Adsorption of Neopentane on Magnesium Oxide as Observed in Thermodynamic Aspect.

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Abstract

The absorption of neopentane on magnesium oxide has been investigated by a conventional static system in the temperature range between -50 to -10°C. With the increase in the pressure of the adsorbate, the amount of adsorption at each temperature rapidly increased in the initial stage of adsorption and then increased proportionally. The saturated amount of monolayer adsorption obtained by the extrapolation of adsorption-pressure relation increased with the rise in the pretreatment temperature of magnesium oxide. The molecular area of neopentane on the surface was calculated from the monolayer capacity and the surface area and was estimated to be 30 Å².

With the increase of the surface coverage, the isosteric heat of adsorption rapidly decreased in the initial stage and then reached a stationary value of 4.5 Kcal/mole. On the other hand, the differential molar entropy of adsorption rapidly increased and then gradually decreased with the increase of the coverage. Both the heat and the entropy of adsorption were independent of the pretreatment temperature of magnesium oxide.

From these points of view, the thermal treatment does not change the adsorptive property of the surface but the number of the sites for neopentane adsorption. Furthermore, it might be considered that neopentane first chemisorbed and then adsorbed physically on the surface of magnesium oxide.
Introduction

Magnesium oxide has been widely investigated in the field of heterogeneous catalysis, especially for catalyst carrier and for structural promoter. It is quite important for understanding the active surface to comprehend adsorptive properties of the materials. However, little investigation has been done in the adsorptive interaction of magnesium oxide. Physical adsorption in the region up to completion of the first layer and slightly beyond is well described by the BET equation (1) when the surface is heterogeneous. This equation also fits isotherms on uniform surfaces when the lateral interaction are small, but when they are large and the surface is highly uniform the isotherms are convex to the pressure axis up to near completion of the first layer and the BET equation does not apply until past the convex region. The isotherm of neopentane-magnesium oxide system is not explained by the BET equation and seems to be separated into two parts, namely, strong interaction and weakly held adsorption. In the present work, the difference between these two kinds of adsorption are discussed in terms of the thermodinamical aspect.

Experimental

Magnesium hydroxide was precipitated from stoichiometric amounts of the nitrate (Fisher Analyzed Reagent Grade) with 20% ammonia solution. After precipitation some excess of the ammonia solution was added to ensure the complete precipitation of the hydroxide. It was thoroughly washed by water and then dried by air at 110°C. The resulting product was evacuated at room temperature for 3 days before use. Magnesium hydroxide obtained was decomposed under vacuum around at 330°C to give magnesium oxide. During the course of the dehydration 31.63% (theoretical value, 30.89%) of water was released. Good crystalities of the hydroxide and of the oxide were revealed by X-ray examination.

2,2-Dimethylpropane (neopentane) of 99.9% minimum purity was supplied by Matheson Co. Prior to use neopentane was distilled twice under vacuum.

Adsorption isotherm of neopentane on magnesium oxide was determined with the aid of a conventional gravimetric gas adsorption apparatus using a silica spring microbalance which has a sensitivity of 2 μg. Since neopentane is highly soluble in stopcock greases, we used greaseless cock made of Tefron. Equilibrium pressure at each adsorption point was measured with a U-type mercury manometer, a McLeod gauge and a sensitive spoon gauge. The details of these gauges have been described in elswhere(2).
Prior to every adsorption measurements, the adsorbent was degassed at 100°C under 10⁻⁶ torr until a constant weight was gained.

Adsorption of neopentane on magnesium oxide was measured at temperatures of -10, -30 and -50°C. The temperature constant bath was consisted of 10 liters-Dewar vessel filled with methanol and a liquid nitrogen tank with a electric heater in it. A constant temperature was obtained by introducing and bubbling cold nitrogen gas into the methanol. The maximum variation of this bath is ±0.5°C.

**Results**

Typical adsorption isotherms of neopentane on magnesium oxide pretreated at 800°C are shown in Fig. 1. With the increase in the pressure of neopentane, the amount of adsorption at each temperature rapidly increased in the low coverage region and then increased proportionally. On the extrapolations of the latter parts to the adsorption-amount axis in this figure, the intercepts show the same value of 330 pmole/g. The identical point of the extrapolations was observed also in the cases of other adsorbents tested, such as magnesium hydroxide pretreated at 200 and 300°C and magnesium oxide pretreated at 400 and 600°C. Therefore, the intercept should provide the saturated amount of monolayer adsorption.
Fig. 1. Adsorption isotherms of neopentane at various temperatures on magnesium oxide treated at 800°C.

Fig. 2. Adsorption isotherms of neopentane at -30°C on magnesium oxide treated at various temperatures. From the extrapolations, the saturated amounts of monolayer adsorption for each adsorbents are estimated to be 120, 270 and 330 µmole/g for magnesium oxide pretreated at 400, 600 and 800°C, respectively. The adsorption isotherm of neopentane was examined also on the parent magnesium hydroxide.
Adsorption of Neopentane on Magnesium Oxide as Observed in Thermodynamic Aspect.

The isotherms on the parent material pretreated at 200 and 300°C showed the similar shape of isotherm to that on magnesium oxide. However, the amounts of monolayer adsorption were quite small in comparison with that on magnesium oxide.

Nitrogen adsorption isotherm at the liquid nitrogen temperature was measured to obtain the surface area of the each adsorbent examined. All isotherms of nitrogen for the samples gave good BET plots under the relative pressure between 0.05 and 0.20. The monolayer capacities (Vm) and the surface areas calculated by BET equation are summerized in Table 1. Both of the monolayer capacity and the surface area of magnesium oxide are much greater than those of the parent magnesium hydroxide. The surface area of the former increased with the rise of pretreatment temperature, while that of the latter was found to be independent of the temperature.

<table>
<thead>
<tr>
<th>Pretreatment temperature (°C)</th>
<th>Monolayer capacity (pmole/g)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>16</td>
<td>4.2</td>
</tr>
<tr>
<td>300</td>
<td>17</td>
<td>4.3</td>
</tr>
<tr>
<td>400</td>
<td>120</td>
<td>34</td>
</tr>
<tr>
<td>600</td>
<td>270</td>
<td>89</td>
</tr>
<tr>
<td>800</td>
<td>330</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 1
Monolayer Capacity and Specific Surface Area of Magnesium Oxide Treated at Various Temperatures.

Over the entire range of the surface coverage measured, the logarithmic plots of neopentane pressure against the reciprocal temperature gave good straight-line relationships. The isosteric heats of adsorption determined from these plots are shown in Fig. 3 for magnesium oxide pretreated at 400, 600 and 800°C. The adsorption heat of neopentane on magnesium oxide over the entire surface coverage was found to be almost independent of the pretreatment temperature of the adsorbent. In the region of surface coverage smaller than 0.4, the isosteric heat of adsorption were rapidly decreased with the increase of the coverage and reached the stationary value of 4.5 Kcal/mole. The initial heat of adsorption at the coverage 0.1 is estimated to be 7-9 Kcal/mole for magnesium oxide. On the other hand, the isosteric heats of adsorption on the parent magnesium hydroxide are 6-7 and 4.4 Kcal/mole at the surface coverage of 0.1 and 2.0, respectively.
Discussion

At higher temperature above $320^\circ$C the transformation of magnesium hydroxide to the oxide takes place (3). The monolayer capacity and the surface area of the adsorbent were strongly influenced by this transformation as shown in Table 1. On the other hand, hardly any variation was observed in the shape of the adsorption isotherm and the isosteric heat of adsorption of neopentane subjected to the treatment between 200 and $800^\circ$C. From these points of view, it can be considered that the thermal treatment above $320^\circ$C does not change the property of adsorption site on the surface but the number of the site for neopentane. This can be confirmed qualitatively with the apparent molecular area of neopentane on the surface which can be calculated from the monolayer capacity and the surface area of the adsorbent. The results are cited in Table 2 in terms of various pretreatment temperatures. The molecular areas of neopentane on the surface of magnesium hydroxide and of magnesium oxide are estimated to be 25 and $30\,\text{Å}^2$, respectively. These two kind of the molecular area are found to be independent of the pretreatment temperature within experimental errors.

\begin{table}[h]
\centering
\caption{Molecular Area of Neopentane on the Surface of Magnesium Oxide}
\begin{tabular}{lcccc}
\hline
Pretreatment temperature ($^\circ$C) & 200 & 300 & 400 & 600 & 800 \\
Molecular Area ($\text{Å}^2$) & 26 & 25 & 28 & 32 & 29 \\
\hline
\end{tabular}
\end{table}
Since the isosteric heat of adsorption of neopentane can be regarded as independent of the pretreatment temperature of the adsorbent as shown in Fig. 3, the adsorption sites on the surface of the adsorbent treated at various temperatures are considered to have the similar strength for the interaction with neopentane. In the region of smaller surface coverage below 0.4, the isosteric heat of adsorption remarkably decreased with the increase of the coverage. On the other hand, the isosteric heat of adsorption at higher coverage above 0.4 was found to show almost constant value of 4.5 Kcal/mole. Furthermore, all the adsorption isotherms measured in this work showed the initial rapid increase and the proportional increase in the region of higher pressure, as shown in Fig. 1 and 2. From these points of view, the surface of magnesium oxide can be divided into two parts with respect to the nature of adsorption sites for neopentane, namely, heterogeneous surface corresponding to the coverage smaller than
0.4 and homogeneous one corresponding to that greater than 0.4. Therefore, neopentane is considered to adsorb on strong heterogeneous surface in the initial stage and then on weak homogeneous surface.

The differential molar entropy for the interaction between neopentane and magnesium oxide were evaluated following the procedure of Young and Crowell (4). The results are shown in Fig. 4 with respect to magnesium oxide pretreated at 400, 600 and 800°C. In the initial stage of neopentane adsorption on magnesium oxide the calculated entropy is very low and rapidly increased with the increase of the surface coverage. The maximum entropy which was estimated to be 32 cal/deg/mole was observed at the coverage of 0.4. The entropy then decreased gradually with the coverage. During the entire course of adsorption tested these three kinds of magnesium oxide showed the same differential molar entropy for the adsorption of neopentane within experimental errors.

![Fig. 4. The differential molar entropy of neopentane on magnesium oxide treated at various temperatures.](image)

○ 800°C; ⋄ 600°C; ⊲ 400°C;
From the results shown in Fig. 4, the mobility of neopentane molecule adsorbed on the surface of magnesium oxide is presumably very small in the initial stage of the adsorption. Since the heat of adsorption in this stage showed extremely high values which seemed to correspond to chemisorption (Fig. 3), neopentane molecules are considered to be strongly held on the sites of magnesium oxide surface, namely, the bonds between neopentane and magnesium oxide is presumably chemical bond. The actual physical adsorption is considered to begin at the coverage of 0.4, from which point the heat of adsorption will correspond to the heat of liquefaction of neopentane, as shown in Fig. 3.

In view of the uncertain crystal structure of magnesium oxide and the equally uncertain surface structure, it would be unwise to ascribe all of the variations in the heat of adsorption to the entropy of adsorption, nevertheless the correlation obtained suggest that the heat and the entropy of adsorption may give us valuable informations.

References