

Thermal Chemistry of 2-Propanol and 2-Propyl Iodide on Clean and Oxygen-Pretreated Ni(100) Single-Crystal Surfaces

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The thermal chemistry of 2-propanol and 2-propyl iodide on clean and oxygen-pretreated Ni(100) single-crystal surfaces was studied by temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and reflection–absorption infrared spectroscopy (RAIRS). 2-Propyl iodide was used as a precursor for the preparation of 2-propyl surface species, in analogy to chemistry reported for other halo hydrocarbons. Those 2-propyl groups were shown to convert to acetone on both oxygen- and hydroxide-covered Ni(100) surfaces by following a two step mechanism, starting with a facile oxygen insertion into the metal–alkyl bond. The resulting 2-propoxide surface moiety, an intermediate that can also be prepared via dehydrogenation of the hydroxyl group in adsorbed 2-propanol, is stable up to about 300 K, at which point it undergoes β -hydride elimination to acetone. Coadsorbed surface hydroxide facilitates the first oxygen insertion reaction, and surface oxygen enhances the latter conversion of 2-propoxide to acetone. Some alcohol dehydration to propene is also observed, presumably by reaction of two hydrogen-bonded alcohol molecules. These results point to the feasibility of designing nickel-based catalysts for the selective partial oxidation of hydrocarbons.

1. Introduction

The most important issue facing heterogeneous catalysis is arguably the need to improve selectivity.¹ A reaction that is highly selective toward the desired product(s) is bound to consume less reactants, minimize the need for expensive and difficult separation processes, and create less polluting byproducts. The problem of achieving acceptable selectivities is particularly acute in hydrocarbon oxidation, where thermodynamics predicts the ultimate products to be carbon dioxide and water;² selectivity toward useful partial oxidation compounds can only be accomplished via kinetic control.^{1,3} As part of our effort to enhance the basic knowledge on hydrocarbon catalytic oxidation reactions,^{4–11} here we report on the surface chemistry of 2-propanol and 2-propyl iodide (a precursor for 2-propyl surface species) on clean and oxygen-pretreated Ni(100) single-crystal surfaces.

The balance between dehydrogenation and dehydration in organic alcohols provides a classical example of the importance of controlling selectivity in catalysis: while acidic oxides such as γ -alumina are often quite active toward alcohol dehydration, basic oxides such as magnesia and calcium oxide typically promote alcohol dehydrogenation instead.^{12,13} In the context of this report, the surface reactivity of alcohols is also closely connected to that of alkyl groups on oxygen-treated substrates, because alcohols dehydrogenate easily to the same alkoxide intermediates reported to form upon oxygen insertion into the metal–carbon bonds of surface alkyl groups.^{9,14}

The reactivity of alcohols has been extensively studied by surface-science techniques on a number of metal and metal oxide surfaces.^{15–17} Most of the efforts in this direction have been focused on the conversion of methanol,^{18–28} but significant work has also been carried out with ethanol^{29–33} and heavier alcohols.^{30,34–40} The most common reactions observed during

the decomposition of alcohols under vacuum have been decarbonylation and extensive dehydrogenation, often to hydrogen and surface carbon. The mechanism of those reactions has not yet been fully determined, but the suggestion has been put forward that it may involve γ -H elimination from alkoxides to yield oxametallacycle moieties.³¹ This path is obviously not available to methanol, where direct extensive dehydrogenation at the β -position is likely.

The mechanisms involved in dehydrogenation and dehydration processes have been less discussed. Dehydrogenation of alcohols to aldehydes or ketones has been reported over a number of late transition-metal surfaces,^{16,35,38} and isotopic labeling experiments have been used to demonstrate that this reaction occurs via direct β -H elimination.^{4,41} In contrast, dehydration has been observed on some early transition metals.⁴¹ Both dehydrogenation and dehydration compete on several oxide surfaces such as TiO₂ (001)³⁴ and ZnO (0001)–Zn,³⁰ where dehydration dominates, and Cu₂O (100), where dehydrogenation prevails instead.³⁷ Changes in selectivity toward C–O bond-breaking steps may also be induced via modification of the surface,⁴² or by selection of the appropriate reactant.^{6,36,43}

Here we report on studies carried out in our laboratory to determine the steps involved in partial oxidation of alcohols and alkyl groups on nickel surfaces. It is widely believed that the catalytic conversion of alkanes requires the initial activation of a C–H bond,^{44,45} in the case of oxide catalysts presumably via an oxidative dehydrogenation,⁴⁶ and the formation of an alkyl surface group. Below, we provide evidence for the fast conversion of adsorbed alkyl moieties to alkoxide intermediates via the insertion of an oxygen surface atom into the surface–alkyl bond. Data are also presented to indicate that from that point on the catalytic chemistry of the alkyls parallels that of alcohols; as mentioned above, adsorbed alcohols dehydrogenate easily at the hydroxyl position to yield similar surface alkoxides. Additionally, our TPD experiments show that alkoxides can undergo β -hydride elimination to form ketones (or aldehydes).

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Finally, our research points to the role that both oxygen and hydroxide surface species play in facilitating the oxygen insertion and hydride elimination reactions.

2. Experimental Section

Most of the experiments reported here were conducted in an ultrahigh vacuum (UHV) apparatus described in detail in previous publications.^{47–49} Briefly, this chamber is evacuated with a turbomolecular pump to a base pressure of less than 1×10^{-10} Torr, and equipped with instrumentation for thermal programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS), and Auger electron spectroscopy (AES).

TPD data were obtained by simultaneous recording partial pressure signals for up to 15 masses in a single experiment using a computer-interfaced mass spectrometer. The quadrupole mass spectrometer used for these TPD experiments is capable of detecting masses in the 1–800 amu range, and has its ionizer located inside an enclosed compartment with 7 mm diameter apertures in its front and back for gas sampling and exit to the quadrupole rods, respectively. The sample is positioned within 1 mm of the front aperture in order to selectively detect the molecules that desorb from the front face of the crystal. Since most of the gases that desorb in this system have complex cracking patterns, the mass spectra of the main hydrocarbons expected were deconvoluted from the raw TPD traces.^{49,50} The TPD signals are reported in arbitrary units, but their intensities are referred to the same standard given by the scale bars shown at the top of each panel. A linear heating rate of 10 K/s, set by a homemade temperature controller, was used in these TPD runs. XPS spectra were taken using an aluminum anode and a hemispherical electron energy analyzer set at a constant pass energy of 50 eV, which in our instrument corresponds to a resolution of about 1.2 eV full-width-at-half-maximum. The Cu $2p_{3/2}$ at 932.7 eV, Ni $2p_{3/2}$ at 852.65 eV, and Ni $3p_{3/2}$ at 66.2 eV peaks were used for calibration of the energy scale.

Reflection–absorption infrared spectroscopy (RAIRS) experiments were performed in a second ultrahigh vacuum (UHV) chamber, also described elsewhere.^{51–53} This system is cryopumped to a base pressure below 1×10^{-10} Torr and is equipped with an ion gun for sputtering of the surface, a UTI-100C quadrupole mass spectrometer for temperature-programmed desorption (TPD), and a Bruker Equinox 55 Fourier transform infrared spectrometer for reflection–absorption infrared spectroscopy (RAIRS). The RAIRS experiments were performed by focusing the IR beam from the FTIR spectrometer through a sodium chloride window onto the sample in the UHV chamber, collecting the reflected beam after passing it through a second sodium chloride window and a polarizer, and refocusing it onto a mercury–cadmium–telluride detector. Grazing incidence was used to optimize the signal from the surface species. Either 1000 or 2000 scans, taken with 4 cm^{-1} resolution, were averaged and ratioed against spectra from the clean surface recorded immediately before dosing. All the RAIRS data were taken at sample temperatures below 100 K.

Similar sample handling arrangements were used in both experimental apparatus, where Ni(100) crystals, cut and polished using standard procedures, were spot-welded to two tantalum rods attached to a manipulator capable of cooling to liquid-nitrogen temperatures and resistively heating to above 1500 K. In each case, the crystal temperature was monitored with a chromel–alumel thermocouple spot-welded to the edge of the crystal. Cleaning of the surface by cycles of oxygen treatment,

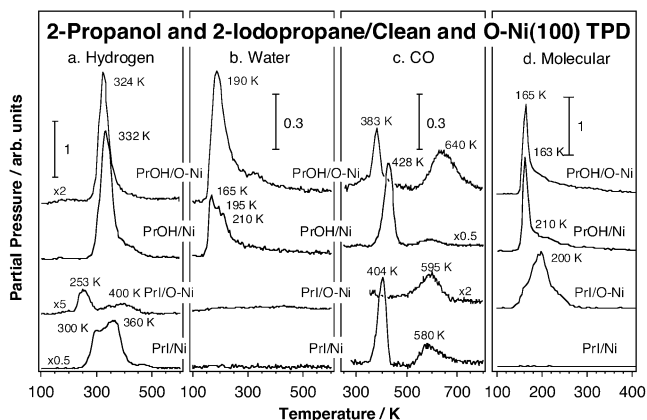


Figure 1. Hydrogen (a, left), water (b, second from left), carbon monoxide (c, second from right), and molecular (d, right) temperature programmed desorption (TPD) data for 4.0 langmuirs of 2-propyl iodide and for 5.0 langmuirs of 2-propanol adsorbed on clean and oxygen-pretreated Ni(100) single-crystal surfaces. The O–Ni surfaces were prepared by dosing 3.0 langmuirs of O_2 at 300 K, after which the hydrocarbons were dosed at 100 K. Heating rates of 10 K/s were used in all TPD experiments. Early alcohol dehydration is identified by the desorption of water (and propylene, see Figure 2) at 160 K, and extensive decomposition in all cases becomes evident by the desorption of H_2 and CO.

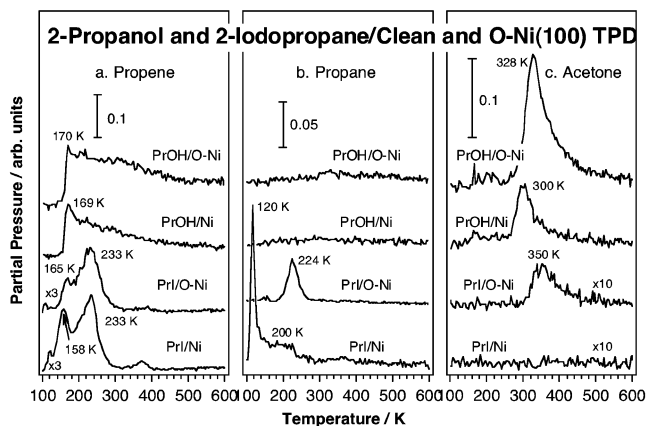


Figure 2. Propene (a, left), propane (b, center), and acetone (d, right) TPD data for 4.0 langmuirs of 2-propyl iodide and for 5.0 langmuirs of 2-propanol adsorbed on clean and oxygen-pretreated Ni(100) single-crystal surfaces. The four traces shown in each panel correspond to the same four systems reported in Figure 1. Acetone detection attests to the feasibility of dehydration steps from alcohols and partial oxidation reactions for alkyl groups.

ion sputtering, and annealing were done prior to each experiment until no impurities were detected by XPS and standard CO and/or H_2 TPD could be reproduced. The 2-propanol and 2-propyl iodide were obtained from Aldrich (99+%) and subjected to several freeze–pump–thaw cycles before being introduced into the vacuum chamber. Oxygen (99.99%) was purchased from Matheson and used as supplied. The purity of all the compounds was checked periodically by mass spectrometry. Gas doses are reported in langmuirs (10^{-6} Torr s), uncorrected for ion gauge sensitivities.

3. Results

The thermal chemistry of both 2-propanol and 2-propyl iodide on clean and oxygen-treated Ni(100) surfaces was first investigated by TPD. The data obtained for saturation coverages are reported in Figures 1 and 2. For these TPD experiments, 2-propanol and 2-propyl iodide saturation layers were obtained

by dosing 5.0 and 4.0 langmuirs of the alcohol and halo-hydrocarbon, respectively, at 100 K. The oxygen-pretreated surfaces were prepared by dosing the clean Ni(100) with 3.0 langmuirs of O₂ at 300 K, a procedure known to deposit a $c(2 \times 2)$ ordered layer of atomic oxygen on the surface.⁵⁴ A number of masses were detected simultaneously during each TPD experiment in order to identify and separate the contributions due to the different products from the raw desorption traces.

Both 2-propanol and 2-propyl iodide display fairly complex chemistry on these nickel surfaces, leading to the desorption of several total and partial oxidation products. The production of hydrogen (2 amu), water (18 amu), and carbon monoxide (28 amu), together with the traces obtained from molecular desorption (45 and 170 amu, respectively), are reported in Figure 1. In the case of 2-propanol, hydrogen desorption occurs mainly in one single peak, about 332 and 324 K for the clean and oxygen-treated surfaces, respectively (Figure 1a). These are temperatures typical for atomic hydrogen recombination,⁵⁵ and therefore do not necessarily reflect the kinetics of decomposition of the adsorbed alcohol. With 2-propyl iodide on clean Ni(100), two intense desorption peaks are seen, with maxima around 300 and 360 K. This behavior, already reported in the literature,⁵⁶ is associated at least in part with a β -hydride elimination from surface propyl groups to yield propene. Much less decomposition is manifested in the H₂ TPD from 2-propyl iodide on the oxygen-covered surface, but the initial dehydrogenation state occurs at quite low temperatures, about 253 K. A small additional amount of hydrogen desorbs in a broad temperature range centered about 400 K.

The thermal decomposition of 2-propanol also leads to the early production of significant amounts of water (Figure 1b). The water TPD traces are somewhat similar for the clean and oxygen-pretreated surfaces, although the yield appears to be a bit higher in the O–Ni(100) case. Also, there are subtle differences in the shape of the desorption feature, which displays a single peak at 190 K on O–Ni(100), but several spikes about 165, 195, and 210 K on the clean surface. Both traces do show a long high-temperature tail, probably because of the slow pumping speed for water out of the vacuum chamber. Water production in these systems is likely to be the result of a facile dehydration reaction that also produces propene (see Figure 2).^{10,17} No water desorption is seen with 2-propyl iodide.

The third panel in Figure 1 displays the results for CO desorption from the systems studied here. Carbon monoxide is detected in all cases. In general, two desorption states are identified in most traces, a low-temperature feature that peaks at 383, 428, and 404 K for 2-propanol on oxygen-covered and clean Ni(100) and for 2-propyl iodide on clean Ni(100), respectively, and a second, broader signal above 500 K (at 640, 595, 595, and 580 K) for all cases. While the low-temperature desorption has been identified in the literature with desorption of molecular carbon monoxide, the high-temperature state is associated with recombination of atomic carbon and oxygen on the surface.⁵⁷ Appreciable low-temperature decarbonylation is seen with 2-propanol, in particular on the clean surface (hence the intense signal reported in Figure 1c around 400 K for those cases), but some complete dissociation is detected as well (the reason for the high-temperature CO recombinative state). The data for 2-propyl iodide are more difficult to understand, and are likely to originate at least in part from impurities on the surface. In any case, much less CO is detected with that reactant.

Because of potential interference from background gas adsorption, a number of blank CO, H₂, and H₂O TPD experiments were carried out using conditions similar to those

employed to acquire the data reported above (data not shown). Leaving a clean Ni(100) surface under our vacuum conditions for extended periods of times leads to the adsorption of small amounts of hydrogen and carbon monoxide, as seen in subsequent TPD experiments as single peaks centered around 380 and 450 K, respectively. On the other hand, no appreciable water adsorption was ever detected under the conditions of the TPD studies. Even the hydrogen and CO adsorption amounts to less than 5 and 2% of that reported in Figure 1, respectively. The CO TPD obtained after a 5.0 langmuirs of CO dose on clean Ni(100) shows the reported asymmetric peak centered around 430 K, together with a broad leading edge, and no high-temperature desorption.^{58,59} Finally, the main effects of preadsorbing oxygen on the adsorption of background gases are a decrease in total uptake and the development of a high-temperature CO TPD peak about 780 K. It appears that the background gases do not significantly contribute to the signals in the TPD traces reported in Figure 1.

Figure 1d reports the molecular desorption traces recorded for all four cases addressed in these TPD studies. Multilayer 2-propanol desorbs from both clean and oxygen-treated surfaces in a sharp peak about 165 K, but some monolayer desorption is also seen as shoulders about 210 and 200 K, respectively. It appears that coadsorbed oxygen weakens the bonding between the 2-propanol and the nickel surface atoms. In the case of 2-propyl iodide, no molecular adsorption is detected from the clean surface (that starts above 7.0-langmuir exposures),⁵⁶ but a broad feature about 200 K is seen with O–Ni(100). Again, coadsorbed oxygen weakens the adsorption of the hydrocarbon.

Partial oxidation products were also detected in these experiments. Figure 2 displays the traces for propene (40 or 41 amu, after deconvolution of the contributions from propane, acetone, and molecular desorption), propane (44 amu), and acetone (58 amu). Extensive propene production is seen with propyl iodide on clean Ni(100), at 158 and 233 K. This is the result of a β -hydride elimination step from adsorbed propyl species, as discussed extensively elsewhere.^{60–64} Almost identical chemistry is seen on the oxygen-pretreated surface, as indicated by the similar shape and intensity of the propene TPD traces in both cases. With 2-propanol, the chemistry is again the same on clean and oxygen-covered surfaces, but with this molecule less propene is produced, and desorption starts sharply about 170 K and is followed by a long tail extending to over 400 K. This propene is likely produced by the dehydration reaction connected to the water desorption.¹¹

Propane production is only seen with 2-propyl iodide, not with 2-propanol (Figure 2b). Propyl groups can undergo a facile reductive elimination with surface hydrogen, but that is limited by the need of a source for the hydrogen (typically hydrocarbon decomposition). A sharp desorption peak is seen on the clean surface at 120 K, accompanied by a smaller and broader feature around 200 K, while a wider peak about 224 K is observed on O–Ni(100). This chemistry has already been reported previously.^{4,56} Last, small but clearly visible amounts of acetone are produced in all but the 2-propyl iodide/clean Ni(100) cases (Figure 2c). For the other three systems, acetone formation raises sharply somewhere between 250 and 300 K and then decays slowly on the high-temperature side. The acetone desorption maxima for 2-propanol on clean and oxygen-covered Ni(100) and for 2-propyl iodide on the O–Ni(100) surface are seen at 300, 328, and 350 K, respectively. It is proposed here that the same kinetics, that of β -hydride elimination from 2-propoxide surface species, apply to all three cases, and that shifts in temperature are observed because of variations in surface

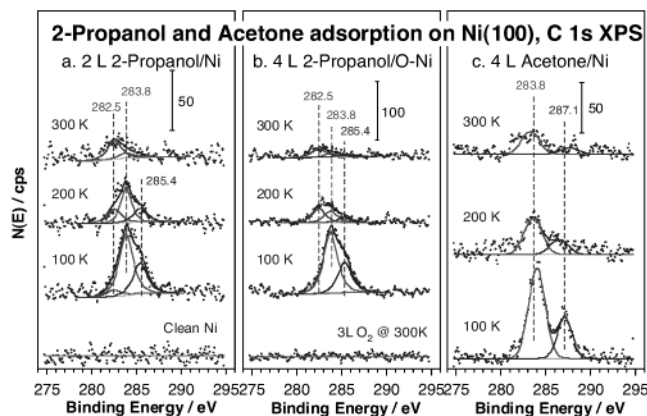


Figure 3. C 1s X-ray photoelectron spectra (XPS) for 2.0 langmuirs of 2-propanol on clean Ni(100) (a, left), for 4.0 langmuirs of 2-propanol on oxygen-pretreated Ni(100) (b, center), and for 4.0 langmuirs of acetone on clean Ni(100) (c, right) as a function of annealing temperature. Gaussian peaks were fitted to the raw data to facilitate the identification of the different surface species. 2-Propanol, adsorbed molecularly at 100 K, evolves into a 2-propoxide species, before 200 K on the oxygen-pretreated surface but only between 200 and 300 K on clean nickel.

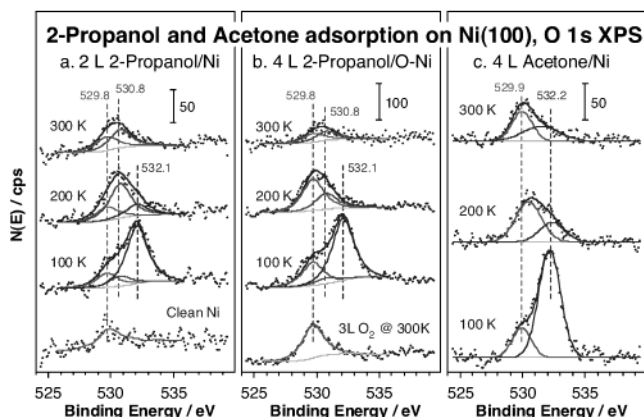


Figure 4. O 1s XPS results for the same systems reported in Figure 3. The conversion of 2-propanol to 2-propoxide is clearly indicated by the red shift of the O 1s XPS signal from 532.1 to 530.8 eV binding energy.

coverages of the reacting species.^{4–6} The mechanism for this reaction will be addressed in more detail in the Discussion.

Complementary XPS data were taken for the systems studied here. Figures 3 and 4 display the respective C and O 1s X-ray photoelectron spectra for (a) 2.0 langmuirs of 2-propanol on clean Ni(100), (b) 4.0 langmuirs of 2-propanol on oxygen-precovered Ni(100), and (c) 4.0 langmuirs of acetone on clean Ni(100), all as a function of annealing temperature. The oxygen-precovered surface was prepared by dosing 3.0 langmuirs of O₂ at 300 K, as in the TPD experiments, while all other doses were carried out at 100 K. Because of the low cross section of the O 1s and, in particular, the C 1s XPS signals, some of the spectra reported here are somewhat noisy, in particular those where the surface coverages are low. Those experiments were repeated several times to corroborate the assignments discussed below. Furthermore, the raw data were fit to Gaussian peaks to facilitate the identification of the different surface species. Once the main species were identified using the most intense spectra, the peak positions were held constant for the other traces in order to minimize the number of adjustable parameters.

The low-temperature C 1s XPS of adsorbed 2-propanol are dominated by a large peak at 283.8 eV and a second feature at about 285.4 eV binding energies. These signals are identified

with the methyl moieties and the central carbon of 2-propanol, in analogy with those reported for 2-propyl iodide on oxygen-covered Ni(100).^{6,7} The two peaks are seen for 2-propanol on both clean and oxygen-predosed Ni(100) surfaces, and also for acetone on clean Ni(100), although in this latter case at slightly blue-shifted values.⁴ Heating adsorbed 2-propanol to 200 K decreases the XPS signals corresponding to the molecular species and leads to the growth of a new feature about 282.5 eV binding energy, which fully develops by 300 K on the clean surface. Such low value is typically associated with surface atomic carbon^{65,66} and argues for extensive decomposition of the adsorbed alcohols at high temperatures. Notice, however, the residual signal at 283.8 eV, most likely due to the persistence of some 2-propoxide intermediates on the surface up to 300 K. The C 1s XPS traces for the clean and oxygen-predosed surfaces are provided in Figure 3 for reference. Despite the low signal-to-noise ratio of the 300 K XPS data, clear features are observed there above the levels displayed in the blank experiments.

The corresponding O 1s XPS data, shown in Figure 4, add to the information gathered from the C 1s XPS results. The spectra for 2-propanol adsorbed at low temperatures is dominated by a peak at 532.1 eV, a value somewhat lower than that reported for adsorbed ethanol.¹⁰ In the case of the oxygen-precovered Ni(100), a clear peak is also seen at 529.8 eV for the surface atomic oxygen⁶⁷ (a small peak is detected there when starting from clean Ni(100), perhaps because of the presence of some subsurface oxygen). Heating up the 2-propanol adsorbed on either clean or oxygen-precovered surfaces to 200 K results in the disappearance of virtually all the signal around 532.1 eV binding energy. This is because of both molecular desorption of some of the adsorbed 2-propanol and dehydrogenation of the rest to 2-propoxide surface intermediates. Dehydrogenation of chemisorbed alcohols at the hydroxyl position to form a surface alkoxide is a facile and well-documented reaction,^{17,68,69} and our O 1s XPS value is consistent with that assignment.¹⁰ Nevertheless, the production of surface OH groups cannot be ruled out,⁷⁰ especially on the oxygen-covered surface.^{71,72} In any case, most of the oxygen associated with hydrocarbons deriving from 2-propanol conversion is gone by 300 K, so adsorbed O and OH are the majority species left on the surface. No adsorbed acetone from 2-propanol decomposition is ever detected (compare the data in parts a and b of Figure 4 with those in part c), but this is not surprising given its low binding energy: molecular acetone desorption from Ni(100) is seen at temperatures as low as 135 K.⁴

Last, the thermal chemistry of 2-propanol and 2-propyl iodide on Ni(100) was characterized by reflection–absorption infrared spectroscopy (RAIRS). The key results from those studies are summarized in Figures 5 and 6, respectively, and the appropriate vibrational assignments are provided in Tables 1–3. Figure 5 shows RAIRS data for 4.0 langmuirs of 2-propanol adsorbed on clean (left panel) and oxygen-pretreated (3.0 langmuirs O₂ at 300 K, right panel) Ni(100) surfaces, initially dosed at 100 K (bottom traces) and after annealing to 200 (middle) and 300 (top) K.

Adsorption of 2-propanol at liquid nitrogen temperatures is molecular on both clean and oxygen pretreated surfaces. The vibrational assignments in those cases were easily made by comparison with liquid 2-propanol⁷³ and with 2-propanol multilayers condensed on a Cu(100) surface,⁷⁴ and are summarized in Table 1. The strongest IR absorption bands are associated with the rocking (956, 1130, and 1166 cm^{−1}), symmetric deformation (umbrella mode, 1366 and 1382 cm^{−1}),

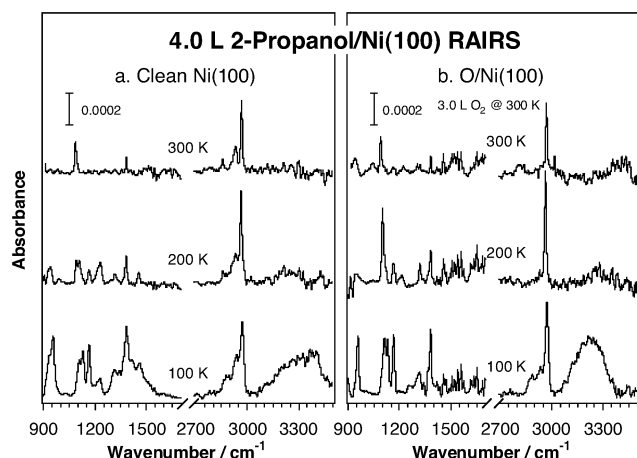


Figure 5. Reflection-absorption infrared spectra (RAIRS) for 4.0 langmuirs of 2-propanol on clean (a, left) and oxygen-predosed (b, right) Ni(100) surfaces as a function of annealing temperature. The conversion of 2-propanol to 2-propoxide on those surfaces is evident by the disappearance of the broad O–H stretching band between 3000 and 3500 cm^{-1} , the slight shifts in the main C–O stretching and methyl stretching and deformation peaks, and the overall simplification of the traces.

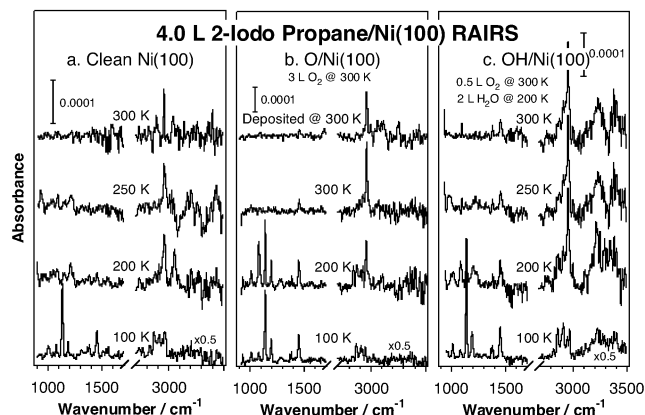


Figure 6. RAIRS for 4.0 langmuirs of 2-propyl iodide on clean (a, left), oxygen-predosed (b, center), and hydroxide-covered (c, right) Ni(100) surfaces. The three lower traces in each panel were obtained by adsorption at 100 K followed by annealing to the indicated temperatures, while the top spectra were obtained by dosing directly at 300 K. The hydroxide-covered surfaces were prepared via the sequential dosing of 0.5 langmuirs of O_2 at 300 K and 2.0 langmuirs of water at 200 K. 2-Propoxide formation is seen in the oxygen- and hydroxide-covered surfaces by the growth of a C–O stretching peak around 1095 cm^{-1} . Surface hydroxide appears to facilitate this reaction.

and asymmetric stretching (2967 cm^{-1}) modes of the methyl groups. It should be noted, however, that the methyl rocking modes are not pure but are mixed with C–C stretching modes. The middle CH group is evident by its deformation (1313 cm^{-1}) and stretching (2940 cm^{-1}) modes, and the stretching of the C–O bond is seen about 1108 cm^{-1} . Perhaps the most relevant features in the RAIRS to support molecular adsorption are the O–H stretching mode, seen as a broad feature between 3000 and 3500 cm^{-1} (the exact position and shape being masked by interferences from baseline features), and a weak peak at 1255–1265 cm^{-1} for the in-plane O–H deformation. The broad nature of the O–H stretching signal indicates extensive hydrogen bonding.

Heating the adsorbed 2-propanol to 200 K initiates some clear changes in the infrared spectra which reach completion by 300 K. These changes appear to occur earlier (by 200 K) on the oxygen-covered surface, and eventually lead to fairly simple

TABLE 1: Vibrational Assignment of the RAIRS Features for 2-Propanol Molecularly Adsorbed on Ni(100) at 100 K, Where All Frequencies Are in cm^{-1} and Relative Intensities Are Given in Parentheses^a

mode ^b	clean Ni(100)	O–Ni(100)	liquid ⁷³	multilayer/Cu(100) ⁷⁴
$\rho(\text{CH}_3)$	956 (s)	956 (s)	952 (s)	960 (vs)
$\nu(\text{CO})$	1108 (m)	1112 (s)	1108 (s)	1114 (sh)
$\nu_s(\text{CC}), \rho(\text{CH}_3)$	1130 (m)	1132 (s)	1130 (s)	1133 (s)
$\nu_s(\text{CC}), \rho(\text{CH}_3)$	1166 (s)	1167 (s)	1162 (s)	1168 (s)
$\delta(\text{CH})$	1313 (w)	1317 (m)	1312 (m, br)	1322 (m)
$\delta_s(\text{CH}_3)$	1366 (sh)	1368 (m)	1369 (m)	1367 (sh)
$\delta_s(\text{CH}_3)$	1382 (s)	1382 (s)	1380 (s)	1381 (s)
$\delta_a(\text{CH}_3)$	1460 (w)	1455 (w)	1470 (s)	1473 (w)
$\nu_s(\text{CH}_3)$	2885 (w)	2885 (w)	2875 (vs, gas)	
$\nu(\text{CH})$	2940 (m)	2935 (m)	2933 (m)	2940 (sh)
$\nu_a(\text{CH}_3)$	2967 (vs)	2967 (vs)	2976 (s)	2972 (vs)
$\nu(\text{OH})$	3300 (m, br)	3250 (m, br)	3650 (m, gas)	

^a vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad. ^b ρ = rocking, ν = stretching, δ = deformation. Subindices: a = asymmetric, s = symmetric.

vibrational spectra on both Ni(100) and O–Ni(100) surfaces. On the basis of the vibrational assignments reported in Table 2, the new species is identified here as surface 2-propoxide. Four clear peaks are seen in the data, at 1087, 1382, 1456, and 2967 cm^{-1} , assigned to the C–O stretching and methyl umbrella, asymmetric deformation, and asymmetric stretching modes, respectively. They approximate the absorptions at 1105, 1316, and 2957 cm^{-1} reported on Cu(100),⁷⁴ although the match is not exact: the strong symmetric methyl rocking mode reported on Cu(100) at 929 cm^{-1} is not evident in our data, and the lower frequency signal of the methyl umbrella mode is only seen here as a weak peak about 1316 cm^{-1} . The inconsistencies between the Ni(100) and Cu(100) cases may be explained by differences in adsorption geometry on the two surfaces. Our identification of the 200–300 K species with 2-propoxide is consistent with the XPS data as well.

The corresponding RAIRS data for 4.0 langmuirs of 2-propyl iodide is provided in Figure 6, in this case for three systems, namely, for clean and oxygen (3.0 langmuirs of O_2 at 300 K) and hydroxide (0.5 langmuirs of O_2 at 300 K + 2.0 langmuirs of H_2O at 200 K) precovered surfaces. The details of the pretreatments used for the latter two cases were extracted from previous reports,^{70,72} and chosen to optimize the reactivity toward oxygen insertion into the nickel–2-propyl bond.⁴ Again, 2-propyl iodide adsorption at 100 K is molecular in all three surfaces. The infrared spectra are easily assigned by comparison with those for liquid 2-propyl iodide,⁷⁵ as well as for multilayers on Pt(111)⁵⁰ and Cu(110)⁷⁶ single-crystal surfaces, as indicated in Table 3. Like with 2-propanol, many of the IR bands seen in adsorbed 2-propyl iodide can be ascribed to methyl groups: rocking modes at 1013 and 1078 cm^{-1} , symmetric deformations at 1367 and 1383 cm^{-1} , an asymmetric deformation about 1453 cm^{-1} , and symmetric and asymmetric stretching modes at 2860 and 2971 cm^{-1} . The middle C–H bond manifests itself by the appearance of bands for its deformation (1187 cm^{-1}) and stretching (2912 and 2957 cm^{-1}) modes. The molecular nature of the adsorbed species is manifested by the strong feature at 1137 cm^{-1} , which corresponds to a combination of C–C stretching and C–C–I deformation modes. The C–I bond is not broken at these low temperatures.

On clean Ni(100), most of the IR features listed above disappear by 200 K. Weak peaks are still identifiable at 1090, 1210, 1380, and 1452 cm^{-1} in both 200 and 250 K traces. Those spectra are likely to correspond to the 2-propyl groups that form

TABLE 2: Vibrational Assignment of the RAIRS Features for 2-Propoxide Species Adsorbed on Ni(100), Where All Frequencies Are in cm^{-1} and Relative Intensities Are Given in Parentheses^a

mode ^b	2-propanol at 300 K		2-propyl iodide at 300 K		Cu(100) ⁷⁴
	clean Ni(100)	O–Ni(100)	O–Ni(100)	OH–Ni(100)	
$\nu(\text{CO})$	1087 (s)	1089 (s)	1095 (vw)	1098 (m)	1105 (s)
$\delta(\text{CH})$	1316 (vw)	1318 (w)			1316 (w)
$\delta_s(\text{CH}_3)$	1382 (s)	1382 (m)		1382 (w)	
$\delta_a(\text{CH}_3)$	1456 (vw)	1456 (w)	1455 (w)	1456 (m, br)	
$\nu_a(\text{CH}_3)$	2967 (vs)	2969 (vs)	2957 (s)	2955 (s)	2957 (vs)

^a vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad. ^b ν = stretching, δ = deformation. Subindices: a = asymmetric, s = symmetric.

TABLE 3: Vibrational Assignment of the RAIRS Features for 2-Propyl Iodide Molecularly Adsorbed on Ni(100) at 100 K, Where All Frequencies Are in cm^{-1} and Relative Intensities Are Given in Parentheses^a

mode ^b	clean Ni(100)	O–Ni(100)	OH–Ni(100)	liquid ⁷⁵	Pt(111) ⁵⁰	Cu(110) ⁷⁶
$\rho(\text{CH}_3)$	1013 (w, br)	1015 (w)	1013 (w)	1017 (m)	1014 (w)	
$\rho(\text{CH}_3)$	1078 (w)	1080 (w)	1079 (w)			
$\nu(\text{CC}) + \delta(\text{CCI})$	1137 (vs)	1143 (vs)	1140 (vs)	1141 (s)	1140 (s)	1139 (s)
$\delta(\text{CH})$	1187 (m)	1194 (m)	1195 (m)		1184 (sh)	1188 (m)
$\delta_s(\text{CH}_3)$	1367 (w)	1367 (w)	1367 (w)	1369 (m)	1366 (m)	
$\delta_s(\text{CH}_3)$	1383 (w)	1383 (w)	1382 (w)	1383 (s)	1381 (m)	1382 (w)
$\delta_a(\text{CH}_3)$	1453 (m)	1449 (s)	1450 (m)	1449 (s)	1450 (m)	1448 (s)
$\nu_s(\text{CH}_3)$	2860 (m)	2857 (m)	2860 (m)	2861 (m)	2863 (m)	2839 (m)
$\nu(\text{CH})$	2912 (m)	2907 (m)	2917 (m)	2913 (Raman)	2916 (sh)	
$\nu(\text{CH})$	2957 (m)	2945 (m)	2946 (w)	2951 (s)	2954 (m)	
$\nu_a(\text{CH}_3)$	2971 (sh)		2967 (m)	2967 (s)	2966 (sh)	2970 (w)

^a vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. ^b ρ = rocking, ν = stretching, δ = deformation. Subindices: a = asymmetric, s = symmetric.

after C–I bond activation,⁷⁶ with the absorption at 1210 cm^{-1} due to a C–C stretching mode and the other three to methyl rocking and deformation vibrations. Notice in particular the absence of the strong $\nu(\text{CC}) + \delta(\text{CCI})$ band seen around 1137 cm^{-1} at low temperatures, a clear indicator that the C–I bond breaks below 200 K (as also determined by XPS).^{56,77} However, another surface species clearly starts to form in that temperature range, as indicated by the C–H stretching modes at 2955 and 3350 cm^{-1} that remain even in the 300 K spectrum. The high frequencies of those modes allow us to rule out a number of potential species, including propylene,⁷⁸ allyl,⁵² nickelacyclobutane,⁷⁹ and propylidyne,⁷⁸ and suggest a highly unsaturated species. Given that 2-propyl groups are known to undergo early β -hydride elimination to propylene,⁵⁶ and by analogy with the chemistry of ethylene on Ni(100),⁸⁰ we suggest here that the species at 300 K may be either propyne or a propynyl moiety.

The chemistry of 2-propyl iodide on Ni(100) surfaces partially covered with oxygen or hydroxide groups also starts with the activation of the C–I bond and the formation of 2-propyl groups on nickel surface atoms. However, some of those propyl groups incorporate adjacent oxygen surface atoms to form propoxide intermediates.^{4,48} The infrared data in Figure 6 indicate that that reaction takes place by 200 K, and that the resulting 2-propoxide species survives until at least 300 K. The summary in Table 2 shows the similarities between the 300 K spectra for 2-propanol on clean and oxygen-treated nickel surfaces and those for 2-propyl iodide on oxygen- and hydroxide-covered substrates. The formation of a C–O bond is highlighted by the appearance of its stretching feature in the experiments with 2-propyl iodide around 1095 cm^{-1} .⁷ This chemistry is easier to observe if the 2-propyl iodide is dosed directly at 300 K rather than carrying out the adsorption at 100 K and then annealing to 300 K, because significant molecular desorption (and other reactions) takes place at lower temperatures in the latter case. Particularly telling is the fact that stronger C–O stretching signals are also seen on the surface precovered with hydroxide groups. Again, the XPS data support this conclusion.

4. Discussion

The TPD, XPS, and RAIRS experiments reported here on 2-propanol and 2-propyl iodide adsorbed on clean and oxygen-treated Ni(100) surfaces were designed to explore the details of the mechanism for the selective oxidation of hydrocarbons. The catalytic oxidation of alkanes is believed to start with a C–H bond activation and the consequent formation of a surface alkyl intermediate. Unfortunately, this is a low-probability reaction difficult to emulate under the vacuum environment needed for our studies with model single-crystal surfaces. To bypass that step, we in our research have resorted to the use of the appropriate precursors for the preparation of alkyl surface groups.^{47,61,81} Iodo compounds are particularly suited for this application, because C–I bonds are relatively weak, and can be broken on many surfaces below 200 K.⁸² In terms of the particular system of interest in these studies, previous work in our group has proven that 2-propyl surface moieties can be produced via the thermal activation of adsorbed 2-propyl iodide at about 160 K on platinum,⁵⁰ nickel,⁵⁶ and copper⁷⁶ single-crystal surfaces. Early dissociation of the C–I bond in 2-propyl iodide coadsorbed with oxygen on Ni(100) is supported by the I 3d XPS data reported by us in a previous publication.⁴

According to ion scattering experiments, the alkyl groups that form from activation of 2-propyl iodide on oxygen-treated Ni(100) surfaces are bonded directly to nickel surface atoms.^{4,48} This means that an appropriate ensemble of surface atoms is required for hydrocarbon oxidation, with alkyl and oxygen adsorbates residing in close proximity to each other. In the case of nickel surfaces, it is clear that only “defective” oxides with open nickel sites are active for this chemistry. Indeed, the production of acetone from conversion of 2-propyl iodide with coadsorbed oxygen is only observed with submonolayer coverages of oxygen.⁴ The subsequent route from coadsorbed 2-propyl and oxygen to acetone involves two elementary steps, an insertion of the oxygen atom into the metal–carbon bond to form an alkoxide (2-propoxide) intermediate, and a following

β -hydride elimination from that moiety to yield the ketone. The mechanism associated with both steps was the focus of the investigation reported here.

Oxygen insertion and 2-propoxide formation on the surface are evident from the infrared spectroscopy data in Figure 6.⁷ Notice in particular the appearance of a new peak at 250 K around 1095 cm^{-1} corresponding to the stretching of the newly formed C—O bond. The identity of the new species was aided in part by the similarities with the RAIRS data obtained for 2-propanol (Figure 5); alcohols are well-known to easily dehydrogenate on most transition metal surfaces to the corresponding alkoxides.¹⁷ Also worth highlighting is the observation that oxygen insertion into the metal–alkyl bond is clearly facilitated by the presence of hydroxide groups on the surface, as indicated by the stronger signals obtained for the propoxide species in that case (compare the 300 K IR traces in Figure 6b vs Figure 6c).^{5,6,9} Surface hydroxide groups have been previously shown to facilitate hydrogen transfer steps between adsorbates with highly electronegative groups such as water and ammonia,^{72,83} but have not been, to the best of our knowledge, been implicated in surface reactions with hydrocarbons before (although we have recently reported the facilitation of α -hydride elimination from methylene by coadsorbed oxygen).⁸⁴ This enhancement in oxygen insertion rate with hydroxylation of the surface may have important implications for the design of catalytic processes.

The chemistry of alkyl groups on other oxygen-exposed metal surfaces appears to be somewhat different to that seen by us on nickel.^{14,85} In particular, it has been reported that alkoxide formation on either rhodium^{86,87} or molybdenum⁸⁸ surfaces involves a direct C—O bond formation between surface oxygen and alkyl gas-phase radicals; no oxygen insertion into adsorbed alkyls was ever observed in those systems. Partial oxidation has also been reported on palladium,⁸⁹ but, again, no direct evidence of alkoxide formation via oxygen insertion was provided for that metal. We, on the other hand, have also seen oxygen insertion on methyl⁹⁰ and methylene⁸⁴ groups on Ni(110). From the other metals studied so far, only on silver oxygen insertion has been proven possible, in that case into ethyl groups to yield diethyl ether.⁹¹ The contrasting behavior among the different transition metal surfaces toward the oxygen insertion step is likely to be related to the relative metal–oxygen and metal–carbon bond strengths of the adsorbates on the surface, but the connection between bond strengths and reactivity needs to be tested in detail via more systematic studies across the periodic table.

2-Propoxide intermediates, from activation of either 2-propanol or 2-propyl iodide + oxygen, are seen at temperatures as low as 200 K, and appear to be stable to up to at least 300 K. On the other hand, our TPD data show that the onset of acetone production is around 300 K. Isotope labeling experiments have proven that acetone production from 2-propoxide involves a β -hydride elimination step,^{63,92} and the high temperatures of the acetone TPD peaks indicate that this is the rate-limiting step for the overall conversion of either 2-propanol or 2-propyl iodide to the ketone. The high stability of the alkoxide and the large activation barrier for its dehydrogenation are quite surprising, in particular when compared with chemistry reported for similar systems. It has been reported that alkoxides from dehydrogenation of adsorbed alcohols decompose rapidly, at temperatures as low as 170 K, on a number of group VIII metals.^{35,93} In fact, on more active metals such as molybdenum, C—O bond scission may take place instead.⁹⁴ Methoxide species (from decomposition of adsorbed methanol) have also been reported to be fairly

unstable on Ni(100),⁹⁵ Ni(111),⁹⁶ and Ni(110)²² and to decompose to carbon monoxide and hydrogen soon after forming. To the best of our knowledge, spectroscopic evidence for alkoxides on nickel single-crystal surfaces has been previously reported only for ethoxide,⁶⁹ and in that case, further decomposition was observed by 260 K.

Oxygen preadsorption on Ni(100) both facilitates the dehydrogenation of 2-propanol to 2-propoxide and increases the stability of that intermediate. In connection with the first observation, both the RAIRS in Figure 5 and the O 1s XPS data in Figure 4 show clear evidence for extensive 2-propoxide formation on O–Ni(100) by 200 K. On clean Ni(100), on the other hand, significant molecular adsorption is still seen at that temperature (as attested by the data in Figures 3–5). The enhancement in 2-propoxide stability by coadsorbed oxygen is manifested by the higher threshold temperature and the higher yield for acetone in the TPD data in Figure 2. These effects have in fact been reported already for other surfaces.^{93,97} Faster dehydrogenation of alcohols to alkoxides can be easily understood in terms of hydrogen bonding, and by transfer of the hydroxyl hydrogen of the alcohol to an adjacent surface oxygen atom. Indeed, similar chemistry takes place with ammonia⁹⁸ and water.⁷² Higher stability of alkoxides, on the other hand, may be simply a consequence of site blocking: the same effect has been reported with coadsorbed sulfur.⁹⁹

The O 1s XPS data in Figure 4 point to another interesting observation: 2-propanol thermal conversion aids in the reduction of oxygen-precovered nickel surfaces. Note in particular the significant reduction in signal intensity for the 529.8 eV peak in Figure 4b when going from 200 to 300 K. This oxygen is most likely removed from the surface in the form of water and/or carbon monoxide. In connection with that observation, it is interesting to also point to the production of propene seen in the TPD data in Figure 2. It appears that the selectivity for alcohol oxidation on nickel surfaces via dehydrogenation to aldehydes or ketones is not 100%, but it is accompanied by a detectable amount of dehydration to the olefin. Alcohol dehydration is known to dominate the catalysis with acidic oxides¹² but may also be possible with more basic oxides such as NiO_x under the right conditions. A more careful investigation of the mechanism of that pathway is underway in our laboratory.^{10,11}

We believe that the chemistry reported here for 2-propanol and 2-propyl groups is quite general. In particular, indirect evidence from other experiments in our laboratory points to the possibility to produce aldehydes from 1-alkoxide intermediates;^{5,6} the difficulty with detecting those products may have more to do with the ease with which they decompose on the surface once formed. In fact, the detection of acetaldehyde from 2-propyl iodide thermal conversion has already been reported on a hydroxide-covered Ni(100) surface,⁵ and the desorption of formaldehyde by activation of either methyl iodide⁹⁰ or diiodomethane⁸⁴ on oxygen-treated Ni(110) surfaces has also been recently observed. Finally, the selective oxidation of alcohols to aldehydes and ketones has been proven in catalytic systems with nickel foils^{6,8} as well as on supported nickel catalysts.¹⁰⁰

5. Conclusions

A number of temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and reflection–absorption infrared spectroscopy (RAIRS) experiments were performed to characterize the chemistry of 2-propanol and 2-propyl iodide on clean and oxygen-pretreated Ni(100) single-crystal surfaces.

These studies were aimed at identifying the elementary steps involved in the catalytic oxidation of hydrocarbons. In terms of 2-propanol, the following was observed:

1. 2-Propanol adsorption on either clean or oxygen-predosed nickel is molecular at 100 K. Evidence for this is provided by the C 1s XPS peaks at 283.8 and 285.4 eV binding energy (with intensity ratios of 2:1), by the main O 1s XPS peak at 532.1 eV, and by infrared spectra similar to those of liquid or condensed 2-propanol. Particularly important is the detection of a broad band between 3000 and 3500 cm^{-1} , which indicates not only that the O–H bond does not break upon adsorption but also that extensive hydrogen bonding occurs among the chemisorbed molecules.

2. Thermal activation of adsorbed 2-propanol leads to an initial activation of the O–H bond, and to the formation of 2-propoxide surface intermediates. This is clearly indicated by the shift in the O 1s XPS peak down from 532.1 to 530.8 eV binding energy, by the disappearance of the O–H features in the IR spectra, and by the red shift of the C–O stretching vibrational mode from approximately 1110 to 1088 cm^{-1} .

3. 2-Propoxide formation is facilitated by coadsorbed oxygen, which leads to a complete conversion by 200 K. On clean Ni(100), on the other hand, significant amounts of nondecomposed adsorbed 2-propanol are still seen in both XPS and IR spectra at that temperature.

4. The 2-propoxide intermediates are stable on the surface to temperatures of up to 300 K; witness in particular the IR spectra obtained for 2-propoxide at that temperature on both clean and oxygen-covered Ni(100). On the other hand, further heating causes β -hydride elimination to acetone, which desorbs immediately after formation (as shown in TPD experiments).

5. Some alcohol dehydration and extensive decomposition are also seen in TPD experiments. The early production of ethylene and water, starting at temperatures as low as 160 K, may be due to intermolecular reactions involving hydrogen-bonded species.¹⁰ Hydrogen and carbon monoxide also desorb from those surfaces at higher temperatures.

With respect to 2-propyl iodide, its surface chemistry can be summarized as follows:

1. 2-Propyl iodide adsorption at 100 K is molecular. The best evidence supporting that conclusion is the detection of a strong feature in the infrared spectra around 1140 cm^{-1} . That peak is assigned to a combination of C–C stretching and C–C–I deformation modes and indicates that the C–I bond of the molecule is intact at 100 K.

2. Thermal activation of 2-propyl iodide adsorbed on nickel surfaces leads to the initial breaking of the C–I bond and to the formation of 2-propyl surface species. Evidence for this comes from earlier I 3d XPS and ion-scattering (ISS) studies.⁴ ISS data also suggest that the alkyl groups bond to nickel surface atoms.⁴⁸

3. On clean Ni(100), 2-propyl surface groups undergo rapid disproportionation to propylene and propene. This takes place via an initial β -hydride elimination from some 2-propyl groups (to yield propylene) followed by rapid reductive elimination of a second alkyl moiety with the released hydrogen (to produce propane). Propylene desorption follows the same kinetics on both clean and oxygen-precovered nickel surfaces, producing TPD peaks at approximately 160 and 230 K. Propane formation, on the other hand, seems to be retarded by coadsorbed oxygen.

4. Some of the propylene produced by β -hydride elimination from 2-propyl groups on clean Ni(100) desorbs molecularly, as indicated above, but the rest remains on the surface, and undergoes further sequential dehydrogenation steps. The high

degree of dehydrogenation of the intermediate formed between 200 and 300 K is indicated by a clear infrared peak about 3050 cm^{-1} , representative of C–H stretchings from either sp^2 - or sp -hybridized carbon atoms. By analogy with the chemistry of ethylene on Ni(100), it is proposed that this species may be either adsorbed propyne or propynyl species.

5. On either oxygen- or hydroxide-precovered nickel surfaces, oxygen atoms can insert into the metal–carbon bond of adsorbed 2-propyl groups. Previous work suggests that this requires both species to be in adjacent surface sites.⁴ This oxygen insertion, which leads to the formation of surface 2-propoxide species, occurs at low temperatures. The best evidence for this chemistry comes from the C–O stretching feature seen in the infrared spectra between 200 and 300 K, and, in general, from the similar spectroscopic characteristics and thermal behavior between these and the 2-propanol systems.

6. Heating of the 2-propyl iodide/O–Ni(100) or 2-propyl iodide/OH–Ni(100) systems to higher temperatures leads to the desorption of acetone. The onset of the acetone TPD peak on the oxygen-pretreated surface is seen at 300 K, and the subsequent kinetics is qualitatively similar to that detected with 2-propanol. Acetone production presumably takes place via the same β -hydride elimination step seen with the alcohol.

7. The preadsorption of hydroxide groups on the surface appears to facilitate the conversion of 2-propyl iodide to acetone. The appearance of stronger bands for 2-propoxide in the infrared spectra obtained for that system indicates that OH surface species modify the kinetics of the oxygen insertion that yields the 2-propoxide. Surface hydroxide also enhances the yield for acetone production in TPD experiments with 2-propyl iodide,^{4,6} but that may be due to the formation of more 2-propoxide moieties in the first step of the reaction.

In general, the results reported here suggest that, under appropriate conditions, a nickel-based catalyst may be used for the partial oxidation of hydrocarbons. Experiments with nickel foils⁸ and supported nickel catalysts¹⁰⁰ have confirmed that it is indeed possible to dehydrogenate alcohols to aldehydes or ketones on those surfaces with high selectivity. It is proposed here that, if an initial C–H bond activation can be achieved under reasonably mild conditions, it may be possible to oxidize alkanes to the same oxygenated molecules on nickel-based catalysts.

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