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Superacid Properties of Sulfated Zirconia as Measured by Raman and ^{1}H MAS NMR Spectroscopy

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Large ^{1}H chemical shifts are suggestive of protonic superacidity of sulfated zirconia catalysts, this property being related to the structure of surface sulfate species.

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Sulfated zirconia attracts significant interest as it is known to develop superacidic properties[1] and may thus find applications as a solid superacid catalyst in hydrocarbon conversion reactions. This might lead to significant technological progress since this relatively harmless and noncorrosive solid that can easily be disposed of could replace extremely corrosive liquid acids and superacids as catalysts. Despite considerable research[2–4] the origin and nature of the superacid sites in sulfated zirconia are still not understood. A detailed interpretation of the acid properties of these materials is required to develop further their high potential for heterogeneously catalysed hydrocarbon transformations, particularly for skeletal isomerizations of aliphatic compounds.

We report here ^{1}H MAS NMR and Raman spectroscopic results which demonstrate the presence of protonic superacidity in sulfated zirconia calcined at 873 K and which permit a correlation of this property to be made with the structure of surface sulfate species.

Pure $Zr(OH)_4$ (type XZO 632/3) and sulfated $Zr(OH)_4$ (type XZO 682/1) (MEL Chemicals, Manchester) were calcined in air for 1 h at 873 K to obtain pure zirconia ZrO_2 and sulfated zirconia ZrO_2-S, respectively. The BET surface areas after this treatment were 41 and 100 $m^2\ g^{-1}$, respectively. The SO_3 content of the ZrO_2-S sample was 4.5% (*m/m*). Although deactivation was very fast, the sulfated zirconia ZrO_2-S developed activity for the skeletal isomerization of *n*-butane to isobutane at temperatures ≥400 K, thus indicating its superacid properties. The sulfate-free zirconia was inactive under identical conditions.

The Raman spectrum (recorded on an OMARS 89 DILOR-spectrometer, at 5 cm^{-1} spectral resolution, 488 nm excitation line, 30 mW at sample position) of ZrO_2 showed the characteristic signature of the monoclinic phase with bands at 98, 183, 220, 303, 335, 376, 473, 536, 554 and 621 cm^{-1}.[5] This structural assignment was consistent with XRD results. The dominant bands in the Raman spectrum of ZrO_2-S (Fig. 1) closely coincide with those of the monoclinic phase, but two additional bands at 155 and 268 cm^{-1} indicate the stabilization of some tetragonal zirconia in the sulfated material. Weak bands are evident at 1000–1030 cm^{-1} and at 1399 cm^{-1} with a weak shoulder at *ca.* 1382 cm^{-1}. These bands are clearly attributed to S–O and S=O stretching modes, respectively, of the surface sulfate species. As only one S=O band is detected, the surface sulfate must contain a single S=O group only. The weak shoulder at 1382 cm^{-1} and the doublet at 1000–1030 cm^{-1} indicate the presence of two sulfate species having slightly different distortions. These Raman spectra are consistent with the IR spectra reported by Bensitel *et al.*[6] and are suggestive of a C_{3v} or C_s symmetry of the surface sulfate. We also observed a new O–H stretching band at 3640 cm^{-1} in the IR spectrum of ZrO_2-S, which was not present on the sulfate-free ZrO_2. Assuming that this new OH group is linked to the sulfate, its probable symmetry is C_s. Furthermore, the frequency of the O–H stretching mode suggests a bridging position for the new OH group. We therefore propose structure **1** for the surface sulfate on ZrO_2-S.

Owing to the high electronegativity of Zr^{4+},[4] the OH group should develop high protonic acidity. ^{1}H chemical shifts have been reported to correlate with the acid strength of surface OH groups.[7–9] MAS NMR spectra were measured on a Bruker MSL 400 spectrometer at a spinning frequency of 8 kHz. The samples were pretreated at 723 K *in vacuo* and measured under dry N_2. The ^{1}H NMR spectra of the two samples ZrO_2 and ZrO_2-S are compared in Fig. 2. The sulfate-free ZrO_2 shows a principal signal at δ 3.86 and a weaker signal at δ 1.60. These chemical shifts, though not identical, are similar to those reported by Mastikhin *et al.*[8] In contrast, the ^{1}H MAS NMR spectrum of the sulfated sample ZrO_2-S is clearly dominated by a single band at δ 5.85 with a weak shoulder at higher field strength. Hence, the sulfate modification induces a very significant downfield shift of *ca.* 2 ppm,

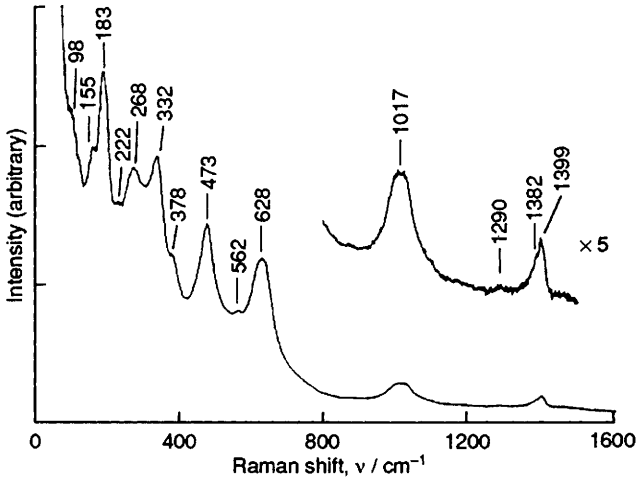


Fig. 1 Raman spectrum of sulfated zirconia ZrO_2-S measured at 773 K in a flow of dry oxygen

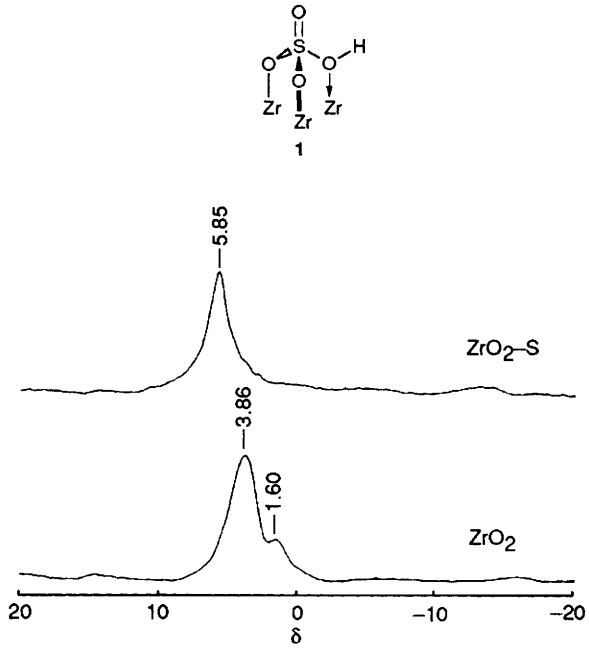


Fig. 2 ^{1}H MAS NMR spectra of ZrO_2 and ZrO_2-S

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which suggests a strongly enhanced proton acid strength relative to the pure ZrO_2. The absolute value of the chemical shift of ZrO_2-S is significantly higher than that reported for the zeolite H-ZSM-5 (δ 4.3)[8] and might therefore be an indication of protonic superacidity, although such comparisons have to be considered with care.[9] We conclude that the observed ^1H chemical shift is a clear indication of the highly acidic—presumably superacidic—properties of sulfated zirconia, and we infer that this property is closely related to the proposed structure of the surface sulfate.

In addition to the protonic acidity, low-temperature IR spectra of adsorbed carbon monoxide have shown the simultaneous presence of Lewis acid centres. The catalytic properties of these materials may well be related to the concerted action of these two types of acid centres.[10] The relative proportion of these centres is expected to depend on sulfate content and calcination temperature. The structural evolution of the surface sulfate species with increasing temperature can be monitored by Raman spectroscopy and detailed studies of the acid properties as a function of calcination temperature are presently being carried out. It is also interesting to note that sulfated zirconia prepared by impregnation of ZrO_2 and calcined at 873 K developed the same structure of the surface sulfate and gave the same proton chemical shift as the material prepared from $Zr(OH)_4$. In contrast to reported data,[4,10] the ZrO_2-derived material was also active for *n*-butane isomerization as expected from the mentioned physical properties. The initial conversions of the two catalysts were proportional to the respective surface areas.

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