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Determination of relative acid strength and acid amount of solid acids by Ar adsorption

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Abstract

Relative acid strength and acid amount of solid acids (alumina, silica-alumina, sulfated zirconia, mordenite, ZSM-5, beta, Y, and reduced MoO_3) are determined by argon adsorption technique. To obtain the heat of Ar adsorption and saturated adsorption amount, the adsorption isotherm is analyzed using the theory reported by Cremer and Flügge. The obtained heats of Ar adsorption and saturated adsorption amounts of sulfated zirconia catalysts and proton-type zeolites correspond well with the activities of acid-catalyzed pentane isomerization of these catalysts. The heats of adsorption were -22 kJ mol^{-1} for sulfated zirconia, and ca. -19 kJ mol^{-1} for mordenite, ZSM-5, and beta. Molybdenum oxides reduced at 623 and 773 K show large heat of adsorption (-19.3 and -19.7 kJ mol^{-1}, respectively), and these are classified into the superacid.

Keywords: Solid acid; Acid strength; Acid amount; Heat of Ar adsorption

1. Introduction

The acid strength, amount of acid sites, and type of acid (Brönsted or Lewis acid) are fundamental properties of solid acids. Niwa and Katada have reported that the measurement of temperature-programmed desorption (TPD) using a typical base of ammonia is the most useful technique for evaluating the relative acid strength and the number of acid sites [1]. They showed that the heat of ammonia adsorption is calculated from the ammonia TPD profile and it relates to the Hammet function (H_o) [2], a scale of acid strength. However, there are several disadvantages associated with this technique when applied to solid acids with high acidity, such as sulfated zirconia and the solid acids containing a component, which is active for ammonia decomposition. For example, during ammonia desorption, temperature is elevated owing to the strong interaction of ammonia with the strong acid sites. This can lead to temperatures higher than $T = 800$ K in some cases [3], and thus, the acid sites can be thermally decomposed on reduction by ammonia. To circumvent this problem, an inert molecule with a low basicity must be used as the probe molecule.

A detailed calorimetric analysis of Ar adsorption was carried out by Llewellyn and Reichert to clarify the pore structures of porous materials, such as graphite [4], MFI-type zeolites [5], and aluminophosphates [6]. Argon exhibits a polarized state that has an acid–base-like interaction with acid sites at low temperatures, owing to an induced dipole [7–10]. Recently, it has been reported that rare gas atoms can exhibit polarizability and even hyperpolarizability [11]. The polarity of silicalite surfaces has been examined calorimetrically using non-polar gases (Ar, O_2, CH_4, C_2H_6, and SF_6) [12]. Wakabayashi et al. have reported that inert gases, including Ar, exhibited a strong interaction with the silanol groups on H-ZSM-5 zeolite, and led to a red shift of the IR stretching bands of the zeolite acidic –OH groups [7]. The interaction strength was found to be related to the proton affinity of inert gases. Michot et al. evaluated the heterogeneity of the strength of surface acid sites on Al-pillared saponites and synthetic Na-saponites by measuring the heat of adsorption of Ar and N_2 [9,13]. The usability of inert gases for evaluation of acid characters has been also reported [14]. These reports indicate that the strength of the interaction between an inert gas and the surface acid sites is mirrored by the relative acid strength of a solid acid.

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Ar atom chemically bonds with Be–O groups, which are a very strong Lewis acid, and it is on the extended line of Be–O bond [15]. The interaction of Ar is analogous to hydrogen bonding, and is also observed to occur with the Brönsted acid of the phenol cation radical [16]. Therefore, Ar has a strong interaction with both Brönsted and Lewis-type acid sites on solid acids.

Previously, we have shown that TPD using Ar as a probe molecule was applicable for the evaluation of the relative acid strength of solid superacids, the activation energy of Ar desorption in the temperature range $T = 113$–223 K being determined [17]. Argon has no chemical effect on the structure of the acid sites, even at elevated temperatures.

The data indicated that Ar is an excellent probe for strong acid sites on solid surfaces.

The measurement of the heat of Ar adsorption was also applied to evaluate an acid strength. The adsorption behavior of Ar is regarded to be of the Henry-type, and so we evaluated the relative acid strength of solid acids by determining the heat of adsorption of Ar using Henry's equation (H-method) [18]. In addition to this calculation procedure, the heat of adsorption can also be determined from Langmuir-type adsorption isotherms (L-method) [19]. Langmuir's adsorption equation provides information regarding the saturated adsorption amount. In the case of a solid acid, the number of adsorption molecules would be equal to that of acid sites on the surface.

According to Cremer and Flügge, the slope of log–log (ln–ln) plot of adsorption isotherm is 1 in lower adsorption amount range, because the Henry's law can be applied [20]. An adsorption isotherm is considered to be composed by several Langmuir-type adsorption isotherms. These adsorptions are possible to be separated by ln–ln plot. In this paper we report a new simple method to calculate the heat of Ar adsorption and adsorption amount based on a theory pointed out by Cremer and Flügge.

2. Experimental

Solid acids tested in this paper are listed in Table 1. Samples marked as JRC are the reference catalysts supplied by the Reference Catalyst Committee of the Catalysis Society of Japan. Sulfated zirconia [21] and MoO_3 [22] were prepared by reported methods. The sample (0.3–2.0 g) was placed in a glass tube and pretreated in a vacuum at 773 or 573 K for a period of 2–3 h. The Ar adsorption isotherm was measured using a volumetrical technique using a conventional BET system of Belsorp 28SA (Nippon Bel Co.) at $T = 163$–243 K in the pressure range $P = 5$–100 kPa.

Henry-type adsorption isotherm is described as follows:

$$\frac{V}{V_m} = bP \quad \text{or} \quad \ln V = \ln P + \ln b + \ln V_m \qquad (1)$$

where b is adsorption constant and V_m is saturated adsorption amount. V_m is regarded as the number of acid sites when there is an acid–base interaction between a probe molecule and surface. The adsorption coefficient, b, relates to the heat of adsorption as follows:

$$b = b_o \exp\left(\frac{-\Delta H}{RT}\right) \qquad (2)$$

where b_o is a constant. Eq. (1) is converted into the following equation:

$$\ln V = \ln P + \left(\frac{-\Delta H}{RT}\right) + \ln b_o + \ln V_m \qquad (3)$$

Table 1
Heat of Ar adsorption and acid amount of various solid acids

Sample	ΔH[a] (kJ mol^{-1})	V_m[a] (mmol g^{-1})	ΔH[b] (kJ mol^{-1})	V_m[b] (mmol g^{-1})	ΔH[c] (kJ mol^{-1})	Al^{3+} cont. (mmol g^{-1})	ΔH of NH_3[d] (kJ mol^{-1})
Al_2O_3 (JRC-ALO-6)	12.5	0.15					
SiO_2-Al_2O_3 (JRC-SAH-1)	14.7	0.015	14.9	0.35	14.4	5.71	
SZ-HM[e]	22.1	0.006	26.3	0.009	22.4		200
SZ-2[f]	22.0	0.002					
SZ-5[g]	21.8	0.004					
Mordenite (JRC-Z-HM20)	18.3	0.90	17.7	1.44	17.3	1.52	145
ZSM-5 (JRC-Z5-70H)	17.6	0.33	17.9	0.39	17.3	0.39	130
ZSM-5 (JRC-Z5-90H)	17.4	0.31				0.36	
Beta (JRC-Z-HB25)	16.8	0.02	17.1	0.10		1.60	
Y (JRC-Z-HY-5.6)	15.1	0.04	15.6	0.35	14.8	4.39	
MoO_3[h]	19.4	0.19					
MoO_3[i]	19.7	0.19					

[a] Calculated by the method presented.
[b] Calculated by L-method in Ref. [18].
[c] Calculated by H-method in Ref. [18,19].
[d] Ref. [23].
[e] Sulfation of zirconia gel obtained by hydrolysis of zirconyl chloride, Ref. [21].
[f] Sulfation of JRC-ZRO-2.
[g] Sulfation of JRC-ZRO-5.
[h] Reduced by H_2 at 623 K.
[i] Reduced by H_2 at 773 K.

When V is a constant, the heat of adsorption (ΔH) in Eq. (3) depends on $\ln P$. The intersection of the tangential line on the horizontal line of desired V relates to the adsorption coefficient. The slope of the values of intersection ($\ln P$) versus $1/T$ plot gives the heat of Ar adsorption, as follows:

$$\ln P_2 - \ln P_1 = \frac{\Delta H}{R(T_2 - T_1)} \tag{4}$$

The intersection of two tangential lines on the adsorption isotherm at low and high equilibrium pressures gives the saturated adsorption amount ($\ln V_m$), the amount of acid sites.

The change of heat of adsorption against adsorption amount is obtained by applying the Clausius–Clapeyron equation to the isotherms measured at various adsorption temperatures. The obtained values are the isosteric heat of adsorption (ΔH_{iso}). These are converted into the differential heat of adsorption (ΔH_{diff}) as follows:

$$\Delta H_{diff} = \frac{\Delta H_{iso2} V_2 - \Delta H_{iso1} V_1}{V_2 - V_1} \tag{5}$$

The skeletal isomerization of pentane was performed in a closed re-circulation system for comparison of catalytic activity of sulfated zirconia catalysts and proton-type zeolites. After the catalyst (0.5–0.8 g, 32–50 mesh) was set in a reactor and pretreated in vacuum at 473 K (sulfated zirconias) or 773 K (zeolites) for 3 h, 6.7 kPa of pentane was introduced into the reactor. The reaction was carried out at 273 K (sulfated zirconia), 473 K (mordenite, ZSM-5, and beta), or 773 K (Y). Products were analyzed by GLC using a capillary column of TC-1 (GL Science) operated at 333 K.

3. Results and discussion

It is considered that an adsorption isotherm is composed of several Langmuir-type adsorption isotherms. Fig. 1 shows a model of adsorption isotherm on a surface with two kinds of acid sites. In lower adsorption amount part, adsorption on the strong acid sites is predominant. In this part, the slope of the adsorption isotherm is 1, because the Henry's Law can be applied. The slope is decreased gradually with increasing the adsorption amount. Afterward, the slope is to be 1 again; Henry-type adsorption on the secondly strong acid sites is predominant. This indicates that the adsorption isotherm is possible to be separated into several Langmuir-type isotherms by ln–ln plot.

In the ln–ln plot, the Langmuir-type adsorption isotherm is approximated by two straight lines. One is the line with slope of 1 in the low equilibrium pressure range, as was explained above. When the equilibrium pressure is high, the adsorption on the acid sites with the strong interaction is saturated. As the result, the slope of another line is smaller than 1. The intersection of these two lines gives $\ln V_m$.

The ln–ln plots of adsorption isotherms measured at various temperatures on mordenite is shown in Fig. 2. The tangential lines of adsorption isotherms in the low equilibrium pressure (lower adsorption amount) were parallel and laid at almost even interval. The slope of tangential lines have to be 1 in this analysis. So the measured data with large error can be eliminated with ease.

Heats of Ar adsorption and adsorption amounts calculated by the method presented are summarized in Table 1 with those calculated by previous methods together with heats of ammonia adsorption reported [23]. The presented heats of adsorption were comparable with those obtained by applying the Henry's and Langmuir's equations. The order of heat of sulfated zirconia, mordenite and ZSM-5 was consistent with that of acid strength evaluated by the heat of ammonia adsorption. In contrast, amounts of acid sites, the values of V_m obtained by applying the present method, are different from those calculated by applying Langmuir's equation. For example, that of sulfated zirconia (SZ-HM) was 0.006 mmol g^{-1} by present method and 0.009 mmol g^{-1} by L-method. In the case of L-method, the amount of acid sites is given as the reciprocal of slope of P/V versus P plot. The Ar adsorption takes place on weak acid sites as well as on the strong acid sites. The resulting

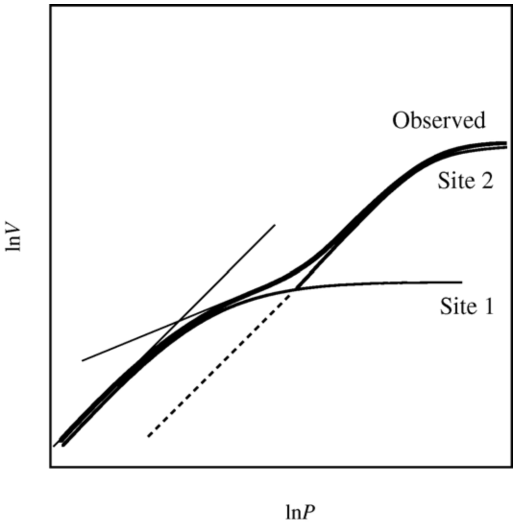

Fig. 1. A model of adsorption isotherm.

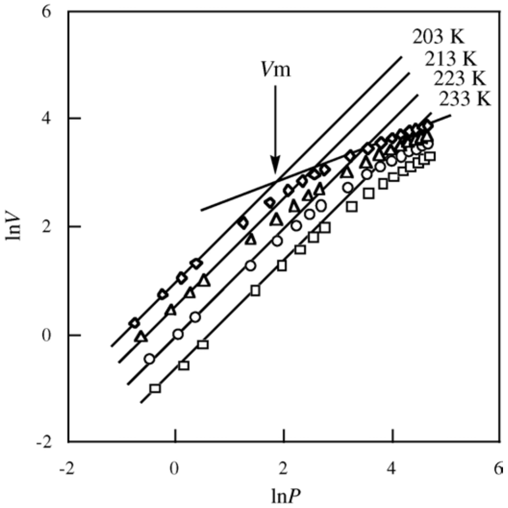

Fig. 2. ln–ln plot of Ar adsorption isotherms on mordenite.

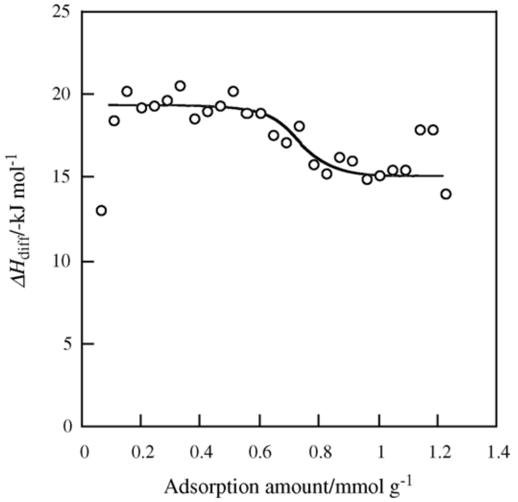

Fig. 3. Differential heat of Ar adsorption on mordenite.

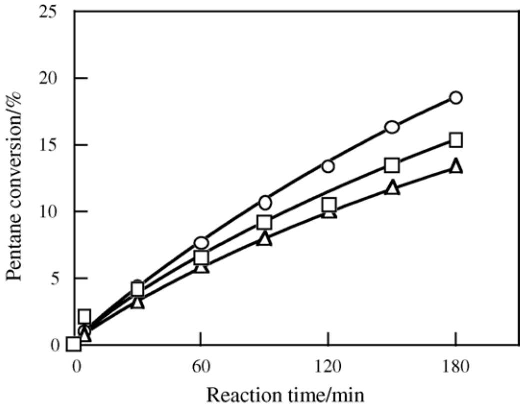

Fig. 4. Isomerization of pentane on sulfated zirconia catalysts at 273 K. (○) SZ-HM, (△) SZ-2, (□) SZ-5. All catalysts were activated at 473 K for 3 h in vacuum.

adsorption amount is measured larger and the slope is smaller by the influence of adsorption on weak acid sites. Consequently, the saturated adsorption amount (V_m), the amount of acid sites, is estimated larger than the expected value.

The differential heat of adsorption of Ar on mordenite is shown in Fig. 3. A decrease of differential heat of adsorption was observed around $V = 0.8$ mmol g^{-1}. This is almost coincident with V_m obtained in Fig. 2, 0.90 mmol g^{-1}. For the proton-type zeolites, the acid sites are composed of Al^{3+} ions incorporated in a silica matrix. The number of acid sites formed on the zeolite surface should therefore, be equal to, or smaller than, the number of Al^{3+} surface ions. The amount of saturated adsorbed Ar on mordenite was 0.90 mmol g^{-1}, and the value was smaller than Al^{3+} content (1.52 mmol g^{-1}). Those of ZSM-5 samples were almost equal to their Al^{3+} contents.

Sulfated zirconia catalysts, a representative solid superacid, were prepared using three kinds of zirconia gels. One was obtained by hydrolysis of zirconium oxychloride [21], and other two were reference catalysts. Sulfated zirconias showed similar values of heat of adsorption, ca. −22.0 kJ mol^{-1}. The pentane isomerization activities of three sulfated zirconias were in the similar level as shown in Fig. 4. It can be said that the result of pentane isomerization is coincident with that of acid strength measurement. The acid amount of sulfated zirconia measured in this study was one-order smaller than those of reported [2,24,25]. This result could be attributed to the very low basicity of Ar. As well known, the acid strength on a solid acid is not uniform. In our case, the quantity of the strong acid sites, which give large heat of Ar adsorption, was counted. The superacid sites, stronger than those on zeolites and have small heat of Ar adsorption than −22 kJ mol^{-1}, are excluded. The acid sites showing the heat of Ar adsorption larger than ca. −18 kJ mol^{-1} should be included for the comparison of the amount of acid sites on SZ with that measured by use of stronger base of ammonia. The change of isosteric heat of Ar adsorption against the adsorption amount on SZ-HM is shown in Fig. 5. From this figure, the amount of acid sites, which showed heat of Ar adsorption larger than those of zeolites (ca. −18 kJ mol^{-1}), was estimated to be 0.016 mmol g^{-1}. This value is in the same order with the reported acid site concentration [2].

It has been reported that MoO_3 catalyst reduced at high temperature has large surface area more than 100 m^2 g^{-1} and shows the heptane isomerization activity [22,26]. Its activity is comparable with that of beta. The heats of Ar adsorption of MoO_3 reduced at 623 and 773 K were −19.4 and −19.7 kJ mol^{-1}, respectively. In general, an acid stronger than 100% H_2SO_4 is called superacid. Among the solid acids, the acid strength of SiO_2–Al_2O_3 is close to that of 100% H_2SO_4. Therefore, an acid which shows the heat of Ar adsorption larger than −15.0 kJ mol^1, can be classified into the solid superacid. The heats of adsorption of the MoO_3 catalysts are much larger than those of SiO_2–Al_2O_3. In addition to this, these are larger than those of proton-type zeolites. From these results, it can be concluded that MoO_3 reduced at high temperature is a kind of solid superacid. This is the first report about the superacidity of reduced MoO_3.

The isopentane formation activities of proton-type zeolites are well represented by the acid properties determined by

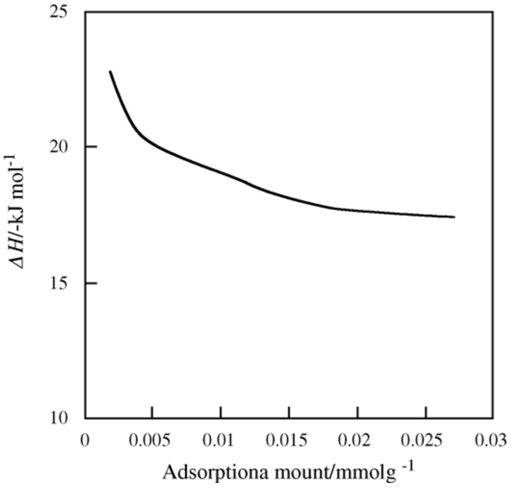

Fig. 5. Change of isosteric heat of Ar adsorption on SZ-HM.

Table 2
Pentane isomerization activity of proton-type zeolites

Catalyst	Reaction temperature (K)	Total conversion activity (% g^{-1} h^{-1})	Isopentane formation activity (% g^{-1} h^{-1})
Mordenite (JRC-Z-HM20)	473	70.1	28.0
ZSM-5 (JRC-Z5-70H)	473	9.8	8.1
Beta (JRC-Z-HB25)	473	3.8	1.4
Y (JRC-Z-HY-5.6)	773	8.4	3.5

presented technique. Results of pentane isomerization on zeolites are shown in Table 2. The order of isopentane formation activity was followed.

$$\text{Mordenite} > \text{ZSM-5} > \text{beta} \gg \text{Y}$$

The heats of adsorption of mordenite, ZSM-5, and beta were ca. -19 kJ mol^{-1}. The difference of acid amounts would reflect the activity order of these three zeolites. The heat of Ar adsorption of Y was -15.1 kJ mol^{-1}; it being much smaller than those of other zeolites. In this case, the reaction temperature was increased by 300 K to obtain the similar formation activity to former three zeolites. Similarly, the difference of reaction temperature was 150–200 K between sulfated zirconias and mordenite or ZSM-5. The differences of catalytic activities are clearly explained by those of heats of Ar adsorption or adsorption amounts. These results indicate that the heat of Ar adsorption and adsorption amount obtained by the present technique are useful for the evaluation of acid properties of solid acids.

4. Conclusion

Argon adsorption isotherms have been analyzed using the theory of Cremer and Flügge to obtain values of the heat of adsorption and saturated adsorption amount. Henry-type adsorption isotherm of the strongest interaction can be separated from the measured adsorption isotherm by ln–ln plot. The slope of the values of ln P at desired V versus $1/T$ plot gives the heat of Ar adsorption. The intersection of two tangential lines on adsorption isotherm at low and high equilibrium pressure parts gives the saturated adsorption amount. The heat of Ar adsorption obtained is indicative of the relative acid strength of the solid acids. The saturated adsorption amount is the number of acid sites having highly acidity. The isopentane formation activities are well represented by the acid properties determined by presented technique. Our results indicate that the technique presented is useful for the evaluation of the acidity of solid acids.

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