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Partial oxidation of hydrocarbons on nickel: from surface science mechanistic studies to catalysis [1]

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Abstract

The mechanistic details of hydrocarbon partial oxidation reactions were studied with both ultra-high vacuum (UHV) modern surface-sensitive techniques and a micro-batch reactor. The focus of this work was to characterize the reactivity of alkyl species and of alcohols on nickel substrates. In the UHV experiments the chemistry of oxides was mimicked via the oxidation of metal surfaces under controlled conditions, and alkyl surface moieties were prepared by thermal excitation of adsorbed alkyl halides. The oxidation of 2-iodopropane on Ni(100) in particular was found to yield several products in a distribution dependent on oxygen pre-coverage, with partial oxidation being favored at low oxygen coverages and total oxidation dominating on thin oxide films. X-ray photoelectron (XPS) I 3d core level spectra indicate that the adsorption of 2-iodopropane below 100 K is always molecular, and ion-scattering spectra (ISS) data strongly suggest preferential bonding to Ni (not O) sites. Annealing the alkyl iodide adsorbed on O/Ni(100) surfaces below 200 K leads to the dissociation of the C–I bond, and generates 2-propyl groups bonded to nickel atoms, the same as on the clean nickel metal. For submonolayer oxygen coverages the 2-propyl groups then follow one of two reaction pathways: they either undergo hydrogenation–dehydrogenation on the nickel sites to form propane, propene, and hydrogen, or, in the case of the moieties adsorbed near the oxygen sites, they incorporate an oxygen atom to form 2-propoxide groups. 2-Propoxide moieties, which can also be prepared by decomposition of 2-propanol, are stable on the surface up to ~ 325 K, at which point they follow a β-hydride elimination step to yield acetone. Additional temperature-programmed desorption (TPD) experiments indicated that propene does not convert directly to acetone on these O/Ni(100) surfaces, and that the presence of hydroxo groups greatly enhances the yield for ketone production. Lastly, preliminary atmospheric pressure experiments proved that alcohols can be oxidized catalytically to aldehydes or ketones on nickel surfaces under controlled conditions, a result that validates the knowledge developed by the mechanistic surface-science studies. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrocarbon partial oxidation; Ultra-high vacuum; Nickel

1. Introduction

The partial oxidation of alkanes is of great industrial importance for the manufacturing of oxygenated hydrocarbons such as alcohols, aldehydes, and ketones. A variety of metal- and metal oxide-based catalysts has been used to oxidize saturated hydrocarbons with moderate

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success, but the challenge in the design of an effective process is in stopping the reaction before total oxidation [1]. The main problem is that while hydrocarbon partial oxidation is thermodynamically possible, carbon dioxide and water are the most favorable products by far, so high yields for partial oxidation products can only be achieved by controlling the relative kinetics of the partial and total oxidation pathways [2]. Much fundamental work has been aimed at the resolution of this difficulty.

It is generally accepted that the rate-limiting step in the partial oxidation of alkanes is the initial scission of a C–H bond to generate alkyl species on the surface of the catalyst [3,4]. Alkanes have very low sticking coefficients, and therefore require the high temperature and pressure conditions used in industrial catalytic processes for their activation. Unfortunately, those conditions are difficult (if not impossible) to emulate under the ultra-high vacuum environment (UHV) normally used in surface-science studies. Instead, in this work the C–H activation step was bypassed, and surface alkyl groups were produced via the adsorption and decomposition of the corresponding alkyl iodides instead. This way the experiments start with the surface intermediates of interest in order to focus on the determination of the parameters that control the selectivity in alkane oxidation. We and others have proven in the past that the C–I bonds in alkyl iodides can indeed be readily activated to yield significant concentrations of the desired alkyl surface species, and that a variety of alkyl moieties can be produced on surfaces this way, the selection being only limited by the availability of the corresponding alkyl iodide precursors [5–9].

As a prototype of the partial oxidation processes mentioned above, the reaction of 2-iodopropane with oxygen on Ni(100) surfaces was investigated here using a combination of surface-sensitive techniques. A variety of products were observed to desorb from the O/Ni(100) system, the selectivity among them depending strongly on the coverage of oxygen on the surface. On the one hand, oxygen coverages close to first-layer saturation (0.50 ML) basically poison the overall activity of the surface, significantly reducing the amounts of propane and propene produced by the clean metal. Even higher oxygen exposures lead to the oxidation of the nickel surface [10] and to the biasing of its activity towards the sole production of CO, CO_2, and H_2O. Interestingly, however, at the other end, for low oxygen coverages, small amounts of acetone are produced. It was determined here that in that case the C–I bond-scission occurs in a temperature range similar to that on the clean metal, between 120 and 180 K, suggesting that 2-propyl fragments are created on the nickel sites at those low temperatures. Complementary experiments have shown that then an oxygen insertion step is followed by β-hydride elimination of the resulting propoxide to yield the acetone. These results differ from those reported previously for the O/Rh(111) system [11,12], apparently because a different mechanism is operative on each of those metals.

Additional studies were performed on the oxidation of 2-propanol. Alcohols are known to readily loose the hydroxo hydrogen atom upon thermal activation on transition metal surfaces; in the case of 2-propanol that step leads to the formation of the same 2-propoxide intermediate proposed during the oxidation of alkanes. Consequently, acetone production was expected, and indeed observed, in this case as well. Furthermore, the partial oxidation of 2-propanol and 2-iodopropane were found to follow essentially the same kinetics behavior. Finally, catalytic studies by using a micro-batch reactor proved that the reaction of 2-propanol with oxygen can indeed be tuned to produce significant amounts of acetone under the right conditions.

2. Experimental

The surface-science experiments reported here were performed in a stainless-steel UHV bell-jar evacuated with a turbomolecular pump to a base pressure below 1×10^{-10} Torr. This chamber is equipped with instrumentation for temperature-programmed desorption (TPD), X-ray photoelectron (XPS), and ion-scattering (ISS) spectroscopies [9,13]. TPD spectra were obtained by simultaneously monitoring the mass spectrometer signal of up to 15 masses with an interfaced computer while heating the sample at a rate of 10 K/s. XPS spectra were taken by using an Al anode and a hemispherical electron-energy analyzer with an overall energy resolution of about 1.2 eV full width at half maximum. The binding energy scale was calibrated against the Pt $4f_{7/2}$ and Cu $2p_{3/2}$ core levels. ISS spectra were obtained using the same hemispherical energy analyzer as for XPS but with the signs of the voltage biases inverted in order to detect ions rather than electrons. The scattering geometry in ISS was such that the angle between the ion source and the analyzer was 115° [14]. A 1–2 μA 500 eV He^+ ion beam was focused to a spot size of about 2 mm diameter on the crystal, and the kinetic energy of the scattered ions was monitored with an interfaced computer. Control experiments on oxygen-covered Ni(100) surfaces, prepared by dosing 3.0 L of O_2 at 300 K, indicated that sputtering by the 500 eV He^+ beam was insignificant [15]. Several methods were also used to calibrate the ISS signal to insure that work function changes due to the various adsorbates do not influence the quantitative analysis of the data reported here in any significant fashion [16].

The nickel (100) single crystal was cut, oriented, and polished using standard procedures, and mounted on a manipulator via spot-welds to tantalum support wires in contact with a liquid nitrogen reservoir. With this set-up the sample could be resistively heated to 1200 K and rapidly cooled back to 90 K. The surface temperature was monitored by a chromel–alumel thermocouple spot-welded to the edge of the crystal. Surface cleaning was done by cycles of Ar^+ ion bombardment and annealing to 1200 K as well as oxygen treatments (to remove atomic carbon) until no impurities were detected by XPS or ISS. The 2-iodopropane and 2-propanol were obtained from Alfa Products (98% purity or better), protected from light, and subjected to several freeze–pump–thaw cycles before use; their purity was routinely checked by mass spectrometry. Compressed oxygen (99.999%), argon (99.999%), and hydrogen (99.999%) were obtained from Matheson and used as supplied. All gas exposures were done by backfilling of the vacuum chamber via leak valves, and are reported in Langmuirs ($1\ L = 1 \times 10^{-6}$ Torr s), not corrected for sensitivity differences in the ionization gauge.

The catalytic studies were carried out in a recirculating batch reactor described in detail elsewhere [17,18]. Briefly, the stainless-steel loop and reactor, which has a total volume of 200 cm^3, is evacuated with a mechanical pump to a base pressure of about 5×10^{-3} Torr and then filled with the reacting gases (oxygen and the alcohol) and topped to a final pressure of 500 Torr by adding argon if needed. The gases are mixed by a recirculation bellows pump, and the time evolution of the partial pressures of the reactants and products is followed with a quadruple mass spectrometer located in a separate chamber and connected to the reactor via a capillary tube. The collection and storage of data for further analysis is accomplished with a personal computer interfaced to the mass spectrometer. A nickel wire of about 1 mm diameter and 2 cm in length was used as the catalyst. It was connected to copper feedtroughs in order to allow for resistive heating, and spot-welded to a chromel–alumel thermocouple for temperature measurement and control. Blank experiments were carried out both with the contaminated Ni wire and with gold and tantalum foils in order to ensure that the activity observed during the kinetic runs was entirely due to the nickel surface [18]. The nickel wire was purchased from Aldrich (99.9% minimum purity), and pretreated in-situ before each reaction by sequential 1 min exposures to 500 Torr of oxygen, 500

Torr of hydrogen, and vacuum while keeping the wire at 1000 K.

3. Results and discussion

The nature of the adsorption sites for 2-iodopropane on the O/Ni(100) surfaces was first probed by ISS. A set of experiments were performed as a function of 2-iodopropane exposure for given fixed oxygen coverages in order to probe the location of the binding sites for the iodide—either on the Ni or on the O atoms [16]. Fig. 1 shows the 2-iodopropane coverage-dependent ISS data obtained for a fixed 3.0 L pre-exposure to oxygen at 300 K. The top trace in the inset, that for the 0.0 L 2-C_3H_7I exposure, corresponds to the oxygen-dosed surface before any 2-iodopropane adsorption, and is the spectrum to which all other traces are compared and normalized. The peaks at 245 and 410 eV kinetic energies in the raw ISS data (inset) correspond to O and Ni, respectively, as determined by using standard elastic collision theory and by taking into account the geometry of our system. What becomes quite clear from these data is that, upon exposures of the oxygen-dosed surface to small amounts of 2-iodopropane, the Ni signal decreases significantly while the O signal remains almost constant (bottom two traces in inset). Specifically, over 80% of the Ni peak disappears after a 1.0 L alkyl iodide exposure, while the oxygen peak still retains over 60% of its initial intensity at that point. This coverage dependence of the ISS signals is better illustrated in the main frame of Fig. 1, in which plots of the normalized Ni and O ISS peak intensities are displayed as a function of the alkyl iodide exposure. This figure highlights the selective titration of the nickel sites by the 2-iodopropane at low exposures, which means that the alkyl iodide binds preferentially to nickel atoms. It is also important to note that the 2-iodopropane exposure at which the oxygen signal starts to be significantly attenuated, around 2.0 L, is the same required to detect any acetone by TPD (see below).

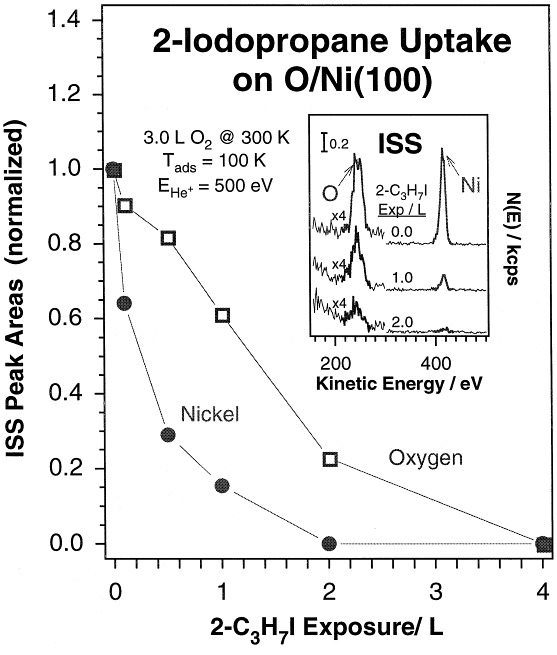


Fig. 1. ISS as a function of 2-iodopropane exposure on a O/Ni(100) surface prepared by adsorption of 3.0 L of O_2 at 300 K. The inset shows the raw data for three key iodopropane doses, while the main frame displays the ISS peak areas normalized to the signal of the Ni and O peaks for the surface with no 2-C_3H_7I. These data highlight the fact that the alkyl iodides prefer to adsorb on the metal sites.

Adsorption of 2-iodopropane at 100 K is molecular regardless of the initial oxygen coverage, but heating the $O_2 +$ 2-C_3H_7I-dosed surfaces between 120 and 180 K induces the dissociation of the C–I bond. This is clearly demonstrated by the I 3d XPS data shown in Fig. 2 [15]. Notice that the I $3d_{5/2}$ peak in that figure is centered around 620.0 eV at low temperatures, when the iodopropane is adsorbed intact on the surface, but shifts to 619.5 eV, a value typical of atomic iodine, once the C–I bond is broken (around 160 K). We propose that this bond-activation step occurs on the Ni sites, because: (1) Ni is the preferred adsorption site for the alkyl iodide; (2) the temperature range for the C–I bond-cleavage on the oxygen-covered surfaces is the same as that on the clean surface; and (3) as the number of nickel sites decreases with increasing oxygen coverage, the

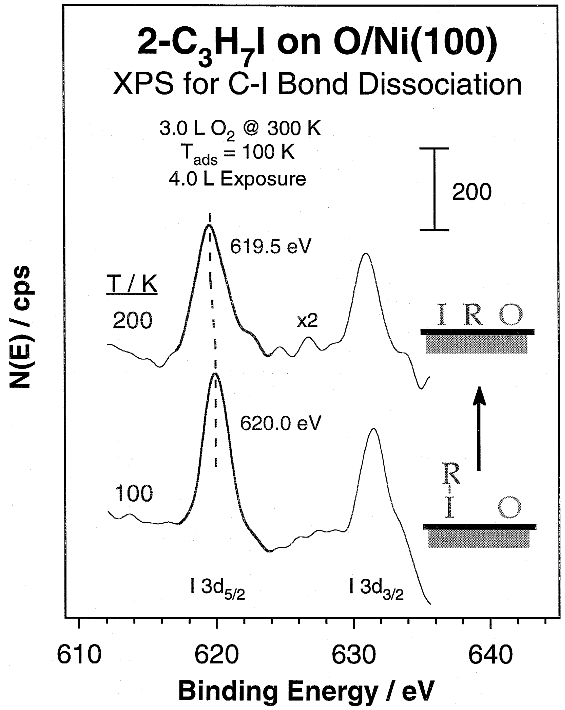


Fig. 2. I 3d XPS as a function of annealing temperature from 2-iodopropane adsorbed on an oxygen-predosed Ni(100) surface. The surface was pretreated by dosing 3.0 L of O_2 at 300 K, and then exposed to 4.0 L of 2-C_3H_7I at 100 K. Data are shown here for the surface right after the low-temperature hydrocarbon dose as well as for the case after annealing to 200 K. Notice the red shift of the peaks by about 0.5 eV binding energy, from 620.0 to 615.5 eV in the case of the I $3d_{5/2}$ feature, indicative of the change in the local environment of the iodine atom: the C–I bond in the alkyl iodide breaks below 200 K to yield alkyl groups and surface iodine.

amount of 2-iodopropane that dissociates decreases as well.

The main species that form at low temperatures upon the breaking of the C–I bond are presumed to be 2-propyl fragments bonded directly to nickel atoms. The reaction of these 2-propyl groups with oxygen on Ni(100) was characterized by TPD. A variety of species were found to desorb from this surface, namely, hydrogen, water, carbon monoxide, propene, propane, carbon dioxide, acetone, and the original hydrocarbon molecule, the relative yields of which were found to depend strongly on the coverage of oxygen on the surface [15,19]. On the one end, the clean nickel behaves in the same way as many other metals, that is, it promotes β-hydride and reductive elimination steps to yield propene and propane, respectively [7,9,20]. At the other extreme, NiO films as thin as 1–2 ML thick passivate the metal and induce total oxidation to CO, CO_2, and H_2O exclusively. It is at the intermediate coverages obtained after doses of less than 10.0 L of O_2 (which yield atomic oxygen coverages below approximately 80% of monolayer saturation [10]) where the most interesting chemistry is seen, because a small amount of partial oxidation to acetone is detected. This is illustrated by the TPD in Fig. 3, which corresponds to the case of a 3.0 L oxygen dose at 300 K followed by a 4.0 L 2-iodopropane exposure at 100 K. The main products in this example still are propane, propene, and the hydrogen resulting

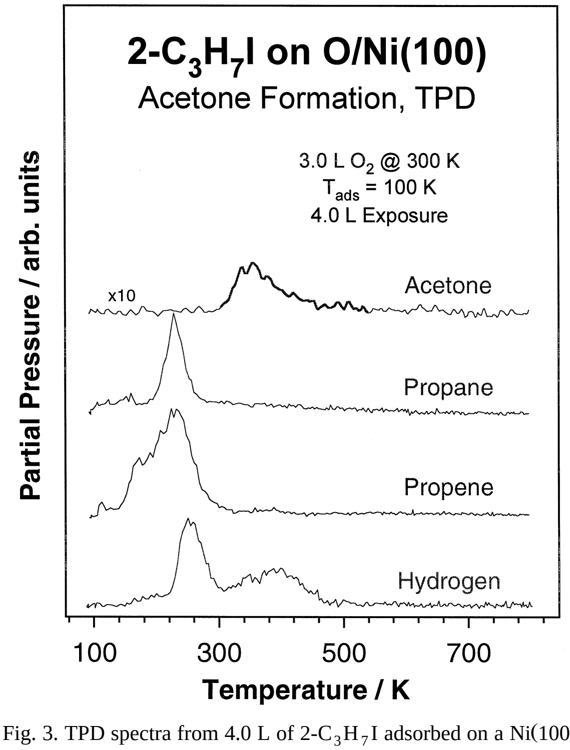


Fig. 3. TPD spectra from 4.0 L of 2-C_3H_7I adsorbed on a Ni(100) surface predosed with 3.0 L of oxygen at 300 K. Propane, propene and hydrogen evolve because of the decomposition of propyl groups on metal adsorption sites, but, in addition, a small amount of acetone is detected around 350 K due to the reaction between 2-propyl and adsorbed oxygen.

from their decomposition, but a clear acetone peak is nevertheless seen around 350 K as well. This acetone production is the focus of our discussion in the next few paragraphs.

One interesting observation from the TPD data as a function of oxygen and 2-iodopropane doses is that, for any given oxygen coverage (in the range where the partial oxidation occurs), the onset of acetone formation is seen only after saturation of the 2-iodopropane monolayer. Indeed, the start of the acetone production also coincides with the point at which all the nickel sites are taken by the iodopropane, as determined by ISS (see Fig. 1). This suggests that in order for acetone to be produced, a particular surface ensemble is required with the 2-propyl groups adsorbed next to oxygen atoms [21,22]. In other words, it seems that the propyl species have limited mobility on the surface, and require close proximity to the oxidizer for its partial oxidation. This may be a key ingredient in the design of optimal partial oxidation catalysts.

Several pieces of evidence point to the fact that the next step in the conversion of 2-iodopropane and oxygen to acetone is the insertion of an oxygen atom into the metal–carbon bond of the adsorbed alkyl species. Fig. 4 shows XPS supporting evidence for this by illustrating the similar behavior of 2-iodopropane and 2-propanol on oxygen-covered Ni(100) surfaces; since propanol is known to produce 2-propoxide groups on most metal surfaces at low temperatures [23], the same intermediate is inferred to be involved in the case of the alkyl halide. In particular, the C 1s XPS traces present in both systems a small shoulder around 285.3–285.7 eV binding energy most likely associated with the carbon atom adjacent to the oxygen. In addition, the two middle traces of Fig. 5 shows the similar peaks seen in the acetone TPD traces from experiments with both compounds. Finally, ISS data obtained after annealing the 2-iodopropane + oxygen system to different temperatures (not shown here) indicate that the O ISS peak never recovers the initial intensity it has before dosing the alkyl halide, a result that suggests that at temperatures slightly above 200 K some of the surface alkyl groups migrate to sites on top of the chemisorbed oxygen atoms [15,16]. It is also worth noticing that acetone molecular desorption from these surfaces occurs at much lower temperatures, which means that acetone detection in the TPD experiments with this iodoalkane is reaction (not desorption) limited.

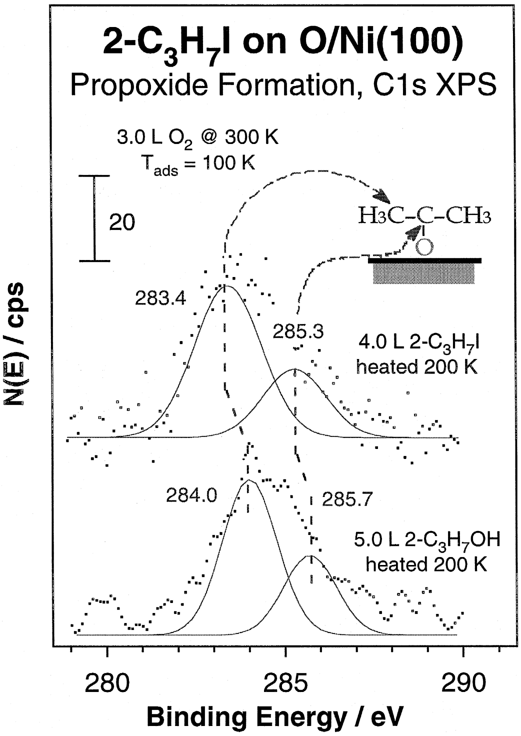


Fig. 4. C 1s XPS data from 2-propanol (bottom) and 2-iodopropane (top) adsorbed on oxygen-precovered Ni(100) and then annealed to 200 K to induce the formation of 2-propoxide groups. The surfaces were first prepared by dosing 3.0 L of O_2 at 300 K, and then dosed at 100 K with either 5.0 L of 2-propanol or 4.0 L of 2-iodopropane. The alkoxide intermediate is identified here by the signal from the middle carbon atom of that species, which is seen as a shoulder around 285.3–285.7 eV binding energy.

The last step in the 2-propyl to acetone conversion is a β-hydride elimination from the 2-propoxide intermediate above 300 K to yield the final product. The selectivity of this step is best illustrated by the acetone TPD traces shown in Fig. 6, which were obtained with the partially labelled CD_3CHICD_3 isotopomer of 2-iodopro-

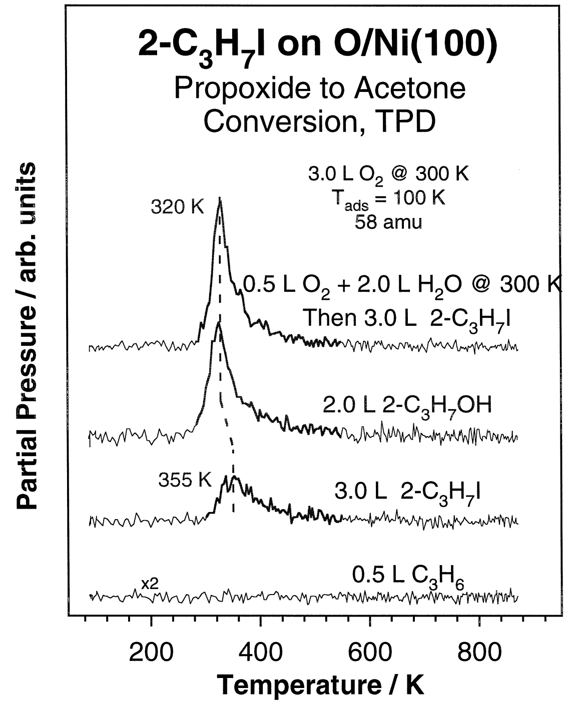


Fig. 5. Acetone TPD from Ni(100) predosed with 3.0 L of O_2 at 300 K and then exposed to different hydrocarbons at 100 K, namely, to 0.5 L of propene (bottom), 3.0 L of 2-iodopropane (second from bottom), and 2.0 L of 2-propanol (third from bottom). The lack of any signal in the bottom trace indicates that the olefin cannot be directly converted to acetone in this system. The two middle spectra show the similarity in kinetic behavior during the oxidation of 2-iodopropane and 2-propanol, an indication that both reactions share the same intermediate, 2-propoxide. The top trace correspond to a surface prepared by sequentially dosing 0.5 L of O_2 and 2.0 L of H_2O at 300 K followed by exposure to 3.0 L of 2-C_3H_7I at 100 K. This procedure was followed with the idea of producing the OH surface groups expected during 2-propanol decomposition for the case of the iodide, thus, mimicking the former TPD experiments more closely. Notice that the experiments corresponding to the two top traces indeed yield almost identical results.

pane. The only acetone detected in these experiments is the perdeutero species, which means that the hydrogen-removing step is regiospecific, and involves only the secondary (middle) hydrogen. This β-hydride step is the rate-limiting reaction of the whole partial oxidation process, and is followed by the immediate desorption of the resulting acetone. As a side point, the TPD data displayed in Fig. 5 (bottom trace) and Fig. 6 also demonstrate that propene is not involved in the production of acetone in such a system. This is a thought-provoking conclusion, because alkene partial oxidation is a viable reaction performed industrially by using oxide catalysts [21,24]. Our results suggest that such a process may occur via an initial hydrogenation of the alkene to alkyl on a metal center followed by the oxygen migratory insertion/β-hydride elimination sequence of steps seen here.

The data presented so far suggest that a few requirements need to be met in order for partial oxidation reactions to take place on oxides. First, there is a need for metal atoms to be exposed on the surface. This in fact is a requisite in the experiments reported here only because the Ni sites are the ones that facilitate the dissociation of the C–I bond in the alkyl halides (a reaction that is not relevant for the oxidation

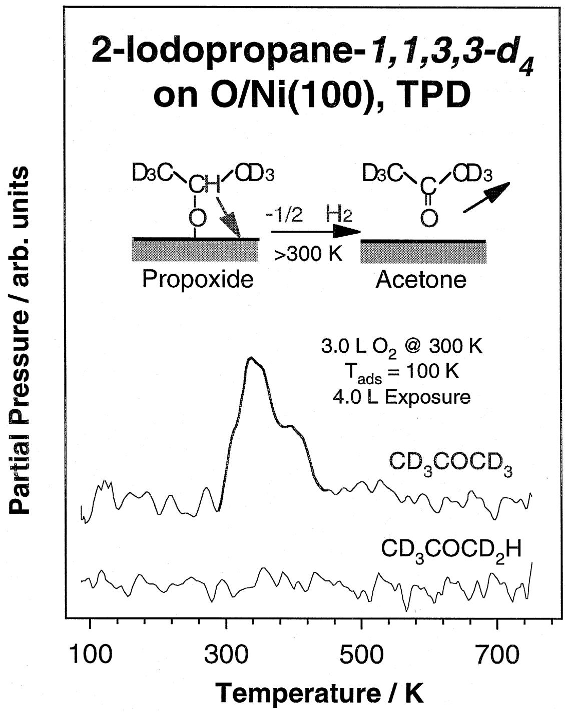


Fig. 6. Acetone TPD traces for the main isotopomers (CD_3COCD_3 and CD_3COCD_2H) expected from the reaction of CD_3CHICD_3 with oxygen on Ni(100) surfaces. The exclusive formation of perdeutero-acetone in this case indicates the high selectivity of the β-hydride elimination step from the 2-propoxide intermediate, and rules out a mechanism where an initial β-hydride elimination from 2-propyl groups on Ni sites is followed by oxygen incorporation.

of alkanes), but they may also be necessary to induce the initial C–H bond-activation in alkanes. Second, the migration of alkyl groups attached to metal atoms seems to be diffusion-limited, which means that they need to form next to oxygen atoms for the reaction to proceed. Third, the partial oxidation reaction involves alkoxide intermediates, and therefore may be favored by anything that stabilizes such species on the surface. Finally, the rate-limiting step appears to be the last β-hydride elimination, so it is important to facilitate the fast desorption of the ketone (or aldehyde) products, because otherwise they may decompose on the surface immediately after their formation.

One final observation is worth reporting here in connection with the surface-science experiments on alkyl partial oxidation, and that is the fact that OH surface groups appear to enhance such processes. As an example to illustrate this point, the top trace in Fig. 5 demonstrate that on surfaces where OH groups are present, the formation of acetone from 2-propyl groups is enhanced to the point of yielding TPD traces similar to those seen for the case of 2-propanol (compare the two top traces of Fig. 5). In fact, although no partial oxidation products at all are seen in TPD experiments with methyl, ethyl, 1-propyl, or 1-butyl iodides on purely oxygen-precovered nickel substrates, some aldehydes are in fact detected from thermal activation of those molecules if hydroxo species are present on the surface [19]. The mechanism by which the OH groups enhance the ability of the surface to induce partial oxidation reactions is still under investigation.

The possibility of extrapolating the surface-science results reported above to more realistic catalytic systems was explored here for the case of the oxidation of alcohols on a nickel wire by using a micro-batch reactor. As an example of the results obtained from those studies, Fig. 7 displays the time evolution of the gas composition during the reaction of a 1:1 2-propanol + oxygen mixture at 800 K. The left panel shows not only the expected monotonic decrease in the

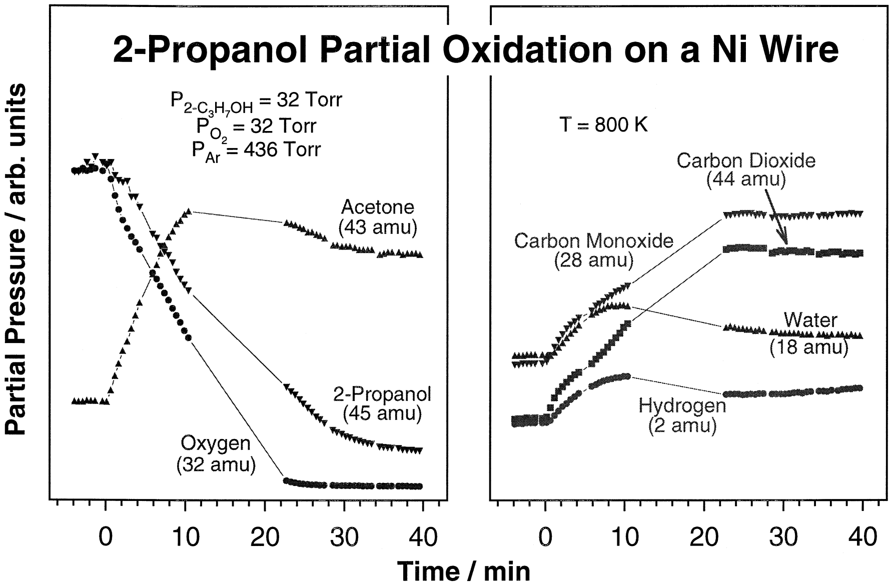


Fig. 7. Results from a typical isothermal kinetic run for the catalytic oxidation of 2-propanol on a nickel wire in a micro-batch reactor. The case presented here is that of the conversion of 32 Torr of 2-propanol with 32 Torr of oxygen at 800 K. The figure displays the temporal evolution of the partial pressures of the reactants, oxygen and 2-propanol (left panel), as well as those for the products, acetone (left panel), hydrogen, water, carbon monoxide, and carbon dioxide (right panel). Notice both the initial production of acetone and its subsequent conversion to CO and CO_2 at later times.

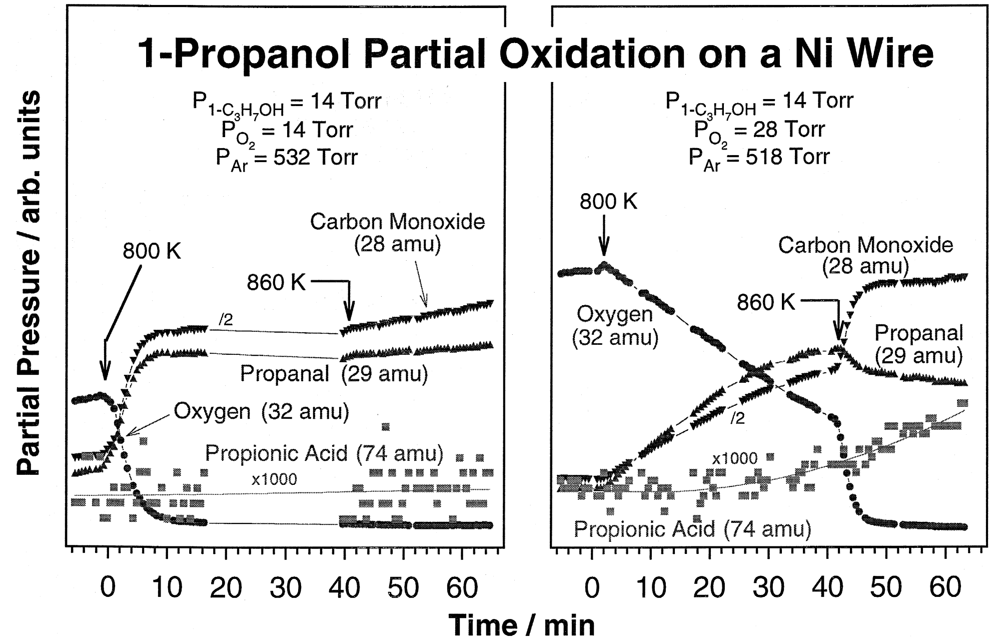


Fig. 8. Pressure-dependence studies for the catalytic oxidation of 1-propanol on a nickel wire. The left panel displays the results from a kinetic run for the conversion of 14 Torr of 1-propanol with 14 Torr of oxygen, while the right panel shows the data for a 14 Torr 1-C_3H_7OH + 28 Torr O_2 mixture. Both reactions were initially run at 800 K and then heated to 860 K after 40 min of reaction. These data show the inhibiting effect of increasing oxygen partial pressures on the partial oxidation of 1-propanol to 1-propanal. Also seen here is the fact that the excess oxygen facilitates further oxidation of the propanal to propionic acid and to carbon monoxide at 860 K.

signals associated with the reactants (2-C_3H_7OH and O_2), but also the production of acetone in the initial 10 min of the reaction. The data shown in the right panel indicate that some hydrogen and water are produced concurrently with the acetone, and that all three initial prod-

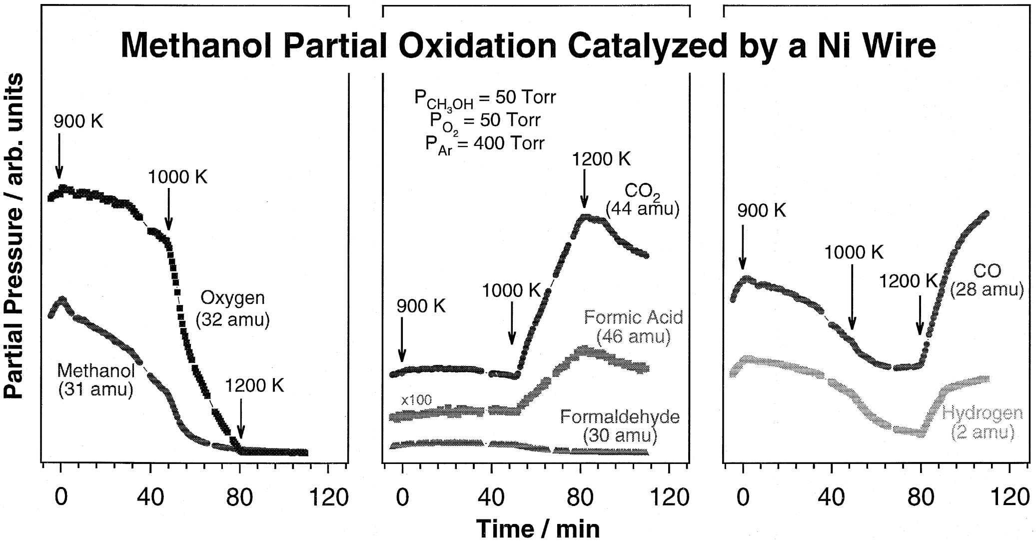


Fig. 9. Results from a kinetic run for the catalytic oxidation of 50 Torr of methanol with 50 Torr of oxygen on a nickel wire at temperatures between 900 and 1200 K. The initial formation of small amounts of formaldehyde at 900 K is overtaken in this case by further oxidation to formic acid and CO_2 at 1000 K, and ultimately to CO and hydrogen above 1200 K.

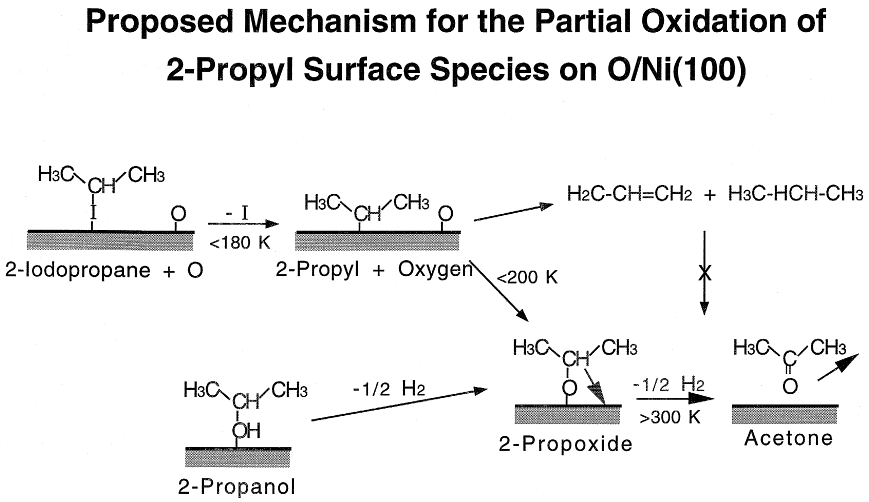
ucts eventually decompose to carbon monoxide and carbon dioxide. The important observation here is that partial oxidation products (acetone) can indeed be produced in significant quantities under the right conditions.

Fig. 8 provides additional data for the oxidation of 1-propanol to highlight the importance of choosing the right composition in the gas mixture in order to control the selectivity of the reaction. The left panel, which shows the results for a 1:1 alcohol:oxygen mixture, indicates that propanal is produced at 800 K within a few minutes of the start of the reaction, and that such a product persists in the mixture even after increasing the temperature of the nickel wire to 860 K. The data on the right, which corresponds to a second run using twice the amount of oxygen, show that excess oxygen inhibits the rate of oxidation (the concentrations of both acetone and CO grow at a much slower pace), and that the propanal can be oxidized further to carbon monoxide by increasing the temperature to 860 K. A small amount of propionic acid was produced in the second experiment as well, but other control experiments suggest that this compound is not an intermediate towards CO or CO_2 formation, but an end product itself.

Finally, other alcohols were found to follow a similar oxidation behavior to that seen with the propanols. Fig. 9 shows what happens with a 1:1 methanol:oxygen mixture as the temperature of the nickel wire is ramped from 900 to 1200 K. A small amount of formaldehyde is seen around 900 K, but that disappears at the expense of formic acid and carbon dioxide formation upon increasing the reaction temperature to 1000 K (Fig. 9, middle panel). Heating the catalysts further to 1200 K leads to the conversion of all other products to carbon monoxide and hydrogen. These are higher temperatures than those needed to oxidize the heavier alcohols, but the reaction sequence appear to be qualitatively the same. More systematic experiments are under way to test these preliminary observations.

4. Conclusions

It was shown here that, under the right conditions, substoichiometric nickel oxides may be capable of catalyzing partial oxidation reactions. A number of criteria were identified for optimizing the activity of this pathway, namely: (1)



Scheme 1. Proposed mechanism for the partial oxidation of 2-iodopropane and of 2-propanol on O/Ni(100) surfaces at low oxygen coverages. A similar mechanism is likely to operate during the catalytic oxidation of alkanes and alcohols on nickel under the appropriate conditions.

nickel atoms need to be exposed in order to promote the initial alkane activation and to stabilize the resulting alkyl surface groups; (2) oxygen atoms need to be present in the proximity of the alkyl groups for the insertion step that leads to alkoxide formation to take place (this oxygen could be located in the immediate subsurface region); (3) alkenes appear to not be direct intermediates in the conversion of alkyl groups to aldehydes or ketones; (4) surface hydroxo groups appear to enhance the partial oxidation pathway, either because they facilitate the formation of alkoxides, or because they help in the limiting H-abstraction step; and (5) the formation of ketones seems to be easier than the production of aldehydes. This latter conclusion is somewhat encouraging, because secondary C–H bonds are weaker than primary ones, and therefore easier to break; alkane activation is likely to yield branched alkyl surface moieties. A schematic representation of the mechanism proposed here for the partial oxidation of 2-iodopropane on oxygen-covered Ni(100) surfaces is provided in Scheme 1. Finally, preliminary catalytic oxidation studies with alcohols have shown that some of the ideas extracted from our surface-science studies do indeed apply to more realistic catalytic conditions.

Acknowledgements

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