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# Mechanism of Strong Metal–Support Interaction in Ni/$TiO_2$

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Catalytic CO hydrogenation reactions were performed on several differently prepared Ni/$TiO_2$(100) and $TiO_x$/Ni(111) model catalysts at 190°C, $P_{H_2}$ = 60 Torr and $P_{CO}$ = 20 Torr. It was found that hydrogen reduction at 500°C before or after Ni deposition on $TiO_2$(100) always results in an enhanced steady-state methanation activity, accompanied by a lower surface carbon level. The ethylene/methane ratio, however, is independent of such treatments and is always about twice that from Ni(111). XPS studies showed that Ni/$TiO_2$ catalysts prepared by different methods have similar surface $Ti^{3+}$ concentration. The $TiO_x$/Ni(111) catalyst has a methanation activity and ethylene/methane ratio similar to Ni/$TiO_2$(100) at an optimum titanium coverage of 8% of a monolayer. Based on these results, we propose one model for strong metal–support interaction in which the presence of titania on the metal surface induced by high-temperature treatment and the possible incorporation of surface or subsurface hydrogen act synergistically to modify and maintain the activity of titania-supported catalysts.

## 1. INTRODUCTION

The anomalous reduction in carbon monoxide and hydrogen sorption capacity of titania-supported group VIII metals prepared by hydrogen reduction at 500°C reported by Tauster *et al.* (*1*) has stimulated much interest in the study of these catalyst systems. It was believed that a strong metal-support interaction (SMSI) is induced by the formation of metal-titanium bonds made possible by oxygen vacancies in titania, thus altering the chemisorption behavior of the catalyst. Horsley's cluster calculation suggested that in the case of Pt on reduced $TiO_2$, a platinum-titanium bond is formed and has a strong ionic component with a charge of −0.6 e on platinum (*2*). Photoemission and energy loss measurements by Chung and co-workers on a number of metal-titania systems confirmed this electron transfer behavior (*3–6*). Recent XPS studies of dispersed Rh/$TiO_2$ catalysts by Haller *et al.* (*7*) and Sexton *et al.* (*8*) showed the same electron transfer direction for catalysts in the SMSI state, i.e., from titania to the metal. The XPS investigation of Huizinga and Prins (*9*) on Pt/$TiO_2$, however, showed no chemical shift of Pt in the SMSI state as compared with Pt/$Al_2O_3$.

Recent studies by Wang *et al.* (*10*) showed that when Pt/$TiO_2$ (SMSI) is prepared by hydrogen reduction at 500°C, large amounts of hydrogen are stored and strongly bound by the catalyst and can only be removed by extended heating at 500°C or above. It was found that there is a correlation between the hydrogen sorption capacity and the amount of hydrogen stored in the catalyst, viz., as the amount of hydrogen stored in the catalyst during the reduction treatment increases (as determined gravimetrically), the amount of hydrogen adsorbed decreases (*10*). The significance of strongly bound hydrogen (even in unsupported catalysts) in heterogeneous catalysis has been emphasized by Menon and co-workers (*11, 12*).

In an earlier publication (*6*), we demonstrated that Ni/$TiO_2$ (SMSI) can be modeled by depositing controlled amounts of Ni on single crystal $TiO_2$(100) reduced by heating

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at 450°C in ultrahigh vacuum (UHV). Using CO hydrogenation as the probe reaction, we obtained initial methanation activity and product distribution data which, when extrapolated, are comparable to those obtained from dispersed catalysts by Vannice and Garten (*13, 14*) and Bartholomew *et al.* (*15*). The important difference is that no deliberate hydrogen reduction was employed in our preparation process for Ni/$TiO_2$(100). It is not clear what the role of hydrogen is in SMSI.

If the formation of metal–titanium bonds is crucial in SMSI, it may be interesting to study this by using a different model system, viz., putting $TiO_x$ ($x < 2$) on Ni(111). By studying the influence of titania on the catalytic activity of Ni as a function of Ti coverage, the role of titania may be revealed.

In this paper, we compare the surface composition and catalytic behavior of Ni/$TiO_2$(100) prepared by different methods. In addition, we investigate the CO hyrogenation activity of Ni(111) with controlled amounts of titania. Based on these results, we propose a possible operating mechanism for SMSI.

## 2. EXPERIMENTAL SECTION

All experiments were performed in a UHV surface analysis–high pressure chamber as described previously (*6*). Metal (Ni and Ti) deposition was done in the UHV part of the chamber by a tungsten evaporator. The amount deposited was estimated from the attenuation of Auger peaks, assuming that the mean free paths for Ni (61 eV), Ti (380 eV), and 0 (510 eV) Auger electrons are 5, 8, and 10 Å, respectively, and that the metal atoms are laid down uniformly. Given these assumptions, we cannot claim absolute accuracy better than 20% for the metal coverage. But the relative accuracy involving comparison of Auger peak ratios should be good (~ a few percent).

Both Ni(111) and $TiO_2$(100) single crystals were prepared by standard metallographic techniques. The backside of each crystal was masked by a sulfided tantalum foil. The active surface area for Ni(111) was 0.66 $cm^2$ while that for Ni/$TiO_2$(100) was defined by an evaporation mask to 0.38 $cm^2$. Surface cleanliness was monitored by Auger electron spectroscopy.

Catalytic CO hydrogenation reactions were performed by first transferring *in vacuo* the prepared model catalyst from the UHV chamber to an attached isolation cell. Once isolated, the cell could be pressurized with the appropriate reactants (99.9995% purity $H_2$ and 99.99% purity CO further purified by a carbonyl trap). Gas products were monitored by a standard FID gas chromatograph equipped with a peak integrator. At the conclusion of the experiment, the cell was evacuated and the specimen transferred back to the UHV chamber for subsequent surface analysis or treatment.

## 3. RESULTS

### *3.1. Effects of Surface Treatment on CO Hydrogenation Activity of Ni/$TiO_2$(100)*

The CO–$H_2$ reaction was performed at a total pressure of 80 Torr with a $H_2$/CO ratio of 3 at a temperature of 190°C. The methane production rate was always high initially and levelled to a steady-state value about 50–60% of the initial rate after a reaction time of 8 to 10 min. Four specimens were compared: (1) a sputtered annealed $TiO_2$(100) with 8 Å Ni deposited (specimen SAD); (2) a sputtered annealed $TiO_2$(100), then oxidized in $5.0 \times 10^{-5}$ Torr oxygen at 450°C for 10 min and followed by deposition of 8 Å Ni (specimen SAOD); (3) sputtered annealed $TiO_2$(100), then reduced in 5 Torr $H_2$ at 500°C for 1 h followed by 8 Å Ni deposition (specimen SARD); and (4) sputtered annealed $TiO_2$(100) with 35 Å Ni followed by hydrogen reduction (specimen SADR) resulting in a final thickness of 8 Å. Part of Ni was lost presumably by dissolution into $TiO_2$ during the hydrogen treatment at 500°C.

TABLE 1

| Ni/TiO$_2$(100) preparation[a] Final $\theta_{Ni}$ = 8 Å | Steady-state methane TOF ($10^{-3}$ s$^{-1}$)[b] | C$_2$H$_4$/CH$_4$ (%) |
|---|---|---|
| SAOD | 1.22 ± 0.12 | 25 ± 3 |
| SAD | 1.50 ± 0.12 | 23 ± 3 |
| SARD | 1.67 ± 0.12 | 24 ± 3 |
| SADR | 2.1 ± 0.12 | 26 ± 3 |

[a] S, argon ion sputtering at 2 kV, 5 to 10 $\mu$A for 10 min; A, annealing in UHV at 500°C for 30 min; D, Ni deposition; O, oxidation in $5.0 \times 10^{-5}$ Torr oxygen at 450°C for 10 min; R, reduction in 5 Torr hydrogen at 500°C for 1 h.

[b] Temperature = 190°C, $P_{H_2}$ = 60 Torr, $P_{CO}$ = 20 Torr. The number of active Ni surface atoms is assumed to be $1.86 \times 10^{15}$/cm$^2$ × masked area of TiO$_2$ (0.38 cm$^2$) = $7.1 \times 10^{14}$.

As seen from Table 1, the methanation activity depends on the surface treatment before or after the Ni deposition, but the ethylene/methane ratio appears to be unchanged. As a comparison, clean ordered Ni(111) prepared by an oxidation–reduction cycle gives a methane turnover frequency of ~(5.0 ± 0.4) × $10^{-4}$ s$^{-1}$ and an ethylene/methane ratio of 13 ± 2%. The C (272 eV)/Ti (380 eV) Auger ratio measured after the reaction and flashing to 300°C to remove adsorbed CO and water vapor appears to bear an inverse relationship to the steady-state methanation activity (Fig. 1). This is in agreement with the dependence found by Kelley and Goodman (*16*) in their methanation studies on Ni single crystal surfaces.

### *3.2. XPS Studies*

Table 2 shows the full-width at half-maximum (FWHM) of the Ti $2p_{3/2}$ peak for differently prepared TiO$_2$ specimens. The Ti $2p_{3/2}$ peak is narrowest after a mild oxidation treatment of TiO$_2$(100) (FWHM = 1.65 eV). Other treatments always give rise to a broader peak due to a shoulder on the small binding energy side. Since it is generally agreed that this shoulder is due to the presence of Ti$^{3+}$ species, the FWHM of the Ti $2p_{3/2}$ can be taken as a measure of the amount of surface Ti$^{3+}$. Data in Table 2 show that when one starts with a TiO$_2$ surface having large amounts of Ti$^{3+}$, Ni deposition decreases the surface concentration of Ti$^{3+}$ consistent with our earlier results (*5, 6*). But when one starts with a TiO$_2$ surface with virtually no Ti$^{3+}$, Ni deposition appears to generate surface Ti$^{3+}$. It is im-

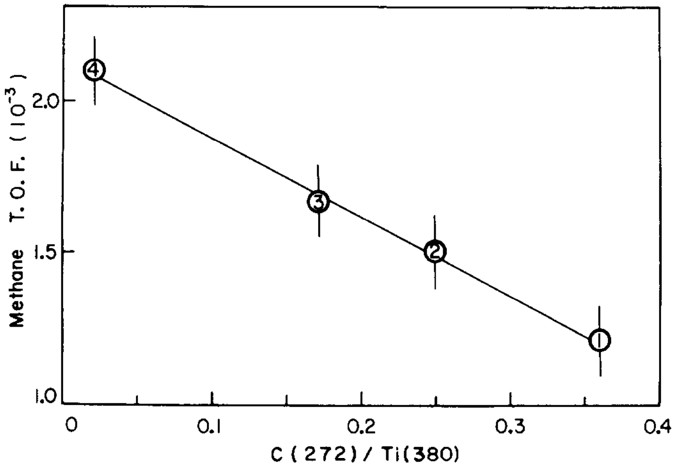

FIG. 1. Plot of the steady-state methane turnover frequency versus the C (272 eV)/Ti (380 eV) Auger peak ratio for several differently prepared Ni/TiO$_2$(100) catalysts. The methanation reaction was performed at 190°C, $P_{H_2}$ = 60 Torr and $P_{CO}$ = 20 Torr. The specimens are (1) SAOD, (2) SAD, (3) SARD, and (4) SADR.

TABLE 2

| Specimen[a] | Ti $2p_{3/2}$ FWHM in eV($\pm$0.05) |
|---|---|
| SAO | 1.65 |
| SAOD | 1.92 |
| SAR | 1.95 |
| SARD | 1.88 |

[a] Symbols explained in footnote of Table 1. $\theta_{Ni}$ = 8 Å in all depositions.

portant to note that the change in peak width is not due to charging. Charging is expected to be more severe in oxidized titania. This is contrary to our observations.

### 3.3. $TiO_x$/Ni(111)

Controlled amounts of titanium metal were first deposited on a sputter-cleaned annealed Ni(111) surface using a tungsten evaporator. The specimen was then oxidized at 450°C in $1 \times 10^{-5}$ Torr oxygen for 100 s, followed by reduction at 450°C in $2 \times 10^{-5}$ Torr hydrogen for 100 s. Inspection of Ti LVV Auger peaks and Ni 2*p* peaks of the resulting specimen showed that after these treatments, the nickel became metallic while titanium was oxidized to $TiO_x$ where $x \sim 1.0$–$1.5$, as estimated from the Auger O/Ti ratio. Catalytic CO hydrogenation reactions were performed on the specimen as a function of Ti coverage at 190°C, 60 Torr hydrogen and 20 Torr CO. The result is summarized in Fig. 2. The steady-state methane turnover frequency achieves a maximum ($1.75 \times 10^{-3}$/s) at a Ti coverage of $1.5 \times 10^{14}/cm^2$. This activity is comparable to that of Ni/$TiO_2$ (specimen SARD and SADR). Furthermore, at the optimum Ti coverage, the ethylene/methane ratio is 22% which is again similar to that of Ni/$TiO_2$. Assuming uniform dispersal of titanium, there is 1 titanium atom per 12 nickel surface atoms at this coverage.

## 4. DISCUSSION

Data in Table 1 indicate that hydrogen reduction before or after nickel deposition results in a marked increase in methanation activity but does not affect the ethylene/methane ratio. Hydrogen reduction leads to generation of oxygen vacancies and $Ti^{3+}$ as well as hydrogen incorporation. XPS data in Table 2 show that Ni deposition alone generates surface $Ti^{3+}$. In fact, the FWHM of the Ti $2p_{3/2}$ peak is about the same for specimen SAOD and SARD, suggesting similar concentration of $Ti^{3+}$. One possible mechanism is that when nickel atoms condense on the $TiO_2$ surface, heat of conden-

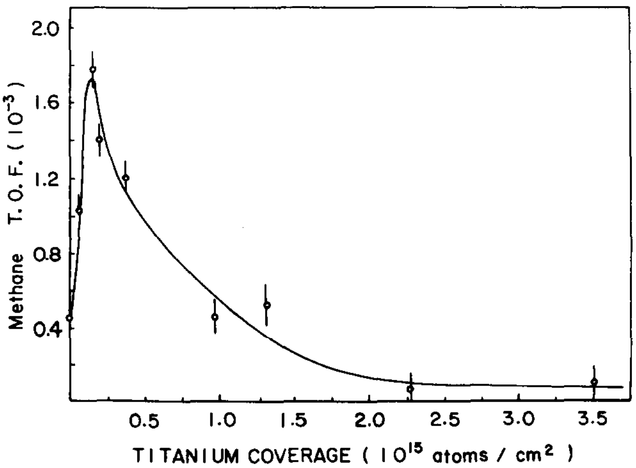

FIG. 2. Plot of the steady-state methane turnover frequency versus the titanium coverage for $TiO_x$/Ni(111). The methanation reaction was performed at 190°C, $P_{H_2}$ = 60 Torr, and $P_{CO}$ = 20 Torr.

sation is released (about 4 eV for Ni on Ni). This may provide enough driving force for displacing surface oxygen, thus generating surface oxygen vacancies and $Ti^{3+}$ species. This mechanism has been proposed to explain electronic properties of metal-compound semiconductor interfaces (*17*). The final surface $Ti^{3+}$ concentration depends on the initial surface $Ti^{3+}$ concentration, the ease with which surface oxygen can be displaced and the removal of surface $Ti^{3+}$ by electron transfer to Ni.

In spite of the similarity in surface $Ti^{3+}$ concentration on specimen SAOD and SARD, the latter shows a steady-state methanation activity appreciably higher than the former. What then is the role of hydrogen? There are several clues. First, the ordering in the steady-state methane TOF is the same as the amount of surface hydrogen expected from the treatment of these catalysts (highest for specimen SADR, lowest for SAOD). Second, the steady-state C (272 eV)/Ti (380 eV) Auger peak ratio varies inversely with the methane TOF. Third, the ethylene/methane ratio is practically the same for all Ni/$TiO_2$ catalysts. It appears that certain surface sites are inert toward methanation, the concentration of which can be decreased by hydrogen treatment. The detailed mechanism is not known. Menon and co-workers (*11, 12*) suggested that strongly bound hydrogen may be incorporated during reduction at 500°C thus changing catalytic behavior.

The oxide support may or may not be relevant in this context. Indeed, we found significant difference in CO chemisorption and hydrogenation activity of Ni(111), depending on whether or not the Ni(111) surface is treated with hydrogen at elevated temperatures (*18*).

It has been proposed by Burch and Flambard (*19*) that the active sites responsible for SMSI in a titania-supported catalyst are located at the periphery of Ni islands. We have performed computer simulations in related studies (*20*), showing that in this case, the number of these peripheral sites acquires a maximum at a metal coverage of ~0.6 monolayer if the metal atoms are randomly dispersed. The reverse problem of putting titania on nickel is identical. Therefore, according to the proposed model of Burch and Flambard (*19*), the methane TOF should be a maximum at an overlayer coverage of ~0.6 monolayer (i.e., 0.6 monolayer Ni on $TiO_2$ or 0.6 monolayer $TiO_2$ on Ni). Increased tendency to clustering will give an optimum coverage larger than 0.6 monolayer. Our earlier work on Ni/$TiO_2$(100) showed that the optimum Ni coverage occurs at about 3 monolayers (*6*). Results in Fig. 2 for $TiO_x$/Ni(111) show that the optimum Ti coverage is much less than 0.6 monolayer. From these observations, we conclude that periphery sites, though unique in their geometric location, cannot be solely responsible for SMSI.

There are remarkable similarities between Ni/$TiO_2$(100) and $TiO_x$/Ni(111) at their respective optimum overlayer coverages in terms of methanation activity and ethylene/methane ratio in the CO hydrogenation reaction. For Ni/$TiO_2$(100) at the optimum Ni coverage, the average distance between the surface Ni atoms and the closest Ti is 5 to 6 Å (*6*). For $TiO_x$/Ni, the optimum Ti coverage occurs at 8% of a monolayer. At this coverage, the average distance between the surface Ni atoms and the closest Ti is ~3.5 Å, assuming random dispersal of titanium. Any tendency for Ti to cluster will increase this number. For example, if Ti pairs are formed uniformly on the surface, this average distance will increase to ~5.5 Å. Thus surface Ti appears to have a certain optimum sphere of influence imparting a promoter effect on the CO hydrogenation activity of Ni. The important point is that SMSI is short-ranged (~ a few Ångstroms). Electron microscopy studies by Baker *et al.* (*21*) concluded that for Pt/$TiO_2$ (SMSI), Pt forms "thin" pillboxes. If "thin" means several atom layers thick, then it will be similar to our Ni/$TiO_2$(100) model system (*6*). But there are microscopy studies (*22*) indicating that they can be as thick as 50 Å. In the latter case, it is unlikely for the underlying support to affect the activity of metal atoms 50 Å away since the effect of Ti is short-ranged. But annealing studies by Kao *et al.* (*5*) showed that extensive interdiffusion takes place between nickel and titania at 300°C or above. This, together with the observation that Ni/$TiO_2$ and $TiO_x$/Ni are so similar in their catalytic behavior, suggests *that during hydrogen reduction at 500°C to induce SMSI, titania diffuses to the metal surface and affects its chemical properties.* Similar conclusions have been arrived at by Dumesic (*23*) and Haller (*24*) for their work on high surface area catalysts of Fe/$TiO_2$ and Rh/$TiO_2$, respectively.

Based on these and other observations, a tentative picture of SMSI in titania-supported catalysts emerges. Hydrogen reduction at 500°C causes small amounts of (reduced) titanium oxide to diffuse to the metal surface. Dispersal of the oxide on the metal surface and the formation of metal–titanium bonds modify the chemisorption and catalytic properties of the surface. The metal–titanium bond formation results in small chemical shifts observed in X-ray photoemission (*4–8*). Hydrogen reduction results in the formation of a high surface energy titanium oxide ($Ti_4O_7$) which allows the metal to wet the support and maintain its dispersion under reaction conditions (*21*). Hydrogen treatment also appears to minimize carbon accumulation. The latter two effects give rise to stable activity.

The reversible nature of the phenomenon can also be explained by the present model. Oxidation gives nickel oxide and titania. Subsequent low-temperature reduction may redisperse Ni and titania into separate clusters (*23*) and result in normal catalytic behavior. Given the low initial concentration of surface titania on Ni, any site-blocking effects may not be observable. Further high-temperature reduction gives titania sufficient mobility to diffuse to the nickel surface again, resulting in anomalous chemisorption and catalytic behavior characteristic of SMSI.

## ACKNOWLEDGMENTS

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