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Electronic Factors in Chemisorption: NH_3 Adsorption

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In this paper experimental verification of the importance of electronic factors in determining the structure of chemisorbed species on various metals is presented. Furthermore, the modification of a single surface so as to change its chemisorption characteristics is demonstrated. Infrared spectra of NH_3 chemisorbed on vanadium and iron films at room temperature indicate adsorption occurs largely without dissociation. The NH_3 surface species are electron-donating with respect to the CO surface species. NH_3 does not adsorb in an undissociated form on our films of nickel and palladium. However adsorption of CO on these latter surfaces conditions them so that a NH_3 surface complex is stable. The stability of NH_3 on particular surfaces and its modification are explicable in terms of the electronic structure of the metal surface and a molecular orbital model of the bonding of NH_3 and CO to the metal surface.

INTRODUCTION

Electronic factors have been frequently proposed to have effects on catalytic reactions on metals but these are difficult to demonstrate in an unequivocal fashion. Ideally, one would like a full quantum-mechanical treatment of surface reactions but this appears to be a considerable distance into the future. In fact, catalytic reaction rates are so dependent on small energy differences that understanding relative rates on the basis of qualitative theory is often impossible. However, structure is a much less sensitive parameter than rate, so we have chosen here to examine surface structures in the light of qualitative theory. This is particularly attractive since infrared spectral techniques have been developed which allow direct determination of surface structures.

The structures of species produced by exposure of metal surfaces to ammonia continue to be of interest since while ammonia synthesis is of major industrial importance and has been much studied, there continues to be disagreement over the mechanism of ammonia synthesis.

EXPERIMENTAL

The wide spectral range experimental technique, which has been described in detail elsewhere (*1*), consists of evaporating a metal from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit on a hydrocarbon oil film on the salt windows of an infrared cell. These dispersed particles are referred to hereinafter as films both for convenience and because it is believed that their behavior is similar to that of vacuum evaporated films. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species obtained. Spectra are recorded before and after admission of the gas to the cell. Five min of pumping has been found sufficient to remove all spectra due to gas phase molecules. The 25°C temperature listed for measurements is an average, as all measurements were taken at room temperature.

The spectra were obtained using a Perkin–Elmer Model 337 Spectrophotometer. This is a grating instrument which

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scans the region 4000–400 cm^{-1}. No unusual spectrometer settings were used.

The adsorbates were obtained as reagent grade chemicals from commercial sources. They were degassed by repeated freeze–thaw cycles in the vacuum system. The CO was passed through an activated charcoal trap cooled with liquid air.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed since many gases have been found to chemisorb readily on the metal. Essentially, the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure.

RESULTS

Evaporated iron films were exposed to anhydrous ammonia at pressures of 30–50 Torr for 2 hr. The cells were evacuated for several hours and infrared spectra were taken in the region 4000–400 cm^{-1}. Table 1 shows the resulting bands and their relative intensities. The N–H stretching bands near 3350 cm^{-1} were weak and unresolved.

The iron films containing preadsorbed NH_3 described above were exposed to CO at a pressure of 30 Torr for 30 min and evacuated. The bands and assignments are also listed in Table 1. The chemisorption of carbon monoxide caused an increase in intensity of all chemisorbed ammonia bands and shifted the symmetric bend of NH_3 to a higher frequency.

Evaporated vanadium films were exposed to NH_3 at a pressure of 50 Torr for 2 hr. Spectra taken after cell evacuation were similar to those of ammonia on iron; so the bands are also listed in Table 1. Vanadium films with chemisorbed NH_3 were exposed to CO for 30 min and the cells evacuated. Spectra were similar to those of NH_3 and CO on iron and are given in Table 1.

Evaporated nickel films were exposed to NH_3 at pressures of 50–70 Torr for periods of 2–18 hr. Spectra taken in the 4000–400 cm^{-1} region after evacuation of the cells showed no bands due to chemisorbed species. When nickel films which had been previously exposed to NH_3 and evacuated were subsequently exposed to CO at a pressure of 30 Torr for 30 min and again evacuated, bands for chemisorbed ammonia appeared as recorded in Table 2. The same bands were also found if the films were first exposed to CO and then to ammonia.

Nickel films which had previously been exposed to NH_3 were exposed to hydrogen at pressures of 100–600 Torr while spectra were taken in the 4000–400 cm^{-1} region.

TABLE 1

FREQUENCIES (CENTIMETERS^{-1}), INTENSITIES, AND BAND ASSIGNMENTS FOR AMMONIA AND CARBON MONOXIDE CHEMISORBED ON IRON AND VANADIUM AT 25°C[a]

NH_3 on iron	CO and NH_3 on iron	NH_3 on vanadium	CO and NH_3 on vanadium	$Fe(NH_3)_6Cl_2$	Transition metal ammines	Assignments
3340 vw	3350 m				3140–3120	N–H Stretch[b]
	3250 w					
1590 w	1590 m	1580 w	1590 m	1597 m	1650–1550	NH_3 bend (asym.)[c]
1140 s	1180 s	1130 s	1160 s	1151 vs	1350–1130	NH_3 bend (sym.)[d]
				641 vs	850–585	NH_3 rock
	1900 vs		2030 w			Added CO
	580 m		1930 m			

[a] Intensities: S: strong; m: medium; w: weak; v: very.

[b] Corresponds to ν_1 for NH_3 gas from Herzberg, G., "Infrared and Raman Spectra." Van Nostrand, New York, 1945.

[c] Corresponds to ν_4 of NH_3 gas.

[d] Corresponds to ν_2 of NH_3 gas.

TABLE 2
FREQUENCIES ($CENTIMETERS^{-1}$), INTENSITIES, AND BAND ASSIGNMENTS FOR AMMONIA AND CARBON MONOXIDE CHEMISORBED ON NICKEL AND PALLADIUM AT 25°C[a]

CO and NH_3 on nickel	CO and NH_3 on palladium	$Zn(NH_3)_2Cl_2$	Assignments
3340 s	3400 vw	3380	N-H Stretch
3270 m		3290	
1600 m	1580 m	1604	NH_3 Bend (asym.)
		1401	
1240 vs	1160 s	1257	NH_3 Bend (sym.)
1200 vs		1241	
650 m		665	NH_3 Rock
1980 vs	2050 w		Added CO
1850 vs	1920 vs		

[a] Intensities are indicated as in Table 1.

Bands attributable to gas phase NH_3 appeared during this period but after evacuation no bands due to chemisorbed species were evident. Addition of CO produces spectra for chemisorbed ammonia but at a very low intensity.

The same sort of behavior is noted when palladium films are exposed to ammonia. When the films are exposed to NH_3 alone, even for several hours, no infrared bands appear. Addition of CO produces spectra resembling those of metal–ammine complexes, also as shown in Table 2.

SPECTRAL ASSIGNMENTS

The infrared bands for chemisorbed ammonia are assigned by analogy to transition metal ammines. In order to be certain of assignments ammonia-D_3 was chemisorbed and in all cases, the corresponding N-D bands were found shifted to the expected region.

An attempt was made to interpret the spectra in terms of either an adsorbed NH_3 model or an adsorbed NH_2 species. NH_3 should be easily distinguished from NH_2 by the NH_3 symmetric bending vibration. Metal-ammine complexes have a strong band in the 1350–1130 cm^{-1} region due to this vibration (*2*, *3*). No bands are found in this region in the spectra of either $(NH_2Hg)_\infty X_\infty$ complexes or primary and secondary alkyl amines.

Every spectrum of adsorbed ammonia obtained in the present study showed a strong band in the 1140–1240 cm^{-1} region. In spectra of adsorbed ammonia-D_3, a strong band appeared in the 875–950 cm^{-1} region, the region in which the corresponding ND_3 symmetric bending frequency occurs in metal-deuteroammines (*2*, *4*). The spectra fit the undissociated NH_3 model quite well except for the absence on iron and vanadium, of any bands below 1100 cm^{-1} which could be attributed to a NH_3 rocking vibration. The absence of such bands does not help distinguish among the models considered, since each should have bands in this region: between 750–815 cm^{-1} for the N_2H_2–metal model (*5*); between 600–850 cm^{-1} for the NH_2–metal model (*5*); and between 585–850 cm^{-1} for the NH_3 metal model (*2*, *3*). A band is found at 650 cm^{-1} in the ammonia–nickel spectrum which can be attributed to this vibration. A shift in band position and/or intensity for a rocking mode of vibration could readily be the result of interaction of the adsorbed NH_3 group with surrounding surface atoms which are of course absent in the transition metal complexes to which comparison is made.

The spectra of ammonia and deuterated ammonia chemisorbed on metal films obtained in the present study are not easily interpreted in terms of the N_2H_2 model proposed by Brill and coworkers (*5*). Whereas Brill found 12 ir bands, the maximum number of bands found in the present study was 7. Furthermore, no bands were observed which could be attributed to a chemisorbed N–N or N=N species. Finally, the spectra of chemisorbed NH_3 were quite different from spectra of hydrazine, N_2H_4, which is found to have chemisorbed in some cases without dissociation (*6*).

The excellent agreement of all bands found with transition metal ammine complexes leaves little doubt that the bands for the chemisorbed species represent undissociated NH_3 groups. The band shifts upon adsorption of ND_3 further confirm this. The presence of the additional bands in the spectrum of NH_3 and CO on nickel cause it to look very much like spectra of bent diammine, $Zn(NH_3)_2Cl_2$, which are included in Table 2 for comparison.

DISCUSSION

Until recently it has usually been suggested that ammonia chemisorbs on metals with dissociation, forming NH_2 or NH groups on the surface (*7, 8*). Recently more divergence of opinion has emerged. Investigations of the adsorption of amines on iron powders using mass spectroscopy and deuterium exchange indicated that the amines chemisorbed on reduced or oxidized iron surfaces with little dissociation (*9, 10*). Dawson and Hansen (*11*) have interpreted their field emission work with ammonia on tungsten in terms of N, NNH_2 and NNH_3^+ species. A field ion mass spectrometric study of ammonia chemisorbed on iron tips by Schmidt (*12*) indicated the presence of N_2H^+ species but no NH_2^+, NH^+, or N^+ ions. Estrup and Anderson (*13*) studied the adsorption and decomposition of NH_3 on a single-crystal tungsten (100) surface using low-energy electron diffraction, flash desorption, mass spectrometry, and work function measurements. They found that at room temperature NH_3 adsorbs without formation of ordered structures and that the NH_3 molecules are undissociated. As the temperature is raised, both desorption and decomposition of NH_3 occur, but decomposition is relatively slow compared to desorption until ammonia coverage has been significantly reduced. Later work by May, Szostak, and Germer (*14*) supports their interpretation.

In the above work the actual measurements are made on gas-phase species. Guessing about surface species on the basis of gas-phase measurements can never be entirely conclusive. Infrared studies have been made of ammonia chemisorbed at elevated temperatures on silica-supported iron (*15*) and on magnesia-supported iron (*5*). In both cases dissociation was thought to occur upon adsorption, but there was no agreement on the structure of the surface species. The results of the work reported here clearly indicate that nondissociative adsorption of NH_3 on transition metals does occur at 25°C.

While the structural information is interesting the most significant aspect of this work is that the experimental data lend credence to the use of simple molecular orbital ideas to gain a theoretical understanding of how electronic factors affect stability of surface structures. In these experiments the modification of a surface so as to change which surface species are stable has been demonstrated.

The metals used as adsorbents may be divided into two groups according to the manner in which adsorption occurs. On iron and vanadium an undissociated NH_3 surface species is intrinsically stable while on nickel and palladium it is not. Ammonia forms a coordinate bond in transition metal complexes and also presumably on a metal surface by the donation of a pair of electrons into the metal orbital system. In the case of iron and vanadium where there are substantial *d* band vacancies this is a stable arrangement, whereas for nickel and palladium, where the extent of *d* band vacancy is quite limited, the donation of a pair of electrons as the sole means of forming a bond does not produce a stable bond. Hence ammonia is intrinsically stable on iron and vanadium but not on palladium and nickel. Carbon monoxide forms a stable bond to nickel and palladium because, while it donates a pair of electrons to the metal to form a sigma bond, there is also a π-bonding system which permits back-donation of electronic charge from the metal to the CO ligand. In the case of NH_3 there are no orbitals available for back-donation of charge.

In the simple molecular orbital model of chemisorbed CO which has been presented (*16, 17*), the highest energy occupied orbital is only partially filled. Since this orbital is antibonding for the C–O bond, the coadsorption of electron donating species with carbon monoxide should weaken the C–O bond. The infrared band positions for the C–O stretch for CO adsorbed alone (*16*) and coadsorbed with NH_3 are listed in Table 3. In all cases the C–O stretching frequency is lower when CO is coadsorbed with NH_3, indicating a weaker C–O bond for the coadsorbed species. Thus the infrared data are in accord with the simple molecular orbital model of adsorbed CO.

The question of how the nickel and palladium surfaces are modified so that undissociated ammonia becomes a stable surface species when it is not intrinsically so will now be considered. It has been noted that NH_3 is not a stable species on nickel and palladium, whereas it is stable on iron and vanadium. This is because nickel and palladium cannot accommodate the charge transferred to form a coordinate covalent bond, which is the only way an undissociated ammonia molecule can form a bond. However, an adsorbed carbon monoxide molecule can accept charge from the metal into its π electron system. Thus coadsorbed CO stabilizes the metal–nitrogen bond for NH_3 on nickel and palladium by removing excess electron density from the metal. That this indeed does occur is seen in the C–O bond stretching frequency shift discussed above.

TABLE 3
INFRARED BAND POSITIONS FOR CO ADSORBED ALONE AND WITH AMMONIA ON TRANSITION METALS

	V	Fe	Ni	Pd
CO alone	2040	1950	2060	2050
	1940		1920	1930
CO with NH_3	2030	1900	1980	2050
	1930		1850	1920

The source of the chemisorbed NH_3 that appears on Ni and Pd films after CO addition is not entirely clear from our infrared data. Since NH_3 does adsorb on Ni at room temperature, it is possible that the initial exposure of the surface to NH_3 produces atomically adsorbed N and H atoms which do not show in our infrared spectra but which reassemble to chemisorbed NH_3 after CO addition. Since the pumping times of .5–2 hr to remove NH_3 may not completely clean the cell walls of NH_3, the addition of CO may induce desorption from the cell walls of NH_3, which chemisorbs on the Ni surface along with CO.

In summary, we have found undissociated ammonia to be a stable surface species on some transition metals. In addition, we have found in simple molecular orbital considerations a viable theoretical framework for handling the different behavior of different metals, and the modification of a particular surface to change the pattern of stability of surface structures. While undoubtedly catalyst promoters and poisons have steric and geometrical effects, such as a controlling sintering, we believe promoters and poisons in many cases have an effect through electronic factors such as those demonstrated here.

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