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[5] Spectroscopic data for **1**: ^{1}H NMR (300.1 MHz, C_5D_5N, 25 °C): $\delta = 6.03$ (br.s, 4H; OH), 3.85 (t, $J = 4.5$ Hz, 8H; OCH_2), 2.49, 2.41 (br., 24H; NCH_2), 1.51 (q, $J = 81.3$ Hz, 4H; BH_4); ^{13}C NMR (75.4 MHz, CD_3CN, 25 °C): $\delta = 51.17$ (NCH_2), 56.45 (NCH_2), 58.96 (OCH_2); ^{11}B NMR (96.23 MHz, CD_3CN, 25 °C, $B(OCH_3)_3$): $\delta = -54.21$ (quintet, $J = 81.4$ Hz; BH_4); ^{11}B MAS NMR (128.33 MHz, 4013 Hz, 25 °C, $B(OH)_3$): $\delta = -45.4$ ($\Delta\nu_{1/2} = 2198$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6028 Hz, 25 °C, NaCl): $\delta = -12.3$ ($\Delta\nu_{1/2} = 1440$ Hz); IR (KBr): $\tilde{\nu} = 2298, 2225$ cm^{-1} (B–H); elemental analysis calcd for $C_{16}H_{40}N_4O_4BNa$ (%): C 49.74, H 10.36, N 14.51; found: C 49.37, H 10.87, N 14.80; m.p. 180–181 °C.

[6] A Siemens SMART CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$) was used for the X-ray single-crystal analyses in this study. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL package (Structure Analysis Program 5.1, Brucker AXS, Inc., Madison, WI, **1997**). Absorption corrections were applied using SADABS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference Fourier maps and refined isotropically. For the borohydride ions in **1**, however, only the hydridic hydrogen atoms involved in dihydrogen bonding could be found; the remaining H atoms from BH_4^- were calculated and placed in idealized positions. The observed O–H and B–H distances appear typically shorter than the ideal values of 0.96 and 1.21 Å, and were not corrected. Crystal data for **1**: crystal dimensions: $0.23 \times 0.18 \times 0.13$ mm; $T = 173$ K; orthorombic, I_{222}; $a = 8.8240(3)$, $b = 14.1344(6)$, $c = 17.3533(7)$ Å, $V = 2164.34(15)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.186$ g cm^{-3}; $2\theta_{max} = 56.4°$; 12854 reflections collected, 2608 unique; 200 parameters; $R_1 = 0.0487$, $wR_2 = 0.1221$ for $I > 2\sigma(I)$; residual electron density: 0.488 e Å^3. Crystal data for **3**: crystal dimensions: $0.47 \times 0.39 \times 0.29$ mm; $T = 173$ K; monoclinic, $P2_1/n$; $a = 8.7696(1)$, $b = 13.0571(1)$, $c = 17.7724(2)$ Å, $\beta = 96.36°$, $V = 2022.50(4)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.301$ g cm^{-3}; $2\theta_{max} = 56.5°$; 20248 reflections collected, 4840 unique; 462 parameters; $R_1 = 0.0352$, $wR_2 = 0.0921$ for $I > 2\sigma(I)$; residual electron density: 0.261 e Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143751 and CCDC-143752. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[8] ^{11}B MAS NMR (128.33 MHz, 4038 Hz, 25 °C, $B(OH)_3$): $\delta = -8.0$ ($\Delta\nu_{1/2} = 2462$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6001 Hz, 25 °C, NaCl): $\delta = -15.6$ ($\Delta\nu_{1/2} = 3421$ Hz).

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[10] ^{11}B MAS NMR (128.33 MHz, 6000 Hz, 25 °C, $B(OH)_3$): $\delta = -6.9$ ($\Delta\nu_{1/2} = 1745$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6000 Hz, 25 °C, NaCl): $\delta = -8.9$ ($\Delta\nu_{1/2} = 2704$ Hz).

[11] For this comparison, the following unit cell parameters derived from powder X-ray diffraction data at room temperature were used for **1**: $a = 8.894(7)$, $b = 14.214(13)$, $c = 17.509(17)$ Å, $V = 2214(3)$ Å^3.

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[14] ^{11}B MAS NMR (128.33 MHz, 6060 Hz, 25 °C, $B(OH)_3$): $\delta = -7.5$ ($\Delta\nu_{1/2} = 1880$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6058 Hz, 25 °C, NaCl): $\delta = -9.0$ ($\Delta\nu_{1/2} = 2476$ Hz).

[15] A topochemical dihydrogen to covalent bonding transformation has been previously reported to occur in the solid-state conversion of cyclotrigallazane to nanocrystalline gallium nitride. However, initial loss of H_2 at 150 °C resulted in an amorphous GaN phase, and subsequent annealing at 600 °C was required to convert it into the final crystalline product. See: J.-W. Hwang, J. P. Campbell, J. Kozubowski, S. A. Hanson, J. F. Evans, W. L. Gladfelter, *Chem. Mater.* **1995**, *7*, 517–525.

NMR and Theoretical Study of Acid Sites Formed by Adsorption of SO_3 onto Oxide Surfaces[**]

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The structure and function of acid sites formed by the treatment of oxide surfaces with sulfur compounds is a current problem in heterogeneous catalysis.[1] While many studies have considered hydrogen sulfate surface complexes as the locus of solid acidity in such materials, other acidic surface sites have also been proposed, including those formed from adsorbed SO_3. Haase and Sauer recently reported a periodic ab initio theoretical study of sulfuric acid adsorbed on low-index surfaces of ZrO_2.[2] One of the stable structures they found on $ZrO_2(001)$ was a tridentate-adsorbed SO_3 species. This conclusion was consistent with an experimental study of Babou and co-workers, who on the basis of infrared studies

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concluded that adsorbed SO_3 formed on sulfated zirconia prepared by using sulfuric acid as the sulfur source.[3] Yamaguchi and co-workers found that generation of strong acid sites on Fe_2O_3 was independent of the sulfur source including sulfate, SO_2, and SO_3.[4]

We treated various oxide materials with SO_3 and studied them using a combination of solid-state NMR spectroscopy and theoretical methods.[5] Here we report results obtained for a material prepared from silica gel (SO_3/silica) and one prepared from zirconia (SO_3/zirconia). Figures 1a and 1b show the ^1H MAS NMR spectra of activated silica and SO_3/silica following evacuation at 473 K, respectively. Activated silica displays isolated silanol groups at $\delta = 1.9$, but SO_3/silica has a new resonance signal at $\delta = 10.6$. The ^{13}C isotropic chemical shift of adsorbed acetone is a useful spectroscopic probe of relative acid strength.[6] Figure 1c shows the ^{13}C MAS NMR spectrum of acetone-2-^{13}C on activated silica; the ^{13}C shift at $\delta = 210$ indicates hydrogen bonding but negligible acidity. Figure 1d shows the ^{13}C MAS NMR spectrum of acetone-2-^{13}C on SO_3/silica. The peak due to unreacted acetone is at $\delta = 217$; this shift indicates acidity, but of slightly lower strength than zeolite HZSM-5, which induces an acetone shift at $\delta = 223$. Figure 1d also shows small peaks at $\delta = 211$ and 189, due to mesityl oxide, which forms from the acid-catalyzed reaction of acetone.[6]

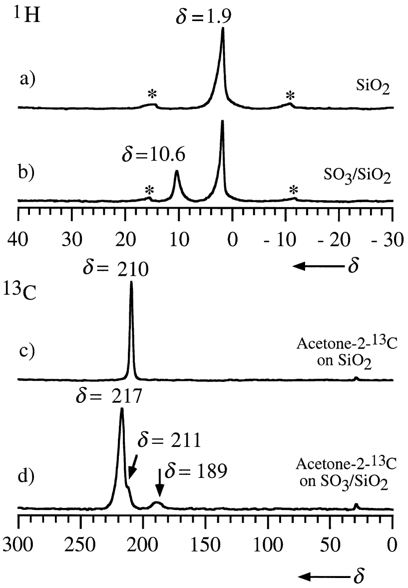

Figure 1. 359.7 MHz ^1H MAS NMR spectra and 50.1 MHz ^{13}C MAS NMR spectra characterizing activated silica and SO_3/silica: a) ^1H MAS spectrum of activated silica; b) ^1H MAS spectrum of SO_3/silica; c) ^{13}C MAS spectrum of acetone-2-^{13}C on silica; d) ^{13}C MAS spectrum of acetone-2-^{13}C on SO_3/silica. Asterisks (*) denote spinning side bands. All spectra were acquired at 298 K.

We probed the nature of the acid sites formed by SO_3 treatment by measuring the ^{15}N MAS NMR spectra of ^{15}N-pyridine on both materials.[7] The ^{15}N spectrum of pyridine on silica (Figure 2a) shows only hydrogen-bonded pyridine ($\delta = -88$) and a small amount of "free" pyridine ($\delta = -65$). Figure 2b shows that much of the pyridine on SO_3/silica is protonated by Brønsted sites ($\delta = -174$). Figure 2c is the ^{15}N spectrum of pyridine on zirconia; the pyridine is complexed to Lewis sites on this sample and resonates at $\delta = -101$. The thermal stability of SO_3/zirconia is remarkable; much of the SO_3 initially adsorbed remains on the surface after evacuation to 773 K. Figure 2d shows that this material contains Brønsted ($\delta = -180$) as well as Lewis ($\delta = -106$) sites. The latter are presumably the adsorbed SO_3 species described by Hasse and Sauer.

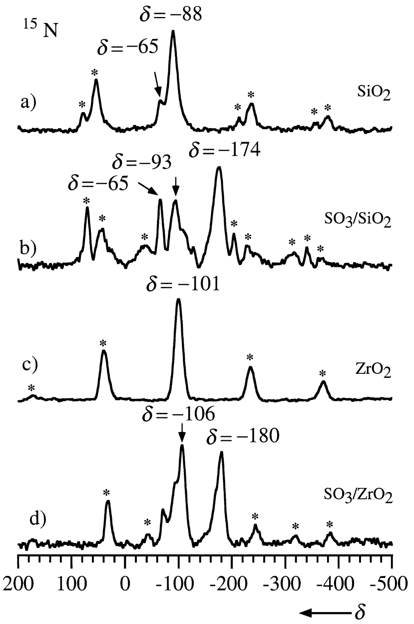

Figure 2. 36.5 MHz ^{15}N CP/MAS NMR spectra of ^{15}N-pyridine on the four oxide materials (0.3 mmol g^{-1} on silica materials and 0.2 mmol g^{-1} on zirconia materials). a) Silica; b) SO_3/silica; c) zirconia; d) SO_3/zirconia. All spectra were acquired at 123 K. Asterisks (*) denotes spinning side bands.

We applied theoretical methods to model the Brønsted sites formed by treatment of silica with SO_3. We used cluster models based on of β-cristabolite to approximate the catalysts and density functional theory to optimize the geometries of the reaction products. Initial calculations used a cluster of stoichiometry $Si_4O_{13}H_{10}$, fixing the terminal OH groups in crystallographic positions[8] and optimizing the inner nine atoms of the cluster and the adsorbed SO_3. Final energies were calculated by using a cluster to which an additional shell of atoms was added ($Si_{13}O_{13}H_{28}$). We considered both the interaction of SO_3 with the silanol lone pairs in a dative fashion, and as an insertion complex which creates an ester of hydrogen sulfate bound to the silica surface (Figure 3). The reaction of SO_3 with the surface silanol to form a dative complex is exothermic by 5.1 kcal mol^{-1}. Formation of the hydrogen sulfate ester is further exothermic by 5.0 kcal mol^{-1}. The theoretical deprotonation enthalpy of the ester is 294.4 kcal mol^{-1}, whereas it is 290.2 kcal mol^{-1} for the dative complex. For comparison, the deprotonation enthalpy of the unactivated silanol group is 326.3 kcal mol^{-}, in good agreement with the experimental value of 332.2 ± 6.0 kcal mol^{-1}.[9] The ester is predicted to be a much stronger acid than the unactivated surface silanols. In fact, the calculated acidity of the ester is comparable to that of a similar model of zeolite H-ZSM5 at the same level of theory (294.1 kcal mol^{-1}). These

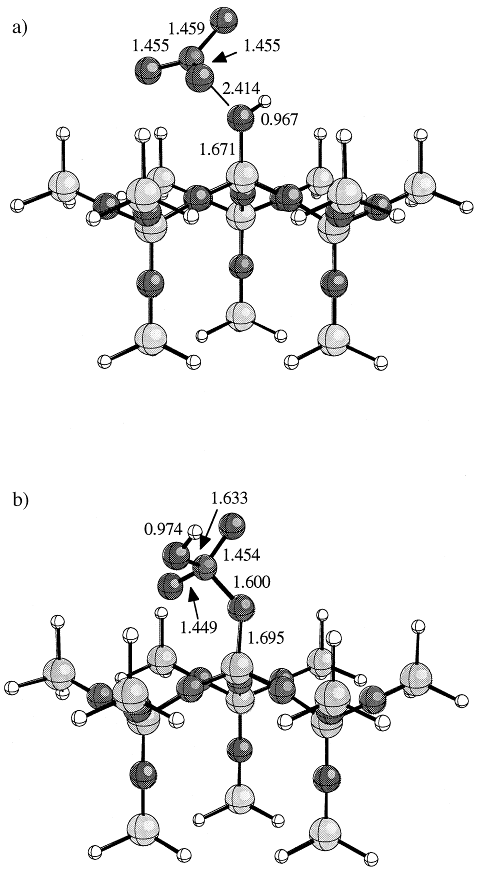

Figure 3. Optimized B3LYP/DZVP2 geometry of the hydrogen sulfate ester formed by reaction of SO_3 on β-cristabolite.

theoretical values compare to experimental deprotonation enthalpies for ZSM-5 of 291–300 kcal mol^{-1}.[10]

In summary, NMR experiments confirm that adsorption of SO_3 onto oxide surfaces introduces acid sites. On SO_3/ZrO_2, both Lewis and Brønsted sites are present, and theoretical modeling, in agreement with NMR studies, supports the formation of Brønsted sites on SO_3/silica.

Experimental Section

Electronic grade silicon(IV) oxide (Puratrem, 99.999%) was obtained from Strem. This was evacuated at 873 K, cooled to 298 K, and then contacted with SO_3 (0.8 mmol g^{-1}). SO_3/silica samples were evacuated at 473 K prior to investigation. Zirconia was prepared by the hydrolysis of zirconyl chloride octahydrate (98%, Aldrich), followed by washing and drying the gel. All zirconia samples were first calcined at 773 K for two hours in flowing air. SO_3 (1.43 mmol g^{-1}) was adsorbed at 298 K and all samples of SO_3/zirconia were further evacuated at 773 K before study. ^1H and ^{15}N MAS NMR spectra were measured at 9.4 Tesla on a Chemagnetics CMX-360 spectrometer and ^{13}C MAS NMR spectra were measured at 4.7 Tesla on a home-built spectrometer.

Theoretical calculations were performed by using Gaussian 94[11] and the B3LYP[12] exchange-correlation functional and the DZVP2[13] basis set. The terminal O and H atoms were held fixed in crystallographic positions, with the OH bond lengths set to 0.9675 Å. Frequency calculations on $H_3SiOHSO_3$ and H_3SiOSO_3H were used to estimate the zero-point and thermal energy contributions for the determination of the deprotonation enthalpies of the larger models.

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Syntheses, Structures, and Magnetic Properties of Two Gadolinium(III)–Copper(II) Coordination Polymers by a Hydrothermal Reaction[**]

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Studies on the syntheses, structures, and properties of lanthanide–transition metal complexes are currently of great interest because they are good models to investigate the nature of the magnetic exchange interactions between 3d and 4f metal ions in magnetic materials that contain rare earth metals.[1–5] Many such studies focused on discrete complexes, which were synthesized from conventional, self-assembly

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