Varied Thermal Chemistry of Hydrocarbons on Nickel Single-Crystal Surfaces

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Abstract Temperature programmed desorption (TPD) results are reported for the conversion of styrene, bromocyclopentane, 1-pentene, 1,5-pentadiene, and 1,5-diiodopentane on Ni(100), and of iodoethane and 1- and 2-iodopropane on Ni(110) single-crystal surfaces. The purpose of these experiments was to illustrate the versatility of nickel in promoting a variety of surface steps for the conversion of adsorbed hydrocarbons. Our examples include the selective hydrogenolysis of styrene to toluene, the migration of carbon–carbon double bonds in cyclopentene and 1-pentene, the ring closure of C₅ metallacyclic surface intermediates, the coupling of alkyl groups, and the growth of hydrocarbon chains starting from ethyl and propyl surface intermediates. Additional information is reported on the relative rates of the hydrogenation and dehydrogenation surface steps responsible for multiple H–D exchange steps.

Keywords Hydrocarbons · Nickel · Thermal desorption · Hydrogenolysis · Cyclization · Double-bond migration · Chain growth

1 Introduction

There have been over the years extensive surface-science studies published by us [1–24] and others [25–45] on the thermal chemistry of small hydrocarbons on nickel single-crystal surfaces. In general, the thermal chemistry observed in those studies is consonant with that expected from the

position of nickel in the periodic table. Indeed, Ni single-crystal surfaces are typically more reactive than those of heavier late-transition metals such as Pd, Pt, or Rh, but still capable of favoring several dehydrogenation and, to a lesser extent, hydrogenation steps [46–48]. Specifically, olefins are readily dehydrogenated at relatively low temperatures to vinyl [3, 6, 35], acetylene [2, 25, 37], and alkylidyne [42] surface species, but can also be hydrogenated in the presence of coadsorbed hydrogen, and can even undergo isotope exchange if deuterium is used instead. Similarly, alkyl groups are prone to dehydrogenation reactions [13, 49], in this case preferentially via β -hydride elimination steps [10, 50], but undergo reductive elimination with coadsorbed hydrogen to produce alkanes as well [11, 22, 51, 52].

In this report, we expand on the previous work cited above to illustrate the variety of surface steps available to hydrocarbon moieties adsorbed on nickel single-crystal surfaces. New results with selected molecules are discussed in terms of their surface chemistry, emphasizing key steps either not previously observed or rarely highlighted in the past. In addition to hydrogenation, dehydrogenation, and H–D exchange processes, carbon–carbon scission and carbon–carbon formation steps are identified. A brief discussion is provided on the potential implications of this diverse chemistry on the uses of nickel in catalysis.

2 Experimental

The experiments reported here were carried out in one of two ultrahigh vacuum (UHV) instruments described in detail previously [7, 53–56]. They both consist of stainless steel vessels pumped with turbomolecular pumps to a base pressure on the order of 1×10^{-10} Torr. Both instruments

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are equipped with a computer-driven quadrupole mass spectrometer for temperature-programmed desorption (TPD) experiments, a manipulator capable of holding the nickel single crystal in place, of x – y – z – θ displacement, and of resistive heating and liquid-nitrogen cooling to any temperature between 80 and 1300 K, and an ion gun for surface cleaning. The temperature of the nickel crystal is controlled by using homemade electronics, and is ramped at a linear rate of 10 K/s for the TPD experiments. The evolution of the partial pressure of up to 15 different masses could be followed simultaneously in a given TPD run by using the computer interface. Deconvolution of the raw data to extract the desorption behavior of the relevant species was done by using a procedure described in detail elsewhere [57]. In this report the signal intensities are reported in arbitrary units (except for the deconvoluted data in Figs. 3 and 5, which were calibrated into units of pressure), but relative scales are provided for relative comparisons.

Two different nickel single crystals were used in these studies, cut along the (100) and (110) orientations, respectively. Their surfaces were cleaned by using a combination of oxygen treatments, ion sputtering, and annealing until no impurities were detected by X-ray photoelectron spectroscopy (XPS) and reported TPD for CO and H₂ could be reproduced. Gas dosing was done via leak valves, by backfilling of the chamber. Exposures were carried out with the crystal at temperatures below 100 K unless otherwise indicated, and are reported in Langmuirs (1 L = 1×10^{-6} Torr s), uncorrected for ion gauge sensitivities. All gases were purchased from Matheson (research purity), and used as supplied. The liquid samples were purchased from Aldrich, and purified via vacuum distillation in situ in the gas manifold before introduction to the UHV chamber.

3 Results and Discussion

The first example to be reported here is that of the thermal conversion of styrene on Ni(100) surfaces. Typical TPD data are shown in Fig. 1, for the conversion of styrene on clean (left) and hydrogen-predosed (right) surfaces. A small amount of molecular desorption is seen in these data, around 217 K from the clean surface and about 190 K on the hydrogen-predosed nickel. Hydrogenation to ethylbenzene is clearly detected at 215 K in the latter case, the product of reductive elimination of styrene with the coadsorbed hydrogen. Dehydrogenation is evident by the evolution of H₂, and the stepwise nature of that process is indicated by the multiple peaks seen in the H₂ traces, with particularly sharp features about 350 and 500 K and broader features extending all the way to 900 K.

Fig. 1 Temperature programmed desorption (TPD) traces for the desorption of hydrogen, toluene, (molecular) styrene, and ethylbenzene from activation of 9.0 L of styrene dosed on a Ni(100) single-crystal surface at 100 K, clean (*left*) and after predosing 2.0 L of H₂ (*right*). Particularly noteworthy here is the detection of toluene, which requires the selective breaking of the carbon–carbon vinyl bond

All these observations are consistent with the hydrogenation and dehydrogenation chemistry seen for other hydrocarbons on nickel surfaces. The new observation here is the clear detection of toluene, at 340 K on clean Ni(100) and at 315 K on the hydrogen-predosed surface. This is indicative of the selective scission of a carbon–carbon bond, perhaps the first time this has been reported in surface-science studies with olefins on nickel single-crystal surfaces. The question arises about the mechanism by which this reaction occurs. The chemisorption and initial conversion of styrene on this Ni(100) surface is most likely initiated at the vinyl group of styrene (see below). It is also quite likely that the carbon–carbon bond-breaking reaction is preceded by one or more dehydrogenation steps, since the toluene production is accompanied by the evolution of significant amounts of hydrogen. It is tempting to suggest that the reaction involves an intermediate bonded to the surface via the terminal carbon atom, an alkylidene or an alkylidyne species. This type of mechanism has been seen previously in the decomposition of neopentyl surface moieties, where the formation of a neopentylidene species is followed by the scission of the C_α–C_β bond to produce isobutene (and a C₁ surface species) [13]. The mechanism proposed for toluene formation from styrene is also consistent with that proposed for chain growth later in this report.

Additional information on the conversion of adsorbed styrene on nickel surfaces can be extracted from the data in Fig. 2, which reports results from TPD experiments on a deuterium-saturated Ni(100). First, some quantitation of

Fig. 2 TPD from 9.0 L of styrene on a 2.0 L D₂-predosed Ni(100) surface. The *left panel* displays the traces for the desorption of the different isotopomers of hydrogen, together with the D₂ TPD obtained after a 2.0 L dose of D₂ alone, provided for reference. The *right panel* displays the results for the desorption of the different isotopomers of styrene and ethylbenzene produced. Deuteration to di-deuteroethylbenzene dominates this chemistry, but additional multiple H–D exchange is indicated by the detection of tri- and tetra-deuteroethylbenzene

the yields was achieved via calibration of the H₂ yields, by comparing with the peak areas obtained from H₂ and D₂ TPD traces on clean Ni(100) versus exposure [58]. It was determined that a 2.0 L dose of hydrogen leads to a coverage of surface atomic hydrogen of approximately 0.8 mL (1 mL $\equiv$ 1 H atom per Ni atom). However, some of that hydrogen is displaced upon subsequent dosing of styrene, so the final hydrogen coverage in the experiments in Figs. 1 and 2 is approximately half a monolayer. In similar fashion, the coverage of the styrene that decomposes to produce the H₂ seen in those TPD was estimated at approximately $\theta(\text{styrene}) = 0.15$ mL. Finally, all the hydrogen detected below 400 K was determined to originate from the vinyl moiety of the styrene, but to account for only two out of the three H atoms in that group; the remaining hydrogen is likely to be removed above 400 K, as the aromatic ring dehydrogenates [12].

The right panel of Fig. 2, which provides the TPD traces obtained for the isotopically substituted styrene and ethylbenzene molecules obtained in the experiments with coadsorbed deuterium, provides some indication on the relative rates of the hydrogenation versus dehydrogenation steps that take place on the vinyl moiety of styrene. First, the main species observed in the TPD is dideuteroethylbenzene (108 amu), the product of the incorporation of two deuterium atoms across the vinyl double bond of the original

styrene. As also made clear by the right panel of Fig. 1, hydrogenation dominates over molecular desorption when hydrogen or deuterium is coadsorbed on the surface. Second, virtually all the styrene detected is in its original isotopomeric form, without any deuterium substitutions. Since hydrogenation and H–D exchange reactions share a common half-hydrogenated (alkyl) intermediate, this means that the incorporation of the second hydrogen here is much preferred over the competing β -hydride elimination that leads back to the olefin [5, 59]. This is in contrast with the chemistry often seen on platinum surfaces, where multiple isotope exchange within the olefin is the norm [60–63]. H–D exchange reactions are nevertheless operative in the styrene/Ni(100) system, since the desorption of small amounts of tri- and tetra-deuteroethylbenzene (109 and 110 amu, respectively) is clear in the TPD experiment reported in Fig. 2 (20 and 15% of the total amount of ethylbenzene produced, respectively). Finally, the H–D exchange stops after two cycles; no significant amount of pentadeuteroethylbenzene (111 amu) is produced. It appears that the initial hydrogenation occurs at the terminal carbon of the vinyl moiety, and that only the hydrogen atoms at that end can be substituted by deuteriums. This is easily explained by steric effects, as already argued in previous studies with similar systems [49, 64, 65].

Another illustration of the competitive nature of hydrogenation, dehydrogenation, and H–D exchange reactions on Ni(100) surfaces is illustrated in Fig. 3. In this

Fig. 3 TPD data from 5.0 L of bromocyclopentane adsorbed on clean (*left*) and 2.0 L D₂-predosed (*right*) Ni(100) surfaces. The *left panel* shows traces for bromocyclopentane molecular desorption as well as for the production of cyclopentane, cyclopentene, and hydrogen. The *right panel* focuses on the products from H–D exchange reactions, and indicate the production of di- and tri-deuterocyclopentane (among other products)

case, the initial reactant is a cyclopentyl surface species, produced in situ via the thermal activation of the corresponding bromocyclopentane precursor [66]. On clean Ni(100), cyclopentyl moieties undergo rapid disproportionation to cyclopentane and cyclopentene (Fig. 3, left panel). The desorption traces for both display similar shapes, sharp peaks centered at 145 K, indicating rapid kinetics limited by the first step, a β -hydride elimination that produces the olefin and the hydrogen atoms required for hydrogenation to the alkane. In fact, the detection of the cyclopentene may be limited by the kinetics of its desorption, which occurs at approximately the same temperature when starting with cyclopentene (data not shown). The same reactions occur in the presence of deuterium on the surface, but there additional H–D chemistry is observed at higher temperatures, with the desorption of di- and tri-deuterocyclopentane (72 and 73 amu, respectively) around 225 K. Much of this chemistry was already mapped out for C₆ cyclic compounds in a previous publication [12]. The interesting addition here is that multiple H–D exchanges may easily be accompanied by migration of the carbon–carbon double bond along the cyclopentyl ring. Similar bond migration has been seen on Pt(111) [67, 68].

The case of double-bond migration can be made more clearly by using TPD data obtained for 1-pentene and 1,4-pentadiene (Fig. 4). In the case of 1-pentene in particular, where the 1- and 2-pentenes can be easily differentiated by mass spectrometry, 2-pentene production is clearly seen even on the clean Ni(100) surface, without any additional hydrogen. Indeed, the two left panels of Fig. 4 (corresponding to two different coverages of 1-pentene) show the clear production of 2-pentene from 1-pentene at about 250 K. Note that this occurs at temperatures much higher than those required to induce molecular desorption

(which takes place in two stages around 170 and 210 K), and is therefore controlled by the kinetics of the half-hydrogenation (to a 2-pentyl surface intermediate) and β -hydride elimination steps. The latter must be relatively fast in this case, though, because it occurs preferentially over the hydrogenation of the 2-pentyl intermediate to pentane (via reductive elimination with coadsorbed hydrogen). Similar chemistry has been seen for 1-butene on Pt(111) [63].

More surprising here is the chemistry reported for 1,4-pentadiene in the two right panels of Fig. 4, because those indicate both hydrogenation and double-bond migration reactions occurring on the same molecule. Moreover, the hydrogenation and bond migration must take place at opposite ends of the adsorbate: while one end incorporates two hydrogen atoms to convert the terminal vinyl moiety to an ethyl group, the other undergoes β -hydride elimination immediately after the first half-hydrogenation step to the alkyl intermediate. This suggests that conformational strains may control the selectivity between alkyl-hydrogen reductive elimination (to produce alkanes) and β -hydride elimination (to produce the olefin) surface reactions. The fact that some 2-pentene is produced here as well suggests that one of the terminal double bonds on a molecule adsorbed via the two C=C bonds is first fully hydrogenated to an ethyl moiety, and that it is the second, remaining double bond that then follows the half-hydrogenation/ β -hydride elimination sequence that results in bond migration. Note that, again, 1-pentene desorption occurs at lower temperatures than 2-pentene production (250 vs. 280 K), and also that the 2-pentene evolves at approximately the same temperatures as when starting with 1-pentene. The first hydrogenation from 1,4-pentadiene to 1-pentene appears to occur rapidly, starting at about 200 K (the temperature at which 1-pentene evolves in this case),

Fig. 4 TPD data from 1-pentene (two left panels) and 1,4-pentadiene (two right panels) adsorbed on clean Ni(100) surfaces. Results are provided in each case for two different doses, 2.0 (first and third panels) and 4.0 L (second and fourth panels). Traces are reported for the desorption of 1,4-pentadiene, 1- and 2-pentene, and pentane. Notice the production of 1-pentene from 1,4-pentadiene, and, perhaps more significant, the fact that 2-pentene, which requires the migration of a carbon–carbon double-bond, is made in all cases

and the remaining chemistry to be similar to that seen when starting with either 1-pentene or 1,4-pentadiene.

Further insights into the chemistry of these dual-functional molecules can be obtained from the TPD data obtained with 1,5-diiodopentane on Ni(100) (Fig. 5). This diiodoalkane is the precursor to a C₅-metallocyclic intermediate bonded to the metal through its two end carbons. Both raw and deconvoluted data are shown in this figure to illustrate the difficulties involved with the data processing [57]. In this particular case, since the iodo-containing compounds are too heavy to be detected by our instrument directly, selected ion fragments needed to be chosen instead. Our analysis indicated that the signal for 43 amu is clearly due to 1-iodopentane, and displays a specific peak at 200 K. A second peak is observed at 175 K in the signals for 39, 67, and 68 amu, which can be assigned to the original 1,5-diiodopentane based on a comparison between the relative intensities measured in the TPD and the cracking pattern seen in its mass spectrum. The 67 amu/68 amu intensity ratio in the TPD is different in the 175 vs. 205 K peaks, indicating that there is a third species that desorbs below 200 K; we identified that product as cyclopentene. Finally, the 55 amu/70 amu intensity ratio is different in the 180–280 K region as compared to the signal at 340 K, again pointing to two different products: 1-pentene in the low-temperature range, and cyclopentane at higher temperatures.

Fig. 5 Raw data (*left*) and deconvoluted traces (*right*) for the TPD obtained starting with 7.0 L of 1,5-diiodopentane adsorbed on Ni(100). A number of interesting products are seen here, including 1-iodopropane (from hydrogenation of a 5-iodopropyl intermediate), 1-pentene (resulting from β -hydride and reductive elimination steps on a 1,5-pentadiyl surface species), cyclopentene, and cyclopentane (from cyclization of a metallacyclic intermediate)

After such deconvolution, it can be seen in Fig. 5 that even though facile β -hydride elimination steps at both ends would be expected to produce 1,4-pentadiene, no pentadiene could be detected in this case. Instead, the main product (besides molecular desorption) is 1-pentene, which desorbs in a broad temperature range between approximately 200 and 280 K. Again, the pentadiene appears to be strained on the surface, so hydrogenation of one alkyl end is favored over dehydrogenation at both positions. In other words, one initial alkyl-hydrogen reductive elimination step yields a 1-pentyl moiety first, and that intermediate then undergoes β -hydride elimination to 1-pentene. In fact, the first hydrogenation step can even precede the elimination of the second halide at the other end; hence the detection of some 1-iodopentane around 200 K. However, this cannot be the full story, because some cyclopentene is produced as well, at about 170 K. Cyclization of dialkyl metallacycles such as the one expected to form here after scission of the two C–I bonds in the diiodo precursor has already been seen with 1,6-diiodohexane, and determined to be initiated by several dehydrogenation steps [17].

Finally, we report on some carbon–carbon bond-formation reactions. Because of the use of vacuum conditions in surface-science experiments, these are in general less commonly seen in those, and are not often expected on nickel surfaces. Nevertheless, several carbon-chain growth processes were detected in the TPD traces reported in Figs. 6 and 7. In the example shown in Fig. 6, the data correspond to the chemistry of ethyl surface groups on clean and hydrogen-predosed Ni(110) surfaces. With coadsorbed hydrogen, a clear peak is seen at 140 K for the evolution of butane, a product easily accounted for by coupling of ethyl moieties on the surface. Couplings such as these are more typical on coinage metals [47, 65, 69–71], but have also been seen (with alkylidenes) on oxygen-passivated early transition metals [54, 72, 73].

In addition, significant amounts of propene are produced around 187 K both on the clean and hydrogen-predosed Ni(110). This suggests a chain growth mechanism involving C₁ surface intermediates produced via prior hydrogenolysis of the ethyl species. A similar mechanism may be operative with propyl intermediates, which can produce butane on Ni(110) (Fig. 7). Notice that in this case the longer-chain hydrocarbon that desorbs is an alkane (butane) instead of an olefin (butene), and that the reaction is seen with the less sterically-hindered 1-propyl group but not with 2-propyl surface species. Interestingly, with both ethyl and propyl groups, this chain-growth reaction is enhanced (the yield increases and the peak shifts to lower temperatures) in the presence of coadsorbed hydrogen on the surface. It is not clear what the C₁ inserting moiety that leads to chain growth may be in these examples, but given that it must be made via the decomposition of the initial

Fig. 6 TPD data from iodoethane dosed on clean (3.0 L, *left*) and 50 L H_2 -predosed (7.0 L, *right*) Ni(110) single-crystal surfaces. Traces are reported for ethane, ethylene, propene, and butane. The latter is produced only on the hydrogen-saturated surface, via coupling of two ethyl surface groups. Propene production, which is seen in both cases, must follow a more complex mechanism

reactants, it is likely to be a somewhat dehydrogenated species, perhaps methylene ($\text{Ni}_n=\text{CH}_2$) or methylidyne ($\text{Ni}_n\equiv\text{CH}$). Regardless, the longer-chain adsorbed hydrocarbon that results from the C_1 insertion step must be hydrogenated afterwards to desorb, hence the need for coadsorbed hydrogen. A less likely but still probable alternative mechanism may involve the direct insertion of an olefin (ethylene or propene) into a metal-alkyl bond followed by the extrusion of a terminal C_1 moiety, perhaps

after the formation of an alkylidyne [13]. A third option is that of a metathesis mechanism [74].

Clearly, the chain-growth reaction reported above is quite complex, since it requires a balance between carbon–carbon bond-breaking and carbon–carbon bond-forming steps. Chain growth reactions have been seen on several metal surfaces before [46–48, 75], even on nickel [19, 22, 76]. Nevertheless, in most of those cases the proposed mechanism has been the insertion of methylene moieties, either dosed on the surface or produced via dehydrogenation of methyl intermediates, into metal-alkyl bonds. In no other system that we are aware of have increases in chain length by one carbon atom been seen when starting with C_n ($n > 1$) intermediates. Since this type of chemistry appears to be more favorable on Ni(110) than on Ni(100) or Ni(111) surfaces, it is possible that it is structure sensitive and favored by more open surface structures. Unfortunately, very limited information is available to date on this type of structure sensitivity from surface-science studies. One exception is our past report on the hydrogenation of methyl groups, where the temperature of the CH_4 desorption peaks in TPD experiments on both copper [65] and nickel [7, 22, 51] only changes slightly across the (111), (100), and (110) series of surface planes [77]. Perhaps carbon–carbon bond formation reactions are more prone to be affected by the structure of the surface used.

4 Conclusions

In this report we have provided several surface-science examples on the thermal chemistry of hydrocarbon fragments on nickel single crystals to illustrate the versatility of

Fig. 7 TPD data from 1- (two left panels) and 2- (two right panels) iodopropane on clean (3.0 L, *first* and *third* panels) and 50 L H_2 -predosed (*second* and *fourth* panels) Ni(110) surfaces. The traces in each case report the desorption of propene, propane, and butane. The detection of the latter with 1-iodopropane is likely to require a reaction mechanism similar to that for the production of propene from iodoethane reported in Fig. 6

that metal in promoting different types of hydrocarbon conversion reactions. Nickel catalysts are certainly well known to promote hydrogenation, dehydrogenation, hydrogenolysis, and methanation. In comparison with platinum and other heavier late transition metals, nickel tends to be more active, and to preferentially promote dehydrogenation steps. This typically limits its use in more subtle reactions such as isomerization and chain growth processes.

The data reported here show that, while the conclusions stated above are in general true, exceptions can be found where other reactions can be favored on nickel surfaces. In our first example, styrene was shown to not only dehydrogenate, ultimately to surface carbon and hydrogen, and hydrogenate (to ethylbenzene), but to also undergo selective hydrogenolysis to toluene. In addition, the fine balance between hydrogenation and dehydrogenation steps in that case is evident by the production of isotope-exchanged ethylbenzene from the conversion of styrene and deuterium. Similar competition among hydrogenation, dehydrogenation, and H–D exchange steps is seen starting with cyclopentyl moieties, and more dramatically in the cases of 1-pentene and 1,4-pentadiene, where such reactions lead to carbon–carbon double-bond migration and 2-pentene production. The sequence of steps involved in the conversion of the pentadiene is in fact somewhat complex, as highlighted by the experiments with 1,5-diiodopentane, a precursor for 1,5-pentadiyl intermediates. With both pentadiene and pentadiyl surface species, initial enhanced reactivity is seen at one end of the hydrocarbon chain, suggesting that steric and conformational strains may play a role in defining the selectivity of hydrogenation versus dehydrogenation steps. Finally, carbon–carbon bond-formation reactions were seen with alkyl species adsorbed on Ni(110), some via simple carbon–carbon coupling steps but others following complex C₁ insertion mechanisms.

The new chemistry reported here suggests that nickel catalysts could be quite versatile for specific hydrocarbon-conversion reactions under the appropriate circumstances. For instance, selective (rather than extensive and uncontrolled) hydrogenolysis may be engineered with certain feedstocks, in, for instance, the conversion of aromatic compounds with side aliphatic chains. Tuning the selectivity between hydrogenation and dehydrogenation steps (by, for instance, choosing the appropriate hydrogen pressure) may open new avenues for the use of nickel as a catalyst to promote the isomerization of olefins and other unsaturated hydrocarbons, a reaction typically catalyzed with more expensive (Pt, Pd, Rh) metals [78, 79]. Even chain-growth processes may be possible; typically, nickel is used as a methanation catalyst but other metals are chosen when chain growth is desired, as in the Fischer–Tropsch process [80, 81].

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