A MULTILAYER MODEL FOR ADSORPTION OF WATER ON ACTIVATED ALUMINA IN RELATION TO ADSORPTION POTENTIAL

KENJI KOTOH*, MIKIO ENOEDA, TETSUYA MATSUI
AND MASABUMI NISHIKAWA

Department of Nuclear Engineering, Kyushu University, Fukuoka 812

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Adsorption of water vapor on activated alumina was examined by a gravimetric method. The experimental results are described by a Freundlich-type polynomial with respect to the adsorption potential. In order to characterize the adsorption, a multilayer of water is assumed here on the alumina surface. Considering the hydrogen-bonding, several types of formation are modeled on structural hydroxyl groups supposed as the surface sites. In the modeling, two kinds of rules are observed in the relationship between the accumulating layers; structural ratios of molecules and allotment ratios of the potentials. In accordance with these rules, an attempt is made to derive an expression for the multilayer adsorption in a model by applying a Freundlich-type equation to the surface monolayer adsorption. The derivation gives a polynomial similar to the empirical expression. It is found from comparison of the parameters of both equations that the model multilayer is consistent in the examined adsorption system.

Introduction

Activated alumina is an effective drying agent. The adsorption of water vapor on the alumina is a classical and widely used operation, but is not fully understood because of its complicated mechanism.

For vapor adsorption systems, Polanyi's potential theory is convenient because isotherms at different temperatures are characterized in common by a single curve with respect to the potential:

$$A = RT \ln(P_s/P) \quad (1)$$

where P and P_s are the vapor pressures in equilibrium and saturation at the temperature T . Dubinin *et al.* developed expressions related to A in the pore-filling concept³⁻⁵. The formulas were satisfactorily applied to describing adsorption equilibria such as on activated carbon^{11-13, 20}. The pore-filling is deduced essentially from the multilayer adsorption on the pore wall surface¹⁹.

Activated alumina is γ -alumina having a hydrated surface, on which structural hydroxyl groups play the role of polar adsorption sites¹⁴. Water molecules are strongly polar, and are known to make clusters with hydrogen-bonding^{1, 6, 9, 17, 21}.

Adsorption equilibria of water vapor on activated alumina were obtained from gravimetric measurements in this study. The experimental results are arranged to the potential and are characterized empirically by a homogeneous polynomial. A multilayer is assumed for the phase of water adsorbed on the hydroxylated surface of alumina, where several types of molecular formation are supposed on the structural hydroxyls. In the mod-

eling of adsorbed phase, the formations are considered in structural and energetic relations between stratified molecules. The characteristics determined empirically are verified by consistencies with one of the model formations.

1. Experimental

The water adsorption was examined by a gravimetric method, using activated alumina made by Nakarai Chemicals, Ltd. The apparatus is composed of a microbalance and a moisture supply system as shown in Fig. 1. The sample moisture is supplied from the system to the microbalance by nitrogen gas as carrier. The system consists of a cold trap as dryer, a water bubbler as humidifier and a pair of glassbeads-bed columns as condenser for gas humidity control, which is submerged in a thermostatic ethanol bath. A gas stream bypassing the bubbler is prepared in order to moderate the overloading of moisture onto the condenser. The gas stream into the gravimetric device was regulated at a flow rate about 400 ml/min. The vapor pressure in the stream was determined from the saturation pressure at a coolant temperature in the bath in the range from 247.5 to 300.9 K.

In the microbalance a specimen of about 400 mg was suspended inside a double-tube finger. The specimen gets the moisture from the gas stream flowing within the inner tube through the outer tube, where the stream is heated by the outer tube wall at controlled temperatures. The counter-flow stabilizes the adsorption atmosphere temperature. The specimen was activated by heating at 593 K in the dry stream over half a day. The weight adsorbed was determined from measurement just

* Received September 14, 1992. Correspondence concerning this article should be addressed to K. Kotoh.

Fig. 1 Apparatus used for gravimetric measurement of water vapor adsorption

Fig. 2 Characteristics of water on alumina with respect to the potential. Experimental temperatures in potential order from 51.0 to 10.1 kJ/mol: 568.0, 547.8, 577.2, 465.6, 550.5, 449.6, 430.4, 510.4, 449.8, 400.0, 442.5, 391.5, 386.7, 376.3, 417.6, 371.5, 387.8, 360.2, 370.9, 348.6, 347.8 and 340.0 K

after stopping the stream in order to eliminate the flow pressure when sufficient equilibrium in the stream was observed.

The equilibria at 52 points were measured under potential conditions from 51,032 to 205 J/mol; the vapor pressures were chosen between 59.5 and 3715 Pa, and the temperatures were adjusted between 300.3 and 577.2 K. The individual temperature conditions are listed in the captions of figures illustrating the relations to the potential. The examination was performed as three series of experiments beginning from the activation in order to check the reappearance of adsorption characteristics: Runs 1, 2 and 3.

2. Experimental Results and Analyses

When equilibrium data are obtained in a wide range from a multilayer adsorption system, the adsorption characteristic of the original layer emerges from the data distribution with decrease in the amount adsorbed. The experimental results are shown in **Fig. 2**, by plotting with

Table 1. Values of parameters for Eq. (4) obtained by multilayer analyses

j [-]	Q_{sj} [mol/kg]	E_j [J/mol]
1	2.981	13,390
2	5.851	2,791
3	10.66	644.4

Fig. 3 Characteristics of water on alumina in suppression of the first characteristic. Experimental temperatures in potential order from 9.04 to 3.51 kJ/mol: 332.9, 328.7, 329.2, 324.1, 318.8, 318.4, 314.7, 311.2, 306.8, 303.2, 301.4, 301.4 and 301.7 K

respect to the potential. Their plots seem to be distributed on a curve. Runs 1, 2 and 3 demonstrate the reappearance of the adsorption examined. By assuming that the potential theory is applicable to this adsorption system, the curve under the plots is calculated from the following analyses.

On a semilogarithmic scale such as in this figure, a straight line is expressed by

$$Q = Q_s \exp(-A/E) \quad (2)$$

where Q_s and Q are respectively the limiting capacity on the adsorption field and the amount adsorbed, and E represents the energetic parameter characterizing the extent of the exponential profile. This equation results in a description of the Freundlich isotherms,

$$Q = Q_s (P/P_s)^{-RT/E} \quad (3)$$

The experimental distribution appears to converge on a line with decrease in the amount adsorbed. We now presume the multilayer and anticipate that the original monolayer is formed by Freundlich-type adsorption but where the relation of the Polanyi potential is held. By approximating the local distribution in **Fig. 2** with the line, the first layer is determined to have the characteristic described by Eq. (2) with the parameters having the values listed in **Table 1**.

The next layer's character emerges from the experimental data by subtracting the amounts estimated for

Fig. 4 Characteristics of water on alumina in suppression of the first and second characteristics. Experimental temperatures in potential order from 2.42 to 0.205 kJ/mol: 301.7, 299.5, 300.3, 301.4, 300.4, 302.7, 302.6, 302.6, 292.6, 302.6, 302.6, 292.6, 302.6, 302.9, 302.9 and 302.4 K

the first layer. The results are shown in **Fig. 3**. The plots of modified data are distributed to converge on a line with increase in the potential as well as in Fig. 2. In the same way, the second layer adsorption is approximated by Eq. (2). The parameters are evaluated as in Table 1.

By the same procedure, the characteristic of the third layer is isolated from the data in Fig. 3 by suppressing the second characteristic. The corrected data are shown in **Fig. 4**. The data appear linearly distributed. The approximate curve is calculated by Eq. (2) with the parameters having the values shown in Table 1.

The adsorption of water on alumina examined in the present range, therefore, is expressed by the three characteristics as follows:

$$Q = \sum_{j=1}^3 Q_{sj} \exp(-A/E_j) \quad (4)$$

where j denotes the ordinal numbers of the adsorption layers, and Q represents the overall amount adsorbed. The comprehensive approximation curve in Fig. 2 is calculated by Eq. (4) with the parameter values obtained from the individual analyses.

The logarithmic graphics such as in Fig. 2 are convenient for showing the characteristic in the low range of adsorption coverage or equilibrium pressure, but the scaling is reduced with increase in the coverage or the pressure. To verify the adsorption in the range near saturation, an isothermal illustration on an ordinary scale is made here from the potential expression. For this purpose, Eq. (4) is modified with Eq. (3) as

$$Q = \sum_{j=1}^3 Q_{sj} (P/P_s)^{-RT/E_j} \quad (5)$$

Since the equilibrium data were obtained at varied temperatures, the equilibria must be rearranged in the relations with pressures corrected from measured values to estimated ones at a common temperature. The estimation is carried out by the following equation derived from Eq.

Fig. 5 Adsorption isotherm estimated for water on activated alumina at 300 K

(1):

$$P = P_s \exp(-A_e/RT) \quad (6)$$

where the subscript e identifies the experimental value. **Figure 5** shows an isotherm at 300 K, for example, where the modified data are plotted. The line drawn under the plots is calculated by Eq. (5). The agreement of plots and line endorses the consistency of the empirical expression on the ordinal scale in this figure.

Desai *et al.*²⁾ recently reported isotherms for water on several activated aluminas. The isotherms are similar to that in Fig. 5. They analyzed the isotherms as a composite by the BET model, however. To verify the stratification by the characterization based on the potential theory, we consider adsorption with models of water decoration on structural hydroxyls of alumina surface.

3. Multilayer Model of Adsorption of Water on Alumina

3.1 Adsorptive sites on the surface

Latent but strong characters lie on an alumina surface that is hydroxylated. The surface, when heated at temperatures near 800 K, begins to be dehydrated by coupling of its structural hydroxyl pairs^{15, 16)}. The dehydration creates two types of ionic defect^{7, 8)}; one is of aluminum ions exposed as electron acceptor (Lewis acid) and the other is of oxygen ions left behind as electron donor (Lewis base)¹⁴⁾. On such a surface the water adsorbed is dissociated to form the structural hydroxyls again; this is identified as chemisorption. The chemisorption is irreversible, however. Some of the defects acting as chemisorptive sites may cease to exist in the thermal process, because crystalline transition takes place in the alumina during heating at dehydration temperatures¹⁸⁾. While the adsorption is expected to operate

Fig. 6a Model of multilayer formation of water adsorbed on hydroxylated alumina surface, Type I

in reappearance, the adsorbent should be regenerated at least so as not to cause the dehydration of the surface.

The surface saturated by hydroxyl groups still has weakly but functionally adsorptive sites. The groups bound by aluminum ions exhibit acidic and basic characters on their hydrogen and oxygen atoms. The acidic and basic sites provide the hydrogen-bonding function to the water molecules. The adsorption on the surface hydroxyls may be the result of physisorption or quasi-chemisorption. This type of adsorption can reappear under regeneration below dehydration temperatures because there is no change in the surface structure. In this study the major object is to gain an insight into the behavior of water in this type.

Water molecules are considered to form a variety of combinations with the surface groups. The variation is influenced by structural conditions of the hydroxylated surface. Several surfaces can be assumed as illustrated in **Figs. 6a** and **6b**. The surface sites can be classified into two types; those with only one acidic site on a hydroxyl group, Type I, and those with one pair of acidic and basic sites on one, Type II. Although real surfaces may comprise mixtures of these types, the adsorption is here accounted for with the simplified surface structures.

3.2 Decoration on surface sites with water molecules

The water molecule has three active sites; one is the basic site on the oxygen atom and the other two are the acidic sites on hydrogen atoms. The molecules gathering around an ionic nucleus tend to construct a cluster by linking together with hydrogen-bonding. In a similar manner, polar sites present on a surface can be decorated by water molecules. Such structural diagrams as in **Figs. 6a** and **6b** were already being drawn; for example, Ishikawa *et al.*¹⁰⁾ introduced the formations of water on an apatite surface through their infrared spectroscopic study.

In Type I in **Fig. 6a**, the surface hydroxyls offer an adsorption stage consisting of acidic sites for a monolayer of water, defined as the first stage. The water molecules are adsorbed there by interaction between their basic sites and the acidic stage sites. As a result, the adsorbed monolayer exposes its surface, exhibiting acidic character to the vapor phase. The layer surface plays the role of adsorption stage as well as the hydroxyl surface, defined as the second stage. The second stage

Fig. 6b Model of multilayer formation of water adsorbed on hydroxylated alumina surface, Type II: (a) Case 1, (b) Case 2-1 and (c) Case 2-2

has but twice as many sites as the first stage. The layer adsorbed on the second stage forms the third stage on its surface in the same way. The third stage provides a capacity twice as large as that of the second stage for the third layer.

In Type II in **Fig. 6b**, water molecules can make several types of combination, which are determined by neighboring conditions of the hydroxyl groups. Case 1 is a situation of the groups ordered in the same direction, where a molecule is adsorbed on a pair of the acidic and basic sites located individually on adjoining groups. This molecule offers one acidic site as the second stage. Cases 2-1 and 2-2 are situations of the groups being arranged in reverse directions to each other, where a molecule is adsorbed on a pair of acidic sites or basic sites on neighboring groups. A molecule perching on the acidic twins issues two acidic sites as the second stage, in Case 2-2, where the molecule is adsorbed by dual reaction of its basic site with the twins. Otherwise, one standing on the basic twins issues only one basic site, in Case 2-1, for the secondary adsorption.

In not only Type I but also Type II, the capacity of the first stage is comparable to the amount of functional hydroxyl groups. The water decorations in Type I and Case 2-2 of Type II are developed progressively with the numbers 1, 2, 4,... of ordinal layer molecules. The decoration in Type II except in Case 2-2 is different from the former, with the numbers 1, 1, 2,... However, the progressional developments are restricted by the geometry of the adsorbent surface and limited by neighboring distances of decorations. The ideal model formations are defective when the decorations are associated. The decorations in growth approach and combine with each other by mediation of such a molecule adsorbed dually on sites as in Case 2-2.

3.3 Structural and potential relationships between the ordinal stages

As before-mentioned, the capacities of the ordinal adsorption stages are estimated to be in two kinds of geometric progressions; in the formations of Type I and Case 2-2 of Type II, the ratio of j -stage to the first-stage capacity is given as

$$C_{sj}/C_{s1} = 2^{j-1} \quad (7)$$

and in the formations of Cases 1 and 2-1 of Type II, it is given as

$$C_{sj}/C_{s1} = 2^{j-2} \quad \text{for } j > 1 \quad (8)$$

where C_s is the stage capacity and its subscript j or 1 denotes the ordinal number of the stage. In both relations the first-stage capacity is equivalent to the number of surface hydroxyls. In addition to these progressions, a relation of the potentials between the stages can be considered.

A vapor molecule, having the free energy μ , is adsorbed on a single site or a pair of sites located at the potential A equal to μ , with release of the latent heat of condensation. The adsorbed molecules are in the liquid state. As the dielectric substance the condensed molecule is induced to polarize by the energy corresponding to A . The polarization produces a difference of polar potential in the molecule, with positive and negative potentials on opposite sides. If the molecule behaves as a perfect dielectric, the potential difference corresponds to A , which is allotted evenly to the opposite sides as reversely polar potentials.

In Type I, on the first stage a molecule adsorbed on a site at A is given a gain of $A/2$ on the acidic side comprising the twin centers; one shares the gain with the other. The molecule hence provides two sites having $A/4$ as the second stage. On the other hand, the basic-side energy of $A/2$ is used for binding the molecule itself to the surface site. In the same manner, molecules adsorbed on the second stage keep themselves there with the energy $(A/4)/2$, then provide the third-stage sites having a quarter of the second-stage potential $(A/4)/4$.

In Type II, Case 1, a molecule on the first stage at A provides one acidic site having $A/4$ as the next stage, on which an adsorbed molecule issues two acidic sites having $(A/4)/4$. In Case 2-1, on the first stage a molecule adsorbed at A provides one basic site having $A/2$ as the second stage, but the next molecule adsorbed produces two different sites as the third stage; one is the acidic site having $(A/2)/4$ and the other is the basic one having $(A/2)/2$. That suggests a complex of potential distribution among the upper stages. If a real surface structure is almost in Type II, it will be difficult to clarify such relationships because Cases 1, 2-1 and 2-2 may be comparably existing in a mixture; Cases 2-1 and 2-2 may be paired at least.

3.4 Verification of experimental results with the model

In the model of Type I, if the adsorption on the first

stage is characterized by the following Eq. (9), similar to Eq. (2):

$$C_1 = C_{s1} \exp(-A/E_1) \quad (9)$$

where C_{s1} and C_1 are the capacity of the first stage and the amount adsorbed. The amount adsorbed on the second stage C_2 in equilibrium at A is estimated as

$$C_2 = 2C_{s1} \exp(-4A/E_1) \quad (10)$$

which is rewritten by

$$C_2 = C_{s2} \exp(-A/E_2) \quad (11)$$

because the second-stage sites at A are produced by the molecules adsorbed on the first-stage sites at $4A$. An aggregate expression is thus obtained:

$$C = \sum_{j=1}^m C_{sj} \exp(-A/E_j) \quad (12)$$

where m denotes the final number of j , and C is the sum of the amounts adsorbed on every stage. The characteristic energy E_j is hence in the geometric progression:

$$E_j/E_1 = (1/4)^{j-1} \quad (13)$$

The empirical Eq. (4) is involved in the expression of Eq. (12) because Q_{sj} is identical to C_{sj} . The experimental Q_s -values are related in the ratios 1.96 and 1.82 as Q_{s2}/Q_{s1} and Q_{s3}/Q_{s2} ; both are smaller than the model ratio 2 but comparable with it. The experimental E -values are in relations of 0.208 and 0.231 as E_2/E_1 and E_3/E_2 ; both are also smaller than the model ratio 1/4 but comparable with it. These results suggest that the examined adsorption system can be elucidated by the model of Type I. The reduced factors compared with the model ratios are considered to result in the deviations from ideality: the presence of Type II sites in part on the real surface and/or local association of the decorations.

Conclusions

The adsorption of water on activated alumina can be characterized in relation to the adsorption potential and described empirically by the Freundlich-type polynomial. The adsorption is interpreted by the model of formation of water accumulating on the polar surface-sites.

Hydrogen-bonding is functional in the adsorption of water molecules. Several types of multilayer can be supposed on the hydroxylated alumina surface. The types depend on the structural conditions of surface sites. In the multilayer formations, geometric progressions can be assumed in the capacity and potential relationships between adsorption stages.

The empirical expression was verified by the derivation of the same type of homogeneous polynomial in accordance with the rules in the model of multilayer adsorption. From the experimental ratios Q_{sj}/Q_s and E_j/E_1 compared with the model ratios, the model of Type I is suitable for the examined adsorption system of water

on activated alumina.

Nomenclature

A	= Polanyi's adsorption potential	[J/mol]
C	= amount adsorbed on stage in model	[mol/kg]
C_s	= capacity of stage for monolayer	[mol/kg]
E	= characteristic adsorption energy	[J/mol]
j	= ordinal number of layers or stages	[-]
m	= final number of j	[-]
P	= equilibrium vapor pressure	[Pa]
P_s	= saturation vapor pressure	[Pa]
Q	= amount of adsorbate adsorbed	[mol/kg]
Q_s	= limiting amount adsorbed	[mol/kg]
R	= gas constant	[J/(mol·K)]
T	= temperature	[K]
μ	= free energy in vapor phase	[J/mol]

<Subscripts>

1,2,3	= identification of ordinal layer or stage
e	= identification of experimental value
j	= identification of j -stage or -layer

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