A Preferable Probe Molecule for Evaluating the Surface Acidic Properties of Sulfated Zirconium and Iron Oxides by Microcalorimetric Adsorption Measurement

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Microcalorimetric adsorption of dimethyl ether as well as ammonia on sulfated zirconium and iron oxides indicated that the former is a preferable probe molecule to evaluate surface acid strength of this kind of strong solid acids.

The surface acidity of solid superacid catalysts have been studied using a variety of methods such as IR, ^{1}H-NMR, TPD and ESR et al. . [1] While structures for the acidic surface sites have been postulated,[2-6] the strengths of these acid sites have not been thoroughly examined. Even more, some authors argued that sulfated zirconium which has long been considered as a superacid pocesses no superacidity.[7-9] So, the acid strengths of these strong acid catalysts which can catalyze the isomerization of light paraffins at low temperature is still a subject of debate. Microcalorimetry of ammonia is an effective method to evaluate acidity, and it has been used to probe the acidic properties of various metal oxides and zeolite catalysts.[10] But it was fairly reported in the study of the acidities of sulfated oxides. Ammonia,[11] H_2O[12], and CO[13] had been used as probe molecules in microcalorimetry studies to evaluate this kind of strong acid. We here report the results of microcalorimetric adsorption of NH_3 and dimethyl ether (DME) on some of these "superacids". To our knowledge, DME is in its first time to be used in microcalorimetric adsorption studies of sulfated metal oxides and it is better than ammonia.

Two sulfated zirconium samples prepared by different methods were provided by Fudan University (Shanghai, PR china). The sample prepared as usual impregnation of zirconium hydroxide (dried overnight at 383 K) with sufuric acid is denoted as SZ while which prepared by a one-step sol-gel synthesis is denoted as SA. These two samples were finally calcined at 923 K for 3 h and sulfur contents were determined by chemical analysis (3.5 wt% for SZ and 6.2 wt% for SA, respectively). Sulfated iron oxide was prepared as described in the literature[4] and denoted as SF. Microcalorimetric adsorption were conducted on a Tian-Calvet heat-flux calorimeter which has been described elsewhere.[14] Adsorption of ammonia and DME were carried out at 423 K and 373 K respectively after the samples being evacuated for 3 h at 523 K.

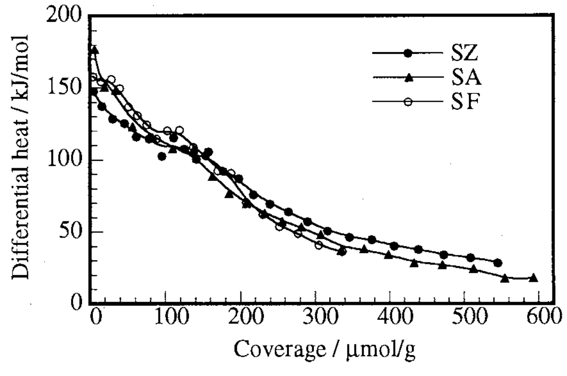

Figure 1. Differential heat of NH_3 adsorption versus adsorbate coverage at 423 K.

Figure 1 shows the microcalorimetric results of NH_3 adsorption at 423 K on the three samples. The initial adsorption heats of them are in the range of 160 kJ/mol to 170 kJ/mol. This is just comparable to that of strong acidic zeolites and could hardly assure their super acidities. It also indicated that differential heat of ammonia adsorption on SA is a little higher than that on SZ. What amazing is SF and SA almost have the same profiles of differential heat versus coverage. This is inconsistent with the common observation that SZ and SA are much more active than SF in the catalytic isomerization of n-butane. However, if DME was used as probe molecule in stead of ammonia, the differential heats of DME adsorption on the three samples depicted in Figure 2 are quite different. The initial adsorption heat of DME on SZ or SA is about 140 kJ/mol and it is much higher than that on SF (105 kJ/mol). This coincides with the reactivity of isomerization reaction. The initial adsorption heats of SA and SZ are identical but SA has much more stronger acid sites than SZ. The acidic sites of SF is homogeneous with adsorption heat around 100 kJ/mol. Differential heat of NH_3 and DME on pure zirconium (obtained by calcining zirconium hydroxide at 923 K for 3 h) is shown in Figure 3 for comparison. It was found that acid strength of zirconium is greatly enhanced by sulfating.

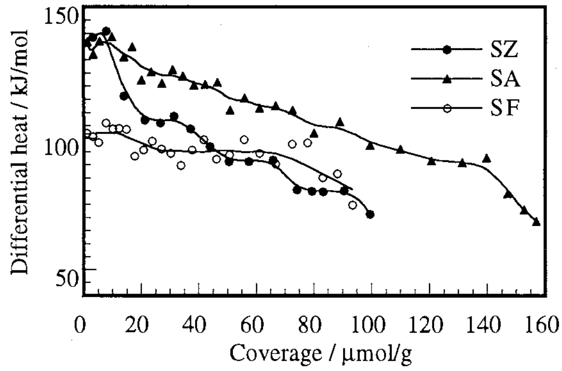

Figure 2. Differential heat of DME adsorption versus adsorbate coverage at 373K.

This sharp difference between NH_3 and DME adsorption is probably due to the different polarizabilities of these two probe molecules (2.26×10^{24} cm^3 for NH_3 and 5.16×10^{24} cm^3 for DME, respectively). Basicity and polarizability of DME are more similar to those of light paraffins than ammonia. So, DME could be more specific to distinguish the interactions of these solid acids with the paraffins.[15]

It is interesting to find out that the initial adsorption heats of

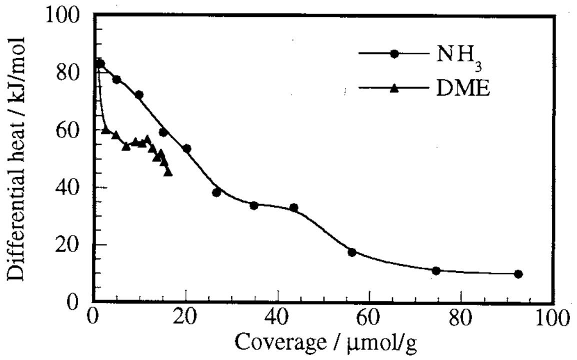

Figure 3. Diiferential heat of NH_3 and DME adsorptions versus adsorbate coverage on ZrO_2.

ammonia on SA and SZ are close to that on H-ZSM5 and H-modernite, but the initial adsorption heats of DME on SA and SZ are 30 kJ/mol higher than that on H-ZSM5 or H-modernite.[16] Thus, the acid strength of our samples should be higher than that of H-ZSM5 and H-modernite based on the initial adsorption heat of DME. This is conflict with the results of IR investigation[17] but coinsistent with the catalytic activities in the isomerization reaction. The differential heat of DME on SF is close to those of above mentioned zeolites.

Although DME seems to be a suitable probe molecule to discriminate surface properties of these strong acids, but more information about the interaction between the probe molecule and the acidic surface is necessary for further investigation.

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