

MULTILAYER ADSORPTION CHARACTERISTICS OF HEAVY WATER ON ACTIVATED ALUMINA

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Introduction

In a previous study³⁾ we reported the characteristic of adsorption of water on activated alumina in relation to the adsorption potential, and proposed a multilayer model of adsorption of water on an alumina surface. The characteristics were described by an empirical Freundlich-type polynomial:

$$Q = \sum_{j=1}^3 Q_{sj} \exp(-A/E_j) \quad (1)$$

$$A = RT \ln(P_s/P) \quad (2)$$

where j denotes the ordinal number of layer, and Q_{sj} and Q represent the capacity of j -stage for monolayer and the sum of the amounts adsorbed. The adsorption potential A is defined by Eq. (2), where P_s and P are the saturation and equilibrium pressures at the relevant temperature T . The factor E_j is the characteristic energy on j -stage.

In the modeling of multilayer formation, two kinds of progressional rules were considered in relationships between ordinal adsorption stages. It was found that the empirical equation is consistent with a polynomial derived in accordance with the rules. This consistency suggested that the real multilayer belongs almost to a type of model formation. The multilayer model is further verified here by examination of the adsorption of heavy water on alumina.

1. Experimental

This study of adsorption of D₂O is continued from the previous study, using the same apparatus, procedure and adsorbent specimen. The adsorbate was water deuterated in a rate of 99.8%. Hill-MacMillan's equation¹⁾ and Van Hook's equations^{2, 4)} were applied to the determination of D₂O vapor pressures from saturation temperatures; the former was for a temperature of/above 277 K and the latter for a temperature below it. The adsorption was examined in three series of experiments beginning

from regeneration at 593 K. The first series, Run 1, was begun from the condition before the alumina was contaminated by D₂O. The second and third, Runs 2 and 3, were from that after contamination. Equilibria were measured for 72 points of potential between 440 and 47,230 J/mol, determined by combinations of a pressure from 39 to 3933 Pa and a temperature from 295.3 to 582.1 K. The temperature conditions are indicated in figure captions.

2. Results and Discussion

Multilayer formations were modeled as decorations on surface hydroxyl groups of alumina with water by hydrogen-bonding, where it was predicted that the molar amount of the functional groups is comparable to the stage capacity for the first layer. If the group or its hydrogen atom is exchangeable for DO- or D- of heavy water D₂O adsorbed, the presence of the groups is suggested by the gravimetric difference of the dry alumina sample between hydroxylated and deuterioxylated surface conditions.

Figure 1a shows the results of Run 1 with plots. Cross keys are the data on the basis of HO-surface, and circle keys are the data corrected on the basis of DO-surface with a difference of 0.1497 mol/kg. This value was estimated as the molar amount of D₂O corresponding to the gain in weight change from HO- to DO-surface, 2.999 g/kg, based on the amount of surface hydroxyl groups predicted as equal to Q_{s1} , 2.981 mol/kg. Otherwise, the amount of the groups was valued at 3.00 or 2.93 mol/kg, from the difference observed in weights of the adsorbent sample regenerated before and after Run 1. These experimental values almost agree with the same value predicted as Q_{s1} .

The curve approximating the circle keys was drawn from the calculation by Eq. (1) with parameter values listed in Table 1. The dotted line shows the characteristics of H₂O, for reference. The parameter values for D₂O were obtained by analyzing the experimental characteristics involving the corrected data of Run 1, as follows.

The characteristics of D₂O were stratified by the

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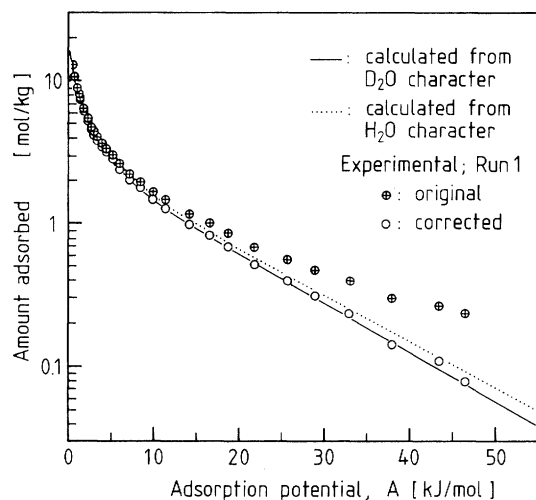


Fig. 1a Influence of difference of gravimetric basis between HO- and DO-surfaces on characteristics of adsorption of D₂O on activated alumina

Table 1. Parameter values for Eq. (1) obtained by multilayer analyses

j [-]	Q_{sj} [mol/kg]	E_j [J/mol]
1	2.981	12,620
2	5.851	2,450
3	10.66	530

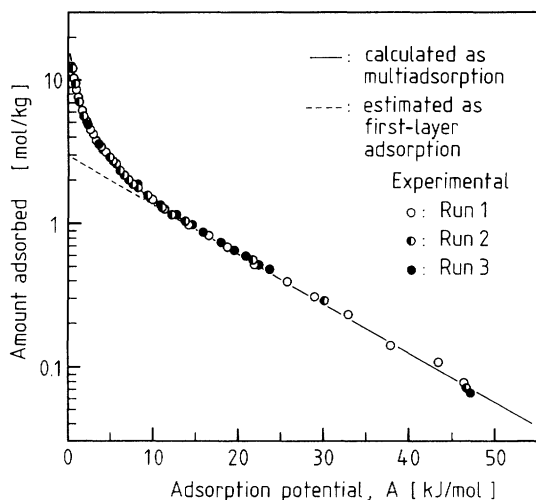


Fig. 1b Characteristics of D₂O on alumina with respect to the potential. Temperatures in potential order from 47.2 to 12.16 kJ/mol: 519.2, 505.0, 582.1, 559.0, 527.4, 493.5, 410.9, 466.7, 444.9, 369.6, 363.0, 419.4, 363.6, 363.0, 363.0, 398.8, 363.0, 384.8, 363.0, 363.0, 369.3, 318.7, 363.0 and 319.3 K

same procedures as for H₂O, but where the Q_{sj} -values were decided beforehand as equivalent to the values for H₂O because of the assumption of the same multilayer structure. The first-layer characteristic is determined by a straight line in **Fig. 1b**. The E_1 -value is comprised in

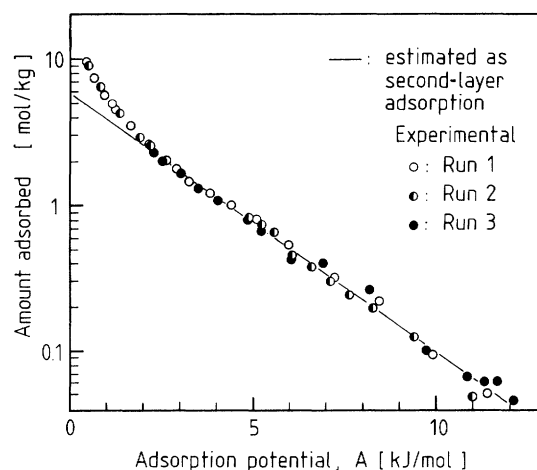


Fig. 2 Characteristics of D₂O on alumina in suppression of the first characteristic. Temperatures in potential order from 12.08 to 2.27 kJ/mol: 362.4, 362.4, 351.4, 362.4, 319.6, 362.4, 342.0, 304.3, 320.1, 332.5, 319.6, 304.3, 319.4, 324.7, 318.3, 304.3, 319.6, 319.6, 304.3, 316.8, 319.6, 319.6, 304.3, 318.0, 319.8, 304.3, 318.0, 304.3, 318.0, 304.6, 318.0, 305.0, 318.0, 318.0, 304.7 and 304.7 K

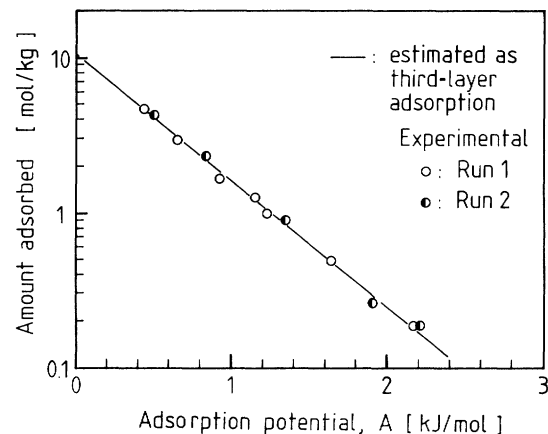


Fig. 3 Characteristics of D₂O on alumina in suppression of the first and second characteristics. Temperatures in potential order from 2.20 to 0.440 kJ/mol: 304.3, 317.4, 302.4, 316.8, 298.9, 311.7, 311.4, 310.2, 296.2, 308.3, 295.3 and 307.1 K

Table 1. **Figure 2** shows the data distribution with the first-layer characteristic suppressed. From the distribution, the second-layer characteristic is isolated as a straight line with the E_2 -value included in Table 1. By eliminating the second characteristic, the corrected data show a linear distribution in **Fig. 3**; the third layer is characterized with the E_3 -value shown in Table 1.

As shown in **Fig. 1b**, the curve calculated by Eq. (1) can describe the adsorption characteristics of D₂O comprehensively. Successful application of the same values of Q_{sj} demonstrates that the multilayer of D₂O has the same structure as that of H₂O. The E_j -values are smaller than the corresponding values for H₂O, but are analogous to them; the energy difference between H₂O and D₂O can be regarded as an isotopic effect. However, notice that the two are fundamentally different; H₂O

adsorption is on the HO-surface of alumina, while D₂O adsorption is on its DO-surface.

Conclusions

The surface-structural hydroxyl group exchanges its hydrogen ion or itself for D- or DO- of D₂O adsorbed. The multilayer model was confirmed by the experimental and analytical results of adsorption of D₂O on activated alumina.

Nomenclature

Symbols are the same as in a previous paper³⁾.

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