

NOTE

A Study of the Thermal Reactions of Methyl Iodide Coadsorbed with Hydrogen on Ni(111) Surfaces: Hydrogenation of Methyl Species to Methane

Despite its importance, the activation of alkanes by solid surfaces, the basis for their conversion to other more useful and easier to handle chemicals, is still not fully understood. Fortunately, the recent development of new preparation methods for alkyl groups on metal surfaces has allowed for the study of some of the most relevant elementary steps involved in those processes by using modern surface sensitive techniques (1-4).

We have adopted a very simple methodology for preparing such alkyl moieties based on the decomposition of chemisorbed alkyl iodides (1). Our previous studies have shown that the thermal activation of methyl iodide on either Pt(111) or Ni(100) surfaces leads to the formation of methyl moieties first and to the desorption of hydrogen and methane afterwards (5-7), and also that the yield for methane formation increases considerably on deuterium precovered surfaces because the main product in that case, CH_3D , is produced via the reductive elimination of methyl groups with surface deuterium (6, 8). By contrast, Johnson *et al.* have reported that on Ni(111) H atoms bound to the surface are unreactive with CH_3 species (which they prepare via the dissociative chemisorption of methane using molecular beams); according to them, only hydrogen in the subsurface is reactive for methane formation on that surface (9).

In order to understand the differences observed between Ni(100) and Ni(111) surfaces with respect to the chemistry of chemisorbed methyl groups, we decided to explore the reactivity of methyl iodide on Ni(111) substrates. The experiments reported here indicate that the methyl moieties generated via the thermal decomposition of adsorbed methyl iodide can indeed react readily with surface hydrogen (or deuterium) to generate methane. A discussion of these results is presented below.

The experiments reported in this paper were carried out in an ultra-high vacuum stainless steel bell jar equipped with instrumentation for thermal programmed desorption (TPD), X-ray photoelectron (XPS), Auger

electron (AES), static secondary ion mass (SSIMS), and ion scattering (ISS) spectroscopies (7, 10). TPD experiments were performed by recording the thermal desorption of up to ten different molecular fragments simultaneously using a computer interfaced to the mass spectrometer and by later deconvolving the cracking patterns of all possible isotopically substituted methane molecules from the raw data in order to separate the contributions of each species to the overall desorption traces (5, 6, 8). Surface coverages, reported as molecules per surface nickel atom, were calculated by using both the TPD areas and results from independent mass spectrometer calibration experiments using a method discussed in detail elsewhere (7). A heating rate of about 10 K/s was used in all TPD experiments.

The Ni(111) single crystal was cut and polished using standard procedures, mounted in a manipulator capable of both resistively heating to up to 1300 K and cooling to liquid nitrogen temperatures, and cleaned before each experiment by oxygen treatments and ion sputtering-annealing cycles until no impurities were detected by either AES or XPS. The temperature was measured by a chromel-alumel thermocouple spot welded to the side of the crystal. The CH_3I (99% purity) was obtained from Alfa Products, kept in the dark, and freeze pumped daily until no impurities were detected by mass spectrometry. The deuterium (99.5%) was purchased from Matheson Gas Products and used as supplied. Gas dosing was done by backfilling the vacuum chamber, measured in Langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr s}$), and not corrected for ion gauge sensitivities.

The thermal behavior of methyl iodide on Ni(111) surfaces, both alone and coadsorbed with deuterium, was studied by thermal programmed desorption spectroscopy. Only hydrogen and methane desorb from this system; no coupling products such as ethylene or ethane were ever detected in these experiments. The hydrogen peak in both cases is centered around 340 K, about the same temperature as for hydrogen adsorbed on a clean surface (because

the desorption rate is limited by hydrogen recombination on the surface (11)), and methane desorption occurs in two regimes around 150 and 235 K.

TPD results for methyl iodide on clean Ni(111) surfaces are given in Fig. 1 as a function of initial exposure. The hydrogen desorption peak (Fig. 1a) first grows with increasing doses, its area going from that corresponding to an initial background coverage of 0.05 of a monolayer of atomic hydrogen to a value of 0.44 after a 2 L methyl iodide exposure, and then reverses to 0.23 at saturation; the peak maximum also shifts with increasing coverages, from 395 to about 340 K. No methane formation is seen for doses below 2 L ($\Theta[\text{CH}_3\text{I}] \leq 0.17$), but a small peak grows then first around 260 K and a second feature develops at about 150 K above 3 L (Fig. 1b). The activation energies for these two temperature desorption regimes were estimated using Redhead's equation (12) to be about 9.5 and 16.5 kcal/mole, respectively (assuming a pre-exponential factor of 10^{13} s^{-1}), and the saturation methyl iodide coverage (about 20% of a monolayer) was determined to occur after exposures of about 3 L, above which molecular desorption is seen around 140 K (not shown).

Desorption of methane (of both CH_4 and CH_3D) from surfaces where 2 L D_2 ($\Theta[\text{D}] \approx 0.80$) was dosed prior to exposures to various amounts of CH_3I is shown in Fig. 2. CH_4 desorption was seen at about 235 K only after CH_3I doses of 2 L and above, and then in a small and relatively constant amount. CH_3D , on the other hand, desorbs initially as a broad peak centered at slightly above 200 K that grows and splits into two around 150 and 235 K as the initial methyl iodide dose is increased from 0.5 to 3 L. The initial methyl iodide saturation coverage in the coadsorbed system amounts to about 20% of a monolayer, the same as on the clean surface, from which about 75% converts into methane during the TPD experiments.

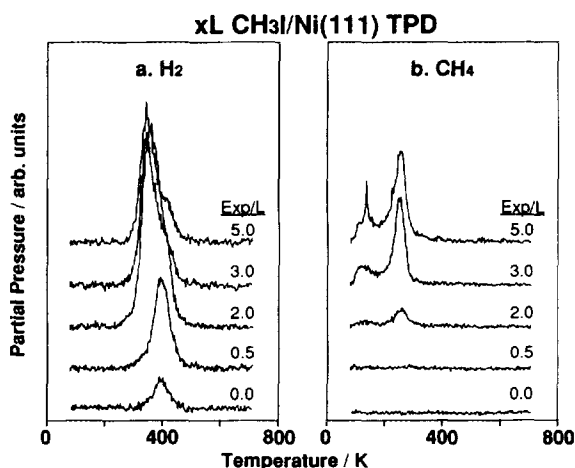


FIG. 1. (a) Hydrogen and (b) methane TPD spectra as a function of initial exposure for CH_3I dosed at 90 K on a clean Ni(111) surface.

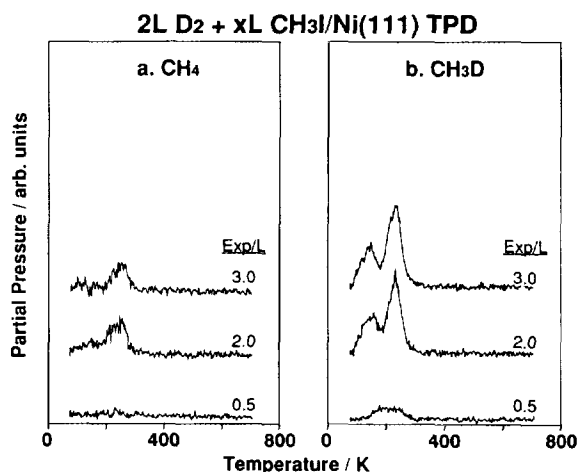


FIG. 2. CH_4 (a) and CH_3D (b) TPD spectra from various exposures of CH_3I adsorbed at 90 K on a Ni(111) surface predosed with 2 L D_2 .

The surface chemistry reported here for methyl iodide adsorbed on Ni(111) surfaces shows a great similarity with that seen in other systems, especially on Ni(100). Previous studies have shown that low-temperature chemisorption of alkyl iodides on most metal substrates is molecular and through the iodine atom, and that at temperatures around 150–200 K the C–I bond dissociates in a reaction that requires an activation energy of only about 5 kcal/mole and that generates iodine atoms and alkyl species on the surface (7, 13–20). Even though we lack spectroscopic data for the identification of the surface species that form during the thermal activation of methyl iodide on Ni(111), it is quite reasonable to expect the C–I bond to break first and methyl and iodine species to form on this surface as well (7, 8). The reactions that the resulting methyl moieties then follow depend on the initial CH_3I coverage: at low doses (below 2 L, $\Theta[\text{CH}_3\text{I}] \leq 0.17$) most of them dehydrogenate completely to surface carbon and hydrogen atoms (which recombine and desorb around 340 K), but at higher coverages a significant fraction undergo a reductive elimination step with surface hydrogen atoms to form CH_4 . Moreover, when deuterium is coadsorbed with CH_3I , methane production is observed mostly in the form of CH_3D , which indicates that such reaction occurs via the recombination of CH_3 species with the deuterium atoms present on the surface. Some CH_4 forms as well, in that case by reductive elimination of CH_3 moieties with surface hydrogen atoms generated by both background adsorption and methyl decomposition, and, in addition, a minority amount of CH_2D_2 desorbs after deuteration of CH_2 surface species. It is important to note that while the methane produced at low temperatures (150 K) may come from a direct reaction between methyl iodide and deuterium, as on Ni(100) surfaces (7, 21), the high-temperature peak (235 K) must involve surface methyl species, since

C-I bond scission reactions on metals occur below 200 K (7, 20). Also, the hydrogen (or deuterium) involved in the reactions reported here is expected to be adsorbed on the surface and not absorbed in the bulk, given that hydrogen absorption is an endothermic process that cannot be easily induced by dosing H₂ at room temperature and low pressures; the surface character of the hydrogen in our experiments is also suggested by the high temperature (300 K) of the desorption of the corresponding hydrogen molecules.

The reactions of alkyl surface species with either hydrogen or deuterium atoms coadsorbed on transition metal surfaces has so far always shown to yield detectable amounts of the alkanes expected from a simple reductive elimination step (6-8, 13, 14, 22). A similar chemistry was seen here on Ni(111), so we are left with the puzzle of why these reactions were not observed in the experiments reported by Johnson *et al.* (9). One obvious difference between their system and ours is in the way the surface methyl groups were prepared in each case. There is a generalized concern that the use of alkyl iodides (our method) has the undesirable consequence of co-depositing iodine atoms on the surface, a species that could alter the chemistry of the alkyl moieties. Several tests have been performed to date to try to assess the magnitude of this problem. For one, vibrational (and other) spectra obtained for species such as ethylidyne formed by decomposition of alkyl iodides (ethyl iodide in this case) have shown to be identical to those acquired after preparing the same species by other means (by activating ethylene) (1). Furthermore, the olefins produced by β -hydride elimination in alkyl groups (from alkyl iodides) on Pt, Ni, and Cu surfaces have shown similar reactivity to that seen when the corresponding olefin is directly adsorbed on the same surface (10, 13, 23). Finally, the chemistry of methyl iodide on Pt(111) and Cu(111) surfaces has been favorably compared to that of species prepared by adsorption of gas phase methyl free radicals (2, 24).

Perhaps the behavior reported by Johnson *et al.* (9) has to do with differences in the effective coverages of both surface hydrogen and methyl moieties. Even though we believe that the iodine atoms coadsorbed in our experiments do not significantly alter the electronic properties of the surface in terms of chemical reactivity, they may nevertheless effectively increase the local concentrations of the other surface species in a similar fashion to that reported for other systems (25). This explanation suggests that perhaps methyl hydrogenation by surface hydrogen is only feasible at the high pressures present in catalytic reactions but not in vacuum surface science experiments. Alternatively, Johnson's results could be understood in terms of a preference for hydrogenation with bulk over surface hydrogen. They did report no methane formation from a surface exposed sequentially to methyl groups

and hydrogen, but since the dosing order is critical in experiments done under vacuum (26), it would be interesting to test the possibility of reacting methyl groups prepared using their method on a surface *predosed* with hydrogen. In any case, we have shown here that surface hydrogen atoms are in fact able to react with methyl groups on Ni(111) as on many other transition metal surfaces to form methane molecules.

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Sariwan Tjandra
Francisco Zaera

Department of Chemistry
University of California
Riverside, California 92521

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