The ketone **11** (entry f) was next examined and in contrast to the corresponding aldehyde **1**, a cyclohexanol was not obtained, the preferred reaction course being that of serial radical cyclization leading to **20** as the principal product. Accordingly, when this preferred pathway was removed by saturation of the double bond to give **11**, no cyclization of any type was observed, the only product being **23**.

In the case of aldehyde **12**, only **24** was detected, there being no evidence of the desired cycloheptanol.

Further studies to determine the full scope of these cyclizations are under way and will be described in due course.

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Absence of the Metal-Support Interaction for Ni/TiO$_2$ Composites Prepared by Ion-Exchange Techniques

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Many recent reports on the surface properties of transition-metal catalysts dispersed on high surface area oxide supports have shown that the support can alter markedly the intrinsic activity of the metal.[1] In particular, when group 8-10 metals are supported on reducible metal oxides, the surface chemistry and the electronic properties of the composite depend on the reduction temperature used for pretreatment. For example, the chemisorption of H_2 at room temperature on metal-TiO$_2$ composites decreases sharply as the reduction temperature used to prepare the catalyst is increased from 573 to 773 K. This change in surface chemistry has been attributed to a strong interaction between the metal and the TiO$_x$ ($x < 2$). By understanding the conditions required to induce this interaction, the acitivity and selectivity of supported metal catalysts can be tailored for specific applications. In this paper, we show that the extent of the interaction can be controlled if the composition at the interface between the nickel and TiO$_2$ is manipulated by varying the method used to disperse the nickel.

In typical preparations of heterogeneous catalysts, group 8-10 metals are dispersed on metal oxides either by incipient wetness or ion-exchange techniques. The initial composition of the interface is quite different in the two cases. If incipient wetness techniques are used, the metal is deposited as a salt; a counterion is codeposited with the metal and the number of hydroxyl groups on the TiO$_2$ surface remains unchanged. By ion-exchange methods, the transition-metal cation is exchanged for H$^+$ from surface hydroxyl groups; no counterion remains behind and surface hydroxyl groups are replaced by metal cations bound directly to surface oxygen. We have prepared samples of nickel dispersed on a low surface area TiO$_2$ (5.1 m^2/g) by both methods and studied their chemisorption properties and magnetism as a function of the pretreatment temperature used to reduce the Ni^{+2} to Ni^0. In agreement with previous studies,[1,2] we find a strong metal-support interaction for the Ni/TiO$_2$ composite prepared by incipient wetness. However, the properties of the sample prepared by ion exchange are strikingly different; the intrinsic activity of the nickel in this sample is not modified by the TiO$_2$. Instead, the properties of this composite are similar to those observed for nickel supported on a more inert support, such as SiO$_2$.

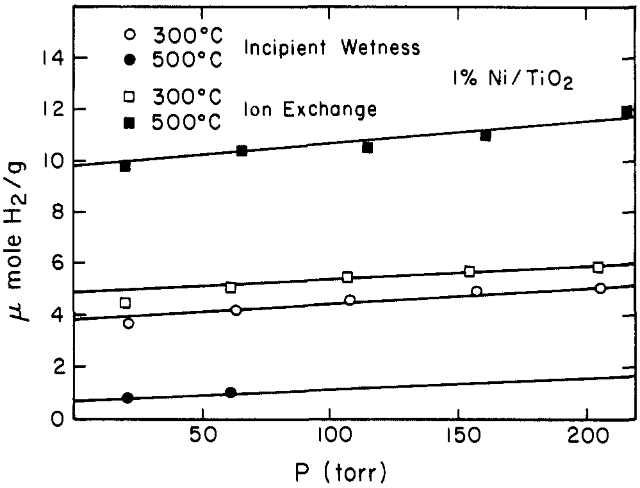

Figure 1. Hydrogen uptake in moles of H per mole of Ni vs. hydrogen pressure for (A) 1.0% Ni/TiO$_2$ prepared by incipient wetness (circles) and (B) 1.0% Ni/TiO$_2$ prepared by ion exchange (squares). Open circles and squares are for samples reduced at 573 K for 4 h. Closed circles and squares indicate samples reduced at 773 K for 4 h.

Two samples of 1.0% Ni/TiO$_2$ were prepared from TiO$_2$ (Cerac, 99.9% pure) which was 10-15% rutile and 85-90% anatase with a surface area of 5.1 m^2/g. Sample A was prepared by incipient wetness techniques using reagent grade Ni(NO$_3$)$_2$·6H$_2$O (99.95% pure) dissolved in distilled, deionized water. Approximately 4 g of TiO$_2$ were slurried with 1 mL of a nickel solution containing the amount of nickel needed to give a 1.0% loading of nickel by weight. After adding 3-4 mL of acetone, the slurry was ground until dry and then further dried for 1 h under vacuum. The unreduced composite consisted of Ni(NO$_3$)$_2$·6H$_2$O deposited on TiO$_2$. To prepare sample B by ion-exchange methods, approximately 4 g of TiO$_2$ was refluxed at 373 K for 20 h in 67 mL of a solution of Ni(NO$_3$)$_2$·6H$_2$O dissolved in an aqueous solution of NH$_4$OH with a pH of 11. The concentration of the nickel solution was adjusted to give a loading of 1.0% nickel by weight. After 20 h the blue solution had turned clear and the pH was 8-9 due to the release of H$^+$ from the TiO$_2$ surface. Although 1.2×10^{-3} mol of protons are released, the pH remains basic due to the buffering of the NH$_3$ solution. The mixture was filtered hot and analyzed for the Ni^{+2} concentration with a Perkin-Elmer Lambda-9 spectrometer with a detection limit for absorbance of 0.001. Since no absorbance due to Ni^{+2} was detected, nearly all the Ni^{+2} ion-exchanged onto the support. The solid was dried at 368 K. Both samples were reduced initially in flowing hydrogen at 573 K for 4 h and then at 773 K for 4 h.

Changes in the surface chemistry of the nickel were monitored by the chemisorption of hydrogen at room temperature. The amount of H$_2$ that chemisorbed on both composites after reduction at 573 K, as shown in Figure 1, was similar; sample A chemisorbed 0.042 mol of H per mol of Ni added to the support and sample B chemisorbed 0.054 mol of H per mol of Ni. After sample A was reduced at 773 K for 4 h, the hydrogen uptake decreased to 0.005 mol of H per mol of Ni. This suppression of hydrogen chemisorption is observed typically for group 8-10 metals supported on TiO$_2$ and is accepted as the signature that there is a strong interaction between the metal and the support.[1] In sharp contrast, the chemisorption on the ion-exchanged sample increased to 0.110 mol of H per mol of Ni after reduction at 773 K for 4 h. This is a value similar to that which we have observed for 1.0% Ni/SiO$_2$. Since no drop in chemisorption is observed for the ion-exchanged sample after reduction at 773 K, we conclude that the reaction of the metal with the support is suppressed.

In order to determine the amount of nickel present as the pure metal,[2] the saturation magnetization M_s was measured at 5 K on

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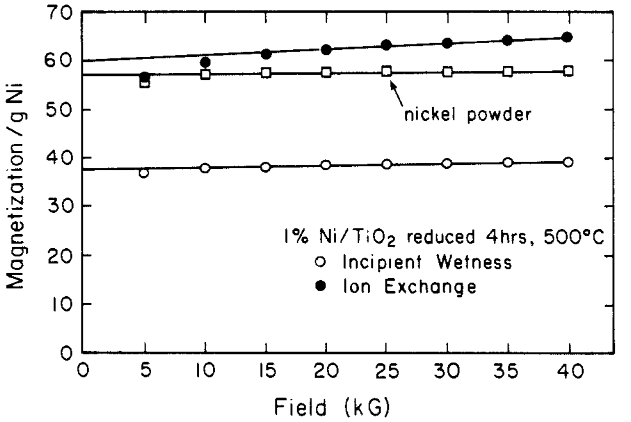

Figure 2. Magnetization per gram of Ni vs. the applied magnetic field measured at 5 K for (A) 1.0% Ni/TiO_2 prepared by incipient wetness (open circles) and (B) 1.0% Ni/TiO_2 prepared by ion exchange (closed circles). Both samples were reduced at 773 K for 4 h. The magnetization of a sample of pure nickel powder is included for comparison.

a SHE SQUID magnetometer. Figure 2 shows the magnetization per gram of Ni for samples A and B reduced at 773 K for 4 h. Data for a sample of nickel powder (Puratronic, 99.999% pure, 100 mesh) are shown for comparison. Extrapolation of the data for fields greater than 25 kG to zero gives the saturation magnetization M_s(A) = 37 per g of Ni for sample A and M_s(B) = 60 per g of Ni for sample B. If all the nickel were present as pure nickel metal, a value of 57.5 per g of Ni is expected, as observed for the sample of nickel powder. The small value of M_s observed for sample A indicates that 36% of the nickel has reacted with the TiO_2 support. In contrast, the sample prepared by ion exchange showed no strong interaction between the nickel and the TiO_2; no loss of ferromagnetic nickel was detected. Since one difference between the two samples is that the composite prepared by ion exchange has less hydroxyl groups on the TiO_2 surface, it is proposed that the surface hydroxyl groups are important in the initial steps in the reaction between nickel and TiO_2. Another possibility which cannot be excluded is that the nitrate groups in the incipient wetness sample produce a reactive intermediate which is not formed in the sample prepared by ion exchange.

The hydrogen chemisorption and magnetism results show that the method used to prepare Ni/TiO_2 composites can be used to manipulate the extent to which the two materials react. We feel that the key difference between the two samples studied here is the number of hydroxyl groups present on the TiO_2 surface. The TiO_2 surface in sample B, prepared by ion-exchange, has very few hydroxyl groups compared with sample A prepared by incipient wetness. In fact, for a 1.0% by weight loading of nickel ion exchanged onto the low surface area TiO_2 used in this study, the entire surface of the TiO_2 is coated with Ni^{+2} and no surface hydroxyl groups should remain. Various studies have shown that at elevated temperatures hydroxyl groups are removed from the surface of the TiO_2 as water, thereby generating Ti^{4+} ions which are coordinatively unsaturated.[4] These unsaturated Ti^{4+} sites are reduced by hydrogen spillover[5] from the metal to form reduced TiO_x ($x < 2$) moieties[6] which diffuse onto and into the metal particles.[7] This reaction of TiO_x with the nickel particles is thought to cause the change in surface chemistry observed for the Ni/TiO_2 composite prepared by incipient wetness. We propose that for the ion-exchanged sample, the reduction of TiO_2 is kinetically slow because the initial concentration of surface hydroxyl groups is too low; for this sample, a strong interaction between the metal and the support is not induced after reduction at 773 K for 4 h.

In summary, we have shown that it is possible to turn off the interaction between nickel and TiO_2 (Cerac, 5.1 m^2/g) if ion-exchange methods are used to disperse the metal onto a low surface area TiO_2 support. For the sample prepared by ion exchange, the chemisorption of hydrogen is not suppressed and the saturation magnetization indicates that the nickel is present as the pure metal. We conclude that the removal of surface hydroxyl groups is important for the facile reduction of the TiO_2 surface at 773 K; if the number of surface hydroxyl groups is too low, the metal–support interaction is suppressed. Since the number of hydroxyl groups initially present on the surface depends also on the preparation and thermal history of the TiO_2, we postulate that the chemistry of metal–TiO_2 composites can be manipulated by controlling the surface properties of the TiO_2 used as the support.

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Total Synthesis of (+)-Aplasmomycin[1]

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Aplasmomycin (**1**)[2] and its congeners **2** and **3**[3] are metabolites of *Streptomyces griseus*[4] that, along with the closely related boromycin (**4**),[5] represent a unique family of ionophoric antibiotics. The elaborate architecture of these natural cryptands, as revealed by X-ray crystallographic studies,[6,7] is centered around a borate core that serves as the anionic companion of the transported alkali-metal cation. Complete elucidation of the stereochemical features of **1** and **4**, including their conformation with and without the borate nucleus,[8] has enabled rational synthetic routes to be designed which have already resulted in syntheses of **1**,[9] the

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