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Supplementary Material Available: Tables of spectroscopic data for all new compounds, crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and an ORTEP drawing for $\{\eta^3\text{-}HB(3\text{-}Bu^tpyz)_3\}MgCH_3$ (20 pages); listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

Oxygen-17 Labeling of Oxides and Zeolites†

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Over the past few years there has been a growth in interest in obtaining ^{17}O-labeled materials for solid-state ^{17}O NMR spectroscopy.[1-10] For many oxides, or complex oxides, we have used wet chemical methods or O-17 labeled precursors (e.g., $Si^{17}O_2$) to make group II oxides, silicates, aluminosilicates (zeolites), and aluminum phosphates (e.g., $AlPO_4$-5), whereas we and other groups have used $^{17}O_2$ gas to label metallic high-T_c superconductors, including $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_{8+x}$, and $Tl_2Ba_2CaCu_2O_{8+x}$.[11] Unfortunately, however, all of the hydrothermal routes are quite lengthy and involve use of significant quantities of $H_2{}^{17}O$, and, in our hands, wet chemical approaches to the preparation of some high-T_c superconductor precursors, such as Y_2O_3, have been somewhat unsuccessful.

Stimulated by the ease of labeling the high-T_c superconductor materials with $^{17}O_2$ gas, together with the previous observations of oxygen diffusion at high temperature in Al_2O_3,[12] three Mg–Al spinels,[13] and in Li_2O,[14] we decided to investigate the possibilities of ^{17}O-labeling a series of metal oxides and zeolites, by using $^{17}O_2$ gas at relatively low temperatures. To our surprise, we found that all materials investigated readily exchange ^{16}O for ^{17}O, producing a variety of ^{17}O-labeled materials, many of which are, we believe, otherwise rather difficult to obtain.

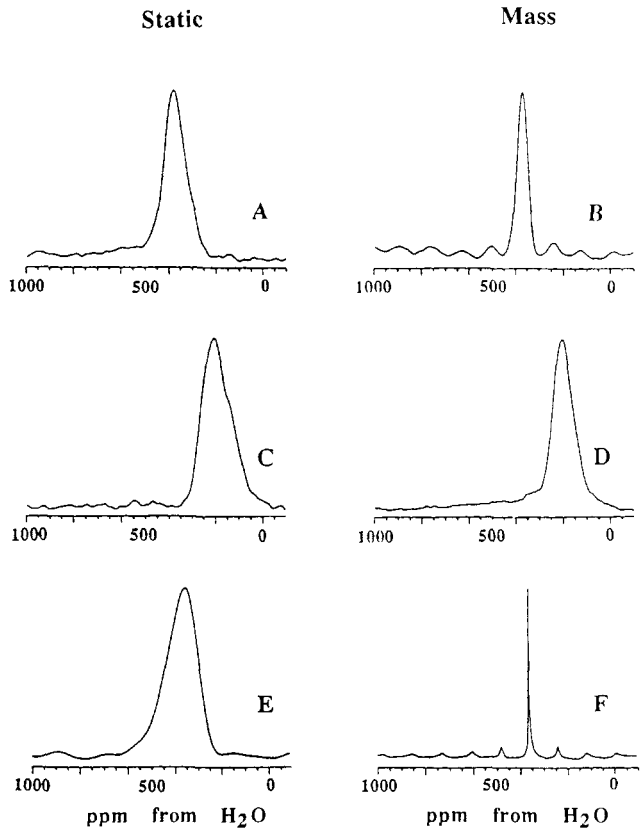

Figure 1. Static and MASS ^{17}O NMR spectra at 11.7 T of ^{17}O-labeled Tl_2O_3, Bi_2O_3, and Y_2O_3: (A) $Tl_2{}^{17}O_3$, static, 1400 scans, 100 ms recycle; (B) $Tl_2{}^{17}O_3$, 7.9 kHz spin rate, 11 330 scans, 1 s recycle; (C) $Bi_2{}^{17}O_3$, static, 380 scans, 10 s recycle; (D) $Bi_2{}^{17}O_3$, 7.9 kHz spin rate, 708 scans, 1 s recycle; (E) $Y_2{}^{17}O_3$, static, 2352 scans, 5 s recycle; (F) $Y_2{}^{17}O_3$, 7.9 kHz spin rate, 31 750 scans, 1 s recycle. Static spectra were recorded with use of a spin-echo pulse sequence with pulse widths of 2.33 μs (solution 90° pulse width = 7 μs) and a 40 μs interpulse delay. MASS spectra used a 3.2 μs pulse width. Line broadenings due to exponential multiplication were in the range of 100–1000 Hz.

We first investigated the M(III) oxides, Tl_2O_3, Bi_2O_3, and Y_2O_3, since they are all precursors to high-T_c superconductors, and their ^{17}O NMR spectra provide a valuable data set with which to begin interpretation of the ^{17}O NMR spectra of the superconductors themselves. $Tl_2{}^{17}O_3$ was prepared by heating Tl_2O_3 (0.5 g) in a gold boat under 0.5 atm $^{17}O_2$ (40%, $^{17}O_2$) for 48 h at 500 °C. Since Tl_2O_3 is metallic, it is perhaps not surprising that ^{17}O exchange occurs readily, and we show in Figure 1A,B the static and magic angle sample spinning (MASS) NMR spectra of Tl_2O_3 taken at 67.8 MHz (corresponding to a magnetic field strength of 11.7 T). For MASS NMR, the sample was diluted 1:9 with Al_2O_3, since the undiluted material would not spin in the high magnetic field used. As can be seen from Figure 1, the isotropic chemical shift of $Tl_2{}^{17}O_3$ is 364 ppm from H_2O (where high frequency, low field, paramagnetic, or deshielded shifts are positive, IUPAC δ scale). Interestingly, the observed chemical shift of 364 ppm is close to the ≈315–345 ppm (two sites) observed in $Tl_2Ba_2CaCu_2O_{8+x}$,[11] one site of which can be attributed to the Tl–O planes in this material.[11]

We then prepared $Bi_2{}^{17}O_3$ by heating 2 g of Bi_2O_3 in a gold boat under 0.5 atm $^{17}O_2$ for 48 h at 600 °C. Bi_2O_3 is a semiconductor, so it was again not very surprising that ^{17}O exchange occurred readily, and we obtained the static and MASS ^{17}O NMR spectra shown in Figure 1C,D. There is little narrowing upon MASS, and the widths are field independent, suggesting exchange interactions or the presence of free Bi(0), as seen previously with

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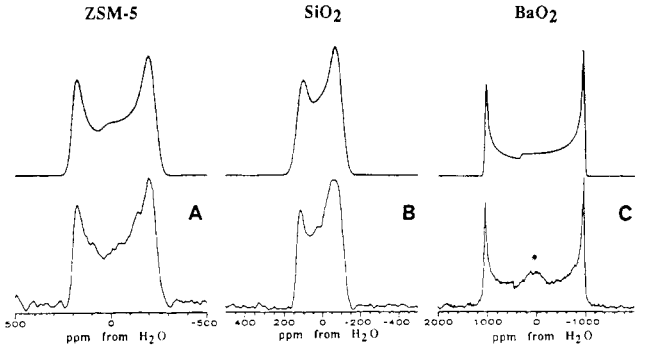

Figure 2. Static ^{17}O NMR spectra and computer simulations of ^{17}O labeled ZSM-5, SiO_2, and BaO_2: (A) Na-ZSM-5 (36 ppm Al), 8.45 T, 300 ms recycle time, 2804 scans. Inset: computer simulation using e^2qQ/h = 5.6 MHz, η = 0.08, δ_i = 43 ppm, and a 2500 Hz Gaussian line broadening. The experimental broadening was 1000 Hz (Lorentzian). (B) SiO_2 (amorphous 99.999% purity), 11.7 T, 3836 scans, 1 s recycle time. Inset: Computer simulation using e^2qQ/h = 5.6 MHz, η = 0.08, δ_i = 46 ppm, and a 4000 Hz Gaussian line broadening. The experimental broadening was 500 Hz (Lorentzian). (C) BaO_2, 11.7 T, 1348 scans, 5 s recycle time. Inset: computer simulation using e^2qQ/h = 17.2 MHz, η = 0.0, δ_i = 334 ppm, and a 3200 Hz Gaussian line broadening. The experimental line broadening was 500 Hz (Lorentzian). The peak marked by an asterisk in the BaO_2 spectrum is thought to arise from an unknown impurity.

the CdO system.[6] The isotropic chemical shift of $Bi_2{}^{17}O_3$ is 195 ppm from $H_2{}^{17}O$, close to the ~200 ppm found in $Bi_2Sr_2CaCu_2O_{8+x}$.[11]

We also show in Figure 1 results obtained on $Y_2{}^{17}O_3$ (Figure 1E,F). Here, we heated Y_2O_3 (0.1 g) in a gold boat under 0.5 atm $^{17}O_2$ for 40 h at 600 °C, and care was taken to keep the sample dry after removal from the furnace to minimize hydration (to e.g., $Y(OH)_3$, $Y_2(CO_3)_3$, etc.). As can be seen from Figure 1E,F, the static spectrum of $Y_2{}^{17}O_3$ contains only a rather broad feature. However, unlike $Tl_2{}^{17}O_3$ and $Bi_2{}^{17}O_3$, MASS in this case is successful in removing the line broadening, which appears to be due to a combination of first-order quadrupolar and chemical shift anisotropy mechanisms. We find the isotropic chemical shift to be 355 ppm from $H_2{}^{17}O$. The observation of ^{17}O-labeling with Y_2O_3 is notable, since $Y_2{}^{17}O_3$ is rather difficult to make with wet chemical methods.

We show in Figure 2 ^{17}O NMR results obtained on the zeolite ZSM-5 (Figure 2A), a 5-9's purity sample of amorphous SiO_2 (Figure 2B), and BaO_2 (Figure 2C). Similar exchange conditions like those for the M(III) oxides were used. Figure 2A shows the spectrum (and its computer simulation) of a Na-ZSM-5 having a low Al content. The line shape is characteristic of a second-order powder pattern having a quadrupole coupling constant (e^2qQ/h) = 5.5 MHz, an electric field gradient tensor asymmetry parameter (η) = 0.08, and an isotropic chemical shift (δ_i) = 43 ppm.

Since we previously observed ^{17}O-labeling of zeolites via hydrothermal routes,[3,4,15] it seemed possible that residual $H_2{}^{17}O$ in our $^{17}O_2$ gas (or just possibly, residual H_2 contamination yielding H_2O on calcination) could be responsible for all ^{17}O labeling we have observed. We feel this possibility is remote for the following reasons: (1) Attempts at preparing ^{17}O-labeled oxides (e.g., Al_2O_3, CaO, Bi_2O_3) using $N_2/H_2{}^{17}O$ (0.2 mL of $H_2{}^{17}O$ in a 400 cm^3 gas volume) were all unsuccessful. (2) ^{17}O labeling using an $^{17}O_2$ gas sample which had been dried over P_4O_{10} for 7 days and then distilled from CO_2/acetone (−70 °C) to LN_2 (−196 °C) yielded highly labeled oxides and ZSM-5. (3) Cross-polarization, H-microanalysis, and X-ray diffraction gave no indications that the oxides investigated contained hydroxides or related basic oxides. Some ^{17}O labeling of the ZSM-5 sample (~10% that obtained with $^{17}O_2$) was observed, but there is no evidence that the hydrothermal route is the major pathway for any of the materials investigated. A porous zeolitic framework is not a prerequisite for ^{17}O-labeling for siliceous materials as shown in Figure 2B where we present the 11.7 T ^{17}O NMR spectrum of SiO_2 (amorphous, 99.999% purity, BET surface area = 269 m^2/g) labeled with carefully dried $^{17}O_2$ (0.1 g of SiO_2, 0.5 atm $^{17}O_2$, 500 °C for 42 h). The spectrum is that expected for SiO_2 (e^2qQ/h = 5.6 MHz, η = 0.08, δ_i = 46 ppm).

Finally, we show in Figure 2C the ^{17}O NMR spectrum of labeled barium peroxide, which was made by heating BaO_2 at 500 °C in a 0.5 atm $^{17}O_2$ atmosphere for 40 h. It is well-known that barium oxide reacts with oxygen to form barium peroxide,[16] and a similar spectrum was obtained from BaO starting material (data not shown). From this observation we suggest that the exchange mechanisms responsible for labeling all oxides and zeolites presented in this communication might involve initial formation of metastable peroxy states, which then form the ^{17}O exchanged oxide:

$$M^{16}O \xrightarrow{1/2\,{}^{17}O_2} [M^{16}O^{17}O] \rightarrow M^{17}O + \tfrac{1}{2}{}^{16}O_2$$

The results we have presented above are important for a number of reasons. First, they show that many metal oxides and mixed-metal oxides, such as zeolites, may be readily ^{17}O-labeled for solid-state ^{17}O NMR spectroscopy simply by heating in $^{17}O_2$ gas at relatively moderate temperatures. This means that many previously well-characterized materials, such as synthetic zeolites, can be ^{17}O labeled without direct synthesis—which can be difficult on a very small scale. Also, processes such as dealumination, which might be encountered by using hydrothermal routes, can presumably be avoided. In addition, species such as Y_2O_3, which are difficult to prepare with wet chemical methods, can be readily produced. The $^{17}O_2$ gas-phase methods outlined should be of particular use in the production of ^{17}O-labeled materials for double-axis rotation (DOR) experiments,[17] where individual ^{17}O sites can be readily detected.[18]

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Ferrapyrrolinone and Ferraazetine Complexes Formed from the Reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with Phosphinimines

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As an extension to our studies of coordinated ketenes,[1] we sought to transform these ligands into ketenimine ligands via deoxygenation with phosphinimines. Described herein are the results of one such attempt with the ketene precursor[2] $Fe_2(\mu\text{-}CH_2)(CO)_8$

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