Molecular Modeling of Amine Dehydrogenation on Ni(111)

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Received September 14, 1992. In Final Form: March 23, 1993

The binding energies of the decomposition products and intermediate surface species formed on Ni(111) from adsorption of ethylamine ($CH_3CH_2NH_2$) have been calculated, using semiempirical model based on the extended-Hückel theory to calculate the energies of the surface ligands and the gas-phase molecules. The results provide information about the energetics of the intermediate surface species which is not directly accessible experimentally. With this insight we have inferred a decomposition pathway which supports the one proposed by a recent experimental study. Furthermore, the calculations suggest a pathway for the hydrogenation to ethylamine ($CH_3CH_2NH_2$) from coadsorption of acetonitrile (CH_3CN) and hydrogen (H_2) on the surface. This proposal awaits experimental examination.

Introduction

The characterization of adsorbed molecules and their decomposition pathways on metal surfaces is of considerable importance to understand the nature of the surface chemical bond. Studies in ultrahigh vacuum (UHV) have increased our understanding of the fundamental molecular processes occurring at the metal surface. Surface vibrational spectroscopies, including high-resolution electron energy loss spectroscopy (HREELS), have shown their ability to follow fundamental molecular processes occurring on various metal surfaces in UHV. This includes measuring molecular structures and orientations, thermal decomposition pathways, and effects of coverage and coadsorption of different molecules on bonding. Although surface intermediates and reaction mechanisms can be inferred from these studies, very little is known usually about the energetics of these systems, and at present no experimental techniques seem to be able to measure the binding energy of intermediate species on surfaces.

In a recent study,[1] we have investigated the thermal decomposition of ethylamine ($CH_3CH_2NH_2$) adsorbed on Ni(111) at low temperature by temperature-programmed desorption (TPD) and HREELS. Ethylamine was found to dehydrogenate to acetonitrile (CH_3CN) and hydrogen (H_2) on the surface. Before the desorption of acetonitrile, at 350 K, different HREELS spectra were observed,[1] which were interpreted to imply the presence of intermediate species (between ethylamine and acetonitrile) adsorbed on the surface. The spectra were consistent with a dehydrogenation process starting by an α-C–H bond cleavage in the amine, leading to an aminomethylcarbene species (CH_3CNH_2) bonded through the carbon to the nickel atoms. Before acetonitrile desorption an acimidoyl species (CH_3CNH) was detected. From these results and the desorption temperature of ethylamine, acetonitrile, and hydrogen, an energy diagram for the transformation of ethylamine ($CH_3CH_2NH_2$) to acetonitrile (CH_3CN) and hydrogen (H_2) on Ni(111) was proposed (Figure 1). Energies of the different species were estimated by use of the data obtained from the experiment and from data found in the literature. The knowledge of the relative stability of the surface species may be useful to understand the selectivity of nickel catalysts toward the formation of primary amines during the catalytic hydrogenation of nitriles.[2]

In the present work, binding energy calculations were performed on the ethylamine–Ni(111) system, and its evolution to acetonitrile–hydrogen–Ni(111). Empirical pair potential repulsive terms were introduced as a correction of the energy calculated within a tight-binding scheme based on the extended-Hückel theory of the molecules. This semiempirical model has been used previously to characterize the energetics and reaction pathways of the ethylene and acetylene decomposition on platinum single crystal surfaces.[3]

The model has enabled us to calculate the binding energies of the stable and metastable surface species. These energies are not directly accessible by TPD or other experiments since the desorption temperatures are above decomposition temperatures.

Binding Energy Calculation

We have calculated the binding energies of species involved in the dehydrogenation of ethylamine ($CH_3CH_2NH_2$) to acetonitrile (CH_3CN) and hydrogen (H_2) on the Ni(111) surface. The reaction pathway considered in this study is the one proposed earlier in a HREELS and TPD study of the decomposition of ethylamine on Ni(111).[1] We have used a semiempirical model based on the extended-Hückel theory. The extended-Hückel parameters for the matrix elements and Slater orbitals are the ones found in the literature.[4] The extended-Hückel theory does not give an adequate description of the repulsive part of the potential, and in general overestimates binding energies. In order to correct for that, we introduce empirical repulsive pair potential terms.[3] This approach is rather similar to the ASED-MO method[5] and other schemes.[6] The repulsive corrections for H–H, C–H, N–H, and C–N bonds are chosen so that the calculated

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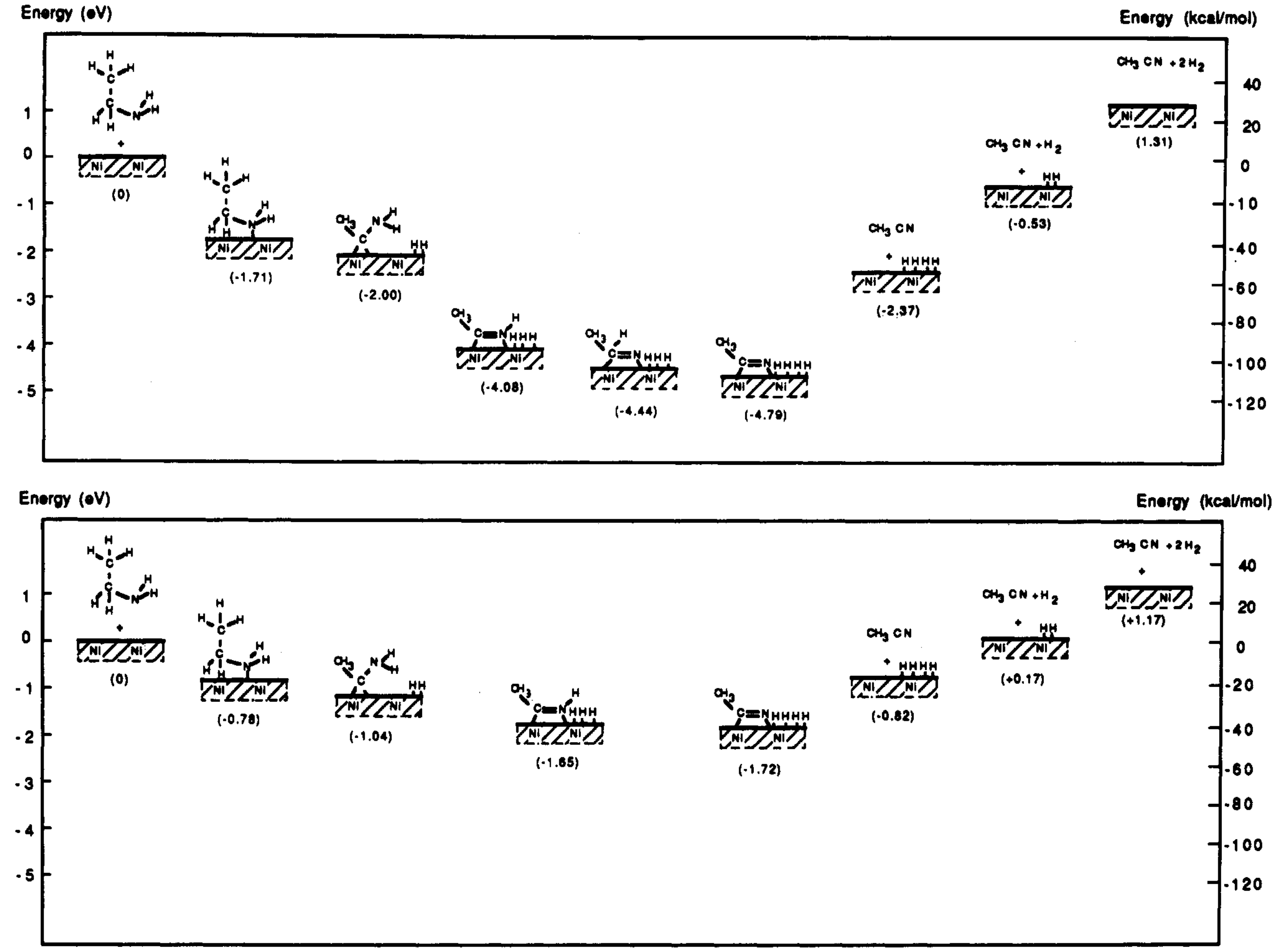

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Figure 1. Energy diagram for the binding of amines to the Ni(111) surface. The upper panel is the calculated diagram and the lower panel is the diagram adopted from the experimental study.[1] We have indicated the binding energy (eV) under each species, with the ethylamine in the gas phase taken to be the reference. The alkylidenimido species (CH_3CHN) was not found in the HREELS study of ethylamine ($CH_3CH_2NH_2$) thermal decomposition on Ni(111), although its calculated binding energy (upper panel) is lower than that of the acimidoyl species (CH_3CNH); see text.

energies of hydrogen (H_2), methane (CH_4), ammonia (NH_3), and hydrocyanic acid (HCN) reproduce the measured values:[7,8]

$$E_{rep}(\text{H-H}) = E_{exp}(H_2) - E_{EHT}(H_2)$$

$$E_{rep}(\text{H-C}) = {}^1/_4(E_{exp}(CH_4) - E_{EHT}(CH_4))$$

$$E_{rep}(\text{H-N}) = {}^1/_3(E_{exp}(NH_3) - E_{EHT}(NH_3))$$

$$E_{rep}(r,\text{C-N}) + E_{rep}(\text{H-C}) = E_{exp}(\text{HCN}) - E_{EHT}(\text{HCN})$$

In the case of C–N bonds, the bond length changes from 1.1 to 1.5 Å when going from the triple bond in CH_3CN to the single bond in $CH_3CH_2NH_2$. So in this case the dependence of the repulsive term on bond length is important. We use an exponential form,

$$E_{rep}(r) = ae^{-r/b}$$

for the repulsion between two atoms separated by a distance r. The parameters a and b are fitted to the measured values of the C–N bond length and the total energy of hydrocyanic acid, and we get

$$a = 607.87 \text{ eV} \quad \text{and} \quad b = 0.20 \text{ Å}$$

Table I. Repulsive Energy Corrections E_{rep} (eV) (r Is the C–N Bond Length)

bond	H-H	H-C	H-N	C-N
E_{rep}	3.10	1.46	1.60	607.87 exp(−r/0.20)

The repulsive energies are listed in Table I. In order to justify the approach, we calculated the energy of methylamine (CH_3NH_2),

$$E(CH_3NH_2) = E_{EHT}(CH_3NH_2) + 3E_{rep}(\text{H-C}) + 2E_{rep}(\text{H-N}) + E_{rep}(r,\text{C-N})$$

and found agreement with experiments to within 0.4 eV.

The main inaccuracy of our binding energy calculation lies in the lack of a realistic pair repulsion between the metal and adsorbate atoms; this can only be obtained when the binding energies to the metal of small adsorbates like ammonia and methyl groups are better known. We have thus omitted any adsorbate–surface repulsion and as a consequence overestimate the binding energies of the molecule to the surface.

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(7) *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Cleveland, 1984.

(8) The binding energies of H_2, NH_3, CH_4, and HCN were calculated from the heats of formation $\Delta H_f°$ found in thermochemical tables[7] like C(atom) + 4H(atom) → C(graphite) + $2H_2 \rightarrow CH_4$, $\Delta H = \Delta E + \Delta(PV) = \Delta H_f°(CH_4) - \Delta H_f°(\text{C(atom)}) - 4\Delta H_f°(\text{H(atom)})$, $\Delta(PV) = -4RT$, so we get $\Delta E = \Delta H_f°(CH_4) = \Delta H_f°(\text{C(atom)}) - 4\Delta H_f°(\text{H(atom)}) + 4R(298 \text{ K})$.

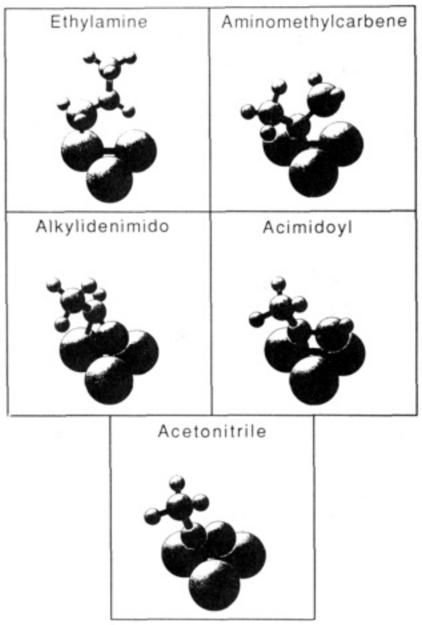

Figure 2. Adsorption geometries of the amines on the Ni(111) surface. The atomic sizes represent, in growing order, H, C, N, and Ni, but have no physical significance.

The adsorption geometries of CH_3CNH, CH_3CHN, and CH_3CN are taken from X-ray crystallography measurements[9] of cluster complexes in which the molecules are bonded to three-atom clusters of Fe. In the case of CH_3CN, the geometry is taken from that of $Fe_3(CH_3CH_2CH_2CN)(CO)_9$[10] by substituting the CH_3CH_2 group with H and adjusting the geometry to that of the methyl group. The three metal atoms form equilateral triangles with bond lengths varying between 2.48 and 2.70 Å. The cluster has been substituted by three surface atoms of the Ni(111) surface, with a nearest-neighbor Ni–Ni distance of 2.49 Å. The adsorption geometry of $CH_3CH_2NH_2$ is taken to be on-top binding through the nitrogen lone pair; the N–Ni bond length is taken to be 1.9 Å, which is a typical value for a nitrogen–metal bond in organometallic complexes. We have calculated the binding energy for different orientations on the surface and for different orientations of the methyl group; this does not alter the binding energy significantly. The adsorption geometry of CH_3CNH_2 is obtained by substituting the two C–H bonds of ethylamine with two C–Ni bonds, thus yielding a bridge-bonded species. The C–Ni bond length is taken to be 2.0 Å. The methyl group has been rotated 60° around the C–C axis in order to obtain optimum binding energy.

The surface is represented in all cases by a periodic slab of three metal layers and a (4×2) lateral unit cell, one amine molecule, and the appropriate number of hydrogen atoms. The geometries of the surface species are shown in Figure 2.

Results

Table II. Calculated Binding Energies (eV) of the Gas-Phase and Adsorbed Amines[a]

		E_{EHT}	E_{rep}	E_{total}	E_b
ethylamine	$CH_3CH_2NG_2(g)$	−364.25	6.50	−357.75	0.00
	$CH_3CH_2NH_2(a)$	−365.96	6.50	−359.46	−1.71
aminomethylcarbene	$CH_3CNH_2(a) + 2H(a)$	−363.33	3.58	−359.75	−2.00
acimidoyl	$CH_3CNH(a) + 3H(a)$	−364.16	2.33	−361.83	−4.08
alkylidenimido	$CH_3CHN(a) + 3H(a)$	−364.47	2.28	−362.19	−4.44
acetonitrile	$CH_3CN(a) + 4H(a)$	−363.65	1.11	−362.54	−4.79
	$CH_3CN(g) + 4H(a)$	−361.98	1.86	−360.12	−2.37
	$CH_3CN(g) + 2H(a) + H_2(g)$	−360.14	4.96	−358.28	−0.53
	$CH_3CN(g) + 2H_2(g)$	−364.50	8.06	−356.44	1.31

[a] The binding energies are defined relative to the energy of ethylamine in the gas phase as $E_b = E_{total} - E_{total}(\text{ethylamine})$.

Table III. Binding Energies (eV) of Hydrogen, Ethylamine, and Acetonitrile[a]

	calculated	measured		calculated	measured
H(a)	3.17	2.75	CH_3CN-η^2	2.42	~0.9
$CH_3CH_2NH_2(a)$	1.71	~0.8	CH_3CN-η^1	2.87	

[a] The measured values are extracted from TPD experiments of H_2,[11] $CH_3CH_2NH_2$,[1] and CH_3CN,[12] assuming first-order desorption kinetics. The geometry of the η^2-bonded acetonitrile is taken from X-ray crystallographic data,[10] and the η^1-bonded acetonitrile is adsorbed end-on with the N–C axis perpendicular to the surface; see text.

The calculated binding energies are shown in Table II. The C–C bond and the methyl group do not change through the reactions so that the C–C and C–H repulsions for the methyl group are omitted from the calculation. The calculated energy change of the gas-phase reaction $CH_3CH_2NH_2 \rightarrow CH_3CN + 2H_2$ is 1.31 eV, in reasonable agreement with the measured value of 1.17 eV.[7] The calculated adsorption energies are expected to be too large since we have not included repulsion terms between the metal atoms and the adsorbates. This is confirmed by comparison with TPD measurements of the adsorption energies for H, CH_3CN, and $CH_3CH_2NH_2$ which are listed in Table III. In this table, we have also reported the binding energy of the acetonitrile (CH_3CN) adsorbed end-on through the nitrogen in a hollow site with the C–N axis perpendicular to the surface. This geometry was proposed previously.[12] We find that the binding energy for the acetonitrile adsorbed perpendicular to the surface is slightly more favorable than for the η^2-bonded acetonitrile, in agreement with extended-Hückel cluster calculations.[13] But acetonitrile bonded perpendicular to the surface is not supported by HREELS measurements.[2,14]

The calculated energy diagram is in close qualitative agreement with the diagram that was proposed from experiments (Figure 1). The general trend, favoring dehydrogenation, is the same for the amines as for the hydrocarbons.[3] The energy diagram (Figure 1) is arranged in order to suggest a decomposition pathway, namely, molecular adsorption of ethylamine ($CH_3CH_2NH_2$), then breaking the C–H bonds to form the aminomethylcarbene species (CH_3CNH_2), and then breaking N–H bonds to form the acimidoyl species (CH_3CNH) and finally acetonitrile (CH_3CN).

The energy of the alkylidenimido species (CH_3CHN) is also estimated and found to be lower than that of the acimidoyl species (CH_3CNH) by about 0.4 eV. This result that the alkylidenimido ligand is more stable than the acimidoyl species on the Ni(111) surface is also observed experimentally for binding to Fe clusters.[15] However, the alkylidenimido species was not detected by HREELS when

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decomposing ethylamine ($CH_3CH_2NH_2$) on the Ni(111) surface.[1] This can be explained by the argument that the abundance of the different surface species observed during TPD experiments (nonequilibrium) is not governed by the thermodynamics of the surface, but by the relative reaction barrier heights of the possible surface reactions. A decomposition pathway to form the alkylidenimido species (CH_3CHN) on the surface could be through initial breaking of the hydrogen–nitrogen bonds via CH_3CH_2N. But this is not observed on Ni(111), the main reason being that the N–H bonds point away from the surface so that the surface cannot easily participate in N–H bond cleavage. Similarly for ammonia (NH_3) on Ni(111), the N–H bond breaking cannot be thermally activated.[16] In contrast, C–H bonds of the adsorbed ethylamine ($CH_3CH_2NH_2$) are pointing toward the surface, allowing bond breaking by hydrogen transfer to the surface.[17]

The alternative pathway to make the alkylidenimido species (CH_3CHN) would involve isomerization of the acimidoyl species (CH_3CNH), but this type of reaction was found in a theoretical study to have a much higher reaction barrier than hydrogenation–dehydrogenation.[3]

From this calculation, on the other hand, we expect that the alkylidenimido species (CH_3CHN) will be seen on the surface when carrying out the hydrogenation reaction by coadsorbing acetonitrile (CH_3CN) and hydrogen (H_2). This experiment is in progress.

Conclusions

We have shown that semiempirical calculations based on extended-Hückel theory can be used to estimate the relative energies of the decomposition products and intermediate species on the Ni(111) surface, in qualitative agreement with experiments.

From our results we see that there are three different species that are very stable on the surface. These are the acetonitrile (CH_3CN), the acimidoyl (CH_3CNH), and the alkylidenimido (CH_3CHN) species. The relative abundances of these species on the surface under equilibrium conditions will probably be important for the selectivity of a nickel surface used as a catalyst. We find the alkylidenimido ligand to be slightly more stable than the acimidoyl ligands, but within the accuracy of the model we expect the alkylidenimido, the acimidoyl, and the acetonitrile species to occur with similar abundance on the surface.

From the calculated binding energies and rough estimates of reaction barriers, which we have not calculated, and the structures of the surface species, we have rationalized the decomposition pathway from ethylamine ($CH_3CH_2NH_2$) to acetonitrile (CH_3CN) on the Ni(111) surface. We have proposed an explanation to why the supposedly stable alkylidenimido species (CH_3CHN) is not formed on the surface during the ethylamine decomposition.

Acknowledgment. Support for this work was provided in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division, under Contract No. DE-AC03-76SF00098, and in part by the Advanced Industrial Concepts Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. D.G. thanks Rhône-Poulenc for fellowship support.

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