Surface Chemistry of Nickel Supported on Ti_nO_{2n-1}

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Received January 13, 1986

Small metal particles dispersed on inorganic oxides are among the most important heterogeneous catalysts. While the primary function of the oxide support is to increase the metal surface area, these supports can cause pronounced changes in the catalytic and chemisorption properties of the metal. In particular, metals supported on TiO_2 have attracted attention due to the observation that activity and selectivity for Fischer-Tropsch synthesis can be altered,[1] depending on the temperature at which the metal-TiO_2 composite is reduced. Furthermore, H_2 and CO chemisorption are suppressed for composites reduced at higher temperatures.[1,2] In this paper, we show that the stoichiometry of the TiO_x support has a large influence on the surface chemistry of the metal.

In a recent paper, we presented our studies of the magnetic properties of Ni on TiO_2.[3] Samples of 0.5% Ni/TiO_2 reduced at 773 K exhibited suppressed hydrogen chemisorption when compared to samples reduced at lower temperatures. This suppression of H_2 chemisorption was accompanied by a decrease in the saturation magnetization of the ferromagnetic nickel, indicating that a large fraction of the nickel was not present as metallic nickel. We proposed that this loss of ferromagnetic nickel at higher reduction temperatures was due to the reaction of Ni with TiO_2. Since metal-support interactions are observed only for reducible supports[1] and since it is known that TiO_2 is reduced partially at higher reduction temperatures,[4] the Ti:O stoichiometry may control the extent to which Ni reacts with the support. To test this hypothesis, we have studied the reaction of Ni with the reduced oxides Ti_nO_{2n-1} ($4 \leqslant n \leqslant 8$).

The titanium oxides Ti_nO_{2n-1}, where $4 \leqslant n \leqslant 8$ and n is an integer, are a homologous series of triclinic phases related to rutile and known as the Magnêli phases.[4,5] These compounds are composed of slabs of rutile extending infinitely in two directions. In the third direction, these slabs have a finite width of n layers of Ti, whereby the slabs are bordered by a layer of octahedra which share faces with the next slab. As n decreases, the Ti:O ratio increases and the thickness of the slabs decreases. Rutile is reduced to these phases at elevated temperatures[4] and partial reduction of rutile is known to occur at 773 K in the presence of certain metals.[6]

Ti_nO_{2n-1} phases with $4 \leqslant n \leqslant 8$ were prepared by reacting TiO_2 (Cerac, 99.9%) and Ti (Alfa, 99.9%) at high temperature. Stoichiometric amounts of the reactants were weighed into quartz tubes previously cleaned with aqua regia. These tubes were evacuated to 10^{-5} torr and sealed, and the samples were heated at 600 °C for 7 days. After grinding and resealing the samples, they were heated further for 1 day at 800 °C, 1 day at 900 °C, 3 days at 1000 °C and then cooled slowly to room temperature. The deep blue products were identified by powder X-ray diffraction.[4] These Ti_nO_{2n-1} supports have low surface areas of 1.1-1.4 m^2/g as measured by the BET method and do not chemisorb H_2 at 295 K.

Samples of Ni/Ti_nO_{2n-1} with nickel loadings of 0.5% by weight were prepared by incipient wetness techniques using Ni-$(NO_3)_2 \cdot 6H_2O$ (Mallincroft, 99.9% pure). TiO_2 (Cerac, 99.9% pure) composed of 15-20% rutile and 80-85% anatase with a surface area of ~5 m^2/g was used for comparison.[7] The samples impregnated with Ni^{2+} were reduced in flowing hydrogen at 473 K for 20 h to produce 0.5% Ni/Ti_nO_{2n-1} composites. In addition, the samples were reduced at 773 K for 1 h. Changes in the surface chemistry of the nickel as a function of Ti:O stoichiometry were monitored by the chemisorption of H_2 at 295 K after reduction at 473 and 773 K.

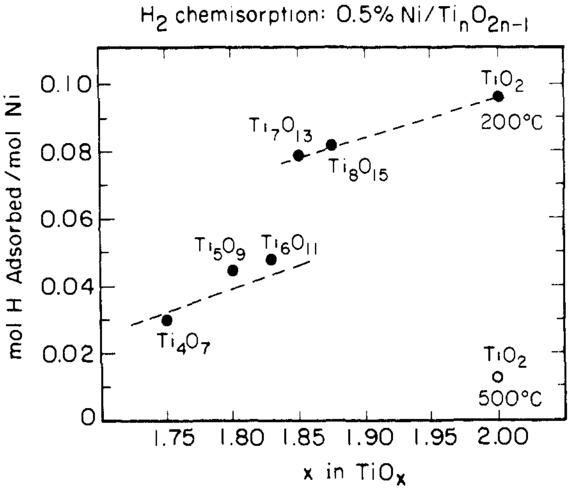

Figure 1. Moles of H adsorbed per mole of Ni as a function of x in TiO_x, where $+2x$ is the oxidation state of the Ti. The closed circles indicate samples reduced in H_2 at 200 °C while the open circle is for the Ni/TiO_2 sample reduced at 500 °C. No H_2 chemisorption could be detected on the Ni/Ti_nO_{2n-1} samples reduced at 500 °C. The error in the measurement is roughly the size of the circles.

The amount of H_2 that chemisorbed on these composites as a function of x in TiO_x is shown in Figure 1, whereby $+2x$ is the oxidation state of the Ti. For samples reduced at 473 K, the amount of H_2 that chemisorbed decreased from 0.096 mol of H/mol of Ni for the least reduced support (TiO_2) to 0.029 mol of H/mol of Ni for the most reduced support (Ti_4O_7). For samples reduced at 773 K, 0.012 mol of H/mol of Ni chemisorbed on Ni/TiO_2 but the chemisorption on all the Ni/Ti_nO_{2n-1} composites was below the detection limit. It is interesting that the chemisorption of H_2 on Ni/Ti_4O_7 reduced at 473 K is similar to that of Ni/TiO_2 reduced at 773 K. This suggests that the effect of the support on the surface chemistry of Ni depends on the degree of reduction of the support.

A large difference in chemisorption is observed between the oxygen-rich phases Ni/TiO_2, Ni/Ti_8O_{15}, and Ni/Ti_7O_{13} and the oxygen-poor phases Ni/Ti_6O_{11}, Ni/Ti_5O_9, and Ni/Ti_4O_7. Since these oxides differ only by changes in the slab thickness and the effective oxidation state of the titanium, smooth changes as a function of stoichiometry are expected. However, large changes in bulk electronic and magnetic properties occur as a function of the Ti:O ratio.[7] While TiO_2 is a large band gap semiconductor, Ti_4O_7 is a metal above 150 K;[9] an insulator-to-metal transition occurs as a function of stoichiometry. While all phases with $n > 4$ show activated conduction and therefore are not metals,[7] the magnetic properties of Ti_8O_{15} and Ti_7O_{13} are quite different from those of Ti_6O_{11} and Ti_5O_9.[10] Both Ti_8O_{15} and Ti_7O_{13} are paramagnetic down to 77 K which suggests that the unpaired spins on the Ti^{3+} sites do not couple strongly to each other. However, in Ti_6O_{11} and Ti_5O_9 the metal-metal separation is smaller and the unpaired spins on the Ti^{3+} sites align antiferromagnetically

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with a Néel temperature near 140 K. As the Ti–Ti distance is decreased and the bulk magnetic properties change abruptly from paramagnetic to antiferromagnetic, the interaction of Ni with the support changes; Ni/Ti_7O_{13} chemisorbs almost twice as much H_2 as Ni/Ti_6O_{11}. This is an interesting example of how bulk electronic properties can effect surface chemistry.

In summary, we have shown that the chemisorption of H_2 at 295 K on Ni dispersed on Ti_nO_{2n-1} decreases as n decreases. Furthermore, the change in H_2 chemisorption is not a smooth function of n but a large drop is observed between Ti_7O_{13} and Ti_6O_{11} where large changes in bulk properties occur. These findings are consistent with the model that Ni reacts with TiO_x to form a metastable Ni–Ti–O composite. We conclude that the energy of activation to form this composite is smaller for more reduced titanium oxides.

Acknowledgment. This research was supported by a Presidential Young Investigator Award from the National Science Foundation (Grant CHE83-51881) and matching funds from E. I. du Pont de Nemours and Co.

Atom-Transfer Cyclization. A Novel Isomerization of Hex-5-ynyl Iodides to (Iodomethylene)cyclopentanes

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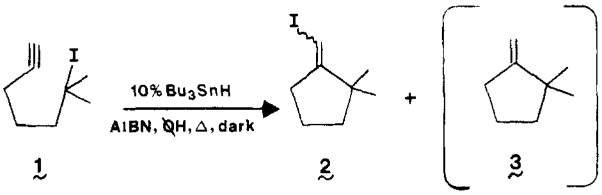
Received November 14, 1985
Revised Manuscript Received February 18, 1986

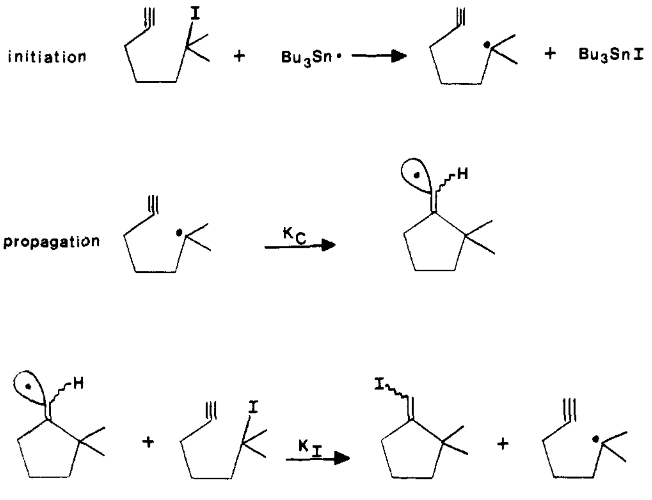
Synthetic sequences based on free radical carbon–carbon bond-forming reactions are generally terminated by a hydrogen atom transfer.[2,3] Clearly, the ability to terminate a sequence of radical reactions with other elements is most desirable.[4] We now report a novel isomerization of hexynyl iodides to iodomethylene cyclopentanes. This reaction occurs via a free radical chain mechanism with near-diffusion-controlled iodine atom transfer from an alkyl iodide to a vinyl radical as the key chain-propagating step. We propose the name "atom-transfer cyclization" for this type of reaction which, in effect, terminates a single or tandem radical cyclization with a synthetically versatile iodine atom.[5,6]

Treatment of 2-iodo-2-methyl-6-heptyne (**1**) with a catalytic amount of tri-*n*-butyltin hydride (10 mol %) and AIBN (5 mol %) in refluxing benzene for 1–2 h induced a smooth isomerization to 2,2-dimethyl-1-(iodomethylene)cyclopentane (**2**). The ratio of **2E**/**2Z** was 15/1 and the combined yield of **2** was 84% as indicated by ^1H NMR integration experiments against an internal standard. A trace amount (2–5%) of the reduced product, 2,2-dimethyl-1-methylenecyclopentane (**3**), was also formed whenever tri-*n*-butyltin hydride was used to initiate this isomerization (eq 1).



(1)

Scheme I



The proposed mechanism for this novel atom-transfer cyclization reaction is outlined in Scheme I. Abstraction of an iodine atom by tri-*n*-butyltin radical initiates the chain. Standard 5-hexynyl radical cyclization[3] is then followed by a rapid iodine atom transfer from a molecule of the starting alkyl iodide to the intermediate vinyl radical. This is the key chain-transfer step. Rapid iodine atom transfer between alkyl radicals and alkyl iodides as illustrated in eq 2 is a well-known process.[5] While a wealth of thermodynamic

$$R\cdot + R'\text{-}I \rightleftarrows RI + R'\cdot \tag{2}$$

and kinetic data is available from such transformations,[5b,c] the reversible nature of this reaction may be undesirable from a synthetic perspective since the product iodides are recycled to the radical pool.[5d]

The intermediacy of the vinyl radical is then central to the above atom-transfer cyclization. It seems likely that the mechanism outlined in Scheme I is under kinetic control. Rapid iodine atom transfer from the alkyl iodide to the vinyl radical is effectively irreversible and the kinetically formed vinyl iodide is *not* recycled to the radical pool due to the increased strength of the vinyl iodide bond relative to an alkyl iodide counterpart.[6,7]

An estimate of the rate constant (k_I) for iodine atom transfer is readily obtained by a simple competition experiment for the vinyl radical. Treatment of **1** with one full equivalent of tri-*n*-butyltin hydride provides mixtures of **2** and **3** with the ratio varying according to reaction time. At low conversion (<20%), vinyl iodide **2** is the major product (3/1), demonstrating that iodine atom transfer from **1** is more rapid than H atom transfer from Bu_3SnH. In fact, k_I approaches the diffusion-controlled limit! An estimate of $k_I \geq 10^9$ mol^{-1} s^{-1} at 80 °C is obtained by using the recent kinetic data of Beckwith and Ingold as a reference for the competitive H atom transfer.[8] Not surprisingly, this rate constant

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[1] Receipient of a Dreyfus Teacher-Scholar Award, 1986–1991. Sloan Foundation Fellow, 1985–1987. Eli Lilly Grantee, 1985–1987. Merck Faculty Development Awardee, 1986.

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