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Chemisorption of *aci*-Nitromethane on Strongly Basic Catalysts: An NMR Probe of Solid Basicity

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Although amorphous oxide and zeolite catalysts are most frequently thought about in terms of acidic properties, the basic properties of oxides such as MgO and CaO and zeolites such as CsX are undergoing a renewal of interest. Amorphous basic oxides are useful for a number of transformations including olefin isomerization, hydrogenation, and functional group elimination.[1] Alkali metal promoted MgO is active for the oxidative coupling of methane at high temperatures.[2] The basic properties of zeolite CsX are evident in the conversion of 2-propanol to acetone[3] and have been implicated in the side-chain alkylation of toluene by methanol to form ethylbenzene.[4] On acidic zeolites the products of those reactions are propene and xylenes, respectively.

Relative to their acidic counterparts, the sites of adsorption and reaction on basic catalysts are poorly understood. One of the strategies by which acid sites on amorphous and zeolite catalysts have been characterized is magic angle spinning (MAS) solid state NMR studies of suitable probe molecules. The considerable literature on acid site NMR probes includes amines,[5-8] phosphines,[9-11] phosphine oxides,[12] and the formation of carbenium,[13] oxonium,[14] sulfonium, and selenonium[15] ions from appropriate precursors. Acid sites in zeolites have also been probed by ^1H NMR studies following adsorption of methanol,[16] water,[17,18] and unsaturated molecules[19] and isotope exchange with deuteriobenzene.[19]

Relative to the rich NMR literature probing acid sites, corresponding NMR studies of basic sites are virtually nonexistent. The most notable exceptions would appear to be the adsorption of CO_2 to form bicarbonates or carbonates on $Cu/ZnO/Al_2O_3$[20] and the formation of bound alkoxy species on basic zeolites from alkyl halides,[21] both of which were examined as potential reactive intermediates rather than probes of basicity per se.

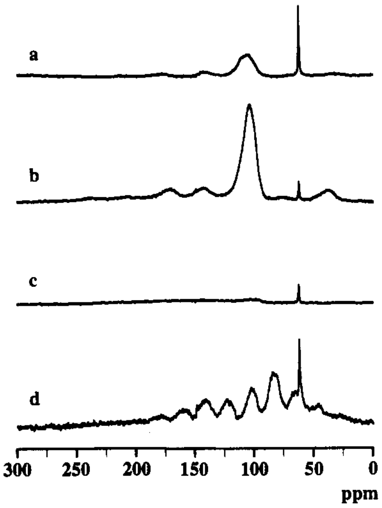
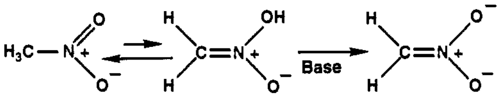


Figure 1. 50.1-MHz ^{13}C MAS NMR spectra showing the formation of chemisorbed *aci* anion on MgO from $^{13}CH_3NO_2$ at 298 K. Spectra a–c were acquired with a spinning speed of 3.5 KHz: (a) Bloch decay spectrum; (b) cross-polarization spectrum; (c) cross-polarization with 50-μs interrupted decoupling; (d) cross-polarization with slow MAS (900 Hz).

In the past year we have been studying the reactions of nitromethane on a variety of solid acids and bases by in situ NMR. These experiments were motivated in part by analogous investigations of other methane derivatives[22] as well as the literature on the rich thermal decomposition chemistry of this energetic compound.[23] In the course of that work we recognized that nitromethane is a useful probe of strong basic sites on solids.

aci-Nitromethane (**1**) is a tautomeric form of nitromethane. The equilibrium constant for the formation of **1** is very small, but strongly basic solutions drive the equilibrium by formation of the *aci* anion (**2**).[24] Figure 1 shows ^{13}C MAS NMR spectra[25] obtained at 298 K from a representative in situ study of nitromethane adsorbed on a high surface area MgO catalyst.[26] Bloch decay spectra (Figure 1a) show both a sharp signal at 62 ppm for gas-phase or physisorbed nitromethane and a broad signal at 104 ppm for the chemisorbed *aci* anion. These isotropic ^{13}C chemical shifts are essentially identical to those observed in solution.[27] The



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(1) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*; Elsevier: Amsterdam, 1989.

(2) Ito, T.; Wang, J.-X.; Lin, C.-H.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 5062–5068.

(3) Hathaway, P. E.; Davis, M. E. *J. Catal.* **1989**, *116*, 263–278.

(4) Engelhardt, J.; Szanyi, J.; Valyon, J. *J. Catal.* **1987**, *107*, 296–306.

(5) Maciel, G. E.; Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Early, T. H.; Mckay, D. R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529–5535.

(6) Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 7206–7207.

(7) Majors, P. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1987**, *109*, 1648–1653.

(8) Earl, W. L.; Fritz, P. O.; Gibson, A. A. V.; Lunsford, J. H. *J. Phys. Chem.* **1987**, *91*, 2091–2095.

(9) Lunsford, J. H.; Rothwell, W. P.; Shen, W. *J. Am. Chem. Soc.* **1985**, *107*, 1540–1547.

(10) Lunsford, J. H.; Tutunjian, P. N.; Chu, P.-J.; Yeh, E. B.; Zalewski, D. J. *J. Phys. Chem.* **1989**, *93*, 2590–2595.

(11) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1987**, *109*, 40–46.

(12) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 7119–7120.

(13) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052–2058.

(14) Munson, E. J.; Haw, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 6303–6305.

(15) Munson, E. J.; Kheir, A. A.; Haw, J. F. *J. Phys. Chem.* **1993**, *97*, 7321–7327.

(16) Anderson, M. W.; Barrie, P. J.; Klinowski, J. *J. Phys. Chem.* **1991**, *95*, 235–239.

(17) Hunger, M.; Freude, D.; Pfeifer, H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 657–662.

(18) Batamack, P.; Dorémieux-Morin, C.; Fraissard, J.; Freude, D. *J. Phys. Chem.* **1991**, *95*, 3790–3796.

(19) White, J. L.; Beck, L. W.; Haw, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 6182–6189.

(20) Lazo, N. D.; Murray, D. K.; Haw, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 8552–8559.

(21) Murray, D. K.; Chang, J.-W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4732–4741.

(22) Munson, E. J.; Lazo, N. D.; Moellenhoff, M. E.; Haw, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 2783–2784.

(23) Nazin, G. M.; Manelis, G. B.; Dubovitskii, F. I. *Russ. Chem. Rev.* **1968**, *37*, 603–612.

(24) Barton, D.; Ollis, W. D. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press: Oxford, 1979; Vol 2, pp 335–336.

(25) ^{13}C MAS NMR experiments were performed at 50.1 MHz on a home built 4.7-T system, and ^{15}N MAS NMR measurements were obtained at 36.5 MHz on a Chemagnetics CMX-360. ^{15}N chemical shifts are reported relative to nitromethane.

(26) MgO (Fischer Scientific, ACS certified grade) and CaO (Aldrich, 99.95% pure) were treated with deionized water (30 mL/g of oxide). The white slurry was then slowly heated to dryness and heated in an oven at 373 K for 12 h. The oxide catalysts were thermally activated to a maximum temperature of 773 K using a multistep procedure described in ref 13. The preparation of CsX was described in ref 21. Nitromethane-^{13}C (Isotech) and nitromethane-^{15}N (Cambridge Isotopes) were purified by several freeze–pump–thaw cycles before introduction to the catalyst at room temperature at loadings well below 1 monolayer based on the N_2 BET surface area.

(27) Bowman, W. R.; Golding, B. T.; Watson, P. W. *J. Chem. Soc., Perkin Trans. 2* **1980**, 5, 731–736.

0002-7863/94/1516-0817$04.50/0

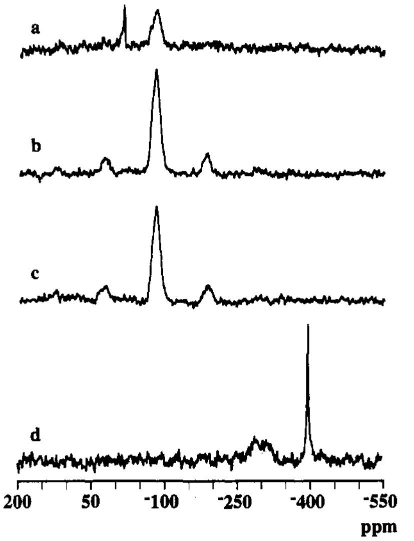

Figure 2. 36.5-MHz ^{15}N MAS NMR spectra showing the formation of chemisorbed *aci* anion on MgO from $CH_3{}^{15}NO_2$ at 298 K (a–c) and subsequent decomposition to NH_3 (d): (a) Bloch decay spectrum; (b) cross-polarization spectrum; (c) cross-polarization with 50-μs interrupted decoupling; (d) cross-polarization spectrum at 298 K after heating to 473 K.

latter signal is emphasized in cross polarization[28] spectra (Figure 1b), while the former is reduced with that mode of excitation. The ^{13}C signal for the *aci* anion is completely attenuated in an interrupted decoupling experiment[29] (Figure 1c), exactly as should happen for a CH_2 species incapable of large amplitude motion on a 50-μs time scale. Chemisorption is also reflected in the spinning side band pattern due to chemical shift anisotropy that becomes more evident with decreased spinning speed (Figure 1d). The principal components of the ^{13}C chemical shift tensor of the surface-bound *aci* anion on MgO were obtained by Herzfeld–Berger analysis,[30] and these values are δ_{11} = 52 ppm, δ_{22} = 86 ppm, and δ_{33} = 173 ppm.[31] Other evidence for strong chemisorption of the *aci* anion on MgO is the fact that the ^{13}C T_1 at 4.7 T and 298 K was 19 s, a very long value for an adsorbate at moderate temperature.

Figure 2 shows representative spectra from an analogous ^{15}N study of $CH_3{}^{15}NO_2$ on MgO. The isotropic chemical shift of the *aci* anion was –80 ppm; a solution value has apparently not been reported, but the upfield shift relative to nitromethane is consistent with the increased negative charge on the adjacent oxygens.

The NMR evidence points to a static structure for chemisorbed *aci* anion on MgO. This is satisfactorily accounted for by bidentate or bridging coordination to exposed cation sites. The fate of the proton is believed to be formation of a surface hydroxyl.

Previous studies in solution[32,33] and in the solid state at high pressure[34] have implicated the *aci* anion in the detonation sensitivity of nitromethane (see note 35 for **safety** issues). At 473 K the *aci* ion on MgO was converted to a carbonate species (spectra not shown) similar in its spectroscopic behavior to surface bicarbonates or carbonates previously characterized.[20] Figure 2d shows that the fate of the nitrogen after heating is formation of ammonia.

Analogous ^{13}C experiments were performed on CaO, and the results were essentially identical to those reported here for MgO. A very small amount of *aci* anion formed on zeolite CsX (not shown), which is thought to be only moderately basic, but strong base sites due to Cs_2O clusters have been proposed to form in this catalyst.[36] No *aci* anion formed in acidic zeolites. Nitromethane was unreactive on zeolite HZSM-5 at room temperature and decomposed to CO_2, CO, ammonia, and urea at 473 K.

The pK_a of nitromethane in aqueous solution is 10.0, which makes it a much more discriminating probe than CO_2, which can, in any event, adsorb in a large number of forms.[1] As has often been pointed out,[1] the activities of adsorbates on surfaces are not well defined thermodynamic quantities, and the Hammett acidity function, H_0, has been defined as a formalism for quantifying surface acid strength, although its usefulness is periodically questioned.[37] The analogous basicity function, H_-, is even more poorly developed, although the term "superbasicity" has been invoked for H_- values higher than +26, and depending on the method of preparation, both CaO and impregnated MgO qualify for this superlative. It should be clear that additional experimental and theoretical work should be directed at basic catalysts to compliment the emerging understanding of acid sites. Probe molecule studies will be one component of this effort.

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(28) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–590.

(29) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.

(30) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021–6030.

(31) It would be worthwhile to compare these values with measurements obtained for a pure salt of the *aci* anion, but ref 24 and the advice of colleagues suggested that these solids would be prone to detonation.

(32) Engelke, R.; Earl, W. L.; Rohlfing, C. M. *J. Phys. Chem.* **1986**, *90*, 545–547.

(33) Engelke, R.; Earl, W. L.; Rohlfing, C. M. *J. Chem. Phys.* **1986**, *84*, 142–146.

(34) Engelke, R.; Schiferl, D.; Storm, C. B.; Earl, W. L. *J. Phys. Chem.* **1988**, *92*, 6815–6819.

(35) **SAFETY NOTE**: In an unrelated experiment, an explosion occurred when 1.4 g of nitromethane was condensed on 5.0 g of zeolite CsX at 77 K, sealed in a glass tube and then warmed to room temperature. No safety problems have been observed in over 100 NMR experiments involving small amounts (≤11.0 mg) of nitromethane on various catalysts, but the authors strongly caution against condensing large quantities of liquid nitromethane on a basic surface.

(36) Hathaway, P. E.; Davis, M. E. *J. Catal.* **1989**, *116*, 263–278.

(37) Farcasiu, D. J.; Ghenciu, A.; Miller, G. J. *J. Catal.* **1992**, *134*, 118–125.