Temperature programmed desorption of argon for evaluation of surface acidity of solid superacids

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The activation energy of Ar desorption from solid acids is determined by temperature programmed desorption (TPD) using Ar as 9.3, 7.6 and 6.0–6.7 kJ mol^{-1} for sulfated ZrO_2, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and zeolites, respectively; the data indicate that Ar TPD is applicable to evaluation of the relative acid strengths of solid superacids.

Temperature programmed desorption (TPD) using ammonia is the most useful technique to evaluate relative acid strengths and the amount of acid sites on solid acids.[1–3] However, there are several problems when this technique is applied to solid acids with high acidity such as sulfated zirconia and zeolites. For instance, the ammonia desorption temperature is elevated owing to the strong interaction of ammonia with strong acid sites, and thus the acid sites may be decomposed by reaction with the adsorbents at such temperatures. Sikabwe *et al.* reported that Fe, Mn and Ni promoted sulfated zirconias were partially or completely decomposed in the temperature range 700–900 K when ammonia, pyridine or benzene were adsorbed.[4] An interaction of ammonia with both the acidic OH group and the basic oxygen site next to the acid site is another problem.[5] Therefore, accurate acid strengths of solid superacids can not be evaluated by TPD using probes such as ammonia or pyridine. To solve these problems, an inert molecule with lower basicity must be used as the probe molecule.

Argon is completely inert towards superacids, but shows an acid–base like interaction with acid sites at low temperature.[6] Argon has an induced dipole when it interacts with a strong dipole. The most polarized site on the solid acids must be the acid sites, and argon would be adsorbed on such sites in a polarized state. The strength of the interaction between Ar and acid sites would be expected to depend on the acid strength. Wakabayashi *et al.* reported that inert gases including Ar showed an interaction with acidic OH sites on zeolites giving 1 : 1 hydrogen-bonded complexes at low temperatures, and there was a linear correlation between the strength of the interaction and the proton affinities of the gases.[6,7] From their results, it is expected that the relative acid strength of solid superacids can be evaluated by TPD using Ar as a probe. Here, Ar TPD was applied to silica–alumina, several types of zeolites, sulfated zirconia and a Cs substituted heteropoly acid; the results clearly showed that Ar TPD was applicable for the evaluation of acid strength of solid superacids.

Silica–alumina and zeolites used in this study were supplied by the Catalysis Society of Japan as reference catalysis. Sulfated zirconia (SO_4^{2-}/ZrO_2) was prepared by the reported method,[8] and the heteropoly acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) was supplied by Professor T. Okuhara, Hokkaido University.[9] Both of these materials can convert *n*-butane into isobutane at room temperature. The solid acid (*ca.* 15–40 mg) was placed in a glass sample tube and pretreated in vacuum at 773 K (SiO_2–Al_2O_3 and zeolites) or 473 K (sulfated zirconia and heteropoly acid) for 2 h. After the pretreatment, the sample was exposed to 6.7 kPa of Ar at room temperature, then cooled to 113 K by N_2 gas which was bubbled out of liquid N_2. The sample cooling system is shown in Fig. 1. The adsorption of Ar was carried out at 113 K for 10 min. Then excess Ar was removed by evacuation at the same temperature. The final pressure of the system was $< 5.0 \times 10^{-3}$ Pa. Ar TPD was performed in the temperature range 113–223 K at a programmed rate of 2–5 K min^{-1}. The sample tube was heated by an electric heater regulated by a temperature controller. Argon desorbed from the surface of solid acid was detected by a mass spectrometer and an ionization gauge connected to the vacuum system.

Ar TPD profiles of solid acids are summarized in Fig. 2. The signal response (m/z = 40) was normalized by the weight of the samples. All the samples showed an Ar desorption peak at *ca.* 120–170 K, *i.e.* much higher than the boiling point of Ar (87.45 K). There was no relation between the BET surface area and the relative amounts of desorbed Ar. The profiles thus show evidence of interaction of Ar with the acid sites on the surface.

For zeolites, an acid site is constructed from Al^{3+} in the framework and the amount of Ar desorbed from the surface is expected to depend on the quantity of Al^{3+}. The amount of Ar desorbed from H-mordenite was much larger than that of H-ZSM-5 reflecting the higher content of Al^{3+} in H-mordenite (Table 1). However, the amount of Ar desorption from H-Y was much smaller than that expected from the Al^{3+} content. Only a small fraction of the acid sites on H-Y or SiO_2–Al_2O_3 appear to show an acid–base interaction with Ar.

An apparent activation energy of Ar desorption was calculated by applying eqn. (1).[10]

$$2\ln T_m - \ln\beta = E_d/RT_m + \text{const.} \qquad (1)$$

Here, T_m is the peak temperature, β is the rate of temperature increase and E_d is the activation energy of desorption. E_d values are obtained from plots of ($2\ln T_m - \ln\beta$) *vs.* $1/T_m$. For the

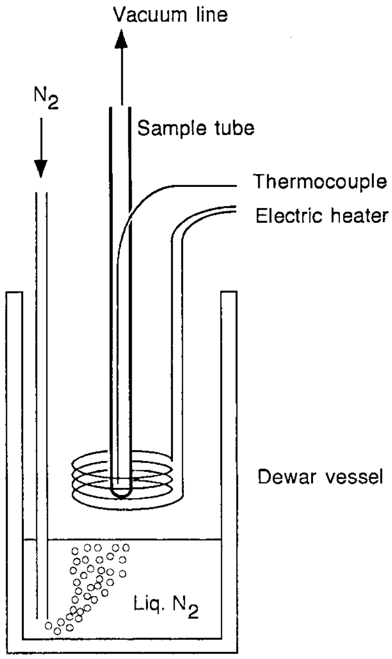

Fig. 1 An outline of the sample cooling system for Ar TPD.

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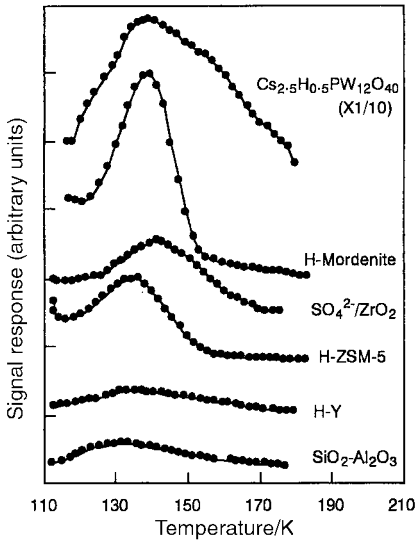

Fig. 2 Ar TPD profiles of solid acids; temperature programmed rate: 2 K min^{-1}.

Table 1 Solid acids and activation energies of Ar desorption

Solid acid	Surface area/ $\mathrm{m^2\ g^{-1}}$	Al_2O_3 content (wt%)	Activation energy/ $\mathrm{kJ\ mol^{-1}}$
SiO_2–Al_2O_3 (JRC-SAH-1)	511	28.61	5.5
H-Y (JRC-Z-HY-5.6)	650	22.0	6.0
H-ZSM-5 (JRC-Z5-70H)		1.99	6.6
H-Mordenite (JRC-Z-HM20)	399	7.76	6.7
SO_4^{2-}/ZrO_2	137		9.3
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	135		7.6

examples shown in Fig. 2, the estimated values of T_m were 131.5, 132.8, 136.0, 139.8, 139.5 and 138.9 K for SiO_2–Al_2O_3, H-Y, H-ZSM-5, SO_4^{2-}/ZrO_2, H-mordenite and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, respectively. The calculated activation energies of Ar desorption are summarized in Table 1. The order of the activation energies is as follows:

$$SO_4^{2-}/ZrO_2 \geqslant Cs_{2.5}H_{0.5}PW_{12}O_{40} \geqslant \text{H-mordenite} \geqslant \text{H-ZSM-5} > \text{H-Y} > SiO_2\text{–}Al_2O_3$$

The termination temperature of Ar desorption also followed this order, *viz.* 159.0, 158.7, 153.8, 153.9, 151.8 and 149.6 K for SO_4^{2-}/ZrO_2, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, H-mordenite, H-ZSM-5, H-Y and SiO_2–Al_2O_3, respectively. The polarization of the Ar molecule is induced by the polarized sites. The interaction between Ar and acid sites should be strong when Ar is adsorbed on strong acid sites because of higher polarization of Ar molecules on the more polarized acid sites. Therefore, the order of the activation energy reflects the acid strength of the solid acid sites. The strength order of zeolites evaluated in this study was consistent with previous reports.[11] From these results, it can be concluded that Ar TPD is applicable to the evaluation of relative acid strengths of solid acids of high acidity on the surface.

The energy of Ar desorption form the solid superacid of sulfated zirconia was 9.3 kJ mol^{-1} the highest among the tested catalysts. The highest acid strength of this sample ($H_0 \leqslant -16.04$) is reflected by the highest value of the desorption energy.[12] The Cs substituted heteropoly acid had a desorption energy (7.6 kJ mol^{-1}) which was higher than for the zeolites. Consequently, it can be stated that the heteropoly acid is a solid superacid.

In summary, the catalysis of solid superacids is characterized by activities for acid-catalyzed reactions at low temperatue and reactions are carried out below room temperature in many cases. The acidity of solid superacids should thus be evaluated at such lower temperatures. TPD using Ar can be performed in the temperature range 113–223 K, close to the reaction temperatures used. Destruction of acid sites can be avoided at these temperatures for themally sensitive sites as found, for example, in Cs-substituted heteropoly acids. In conclusion, TPD using Ar is a very useful technique to evaluate the acidity of solid superacids.

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Notes and references

1 M. Niwa, M. Iwamoto and K. Segawa, *Bull. Chem. Soc. Jpn.*, 1983, **59**, 3735.
2 H. G. Karge and V. Dondur, *J. Phys. Chem.*, 1990, **94**, 765.
3 T. Miyamoto, N. Katada, J.-H. Kim and M. Niwa, *J. Phys. Chem. B*, 1998, **102**, 6738.
4 E. C. Sikabwe, M. A. Coelho, D. E. Resasco and R. L. White, *Catal. Lett.*, 1995, **34**, 23.
5 E. H. Teunissen, A. P. J. Jansen and R. A. van Santen, *J. Phys. Chem.*, 1995, **99**, 1873.
6 F. Wakabayashi, J. N. Kondo, K. Domen and C. Hirose, *J. Phys. Chem.*, 1996, **100**, 4154.
7 F. Wakabayashi, J. N. Kondo, K. Domen and C. Hirose, *Microporous Mater.*, 1997, **8**, 29.
8 T. Tatsumi, H. Matsuhashi and K. Arata, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1191.
9 K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 367.
10 R. J. Cvetanovic and Y. Amenomiya, *Adv. Catal.*, 1967, **17**, 103.
11 H. Stach, J. Jänchen, H. Jerschkewitz, U. Lohse, B. Parlitz and M. Hunger, *J. Phys. Chem.*, 1992, **96**, 8480.
12 K. Arata, *Adv. Catal.*, 1990, **37**, 165.

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