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A Study of Acidic Titania/Silica Mixed Oxides and Their Use as Supports for Nickel Catalysts

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A series of titania/silica (TiO_2/SiO_2) mixed oxides, containing between 25 and 75 wt% TiO_2, was prepared by the coprecipitation method. After a calcination temperature of 773 K, these mixed oxides were found to be amorphous by X-ray diffraction and to be acidic by Hammett indicators, *n*-butylamine titration, and 1-butene isomerization. Both the acid amounts and isomerization activity were higher than those of either of the pure components. When Ni catalysts were prepared onto these acidic oxides, support effects were observed after a reduction at 773 K in the form of suppressions in hydrogen chemisorption and ethane hydrogenolysis. Furthermore, CO hydrogenation showed a catalytic behavior different from what is normally expected from strong metal–support interactions. These results demonstrated that the environment of TiO_2 could affect its role as an interacting oxide. © 1987 Academic Press, Inc.

INTRODUCTION

Ever since the report of strong metal–support interactions (SMSI) by Tauster *et al.* (*1*), there have been numerous studies on titania as a support for metal catalysts. As an outgrowth of this interest, many researchers have synthesized supports containing TiO_2 and other oxides such as silica (SiO_2) (*2–4*) and alumina (*5–7*). In these studies the two oxides are combined in one of two approaches. In the first approach TiO_2 is placed onto the surface of another oxide by either liquid-phase impregnation (*2–4, 6, 7*) or vapor-phase deposition (*7*) of a precursor followed by calcination. In the second approach the two precursors are coprecipitated and the precipitate is then calcined (*5, 7*).

In the literature various names have been used for materials prepared by these two approaches. Hence it is necessary to adopt a common nomenclature to avoid confusion when results from different laboratories are discussed. In the following sections we refer to materials prepared by the first approach as *surface oxides* and denote them as AO_x–BO_y (e.g., TiO_2–SiO_2). Materials prepared by the second approach are referred to as *mixed oxides* and denoted as AO_x/BO_y. The general term *binary oxide* is used to include both surface and mixed oxides.

One topic of interest is whether a binary oxide containing a SMSI oxide such as TiO_2 will also be an interacting support. The results of Murrell and Yates (*2*) and of Ko *et al.* (*3, 4*) showed that TiO_2–SiO_2 exhibits SMSI behavior for supported Ir and Ni, respectively. The same appears to be true for Pt and Ir supported on TiO_2–Al_2O_3 (*6*) and for Pt (*5*) and Ir (*7*) supported on TiO_2/Al_2O_3. However, a complication arises for mixed oxides due to the fact that these materials are often acidic (*8, 9*) and that an acidic support could also interact with a metal (*10*).

In view of the acidic properties of TiO_2/SiO_2 demonstrated by Itoh *et al.* (*11*), we decided to use them as supports for Ni catalysts with two goals in mind: (i) to determine if there is a support effect and (ii) to compare them with TiO_2 to see how TiO_2 in different environments would affect the interaction. Since our samples were prepared from precursors which are different from

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those used by Itoh *et al.*, we first present results to establish their acidic behavior. Their effects on the activation of catalysts as well as on the reduced metal are then discussed.

EXPERIMENTAL

Sample Preparation

Mixed oxides of TiO_2/SiO_2 were prepared by a conventional coprecipitation method. Ammonium hydroxide was added dropwise to a well-stirred methanol solution of $TiCl_4$ and $SiCl_4$ until a final pH of 7 was reached. During this process the temperature was maintained at or below 308 K by surrounding the reaction flask with a cold water bath and by controlling the rate of addition of NH_4OH. The resulting precipitate was filtered by many cycles of washing with deionized water until no chloride ions were detected in the filtrate by a silver nitrate test. The cake was then dried in an air oven at 383 K overnight. The dried sample, after being crushed to a fine powder, was heated in flowing N_2 (18 liters/h) at 673 K for 2 h and calcined in flowing oxygen (18 liters/h) at 773 K for 2 h. The product was then cooled to room temperature under a small oxygen flow and stored in a vial. The same procedure was followed in preparing pure TiO_2 and SiO_2.

Nickel catalysts containing 10 wt% Ni were prepared by incipient wetness impregnation of these oxides using $Ni(NO_3)_2 \cdot 6H_2O$ as a precursor. The impregnated samples were dried in an air oven at 383 K overnight and then stored. Prior to chemisorption and reaction, the sample was reduced *in situ* by heating in flowing hydrogen from room temperature to 773 K at a rate of 10 K/min and holding at 773 K for 1 h.

Physical Characterization

The BET surface areas of mixed oxides were measured with a commercial Quantasorb unit (Quantachrome Corp.). X-Ray powder diffraction experiments to identify the phases present in the mixed oxides and to estimate the average Ni crystallite size were performed on a Rigaku D/Max diffractometer with a Mo source. The actual Ni loading was determined by extracting the metal with nitric acid and measuring its concentration with an atomic absorption spectrometer (Perkin–Elmer Model 4000). The percentage reduction to metallic Ni was quantified by measuring the weight gain from the oxidation of nickel to nickel oxide at 673 K with a Cahn TGA System 113.

Representative samples of the oxides prepared above were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX). The powdered oxides were embedded in epoxy resin, the surface of which was then polished to reveal cross sections through the oxide powders. These were then carbon coated and observed using a Cam Scan Series 4 SEM. Quantitative analysis and elemental mappings were performed using a Princeton Gamma-Tech Si(Li) detector and a System-4 X-ray analyzer. For several grains of each of the oxides, a point-to-point analysis for Si and Ti, as well as an analysis of the bulk grain, was made. These were computed in terms of the oxide weight percentage. In addition, elemental mapping for Si and Ti was done for each of the grains analyzed.

Acidity Measurements

The following indicators were used in the determination of acid strength: methyl red ($pK_a = +4.8$), methyl yellow ($pK_a = +3.3$), 4-(phenylazo)-diphenylamine ($pK_a = +1.5$), dicinnamalacetone ($pK_a = -3.0$), benzalacetophenone ($pK_a = -5.6$), and anthraquinone ($pK_a = -8.2$). The acidity was determined by titrating a sample in benzene with *n*-butylamine following the Benesi method (*12*). All titrations were run using a microburette of 0.01-ml resolution with the sample stirred by a micromagnetic bar.

Isomerization of 1-butene was run in a continuous-flow reactor operated at 1 atm.

TABLE 1

BET Surface Areas of TiO_2/SiO_2

Composition		Surface area (m^2/g oxide)
wt%	mol%	
(0/100)	(0/100)	365
(25/75)	(20/80)	213
(50/50)	(43/57)	110
(75/25)	(69/31)	190
(100/0)	(100/0)	113

In a typical run, a sample of 200–300 mg was pretreated in flowing He (3 liters/h) at a specific temperature for 1 h, then cooled to the reaction temperature. A reaction mixture containing 5 mol% 1-butene and 95 mol% He was then passed through the reactor. A sample was taken for analysis every 10–20 min until a steady-state activity was reached. At all times the conversion was kept low to assure a differential operation. Analysis of the sample was done with a Gow-Mac gas chromatograph (Model 69-550P) using a 2 m × ⅛ in. column containing 0.19% picric acid on 80/100-mesh Carbopack C packing (Supelco, Inc.). Details on the reactor system and experimental procedure can be found elsewhere (*13*).

Chemical Characterization

The chemical behavior of the reduced Ni catalysts was studied with hydrogen chemisorption, ethane hydrogenolysis, and CO hydrogenation. Temperature-programmed desorption of H_2 was performed with a system manufactured by Altamira Instruments, Inc. The procedures for carrying out the other two reactions were previously described (*14*).

RESULTS AND DISCUSSION

Synthesis and Characterization of Titania/Silica

Titania/silica mixed oxides of three different compositions were prepared with the coprecipitation method described earlier. By using a single precursor in each case, pure TiO_2 and SiO_2 were prepared following the same procedure so that a comparison could be made over the entire range of composition. We use the notation (x/y) to denote the composition of each oxide, where x and y represent the weight percentages of TiO_2 and SiO_2, respectively. For example, pure SiO_2 will be represented as (0/100) in this series.

Table 1 lists the five compositions in weight as well as mole percentage. Shown in the same table are the BET surface areas of the calcined oxides. Four of the five oxides were amorphous after a calcination temperature of 773 K, as shown by the absence of any diffraction features in Fig. 1. The one exception is pure TiO_2 which crystallized to the anatase phase.

SEM experiments were performed to determine if the two components distribute homogeneously in the mixed oxides. Figure 2 shows typical results for a (50/50) sample. The strong correspondence between the Ti and Si maps of the sample region is apparent. Table 2 lists the compositions determined by EDAX at the various locations

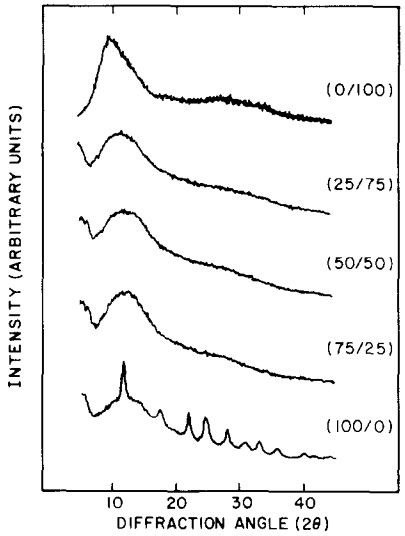

FIG. 1. X-ray diffractograms for SiO_2, TiO_2, and TiO_2/SiO_2. Numbers in parentheses indicate weight percentages of TiO_2 and SiO_2, respectively.

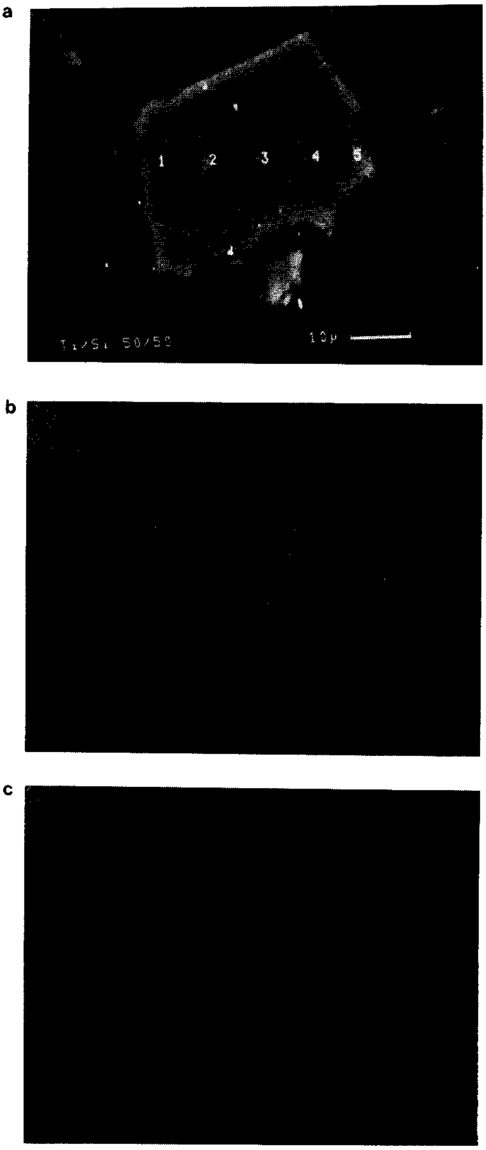

FIG. 2. (a) SEM micrograph of a (50/50) TiO_2/SiO_2 sample. (b) Ti map obtained with energy-dispersive analysis. (c) Si map.

marked in Fig. 2a. There is only a slight variation from one point to another. Furthermore, the composition at each point agrees well with the bulk analysis and with the expected stoichiometric ratio. Since similar observations were found for the other samples, we believe our preparation method was successful in producing amorphous, chemically mixed samples.

TABLE 2

EDAX Analysis of a TiO_2/SiO_2 (50/50) Sample

Location[a]	Composition (wt%)		
	TiO_2	SiO_2	TiO_2/SiO_2
Point 1	50.8	49.2	1.03
2	51.7	48.3	1.07
3	51.0	49.0	1.04
4	50.7	49.3	1.03
5	53.0	47.0	1.13
Bulk	52.6	47.4	1.11

[a] See Fig. 2a.

EDAX was also performed on these samples to detect any residual chlorine, and none was found. This is consistent with the analysis performed by Galbraith Laboratories, Inc. on selected samples which showed the chlorine content to be less than 0.01 wt%. These results confirm that the chlorine ions were successfully removed by the repeated washings.

Acidic Properties of the Mixed Oxides

Table 3 shows the results when the acid strengths of the mixed oxides were determined with six Hammett indicators. When an indicator is in its acid color (as indicated by a + in the table), it means the surface has an acid strength that is equal to or greater than the corresponding pK_a value. In this series of samples, silica showed the

TABLE 3

Acid Strength of TiO_2/SiO_2 as Determined by Hammett Indicators

	pK_a					
Sample	4.8	3.3	1.5	−3.0	−5.6	−8.2
(0/100)	+[a]	−	−	−	−	−
(25/75)	+	+	+	+	+	+
(50/50)	+	+	+	+	+	−
(75/25)	+	+	+	+	+	−
(100/0)	+	+	+	+	+	−

[a] +, acid color; −, base color.

TABLE 4

Acidities of TiO_2/SiO_2 at Different Acid Strengths

Sample	Acid amount					
	mmol/g			mmol/m^2 ($\times$ 10^{-3})		
pK_a	+3.3	+1.5	−3.0	+3.3	+1.5	−3.0
(0/100)	—	—	—	—	—	—
(25/75)	1.26	1.14	0.72	5.92	5.35	3.38
(50/50)	0.65	0.51	0.36	5.91	4.64	3.27
(75/25)	1.08	0.84	0.69	5.68	4.42	3.63
(100/0)	0.28	0.18	0.13	2.44	1.59	1.14

weakest acid strength. The acid strengths of the mixed oxides were equal to or greater than that of pure TiO_2.

The acidities of the mixed oxides were measured by *n*-butylamine titration. Table 4 shows the titration results for samples which had been pretreated in a vacuum oven at 373 K for 1 h and then cooled in oxygen to room temperature. Three indicators that give distinct color changes were used so that the endpoint could be easily discerned. No titration could be done on SiO_2 which had too weak an acid strength for these indicators. All three mixed oxides showed similar acid amounts on a per surface area basis and had a larger value than that of TiO_2.

Our observation of TiO_2/SiO_2 mixed oxides possessing higher acidities than either of the pure components is consistent with the hypothesis of Tanabe *et al.* (*15*) and the model of Kung (*16*). Itoh *et al.* (*11*) also reported the generation of strong acid sites on TiO_2/SiO_2 prepared from ethyl orthosilicate and titanium tetrachloride. In fact, these authors found that on a per-gram basis, their TiO_2/SiO_2 mixed oxide with a 1 : 1 mole ratio has a higher acidity than two silica/alumina samples used in the same study. On a per-surface-area basis, this particular TiO_2/SiO_2 mixed oxide has a maximum acidity of 1.83×10^{-3} mmol/m^2 for a Hammett acidity function of $H_0 \leq 1.5$.

Table 4 shows that at the same Hammett acidity, our (50/50) sample has an acid amount of 4.64×10^{-3} mmol/m^2, which is about 2.5 times the value of Itoh *et al.* This is not too alarming a discrepancy in view of the different experimental conditions used in the two studies and the limitations that are intrinsic to the titration method. Deeba and Hall (*17*) recently noted that titration data in the literature for the same material (silica/alumina) could vary by up to a factor of 4 from one laboratory to another. One particular important issue is that the assumption of chemical equilibrium is often not valid, in which case the Benesi method could lead to an overestimation of acidity (*18*).

In our titrations we used a standard set of parameters including particle size, titrant concentration, and pretreatment. Furthermore, each titration was allowed to proceed over a long time in a continuously stirred solution in an attempt to reach an accurate endpoint. With these precautions results could be reproduced to ±10%, which gave us confidence in establishing qualitatively the acidic nature of our samples and in comparing their acidities on a relative basis within a group. However, a comparison of our results with others in the literature on an absolute basis must be done with caution due to the limitations stated above.

We studied the isomerization of 1-butene over the TiO_2/SiO_2 mixed oxides to further characterize their acidic properties. In the initial experiments, all samples were pretreated at 473 K in flowing He and the activities were measured at 423 K. No activity was found for SiO_2. As shown in Fig. 3, the activities of the other samples declined over time and reached their steady-state values after about 2 h. Table 5 shows the steady-state activities both on a per-mass and on a per-surface-area basis. Pure TiO_2 was significantly less active than the three mixed oxides in isomerizing 1-butene.

Table 5 also shows the selectivities of these samples, defined in terms of the ratio of *cis*- to *trans*-2-butene. A *cis*/*trans* ratio near unity was found for all the mixed oxides, suggesting that the reaction proceeded through a 2-butyl carbonium ion intermedi-

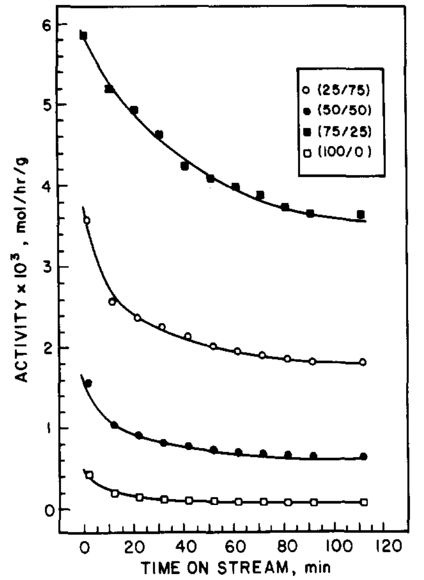

FIG. 3. Time-on-stream data showing the activities of 1-butene isomerization over TiO_2 and TiO_2/SiO_2.

ate (*19, 20*). Since this intermediate is formed by abstracting a proton from the surface, we believe the isomerization activity is a good measure on the Brønsted acidity of the mixed oxides.

Several experiments were performed to confirm that the isomerization reaction was catalyzed by Brønsted acidity. The *cis*/*trans* ratios were measured at four different temperatures ranging from 393 to 453 K and found to be invariant with temperature as expected for a mechanism involving a 2-butyl carbonium ion intermediate (*19*). Furthermore, the activity of each mixed oxide decreased with successively higher pretreatment temperatures. Figure 4 shows the results of the (75/25) sample. Although the activity of 1-butene isomerization decreased by a factor of 3 as the pretreatment temperature was increased from 473 to 773 K, the acid amount as titrated by *n*-butylamine varied by no more than 10% over the same range of pretreatment temperature.

TABLE 5

Activity and Selectivity of 1-Butene Isomerization over TiO_2/SiO_2

Sample	Activity		*cis*-/*trans*-2-butene
	mol/h/g ($\times 10^{-3}$)	mol/h/m² ($\times 10^{-5}$)	
(0/100)	—	—	—
(25/75)	1.78	0.84	1.05
(50/50)	0.62	0.56	1.21
(75/25)	3.64	1.92	1.26
(100/0)	0.07	0.06	1.89

The effect of pretreatment can be understood in terms of the dehydroxylation of the surface. As found for other acidic oxides, dehydroxylation converts Brønsted acid sites to Lewis acid sites (*21–23*). Such a conversion lowers the concentration of Brønsted acid sites and, in turn, the isomerization activity. On the other hand, the total acid amount is less affected since *n*-butylamine titrates both Brønsted and Lewis acid sites. As a final test of this hypothesis, water was injected after a (75/25) sample had been pretreated at either 573 or 773 K and cooled to room temperature. The sam-

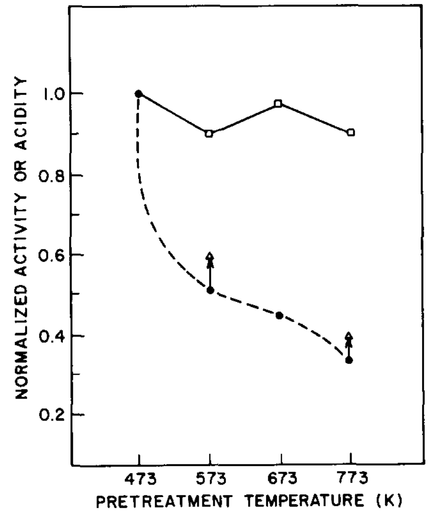

FIG. 4. Effects of pretreatment on activity and acidity over a (75/25) TiO_2/SiO_2 sample. (●) Activity determined from 1-butene isomerization, (□) acidity titrated with *n*-butylamine, (△) restoration of isomerization activity following water injection.

ple was then pretreated at 473 K following the standard procedure. Figure 4 shows there was indeed an increase in activity after water injection, which presumably hydroxylated the surface and converted part of the Lewis acid sites back to Brønsted acid sites. A total restoration in activity was not achieved due possibly to the insufficient amount of water injected. However, these experiments qualitatively demonstrated the reversible interconversion between the two types of acid sites.

Itoh *et al.* (*11*) also studied the isomerization of 1-butene over TiO_2/SiO_2. By using a closed circulation reactor, they observed results which are similar to ours. For example, they reported *cis/trans* ratios of around 1.5. Over their studied range of composition, they found that the acidity varies by no more than a factor of 2 but the isomerization activity varies by about a factor of 10.

A comparison between Tables 4 and 5 shows that for the three mixed oxides in this study, there is also a larger variation in isomerization activity than in acidity on a per-surface-area basis. We believe this difference is due to the fact that isomerization measures Brønsted acidity, whereas titration measures both Brønsted and Lewis acidities. This would then imply that the relative concentration of the two types of acid sites varies as a function of composition over this series of samples. Since the acidities of all three samples are comparable, under this hypothesis we would expect an inverse relationship between the isomerization activity and the amount of Lewis acid sites. In other words, the order of increasing Lewis acid sites should be (75/25) < (25/75) < (50/50). In the next two sections, we examine how the acidic properties of these mixed oxides affect their behavior as supports for Ni catalysts.

TABLE 6

Characteristics of Supported Ni Catalysts

Support composition	Ni loading[a] (wt%)	Percentage reduction[b]	Average crystallite size[c] (nm)
(0/100)	10.5	100	5
(25/75)	10.7	94	10
(50/50)	10.8	86	13
(75/25)	10.7	99	9
(100/0)	10.8	100	8

[a] Determined with atomic absorption.

[b] Determined by thermogravimetric measurement of oxygen uptake at 673 K.

[c] Determined with the X-ray line broadening technique.

Characterization of Supported Nickel Catalysts

Nickel catalysts were prepared onto SiO_2, TiO_2, and TiO_2/SiO_2 by incipient wetness impregnation to achieve a nominal metal loading of 10 wt%. As shown in Table 6, the actual Ni loadings determined from atomic absorption varied from 10.5 to 10.8 wt%.

To study the effect of composition on chemical behavior, all catalysts were reduced with one standard procedure in which the sample was heated at a rate of 10 K/min from room temperature to 773 K and held at 773 K for 1 h. This procedure led to a complete reduction for Ni supported on SiO_2 and TiO_2. The extent of reduction for Ni supported on TiO_2/SiO_2 varied in the order (75/25) > (25/75) > (50/50) (see Table 6). It is interesting to note that there is an inverse relationship between the extent of reduction and the amount of Lewis acid sites on the three mixed oxides. We believe this was due to an interaction between the Lewis acid sites and NiO which was formed from the decomposition of the nickel precursor. A similar type of interaction between metal ions and coordinately unsaturated sites (Lewis acid sites) on metal oxides has been reported for Rh on TiO_2-doped SiO_2 (*24*) and FeO and Ir–Fe on TiO_2 (*25*). In the latter case the interaction prevents the reduction of FeO to metallic Fe, which is similar to our observation.

TABLE 7

Kinetic Results for Ethane Hydrogenolysis over $Ni/TiO_2/SiO_2$ Catalysts

Support	E_a[a] (kJ/mol)	n[b]	m[b]	Activity at 478 K (molecules/s/surface Ni atom)
(25/75)	181	0.8	−1.7	7.1×10^{-6}
(50/50)	188	0.9	−1.8	1.5×10^{-5}
(75/25)	181	0.9	−1.7	2.4×10^{-6}

[a] Determined from the temperature dependence of the rate at ethane and hydrogen partial pressures of 0.03 and 0.2 atm, respectively.

[b] Exponents in the experimental power rate law, $kp_E^n p_H^m$.

Table 6 also lists the average sizes of the reduced Ni crystallites as determined from X-ray line broadening measurements. The variation in sizes follows the general trend in the variation in surface areas of these samples, especially at the two extremes of (0/100) and (50/50).

Results in this section show that TiO_2/SiO_2 mixed oxides exhibited an indirect support effect in changing the physical characteristics of reduced Ni catalysts. In the next section we present experimental evidence that they also affected the chemical behavior of these samples.

Support Effects on Chemical Behavior

Three chemical probes which have previously been used in characterizing SMSI catalysts (*14*) were used in this study. Hydrogen chemisorption and ethane hydrogenolysis were run only over Ni supported on the three mixed oxides. Results for the two pure oxides were not obtained since there are abundant data in the literature for comparison. In addition, support effects led to suppressions in chemisorption and hydrogenolysis activity which represent negative observations. A more meaningful probe is CO hydrogenation, which was run over Ni on all five supports prepared in this study.

Temperature-programmed desorption studies of H_2 on the $Ni/TiO_2/SiO_2$ catalysts showed that each catalyst adsorbed only a very small amount of hydrogen at room temperature. Based on the quantity of hydrogen desorbed, dispersions of these catalysts were calculated to be between 0.1 and 0.3%. By contrast, dispersions ranging from 6 to 9% were obtained if crystallite sizes determined from X-ray line broadening were used. This underestimation of dispersion (or overestimation of crystallite size) from TPD results suggests a strong suppression in H_2 chemisorption.

Table 7 shows the kinetic results for ethane hydrogenolysis over these catalysts. As a comparison, the activities of ethane hydrogenolysis over bulk Ni or Ni on an inert support range from 2.4 to 7.6×10^{-4} molecules/s/Ni in the range 473–478 K (*26*). There was thus a factor of 10–100 decrease in ethane hydrogenolysis activity over Ni supported on TiO_2/SiO_2 mixed oxides.

The above results clearly indicate a support effect for the mixed oxides. The suppression in hydrogen chemisorption and decrease in ethane hydrogenolysis activity are typical of the behavior of SMSI catalysts (*14*). However, results for CO hydrogenation suggest that there may be another mechanism at play. As shown in Table 8, there was no appreciable enhancement in CO hydrogenation activity as observed for Ni supported on TiO_2. The characteristic shift in product distribution toward higher hydrocarbons for SMSI catalysts (*14, 27*) was also less apparent for Ni supported on TiO_2/SiO_2.

It is significant that the TiO_2/SiO_2 mixed oxide does not behave like a SMSI support, whereas a surface-phase oxide consisting of TiO_2 deposited onto SiO_2 does (*3, 4*). Recent evidence has suggested that for Ni catalysts, the SMSI behavior is related to the decoration of the metal surface by a migrating adspecies (*28–31*). Within this framework, our results suggest that the coexistence of TiO_2 and SiO_2 in a chemically mixed system affects the process of migration. The important point is that a binary

TABLE 8

CO Hydrogenation over $Ni/TiO_2/SiO_2$ Catalysts

Support	Activation energy, E_{CO} (kJ/mol)	Turnover frequency at 548 K, N_{CO} ($\times 10^{-2}$ s^{-1})	Selectivity		
			CO conversion (%)	CH_4 yield (mol%)	C_2^+/C_1[a]
(0/100)	84	2.4	2.4	83.0	0.20
(25/75)	124	2.4	2.0	81.8	0.23
(50/50)	118	5.4	1.6	71.0	0.41
(75/25)	112	1.0	1.6	68.8	0.45
(100/0)	129	16.7	1.8	57.8	0.73

[a] C_2^+ denotes the sum of hydrocarbons from C_2 to C_5.

oxide containing a SMSI oxide is not necessarily a SMSI support.

In view of the acidic nature of TiO_2/SiO_2, it is not surprising that our kinetic results are similar to those obtained for Ni on other acidic supports. Taylor *et al.* (*32, 33*) found that the activity of ethane hydrogenolysis is a factor of 50 lower for Ni supported on SiO_2/Al_2O_3 than on SiO_2. Richardson (*34*) reported that the activity of ethane hydrogenolysis decreases with increasing acidity over a series of supports including silica, alumina, silica/alumina, and Y-faujasite. The more recent work of Burch and coworkers (*35, 36*) showed that $Ni/SiO_2/Al_2O_3$ is equally as active as Ni/SiO_2 for the hydrogenation of benzene and CO, but less active for the hydrogenolysis of hexane. Thus, placing SiO_2 into TiO_2 may hinder its SMSI behavior; the resulting acidity makes the mixed oxide an interacting support for Ni nonetheless.

The mechanism of interaction between a metal crystallite and an acidic support remains unclear. The traditional view of electron-withdrawing Lewis acid sites is probably inadequate in our system since the Ni crystallite sizes are quite large. One other possibility is that Lewis acid sites interact with nickel oxide (as stated earlier) to form a new phase which, in turn, interacts with nickel. However, Burch and Flambard (*36*) found no evidence of nickel silicate or nickel aluminate in a $Ni/SiO_2/Al_2O_3$ system. The role of NiO is also unlikely to be important in the work of Taylor *et al.* (*33*) since all the nickel catalysts are believed to be completely reduced. Work is in progress in our laboratory to further define the mechanism of metal–acidic support interaction and how it is different from SMSI.

SUMMARY

We have prepared a series of TiO_2/SiO_2 mixed oxides which are amorphous and chemically mixed after a calcination temperature of 773 K. They exhibit surface acidity larger than that of either of the pure components as shown by *n*-butylamine titration and 1-butene isomerization. The results further suggest that the relative concentrations of Brønsted and Lewis acid sites vary with the composition of these mixed oxides.

The TiO_2/SiO_2 oxides exert both direct and indirect support effects when used as supports for Ni catalysts. An interaction between Lewis acid sites and NiO could account for the observed trend in percentage reduction. Support effects on the reduced metal manifest themselves in the catalytic behavior toward hydrogen chemisorption, ethane hydrogenolysis, and CO hydrogenation. The behavior, however, is not identical to what is usually associated with a SMSI system. The role of

TiO_2 as an interacting oxide is thus dependent on its environment in a binary system. Specifically, surface acidity should be considered whenever the preparation method results in an acidic support. Chemical probes other than hydrogen chemisorption (which could be suppressed for metals supported on both SMSI and acidic oxides) are needed to properly characterize a specific type of metal–support interaction.

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