

Induction of an Electronic Perturbation in Supported Metal Catalysts

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The debate as to whether an “electronic” effect is responsible for perturbations in the normal behavior of supported metal catalysts has seized the attention of scientists for many years. Unfortunately, many of the proposed so-called “electronic” models can now be more satisfactorily explained in terms of either the surface concentration or the size of the ensembles present on the support surface. In this study we have used both ferroelectric and selected ceramic support media to demonstrate that at specific temperatures the catalytic activity of a supported metal particle can be enhanced to a significant degree. The observed improvement in the performances of these systems can be correlated with changes in the structure of the support media and to the different dielectric constants exhibited by these materials. A further aspect that must be taken into consideration is the finding from high-resolution TEM examinations that even after mild reduction at 350 °C there was evidence that in the vicinity of metal particles the support underwent transformation to a lower oxide state.

Introduction

Metal particles can undergo substantial modifications in catalytic behavior when dispersed on different support materials. The impact of the establishment of chemical and physical interactions between metal particles and the support on the catalytic activity and selectivity for a given reaction has been the subject of numerous papers and excellent reviews have been written about this topic.^{1–7} The most dramatic changes in the catalytic performance were found when titania or other readily reducible oxides were employed as support media.^{3,4,8–17} Indeed, the investigations of the so-called strong metal–support interaction (SMSI effect) reported by Tauster and co-workers^{3,4} gave rise to an avalanche of papers and a debate that centered around the origin of the observed changes in catalytic activity. Several explanations were proposed to account for the decrease in hydrogen chemisorption capacity of various metal/TiO₂ systems, following reduction at temperatures of about 500 °C. The main theories can be summarized as follows: (a) the formation of new active sites at the metal-support interface,^{8–10} (b) an electron-transfer process between the metal and support,^{11–14} and (c) hydrogen spillover onto the titania support that resulted in the formation of a reduced oxide phase, Ti₄O₇.^{15,16} It was demonstrated via the use of geometrically designed model catalyst systems that the metal particles served as dissociation centers for hydrogen and that when the atomic species created in this process subsequently diffused onto the support, regions where this phenomenon occurred underwent reduction to a lower oxide state.¹⁸ Later it was established that, during reduction, TiO_x species generated at the metal/support interface were capable of diffusing onto the metal particle surfaces and this phenomenon was deemed to be responsible for the modifications in both hydrogen chemisorption and subsequent catalytic activity.^{19,20}

It was found that a more subtle yet equally important change could be induced in both the catalytic activity and selectivity of nickel particles when highly electrical conductive graphitic

nanofibers were used as support media in a series of hydrogenation reactions.^{21–24} Park and Baker^{23,24} demonstrated that with these types of tailored materials one of the key factors in determining the catalytic behavior of the supported metal particles was the orientation of the graphitic platelets constituting the nanofiber structure. Dramatic differences in both activity and selectivity could be achieved when the nickel particles were dispersed on certain types of graphite nanofibers compared to that found with other amorphous and graphitic forms of carbon and traditional oxide carriers containing the same metal loading. A further feature to emerge from this work was the finding that the active state of nickel was one where the particles preferentially located on the “zig-zag” faces of the nanofiber structures.²⁴

Certain dielectric materials such as barium titanate and lead zirconate titanate exhibit electrical polarization in the absence of an applied field, a property known as ferroelectricity. At the molecular scale, ferroelectrics consist of structural units with small localized electric dipoles oriented in various directions in such a manner that the bulk polarization of the material is zero.^{25,26} Typically ferroelectrics possess a high relative dielectric constant (relative permittivity) which can vary dramatically with temperature upon reaching the Curie point. It is the effect of this dramatic increase in the value of the dielectric constant at the Curie temperature that we intend to exploit in the quest to induce electronic perturbations in the properties of supported metal particles. It is our belief that such behavior should be manifested by a abrupt change in the catalytic performance of the system as one approaches the Curie temperature of the support medium.

The use of ferroelectric materials as catalyst supports has been limited to a few areas in catalysis, but on the whole these unique materials have gone unnoticed and untested as possible alternatives to conventional oxides such as magnesia, silica and γ -alumina. Parravano²⁷ investigated the use of ferroelectric sodium and potassium niobates and lanthanum ferrite for the catalytic oxidation of CO and reported that the rate of reaction was directly influenced by the ferroelectric transitions taking

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place in these materials at specific temperatures. These results were interpreted according to the notion that an electronic mechanism was operative in these systems, which had a substantial impact on the rate-determining step for the catalytic oxidation of CO.

In more recent years, Inoue and co-workers^{28–32} have employed various ferroelectric materials as novel catalyst supports in conjunction with surface acoustic waves (SAWS). Using this technique they demonstrated that the catalytic activity of both palladium and copper could be substantially enhanced when supported on ferroelectric materials. This enhancement was accounted for in terms of a displacement of the metal lattice atoms caused by the resonance oscillations, which in turn influenced the local density of the electrons at the particle surface resulting in the observed changes in the behavior of the catalyst system.

In other investigations, ferroelectric and perovskite type oxides have been used as oxidation catalysts for a variety of hydrocarbons, especially those related to exhaust control devices.³¹ In these studies the activation of oxygen in the bulk of the materials and the subsequent mobility of such species onto the surface of these perovskite oxides was exploited by varying the valence states of the A and B sites.^{34–37} Recent advances in the understanding of the mechanism whereby these oxide catalysts operate have resulted in their use for the partial oxidation of hydrocarbons rather than depending on systems that merely result in an uncontrolled reaction leading to complete oxidation.^{38,39}

In the current study we have elected to investigate the modifications in catalytic action of nickel that result from supporting the metal on various types of ceramic materials using the hydrogenation of a simple olefin, ethylene as a probe reaction. The objective of the study was to ascertain whether the choice of support could have an influence not only on the catalytic activity of the nickel particles, but also if one could enhance the performance of the system by selectively inducing an electronic perturbation in the deposited metal. In this regard, the choice of BaTiO₃ as a catalyst support has been investigated at specific temperatures where a spontaneous polarization is known to be generated due to the positively and negatively charged domains contained within this material. The results suggest that this concept has distinct merit, since significant changes in the catalytic behavior of nickel were observed when such particles were supported on certain types of ceramic media.

Experimental Section

Materials. The 5 wt % nickel supported catalysts used in this study were prepared by a standard incipient wetness technique. Each support media was impregnated with a solution of nickel nitrate containing the appropriate amount of metal required to achieve the desired 5 wt % loading. The nickel nitrate was dissolved in 25 mL of 2-butanol before being added dropwise to the support media with constant stirring at approximately 80 °C. When all of the nickel solution had been added and the solvent evaporated off, the impregnated powder was dried overnight in an oven at 110 °C. The catalyst precursor was initially calcined in air at 250 °C for 4 h to convert the metal nitrate to the respective oxide. Following this step the powder was then flushed in He at ambient temperature before being reduced at 350 °C in a 10% H₂/He mixture for 24 h. The low temperature was chosen in order to prevent the reduction of the support to a lower oxide state. The reduced catalyst was cooled in He and finally passivated at ambient temperature in a 2% O₂/He mixture for 1 h prior to removal from the reactor and stored for future use.

The gases used in this work, helium (99.999%), hydrogen (99.999%), carbon monoxide (99.99%), and ethylene (99.95%) were obtained from Medical Technical Gases and were used without any further purification. Reagent grade nickel nitrate [Ni(NO₃)₂·6H₂O], used in the catalyst preparation, and the TiO₂ was obtained from Fisher Scientific. The γ -Al₂O₃ was supplied by the Degussa Corporation, Ta₂O₅ was obtained from Alfa Aesar, BaTiO₃ and CaTiO₃ were supplied by Rhone-Poulenc and all powders were used as received.

Apparatus and Procedures. The apparatus used in all the experiments performed in this study consisted of a quartz flow reactor, fitted with a quartz frit situated approximately in the middle of the reactor tube and heated by a split vertical tube furnace. The gas flow to the reactor was precisely regulated by the use of MKS mass flow controllers allowing a constant composition of a desired reactant feed to be delivered to the catalyst system. Catalyst samples (100 mg) were placed on the quartz frit and the tube was positioned in such a manner that the frit was always in approximately the same location in the reactor. After reduction in a 10% H₂/He mixture for 2 h at 350 °C the system was cooled to the desired reaction temperature. Once the desired reaction temperature was attained, the reactant hydrocarbon gas, or a predetermined C₂H₄/H₂/He mixture was introduced to the reduced catalyst sample for periods of up to 3 h. The progress of the reaction was followed as a function of time by sampling the inlet and outlet gas streams at regular intervals. The reactants and products were analyzed by gas chromatography using a 30 m megabore (GS-Q) capillary column in a Varian 3400 G.C.

The nature and characteristics of all the catalyst support materials were established using a combination of techniques, including high-resolution transmission electron microscopy (HRTEM), temperature programmed oxidation/reduction (TPO/TPR), X-ray diffraction (XRD), and nitrogen BET surface area measurements. The nickel catalysts were examined before and after use by HRTEM to establish any changes in the support structure and in the morphology of the impregnated metal particles. These studies were carried out in a JEOL 2000EX II electron microscope fitted with a high-resolution pole piece capable of giving a lattice resolution of 0.18 nm. Suitable TEM specimens were prepared by the ultrasonic dispersion of catalyst samples in isobutanol followed by application of a drop of the resultant suspension to a holey carbon support grid.

BET surface areas, calculated from nitrogen adsorption isotherms at –196 °C, were carried out on the different support media using a Coulter Omnisorp 100CX surface analysis unit. Powder XRD patterns of the pristine support materials and the catalyst samples were performed with a Scintag diffractometer using nickel filtered Cu K α radiation. Diffraction patterns were recorded over a range of 2 θ angles from 10 to 90° and compared with the known X-ray powder files to establish the phase identities.

Temperature programmed oxidation and reduction experiments were performed using a Cahn 2000 microbalance in a 10% air/He mixture for the TPO studies and a 10% H₂/He mixture for the TPR studies. The catalyst samples under investigation were ramped from ambient to 500 °C at a rate of 5 °C/min and held at this temperature for a further 2.0 h. The data obtained from these studies were used to determine the stability of all the support powders under both oxidizing and reducing conditions.

Results

1. Characterization Studies. 1.1. XRD Analysis. X-ray diffraction analysis of the ceramic support materials and the

TABLE 1: Measured N₂ BET Surface Areas for the Catalyst Support Materials Used in This Study

support material	N ₂ BET surface area (m ² g ⁻¹)
BaTiO ₃	6.3
CaTiO ₃	9.1
TiO ₂	10.8
Ta ₂ O ₅	7.1
γ -Al ₂ O ₃	115.1

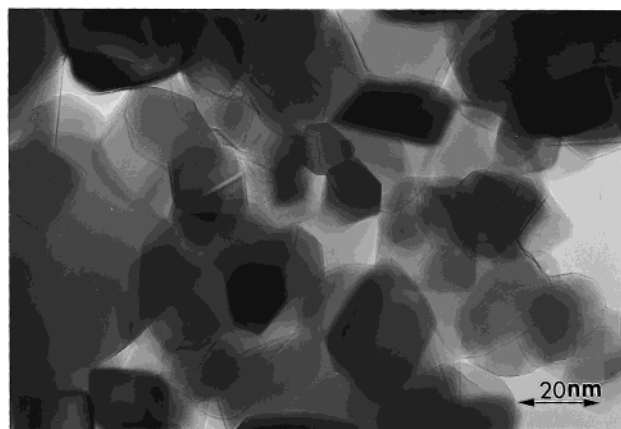
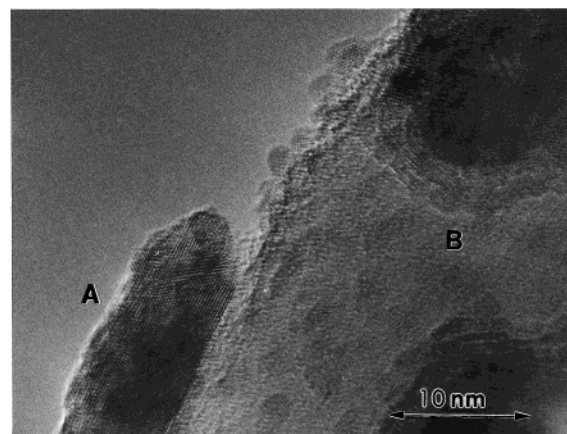
catalysts were conducted both before and after use. This procedure enabled one to identify the existence of any changes in the structure of the support media or the creation of interactions between the dispersed metal particles and the various carrier materials. XRD analysis of the supported nickel catalysts showed the existence of peaks matching those of the metallic species and the corresponding peaks for each support material with no appearance of lower oxide states. No evidence for nickel oxide could be discerned in any of the catalyst samples after passivation demonstrating the effectiveness of the reduction procedure. Furthermore, the catalysts did not display any unusual or unexpected XRD peaks following the hydrocarbon hydrogenation reaction, indicating that there was very little change in the characteristics of catalyst during the typical reaction period.

1.2. Temperature-Programmed Oxidation/Reduction Studies. This technique is used to monitor possible weight changes accompanying a chemical reaction as a result of the formation of volatile products such CO₂ and H₂O vapor. When samples of the various supported nickel catalysts were heated in either 10% air/He or 10% H₂/He mixtures no changes in weight were recorded over the range room temperature to 500 °C. On the basis of these observations, one may assume that the supported nickel catalysts were relatively stable under these conditions.

1.3. Surface Area Measurements. The N₂ BET surface areas of all the materials used as catalyst supports in this current investigation, measured at -196 °C, are summarized in Table 1. Inspection of these data shows that, as expected, the ceramic and ferroelectric materials possess a very low surface area when compared with that of a traditional support material, γ -Al₂O₃.

1.4. Transmission Electron Microscopy Examinations. High-resolution transmission electron microscopy studies enabled one to determine the location and morphological characteristics of the nickel particles when supported on ceramic materials and the more conventional γ -Al₂O₃ carrier. From an inspection of the various supported nickel samples it became evident that there were significant differences in the morphological characteristics exhibited by the metal particles on each of the carrier materials.

The appearance of nickel particles supported on TiO₂ is presented in the electron micrograph, Figure 1. In this system the 2-D transmission image shows that the metal particles adopted a faceted hexagonal-shaped outline. Examination of particles that are tilted at a critical angle with respect to the support surface shows that these structures are sufficiently thin to enable one to detect features of the underlying carrier. Furthermore, it is evident that the electron density is quite uniform across any given particles indicating that they are relatively flat. These morphological characteristics are consistent with the existence of a strong interaction between the metal and the support. Figure 2 is a high-resolution micrograph where one can see the lattice fringe image of a (A) nickel crystallite that is located on the (B) edge of the TiO₂ support. The *d* spacing of the metal particle measured from the negative of this micrograph was 0.202 nm, which can be compared with the literature value of 0.203 nm for the (111) face of nickel. Perhaps the most interesting features were the values measured for the

**Figure 1.** Electron micrograph showing the formation of highly faceted nickel particles on TiO₂ after reduction at 350 °C.**Figure 2.** High-resolution micrograph showing the lattice fringe images of a (A) nickel crystallite sitting on the (B) edge of TiO₂.

d spacings of the support in close proximity to the nickel, which were found to be 0.332 and 0.304 nm, and can be compared with those reported for Ti₄O₇₍₁₂₀₎ of 0.338 nm and Ti₄O₇₍₁₂₂₎ of 0.302 nm, respectively. On the other hand, if one measured the *d* spacing of the support in a region remote from the metal crystallite a value of 0.323 nm was obtained, which is very close to that of 0.325 nm for TiO₂₍₁₁₀₎.

In comparison when the nickel was supported on Ta₂O₅ the shapes of the particles were not as well defined as those on the TiO₂. The typical appearance of the nickel particles that accumulated at the edges of Ta₂O₅ support material is shown in Figure 3. It is evident that the particles acquired a faceted outline that tends to follow a hexagonal geometry albeit with slightly rounded edges. A similar set of morphological characteristics was displayed by nickel particles when supported on CaTiO₃ and BaTiO₃, as shown in Figures 4 and 5, respectively, and in many respects matched those found for the Ni/Ta₂O₅ system. Examination of the particles shown in Figures 4 and 5 reveals the existence of relatively thin crystallites whose shapes appear to be somewhat hexagonal in outline. The failure to observe the growth of well-defined faceted particles in these latter three systems may be taken as an indication that in these cases, the strength of the interaction between these support materials and nickel is marginally less than that of the metal with TiO₂. If a weaker metal-support interaction existed between the two components then the particle shapes would tend to be more spherical in form, as is the situation encountered when nickel is supported on γ -Al₂O₃, as shown in the electron micrograph, Figure 6.

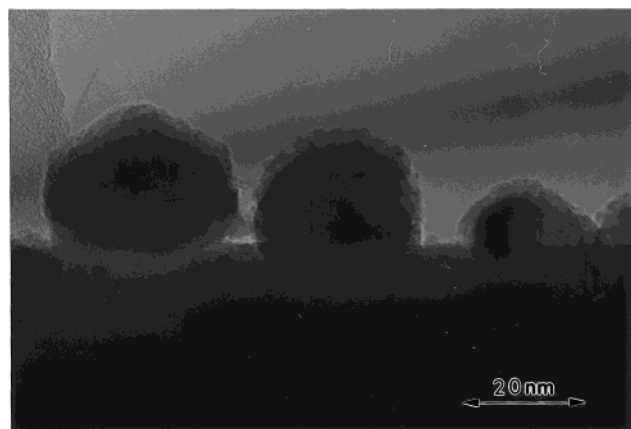


Figure 3. Electron micrograph showing the appearance of nickel crystallites when impregnated on a Ta₂O₅ support material.

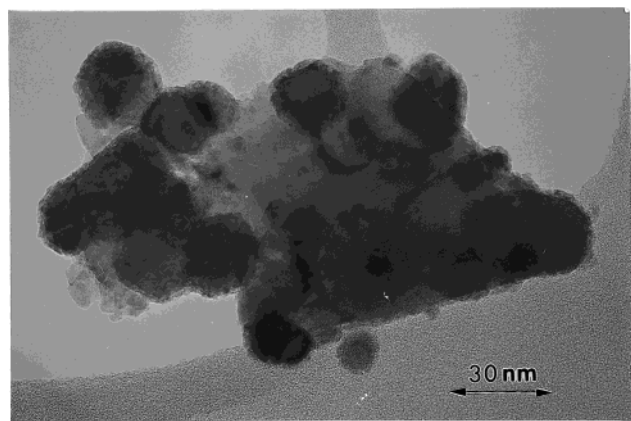


Figure 4. Electron micrograph showing the appearance of nickel crystallites when dispersed on a CaTiO₃ support material.

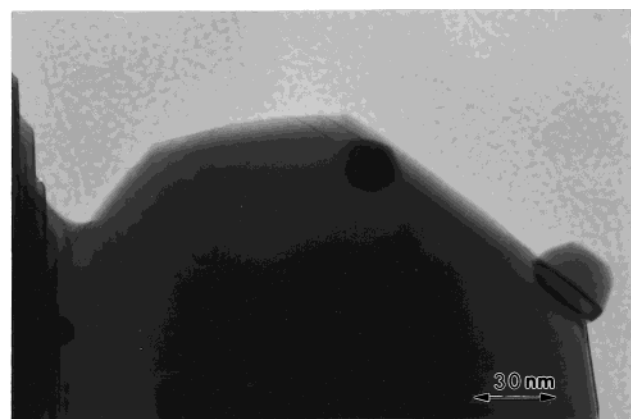


Figure 5. Electron micrograph showing the appearance of nickel crystallites when deposited on a BaTiO₃ support material.

Particle size distribution measurements of the various supported nickel catalysts are presented in Figure 7, with the weighted average particle sizes being reported in Table 2. These distributions are based on the measurements of over 300 particles in each system. From Table 2 it is clearly apparent that when nickel is supported on γ -Al₂O₃ the average particle size is substantially smaller than when the same metal loading was dispersed on the ceramic media employed in this study.

2. Flow Reactor Studies. To establish that the various oxide support media did not exert any catalytic influence on the hydrogenation reaction, blank experiments were carried out by passing ethylene/hydrogen mixtures over the respective materials for 90 min periods at temperatures ranging from 100 to 140

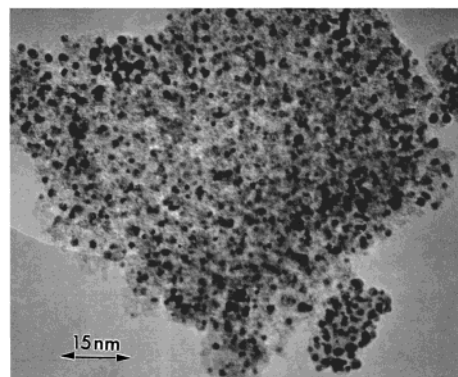


Figure 6. Electron micrograph showing the appearance of nickel particles on γ -Al₂O₃.

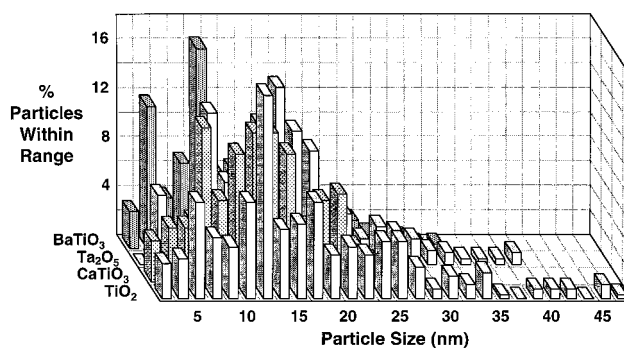


Figure 7. Comparison of the particle size distributions of freshly prepared nickel catalysts when impregnated on TiO₂, CaTiO₃, Ta₂O₅, and BaTiO₃.

TABLE 2: Comparison of the Weighted Average Particle Size of the Nickel Particles Formed on Each Support Material Used in This Investigation

5 wt % Ni/catalyst support	weighted average particle size (nm)
BaTiO ₃	8.99
CaTiO ₃	9.41
TiO ₂	11.64
Ta ₂ O ₅	11.41
γ -Al ₂ O ₃	1.60

°C. Under these conditions there was no evidence to suggest that any of the ceramic support media exhibited an ability to catalyze the hydrogenation of ethylene.

2.1. Nickel Catalyzed Hydrogenation of Ethylene. All the 5 wt. nickel/oxide catalyst systems were investigated over a wide range of temperatures in order to assess their ability to hydrogenate a simple probe molecule, ethylene. The results are summarized in Figure 8, where the percentage conversion of ethylene to ethane is plotted as function of the reaction temperature for each catalyst system. From the data presented in Table 3, it is apparent that, with the exception of the Ni/ γ -Al₂O₃ system, when the metal was supported on the various oxides the catalytic activity was observed to pass through a maximum value at specific temperatures and then exhibited a sharp decrease at higher levels. In contrast, the activity of a Ni/ γ -Al₂O₃ catalyst toward the decomposition of ethylene exhibited a steady increase as the temperature was progressively raised. In all cases, the conversion of ethylene over the supported nickel catalysts was primarily to ethane with a small amount of solid carbon being produced.

A further interesting feature of this study of ceramic media was that although the activity of nickel showed significant variations when supported on TiO₂, BaTiO₃ and CaTiO₃ at low temperatures, as the level was raised to 200 °C the conversion

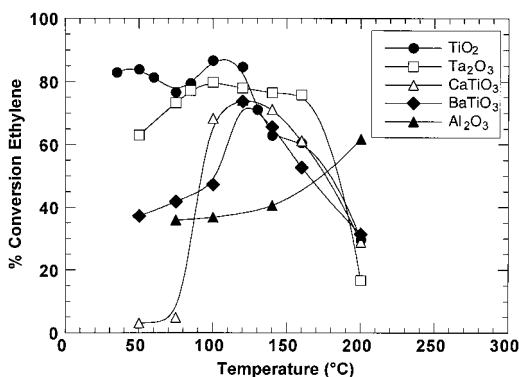


Figure 8. Comparison of the percent conversion of ethylene with respect to the reaction temperature for all the supported 5 wt % nickel catalysts.

TABLE 3. Comparison of the Measured Catalytic Activity Maximum of the Supported Nickel Systems with the Corresponding Dielectric Constants of the Various Carriers

support material	temperature at which maximum conversion is achieved (°C)	dielectric constant ϵ_r^a
BaTiO ₃	120	7000
CaTiO ₃	120	170
TiO ₂	100–140	104
Ta ₂ O ₅	100–140	40
γ -Al ₂ O ₃		10

^a Values for the dielectric constants are taken from refs 25, 56–59.

of ethylene was almost identical on all these catalysts. It is evident, therefore, that any influence that a particular ceramic material exerted on the catalytic behavior of the metal particles apparently was negated by increasing the temperature to 200 °C or higher. The observed promotional effect must be deemed to be very subtle in nature and only effective over a very limited temperature range.

Discussion

Previous studies using graphite nanofiber supported nickel catalysts demonstrated that the crystallographic orientation adopted by the impregnated metal particles was a more important factor in determining the catalyst activity and selectivity for hydrocarbon hydrogenation reactions than the particle size.^{21–23} In the current investigation we have found that when nickel was supported on γ -Al₂O₃ a much smaller average particle size (1.4 nm) was achieved compared to those obtained from the same metal loading on the various ceramic support media (9 to 12 nm) as listed in Table 2. The existence of such a large difference in average metal particle sizes on these oxide supports can be directly correlated to the respective surface areas of each material as shown in Table 1. Since this substantial difference in metal dispersion is not reflected by a corresponding trend in catalytic activity it is clear that other factors must be responsible for dictating the performance of the supported nickel particles.

It has been argued that the relative strength of a metal–support interaction could be gauged from the morphological characteristics adopted by the particles when dispersed on the surface of the material.^{40–42} The existence of a strong metal–support interaction is believed to result in a wetting and spreading action of the metal species on the surface of the support to generate thin flat crystallites, frequently referred to as “pillbox” structures. In sharp contrast, under conditions

where the interaction between the two components is relatively weak, one would predict that the metal particles would acquire a globular geometry. It should be appreciated, however, that this set of diagnostics does not always hold for all titania supported metal systems. Many metals, including Ir, Pd, and Rh, when supported on TiO₂, do not appear to wet the support, but the behavioral patterns of such systems are consistent with the existence of a strong interaction between the two components.^{42,43} Therefore a degree of caution must be exercised when making comparisons between various supported metal catalyst systems.

There is a general consensus that in supported metal catalyst systems the formation of thin flat faceted particle morphology is indicative of the existence of a strong interaction with the support.⁴⁴ On the basis of these criteria, one may conclude that of the systems examined in the current investigation, the Ni/TiO₂ exhibits the strongest metal–support interaction, since electron microscopy studies showed that the metal crystallites adopted a thin hexagonal-shaped geometry. This finding is consistent with the reports by other workers, using similar TEM techniques, who found that when metals such as nickel and platinum, were dispersed on TiO₂, the particles acquired thin well-defined morphological characteristics.^{40,45}

Examination of the nickel particles dispersed on the CaTiO₃ and BaTiO₃ substrates showed that while a thin hexagonal morphology was attained, many of the crystallites tended to possess slightly rounded corners and edges, features associated with the existence of a degree of atomic mobility within the metal. As a consequence, it is reasonable to assume that the strength of the metal–support interaction in these systems was not as strong as that encountered with Ni/TiO₂. Finally, it was evident that when Ta₂O₅ was utilized as a support material a significantly weaker metal–support interaction is observed. In this case the particles tended to adopt a somewhat more globular form.

Temperature programmed oxidation and reduction experiments and X-ray diffraction analysis failed to indicate the existence of any significant chemical changes in the bulk state of the various ceramic support media under the conditions used in the current studies. It is important to be aware, however, that at higher reduction temperatures the formation of a reduced titania species is known to take place and this process results in the creation of mobile TiO_x species that have a tendency to diffuse onto the metal particle surfaces, thereby inducing extensive changes in the catalytic behavior of the system.^{18–20} On the other hand, high-resolution TEM examination of a Ni/TiO₂ specimen that had been reduced in hydrogen at 350 °C demonstrated that the surface regions of the support in close proximity to the metal crystallites had undergone reduction to form Ti₄O₇. Under these circumstances it is possible that the reduction of the support arises from interaction with atomic hydrogen species generated from the dissociation of molecular hydrogen on nickel.^{18,46} This subtle change in the chemical characteristics of the support surface in the vicinity of nickel is unlikely to exert any effect on either the TPO/TPR or XRD data, since these techniques would only indicate modifications in the bulk state.

The hydrogenation of a simple molecule, such as ethylene, over selected ceramic supported nickel catalysts produced some extremely interesting results. Inspection of the data presented in Table 2 and Figure 1 shows that the nature of the support material and the reaction temperature plays a critical role in determining the catalytic behavior of the nickel particles. The nickel catalyzed hydrogenation of ethylene was observed to pass through a maximum at 120 °C when supported on either BaTiO₃

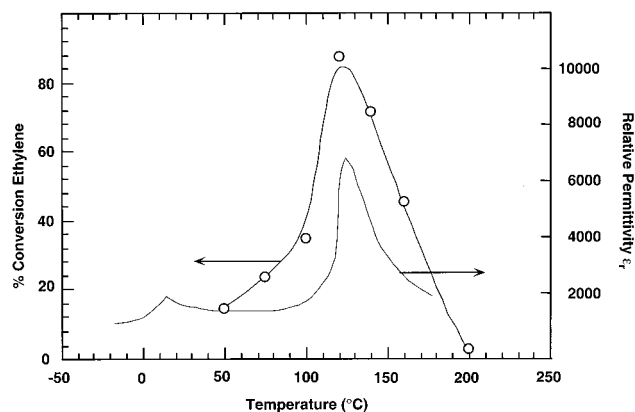


Figure 9. Comparison of the catalytic performance of Ni/BaTiO₃ for the hydrogenation of ethylene with that of the relative permittivity of the oxide as a function of temperature. This latter data is taken from ref 25.

or CaTiO₃; materials that possess perovskite structures. In this regard it is illuminating to compare the profile of the observed catalytic performance of the Ni/BaTiO₃ system with that for the relative permittivity of the support as a function of temperature, Figure 9, where it can be seen that there is a close correspondence between the two plots. At this maximum temperature BaTiO₃ is known to undergo a transition from a ferroelectric tetragonal to a para-electric cubic phase.^{25,26,47} It is significant to find that this phase transition is also accompanied by a significant increase in the relative permittivity of BaTiO₃, and under these circumstances it is reasonable to expect that when nickel is dispersed on this support medium there is the potential for major modifications to occur in the structural and electronic characteristics of the metal particles when the reaction temperature approaches 120 °C. It is highly likely that such perturbations would induce major changes in the catalytic properties of the system, a feature which was indeed observed experimentally. Similar conclusions were reached by Parravano,²⁷ who found that the activity of ferroelectric sodium and potassium niobates and lanthanum ferrite catalysts when used for the oxidation of CO increased significantly at the transition points of these materials.

The increase and subsequent decrease in the catalytic activity was not as prominent when nickel was supported on CaTiO₃. This would suggest that a lesser degree of perturbation of the metal particles occurs when supported on CaTiO₃, which is consistent with the much lower dielectric constant exhibited by this material. In contrast, the activity of nickel when supported on either Ta₂O₅ or TiO₂ did not show the same pattern of behavior as that displayed in the previous two systems. In these cases, the activity was substantially higher and more stable at low temperatures before exhibiting a sharp decrease at 120° and 160 °C, respectively. The magnitudes of the observed activity peak maxima attained by nickel supported on either TiO₂ or Ta₂O₅ were relatively small, when compared to that achieved when the metal was dispersed on BaTiO₃. Once again, this feature may be correlated to the lower dielectric constants associated with both of these oxides (Table 3).

A further contributory factor to the observed pattern of catalytic behavior is that the partial reduction of the support media is also going to exert a significant impact on the electronic properties of the dispersed metal particles as a result of electron enrichment. Under such conditions the catalytic properties of the nickel are likely to exhibit a significant perturbation due to the transfer of electrons from the reduced cation to the *d* orbitals of the adjacent metal atoms.⁴⁸

Classical studies of ethylene hydrogenation over nickel surfaces have demonstrated that the kinetic behavior can exhibit significant variations as a function of reaction conditions.^{49–51} The rate of the reaction was found to decline at high ethylene pressures⁵² and also depend on which gas was first introduced to the nickel surface.⁵³ A mechanism was proposed⁵⁴ that takes into consideration two discrete steps, one involving the associative adsorption of ethylene on a pair of metal sites and on the other, the interaction of a gas-phase ethylene molecule with an adsorbed hydrogen atom to form a C₂H₅ radical. Thomson and Webb⁵⁵ attempted to present a unifying mechanism for catalytic hydrogenation of olefins, which they claimed could be applied to all metal systems.

In the current investigation it is difficult to attribute the observed behavior of some of the oxide supported nickel particles to differences in the rate controlling steps of the ethylene hydrogenation reaction as a function of temperature. In experiments where the metal was supported on the more traditional carrier, γ -Al₂O₃, the catalytic activity was observed to exhibit a steady rise with increasing temperature. In direct contrast to the situation encountered with all other support materials used in this study the activity did not pass through a maximum. This aspect is a consequence of the relative stability of the γ -Al₂O₃ at these temperatures coupled with the absence of any phase transitions over the temperature range studied and the low dielectric constant of the oxide. In this regard it is also worth noting that when the hydrogenation of ethylene was conducted over nickel supported on graphite nanofibers, a highly electrically conductive material, no evidence of an activity maxima was found over the temperature range 100–200 °C.²³

Examination of the literature reveals the possibility of manipulating the influence of the substrate, by not only following standard semiconductor doping procedures but also by the exploitation of other tunable electrical properties that exist in dielectric and ferroelectric materials. The notion of designing a supported metal catalyst system having artificially controllable functions that can induce major improvements in the performance is an exciting prospect.

Conclusions

From this current investigation it is evident that by using materials which possess significantly different dielectric constants as support media one can induce dramatic changes in the catalytic behavior of impregnated metal particles. The most striking enhancements in the catalytic performance of nickel were observed on ferroelectric BaTiO₃ where at the Curie temperature the activity exhibit a sharp increase, which was followed by a precipitous drop when the temperature was increased to higher levels. This peak in activity is believed to be related to an electronic perturbation in the nickel particles caused by the substantial structural and electronic changes associated with a phase transition at the Curie temperature. It was interesting to find that when nickel was dispersed on materials which possess a lower dielectric constant than BaTiO₃ then similar perturbations in activity occurred, albeit at a considerably lower intensity, at temperatures which are specific to each material. It is tentatively proposed that the intensity of the perturbations induced in the metal particles by a given support material show a direct correlation with the value of the dielectric constant.

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