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Electronic Factors in Chemisorption: H_2O Adsorption

The different structures found here for water adsorbed on V and Ni evaporated films at 20°C alone and in the presence of other adsorbates may be rationalized by the same electronic factors as were found to be useful in dealing with NH_3 adsorption (*1*). Although the interaction of water with metal surfaces is important in steam reforming processes and because of the unbiquitous presence of water as a contaminant and corrosive agent, relatively few studies of the structure of adsorbed water have appeared in the literature. The exchange reactions between D_2O and H_2 on metals have been reviewed by Bond (*2*). Suhrmann and co-workers (*3*), in measuring electrical resistance and electron work function changes as water was adsorbed on Ni films, found that water molecules were adsorbed without decomposition at 77°K but that when the temperature was raised to 273°K some of the adsorbed molecules decomposed. The exchange reaction between D_2O and propylene has been investigated by Hirota (*4*). McNaught *et al.* (*5*) determined the rates of exchange between D_2O and H_2 or propylene on Pt, Rh, Pd, and Ni. From H–O bond energies and heats of adsorption of H_2 and O_2 they predicted that water would dissociate completely to adsorbed H and O atoms on Ni. Our infrared data for water adsorbed on Ni supports this proposition for water as a lone adsorbate but we also find that in the presence of a coadsorbed Lewis acid there are undissociated adsorbed water molecules.

The wide spectral range experimental technique, which has been described in detail elsewhere (*6*), 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 in a hydrocarbon oil on the salt windows of an infrared cell. These dispersed particles are referred to hereafter 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 is obtained. Spectra are recorded before and after admission of the gas to the cell. Five minutes of pumping have been found sufficient to remove all spectra due to gas phase molecules.

The spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer. This is a grating instrument which scans the region from 4000 to 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. This technique has the advantage that a wide infrared spectra 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 be chemisorbed 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.

The observed infrared bands are listed in Table 1. For the first column the evaporated vanadium was exposed to a water vapor pressure of 10 Torr for 30 min and evacuated to 10^{-6} Torr. The bands at 3650

TABLE 1

FREQUENCIES (cm^{-1}), INTENSITIES[a] AND BAND ASSIGNMENTS FOR H_2O CHEMISORBED ON V AND Ni AT 20°C

H_2O on V	H_2O and air on V	BF_3 and H_2O on V	H_2O on Ni	BF_3 and H_2O on Ni	Assignments
3650 m	3450 m, b		No Bands		M–O–H str.
		3450 m		3600 m	H_2O str.
		1630 m		1590 m	H_2O bend
	1010 sh	1030 s			V=O str.
970 m	970 m				M–O–H bend

[a] Intensities: s, strong; m, medium; b, broad; sh, shoulder.

and 970 cm^{-1} are assigned to M–O–H stretching and bending vibrations by analogy to aquo and hydroxy coordination complexes (*7*). No bands near 1600 cm^{-1} which could be attributed to H_2O bending vibrations were observed. Exposure of this film to CO had no effect on the spectrum. No chemisorbed CO bands were observed. When this film was exposed to the atmosphere the intensity of the 970 cm^{-1} band increased and a shoulder which is assigned to the V=O stretch (*8*), appeared at 1010 cm^{-1}. The O–H stretching vibration shifted and broadened as is typical when hydrogen bonding interactions with neighbors occur.

Exposure of a vanadium film with preadsorbed BF_3 to 10 Torr of water vapor for 30 min produced bands at 3450, 1630, and 1030 cm^{-1} which are assigned as indicated in Table 1. The infrared bands for adsorbed BF_3, which chemisorbs without dissociation (*9*), completely disappeared upon the water addition. This indicates that the BF_3 is not strongly enough coordinated to the vanadium surface to prevent it from being displaced by water. Water reacts readily with free BF_3 to form hydrates and a variety of hydrolysis products (*10*). In the course of water reacting with the BF_3 covered surface, the surface is oxidized as indicated by the formation of the band at 1030 cm^{-1} assigned to V=O. This oxidized surface chemisorbs undissociated H_2O as is shown by the presence of the H–O–H bending frequency at 1630 cm^{-1}. This is not removed by 16 hr evacuation at 10^{-6} Torr.

The exposure of evaporated nickel to 20 Torr of water vapor for periods of up to 18 hr did not produce any observable bands, although subsequent exposure of these films to CO resulted in strong adsorption of the CO. When a nickel film was first exposed to BF_3, however, subsequent exposure to 5 Torr of water vapor for a few minutes was sufficient to produce bands at 3600 and 1590 cm^{-1}, which are characteristic of coordinated H_2O (*7*). The infrared bands for chemisorbed BF_3 remained completely unchanged by the water adsorption.

The data in Table 1 provides direct experimental verification that the following simple molecular orbital ideas are useful in understanding surface processes. The electronic factors which determine the stability of water molecules on metal surfaces are the same as those previously discussed for NH_3 adsorption (*1*). In order for water to chemisorb as an undissociated molecule it must either be hydrogen bonded to some electronegative atom on the surface or form a coordinate covalent bond with a surface atom by donation of a pair of electrons from oxygen into a bond with the surface. In the case of clean surfaces of the zero valent metals V and Ni used here the undissociated structure is not stable with respect to dissociation of water into fragments. For the oxidized vanadium surface formed by the interaction of BF_3 and water, it is not entirely clear whether the undissociated water is hydrogen bonded or coordinated through oxygen to the surface. But the usual hydrogen bonding strength of 6 or 7 kcal/mole would not be expected to make the adsorbed water stable to desorption during the 16 hr evacuation at 10^{-6} Torr which the adsorbed water withstood.

On metallic Ni with its nearly filled *d* band, a coordinate bond formed by donation of electrons from the oxygen atom of water is not stable because of the high electron density already on the Ni atoms. However, in the presence of the coadsorbed strong Lewis acid BF_3 which withdraws electrons from surface atoms, a coordinate bond by undissociated water to the surface is stable. This undissociated water found on Ni is believed to be coordinated rather than hydrogen bonded not only because it withstands evacuation at 10^{-6} Torr but also because the only species to which it could be hydrogen bonded, BF_3, has its infrared B–F stretching bands completely unchanged by the water adsorption.

In summary we have shown that the dissociation of a molecule, H_2O in this case, can be strongly affected by the coadsorption of another species and that the effect may be understood in terms of simple electronic factors. This is believed to have considerable relevance to understanding the effects of promoters and poisons in catalytic reactions.

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