.691	0.053
0.789	0.139	1.289	0.120	0.901	0.061
1.118	0.163	1.678	0.135	1.230	0.072
1.474	0.184	2.033	0.146	1.539	0.081
1.803	0.198	2.329	0.155	1.822	0.088
2.197	0.212	2.592	0.163	2.191	0.098
2.546	0.225			2.546	0.105
		Toluene			
0.040	0.070	0.046	0.055	0.046	0.028
0.079	0.107	0.132	0.079	0.118	0.043
0.184	0.136	0.270	0.101	0.237	0.058
0.283	0.155	0.474	0.123	0.401	0.070
0.428	0.176	0.776	0.144	0.592	0.082
0.592	0.195	1.013	0.156	0.849	0.092
0.842	0.216	1.283	0.167	1.204	0.103
1.105	0.236	1.614	0.177	1.507	0.110
1.382	0.256	2.039	0.190	1.743	0.114
1.678	0.275			2.026	0.118
2.000	0.294				

Table 4. Equilibrium Data of 2,2,4-Trimethylpentane and Toluene on HA #2 and HA #3 at 323.15 K

HA #2		HA #3	
P/kPa	Q/mol·kg^{-1}	P/kPa	Q/mol·kg^{-1}
	2,2,4-Trimethylpentane		
0.072	0.034	0.092	0.051
0.224	0.057	0.250	0.076
0.428	0.080	0.454	0.102
0.776	0.108	0.724	0.126
1.164	0.130	0.987	0.144
1.566	0.152	1.276	0.161
1.941	0.168	1.645	0.183
2.309	0.182	2.013	0.199
2.724	0.196	2.329	0.214
		2.697	0.230
	Toluene		
0.033	0.065	0.039	0.091
0.112	0.097	0.099	0.123
0.224	0.119	0.250	0.160
0.395	0.141	0.539	0.198
0.618	0.163	0.809	0.228
0.934	0.182	1.171	0.251
1.296	0.200	1.533	0.270
1.658	0.216	1.796	0.285
2.079	0.232	2.092	0.301

For all adsorbers micropores were distributed between 4 Å and 10 Å. Pore volumes at pore diameters under 10 Å were increased with the increase of cell density and geometric surface area. The BET surface area and micropore volume (<20 Å) of the adsorbers are shown in Table 2. The surface area and micropore volume seem to increase in the order HA #1, HA #2, and HA #3. This result notes that the increase of the cell density and the geometric surface area of the substrate leads to an increase of the BET surface area and micropore volume of the adsorber.

CO Isotherms and Metal Dispersion. Isotherms for CO on the three adsorbers at 303.15 K are shown in Figure 3. Two isotherms for each adsorber were obtained. The first isotherm is the measure of irreversible and reversible CO, and the second one is only that of the reversible CO.[10] In this figure, closed symbols are the data of the first isotherm and open symbols are those of the second one. As cell density and geometric surface area increase, CO amount adsorbed was increased at constant pressures. The irreversible CO from the difference of two isotherms was also increased. Metal dispersion may be advanced by the increase in the cell density and geometric surface area. Metal dispersion was calculated using an extrapolation method and assuming a 1:1 stoichiometry for Pd:CO and Rh:CO. The values for metal dispersion of the three adsorbers are shown in Table 2. As expected, the value increased with the increase of cell density and geometric surface area.

VOC Isotherms. Equilibrium data of 2,2,4-trimethylpentane and toluene vapors on HA #1 at three different temperatures of 303.15 K, 323.15 K, and 343.15 K and pressures up to 3 kPa were measured. The values are presented in Table 3. The adsorbed amount of 2,2,4-trimethylpentane and toluene vapors on HA #2 and HA #3 at 323.15 K and pressures up to 3 kPa was also measured. The results are listed in Table 4. Tables 3 and 4 represent that toluene was more adsorbed than 2,2,4-trimethylpentane on the adsorbers. This means that the adsorption affinity of toluene is superior to that of 2,2,4-trimethylpentane.

The Langmuir and Langmuir–Freundlich isotherms[10] are used to correlate the experimental results.

Langmuir isotherm

$$Q = \frac{Q_m bP}{1 + bP} \tag{1}$$

Langmuir–Freundlich isotherm

$$Q = \frac{Q_m bP^{1/n}}{1 + bP^{1/n}} \tag{2}$$

Here, Q_m is the monolayer adsorption amount, and b and n are empirical isotherm parameters.

Figure 4 shows the equilibrium data of 2,2,4-trimethylpentane on HA #1 at 303.15 K, 323.15 K, and 343.15 K, and corresponding amounts fitted with the Langmuir and the Langmuir–Freundlich isotherms. Figure 4 shows there are large deviations between experimental values and the Langmuir isotherm. However, the Langmuir–Freundlich isotherm fitted the data well. This pattern appeared to be similar for toluene. From this result, it is expected that the Langmuir–Freundlich isotherm can predict equilibrium data at the temperature range of the cold start period.

Table 5. Langmuir and Langmuir−Freundlich Isotherm Parameters To Fit Equilibrium Data at 303.15 K, 323.15 K, and 343.15 K

	Langmuir			Langmuir−Freundlich			
	Q_m/mol·kg^{-1}	b/kPa^{-1}	E	Q_m/mol·kg^{-1}	b/kPa^{-1}	n	E
			303.15 K				
224TMP[a]/HA #1	0.259	1.898	9.363	0.680	0.296	1.823	0.681
toluene/HA #1	0.313	3.775	12.151	2.060	0.127	2.709	2.636
			323.15 K				
224TMP/HA #1	0.201	1.354	7.930	1.140	0.102	1.945	1.180
toluene/HA #1	0.204	3.999	9.488	0.600	0.347	2.475	0.557
224TMP/HA #2	0.238	1.308	9.481	1.980	0.066	1.924	0.408
toluene/HA #2	0.245	4.367	12.113	1.600	0.132	3.021	0.456
224TMP/HA #3	0.276	1.356	8.603	1.800	0.088	2.004	0.474
toluene/HA #3	0.317	4.443	12.180	2.920	0.090	3.167	0.754
			343.15 K				
224TMP/HA #1	0.137	1.049	7.385	2.820	0.024	1.878	1.375
toluene/HA #1	0.128	3.705	8.025	0.600	0.192	2.315	2.250

[a] 224 TMP = 2,2,4-trimethylpentane.

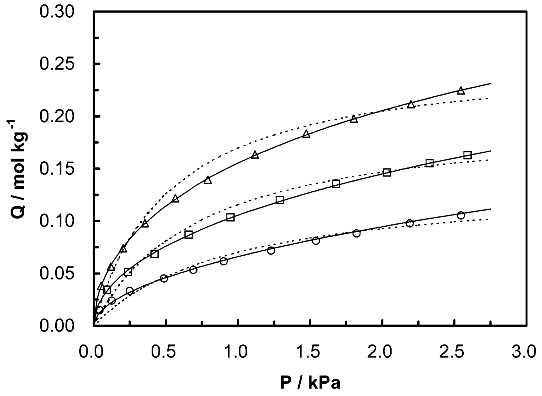

Figure 4. Adsorption isotherms of 2,2,4-trimethylpentane on HA #1 at 303.15 K, 323.15 K, and 343.15 K: △, 303.15 K; □, 323.15 K; ○, 343.15 K; ⋯, Langmuir; —, Languir−Freundlich.

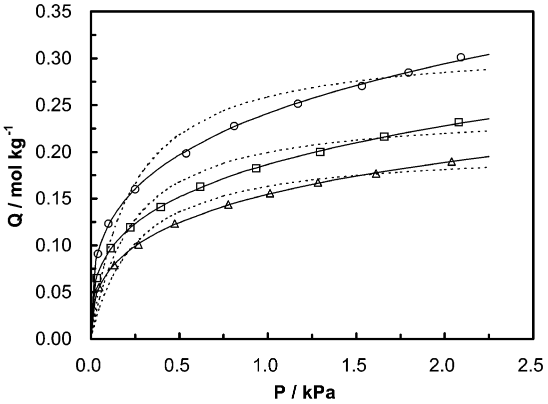

Figure 5. Adsorption isotherms of toluene on HA #1, HA #2, and HA #3 at 323.15 K: △, HA #1; □, HA #2; ○, HA #3; ⋯, Langmuir; —, Languir−Freundlich.

Figure 5 shows the experimental values of toluene on the three adsorbers at 323.15 K, and the data fitted with the Langmuir and the Langmuir−Freundlich isotherms. As the cell density and geometric surface area were increased, the adsorbed amount at any determined pressure was increased. This result was found to be the same as that for 2,2,4-trimethylpentane. This is probably due to the difference of BET surface area and micropore volume between the three adsorbers. The Langmuir−Freundlich isotherm was better than the Langmuir isotherm for fitting the equilibrium data. The Langmuir and the Langmuir−Freundlich isotherm parameters and deviations for the adsorption of 2,2,4-trimethylpentane and toluene on the three adsorbers (HA #1, HA #2, HA #3) at 303.15 K, 323.15 K, and 343.15 K are listed in Table 5.

In this study, E represents the average deviation between the experimental (Q_{exp}) and calculated results (Q_{cal}) as follows.

$$E = \frac{100}{N}\sum_{k=1}^{N}\left[\frac{Q_{\mathrm{exp}} - Q_{\mathrm{cal}}}{Q_{\mathrm{exp}}}\right]_n$$

Conclusions

Three hydrocarbon adsorbers of honeycomb shape were prepared using the slurry coating method. Adsorption isotherms of CO and 2,2,4-trimethylpentane and toluene on the three adsorbers were measured using a volumetric method. The isotherms of CO were measured at 303.15 K, and equilibrium experiments for 2,2,4-trimethylpentane and toluene were carried out at 303.15 K, 323.15 K, and 343.15 K. The amount of CO adsorbed and metal dispersion increased with the increase of geometric surface area. The amount of toluene adsorbed was higher than that of 2,2,4-trimethylpentane for all samples. The increase of geometric surface area led to the increase of the two vapors adsorbed. The equilibrium data of two VOCs were correlated by the Langmuir and the Langmuir−Freundlich isotherms. The Langmuir−Freundlich isotherm predicted the equilibrium data better than the Langmuir isotherm.

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