

## FINAL REPORT

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Title: "Molecular Design of Hydrocarbon Oxidation Catalytic Processes"

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### Abstract

The main goal of this project had been to use model systems to correlate selectivities in partial oxidation catalysis with the presence of specific sites on the surface of the catalyst. Extensive work was performed this year on characterizing oxygen-treated nickel surfaces by chemical means. Specifically, the surface chemistry of ammonia coadsorbed with atomic oxygen on Ni(110) single-crystal surfaces was studied by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). It was determined that at intermediate oxygen coverages direct ammonia adsorption on nickel sites is suppressed, but a new high-temperature reaction regime is generated at 400 K where  $\text{NH}_x$  surface fragments are rehydrogenated concurrently with the production of water and molecular hydrogen. The extensive isotope scrambling and hydrogen transfer seen from nitrogen- to oxygen-containing surface intermediates, and the optimum yields seen for this 400 K state at intermediate oxygen coverages, strongly suggest the direct interaction of the adsorbed ammonia with oxygen atoms at the end of the  $-\text{Ni}-\text{O}-$  rows that form upon reconstruction of the surface. Hydrogen transfer between ammonia and oxygen appears to take place directly via hydrogen bonding, and to be reversible but biased towards water formation. An equilibrium is reached between the produced water and the reacting surface oxygen and hydrogen. The strong influence of the OH surface groups on the thermal chemistry of the adsorbed ammonia was interpreted in terms of the adsorbing geometry of the OH groups on the surface, and of hydrogen bonding between adsorbed OH and  $\text{NH}_3$  species. In terms of alcohol reactivity, the adsorption of 2-iodoethanol, a precursor for the preparation of 2-hydroxyethyl and oxametallacycle surface species, was found to lead to two configurations involving either just the iodine atom or both iodine and hydroxyl ends of the molecule. A complex chemical behavior starts around 140 K with the production of small amounts of ethylene and water, most likely via the concerted decomposition or disproportionation of the adsorbed molecular species. The bulk of the 2-iodoethanol decomposes at about 150 K via an initial carbon-iodine scission to form  $-\text{O}(\text{H})\text{CH}_2\text{CH}_2-$  (~80%) and 2-hydroxyethyl (~20%) intermediates. Two competing reactions are involved with the subsequent conversion of the 2-hydroxyethyl species around 160 K, a reductive elimination with surface hydrogen to yield ethanol, and a  $\beta$ -H elimination to surface vinyl alcohol. The  $-\text{O}(\text{H})\text{CH}_2\text{CH}_2-$ , on the other hand, dehydrogenates to a  $-\text{OCH}_2\text{CH}_2-$  oxametallacycle species

about the same temperature. Both 2-hydroxyethyl and oxametallacycle species tautomerize to acetaldehyde, around 210 K and above 250 K, respectively, and some of that acetaldehyde desorbs while the rest decomposes to hydrogen and carbon monoxide. We contend that a better understanding of the surface chemistry of oxygen-containing surfaces can lead to better selectivities in catalysis. This is arguably the most important issue in the field of catalysis in the near future, and one that impacts several technologies of interest to DOE such as the manufacturing of speciality chemicals and the control and removal of pollutants.

Additional work was performed on the characterization of the chemistry of methyl and methylene adsorbed species on oxygen-treated nickel surfaces. Complex chemistry was observed involving not only hydrogenation and dehydrogenation steps, but also C-C couplings and methylene insertions to produce heavier hydrocarbons, and oxygen insertion reactions that yield oxygenates. Finally, a dual titration technique employing xenon and a chemically sensitive probe was developed to identify minority catalytic sites on oxide surfaces. In the case of oxygen-treated Ni(110) single crystals, it was found that both hydrogen transfer with adsorbed water or ammonia and certain hydrocarbon hydrogenation reactions take place at the end of the –Ni–O rows that form in this system. Carbon and nitrogen oxides, on the other hand, display no preference for adsorption on those sites.

## Technical Report

### 1. *Introduction.*

One of the most critical aspects in hydrocarbon conversion is selectivity towards the production of the desired products. 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. 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 have striven 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. Below we summarize key results illustrating the usefulness of this approach and highlight the results obtained from our work in the one-year period of this DOE-funded project.

The work in this area has focused on the characterization of the surface chemistry of hydrocarbons on metal oxide surfaces, on nickel oxide in particular because of the ease with which the electronic and acid-base properties of that solid can be modified. This is crucial because catalytic reactivity is closely tied to the electronic properties of the catalyst. For instance, it has been shown that the activation energy for the catalytic oxidation of carbon monoxide on NiO decreases monotonically with lithium doping, and that the selectivity during ammonia oxidation can be predicted in terms of the  $p$  character of the nickel oxide. A growing interest has also developed more recently on the tuning of the electronic properties of nickel oxide as a catalyst for the conversion of methane. In our research, nickel single-crystal surfaces have been oxidized and characterized in situ under ultrahigh vacuum by both physical and chemical means. Novel ways of enhancing the growth of these oxide films were found via its assistance by ion bombardment. 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). The chemistry of ammonia on those surfaces was found to be more complex, but to still be helpful at probing the lability of hydrogens in O-H surface groups (via H-D exchange reactions). Both chemical probes, CO, and ammonia, as well as a few others (water, nitrogen oxide, methyl iodide), were also used in combination with xenon to identify minority surface catalytic sites.

In a second parallel direction of research, studies are being performed on the conversion of alkyl groups on oxide surfaces. Our initial work showed 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  $\beta$ -hydride elimination of the resulting alkoxide, and to be promoted by the presence of hydroxyl groups on the surface. Also, the selectivity of nickel catalysts in the form of either foils or supported particles was tested in partial oxidation of alcohols under catalytic conditions. It was found that, under the right conditions, high selectivity for acetone formation can be achieved in those systems, as predicted

from our previous surface-science work. Specifically, it was determined that 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. A thin oxide-like layer 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. Our kinetic evidence also indicates that the undesirable complete oxidation of the alcohol to  $\text{CO}_2$  and water is mainly a sequential reaction that takes place on the acetone produced from the alcohol, not a primary alcohol oxidation step. The work was then expanded to the characterization of methyl and methylene fragments on these surfaces. Below we describe the results from these studies in more detail.

## 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, and was successfully reproduced in our laboratory during the growth of NiO films on nickel foils and on Ni(100) and Ni(110) single crystals. Ion bombardment was found to enhanced deep oxidation, 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. In addition, the oxidized nickel surfaces are being characterized by using a number of physical and chemical techniques. For one, different peaks were seen in CO temperature-programmed desorption (TPD) titration traces from oxygen-treated Ni(110) surfaces under ultrahigh vacuum, 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  $\text{Ar}^+$  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(110) surfaces by TPD indicated limited decomposition leading to the formation of  $\text{NH}_2(\text{ads})$  about 300 K, and further dehydrogenation to  $\text{NH}(\text{ads})$  and  $\text{N}(\text{ads})$  around 380 K. Additional  $\text{NH}_2(\text{ads}) + \text{H}(\text{ads})$  recombination to  $\text{NH}_3(\text{g})$  was identified about 360 K. More to the point, enhancement of the dissociative pathway by surface oxygen was observed in work performed by us this year. Specific TPD and X-ray photoelectron spectroscopy (XPS) results to support this latter claim are provided in Figure 1. Of particular interest in this case is the new high-temperature ( $\sim 400$  K) desorption state observed at intermediate oxygen coverages. Our work, as well as that of others, strongly suggest that ammonia dissociates easily below 400 K, and that the chemistry observed in that high-temperature state may involve  $\text{NH}_2$  (and perhaps  $\text{NH}$ ) surface intermediates.

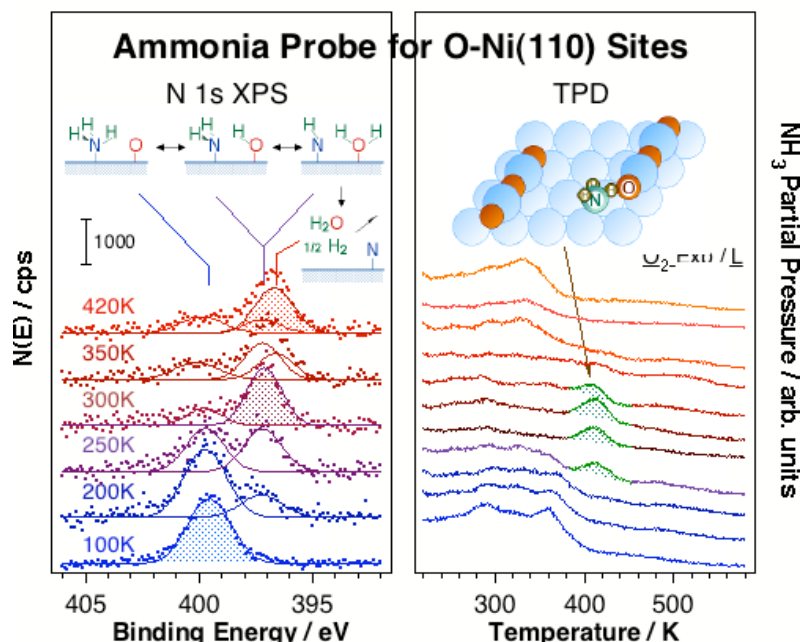


Figure 1

Our work with oxygen-treated nickel surfaces was expanded to describe the thermal chemistry of ammonia on hydroxyl-precovered Ni(110). In the  $\text{NH}_3/\text{O}/\text{Ni}(110)$  system, it was found that the  $\text{N}_2$  TPD peak, indicative of ammonia decomposition, increases in intensity continuously with increasing oxygen exposure between 0 and 0.25 L, and reaches saturation above 0.30 L  $\text{O}_2$ . On the other hand, the new high-temperature ( $\sim 400$  K)  $\text{NH}_3$  feature reaches a maximum yield at about 0.10 L  $\text{O}_2$ , but then disappears above 0.40 L  $\text{O}_2$ . This suggests that oxygen always aids in the dehydrogenation of ammonia, but that only at intermediate O coverages rehydrogenation is possible. The studies reported here confirmed the similarities in the chemistry of  $\text{NH}_3$  on both  $\text{OH}/\text{Ni}(110)$  and  $\text{O}/\text{Ni}(110)$  surfaces. As with oxygen coadsorption or electron radiation, OH predosing on Ni(110) leads to the production of ammonia above 400 K. In contrast to the case of coadsorbed oxygen, however, the OH-precovered surface leads to additional changes in the  $\alpha$ - and  $\beta$ - $\text{NH}_3$  desorption states, those associated with direct bonding to the Ni sites and to hydrogen bonding to the first layer of adsorbates, respectively. These intensity variations are explained by OH adsorption geometry arguments. Both the emergence of the high-temperature ammonia feature and the shifts of the  $\beta$ - $\text{NH}_3$  states to higher desorption temperatures are suggested to be caused by H-bonding among the  $\text{NH}_3$  and OH adsorbates: H-bonding provides an additional mechanism for trapping  $\text{NH}_3$  molecules on the surface.

In a more recent advance, a dual titration methodology was developed to probe minority sites on solid surfaces with unique chemical properties of potential relevance to heterogeneous catalysis. Our approach involves the initial dosing of a chemical probe such as carbon monoxide or ammonia to drive their selective adsorption onto specific sites with particular chemical activity, and the subsequent adsorption of Xenon to help identify the nature of those sites. A combination of photoelectron (PAX) and temperature-programmed desorption (TPD) spectroscopies are used to characterize the Xe adsorption. The chemistry of oxygen-modified Ni(110) single crystals was probed to test this methodology. It was observed that while CO does not discriminate

among the various sites present on those surfaces, ammonia binds preferentially to the end of -Ni-O rows and modifies the local electrostatic potential of those sites. In addition, it was determined that adsorbed CO aids in a reversible surface reconstruction involving the coalescence of fragmented surface -Ni-O rows at high (>350 K) temperatures. This work was published in the prestigious journal *Nature Materials*.

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

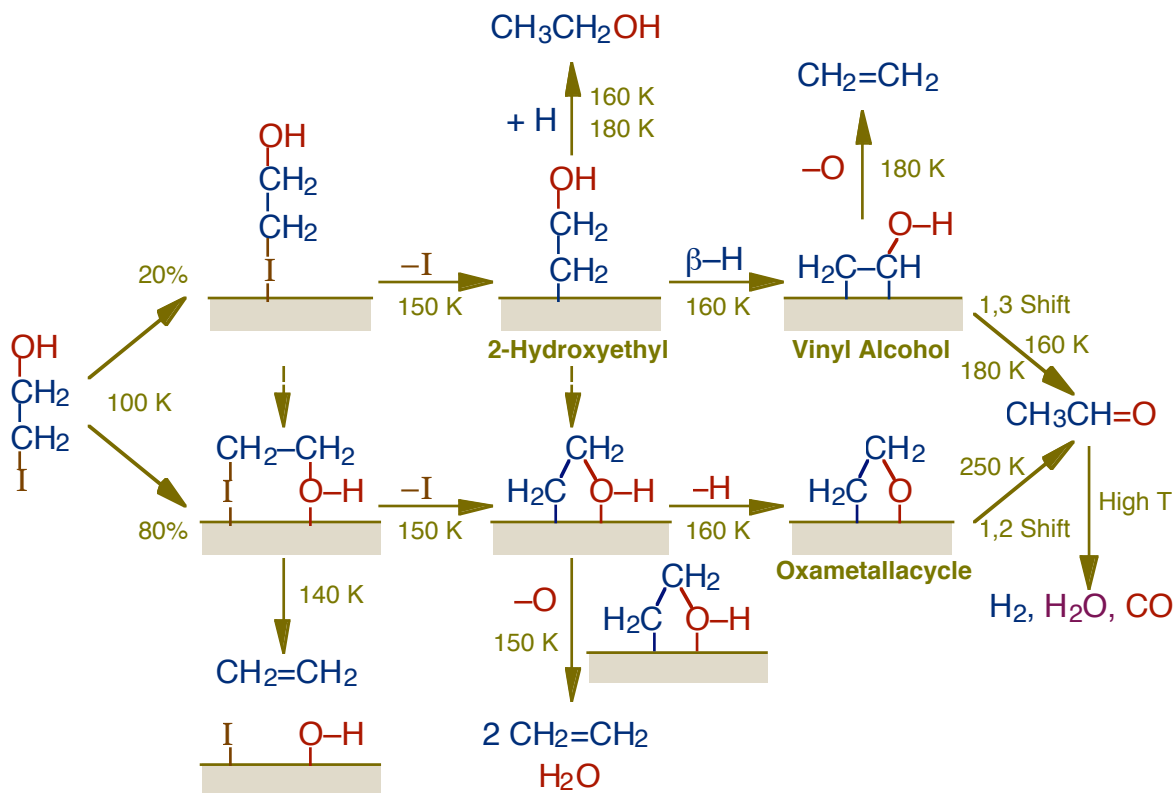
The second direction of our research has focussed on the study of the reactivity of oxidized surfaces towards the conversion of hydrocarbons, specifically on the steps related to partial oxidation processes. For this, alkyl surface moieties were prepared via thermal excitation of alkyl halides adsorbed on oxygen-treated surfaces. In the case of the oxidation of 2-iodopropane on Ni(100), it was found that, at submonolayer oxygen coverages, 2-propyl moieties incorporate oxygen atoms to form 2-propoxide groups. 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 temperature, the 2-propoxide does follow a  $\beta$ -hydride elimination step to yield acetone. Additional TPD experiments indicated that propene does not convert directly to acetone on these O/Ni(100) surfaces. This is a thought-provoking conclusion, because alkene partial oxidation is in fact performed industrially by using oxide catalysts. 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  $\beta$ -hydride elimination steps.

In terms of alkoxide dehydration, the order in which the C-O and  $\gamma$ -C-H bond-breaking steps take place is being interrogated via the use of appropriate surface precursors. Early gamma elimination should lead to the formation of an oxametallacycle intermediate, a reaction that is not facile on late transition metals but could be enhanced by appropriate substitutions. Barteau et al. has recently demonstrated that HOCH<sub>2</sub>CH<sub>2</sub>I can be used to prepare a surface oxametallabutane surface moiety. We have explored the chemistry of that molecule on Ni(100) surfaces. I 3d and O 1s XPS data indicated that 2-iodoethanol adsorbs in two geometries at 100 K, a majority -O(H)CH<sub>2</sub>CH<sub>2</sub>I- species anchored to the surface through both the iodine and oxygen atoms, and a minority configuration attached only via the iodine end of the molecule. The initial activation of both species occurs around 150 K, and involves the scission of the C-I bond to yield -O(H)CH<sub>2</sub>CH<sub>2</sub>- and 2-hydroxyethyl intermediates, respectively. A low-temperature decomposition channel does seem to precede that reaction, producing small amounts of ethylene and water starting around 140 K. This pathway most likely involves either the simultaneous breaking of both C-I and C-O bonds in the -O(H)CH<sub>2</sub>CH<sub>2</sub>I- molecular species, and/or a disproportionation between two interacting (hydrogen-bonded) -O(H)CH<sub>2</sub>CH<sub>2</sub>- surface moieties once the C-I bond has been broken.

The 2-hydroxyethyl intermediate resulting from iodine removal in iodine-bonded molecular species reacts further around 160 K via two competing steps, a reductive elimination with surface hydrogen to produce ethanol, and a  $\beta$ -hydride elimination to yield surface vinyl alcohol. Ethanol desorption is seen in TPD experiments in two peaks around 175 and 210 K; its origin from hydrogenation of 2-hydroxyethyl intermediates is corroborated by the incorporation of only

one deuterium atom when  $D_2$  is predosed on the Ni(100) surface. The vinyl alcohol converts further on the surface, a small amount losing its oxygen atom to produce ethylene (detected around 210 K), and the rest tautomerizing to acetaldehyde (180 and 210 K peaks in TPD).

## Reaction Scheme for 2-Iodoethanol on Ni(100)



Based on O 1s XPS data as a function of temperature, it is proposed that the  $-O(H)CH_2CH_2I-$  intermediate dehydrogenates around 160 K to produce a  $-OCH_2CH_2I-$  surface oxametallacycle. This intermediate has previously been identified on silver single crystal surfaces, and proposed on rhodium, palladium, and other transition metals. At higher temperatures, that oxametallacycle isomerizes via a 1,2 hydrogen shift to yield acetaldehyde, some of which desorbs in a wide temperature range starting around 250 K and peaking about 300 K. Hydrogenation of the oxametallacycle to ethoxide can be ruled out by the absence of significant production of acetaldehyde from adsorbed ethanol (a good precursor for the ethoxide species), and also by the absence of any ethanol- $d_2$  production in experiments with coadsorbed 2-iodoethanol and deuterium. Formation of acetaldehyde via a  $\beta$ -hydride elimination of oxametallacycle to an allylic species followed by rehydrogenation at the terminal methylene moiety is also discarded based on the inhibition of high-temperature acetaldehyde production in the presence of surface hydrogen. Finally, high-temperature  $H_2$  and  $CO$  desorption may be accounted by decomposition of adsorbed acetaldehyde, since similar chemistry is observed when starting from that adsorbate.

The overall reaction network associated with this system is summarized in the scheme in the previous page.

We are also interested in the study of oxidative coupling reactions. There have been a number of catalytic studies on these potentially commercial processes, but virtually no atomic-level characterization of the corresponding surface steps has been performed to date. To the best of our knowledge, only polymerization of methyl groups on nickel and molybdenum oxides has been reported. The experiments we have carried out on this system indicate much more complex chemistry, including the polymerization reported previously, but also the formation of methane and oxygenated hydrocarbons. It should be pointed out that the raw TPD data contain extensive and overlapping information, and therefore need careful analysis, in particular proper deconvolution. An example of how this works is shown in Figure 2 for the results from a Ni(110) surface first dosed with 0.3 L of oxygen at room temperature followed by 3.0 L of methyl iodide. The focus on those data is on the detection of high molecular weight hydrocarbons. The left panel shows the raw data for a number (15) of key masses, while the right frame reports the results from our deconvolution procedure.

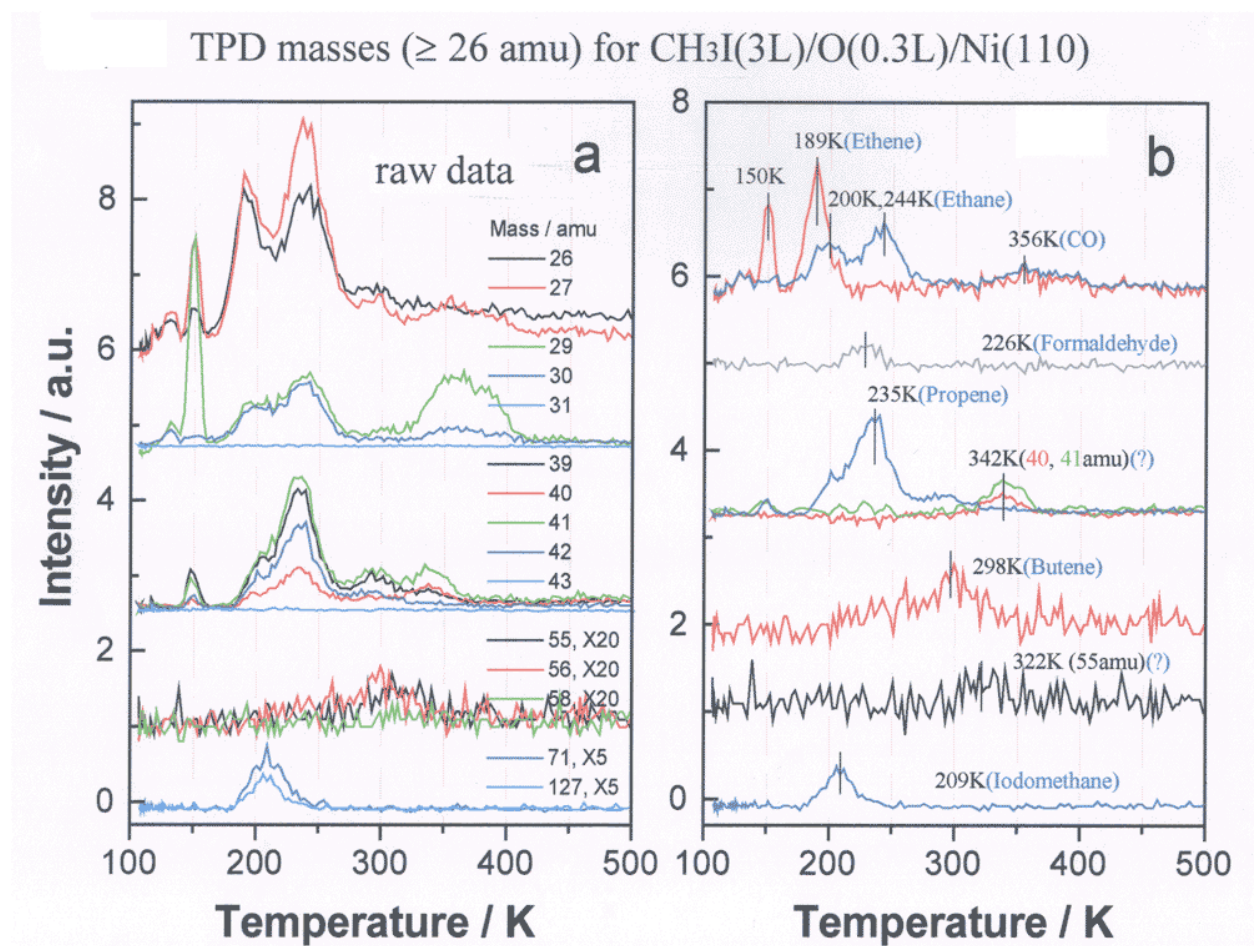


Figure 2



A number of observations derive from the data in Figure 2. Specifically, those TPD show the production of a number of olefins, including ethylene, propene and butene. When combined with experiments using diiodomethane, a precursor for methylene surface groups, these data suggest that methyl groups may first dehydrogenate to form methylene surface species, and then recombine to yield ethylene; chain growth is then likely via methylene insertion steps. Extensive ethane production is also seen at 200 and 244 K, the product of coupling of two methyl groups. Finally, detectable amounts of formaldehyde production are reported. Oxygen insertion into metal-carbon bonds may lead to methoxide formation, and  $\beta$ -hydride elimination from those to the production of the aldehyde. This mechanism appears to be optimized at intermediate oxygen coverages. The evolution of the most important TPD traces versus oxygen precoverage is shown in Figure 3.

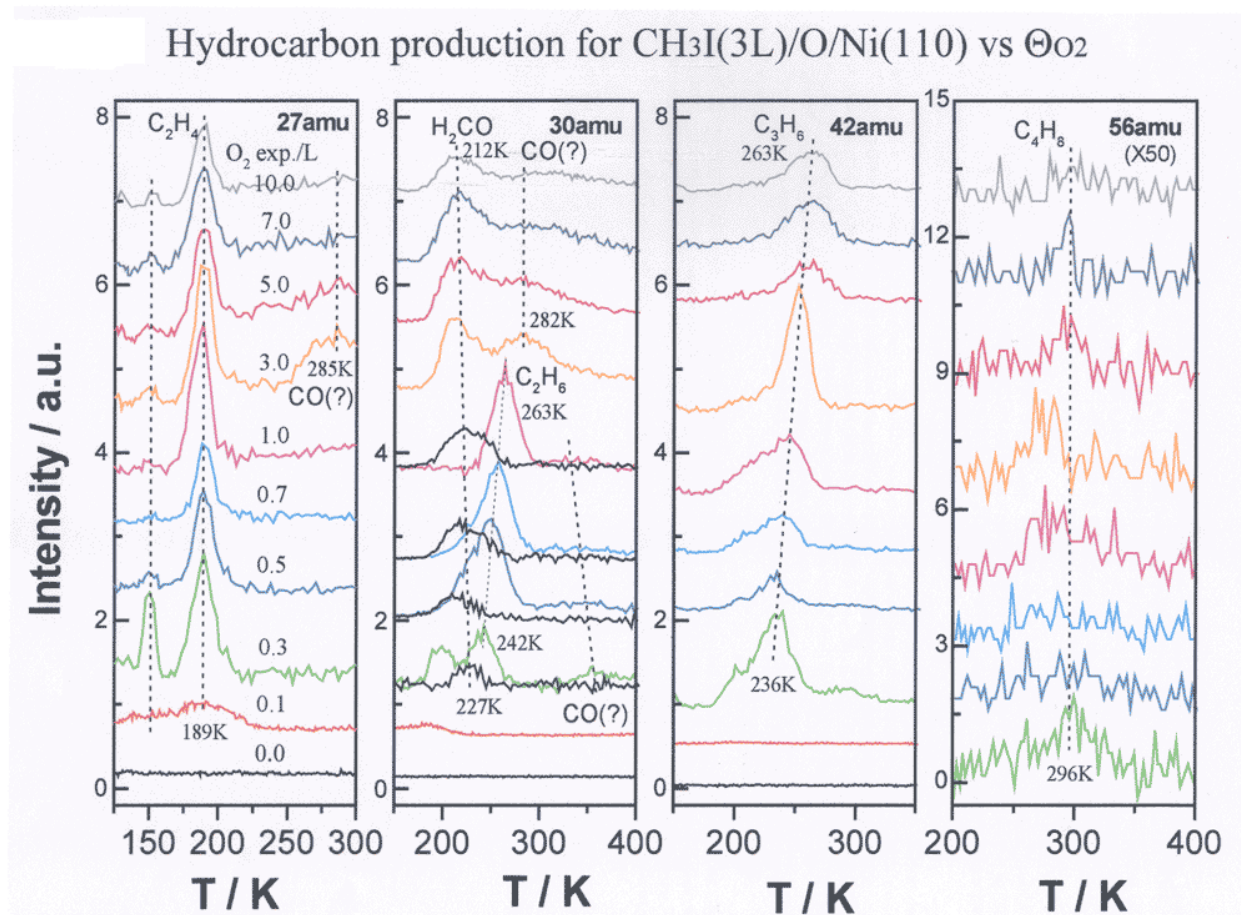


Figure 3

The effect of coadsorbed oxygen was also explored for the thermal chemistry of diiodomethane on Ni(110) single-crystal surfaces. Significant amounts of methane and other heavier hydrocarbons are produced after further thermal activation of chemisorbed methylene groups, the same as with the methyl moieties. The production of alkanes and alkenes, which is accounted for by a chain-growth mechanism where the initial hydrogenation of some adsorbed methylene to methyl moieties is followed by a rate-limiting methylene insertion step to yield ethyl intermediates, is inhibited but not fully blocked by the coadsorbed oxygen. A few new avenues

are also added by oxygen in this system, including a direct coupling of two methylene groups to ethylene, the insertion of an oxygen atom into a nickel-methylene group to produce formaldehyde, and a parallel methylene insertion chain-growth sequence starting from a  $\text{CH}_2\text{I}_{\text{ads}}$  intermediate to ultimately yield  $\text{C}_3\text{H}_5\cdot$  and  $\text{C}_4\text{H}_7\cdot$  unsaturated gas-phase radicals.

#### 4. Catalytic studies.

We have also tested alcohol dehydration and dehydrogenation processes on nickel foils as well as on alumina- and silica-supported catalysts by using both transmission infrared spectroscopy and a microbatch reactor kinetic setup. 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. 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.

### Alcohol Catalytic Selective Oxidation On Ni Foils

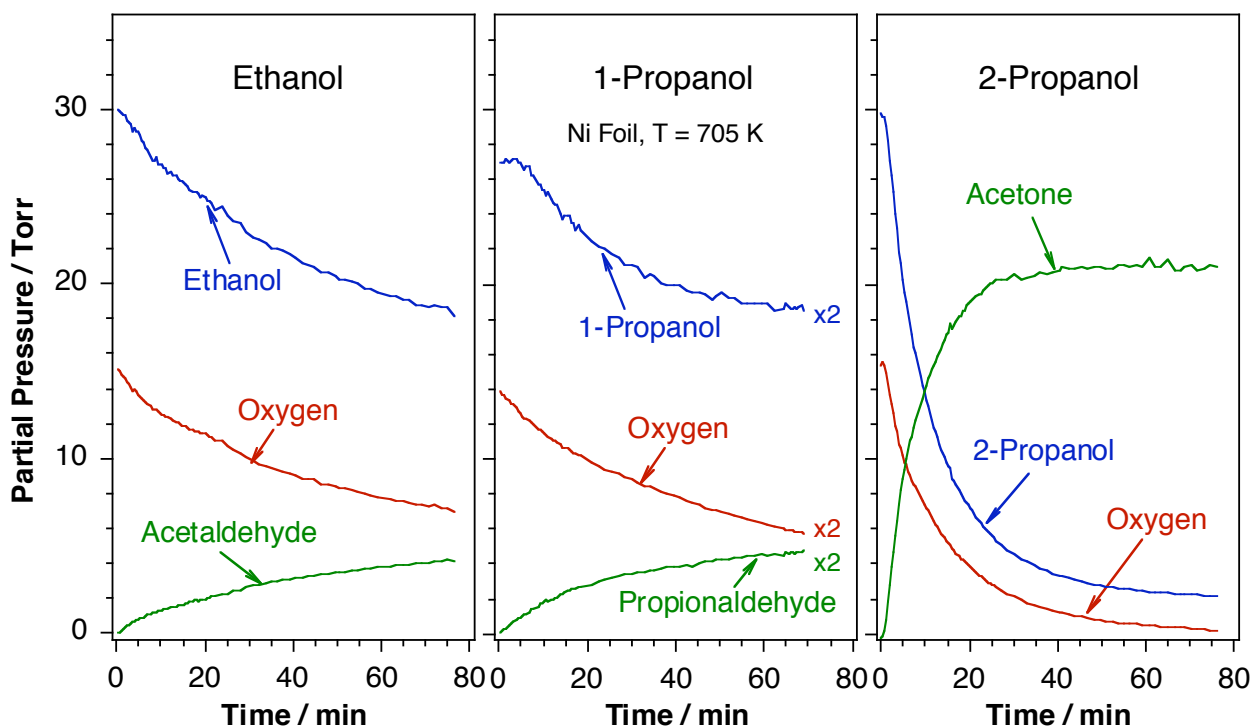


Figure 4

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. 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. A thin (but non-stoichiometric)

oxide-like layer 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 initial studies were performed using 2-propanol because it is easier to isolate the ketone product from that reaction, but the conversion of primary alcohols to aldehydes proved to be quite efficient as well. Examples of the kinetic runs carried out with our micro-batch reactor are shown in Figure 4.

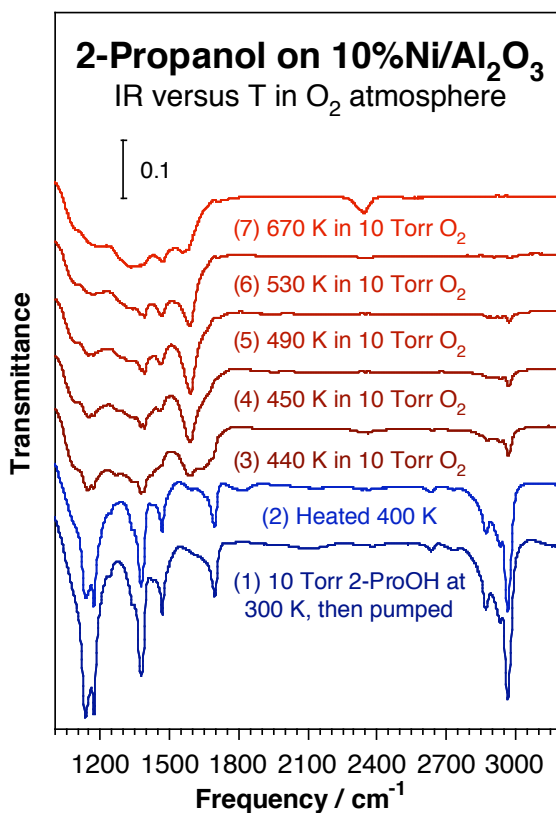


Figure 5

The kinetic behavior seen on nickel foils was by and large reproduced this year 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 allow for the identification of most of the intermediates in these reactions. An example of this is provided in Figure 5, 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. 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  $\text{cm}^{-1}$  (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  $\text{CO}_2$ , were sequentially identified with increasing temperature. The effect of surface oxidation on these reactions was also studied. Again, a thin partially oxidized layer (as identified by CO infrared probing experiments) seems to optimize the selectivity towards partial oxidation.

Finally, both kinetic and spectroscopic evidence from our work indicate that the undesirable complete oxidation of the alcohol to  $\text{CO}_2$  and water is mainly a sequential reaction that takes place on the acetone produced from the alcohol, not a primary alcohol oxidation step. This is somewhat odd, because partial and total oxidation reactions are commonly believed to follow different mechanisms. It has been suggested that while oxygen molecules, either adsorbed on the surface or in the gas phase, are responsible for the formation of carbon dioxide, lattice oxygen atoms are required for the formation of alcohols, aldehydes, and other oxygenated hydrocarbons. 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. None of these conclusions seem to apply to the nickel catalytic system studied here.

## Technical Reports funded by this DOE Grant

### 1. Publications (Scientific Journals).

1. F. Zaera, The Surface Chemistry of Hydrocarbon Partial Oxidation Catalysis, *Catal. Today*, **81(2)**, 149-157 (2003).
2. H. Guo and F. Zaera, Reactivity of Hydroxyl Species from Coadsorption of Oxygen and Water on Ni(110) Single-Crystal Surfaces, *Catal. Lett.*, **88(3-4)**, 95-104 (2003).
3. Q. Zhao and F. Zaera, Switching of Alcohol Oxidation Mechanism on Nickel Surfaces by Fluorine Substitution, *J. Am. Chem. Soc.*, **125(36)**, 10776-10777 (2003).
4. Q. Zhao and F. Zaera, Adsorption and Thermal Conversion of 2-Iodoethanol on Ni(100) Surfaces: Hydroxyalkyls and Oxametallacycles as Key Intermediates during the Catalytic Oxidation of Hydrocarbons, *J. Phys. Chem. B*, **107(34)**, 9047-9055 (2003).
5. N. Gleason, J. Guevremont and F. Zaera, Thermal chemistry of 2-Propanol and 2-Propyl Iodide on Clean and Oxygen-Pretreated Ni(100) Single Crystal Surfaces, *J. Phys. Chem. B*, **107(40)**, 11133-11141 (2003).
6. H. Guo and F. Zaera, Thermal Chemistry of Diiodomethane on Ni(110) Surfaces: I. Clean and Hydrogen Predosed, *Surf. Sci.*, **547(3)**, 284-298 (2003).
7. H. Guo and F. Zaera, Thermal Chemistry of Diiodomethane on Ni(110) Surfaces: II. Effect of Coadsorbed Oxygen, *Surf. Sci.*, **547(3)**, 299-314 (2003).
8. F. Zaera, Mechanistic Requirements for Catalytic Active Sites, *J. Phys.: Cond. Matter*, **16(22)**, S2299 -S2310 (2004).
9. H. Guo and F. Zaera, Thermal Chemistry of Iodomethane on Ni(110): 1. Clean and Hydrogen Predosed Surfaces, *J. Phys. Chem. B*, **108(41)**, 16220-16225 (2004).
10. H. Guo and F. Zaera, Thermal Chemistry of Iodomethane on Ni(110): 2. Effect of Coadsorbed Oxygen, *J. Phys. Chem. B*, **108(41)**, 16226-16232 (2004).
11. Hansheng Guo and Francisco Zaera, Xenon as a Probe for Minority Sites on Solid Surfaces, *Nature Mater.*, **5(6)**, 489-493 (2006).

### 2. Presentations: I. Invited.

1. Davison Catalysts, W. R. Grace and Company, November 2003
2. 2nd University of California Symposium on Surface Science and its Applications, San Diego, California, February 2004
3. The Third San Luis Symposium on Surfaces, Interfaces and Catalysis, Mérida, Venezuela, March 2004
4. 227th ACS National Meeting, Anaheim, California, March-April 2004
5. Catalysis Club of Chicago 2004 Spring Symposium, Chicago, Illinois, May 2004
6. DOE 2004 Catalysis and Chemical Transformations Contractors' Meeting, Rockville, Maryland, May 2004
7. 2004 Gordon Research Conference on Catalysis, New London, New Hampshire, June 2004
8. Molecule-Surface Interactions: Elementary Reactive Processes, San Sebastian, Spain, September 2004
9. The 15th CRC International Symposium on Catalytic Reaction Dynamics and Surface Nano-structures, Sapporo, Japan, October 2004

3. *Presentations: II. Contributed.*

1. 227th ACS National Meeting, Anaheim, California, March-April 2004 (presented by Hansheng Guo)
2. 51st AVS Annual Symposium, Anaheim, California, November 2004 (presented by Hansheng Guo)

**Special Recognition Received by the PI in this period**

2003 North American Catalysis Society Paul H. Emmett Award  
2004 Humboldt Research Award for Senior U.S. Scientist  
Editor, *The Journal of Molecular Catalysis A: Chemical*.