Distinction of Acid-type on Solid Acid Surface by Comparison of Adsorption Heats of Nitrogen and Argon

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The heats of adsorption of N_2 and Ar on solid acids were compared by applying the Clausius–Clapeyron equation to isotherms. The heats on H-mordenite and $H_4SiW_{12}O_{40}$ supported on SiO_2 decreased gradually with increasing the adsorption amount in parallel with each other, while sulfated zirconia and Al_2O_3 gave large difference between N_2 and Ar in low adsorption range more than 30 and 15 kJ mol^{-1}, respectively, enabling the result to distinguish the Brönsted- and Lewis-acid types.

The acid-type, Brönsted- and Lewis-types, is a fundamental property of solid acids as well as the strength and amount of acid sites. The measurement of IR spectrum of adsorbed pyridine is the most useful technique to distinguish the acid type on the surface of solids.[1] However, there is a problem when this technique is applied to solid acids with high acidity such as sulfated zirconia and proton-type zeolites. Pyridine is adsorbed on weak acid sites which are not active for the acid-catalyzed reactions like the skeletal isomerizations of alkanes because of the strong basicity of pyridine.

Argon shows an acid-base-like interaction in a polarized state with acid sites at low temperature owing to its induced dipole.[2–4] Inert gases such as Ar had an interaction with the acidic silanol groups on H-ZSM-5.[2] Michot et al. evaluated heterogeneity of the strength of surface acid sites on saponites by the measurement of adsorption heats of Ar and N_2.[4] These reports indicate that the strength of interaction reflects the relative acid strength of solid acids. We had shown that temperature programmed desorption (TPD) of Ar is applicable for the evaluation of relative acid strength of solid superacids.[5] The measurement of heat of Ar adsorption was also applied to evaluation of the acid strength using the Langmuir's[6] and the Henry's equation.[7] The adsorption is a kind of hydrogen-bonding interaction in the case of the Brönsted sites.[8] On the contrary, CO and N_2 are adsorbed on Lewis acid sites by the interaction between the electron pair of 5σ of the adsorbed molecule and the vacant molecular orbital of Lewis sites.[9]

In this study, we would like to show that the heat of adsorption of N_2 on Lewis acid sites is much larger than that expected from the Ar adsorption, and that the distinction of acid site character, Brönsted- and Lewis-types, is possible by the comparison of heats of adsorption between N_2 and Ar.

Among the solid acids used in this study, Al_2O_3 and H-mordenite (H-MOR) were reference catalysts supplied by the Catalysis Society of Japan, JRC-ALO-6 and JRC-Z-HM20, respectively. Sulfated zirconia (SZ) was prepared by the reported methods[10] using the reference catalyst of JRC-ZRO-2, and $H_4SiW_{12}O_{40}$ supported on SiO_2[11] (SW/S) was supplied by Professor T. Okuhara, Hokkaido University. The sample (ca. 0.2–2.0 g) was placed in a glass tube and pretreated in vacuum at 773 K (Al_2O_3 and H-MOR), 573 K (SZ), or 473 K (SW/S) for 3 h. The adsorption isotherm of N_2 or Ar was measured by means of volumetrical method using Belsorp 28SA BET system (Nippon Bel Co.) at 193–243 K. The heat of adsorption was obtained by applying the Clausius–Clapeyron equation to the isotherms measured at various adsorption temperatures.

Figure 1 shows the adsorption isotherms of Ar and N_2 on SW/S and Al_2O_3 at 193 K. The profiles of Ar and N_2 isotherms on SW/S were very similar. In contrast to that, a large difference of adsorption amounts between them was seen on Al_2O_3. Especially, steep increase of adsorption amount was observed on the isotherm of N_2 in lower pressure range.

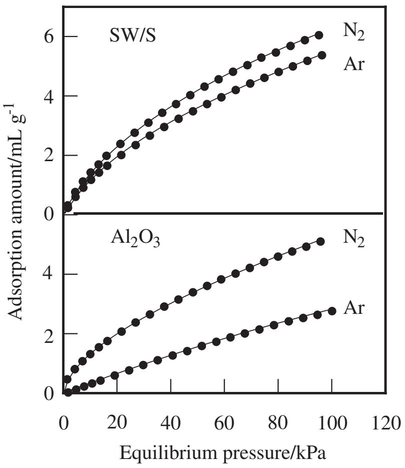

Figure 1. Adsorption isotherms of Ar and N_2 on SW/S and Al_2O_3 at 193 K.

Figure 2 shows the heats of adsorption of N_2 and Ar plotted against the adsorption amounts on H-MOR and SW/S. The heat of adsorption of N_2 was larger than that of Ar; the difference being 2–3 kJ mol^{-1}. Both the heats decreased gradually with increasing the adsorption amounts, drawing almost parallel lines. Similar result was reported on synthetic saponite by a calorimetric analysis of N_2 and Ar adsorption.[4] The red shift of IR band of acidic OH was observed on H-ZSM-5 zeolite by the adsorption of inert gases. N_2 adsorption provided larger red shift than Ar.[2] The difference of the heats can be attributed to the strength of hydrogen bonding brought by the interaction between the acidic OH groups and N_2 and Ar. On the other hand, changes of the heats of adsorption of N_2 and Ar are not parallel in the cases of SZ and Al_2O_3 as shown in Figures 3 and 4, respectively. In particular, very large heat of adsorption, more than 60 kJ mol^{-1}, was obtained by N_2 adsorption on SZ, much larger than that of H-MOR; the difference in the adsorption heats of two gases was more than 30 kJ mol^{-1}.

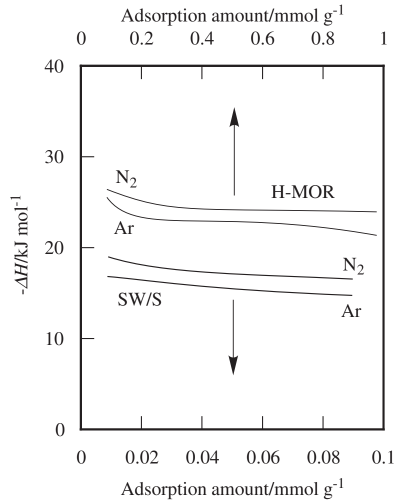

Figure 2. Heats of adsorption of Ar and N_2 on H-MOR and SW/S.

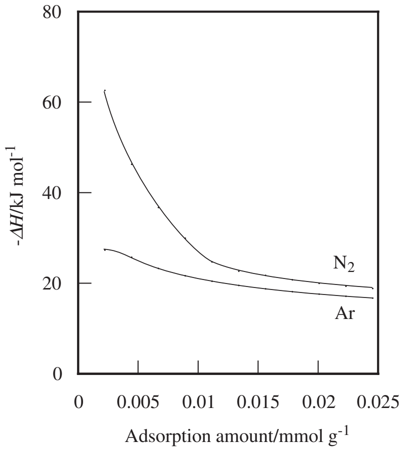

Figure 3. Heats of adsorption of Ar and N_2 on SZ.

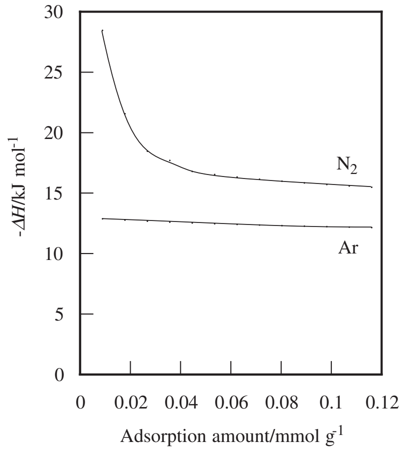

Figure 4. Heats of adsorption of Ar and N_2 on Al_2O_3.

SZ has strong Lewis-acid character,[12] and the Al_2O_3 is well known to consist mainly of Lewis sites.[13] The acid sites on SW/S is of Brönsted-type.[14] Although H-MOR has a small amount of Lewis acid sites by the treatment at high temprature,[15] the acid sites on H-MOR are regarded as the Brönsted-type basically. When the Lewis acid sites coexists with the Brönsted acid sites, the adsorption of gaseous molecules is predominant on Lewis acid sites.[2,15,16] Therefore, the large difference of the heats in lower pressure range was observed when they were adsorbed on Lewis-type acid sites. The upward shift of IR bands of N_2 and CO has been reported. Since the 5σ orbitals of N_2 and CO have an antibonding nature, N–N and C–O bond would be stronger by σ electron donation to Lewis acid site.[9] The stabilization of the N–N bond in addition to the stabilization by adsorption on the acid sites gives the large heat of N_2 adsorption. This result indicates that the type of acid sites can be clarified by comparison of the adsorption heat of N_2 with that of Ar.

It is reported that N_2 can be adsorbed by Lewis acid sites, but not by Brönsted sites under the conditions of the adsorption temperature around 270 K and N_2 pressure of 14.6 kPa.[15] The adsorption amount of N_2 was measured by $0.05\,\text{mmol}\,\text{g}^{-1}$ in the similar conditions. The amount of Lewis acid sites was estimated to be $0.12\,\text{mmol}\,\text{g}^{-1}$ at most. Unfortunately, this is out of the measurement region in the present study because there were large measurement errors. It is expected that the measurement with high resolution provides the steep increase of the heat of adsorption of N_2 in low equilibrium pressure range. Further study should be done to clarify the acidity of H-MOR. Additionally, the present technique will be applied to solid acids whose properties are defined well by spectroscopic and/or thermal analysis to confirm the usability.

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