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# Effects of Support on the Kinetics of Carbon Hydrogenation on Nickel

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The kinetics of carbon hydrogenation on 3% $Ni/Al_2O_3$, 3% $Ni/SiO_2$, and 3% $Ni/TiO_2$ were determined gravimetrically under conditions representative of CO hydrogenation, i.e., 423–503 K, 1 atm total pressure, $P_{H_2}$ = 5–10 kPa, and carbon coverages of 0.1–0.3. The activation energy for carbon hydrogenation on nickel is independent of support. However, specific rates of these catalysts vary by as much as a factor of 10 and decrease in the order $Ni/TiO_2$, $Ni/Al_2O_3$, $Ni/SiO_2$; moreover, the reaction order with respect to hydrogen is significantly higher for $Ni/TiO_2$ relative to $Ni/Al_2O_3$ and $Ni/SiO_2$. Thus, the differences in rates for carbon hydrogenation on $Ni/TiO_2$ relative to those on $Ni/Al_2O_3$ and $Ni/SiO_2$ are even greater at high $P_{H_2}$. CO also dissociates more rapidly on $Ni/TiO_2$. Accordingly, the higher activity of $Ni/TiO_2$ in CO hydrogenation is explained by its higher activities for both CO dissociation and carbon hydrogenation. © 1985 Academic Press, Inc.

## INTRODUCTION

The interaction between metals and supports in supported metal catalysts is a topic of significant current interest to catalysis researchers. For example, recent investigations (*1–3*) have provided evidence that supports can significantly influence the adsorption and CO hydrogenation activity/selectivity properties of nickel. Since hydrogenation of atomic, "carbidic" carbon from CO dissociation has been proposed as one of the important elementary steps in CO hydrogenation on nickel (*4–13*), it would be interesting to determine how nickel-catalyzed carbon hydrogenation is affected by the choice of support.

The kinetics of hydrogenation of atomic carbon (from CO dissociation) have been studied on supported and single crystal nickel surfaces (*8, 11, 12, 14–16*). In these previous studies rates of hydrogenation, activation energies, and hydrogen partial pressure dependencies (for $Ni/SiO_2$) were determined. In a very recent study (*16*), it was reported that the unsteady-state rates of carbon hydrogenation on $Ni/Al_2O_3$, $Ni/SiO_2$, and $Ni/TiO_2$ determined by temperature-programmed reaction are independent of support. However, these rates were measured at high carbon coverages on catalysts of moderately high nickel loadings (5–16%). Since the active, atomic carbon produced by CO dissociation on nickel is present only at low carbon coverages (*11*) and since metal–support effects are more likely to be observed at low metal loadings and high dispersions (*2, 3*), the choice of conditions in this previous study (*16*) was not well-suited for observing support effects or for observing kinetics of hydrogenation of carbidic carbon on nickel.

The present study involving well-characterized nickel catalysts of 3 wt% nickel on alumina, silica, and titania supports was undertaken to determine effects of support on the kinetics of carbon hydrogenation on nickel under conditions representative of CO hydrogenation, i.e., low reaction temperatures and low carbon coverages. These conditions were also chosen to ensure the absence of competing reactions, heat and

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TABLE 1

$H_2$ Adsorption Uptakes and Nickel Metal Dispersions for $Ni/Al_2O_3$, $Ni/SiO_2$, and $Ni/TiO_2$ Catalysts

| Catalyst | $H_2$ uptake[a] (μmol/g) | Dispersion[b] (%) |
|---|---|---|
| 3% $Ni/SiO_2$ | 71.6 | 39 |
| 3% $Ni/Al_2O_3$ | 16.3 | 9.9 |
| 3% $Ni/TiO_2$ | 14.3 | 7.5 |

[a] Total $H_2$ uptake at 298 K.

[b] Percentage of nickel atoms exposed to the surface (see Ref. 17 for details of calculation).

mass transport disguises, and inactive forms of carbon which would otherwise affect the kinetic measurements.

## EXPERIMENTAL

*Materials.* Hydrogen (99.99%) was purified with a palladium Deoxo unit (Engelhard) followed by a molecular sieve trap. Nitrogen was purified by passing it through a heated copper trap followed by a molecular sieve trap or when it was used with hydrogen, both gases were passed through a Deoxo unit and a molecular sieve trap together. Carbon monoxide (99.99%, Matheson) was purified of iron carbonyl by passing it through a molecular sieve trap heated to 525 K.

Catalysts containing 3 wt% nickel were prepared by impregnation of γ-alumina (SAS, Kaiser), silica (M-5, Cabot Corp.), and titania (P-25, Degussa) with an aqueous solution of nickel nitrate, dried in air at 323 K for 24 h, and reduced in flowing hydrogen at 723 K according to procedures described elsewhere (*17*). $H_2$ adsorption uptakes were measured at 298 K and dispersions were calculated according to previously described procedures (*17, 18*); $H_2$ uptake and dispersion data are summarized in Table 1.

*Apparatus and procedure.* Experiments were performed using a thermogravimetric (Perkin-Elmer TGS-II) flow system (*12, 19, 20*). Catalyst temperatures were measured with a K-type thermocouple placed 1 mm below the sample pan. The thermocouple readout and sample temperatures were calibrated to within 2 K of each other using magnetic transition standards.

A 10–25 mg sample of prereduced and passivated catalyst was loaded in a platinum pan and rereduced *in situ* in flowing $H_2$ ($3.7 \times 10^{-3}$ mol/min) by heating at 20°/min to 723 K and holding there for 4 h. The steady-state weight of the reduced sample (usually reached after 3 h) was used for subsequent calculations. The sample was then cooled in flowing $N_2$ to the desired deposition temperature (423–493 K). Hydrogen was added, adjusting the flows to $6.5 \times 10^{-3}$ mol/min $N_2$ and $1.6 \times 10^{-3}$ mol/min $H_2$, and the catalyst weight was allowed to stabilize before the catalyst was exposed to CO.

Carbon monoxide at $4.1 \times 10^{-4}$ mol/min was then added to the reactant gas giving a mixture with a $H_2/CO$ ratio of 4. This was passed over the catalyst for one minute resulting in a rapid weight increase (see Fig. 1) after which both $H_2$ and CO flows were shut off and the $N_2$ flow was increased to $8.2 \times 10^{-3}$ mol/min. In a previous study in this laboratory (*12*), it was determined that a $N_2$ purge at reaction temperature quantitatively removes adsorbed CO and $H_2$ from the nickel surface, while leaving active carbon formed during reaction on the surface. Previous studies of temperature-programmed desorption of CO (*16*) and $H_2$ (*21*) from these catalysts show that peak desorption temperatures are generally within or below the range of desorption temperatures (423–493 K) used in this study and thus provide further evidence that adsorbed $H_2$ and CO were quantitatively removed.

After the catalyst weight had again stabilized, the catalyst was quickly heated or cooled to the desired gasification temperature, and $H_2$ was added to the gas stream. The $H_2$ and $N_2$ flows were adjusted to give the desired partial pressure of hydrogen while still maintaining a total flow of $8.2 \times 10^{-3}$ mol/min over the catalyst. The weight loss due to reaction of surface carbon with hydrogen was measured as a function of

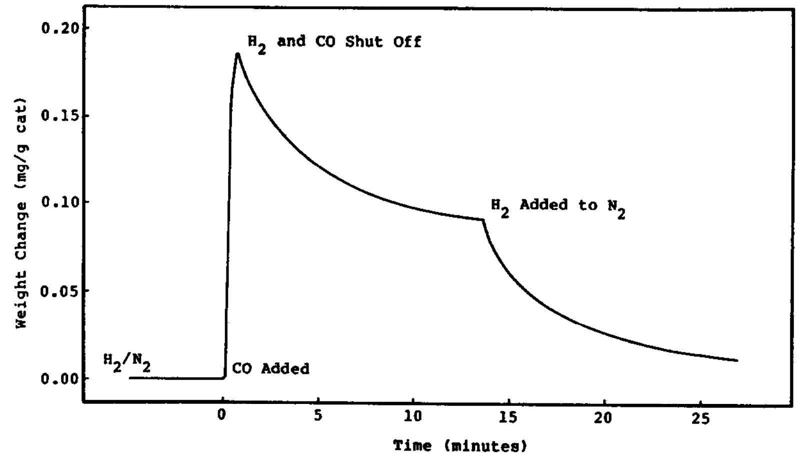

FIG. 1. Typical TGA plot to determine the rate of carbon hydrogenation.

time (see Fig. 1) from which carbon hydrogenation rates were calculated.

To determine the dependence of the partial pressure of $H_2$ on the rate of carbon hydrogenation, runs were conducted at hydrogen partial pressures of 5.07, 7.60, and 10.1 kPa while the deposition and gasification temperatures were kept constant. Carbon coverage dependency was found by depositing carbon generally at less than 0.3 monolayers at three temperatures and reacting it off with $H_2$ at a partial pressure of 7.60 kPa. The activation energy was determined by gasifying the carbon at three different temperatures with $H_2$ at 7.60 kPa.

Corrections for reversible and irreversible $H_2$ and CO uptakes on each support were also determined by following the same procedure as above to determine the carbon coverage dependency using pure supports instead of catalyst samples. Corrections for changes in buoyancy with temperature were also made.

## RESULTS

Carbon was deposited by CO dissociation in the presence of $H_2$ at less than 0.3 monolayers on $Ni/SiO_2$ and $Ni/Al_2O_3$ between 453 and 493 K, but in the case of $Ni/TiO_2$, it was necessary to keep the deposition temperature below 423 K in order to keep the carbon coverage below 30%. The order of increasing temperature to obtain approximately the same carbon coverage was $Ni/TiO_2$, $Ni/Al_2O_3$, $Ni/SiO_2$.

In experiments with the pure supports a weight gain was not observed with CO flowing over silica in the temperature range of this study. Uptakes by the titania support were small and were completely removed with flowing $N_2$. However, substantial irreversible uptakes (15–42% of the total uptakes of 3% $Ni/Al_2O_3$) were measured for the alumina support at the same temperatures at which rates were determined. Thus, the initial and final adsorption uptakes for $Ni/Al_2O_3$ and $Ni/TiO_2$ were corrected for adsorption on the support.

Upon adding $H_2$ to a carbon-containing catalyst, a rapid initial weight loss was observed after which the rate of gasification slowly decreased, until after about 8 min, it was less than 10% of its maximum value. In most cases nearly all of the adsorbed carbon was removed with $H_2$ after 20–25 min as indicated by a return of the baseline to its original position before adsorption (see Fig. 1). Since the rates of hydrogenation were maximum and constant during the first few minutes of reaction, the initial rates were used in comparing catalyst activities.

Initial rates of hydrogenation are re-

TABLE 2

Carbon Hydrogenation Rates over Supported Nickel Catalysts

| Catalyst | T (K) | $\theta_C$[a] | $P_{H_2}$(kPa) | Turnover frequency[b] $\times 10^3$ ($s^{-1}$) |
|---|---|---|---|---|
| 3% $Ni/SiO_2$ | 453 | 0.078 | 7.60 | 0.54 |
| | 473 | 0.078 | 7.60 | 1.2 |
| | 493 | 0.078 | 7.60 | 2.6 |
| | 473 | 0.060 | 7.60 | 1.1 |
| | 473 | 0.071 | 7.60 | 1.2 |
| | 473 | 0.084 | 7.60 | 1.5 |
| | 473 | 0.077 | 5.07 | 1.4 |
| | 473 | 0.077 | 7.60 | 1.6 |
| | 473 | 0.077 | 10.1 | 1.9 |
| 3% $Ni/Al_2O_3$ | 473 | 0.13 | 7.60 | 4.1 |
| | 488 | 0.13 | 7.60 | 7.1 |
| | 503 | 0.13 | 7.60 | 11 |
| | 473 | 0.20 | 7.60 | 6.5 |
| | 473 | 0.27 | 7.60 | 7.6 |
| | 473 | 0.34 | 7.60 | 8.5 |
| | 473 | 0.22 | 5.07 | 5.3 |
| | 473 | 0.22 | 7.60 | 6.4 |
| | 473 | 0.22 | 10.1 | 7.6 |
| 3% $Ni/TiO_2$ | 423 | 0.24 | 7.60 | 3.3 |
| | 433 | 0.24 | 7.60 | 5.1 |
| | 443 | 0.24 | 7.60 | 7.6 |
| | 423 | 0.14 | 7.60 | 1.5 |
| | 423 | 0.24 | 7.60 | 2.7 |
| | 423 | 0.29 | 7.60 | 3.1 |
| | 423 | 0.25 | 5.07 | 2.2 |
| | 423 | 0.25 | 7.60 | 3.3 |
| | 423 | 0.25 | 10.1 | 4.4 |

[a] $\theta_C$ is the fractional coverage of carbon on the surface determined from the total weight loss during hydrogenation.

[b] Rate of carbon removal in atoms of carbon per catalytic site (measured by $H_2$ adsorption) per second. Carbon was deposited at 423–493 K, $P_{H_2}$ = 19.3 kPa, and $P_{CO}$ = 4.83 kPa.

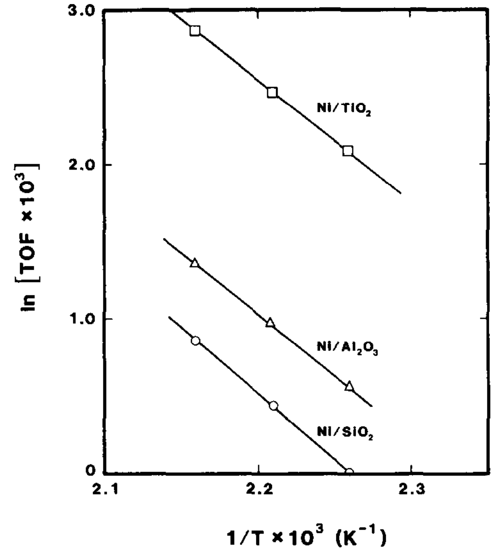

FIG. 2. Arrhenius plot of carbon hydrogenation rates for supported nickel catalysts calculated from the data in Table 2 according to Eq. (1) at $P_{H_2}$ = 7.60 kPa and $\theta$ = 0.25. ○, 3% $Ni/SiO_2$; △, 3% $Ni/Al_2O_3$; □, 3% $Ni/TiO_2$.

ported in Table 2 in the form of carbon turnover frequencies (the TOF is the rate of hydrogenation in atoms of carbon per catalytic site per second). It is evident that TOF values vary considerably with temperature, carbon coverage, and $H_2$ partial pressure for each catalyst.

Assuming the rate of carbon hydrogenation follows a simple power law model, it can be written

$$r = k_0 \exp(-E_a/RT)\theta_C^x P_{H_2}^y \qquad (1)$$

where $\theta_C$ is the fraction of sites covered with active carbon and $P_{H_2}$ is the hydrogen partial pressure. The carbon coverage, $H_2$ partial pressure, and temperature dependencies calculated from the rate data are summarized in Table 3. The reaction orders vary significantly from catalyst to catalyst while the activation energies are almost the same within experimental error (±10%). TOF values calculated from the data in Table 2 according to Eq. (1) and compared at the same temperature, carbon coverage, and partial pressure of hydrogen decrease in the order $Ni/TiO_2$, $Ni/Al_2O_3$, $Ni/SiO_2$ (see Table 3 and Fig. 2). These differences are

TABLE 3

Turnover Frequencies and Rate Parameters for Hydrogenation of Atomic Carbon on Supported Nickel Catalysts

| Catalyst | Turnover frequency[a] $\times 10^3$ ($s^{-1}$) | Reaction orders[b] | | $E_a$[c] (kJ/mol) |
|---|---|---|---|---|
| | | $x$ | $y$ | |
| 3% $Ni/SiO_2$ | 1.0 | 0.9 | 0.44 | 70 |
| 3% $Ni/Al_2O_3$ | 1.8 | 0.48 | 0.55 | 67 |
| 3% $Ni/TiO_2$ | 8.1 | 1.0 | 0.97 | 65 |

[a] Rate of carbon removal in atoms C per catalytic site per second calculated at 443 K, $P_{H_2}$ = 7.60 kPa, and $\theta_C$ = 0.25 atoms C per surface Ni atom from the data in Table 2.

[b] Based on $r = k(T)\,\theta_C^x P_{H_2}^y$.

[c] Determined over the temperature ranges 453–493, 473–503, or 423–443 K from plots of ln (turnover number) versus $1/T$.

clearly significant within the experimental precision estimated to be ±10–15%.

## DISCUSSION

Previous studies (*4–15*) provide strong evidence for the existence of two carbon forms on the surface of nickel catalysts during CO hydrogenation: $\alpha$-carbon ($C_\alpha$) and $\beta$-carbon ($C_\beta$). $C_\alpha$, an atomic or carbidic carbon of high reactivity is formed by CO dissociation (*4–8*); the evidence strongly suggests that it is the principal intermediate in CO methanation on nickel (*4–15*), i.e., it reacts with hydrogen on the nickel surface to form methane. $C_\beta$ is a relatively inactive, polymeric, graphitic carbon formed by transformation or polymerization of $C_\alpha$ at relatively high reaction temperatures and/or low $H_2$/CO ratios (*8, 22*); it is significantly less reactive in the presence of $H_2$ than $C_\alpha$ and under typical reaction conditions serves mainly to deactivate the nickel surface (*22*). Data of Goodman *et al.* (*11*) indicate that during CO dissociation on Ni(100) carbidic carbon is formed below carbon coverages of 0.5 at temperatures below 650 K; above carbon coverages of greater than 0.5 (which occur above 650 K) graphitic carbon is formed. The carbidic carbon coverage following methanation at 120 Torr and 450–700 K ($H_2$/CO = 4) is about 0.05; no graphitic carbon is formed under these conditions (*11*).

In the preliminary stages of this investigation it was found that a relatively inactive carbon (presumably graphitic carbon) was formed on supported nickel at coverages of greater than about 0.3 at lower temperatures (e.g., 500 K) than observed by Goodman *et al.* (*11*) on single crystal nickel; in the case of Ni/titania it was found that a relatively less active carbon formed at carbon coverages of greater than 0.3 at temperatures above about 430 K. It was determined that generally the key to obtaining reproducible kinetics for hydrogenation of active, carbidic carbon was to deposit the carbon at a sufficiently low temperature to ensure carbon coverages of less than about 0.3.

The principal objective of this investigation was to measure the kinetics of hydrogenation of carbidic carbon under conditions representative of the methanation reaction. The *deposition conditions were therefore carefully limited* to temperatures below 493 K (423 K in the case of $Ni/TiO_2$) in order to limit carbon coverages to less than 0.3 *thereby ensuring that only active, carbidic carbon ($C_\alpha$) was deposited.* While surface intermediates having higher activity than carbidic, alpha-carbon, such as the $\alpha'$-carbon reported by McCarty and Wise (*8*) or $CH_x$ species (*10, 13*), may have been present on the surface under these conditions of deposition, recent investigations (*23, 24*) suggest these high activity intermediates are present at very low concentrations relative to $\alpha$ or $\beta$ carbons, i.e., less than 1–2% coverage. Thus, the presence of these species at such low levels would have had little effect on the measurements of carbidic carbon hydrogenation kinetics in this study.

The activation energies and hydrogen reaction orders for carbon hydrogenation on $Ni/SiO_2$ and $Ni/Al_2O_3$ obtained in this study are in good agreement with those reported previously for hydrogenation of carbidic, $\alpha$-carbon, or carbon deposited during CO hydrogenation at low reaction temperatures (*11, 12*). For example, the activation energy of 70 kJ/mol and $H_2$ reaction order of 0.44 for 3% $Ni/SiO_2$ (Table 3) compare well with the values of 63 kJ/mol and 0.5 reported by Ho and Harriott (*14*) for 2% $Ni/SiO_2$ (at a carbon coverage of 0.3). The activation energy for 3% $Ni/Al_2O_3$ of 67 kJ/mol (Table 3) agrees remarkably well with values of 71 ± 19, 70 ± 8, and 73.6 kJ/mol reported by McCarty and Wise for 25% $Ni/Al_2O_3$ (*8*); the $H_2$ reaction order of 0.55 also agrees well with the value of 0.5 ± 0.1 reported by Gardner and Bartholomew (*12*). The activation energy of 65 kJ/mol for 3% $Ni/TiO_2$ (Table 3) is significantly higher than values of 40–44 reported by Ozdogan *et al.*

(*16*) for 5 and 10% Ni/$TiO_2$ catalysts at high carbon coverages. Their values for Ni/$SiO_2$ and Ni/$Al_2O_3$ of 40–44 kJ/mol determined at high carbon coverages are also much lower than reported here or in previous work, with the exception of the activation energy of 38 kJ/mol reported by Ho and Harriott for hydrogenation of carbon on 10% Ni/$SiO_2$ at a carbon coverage of 0.9. Thus data obtained by previous workers (*14, 16*) at high carbon coverages are probably valid for hydrogenation of a graphitic rather than carbidic carbon.

The data of this study provide strong evidence that the support significantly influences the hydrogenation of $\alpha$-carbon on nickel. This conclusion is contrary to that of Ozdogan *et al.* (*16*), who found their carbon hydrogenation rates to be independent of support. However, since their measurements apparently involved surfaces highly covered with relatively inactive carbon, the inaccessibility of reactants to active nickel sites may have limited the extent to which changes in the surface properties due to metal-support interactions could be observed. Moreover, due to the predominance of large metal crystallites in their catalysts of moderately high nickel loading, metal support effects would have been more difficult to observe.

On the other hand, the measurements of hydrogenation rate in this study were carried out on nickel surfaces partially covered with only reactive, atomic carbon. Since the nickel surface was largely accessible to hydrogen at the nickel/carbon interface, changes in the surface due to metal–supports effects were facilitated. The observation of metal–support effects was further facilitated by the choice of low loading catalysts containing relatively smaller nickel crystallites.

The results of this study also provide evidence that the rate of carbon dissociation on nickel is affected by the support. The observation of a much lower temperature for carbon dissociation on Ni/$TiO_2$ relative to Ni/$SiO_2$ and Ni/$Al_2O_3$ provides evidence that carbon dissociation occurs at a significantly faster rate on Ni/$TiO_2$.

Although activation energies for CO hydrogenation were found to be independent of support, the significantly different reactions orders observed in this study provide further evidence that the kinetics of carbon hydrogenation on nickel are not independent of support. For example, since the reaction order for $H_2$ on Ni/$TiO_2$ is higher compared to the other catalysts, the rate of carbon hydrogenation on Ni/$TiO_2$ would be even greater compared to Ni/$Al_2O_3$ or Ni/$SiO_2$ at high partial pressures of $H_2$ (which may occur in commercial methanators). Moreover, these differences in the kinetics of carbon hydrogenation could significantly influence the rate of CO hydrogenation on Ni/$TiO_2$ relative to Ni/$SiO_2$ and Ni/$Al_2O_3$ at higher reaction temperatures where carbon hydrogenation (rather than CO dissociation) becomes rate determining (*12, 25, 26*). The effects of support on CO dissociation would play a more important role in CO hydrogenation on nickel at relatively low reaction temperatures where CO dissociation is apparently the rate determining step (*25, 26*).

The observation of a higher reaction order with respect to $H_2$ for Ni/$TiO_2$ relative to the other catalysts suggests that $H_2$ is less strongly adsorbed on Ni/$TiO_2$ relative to Ni/$Al_2O_3$ and Ni/$SiO_2$. Indeed, this is consistent with a recent TPD study (*21*) showing that the heat of adsorption of $H_2$ on Ni/$TiO_2$ after high temperature reduction is significantly lower than on Ni/$Al_2O_3$ or Ni/$SiO_2$.

While the data of this study provide strong evidence that the kinetics of CO dissociation and $\alpha$-carbon hydrogenation on nickel are influenced significantly by the support, they do not provide a basis for choosing among the various alternative explanations recently advanced for such phenomena (*27–29*) which include (i) changes in electronic structure of metal crystallites due to adjustments in the Fermi level at the metal–support interface (*27, 28*) and (ii) decoration of the metal crystallites with reduced species from the support (e.g., $TiO_x$) (*29*). The possibility that effects of dispersion or structure-sensitivity account for these observations can probably be ruled out, since several recent studies have shown that CO hydrogenation on nickel is a structure-insensitive reaction (*2, 30, 31*). If effects of dispersion contributed to the differences in the behavior of $Ni/SiO_2$ ($\%D = 39$) and $Ni/Al_2O_3$ ($\%D = 9.9$), they could not explain the differences in behavior of $Ni/Al_2O_3$ and $Ni/TiO_2$, since their dispersions are essentially the same (9.9 versus 7.5%).

## CONCLUSIONS

1. The kinetics of carbon hydrogenation on nickel vary significantly with support. The order of decreasing specific rate is $Ni/TiO_2$, $Ni/Al_2O_3$, $Ni/SiO_2$. Although activation energies are independent of support, the reaction order for $H_2$ is significantly higher for $Ni/TiO_2$ relative to $Ni/Al_2O_3$ and $Ni/SiO_2$. Thus, the rate of carbon hydrogenation will be even higher for $Ni/TiO_2$ at high partial pressures of hydrogen.

2. The rate of CO dissociation is higher on $Ni/TiO_2$ compared to rates on $Ni/Al_2O_3$ and $Ni/SiO_2$. Thus, at low reaction temperatures and $P_{H_2}$ values, the significantly higher rate of CO hydrogenation on $Ni/TiO_2$ is due to its higher activity for CO dissociation. Generally speaking, the higher activity of $Ni/TiO_2$ in CO hydrogenation is explained by its higher activities for both CO dissociation and carbon hydrogenation.

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