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The surface chemistry of hydrocarbon partial oxidation catalysis[☆]

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Abstract

The catalytic oxidation of simple alkyl moieties and alcohols on nickel surfaces has been studied by a combination of surface-science and catalytic techniques on increasingly more complex model systems. Initial work was carried out on oxygen-treated nickel single-crystal surfaces under ultrahigh vacuum conditions. The emulation of sub-stoichiometric nickel oxides was corroborated by a number of physical and chemical means, in particular by the use of carefully chosen probe molecules. The mechanism for partial oxidation was then determined. In the case of alkyl groups, an initial facile oxygen insertion was determined to lead to the formation of surface alkoxides, and to a subsequent dehydrogenation of those intermediates at the beta position to yield aldehydes or ketones. Alcohols were found to dehydrogenate by the same β-hydride elimination step, and surface OH groups to enhance that partial oxidation pathway. High selectivity towards dehydrogenation was observed on most nickel-based catalysts, except when alumina was used as a support, where the new acid sites favored dehydration instead. Total oxidation appears to be a secondary reaction on the initial dehydrogenation products, not a parallel pathway.

Keywords: Single-crystal surfaces; Partial oxidation; Alkyls; Alcohols; Nickel

1. Introduction

One of the most critical aspects in hydrocarbon conversion is selectivity towards the production of the desired products [1]. The problem of achieving acceptable selectivities in industrial processes is particularly acute when oxidation processes are involved, because the most thermodynamically favorable reactions usually lead to the formation of undesirable products such as carbon oxides and water [2]. Selectivity towards useful partial oxidation compounds can only be accomplished via kinetic control, but that requires a good understanding of the surface reaction mechanisms. Over the past few years, we in our laboratory have stridden to enhance the basic knowledge on hydrocarbon catalytic oxidation by combining surface-science and catalytic experiments. Fundamental mechanistic questions have been addressed by increasing the complexity of the systems studied in a stepwise manner, from single crystals in ultrahigh vacuum to supported catalysts under atmospheric catalytic conditions.

Our work in this area has focused on the characterization of the surface chemistry of hydrocarbons on metal oxide surfaces. Nickel oxide has been chosen as a prototypical surface because of the ease with which its electronic and acid–base properties can be changed. In pure nickel oxide, which has a rock-salt structure, the $3d^8$ orbitals of the metal do not overlap significantly, for the stoichiometric oxide is an

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insulator. However, the introduction of a few Li^+ ions, for example, gives rise to a controlled change in the number of Ni^{3+} ions in the solid while lowering the Fermi level and making the material a p-type semiconductor [3,4]. This is a particularly interesting property for catalysis because, according to classical electronic theory, an increase in the work function of the surface may favor catalysis in which the rate-limiting step is a donor-type reaction (and a decrease in those involving an electron acceptor) [3,5]. Early reports had indeed shown that the activation energy for the catalytic oxidation of carbon monoxide on NiO decreases monotonically with lithium doping [6], and that the selectivity during ammonia oxidation can be predicted in terms of the p character of the nickel oxide [7,8]. A growing interest has also developed more recently on the use of nickel oxide as a catalyst for the conversion of methane, because the exclusive production of carbon dioxide and water seen on pure NiO is suppressed if alkali salts are added to its surface, at which point the selectivity for oxidative coupling to ethylene and ethane is enhanced [9–11].

In our research, nickel single-crystal surfaces have been oxidized and characterized in situ under ultrahigh vacuum by both physical and chemical means [12,13]. Novel ways of enhancing the growth of these oxide films were found via its assistance by ion bombardment [14,15]. CO was shown to be a very useful local probe for the investigation of defective NiO surfaces, specifically for the identification of nickel surface atoms with different oxygen coordination numbers (different oxidation states) [16]. The chemistry of ammonia on those surfaces was found to be quite a bit more complex, but to still be helpful at probing the lability of hydrogens in O–H surface groups (via H–D exchange reactions) [17].

In a second parallel direction of research, studies were performed on the conversion of alkyl groups on oxide surfaces [13,18–20]. Specifically, it was found that it is possible to induce the conversion of 2-propyl moieties to acetone, a partial oxidation product. This reaction was shown to occur via a facile oxygen insertion into the metal–carbon bond followed by β-hydride elimination of the resulting alkoxide, and to be promoted by the presence of hydroxyl groups on the surface. Finally, the selectivity of nickel catalysts in the form of either foils or supported particles was tested in partial oxidation of alcohols under catalytic conditions [13,21]. Below we expand on the results obtained from all these studies.

2. Preparation and characterization of nickel oxide surfaces

Most of our surface-science research has been carried out on well-defined model surfaces, typically single crystals, and under ultrahigh vacuum conditions. A convenient way to study the chemistry of oxides with this approach is via the in situ oxidation of metal solid samples. The growth of nickel oxide films by oxidation of nickel substrates has been characterized in great detail in the past [22,23], and can be described as follows: (1) oxygen molecules chemisorb dissociatively and with high initial sticking coefficients; (2) a few ordered oxygen overlayers form on most single-crystal surfaces; (3) NiO nucleation starts before the build-up of the chemisorbed layer is complete (before the $c(2 \times 2)$ structure covers the nickel surface in the case of Ni(1 0 0)); (4) the sticking coefficient for oxygen drops by two to three orders of magnitude as the saturation of that first monolayer is reached; (5) a thin (3–5 ML) NiO film grows around the nucleation sites at much higher exposures, on the order of hundreds/thousands of langmuirs; and (6) the oxide growth slows down even further after the NiO initial islands coalesce. This behavior was successfully reproduced in our laboratory during the growth of NiO films on both nickel foils and Ni(1 0 0) and Ni(1 1 0) single crystals, as illustrated by the data in Fig. 1, which shows ion scattering spectroscopy (ISS) data recorded during the initial stages of uptake of oxygen on Ni(1 0 0). In addition, ion bombardment was found to enhanced deep oxidation [14], and simultaneous exposure to small amounts of water to lead to the formation of a monolayer of surface hydroxyl groups on top of nickel oxide films [15].

The oxidized nickel surfaces were characterized by using a number of physical [12] and chemical [16,17] techniques. Site titration using specific probe molecules proved a particularly informative method for obtaining chemical information. For one, CO was shown to be a useful local probe for the investigation of the electronic nature of the metal atoms in defective NiO surfaces. Different peaks were seen in CO temperature-programmed desorption (TPD)

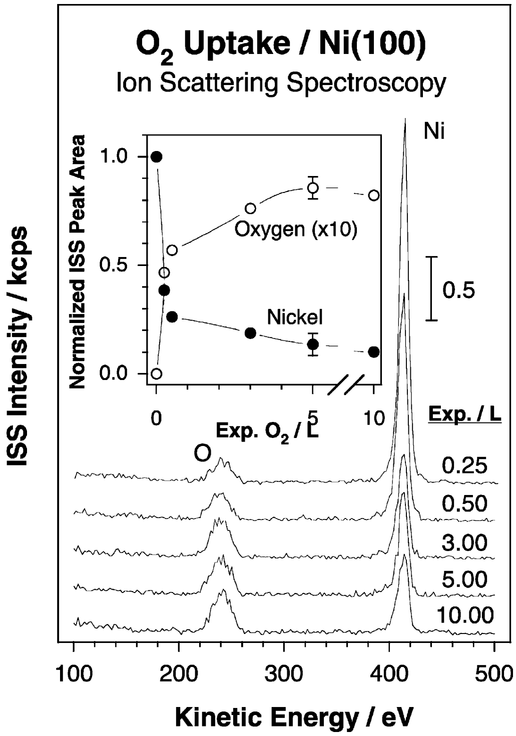

Fig. 1. Ion scattering spectroscopy (ISS) data for the uptake of oxygen on Ni(1 0 0) at 300 K. The main frame displays the raw data, while the inset shows the normalized Ni and O ISS signals vs. exposure. Note the rapid decrease in the Ni signal and the corresponding increase in the O signal during the initial exposures to oxygen, and their subsequent leveling off as the first oxygen monolayer saturates and the O_2 sticking coefficient decreases. The oxygen absolute coverage, calibrated by XPS, is estimated to be about 0.3 ML after a 3.0 L O_2 exposure.

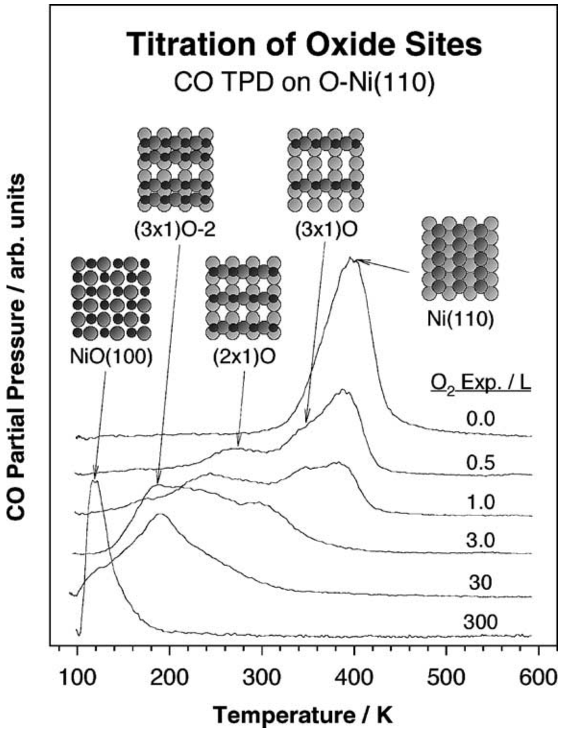

Fig. 2. CO titration of local adsorption sites on a Ni(1 1 0) single-crystal surface treated with different amounts of oxygen. The different peaks in the resulting CO temperature-programmed desorption (TPD) traces are indicative of different adsorption strengths, from approximately 30 kcal/mol on clean nickel (the 400 K peak), to less than 10 kcal/mol in the case of NiO (the feature about 120 K). The five adsorption states detected in these experiments can be directly identified with different coordination numbers of oxygen atoms around the nickel adsorption sites based on the known structures for this O–Ni(1 1 0) system. The establishment of correlations between the formation of different O–Ni sites and the selective reactivity toward specific reactions (like the partial oxidation of alkanes illustrated in the Figs. 5 and 6) can aid in the design of better catalysts.

titration traces from oxygen-treated Ni(1 1 0) surfaces under ultrahigh vacuum (Fig. 2), indicative of different adsorption strengths going from approximately 30 kcal/mol on clean nickel (the 400 K peak) to less than 10 kcal/mol in the case of NiO (the feature about 120 K). The CO probing experiments also revealed that Ar^+ bombardment of thin NiO films leads to the formation of Ni–O phases similar to those found during the early oxidation stages of the Ni metal surface.

Ammonia can also be used as a probe molecule, in this case to identify acidic surface sites. Unfortunately, the complexity of the surface chemistry of that molecule, a result of its ability to form multiple hydrogen bonds, makes the data from TPD experiments difficult to interpret. Initial studies on the reactivity of ammonia on clean Ni(1 1 0) surfaces by TPD indicated limited decomposition leading to the formation of NH_2 (ads) about 300 K, and further dehydrogenation to NH (ads) and N (ads) around 380 K [24]. Additional $NH_2(ads) + H(ads)$ recombination to NH_3 (g) was identified about 360 K. More to the point, enhancement of the dissociative pathway by surface oxygen was also observed [1,17]. Specific TPD and X-ray photoelectron spectroscopy (XPS) results to support this latter claim are provided in Fig. 3. Of particular interest in this case is the new high-temperature

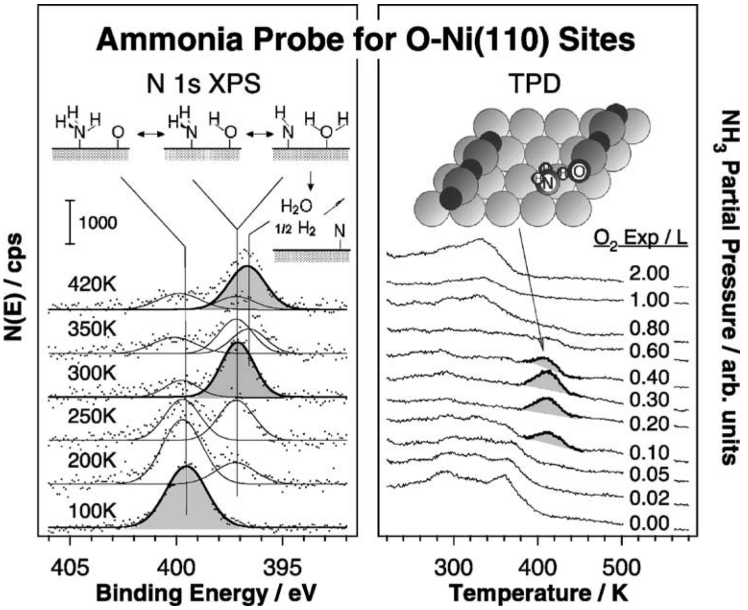

Fig. 3. Evidence for the high reactivity of some surface oxygen atoms towards ammonia activation on partially oxidized Ni(1 1 0) surfaces. Left panel: sequence of N 1s X-ray photoelectron spectroscopy (XPS) data for ammonia coadsorbed with oxygen as a function of temperature illustrating the facile interchange of hydrogen atoms between the two species. Rapid interconversion between ammonia and water is attained via the formation of NH_2, NH, and OH surface intermediates. Right panel: sequence of TPD traces for ammonia desorption from Ni(1 1 0) surfaces treated with different amounts of oxygen. A new high-temperature state is seen above 400 K at the intermediate oxygen doses associated with O atoms at the end of O–Ni–O surface chains (see diagram). These oxygen atoms are believed to be particularly active towards the abstraction of hydrogen atoms from adsorbed ammonia, the step responsible for the reactions indicated in the left panel. These experiments exemplify the importance of specific local ensembles of surface atoms in defining sites for selective catalysis.

(∼400 K) desorption state observed at intermediate oxygen coverages. Our work, as well as that of others [25,26], strongly suggest that ammonia dissociates easily below 400 K, and that the chemistry observed in that high-temperature state may involve NH_2 (and perhaps NH) surface intermediates. We propose a facile interchange along the $NH_3(ads) + O(ads) \leftrightarrow NH_2(ads) + OH(ads) \leftrightarrow NH(ads) + H_2O(ads)$ reaction coordinate [17]. Experiments with coadsorbed OH groups on the surface corroborate this hypothesis [27].

3. Alkyl reactivity on oxygen-treated nickel single-crystal surfaces

The second direction of our research has focussed on the study of the reactivity of oxidized surfaces towards the conversion of hydrocarbons, specifically on the steps related to partial oxidation processes [18,19]. For this, alkyl surface moieties were prepared via thermal excitation of alkyl halides adsorbed on oxygen-treated surfaces [28,29]. Specifically, the oxidation of 2-iodopropane on Ni(1 0 0) 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 [18]. Of particular interest are the observations derived from experiments with submonolayer oxygen coverages, where reflection–absorption infrared spectroscopy (RAIRS) data pointed to the fact that, when in close proximity, 2-propyl moieties incorporate oxygen atoms to form 2-propoxide groups (Fig. 4). The oxygen insertion step occurs at low temperatures, perhaps below 200 K, but the resulting 2-propoxide moieties, which can also be prepared by decomposition of 2-propanol, are stable on the surface up to ∼325 K. Above that

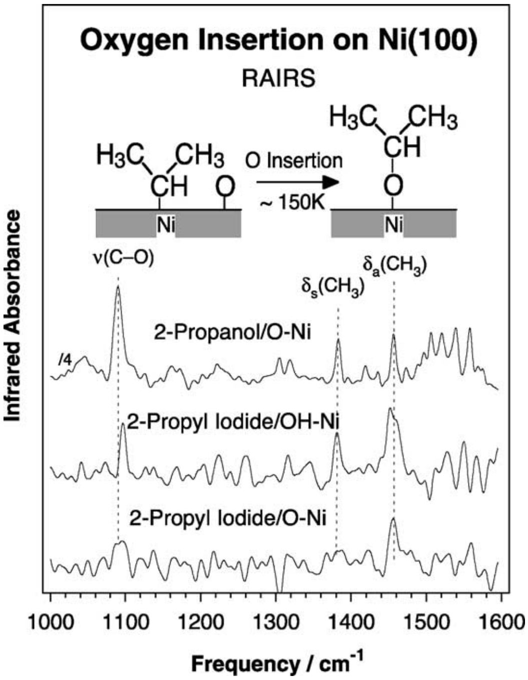

Fig. 4. Evidence for the first of the two steps responsible for the oxidation of 2-propyl groups to acetone on an oxygen-treated Ni(1 0 0) single-crystal surface. Reflection–absorption infrared spectroscopy (RAIRS) data is provided to highlight the early insertion of an oxygen atom into the metal–carbon bond to form an alkoxide intermediate; notice in particular the development of the C–O stretching vibration about 1100 cm^{-1}. This reaction appears to take place at temperatures as low as 200 K. The data also indicate that the partial oxidation reaction can be enhanced by prior deposition of hydroxyls on the surface, as those groups lead to an increase in IR signal intensities (middle spectrum). The top trace corresponds to the reactivity of 2-propanol on the same surface, and was used to help in the identification of the 2-propoxide intermediate.

temperature, the 2-propoxide does follow a β-hydride elimination step to yield acetone (Fig. 5).

Additional TPD experiments indicated that propene does not convert directly to acetone on these O/Ni(1 0 0) surfaces, at least under ultrahigh vacuum conditions. This is a thought-provoking conclusion, because alkene partial oxidation is in fact performed industrially by using oxide catalysts [30,31]. Our results suggest that such a process may occur via an initial hydrogenation of the alkene to an alkyl intermediate on a metal center followed by a sequence of oxygen migratory insertion and β-hydride elimination steps.

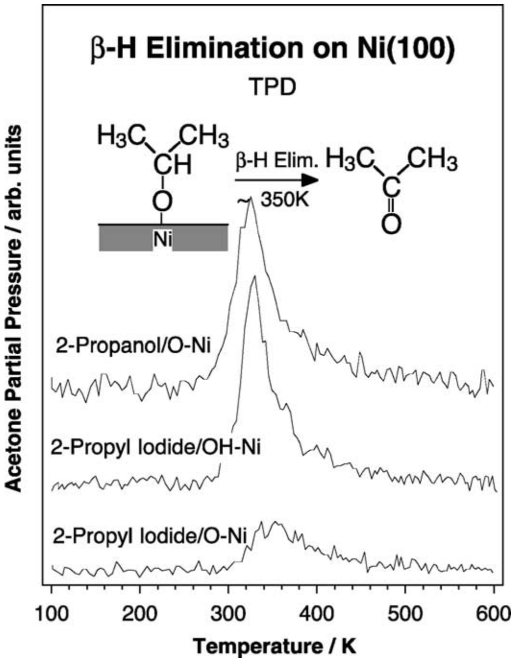

Fig. 5. Evidence for the second of the two-step mechanism responsible for the oxidation of 2-propyl groups to acetone on an oxygen-treated Ni(1 0 0) single-crystal surface, namely, a β-hydride elimination from 2-propoxide intermediates to yield acetone. The production of acetone is indicated by its desorption above 300 K in these TPD traces. Notice also the larger yield in the TPD results from the hydroxyl-covered surface shown in the middle trace. The corresponding data for 2-propanol is again provided to illustrate the similar chemistry followed by the adsorbed alkyls and alcohols, an observation that suggests that both react via the formation of the same alkoxide intermediate.

4. Role of surface hydroxyl groups

One of the issues that in our opinion has not received enough attention by the surface-science community is the role of surface hydroxyl groups in modifying the selectivity of hydrocarbon oxidation reactions. OH surface species are known to influence catalytic activity, but the details of how this happens are so far sketchy. It has been reported, for instance, that 2-propanol dehydrogenation can be favored over dehydration on anatase TiO_2 by addition of water to the reaction mixture [32]. This change in selectivity is presumably due to the formation of OH species on the surface. In another example from the surface-science community, TPD data from ethoxide moieties on

TiO_2(1 1 0) point to a competition between two reaction regimes, a hydrogen incorporation from a neighboring OH group to yield ethanol between 250 and 400 K, and a β-H elimination involving bridging oxygen vacancies created by recombination of hydroxyl groups to produce a 1:1 ethanol + ethylene mixture at 650 K [33,34]. Again, the role of surface OH is critical in defining reaction selectivities there. Finally, the formation of surface hydroxyl groups during the initial dehydrogenation of alcohols has been reported on a number of oxygen-treated transition metal single-crystal surfaces, including molybdenum [35], iron [36], rhodium [37,38], palladium [39], copper [40], and silver [41].

Our work on the conversion of 2-propyl and 2-propanol on O/Ni surfaces has also indicated that surface hydroxyl groups play an important role in helping partial oxidation pathways [13,19]. This is illustrated by the data in Fig. 5, which shows that OH surface groups enhance the formation of acetone from 2-propyl groups, to the point of yielding TPD traces similar to those obtained with 2-propanol [13,19]. Moreover, the lack of any partial oxidation products in TPD experiments with methyl, ethyl, 1-propyl, or 1-butyl iodides on oxygen-precovered nickel substrates is to be contrasted with the chemistry seen on hydroxyl-covered surfaces, where desorption of detectable amounts of the aldehyde is observed (Fig. 6) [19]. It has recently been reported that surface hydroxyl groups also promote the activation of methyl iodide on TiO_2 [42].

The enhancing effect of OH surface groups towards aldehyde and ketone production is most likely associated with at least one of the reaction steps identified above. Our infrared data in Fig. 4 indicate that the initial oxygen insertion and the formation of the alkoxides may be the key reaction modified by surface hydroxides. Were this to be the case, the selectivity for partial oxidation would be defined during the early stages of the conversion, much before the rate-limiting β-hydride elimination step takes place. However, additional preliminary results from our lab suggest that OH surface species may influence that latter reaction as well. In addition, the lack of aldehyde desorption in TPD experiments on oxygen-covered nickel may be due to the fast decomposition of that product on the surface. In that case, OH species may contribute to the passivation of further dehydrogenation steps. These issues need to be explored in more detail.

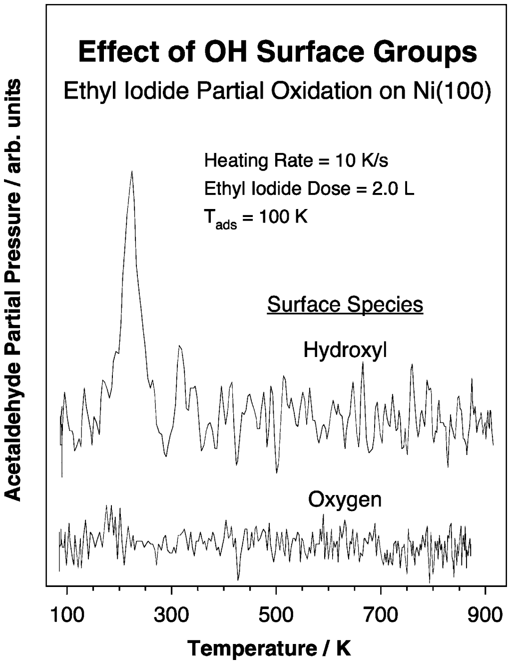

Fig. 6. Thermal desorption data illustrating the importance of surface hydroxyl groups in enhancing the selectivity of partial oxidation reactions. Shown here are TPD traces for the formation of acetaldehyde from ethyl iodide adsorbed on oxygen (bottom) and hydroxyl (top) precovered Ni(1 0 0) surfaces. An increase in acetone yield with increasing OH concentration was illustrated in the previous figure.

5. Catalytic studies

The dehydration and dehydrogenation of alcohols on nickel foils as well as on alumina- and silica-supported catalysts has also been tested by using both transmission infrared spectroscopy [43,44] and a microbatch reactor kinetic setup [21,45]. The selective oxidation of alcohols is mainly used for the production of fine chemicals, and is traditionally carried out via aqueous reactions with a variety of oxidants such as chromium, manganese, selenium, or lead oxides [46]. Unfortunately, those reactions are stoichiometric, and yield large amounts of toxic inorganic salts. In heterogeneous catalysis, selective oxidation is normally performed with silver- or copper-based catalysts [47].

Our kinetic studies on the partial oxidation of alcohols have assessed the feasibility of converting alcohols to aldehydes or ketones on nickel substrates with high selectivity (up to 95%) under appropriate conditions [13,21]. Specifically, it was determined that, on nickel foils, high partial oxidation selectivity requires the use of temperatures below 700 K and oxygen partial pressures higher than stoichiometric, that is, oxygen-to-alcohol ratios above 1:2. Zero- and half-order kinetics with respect to 2-propanol and oxygen pressures, respectively, were observed for the conversion of 2-propanol to acetone on the clean Ni catalyst; typical data for the case of the oxygen dependence is given in Fig. 7. A thin oxide-like layer with labile oxygen-containing surface species was determined to be the active catalyst for this reaction, and the rate of oxidation was found to be significantly higher on oxygen-pretreated Ni surfaces.

The kinetic behavior seen on nickel foils was by and large reproduced qualitatively on supported nickel catalysts. Indeed, nickel particles deposited on neutral silica powders display similar high selectivities towards alcohol dehydrogenation to aldehydes or ketones. When supported on alumina, however, significant dehydration is seen as well. For instance, when using a 2-propanol:oxygen 2:1 mixture, the selectivity for 2-propanol dehydrogenation to acetone on a nickel foil yields reached as high as 75%, but only about 30% on alumina. That difference is due to the formation of propene on the acidic sites of the support. In any case, transmission infrared (IR) spectroscopy characterization studies allowed for the identification of most of the intermediates in these reactions. An example of this is provided in Fig. 8, where a set of transmission IR spectra is shown for the thermal chemistry of 2-propanol on a 10% nickel catalysts supported on alumina in the presence of gas-phase oxygen [44,48]. In this particular instance, it is clear that the original alcohol decomposes between 440 and 450 K to yield surface acetone, as indicated by the new absorption bands around 1378, 1472, and 1590 cm^{-1} (the symmetric and asymmetric methyl deformations and the carbonyl stretching modes, respectively). Interestingly, additional vibrational modes associated with acetate surface species were detected under certain conditions, and, in the case of ethanol conversion on nickel supported on silica, ethoxide, acetaldehyde, acetate and formate moieties, and ultimately CO_2, were sequentially identified with increasing temperature. The effect of surface oxidation on these reactions was also studied. Again, a thin and partially oxidized layer (as identified by CO infrared probing experiments) seems to optimize the selectivity towards partial oxidation.

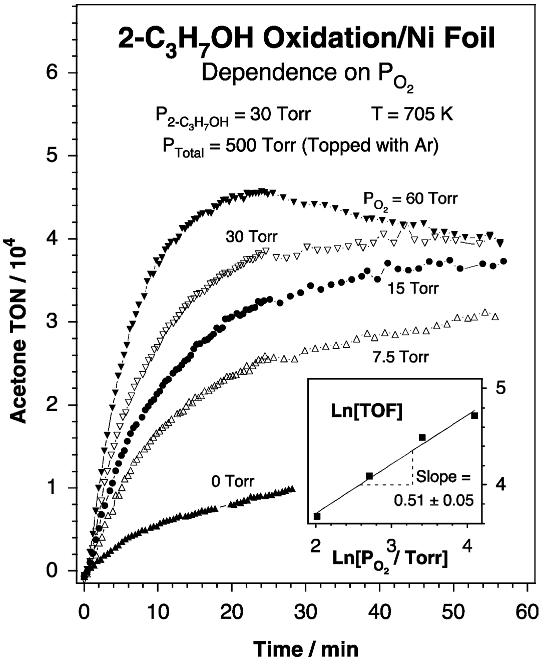

Fig. 7. Typical kinetic data for the partial oxidation of alcohols by nickel catalysts. The data in this figure show the dependence of the rate of oxidation of 2-propanol on the partial pressure of oxygen over a Ni foil at 705 ± 2 K. The main panel displays the raw data from experiments using a batch reactor, in the form of the accumulation of acetone (in turnover numbers, TON = molecules/Ni surface atoms) as a function of reaction time. The inset provides a ln–ln plot of the initial rates of formation of acetone (in turnover frequencies, TOF = TON/time) vs. oxygen pressure, as calculated from the raw kinetic data. The order of the reaction with respect to oxygen was estimated to be 0.51 ± 0.05. These experiments prove that the partial dehydrogenation of alcohols to aldehydes or ketones can be accomplished with good selectivity by using nickel foils and oxygen-rich mixtures. Similar results were obtained on silica-supported nickel catalysts, but significant dehydration was seen on alumina-based solids because of the acidity of that oxide.

Finally, both kinetic and spectroscopic evidence from our work indicate that the undesirable complete oxidation of the alcohol to CO_2 and water is mainly a sequential reaction that takes place on the acetone produced from the alcohol, not a primary

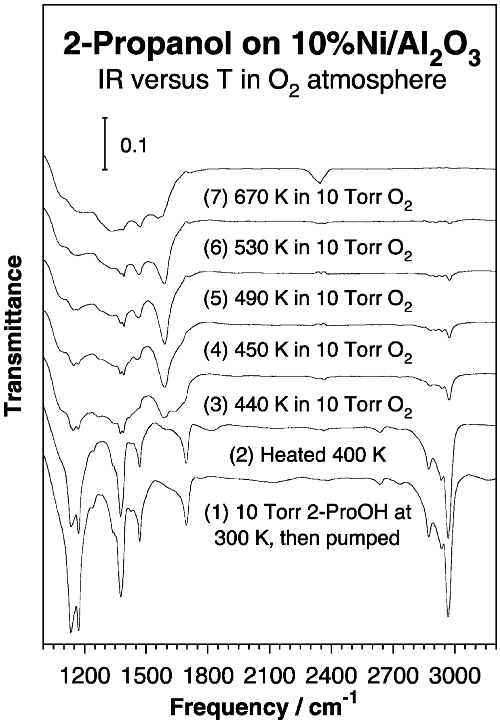

Fig. 8. Transmission infrared absorption spectra for the oxidation of 2-propanol on a 10% Ni catalyst supported on alumina after sequential exposures to 10 Torr of the alcohol and 10 Torr of oxygen. The data are shown here as a function of sample temperature. A change in the nature of the adsorbed species is seen about 440 K, from molecular adsorption to a new species, most likely acetone bonded to the metal surface. Experiments such as these allow for the identification of potential surface intermediates during catalysis.

alcohol oxidation step. In particular, infrared studies with methanol and ethanol led to the identification of the same formate and acetate surface intermediates seen with formaldehyde and acetaldehyde, and with formic and acetic acids. Also, the kinetics for the total oxidation of the alcohols to CO_2 parallel those seen with the corresponding aldehydes and ketones. This is somewhat odd, because partial and total oxidation reactions are commonly believed to follow different mechanisms. It has been suggested that, in general, oxygen molecules, either adsorbed on the surface or in the gas phase, are responsible for the formation of carbon dioxide, and that, in contrast, lattice oxygen atoms are typically required for the formation of alcohols, aldehydes, and other oxygenated hydrocarbons [49]. It is also thought that the latter steps most often require metals with more than one oxidation state, because lattice oxygen incorporation into the desorbing products leaves a vacancy in the solid that needs to be replenished by the adsorption of additional oxygen from the gas phase [50]. None of these conclusions seem to apply to the nickel catalytic system studied here.

6. Concluding remarks

In this article, a brief summary of our surface-science and catalytic work on the conversion of alkyls and alcohols on oxygen-treated nickel surfaces was provided. We believe that comprehensive studies such as this are ideally suited for the determination of the key parameters that control selectivity in partial oxidation processes. It is important to remember that the chemistry observed on model systems under vacuum not always extends directly to more realistic conditions [51–53]. In particular, it is not straightforward to assume that oxygen-treated single-crystal and foil surfaces can reproduce non-stoichiometric supported metal oxide particles. This needs to be probed by titration experiments such as those shown above. It is also not a foregone conclusion that the species isolated during the surface-science vacuum work are in fact directly involved in catalytic reactions. By carefully considering these issues, however, knowledge relevant to industrial processes can be drawn from studies on model systems. In our case, the selective dehydrogenation (versus dehydration) of alcohols on nickel surfaces could be extrapolated from the simplest solids to more realistic catalysts. The sequential nature of the oxidation, to aldehydes or ketones first, and to CO and CO_2 later, was also shown to hold in all the systems studied here. Initial advances were made on understanding how hydroxyl surface groups participate in oxidation catalysis, but more work lies ahead.

Acknowledgements

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