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Detection of Superacidity on Solid Superacids; a New Approach

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Substituted benzenes having proper basicities have been used as adsorbates to differentiate between superacidities of various solid superacids employing a temperature programmed desorption (TPD) method.

A new class of solid superacids, sulfated metal oxides containing Fe, Mn, and Zr (SFMZ), has recently been developed[1] and shown to be the most active non-halide catalyst for isomerization of n-butane.[2] Kinetic results indicate that the new catalyst is about three orders of magnitude more active than a sulfated ZrO_2 (SZ). The latter has an acid strength of $H_0 \leqslant -16.04$.[3] However, the acid strength of this new catalyst could not be measured by using Hammett indicators since the catalyst is grey. We have applied the TPD method using a series of substituted benzenes as adsorbates to demonstrate the very strong acidity of our new SFMZ.

The conventional TPD method using desorption temperature to measure the acid strength is not applicable to SFMZ because its acidity is so strong that the adsorbate decomposes before it desorbs. Our approach utilizes TPD to monitor the acidity in which the observation of a TPD peak with a base indicating a certain level of acidity is similar to the observation of a Hammett indicator colour change registering a certain level of acidity.

Substituted benzenes, alkyl and fluorobenzenes, are weak Lewis bases and have been used to measure the relative acid strengths of the metal halide superacids[4] and the zeolitic Brønstead acidity.[5] The interaction was attributed to be between π-electrons of the aromatic ring and the protons or the acidic hydroxy groups. The basicities of the substituted benzenes can be fine-tuned in a controlled manner by attaching different types and numbers of electron-withdrawing or -releasing functional groups to the benzene ring in order to study catalysts having a wide range of acidities. For example, more basic alkylbenzenes can be used to probe the weaker acid sites, whereas the less basic fluorobenzenes can be used to probe the stronger ones.

TPD experiments were performed using a Model AMI-1 instrument obtained from Altamira, Inc. Before introducing the adsorbate, the catalyst was dried at 773 K for 1.0 h in dry air flowing at 30 cm^3 [normal temperature and pressure (NTP)] min^{-1}. The adsorptions were conducted by introducing 10 μl of an adsorbate into the reactor at 373 K for 1.0 h in He flowing at 30 cm^3 (NTP) min^{-1}. After adsorption, the He flow was continued for an additional 30 min to remove the excess of adsorbate. The reactor temperature was then raised at a rate of 15 K min^{-1} to 1073 K, and maintained at this temperature for 10 min. All the desorbed gases were analysed by a thermal conductivity detector (TCD). Measurements of catalyst activities for n-butane isomerization were made in a fixed-bed flow reactor containing 10 cm^3 of catalyst. The catalysts were dried at 523 K for 4.0 h with dry air flowing at 30 cm^3 (NTP) min^{-1}. The n-butane conversions were measured at 363 K, 28 bar and liquid hourly space velocity (LHSV) = 1.0. Unless otherwise indicated the catalyst SFMZ contains 1.5% Fe, 0.5% Mn, and 4.0% SO_4^{2-} on ZrO_2 prepared according to patented procedures.[1] The SZ sample in this paper is 4.0% SO_4^{2-} on ZrO_2.

A TPD spectrum of SFMZ is shown in Fig. 1(*a*). The only detected desorption peak centred at 1053 K is related to the decomposition of SO_4^{2-} in the catalyst. Fig. 1(*b*) is the spectrum of SZ with benzene as the adsorbate. In addition to the SO_4^{2-} decomposition peak (1058 K), a very weak and broad peak at 800 K and an asymmetric peak at 500 K were also observed. The latter is associated with the weakly adsorbed benzene and is characteristic for all the catalysts tested. In contrast, a well-defined peak at 835 K was observed upon adsorption of benzene on SFMZ [Fig. 1(*c*)]. To assure that this peak is not generated by the adsorption of benzene on iron or manganese oxides, a catalyst with the same metal

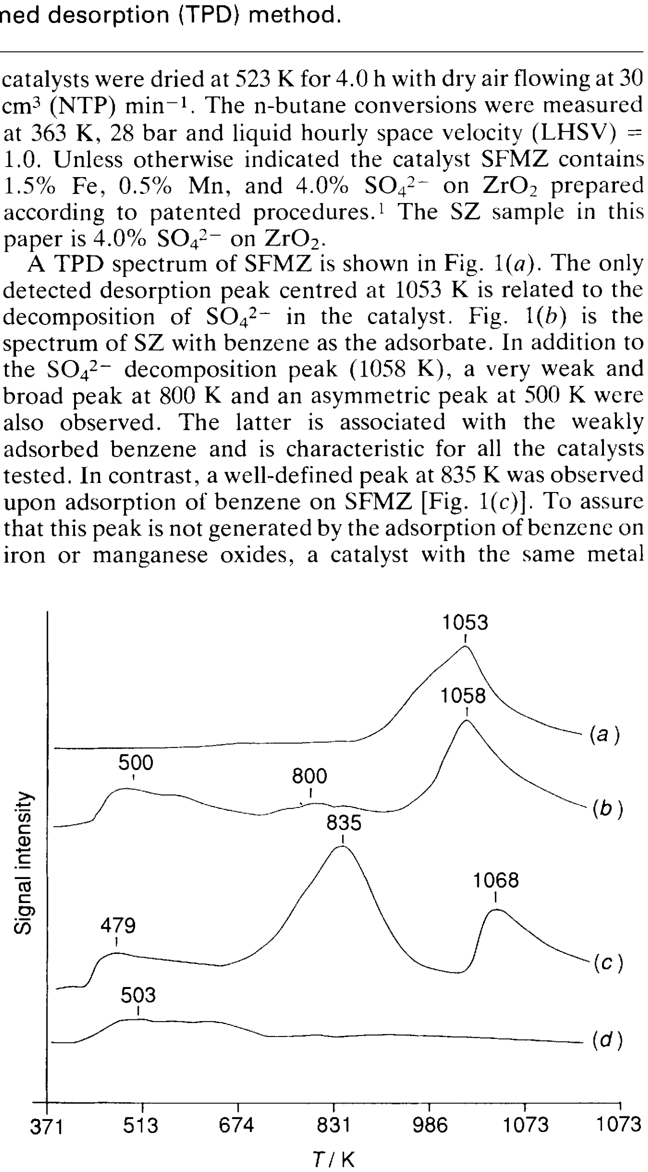

Fig. 1 TPD profiles of (*a*) SFMZ without adsorbate, (*b*) SZ with 10 μl of benzene as adsorbate, (*c*) SFMZ with 10 μl of benzene as adsorbate and (*d*) 1.5% Fe/0.5 Mn/ZrO_2 (FMZ) with 10 μl of benzene as adsorbate

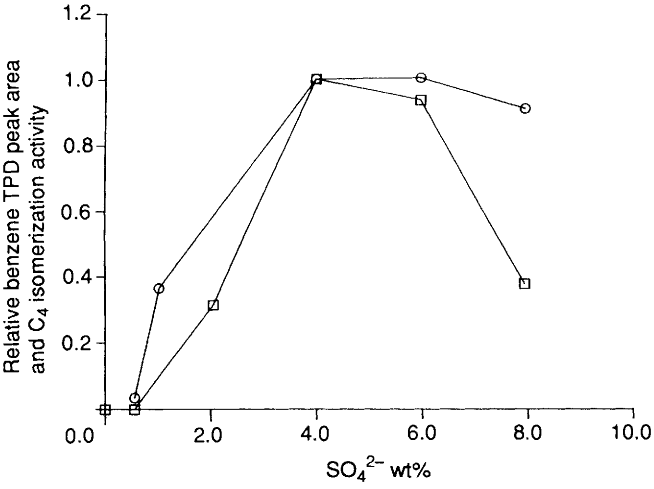

Fig. 2 Variation of the relative benzene TPD peak area □ and butane isomerization activity ○ with SO_4^{2-} wt% in SFMZ. The relative ratio of area and activity at 4% SO_4^{2-} is arbitrarily set to 1.

contents but containing no SO_4^{2-} was prepared and tested. Only a peak associated with the weak adsorption centred at 503 K was observed [Fig. 1(*d*)]. Thus, we conclude that SFMZ contains additional strong acid sites whose strength is high enough to adsorb a very weak base like benzene.

It is generally believed that the strong acidity of sulfated solid superacids is originated from the induction effect of the SO_4^{2-} group in the catalyst.[6] Increasing the amount of SO_4^{2-} in the catalyst increases the number of strong acid sites and enhances the adsorption of benzene. Fig. 2 shows that there is a volcano-type of relationship between the amounts of SO_4^{2-} in SFMZ and the area of the peaks at 835 K. The peak area is proportional to the amount of benzene adsorbed on acid surface. The significant reduction in the peak area of 8% SO_4^{2-} catalyst may be due to the saturation of the surface with less acidic SO_4^{2-} group or the reconstruction of the catalyst structure by the excess amount of SO_4^{2-}. Fig. 2 also includes the relationship between the SO_4^{2-} content and the catalytic activity for butane isomerization. These results clearly show that the presence of SO_4^{2-} is necessary for the catalyst to be active for the isomerization reaction. Furthermore, there is a remarkable correlation between the benzene TPD peak area and the butane isomerization activity. Such correlation clearly indicates that the adsorption of benzene is probing exactly the same strong acid site participating in isomerization of butane.

Since benzene does not readily adsorb on SZ, it is apparently necessary to use a stronger base as adsorbate so that we can compare the acidity of SFMZ and SZ on the same basis. Moreover, one may argue that SFMZ only has a large number of acid sites rather than a greater acid strength because a weak peak at 800 K was indeed observed with SZ. Toluene, *p*-xylene, and mesitylene were chosen as adsorbates for their increasing basicity.[4,5] All three molecules adsorbed on the SFMZ and displayed a TPD peak as shown in Fig. 3. This is expected because their basicities are greater than benzene and should adsorb on the more acidic SFMZ. It is interesting to note that TPD peak areas of all three molecules on the SFMZ are greater than those on the SZ. Such observation is consistent with the notion that SFMZ contains additional strong acid sites. In contrast, most of the sites on the SZ surface are only acidic enough to adsorb more basic *p*-xylene and mesitylene. Again, the result implies that acid sites on the SZ surface are weaker in strength than those on SFMZ. Following the same argument, none of the less basic fluorinated benzenes, monofluorobenzene, 1,4-difluorobenzene, 1,3,5-trifluorobenzene and hexafluorobenzene, is expected to adsorb on less acidic SZ. This was exactly what we observed. On the other hand, more acidic SFMZ did absorb a considerable amount of monofluorobenzene and 1,4-difluorobenzene. These sites are the very strong acid sites and only exist on the SFMZ. The above result is summarized in Fig. 3 which can be regarded as a distribution curve for the strength and concentration of strong acid sites on the SFMZ and SZ surface. The *y*-axis of Fig. 3 is the TPD peak area which is proportional to the number of acid sites. The *x*-axis is arranged according to the decreasing basicity of adsorbate such that it is a scale for measuring the strength of an acid site.

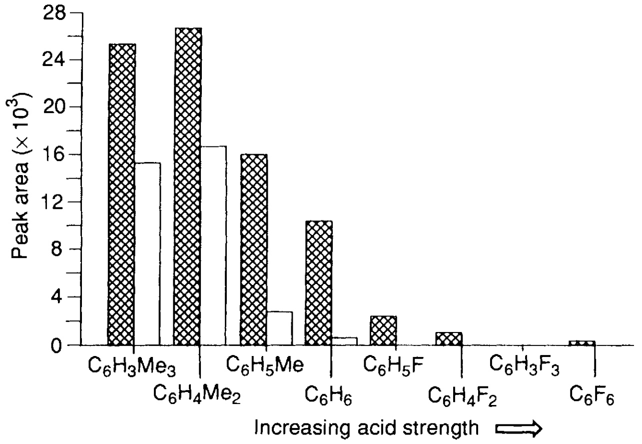

Fig. 3 The distribution of strength and number of acid sites on the surfaces of SFMZ ▨ and SZ ☐

In conclusion, we have coupled the TPD method with a series of adsorbates based on substituted benzenes whose basicities can be fine-tuned at the molecular level to investigate acid sites with strength less, equal or greater than that of SFMZ. The acid site concentration is proportional to the TPD peak area and its strength is determined by the basic nature of the adsorbate. Furthermore, through adsorption of fluorinated benzenes, we clearly demonstrated that there are much stronger acid sites in SFMZ which can not be found in SZ. To further substantiate our claim of strong acidity, we want to point out that SFMZ is capable of catalytically converting methane into ethane at temperatures of less than 573 K.[7] The reaction is believed to proceed through acid-catalysed oligocondensation mechanism as suggested by Olah and Schlosberg.[8]

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