

the longest C<sub>1</sub>-F bond since only one fluorine hyperconjugative resonance structure is available to delocalize charge, whereas in CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup> and CF<sub>3</sub>O<sup>-</sup> there are two and three, respectively. The increase in C<sub>1</sub>-F bond lengths, however, might simply reflect the well-known dependence of C-F bond length on the number of fluorines attached to the carbon atom.<sup>7a,28</sup> For CF<sub>3</sub>-F, CF<sub>3</sub>CF<sub>2</sub>-F, and (CF<sub>3</sub>)<sub>2</sub>CF-F the calculated bond lengths are 1.306, 1.312, and 1.328 Å, respectively.<sup>29</sup> The C-F bond lengths in the perfluoroalkoxides show a much larger change than in the perfluoroalkanes, which clearly supports the importance of negative HCl in the alkoxides.

**Registry No.** (Me<sub>2</sub>N)<sub>3</sub>S<sup>+</sup>CF<sub>3</sub>O<sup>-</sup>, 96898-10-1; F<sub>2</sub>CO, 353-50-4; (Me<sub>2</sub>N)<sub>3</sub>S<sup>+</sup>Me<sub>3</sub>F<sub>2</sub>Si<sup>-</sup>, 59218-87-0; CF<sub>3</sub>O<sup>-</sup>, 57178-38-8; CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup>, 94295-10-0; (CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup>, 44967-50-2.

**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and structure amplitudes (5 pages). Ordering information is given on any current masthead page.

(27) The TAS salts of CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup> and (CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup> were easily prepared by adding CF<sub>3</sub>C(O)F and (CF<sub>3</sub>)<sub>2</sub>C=O, respectively, to TASF following the procedure to make 1;<sup>4</sup> TAS<sup>+</sup>CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup>: mp 189-191 °C dec; <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) δ -83.52 (s, CF<sub>3</sub>), -34.56 (s, CF<sub>2</sub>); TAS<sup>+</sup>(CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup>: mp 129 °C dec; <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, -30 °C) δ -81.24 (d, J = 4.5 Hz, CF<sub>3</sub>), -71.17 (sept, J = 4.5 Hz, CF); δ (20 °C) -81.21 (s, CF<sub>3</sub>), -69.30 (s, CF, w<sub>1/2</sub> = 12 Hz). Unfortunately we have not yet been able to obtain crystals of either salt suitable for X-ray analysis. Unlike their Rb<sup>+</sup> and Cs<sup>+</sup> salts, which rapidly decompose at or below 50 °C,<sup>1f</sup> the TAS<sup>+</sup> salts of CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup> and (CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup> are both stable up to their respective melting points. Solution dynamic properties and synthetic use of TAS perfluoroalkoxides and related stable TAS perfluorocarbanions will be discussed in a forthcoming publication: Smart, B. E.; Middleton, W. J.; Farnham, W. B., unpublished results.

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(29) Ab initio (6-31G+ polarization functions on C) values: Van-Catledge, F. A.; Dixon, D. A. Experimental differences:  $r(\text{CF}_3\text{-F})^{10} - r(\text{CF}_3\text{CF}_2\text{-F})^{30} \approx 0.007 \text{ \AA}$ ;  $r(\text{CF}_2\text{H-F})^{10} - r(\text{CF}_3\text{CFH-F})^{31} \approx 0.009 \text{ \AA}$ . No experimental (CF<sub>3</sub>)<sub>2</sub>CX-F bond lengths have been reported to date.

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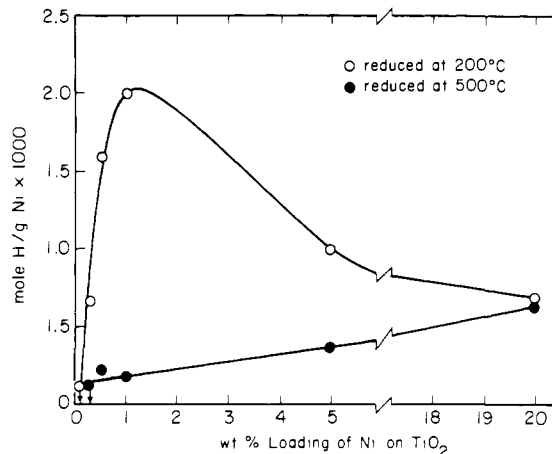
## Changes in the Electronic Structure of Ni/TiO<sub>x</sub> Composites as a Function of Reduction Temperature<sup>†</sup>

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Transition-metal catalysts are dispersed on high surface area oxide supports in order to obtain a large catalytic activity per metal atom. Many supports, such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, are considered to be inert; that is, these supports do not alter the intrinsic activity of the metal significantly but only serve to increase the surface area of the metal and prevent sintering. For some oxide supports, however, there is a strong interaction between the metal and the support.<sup>1</sup> In particular, TiO<sub>2</sub> can affect the activity of the supported metal depending on the conditions under which the metal-titanium dioxide composite is prepared. It is our goal to learn how to control the chemistry of supported metals by mod-



**Figure 1.** Dependence of H<sub>2</sub> chemisorption at room temperature on the weight percent of Ni supported on TiO<sub>2</sub>.

ifying the support composition and the composite preparation temperature.

Typically, transition metals are dispersed on oxide supports by impregnation of the support with a metal salt and subsequent reduction to the metal in flowing hydrogen. The catalytic activity and chemisorption properties of group 8-10 metals supported on TiO<sub>2</sub> depend on the reduction temperature used to prepare the catalyst. In particular, the chemisorption of H<sub>2</sub> and CO at 295 K decreases sharply as the reduction temperature is increased from 473 to 773 K. This suppression of chemisorption can be attributed to (1) the migration of TiO<sub>x</sub> species from the support onto the metal particles, thereby decreasing the number of metal sites exposed for chemisorption,<sup>2</sup> (2) an electronic effect, due to charge transfer from the reduced support to the metal,<sup>3</sup> or (3) the formation of a new metastable Ni-Ti-O phase. We have studied the magnetic properties of Ni/TiO<sub>2</sub> and have shown that an electronic change occurs as a function of reduction temperature.

We chose to study nickel supported on TiO<sub>2</sub> because the magnetic properties of the nickel provide an excellent probe of changes in the electronic properties of the Ni/TiO<sub>2</sub> composites. Nickel is ferromagnetic below its Curie temperature of 627 K with a saturation magnetization  $M_s = 57.50 \text{ emu/g}$  at absolute zero.<sup>4</sup> By measuring the saturation magnetization of the Ni/TiO<sub>2</sub> samples, the amount of Ni present as bulk metal can be determined. TiO<sub>2</sub>, on the other hand, is an insulator and is diamagnetic. It can be reduced, however, in hydrogen to a series of paramagnetic phases known as the Magneli phases of formula Ti<sub>n</sub>O<sub>2n-1</sub> for  $n \geq 3$ .<sup>5</sup> Whereas this reduction does not occur for pure TiO<sub>2</sub> below ~1000 K, it occurs at much lower temperatures in the presence of metal impurities.<sup>6</sup> These Magneli phases are all paramagnetic due to the presence of Ti<sup>3+</sup> species.<sup>7</sup> By measuring the paramagnetic moment of the Ni/TiO<sub>2</sub> samples it is possible to determine the degree of support (TiO<sub>2</sub>) reduction. Therefore, in a single magnetic measurement one can determine both changes in the electronic properties of the nickel and the degree of reduction of the support.

Samples of Ni/TiO<sub>2</sub> were prepared from TiO<sub>2</sub> (Cerac, 99.9% pure) which was 15-20% rutile and 80-85% anatase with a surface area of 51 m<sup>2</sup>/g. Samples with nickel loadings from 0.1% to 20% by weight were prepared by incipient wetness techniques using

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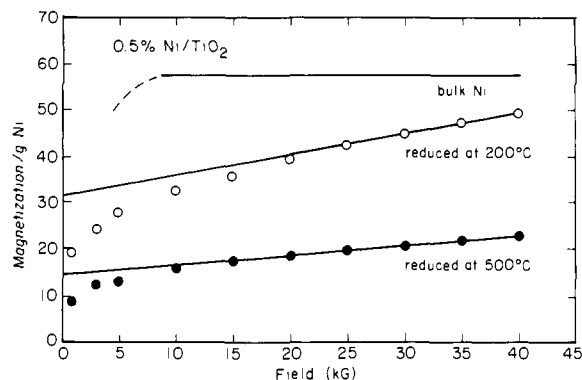
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<sup>†</sup> In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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**Figure 2.** Magnetization vs. field for 0.5% Ni/TiO<sub>2</sub> reduced at 200 and 500 °C. The magnetization expected for bulk nickel is shown.

reagent grade Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Mallinckroft, 99.95% pure). These samples were reduced initially in flowing hydrogen at 473 K for 20 h and then at 773 K for 1 h. Changes in the surface chemistry of the nickel were monitored by the chemisorption of hydrogen at room temperature.

The amount of hydrogen that chemisorbed at 295 K on these composites was sensitive both to the amount of nickel present and to the preparation temperature as shown in Figure 1. A suppression of hydrogen chemisorption was observed as the reduction temperature of the composite was increased from 473 to 773 K. As the nickel loading was increased, the amount of hydrogen chemisorbed became nearly independent of reduction temperature as expected for bulk nickel. The trends in chemisorption observed for the lower nickel loadings are due to two effects: (1) interactions of the nickel with the TiO<sub>2</sub> and (2) changes in the dispersion of the nickel. We present here magnetic studies on the 0.5% Ni/TiO<sub>2</sub> sample which show that the large changes in chemisorption as a function of reduction temperature are due to a strong interaction between nickel and TiO<sub>2</sub>.

Magnetization vs. field was measured for these samples with a SHE SQUID magnetometer at 5 K in fields from 1 to 40 kG. Figure 2 shows the magnetization per gram of nickel vs. field for 0.5% Ni/TiO<sub>2</sub> reduced at 473 and 773 K. Extrapolation of the data for fields greater than 30 kG to zero gives the saturation magnetization  $M_s(473\text{ K}) = 31.7$  per g of Ni for the sample reduced at 473 K and  $M_s(773\text{ K}) = 14.8$  per g of Ni for the sample reduced at 773 K.  $M_s(473\text{ K})$  is 55% of the value expected if all the nickel were present as bulk nickel, indicating that some unreduced NiO remains. A temperature of 773 K is high enough to reduce all the NiO to Ni<sup>0</sup> and therefore  $M_s$  should increase to the value observed for bulk nickel. The fact that  $M_s(773\text{ K})$  is less than  $M_s(473\text{ K})$ , however, suggests that much of the nickel (~75%) is not present as bulk nickel. Furthermore, since this loss of bulk nickel after the high-temperature reduction correlates well with the suppression of hydrogen chemisorption we conclude that the change in chemisorption properties is associated with the change in the form of nickel present in the system.

The slope of the magnetization vs. field curves for fields greater than 30 kG shows that the samples contain localized, unpaired electrons. Since the TiO<sub>2</sub> starting material is temperature independent and diamagnetic down to 5 K, this result suggests that part of the TiO<sub>2</sub> has been reduced. Although the analysis is complicated by the exchange field of the ferromagnetic nickel, the magnitude of the moment indicates that ~5% of the Ti<sup>4+</sup> in the support has been reduced to Ti<sup>3+</sup>. We have obtained electron spin resonance spectra of these materials and the presence of a resonance due to Ti<sup>3+</sup> supports this conclusion. This reduced titanium oxide is present after reduction at both 473 and 773 K.

In summary, we have shown that for 0.5% Ni/TiO<sub>2</sub> reduced at 773 K, a large fraction of the nickel is not present as bulk nickel. Furthermore, a significant fraction of the support is present as paramagnetic reduced titanium oxide, TiO<sub>x</sub> (where  $x < 2$ ), after

reduction at both 473 and 773 K. We conclude that the changes in chemisorption properties for samples reduced at 773 K are due to a change in the electronic structure of the material and not just a change in the number of metal sites exposed for chemisorption. To account for the loss of bulk nickel at the 773 K reduction temperature, we propose the formation of a metastable Ni-Ti-O phase. To substantiate the presence of such a composite and to determine its properties, we have begun electron spin resonance studies of the Ni/TiO<sub>2</sub> system and are beginning magnetic studies on other metal/TiO<sub>2</sub> systems.

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Registry No. TiO<sub>2</sub>, 13463-67-7; Ni, 7440-02-0.

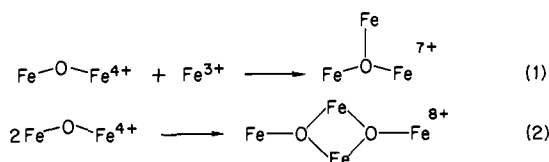
### Synthesis, Structure, and Magnetic Properties of an Asymmetric $\mu_3$ -Oxotriiron(III) Complex: A New Type of {Fe<sub>3</sub>O}<sup>7+</sup> Core

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Polynuclear iron oxo complexes have interested inorganic and biological chemists for many years.<sup>1-3</sup> Recently  $\mu$ -oxodiron(III) complexes having properties comparable to those of the met forms of hemerythrin, a marine invertebrate oxygen transport protein, were prepared and characterized.<sup>4</sup> Further studies led to the synthesis of hydroxo- and phosphodiester-bridged analogues,<sup>5,6</sup> the latter being of likely relevance to several biologically occurring iron-phosphate systems.<sup>7</sup> Binuclear oxo-bridged iron centers have also been suggested to be important for initiating the formation of the polynuclear iron core in the iron storage protein ferritin.<sup>7d,e</sup> We were therefore interested to investigate whether larger iron-oxo aggregates might be constructed by controlled oligomerization in a nonaqueous solvent from {Fe<sub>2</sub>O}<sup>4+</sup> and Fe<sup>3+</sup> building blocks, as illustrated for example by eq 1 and 2. It is of value to compare



properties of the resulting polynuclear iron oxo complexes with those of ferritin, the polynuclear iron core of which has been postulated<sup>7a,8</sup> to be comprised of such units. As described in the

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