

COADSORPTION AND REACTION OF H₂ AND CO ON RANEY NICKEL:
NEUTRON VIBRATIONAL SPECTROSCOPY

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Neutron inelastic scattering (NIS) has been used in several laboratories to measure the vibrational spectra of adsorbed species on high surface area transition metal catalysts (1,2,3). In a recent publication (4) we have reported the assignment of the vibrations of chemisorbed H on Raney nickel (a high surface area commercial catalyst) measured with NIS. The use of normal mode analysis has made possible the identification of the binding site symmetry and the geometry and vibrational force constant of the dominant H-Ni species on this polycrystalline powder. We report here an extension of this study to the low temperature coadsorption of hydrogen and carbon monoxide and to the first attempt to use NIS as a surface spectroscopy following the catalytic methanation reaction at one atmosphere pressure in a flowing H₂-CO gas mixture. Such measurements can allow not only a determination of the concentration of atomic hydrogen on the catalyst surface under reaction conditions but also permit the detection and identification of stable hydrogenous surface fragments (such as HCO or CH_x intermediates).

An extensive discussion of the preparation and treatment of the Raney nickel catalyst including a detailed description of the sample cell used in these coadsorption and reaction studies can be found in a previous publication (4). Also included in that publication are details and extended discussion of the neutron spectrometer, of the Raney nickel material (essentially a nickel powder with an average crystallite size of 7nm), of the techniques used to obtain neutron vibrational spectra of surface species, as well as spectra of the "clean, hydrogen-free" Raney nickel catalyst used in these adsorption and reaction studies.

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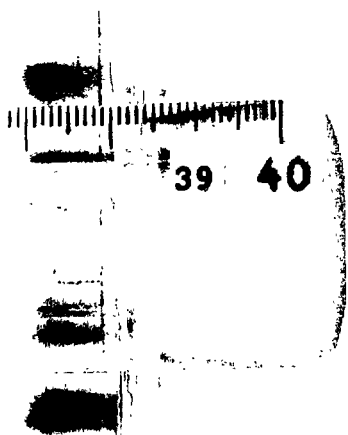
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Prior to a typical adsorption experiment the Raney nickel catalyst (~85 gm contained in the sample cell) was heated in flowing H₂ at 573 K to remove or minimize oxide and other impurities. The hydrogen was subsequently removed in flowing helium at the same temperature, the cell mounted in a variable temperature cryostat on the neutron spectrometer, cooled to 80 K, and a NIS spectrum was then taken. Such a spectrum was used as a blank in each experiment. The sample was then saturated with H₂ at 300 K with an equilibrium pressure of 100 Torr. The NIS spectrum was measured for this hydrogen saturated sample at 80 K (to reduce multiphonon scattering and improve the signal to background ratio) and is shown in Fig. 1. This spectrum is essentially identical to that reported previously (4). The two dominant vibrational modes have been assigned to hydrogen bound in a three-fold site in which the doubly degenerate mode, having H motion parallel to the surface, occurs at an energy of 936 cm⁻¹ (117 meV) and the mode involving H motion perpendicular to the surface plane is found at an energy of 1128 cm⁻¹ (141 meV). This assignment is discussed in the previous publication (4). It should be noted that the intensity of the neutron scattering is a quantitative measure of the number of H atoms vibrating at these frequencies. Thus, the vibrational spectrum in Fig. 1 is directly related to the number of H atoms chemisorbed on Raney nickel in three-fold sites (i.e., changes in the intensity of these peaks can be interpreted directly as changes in site occupation and coverage).

Following the pure hydrogen measurement, the sample was maintained at 150 K and exposed to CO. The total quantity of CO which adsorbed on the catalyst (final gas pressure: P_{CO} ~ 50 Torr, P_{H₂} ~ 1 Torr) was found to approximately equal the total number of H atoms on the nickel surface. The NIS spectrum was then measured at 80 K and is shown as the solid curve in Fig. 1. Aside from a slight broadening of the 936 cm⁻¹ peak and a small change in the low energy region, there is little difference in the two spectra of Fig. 1. We can conclude from this result that, at temperatures less than 150 K adsorbed CO does not displace H from the three-fold binding site and even more strikingly, has only a small effect on the H-Ni vibrational force



constant. This conclusion follows from the fact that significant changes in the vibrational motion of H in the three-fold site would produce measureable changes in both the energy and the relative scattering intensity of the H-Ni vibrational modes (4).

Such changes are in fact observed at higher temperatures. We have investigated these interactional effects at 300 K and at 450 K in a flowing 7:1 H₂:CO reactant gas mixture at one atmosphere pressure. The NIS sample cell served as the reactor and the gas exiting the reactor was analyzed for low molecular weight hydrocarbons, CO and CO₂. To measure the NIS spectrum, the sample cell was isolated from the gas flow and rapidly cooled to room temperature. The sample cell was mounted in the cryostat and placed in the spectrometer. The NIS spectra were measured at 80 K and are shown in Fig. 2. At 300 K no reaction products were detected in the gas stream. At 450 K, the reaction products were CH₄, C₂, C₃ and C₄ hydrocarbons, water and a small quantity of CO₂. The quantity and distribution of these products was unchanged over a period of 24 hours, indicating a constant reaction rate in which approximately 50 % of the reactant CO was converted to products.

The striking feature of Fig. 2 is the similarity in the spectra at 300 K where no products are formed and at 450 K where 50 % of the CO is converted to products. While there are quantitative differences between the two spectra, it is clear that the same surface species are present at both temperatures. The NIS spectra show decreased intensity and some broadening of the modes due to H bound in three-fold nickel sites and a relative increase in the low energy region, including a distinct band centered at ~650 cm⁻¹ and a second feature around 400 cm⁻¹. In contrast, the chemisorbed H spectrum in Fig. 1 shows a broad shoulder at ~600 cm⁻¹ (which has been associated with H bound in four-fold sites (4)), and little intensity at lower energies. The peaks centered at 970 and 1160 cm⁻¹ in Fig. 2 show the presence of H in 3-fold sites. Comparison with the results of spectra measured under identical H₂ flow conditions without CO, suggests that this chemisorbed H represents 30 % or less of the available three-

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fold sites. The feature near 400 cm^{-1} (and possibly at 650 cm^{-1}) in Fig. 2 strongly indicates the existence of carbon-hydrogen fragments on the surface at both 300 K and 450 K. Future in situ experiments are planned under varying reaction conditions to better characterize the surface spectroscopy of this catalytic reaction.

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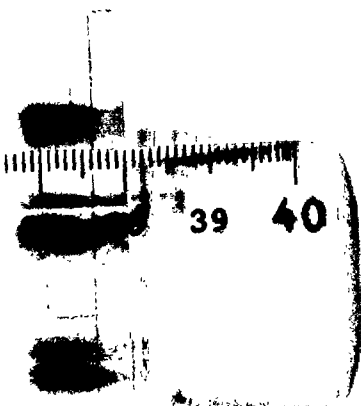
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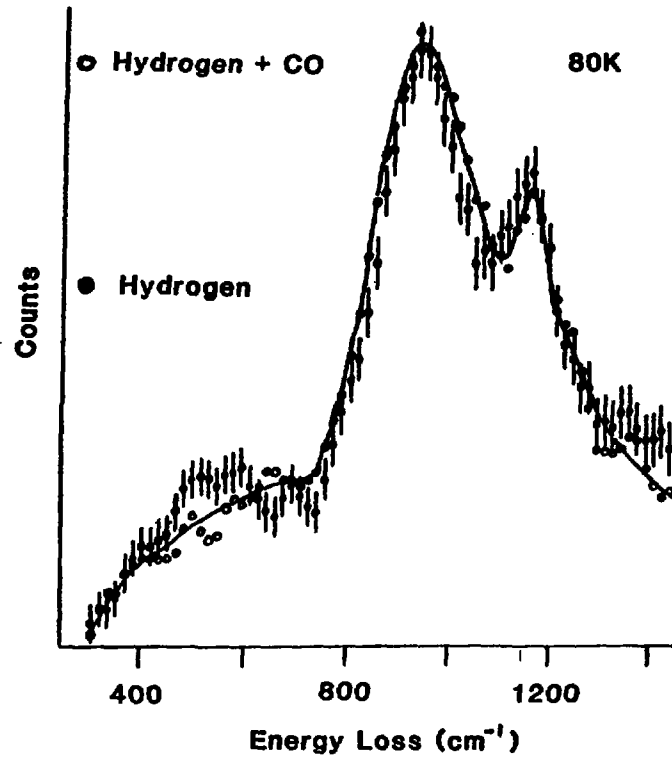


Figure 1

NIS intensity as a function of energy loss recorded at 80 K. The solid points indicate the spectrum of hydrogen adsorbed at room temperature on Raney nickel. The solid line (open points) indicates the spectrum observed for CO adsorbed at 150 K on the hydrogen covered sample. Both spectra have been corrected for scattering due to bulk nickel.

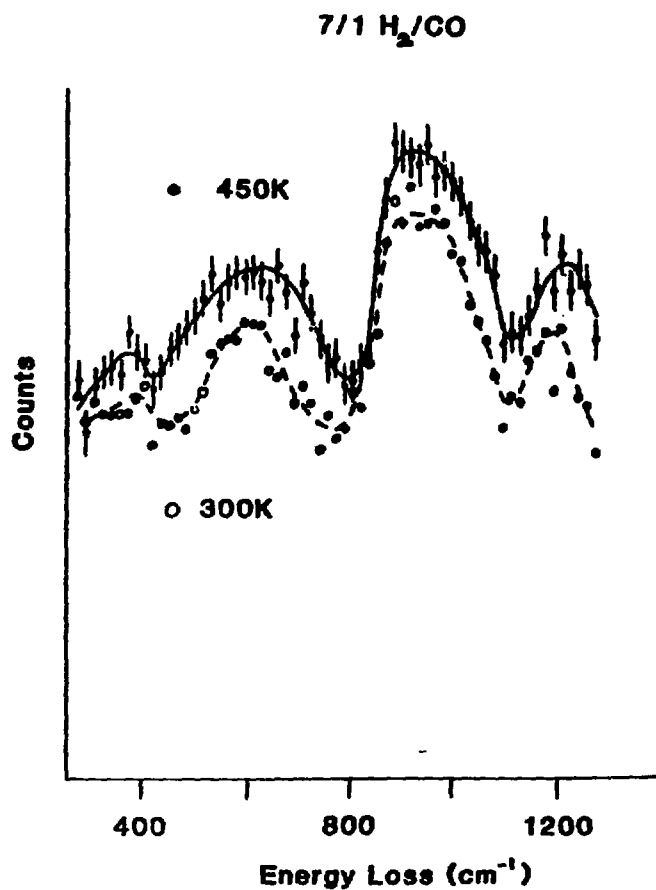


Figure 2

NIS intensity as a function of energy loss recorded at 80 K. The broken line indicates spectrum observed from sample held at 300 K while flowing H₂/CO=7, no conversion of CO to hydrocarbons observed. Solid line indicates spectrum after flowing the same gas mix, but with the sample held at 450 K where 50 % of the CO was converted to hydrocarbons.

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