ETHZ granted free computer time.

Registry No. HBO_2, 13460-50-9; H_2O_2, 7722-84-1; HCOOH, 64-18-6; HC(O)OOH, 107-32-4; HC(O)OOD, 84057-56-7; DC(O)OOH, 84057-57-8; $H^{13}C(O)OOH$, 84057-58-9; $HC(^{18}O)OOH$, 84057-59-0; $HC(O)O^{18}OH$, 84082-02-0; $HC(O)^{18}OOH$, 84057-60-3; $HC(O)^{18}O^{18}OH$, 84057-61-4.

Supplementary Material Available: Listings of measured rotational transition frequencies of HCOOOH, HCOOOD, DCOOOH, $H^{13}COOOH$, $HC^{18}OOOH$, $HCO^{18}OOH$, $HCOO^{18}OH$, and $HCO^{18}O^{18}OH$ in the vibrational ground state (Table VI) (3 pages). Ordering information is given on any current masthead page.

Small-Molecule Chemisorption on $NiSi_2$: Implications for Heterogeneous Catalysis

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Contribution from Bell Laboratories, Murray Hill, New Jersey 07974. *Received July 2, 1982*

Abstract: The chemisorption of O_2, CO, CO_2, H_2, N_2, and CH_3OH on the clean (111) surface of nickel disilicide ($NiSi_2$) was studied under ultrahigh vacuum conditions. Samples were characterized by high-resolution electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) with experiments carried out between 170 and 300 K. The vibrational spectra clearly indicate that O_2, CO, and CO_2 dissociate on $NiSi_2(111)$ at 170 K. Adsorbed CH_3OH yielded only a methoxide species, even at 300 K. We found no evidence for either molecular H_2 or molecular N_2 adsorption, although atomic hydrogen is strongly bound to the silicide surface. The implications of these unusual findings with respect to both heterogeneous catalysis by supported metal particles and strong metal-support interactions (SMSI) are discussed.

It is generally accepted that of the factors which most significantly influence the performance of a catalyst (as measured by parameters such as activity and selectivity), many are "local" in origin.[1] These can be structural—steps, kinks, and other surface defects[2]—or perturbations in site geometries and local band structure due to alloying and/or compound formation.[3] The catalytic consequences of the latter processes can be both dramatic and technologically important. It is largely for this reason that there continues to be considerable interest in the characteristics of metals in unusual chemical and structural environments. While single-crystal metal and alloy surfaces have been well studied,[2,3] little attention has been given to the corresponding surfaces of intermetallic compounds. This omission is significant in that both the nature of the chemistry exhibited by these materials and their structure can be unique. For example, in recent studies on the activity of nickel-silicon intermetallic compounds as catalysts for CO hydrogenation, unusual chemisorption behavior was observed.[4,5] It was found that these materials have chemisorption properties similar to those of supported metal catalysts which are believed to be influenced by strong metal-support interactions (SMSI).[6] The origin of the SMSI effect, an abnormally low activity for both CO and H_2 chemisorption, is unknown at present. It has been postulated by Tauster[6] and others[7] that SMSI, induced by the high-temperature reduction of supported metal salts, *may* be the result of intermetallic compound formation. Thus, data on the chemistry of well-characterized intermetallic compound surfaces would address several important issues in catalysis by transition metals.

In this paper we describe a detailed study of the chemisorption properties of a well-ordered, single-crystal (111) surface of nickel disilicide ($NiSi_2$). This material is easily prepared[8] and is characterized by an unusual structure in which coordinately unsaturated nickel surface atoms are bonded *only* to silicon nearest neighbors. The chemisorption properties of nickel in this material, with respect to small adsorbate molecules (H_2, O_2, N_2, CO, CO_2, CH_3OH) incapable of bridging between Ni atoms, is found to be dramatically different from that of bulk metal. The implications of these findings with respect to heterogeneous catalysis by supported metal particles is discussed.

Experimental Section

$NiSi_2$ samples were grown epitaxially on highly polished and etched Si(111) single crystal wafers. In a typical preparation, nickel was electron beam evaporated onto the substrate at a pressure of the order of 10^{-7} torr to a film thickness of 1200 Å. Vacuum-annealing ($\lesssim 10^{-7}$ torr) at 573 K for 30 min produced a polycrystalline Ni_2Si film, while further annealing at 1073 K resulted in the growth of an epitaxial disilicide.[9] Previous studies have shown that comparable procedures produce well-ordered, stoichiometric surfaces.[9]

Our analysis is based primarily on data obtained by high-resolution electron energy loss spectroscopy (EELS).[10,11] In this technique a collimated beam of monoenergetic electrons (1-10 eV incident energy, 5-10 meV, or 40-80 cm^{-1} full width at half-maximum) is scattered from a crystal surface and the energy distribution of the specularly reflected beam recorded. The incident electrons excite surface vibrational modes (surface phonons, adsorbate and adsorbate-substrate vibrations) and therefore lose energy corresponding to the frequency of the vibration involved. Both theory and experiment have shown this inelastic scattering process to occur by a long-range electron-dipole interaction.[11] Due to the nature of this interaction and to the high dielectric constant of the substrate, the incident electrons will couple only to vibrations which are perpendicular to the sample surface. This orientational selection rule greatly simplifies the interpretation of the observed spectra.

All experiments were carried out in an ultrahigh vacuum chamber (diffusion and titanium-sublimation pumped) with a base pressure near 1×10^{-11} torr. The system was equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), ion sputtering, as well as for high-resolution electron energy loss spectroscopy. The design of the high-resolution EELS spectrometer is similar to that described by

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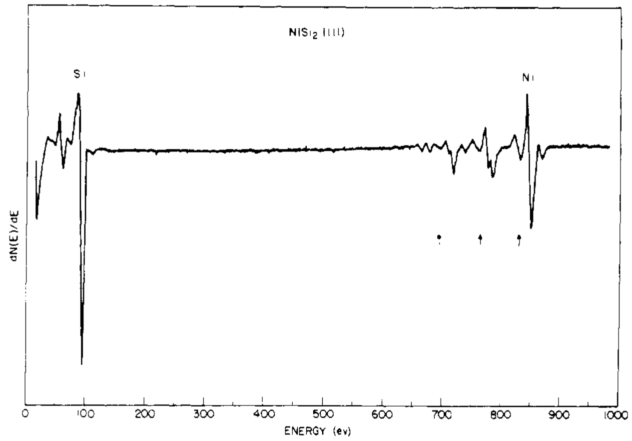
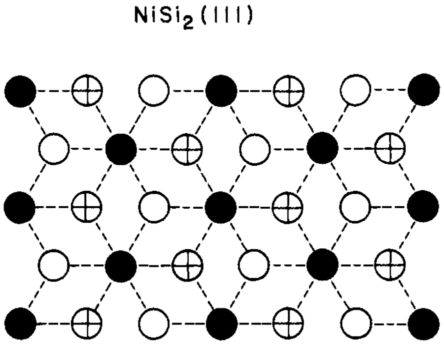
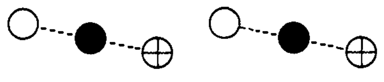


Figure 1. Auger electron spectrum of clean $NiSi_2(111)$ shows a Ni (848 eV) to Si (92 eV) peak-to-peak ratio of 0.47 ± 0.02. There is no evidence for sulfur (152 eV), carbon (272 eV), or oxygen (~505 eV) contamination. The arrows in the Ni LMM region of the spectrum point to features which are not observed on clean nickel surfaces.



(a) Top View



(b) Side View

Figure 2. Structure of the silicon-terminated surface of $NiSi_2(111)$ shows that each nickel atom (●) is surrounded by a hexagon of surface silicon atoms. Each silicon atom is tetrahedrally coordinated and one is located above (○) and the other below (⊕) the plane of the nickel atoms. There are no Si–Si bonds in the idealized crystal structure.[13]

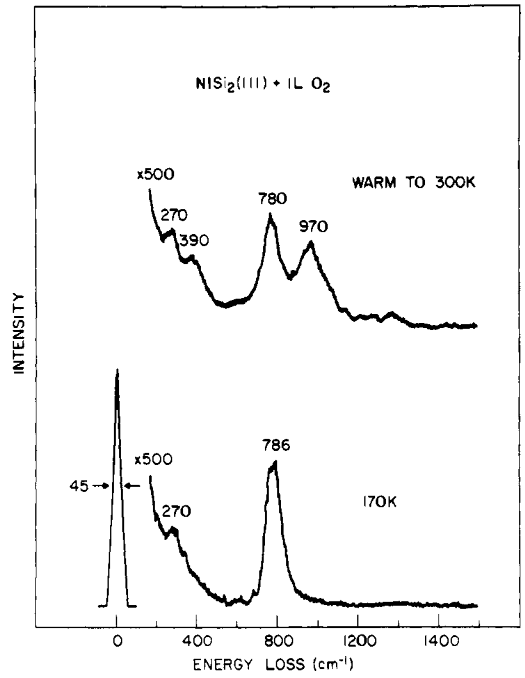


Figure 3. High-resolution EELS spectra of a clean $NiSi_2(111)$ surface exposed to 1 L of O_2 at 170 K (lower trace) and allowed to warm slowly to 300 K (upper trace) clearly show only atomic oxygen adsorption. The mode assignments are discussed in the text. A 1-L O_2 exposure corresponds to approximately saturation coverage.

Sexton.[12] For these experiments, the angle of the incident electron beam (60° to the surface normal) and its energy (5–6 eV) were held constant; electrons were collected only in the specular direction. The elastic scattering peak from a clean silicide surface had a maximum intensity near 1×10^5 counts sec^{-1} and a full width at half-maximum (fwhm) between 40 and 80 cm^{-1}. Scattering from an adsorbate-covered surface reduced the total intensity by as much as an order of magnitude and increased the width of the elastic peak up to 100 cm^{-1} in several cases.

Results

Clean Surface: Auger and LEED Studies. Clean $NiSi_2(111)$ samples were prepared by argon ion bombardment (1000 eV at ~10 $\mu A/cm^2$ for 3 min) followed by annealing at 1150 K (temperature measured at a tantalum foil pressed against the rear of the sample) for 20 min to remove any surface damage. Auger electron spectroscopy (Figure 1) showed only nickel and silicon present on the surface with no evidence of carbon, oxygen, or sulfur impurities. Clean samples had a nickel (848 eV) to silicon (92 eV) peak-to-peak ratio of 0.47 ± 0.02. The small arrows in the right portion of Figure 1 point to features in the nickel LMM region of the Auger spectrum which are not found on pure nickel samples; the origin of these peaks is not completely understood.

Bulk $NiSi_2$ has the CaF_2 structure with a lattice constant (5.40 Å)[13] well matched to that of silicon (thus promoting the growth of a highly oriented, monocrystalline epitaxial film).[9] Low-energy electron diffraction patterns of the clean (111) disilicide showed only integral order spots at all energies (20–200 eV), with low background intensity. A real space drawing of this surface is shown in Figure 2a. The nickel disilicide film consists of Si–Ni–Si triple layers (Figure 2b) and is drawn as silicon terminating, although we have no conclusive evidence for this. We believe this to be the most chemically reasonable type of surface termination, however. Although the surface terminates in a ridged structure, the lack of extra diffraction features in the LEED pattern indicates that no major surface reconstruction occurs. Figure 2a shows that each nickel atom is surrounded by a hexagon of surface silicon atoms, but as clearly shown in 2b, these silicon atoms are of varying heights. Each nonsurface silicon atom is tetrahedrally coordinated and bonded only to adjacent nickel atoms. The isolated, coordinately unsaturated nickel atoms and the textured surface may account for some of this material's unique chemisorption properties (see below).

Adsorption of Oxygen. The initial sticking probability of O_2 on clean $NiSi_2(111)$ at 170 K is near unity. A high-resolution EELS spectrum of 1 L (1 L = 1 langmuir = 10^{-6} torr sec) of oxygen chemisorbed on this surface at 170 K is shown in the lower trace of Figure 3. A single energy loss peak and shoulder are visible at 786 and ~270 cm^{-1}, respectively. The low-frequency shoulder is due to an intrinsic $NiSi_2$ surface phonon and is seen in all spectra. The nature of this mode is discussed in detail elsewhere.[14]

Although molecular oxygen chemisorption on metal surfaces is known to take place at low temperatures ($T \lesssim 150$ K),[10] the 786-cm^{-1} energy loss cannot be due to an undissociated species for three reasons. First, this peak is also observed at 300 K (see Figure 3, upper trace) where a dioxygen species should not be stable. Second, the substrate-oxygen stretch (expected to be between 300 and 500 cm^{-1})[10] is missing. Finally, a similar peak

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arises from the dissociative chemisorption of both carbon monoxide and carbon dioxide, as well as from the chemisorption of methanol on this surface (see below).

We assign the loss at 786 cm^{-1} to the surface–oxygen stretch of an atomically adsorbed species. The assignment of this species to a specific surface site is difficult; however, three possibilities exist: (1) the adsorbed oxygen is bonded only to nickel; (2) the adsorbed oxygen is bonded only to silicon; (3) the adsorbed oxygen is bridge bonded to both nickel and silicon. We can easily rule out the first possibility since the mode at 786 cm^{-1} is much too high in frequency to be a simple Ni–O stretch (ν_{NiO}(gas phase) = 615 cm^{-1}).[15] The second possibility is equally unrealistic as this mode is far too low in frequency to be either a linear SiO (ν_{SiO}(gas phase) = 1230 cm^{-1})[15] or a bridged Si_2O(ν_{Si_2O} = 1100–1200 cm^{-1})[16] species. It is known that the sticking probability of molecular oxygen on clean silicon is quite low,[17] further indicating that nickel atoms must be intimately involved in the bonding. This leaves the third possibility, in which the adsorbed oxygen atoms interact with both nickel and silicon. Recent electronic structure calculations on bulk $NiSi_2$ suggest significant charge accumulation along the nearest neighbor nickel–silicon directions,[18] further supporting the placement of these adsorbed species at bridged Ni–Si sites. Finally, it is interesting to note that high-resolution EELS studies of oxygen chemisorption on Pt(111),[19] where there is a high probability of silicon contamination,[20] show a single, intense vibrational band at 760 cm^{-1}.

When an oxygen-covered surface is allowed to warm slowly to 300 K (overnight), the spectrum in the upper trace of Figure 3 is obtained. Two additional features at ~390 and ~970 cm^{-1} are observed. These bands are most likely associated with oxygen atoms bridge-bonded to two silicon neighbors:[17] the 970-cm^{-1} peak is believed to be the symmetric Si_2–O stretch and the 390-cm^{-1} peak the low frequency bending mode for this species. Both vibrations are of A_1 symmetry[16] and are therefore dipole allowed. The asymmetric stretching vibration (B_1 symmetry and approximately parallel to the surface) is expected to lie between 750 and 850 cm^{-1}. This peak (which should be quite low in intensity) may be obscured by the strong 780-cm^{-1} mode resulting from the low-temperature chemisorption of oxygen. A similar vibrational spectrum (387, 726, and 1008 cm^{-1}) for O_2 chemisorption on Si(111) has been reported previously by Ibach,[17] further supporting the suggested assignments.

It is interesting to note that the kinetics of formation of the stable oxygen species are quite slow. Warming an oxygen-covered surface to room temperature does not, in itself, produce the two new energy loss features; these peaks appear only after the sample has been held at 300 K for several hours. It should be emphasized that the 390- and 970-cm^{-1} modes are not due to the adsorption of background impurities since allowing either a warm or cold silicide surface to sit for several hours in the vacuum system did not produce new energy loss peaks.

LEED studies of the chemisorption of oxygen on $NiSi_2$(111) at both 170 and 300 K showed no evidence for ordered overlayer formation. We also found no evidence for ordered overlayer formation with any of the adsorbates studied. This is not too surprising since, due to the large substrate unit cell, adsorbate–adsorbate interactions, which are generally required for ordered overlayer formation,[2] will be minimized. Electron-stimulated desorption and/or disordering may be playing a more crucial role, however, since all of the adsorbates studied were extremely sensitive to the electron beam. Attempts at measuring good quality vibrational spectra after looking for LEED patterns (~1 μA incident beam current at 25–100 eV for several seconds) or recording an Auger spectrum (5μA incident beam current at 3 kV for ~6 min) were consistently unsuccessful. Because of this sensitivity to the electron beam, the absence of ordered overlayers cannot be rigorously concluded. Despite the adsorbate sensitivity to low-energy electrons, the high-resolution EELS spectrometer is unlikely to be causing the observed reactivity since incident beam currents and voltages are on the order of 10^{-10} A and 5 eV, respectively.

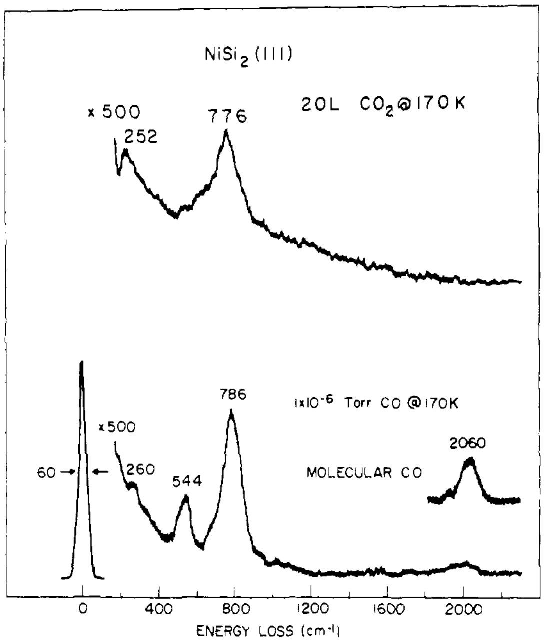

Figure 4. Vibrational spectra of carbon monoxide chemisorbed on $NiSi_2$(111) at 170 K show both molecular (insert) and dissociative (lower trace) adsorption. The dissociative chemisorption of carbon dioxide on this surface is shown in the upper trace.

Adsorption of Carbon Monoxide and Carbon Dioxide. Molecular chemisorption of carbon monoxide on $NiSi_2$(111) is difficult to detect even at low temperatures. After exposure of a clean silicide surface to 1 × 10^{-6} torr of CO at 170 K, a weak energy loss feature centered at 2060 cm^{-1} is observed (see insert to lower trace of Figure 4). The frequency of this mode is characteristic of linearly bonded, molecular CO with the carbon coordinated to a single nickel atom[21] (carbon monoxide is not known to bond to silicon). The low-frequency (400–500 cm^{-1}) Ni–C stretching vibration for this species could not be detected.

The band at 2060 cm^{-1} disappears at this temperature on the order of minutes and the spectrum in the lower trace of Figure 4 is obtained. Two new energy loss peaks are observed at 544 and 786 cm^{-1} as well as the $NiSi_2$ surface phonon at ~260 cm^{-1}. This new spectrum did not change over a period of several hours at 170 K. The presence of the two new low-frequency modes and the lack of any bands near 2000 cm^{-1} strongly indicate that CO chemisorbs dissociatively. Auger electron spectroscopy shows that both the carbon and oxygen atoms remain on the surface. We assign the 786-cm^{-1} mode to the surface–oxygen stretch on the basis of and in agreement with the data obtained for oxygen chemisorption. The 544-cm^{-1} mode is assigned to adsorbed carbon. This latter species is also likely to be bridge bonded, as gas-phase diatomic carbides typically have vibrational frequencies near 1000 cm^{-1}.[15] On warming to 300 K, a new band at ~938 cm^{-1} slowly grows into the spectrum, consistent with the presence of an atomic oxygen species on the surface.

We note that the best quality (highest intensity, narrowest peaks) vibrational spectra were always obtained with a background pressure of CO in the chamber. Due to electron–gas collisions inside the spectrometer, pressures were kept below a few ×10^{-6} torr. Lowering the surface temperature further would no doubt

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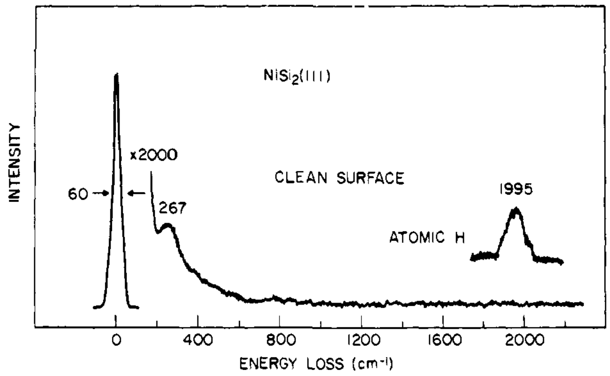

Figure 5. Clean $NiSi_2(111)$ surface shows only a single, weak energy loss peak at 267 cm^{-1}. Exposure of this surface to >1000 L of either molecular H_2 or N_2 also shows only a single peak. When $NiSi_2$ is exposed to atomic hydrogen between 170 and 300 K (insert), however, a new mode characteristic of singly bonded hydrogen is observed.

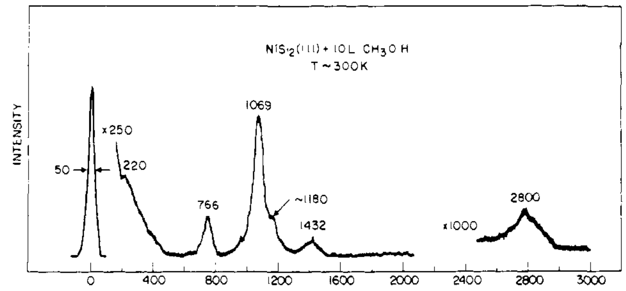

Figure 6. Adsorption of 10 L of methanol on $NiSi_2(111)$ at 300 K results in the formation of a surface methoxide. An identical spectrum is obtained by exposing the clean $NiSi_2(111)$ surface to CH_3OH at 170 K and allowing the sample to warm slowly to 300 K. The mode assignments are discussed in the text.

help to stabilize the observed species. Thus despite the low sticking probability of molecular CO on this surface, it appears that, once absorbed, dissociation is a facile process.

The dissociative chemisorption of carbon dioxide on $NiSi_2(111)$ was also observed. The upper trace of Figure 4 shows a spectrum of a 20-L CO_2 exposure (saturation coverage) with the sample temperature at ~160 K. The two peak spectrum (252 and 776 cm^{-1}) is almost identical with that for adsorbed oxygen (except for the tailing of the mode at 776 cm^{-1} to lower energies) and indicates that oxygen atoms are present on this surface. It should be emphasized that this surface oxygen does not originate from O_2 or water vapor present either as impurities in the inlet gas stream or as a result of displacement from the walls of the vacuum chamber. In situ mass spectroscopic analysis showed that the sum of all mass 32 and mass 18 species present was less than 1 part in 10^4 of the parent CO_2 peak (mass 44). On geometric grounds we can also rule out the importance of cracking of CO_2 to CO and atomic oxygen on the ionization gauge filaments as a source of reactive oxygen: the ions (or atoms) would have to make numerous collisions with the walls of the chamber, the spectrometer, etc., before impinging on the front surface of the sample. Furthermore, no such effects have been seen in other systems or on other samples where both molecular CO and oxygen have high sticking probabilities. Both AES and high-resolution EELS show, at most, trace amounts of residual carbon adsorption, and we can therefore rule out the total decomposition of CO_2 to surface carbon and oxygen species. We also find no evidence for molecular CO adsorption. This latter result is not too surprising inasmuch as the binding energy of the molecular species is low. In addition, the adsorbed oxygen atoms may be blocking the sites on which molecular CO adsorption and decomposition occur.

Hydrogen and Nitrogen. We find no spectroscopic evidence for either hydrogen or nitrogen chemisorption on $NiSi_2(111)$. The lower trace of Figure 5 shows a vibrational spectrum of a clean disilicide surface at 170 K. Only a single loss corresponding to the excitation of a $NiSi_2$ surface phonon is observed. Exposing this sample to >1000 L of either H_2 or N_2 between 170 and 300 K causes no changes in the observed spectrum. Although the sticking probability of hydrogen on clean nickel surfaces is quite high, previous high-resolution EELS studies have shown that molecular hydrogen does not chemisorb on clean silicon.[22] Molecular nitrogen is also not known to chemisorb on either nickel or silicon surfaces. The absence of adsorbed nitrogen (either molecular or atomic) on NiSi(111) was further confirmed by Auger electron spectroscopy.

Filling the ultrahigh vacuum chamber with 5×10^{-5} torr of H_2 and placing the sample in front of the mass spectrometer filament during the degassing procedure caused the growth of a new energy loss feature at 1995 cm^{-1} (insert in Figure 5). The filament both ionizes and atomizes hydrogen, exposing the surface to a variety of species including H_2^+, H^+, and H. This latter species is known to chemisorb strongly on a number of clean surfaces which are unreactive toward H_2.[22,23] We can conclude on the basis of the high frequency of this adsorbate mode that hydrogen atoms bonded to a single substrate atom are produced in this procedure. This species is most likely SiH since the corresponding gas phase diatomic molecule has a Si–H stretching vibration at 1971 cm^{-1}.[15] We cannot completely rule out that the chemisorption of hydrogen on coordinately unsaturated nickel may also be occurring under these conditions. Diatomic nickel hydride is known to have a stretching frequency of 1851 cm^{-1}.[15] Careful examination by high-resolution EELS showed no evidence of a lower frequency mode which might be ascribed to such a species. We also find no evidence for adsorbed molecular hydrogen (ν_{HH}(gas phase) = 4159 cm^{-1}).

Similar experiments to activate molecular nitrogen were not attempted.

Adsorption of Methanol. The observation of dissociative chemisorption of CO, O_2, and CO_2 on $NiSi_2(111)$ might lead one to expect the decomposition of methanol to adsorbed carbon, oxygen, and hydrogen on this surface. This is not the case, however. Clean $NiSi_2(111)$ surfaces, when exposed to ~10 L of CH_3OH at either 300 K or at 170 K (giving a layer of physisorbed methanol) and slowly warmed to ambient temperature, yield identical vibrational spectra (Figure 6). In close analogy with the low-temperature adsorption of CH_3OH on Ni(111),[24] Cu(100),[25] and Pt(111),[26] we can assign this spectrum to a surface methoxide species: the low-frequency shoulder at ~220 cm^{-1} is the intrinsic $NiSi_2$ surface phonon; the band at 766 cm^{-1} is the substrate–oxygen stretch, downshifted as a result of the larger reduced mass of the methanol moiety; the intense mode at 1069 cm^{-1} is the C–O stretch; the band at 1437 cm^{-1} is a CH_3 deformation; the broad loss feature centered at ~2800 cm^{-1} contains both the symmetric and asymmetric CH_3 stretching vibrations. The origin of the shoulder at ~1180 cm^{-1} is unclear but may be associated with adsorbed hydrogen.[26] No evidence for an O–H stretch between 3200 and 3600 cm^{-1} was detected. Methanol has a very high initial sticking coefficient on $NiSi_2(111)$ at 300 K and this surface is saturated with methoxide at a 10-L gas exposure.

The orientation of this species with respect to the surface is unknown. We can conclude, however, on the basis of the similarity of the substrate–oxygen stretches, that adsorbed methoxide and atomic oxygen bond to the surface in similar sites.[24-26]

Discussion

In Table I we compare the chemisorption of a number of small molecules on $NiSi_2(111)$, Ni(111), Ni/SiO_2, and Si(111) surfaces (albeit under a variety of conditions). All of the cited experiments were performed with either high-resolution EELS or infrared

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Table I. Small-Molecule Chemisorption on $NiSi_2(111)$, Ni(111), Ni/SiO_2, and Si(111)

adsorbate	$NiSi_2(111)^a$	Ni(111)	Ni/SiO_2 [b]	Si(111)
O_2	O	O^c	O	O
CO	C + O	CO^d	CO	
CO_2	O + CO(g)		CO_2 [f]	
H_2		H^c	H	
N_2			N_2 [f]	
CH_3OH	CH_3O + H	$CH_3O + H \rightarrow$ CO, O^e	CO, H	

[a] This work. [b] Reference 27. [c] Reference 28. [d] Reference 29. [e] Reference 24. [f] Physisorbed at low temperature.

spectroscopy. These studies clearly establish that the surface chemistry of nickel in $NiSi_2$ differs substantially from that observed on the surface of the bulk metal. The trends exhibited by these differences are particularly interesting in that they simultaneously represent both a decreased and an increased reactivity of nickel. The most striking feature of the chemisorption data is the reactivity of the surface toward carbon monoxide and carbon dioxide.

CO binds, without exception, to all nickel surfaces under the conditions employed in this study as the molecular species (heat of adsorption ~28 kcal/mol on bulk Ni).[2] In stark contrast, molecular CO interacts only weakly with $NiSi_2(111)$. Once bound, however, dissociation to atomic carbon and oxygen occurs in a facile reaction. It is this particular process which is highly uncharacteristic of nickel and other group 8 metal surfaces. Indeed, most documented cases of dissociative CO chemisorption involve surfaces of the early transition metals.[2] This analogy between the chemistry observed on $NiSi_2(111)$ and on the surfaces of early transition metals is not a rigorous one. These latter surfaces are known to be very active in the dissociation of both molecular hydrogen and molecular nitrogen.[2] No such reactivity is seen for this system.

It is unclear whether the coordinately unsaturated silicon nearest neighbors present on this surface assist in the dissociation of carbon monoxide. In general, clean silicon surfaces are not known to react with CO or other common adsorbates at these temperatures. While the precise bonding geometries of the carbon and oxygen fragments generated are unknown (LEED does not indicate an ordered overlayer), Figure 4 provides clear evidence for the occupation of bridged Ni–Si sites.

The disproportionation of carbon dioxide to CO and chemisorbed oxygen is equally unusual. As with CO, oxygen extrusion from this normally "unreactive" adsorbate is extremely facile. On the basis of the arguments developed above, we infer that this reaction occurs on the same sites as those responsible for CO and O_2 dissociation.

Given the remarkable activity of this surface for dissociating both CO and CO_2, it is somewhat surprising to find that methanol adsorbs as a stable alkoxide. Although methoxide formation is known to take place in the chemisorption of methanol on Ni(111), this species decomposes to adsorbed CO and oxygen at temperatures below 300 K. Similarly, methanol decomposition to CO and hydrogen on silica-supported nickel has also been noted.[27] In stark contrast, only physisorbed methanol was detected on $NiSi_2(111)$ under similar experimental conditions. While the underlying cause for this behavior is not immediately obvious, it suggests that both the dehydrogenation of methanol to CO and oxygen extrusion from methanol are higher activation energy processes on this surface.

Hydrogen presents another enigma. On the basis of studies of numerous homogeneous systems, single metal atom complexes are among the most efficient materials known for dissociating molecular hydrogen.[30] By analogy, single atom sites on many group 8 metal surfaces have long been considered to be similarly effective.[1,2] The inability of the isolated nickel sites in $NiSi_2$ to dissociate and coordinate hydrogen is for this reason all the more puzzling. Since the adsorption of hydrogen atoms on $NiSi_2(111)$ (H_2 predissociated on a hot filament) is both facile and strong, we infer that the low activity of this surface in H_2 chemisorption is kinetic in origin.

It is interesting to note that the low activity of $NiSi_2$ in adsorbing both H_2 and molecular CO is analogous to the behavior of supported metal catalysts exhibiting the effects of strong metal–support interactions (SMSI).[6,31] These latter systems are characterized by dramatically altered chemisorption properties and catalytic activity when compared to either a bulk metal or to a typical supported catalyst. In past discussions, the exact structure of the surfaces in materials displaying SMSI were not known. While sintering and encapsulation were tentatively ruled out as causes of the decreased chemisorption activity, the importance of compound formation could not be rigorously excluded. Our data clearly show that these effects can originate from surface compound formation. In only one regard is the reactivity of $NiSi_2(111)$ different from that of systems with SMSI, namely in its ability to dissociate CO. On the basis of the data available in the literature, it is unclear whether the earlier work could have detected such a reaction. As such, this distinction remains tentative. On the basis of the results obtained above, we feel that the importance of compound formation[32] in SMSI should be seriously reconsidered.

It is important to note that the reactions we have studied are not catalytic in nature (i.e., the surface does not "turn over"). Still, the chemistry of $NiSi_2(111)$ counters many of the simple but popular notions which have come to characterize mechanistic thinking in heterogeneous catalysis. In particular, the debate engendered over the relative importance of ensemble and electronic factors in catalysis has overly emphasized the interpretation of simple trends.[1,3] (A reaction either is or is not "site intensive". Chemically dissimilar nearest neighbors make a catalytically active metal either more or less reactive.) In $NiSi_2$, the trends observed in chemical activity relative to bulk Ni are not simple nor are they easily rationalized. The subtle interplay of geometric and electronic influences suggested by the chemistry of this system illustrates the caution which should be exercised in interpreting, mechanistically, isolated pieces of experimental data.

We will report on further studies in this area in subsequent publications.

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Registry No. $NiSi_2$, 12201-89-7; O_2, 7782-44-7; CO, 630-08-0; CO_2, 124-38-9; H, 12385-13-6; CH_3OH, 67-56-1.

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(32) We note that $NiSi_2$ represents only one type of possible compound formation; in this case, one in which the catalytically active metal is in the zerovalent state. In practice other possibilities could pertain, among these the formation of stoichiometric intermetallic oxides. The choice of $NiSi_2$ for this study is not intended to suggest any special significance for zerovalent intermetallics. Rather, we wish to illustrate that intermetallic compounds can exhibit reactivity strikingly different from that of the bulk metal, reactivity which, in many regards, is indistinguishable from that of systems exhibiting SMSI.