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Activation behavior of Ni/hydrous titanium oxide (HTO) catalysts

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The activation of Ni-TiO_2 catalysts prepared via both impregnation on commercial TiO_2 and by ion exchange on hydrous titanium oxide (HTO) supports was investigated. The reactivity of these catalysts for a structure-sensitive reaction (*n*-butane hydrogenolysis) was investigated as a function of different activation treatments (temperature, time) in a H_2 atmosphere. Complete activation of the ion exchanged Ni/HTO catalyst in H_2 required temperatures > 623 K and times > 18 h. Low temperature (573 K) activation of the ion exchanged Ni/HTO catalyst in H_2 was not possible without performing a mild (573 K) reduction/oxidation/reduction cycle. Observations of the ion exchanged Ni/HTO catalyst microstructures by transmission electron microscopy revealed that inactive samples contained a distinct film which covered Ni particle surfaces. The exact nature of this film has not yet been determined; experimental evidence is consistent with the film being composed of either carbonaceous residue or TiO_x which has migrated to the Ni particle surfaces from the bulk support phase.

Keywords: Catalyst activation; ion exchange; Ni; hydrous titanium oxide; *n*-butane hydrogenolysis

1. Introduction

Ion-exchangeable hydrous metal oxides have generated considerable interest as catalyst support materials [1]. Under certain conditions, high loadings of uniformly dispersed metals can be obtained, resulting in significant improvements in catalytic activity for such reactions as pyrene hydrogenation [1,2]. However, it has recently been shown that Ni/hydrous titanium oxide (HTO) catalysts prepared by ion exchange were not significantly different from conventionally prepared Ni/TiO_2 catalysts in terms of catalytic activity for both structure-sensitive (*n*-butane hydrogenolysis) and structure-insensitive (benzene hydrogenation) reactions [3]. This was due to the formation of large Ni particles when the Ni/HTO catalysts were activated by heating in H_2 at 673 K. The activation of HTO catalyst materials is considerably complex, involving many separate and potentially competing processes such as metal reduction, loss of surface area, loss of volatiles, and metal/support structural evolution. We felt that the proper activation of these Ni/HTO materials might result in the retention of the high dispersion characteristic of the as-prepared catalyst. Therefore, in this paper we present a careful study of the activation of ion exchanged Ni/HTO catalyst materials and a comparison with conventionally prepared Ni/TiO_2 catalysts.

2. Experimental

Two Ni catalysts, each containing nominally 5 wt% Ni, were evaluated in this study. Ion exchanged Ni/HTO catalysts were prepared utilizing a preparation procedure described in detail elsewhere [1,4]. Briefly, hydrous sodium titanate with the approximate stoichiometry $NaTi_2O_5H$ was synthesized by hydrolyzing a mixture of tetraisopropyl titanate, sodium hydroxide, and methanol with an acetone/water solution. Controlled ion exchange of Ni^{2+} for Na^+ was achieved by first preparing a slightly acidic (pH = 6) $NaTi_2O_5H/H_2O$ slurry, resulting in the exchange of a significant portion of Na^+ with H^+. Subsequently, a pH-adjusted (pH = 5.6) 0.5 M $Ni(NO_3)_2$ solution was added to affect Ni^{2+} ion exchange with H^+ or Na^+. The chemistry involved in the ion exchange process and its optimization have been reported elsewhere [4,5]. In short, the solution chemistry conditions (i.e. pH) were chosen to maximize the cation exchange capacity of the HTO support while avoiding precipitation of $Ni(OH)_2$, which occurs at pH values > 7 [6]. After washing and filtering, the catalyst was dried at room temperature under vacuum for a minimum of 16 h. The second catalyst was prepared using conventional wet impregnation, utilizing $Ni(NO_3)_2 \cdot 6H_2O$ and TiO_2 (Degussa, P25 grade) as raw materials.

For reactivity measurements, all catalyst samples were activated in flowing H_2 at temperatures ranging from 573 to 673 K and times ranging from 2 to 100 h. The model reaction used to determine the reactivity of the catalyst materials was *n*-butane hydrogenolysis, a known structure-sensitive reaction. A flow reactor system composed of a 0.635 cm o.d. quartz U-tube packed with quartz wool supporting nominally 0.050 g of raw (as-prepared) catalyst was used. Hydrogen and *n*-butane flow rates to the reactor were 20.0 and 1.0 standard cubic centimeters per minute (sccm), respectively, and were selected to prevent catalyst deactivation. Product gas analysis was determined by on-line gas chromatography with a flame ionization detector. Reaction temperatures investigated ranged from 503 to 583 K, depending on the particular catalyst and its state of activation. Reactivity data were supplemented with static H_2 chemisorption measurements performed at room temperature (after evacuation to 10^{-5} Pa) using a glass volumetric apparatus and a standardized procedure [7]. Prior to these chemisorption measurements, catalyst activation treatments were performed in a static atmosphere (nominal pressure $\approx$ 27–40 kPa H_2).

The final catalyst samples were analyzed after heat treatment and reactivity measurements by both X-ray diffraction and transmission electron microscopy (TEM). Samples of both raw (as-prepared) catalysts were also analyzed by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) in both oxidizing (air) and reducing (5% H_2 in Ar) atmospheres.

3. Results and discussion

Figs. 1 and 2 contrast the activation behavior of the conventionally prepared Ni/TiO_2 and the ion exchanged Ni/HTO catalysts, respectively. For simplicity, these two catalysts will be hereafter referred to as Ni/TiO_2 and Ni/HTO, respectively. For the Ni/TiO_2 catalyst (see fig. 1), reactivity was independent of activation time suggesting that the reduction of $Ni(NO_3)_2$ to metallic Ni occurs very rapidly at 573 K and is essentially complete within the first hour. Factors

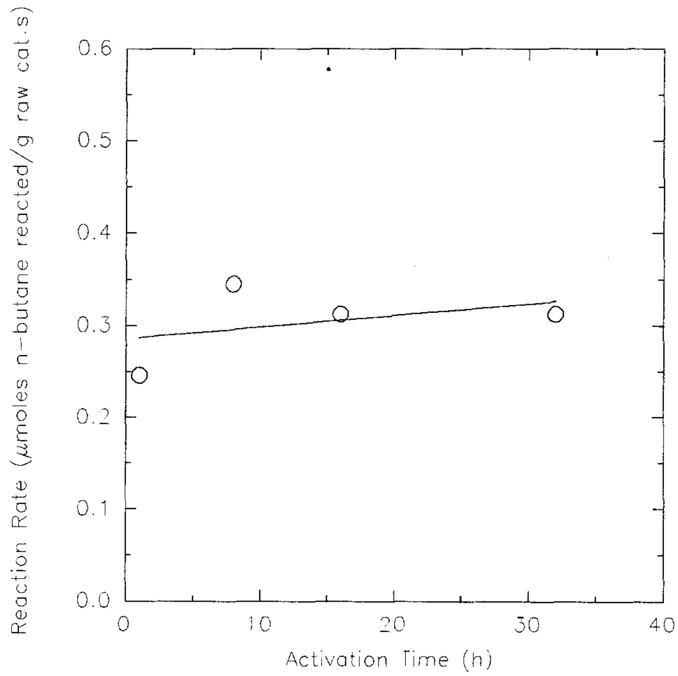

Fig. 1. Reaction rate as a function of activation time for the Ni/TiO_2 catalyst heat treated at 573 K in H_2. All reaction rates were measured for the model reaction (n-butane hydrogenolysis) at a reaction temperature of 523 K.

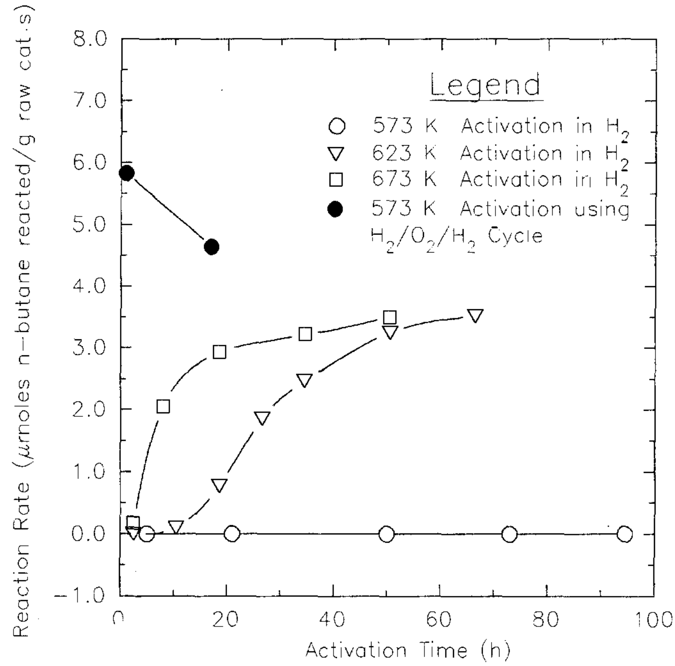

Fig. 2. Reaction rate as a function of activation time for the Ni/HTO catalyst heat treated at various temperatures in H_2. All reaction rates were measured for the model reaction (*n*-butane hydrogenolysis) at a reaction temperature of 573 K.

which contribute to the facile nature of this process are the ease of decomposition of the $Ni(NO_3)_2$ salt in a H_2 atmosphere and the fact that the support (Degussa P25 TiO_2) is stable with respect to its surface area (≈ 50 m^2/g) and crystallinity (anatase/rutile mixture) [8]. Previous work has shown that the reactivity of these catalysts is unaffected by exposure to oxidation (773 K) and reduction (673 K) cycling [3].

The activation behavior of the Ni/HTO catalyst (see fig. 2) was significantly different from the Ni/TiO_2 catalyst. In contrast to the Ni/TiO_2 catalyst, heat treatment of the Ni/HTO catalyst at low temperature (573 K) for times up to 100 h yielded catalysts with negligible hydrogenolysis reactivity (at 573 K). At higher activation temperatures ($\geqslant 623$ K), catalyst reactivity increased with activation time in the 2–40 h range. Both of these observations indicate a relatively complex activation process for this material. Fig. 2 also shows the change in reactivity of the previously inactive Ni/HTO catalyst (573 K activation in H_2) upon exposure to a mild oxidation/reduction cycle at 573 K. As a result of the oxidation/reduction cycle, the catalyst reactivity changed from essentially negligible to the highest activity measured for the Ni/HTO catalyst.

The chemisorptive uptake of H_2 was also monitored as a function of activation time and temperature. As shown in table 1, there was some improvement in

Table 1
H_2 chemisorption results

Catalyst	Activation treatment temperature/atmosphere/time	H_2 uptake (μmol H_2/g raw cat.)
Ni/TiO_2	573 K/H_2/16 h	31.4
Ni/HTO	573 K/H_2/5 h	3.7
	573 K/H_2/50 h	5.1
	573 K/(H_2/O_2/H_2)/1 h [a]	7.0
	623 K/H_2/2.5 h	5.5
	623 K/H_2/66 h	8.2

[a] This exact activation treatment was as follows: 573 K/H_2/50 h+573 K/9.1% O_2 in He/2 h+573 K/H_2/1 h.

H_2 uptake for the Ni/HTO catalyst with both increasing activation temperature and time. However, these changes are insignificant compared to the large changes in reaction rate observed for the Ni/HTO catalyst in fig. 2. The H_2 uptake results for the Ni/TiO_2 catalyst were independent of activation time at 573 K. From the overall results shown in table 1, we can infer that a plot of turnover frequency versus activation time for either catalyst would be very similar in nature to figs. 1 and 2, respectively. The low H_2 uptake values for the Ni/HTO catalyst relative to the Ni/TiO_2 catalyst are consistent with previous work [3,5,9]. Although this trend has not been fully characterized, it is believed that Ni particle encapsulation by the TiO_2 support matrix during catalyst activation is responsible for these low H_2 uptake values and the low Ni dispersions observed for these samples [3,5,9]. Oxygen and hydrogen titration data from previous work has shown that only ≈ 1/3 of the total Ni in the Ni/HTO catalyst is reducible during activation, indicating that a large portion of the total Ni present in the as-prepared Ni/HTO catalyst is encapsulated during the activation treatment [3].

Turnover frequency values calculated for the most active catalyst samples shown in figs. 1 and 2 revealed that for reaction temperatures ranging from 513 to 543 K the reactivities of the Ni/TiO_2 and the Ni/HTO catalysts were very similar. Arrhenius plots for the most active Ni/HTO and Ni/TiO_2 catalysts are shown in fig. 3. Activation energy values were calculated to be ≈ 50 kcal/mol for all catalysts which were completely activated, and these values are consistent with previous work [3,5]. Slightly higher activation energy values (up to 70 kcal/mol) were observed for Ni/HTO catalyst samples in transition from an inactive to a highly reactive state.

Microstructural evaluation via transmission electron microscopy (TEM) provided insight into the activation behavior of the Ni/HTO catalyst. Fig. 4 shows a transmission electron micrograph of the as-prepared Ni/HTO catalyst. The microstructure of this sample is featureless, indicating an amorphous support

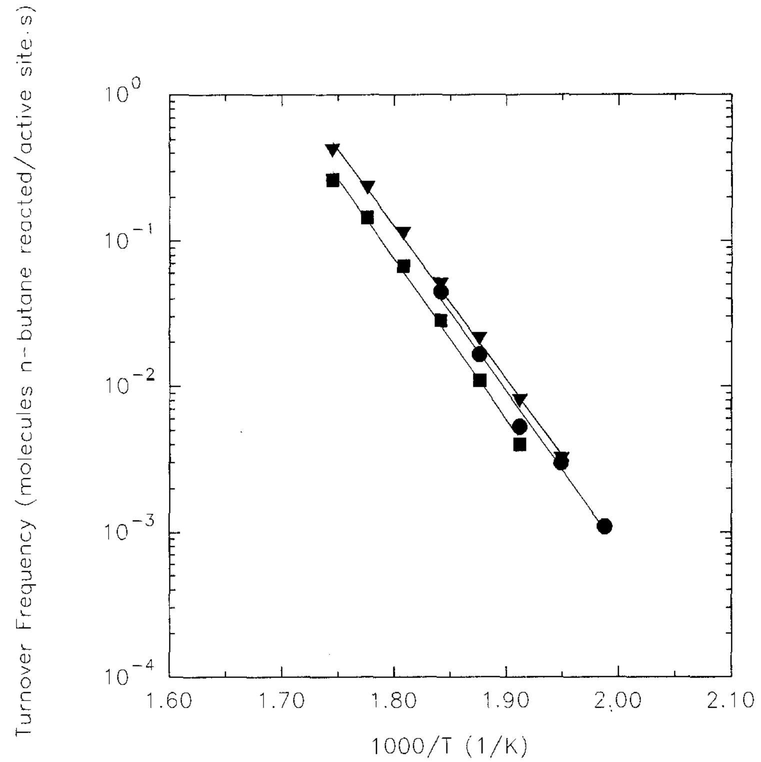

Fig. 3. Arrhenius plots for the most active Ni/HTO and Ni/TiO$_2$ catalysts using *n*-butane hydrogenolysis as a model reaction. (●) Ni/TiO$_2$ catalyst activated in H$_2$ at 573 k/8 h; (■) Ni/HTO catalyst activated in H$_2$ at 623 K/66.5 h; (▼) Ni/HTO catalyst activated at 573 K using H$_2$/O$_2$/H$_2$ cycle.

phase and no distinct Ni particles. Energy dispersive X-ray analysis showed that the as-prepared Ni/HTO catalyst possessed a homogeneous distribution of Ni. This supports the fact that the as-prepared Ni/HTO catalyst contains a uniform dispersion of Ni^{2+} ions.

The effects of heat treating the Ni/HTO catalyst at various conditions are shown in figs. 5 and 6, which show transmission electron micrographs of inactive and active samples, respectively. The inactive sample was heat treated at 573 K in H$_2$ for 30 h and exhibited negligible hydrogenolysis activity. The active sample was produced by heat treating the Ni/HTO catalyst at 673 K in H$_2$ for 33 h. The data shown in fig. 2 illustrate the reactivity of this particular sample. There are a number of features worth noting regarding the catalyst microstructures. First, although the as-prepared Ni/HTO catalyst possesses a uniform dispersion of Ni^{2+} ions (see fig. 4), the relatively high temperatures (> 573 K) required to produce an active Ni catalyst result in the production of large (10–20 nm) Ni particles. It is apparent from figs. 5 and 6 and additional detailed microstructural evaluation that an increase in activation temperature from 573

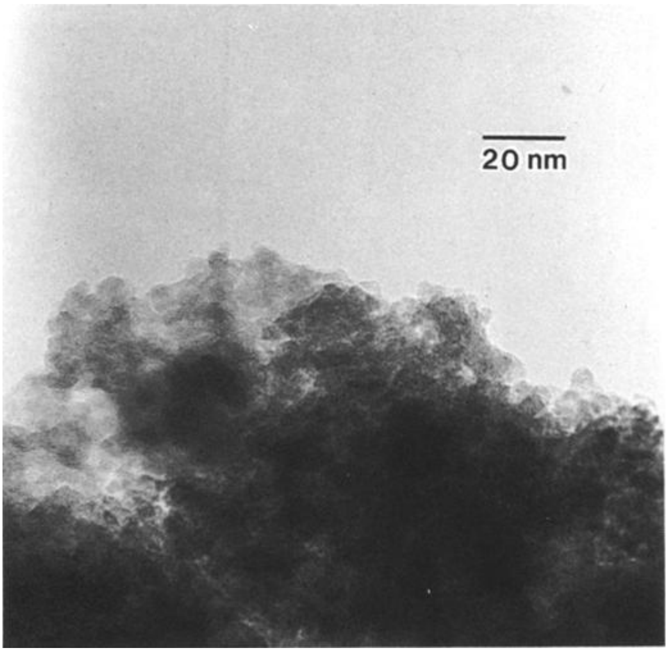

Fig. 4. Transmission electron micrograph of the as-prepared Ni/HTO catalyst. No distinct Ni particles are distinguishable, indicating a uniform dispersion of Ni^{2+} ions within the HTO support.

to 673 K does not result in a significant increase in Ni particle size (less than a factor of 2) in the Ni/HTO catalyst. Increasing activation temperature or time at a given temperature does result in crystallographic changes in the support. X-ray and electron diffraction results showed that these changes were manifested in the formation of anatase and rutile for activation temperatures $\geqslant 623$ K. These structural changes in the support cannot be directly responsible for catalyst activation because in the case of the most active catalyst shown in fig. 2 (573 K oxidation/reduction cycle following a 573 K activation in H_2) the HTO support material remained amorphous. This result also reinforces recent evidence that HTO support crystallization is not a necessary consequence of the reduction of Ni^{2+} ions to form metallic Ni particles [3].

The most striking difference between the inactive and active catalysts is the nature of the Ni particle surfaces. High resolution imaging of small particle surfaces can provide detailed information on atomic level structure, adsorbed layers, and the presence of oriented second phases [10–14]. In the inactive catalyst, a distinct film (indicated in fig. 5 by the unlabeled arrows) is consistently observed on the Ni particle surfaces and the Ni particles appear at least partially buried in the TiO_2 matrix. In contrast to the inactive catalyst, the active catalyst contains distinct, well-defined Ni particles with extremely clean surfaces (see fig. 6). These microstructural observations were consistently observed

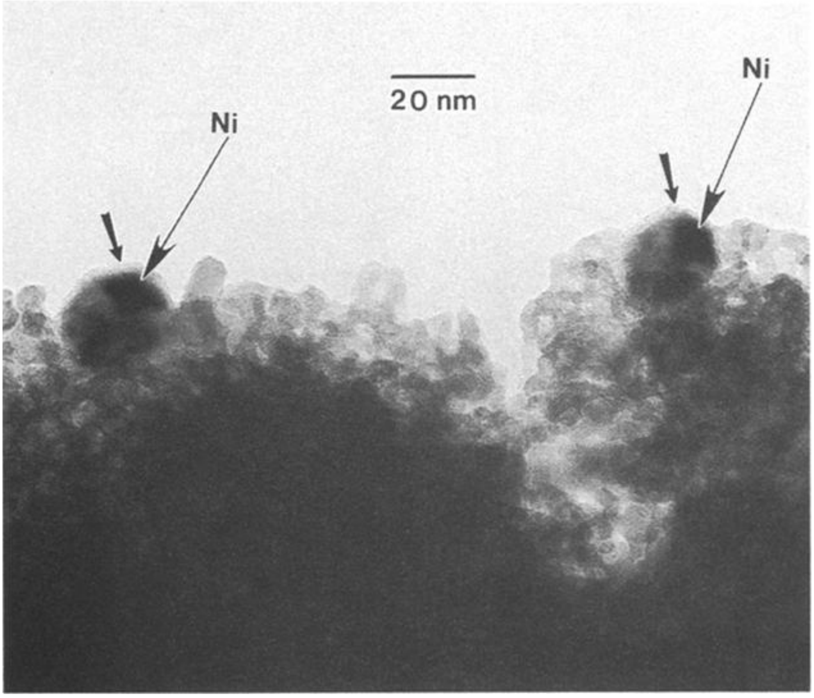

Fig. 5. Transmission electron micrograph of an inactive Ni/HTO sample (activation treatment: 573 K/H_2/30 h). A distinct film is noted on the surfaces of Ni particles located near the edge of the support.

throughout the respective catalyst microstructures. High resolution transmission electron microscopy of the highest reactivity Ni/HTO catalyst (after the 573 K reduction/oxidation/reduction treatment) was not possible due to significant sample charging, but low magnification views confirmed the general observation that the Ni particle surfaces are clean.

This microstructural evidence therefore indicates that the activation behavior of the Ni/HTO catalyst is related to a process involving cleaning of Ni particles. Thus far we have been unable to identify the composition of this surface film observed on the Ni particles. However, two distinct possibilities exist. First, the film could be carbonaceous in nature, resulting from the incomplete removal of volatile organics from the Ni/HTO catalyst during the activation treatment. The ion exchanged metal/HTO catalysts contain a high volatiles content, typically ranging from 20–30 wt%. These volatile species consist predominantly of water and methanol, but carbonate species resulting from adsorption of CO_2 during a prolonged exposure of the material to air, and residual acetone are also possible. Thermal analysis results for the Ni/HTO catalyst in both air and 5% H_2/95% Ar atmospheres showed that temperatures exceeding 773 K (in either

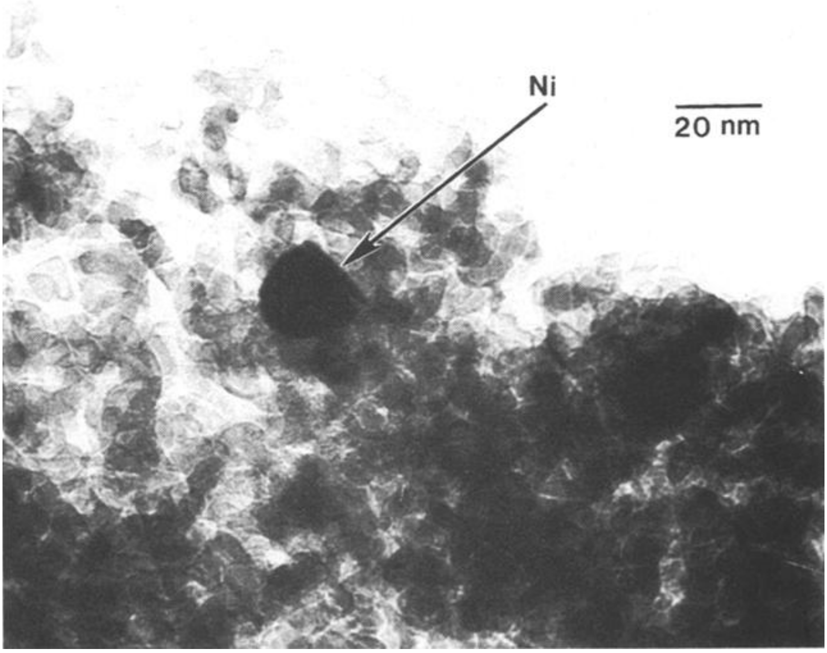

Fig. 6. Transmission electron micrograph of a reactive Ni/HTO catalyst sample (activation treatment: 673 K/H_2/33 h). A clearly defined Ni particle with clean surfaces is visible.

atmosphere) were required to completely remove all volatiles from this material. It is possible that the reducing atmospheres used in this study for activation treatments were not sufficient to completely pyrolyze organic residue from the ion exchanged Ni/HTO catalyst materials. Residual organic species might be expected to foul Ni particle surfaces and result in poor or negligible reactivity [15]. This might explain the fact that higher temperatures ($\geqslant 623$ K) and long (18–40 h) activation times were required to completely activate the Ni/HTO samples, as well as the beneficial effect of the mild oxidation/reduction cycle at 573 K on the inactive sample (previously heat treated at 573 K in H_2).

The film could also result from the diffusion of reduced titanium oxide (TiO_x) species from the bulk support phase to the Ni particles during the activation treatment and/or Ni diffusion into the TiO_2 matrix. These diffusional processes are also the possible cause for support encapsulation of the Ni phase, resulting in low H_2 uptake values for this material. Substantial previous work has been performed which links the diffusion of TiO_x species during high temperature reduction (HTR) with strong metal–support interaction (SMSI) phenomena [16,17]. This film composition may be consistent with the lack of significant contrast difference between the film and the matrix for the inactive sample shown in fig. 5. However, indirect evidence, such as decreased H_2 chemisorption capacity or hydrogenolysis reaction rates, for the presence of such TiO_x species on Ni particle surfaces has only been observed after reduction at temperatures $\geqslant 723$ K [18]. Migration of TiO_x species in the Ni/HTO catalysts was not expected in this study because the maximum activation temperature was only 673 K, but it is possible that the chemically prepared, highly reactive HTO material is more susceptible to reduction than standard commercial forms of TiO_2. The fact that low temperature oxidation (573 K) followed by low temperature reduction (573 K) changed the reactivity of the sample activated at 573 K in H_2 from negligible to highly active is also consistent with previous SMSI-related work [19,20].

Although two distinct film compositions are possible, it appears that the carbonaceous film may be more plausible. One would expect that if significant TiO_x migration occurred at 573 K in H_2, higher activation temperatures or longer times at a given temperature in H_2 would exacerbate this problem. However, the microstructural and reactivity data clearly indicate that the surface film is removed from the HTO-supported Ni particles under these conditions. Also, recent Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) studies on Ni/HTO thin film catalysts have shown that a low temperature oxidation/reduction cycle significantly reduces the carbon to nickel signal ratio, which supports the removal of carbonaceous material as a result of a low temperature oxidation treatment [9]. It is also possible that the activation process involves rediffusion of previously encapsulated Ni to the surface of TiO_2 matrix particles, but this mechanism is difficult to distinguish from the TiO_x migration hypothesis [21]. It is unclear whether a low temperature oxidation/reduction cycle would enhance Ni rediffusion to the surface of the support particles.

Further work is necessary to determine the nature of the surface film which prevents activation of Ni/HTO catalysts at low temperature (573 K) in H_2. An optimized activation treatment that takes full advantage of the desirable characteristics of HTO materials could ultimately result in the preparation of highly dispersed Ni/HTO catalysts.

4. Summary

The activation process for ion exchanged Ni/HTO catalysts is much more complex than that for conventionally prepared Ni/TiO_2 catalysts. Activation temperature, time, and atmosphere all play important roles in determining the reactivity of the ion exchanged Ni/HTO catalyst materials. Although conventionally prepared Ni/TiO_2 catalysts were completely activated after short times (1 h) at low temperature (573 K) in a H_2 atmosphere, ion exchanged Ni/HTO catalysts required higher temperatures ($\geqslant 623$ K) and longer times ($\geqslant 18$ h) to complete the activation process. A low temperature (573 K) oxidation/reduction cycle following low temperature (573 K) activation in H_2 was found to transform the ion exchanged Ni/HTO catalyst from an inactive to a highly reactive state. Microstructural observations showed that inactive ion exchanged Ni/HTO catalysts contained a distinct film which covered Ni particle surfaces, while highly reactive ion exchanged Ni/HTO catalysts contained well-defined Ni particles with clean surfaces. It appears that the activation process for the ion exchanged Ni/HTO catalyst is controlled by the surface cleaning of existing Ni particles. Experimental evidence is consistent with films consisting of carbonaceous residue or TiO_x species which have migrated from the bulk support phase.

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