

Coadsorption and Reaction of H₂ and CO on Raney Nickel: Neutron Vibrational Spectroscopy

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Neutron inelastic scattering (NIS) has been used to monitor vibrational modes during the adsorption and reaction of hydrogen and CO on Raney nickel. Evidence for a temperature dependent hydrogen/CO interaction is observed. The results show that CO coadsorbed in equivalent amounts with a saturation layer of H at 80 K has little impact on the H vibrational spectrum and thus on the force constant or configuration of the threefold binding sites occupied by hydrogen. Raising the temperature of the CO + H layer to 295 K shows significant H-CO interactions. Preliminary NIS experiments for H₂/CO gas mixtures under flow conditions indicate that the adsorbed layer present under reaction conditions, i.e., during substantial (~50%) conversion of CO to hydrocarbons (450 K) is dominated by the same adsorbates which are found under non reactive (i.e., no conversion of CO to hydrocarbons) conditions (300 K).

INTRODUCTION

Due to the sensitivity of neutron inelastic scattering (NIS) to the motion of hydrogen atoms, NIS has been used in several laboratories to measure the vibrational spectra of adsorbed hydrogenous species on high surface area transition metal catalysts (1-3). 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. We also report here the first attempt to use NIS as a reaction spectroscopy through NIS measurements of the Raney nickel surface following the catalytic methanation reaction at 1 atm 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).

EXPERIMENTAL

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 7 nm), 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.

Prior to a typical adsorption experiment the Raney nickel catalyst (~85 g 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 was mounted in a variable temperature cryostat on the neutron spectrometer, cooled to 80 K, and a

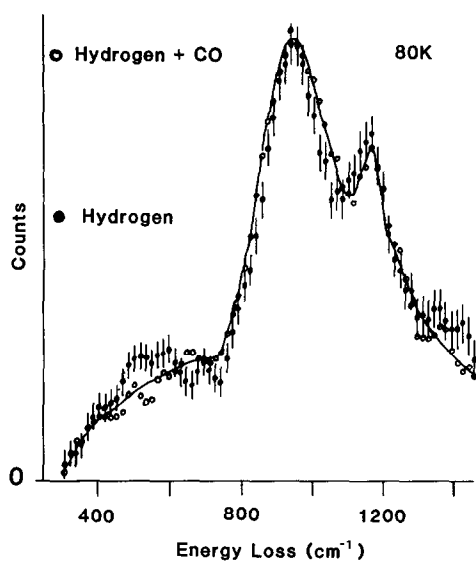


FIG. 1. NIS intensity as a function of energy loss recorded at 80 K. The solid points indicate the spectrum of hydrogen adsorbed at room temperature on Raney nickel. The solid line (open points) indicates the spectrum observed for CO adsorbed at 80 K on the hydrogen-covered sample. Both spectra have been corrected for scattering due to bulk nickel.

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 40 Torr. The quantity of H₂ chemisorbed by the catalyst (~ 14 m²/g) was measured using a capacitance manometer in a calibrated volume. The sample cell volume and the total surface area of the sample was such that at 40 Torr pressure, the quantity of gas phase H₂ in the cell was less than 1% of the quantity of H₂ adsorbed on the nickel surface. The NIS spectrum for such a hydrogen-saturated sample was measured at 80 K (to reduce multiphonon scattering and improve the signal to background ratio) and is shown in Fig. 1 (solid points). The error bars indicate the uncertainty following subtraction of the blank. In all figures the zero scattering signal (baseline) is determined by such a difference measurement. Since all spectra have comparable statistical uncertainties, error bars are indicated for only one spectrum in each figure.

Coadsorption. The adsorbed H spectrum in Fig. 1 is essentially identical to that reported previously (2, 4). The two dominant vibrational modes have been assigned to hydrogen bound in a threefold site in which the doubly degenerate mode, having H motion parallel to the surface, occurs at an energy of 940 cm⁻¹ (117 meV) and the mode involving H motion perpendicular to the surface plane is found at an energy of 1130 cm⁻¹ (141 meV). This assignment is discussed in a previous publication (4). The scattering at lower energy (~ 600 cm⁻¹) has been associated with hydrogen in fourfold sites (2). 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 dominated by H atoms chemisorbed on Raney nickel in threefold sites. Changes in the intensity of the peaks at 940 and 1130 cm⁻¹ can be interpreted directly as changes in site occupation and coverage of such sites.

Following the pure hydrogen measurement, the sample was maintained at 80 K and exposed to CO. The total quantity of CO which was introduced to the catalyst was approximately equal to the total number of H atoms on the nickel surface. Upon equilibration at 80 K, the total gas pressure corresponded to less than 1% of all the adsorbed species. Since virtually no hydrogen has been displaced into the gas phase, the surface concentration of H and CO are approximately equal. The NIS spectrum was then measured at 80 K and is shown as the solid curve in Fig. 1.¹ Aside from a slight broadening of the 940-cm⁻¹ peak, there is little difference in the scattering associated with hydrogen bound in threefold sites in the two spectra of Fig. 1. We can conclude from this result that, at 80 K, adsorbed CO does not displace H from the threefold binding site and even more strikingly, has

¹ Due to the much higher inelastic incoherent neutron scattering cross section for hydrogen (2), vibrations due to chemisorbed CO will not be observed under these experimental conditions.

only a small effect on the H-Ni vibrational force constant. This conclusion follows from the fact that, as indicated earlier, changes in the binding or geometry of H in the threefold site would produce distinct changes in both the energy and the relative scattering intensity of the H-Ni vibrational modes (4). While there is some relative change in the NIS spectra near 600 cm^{-1} the small net change is probably not significant.

Single crystal studies of the low temperature coadsorption of H_2 and CO on Ni(100) using temperature programmed desorption (TPD) (5) and ultraviolet photoemission (UPS) (6) have found a strong perturbation of both H and CO adsorption on this fourfold symmetric surface. Electron energy loss spectroscopy (EELS) studies (7) of H_2 and CO coadsorption have shown no evidence for C-H or O-H vibrations but have demonstrated that CO was bound predominantly on bridge sites in the presence of hydrogen, in contrast to the occupation of atop sites in its absence. However, in recent studies (8) on the Ni(111) surface no perturbation of either H or CO adsorption was detected. Interestingly, while the NIS measurements at 80 K cannot unequivocally address the CO-H interactions on fourfold (001) faces, they do clearly show little interaction of coadsorbed CO with H bound in threefold sites.

As the sample temperature is raised, H_2 is released to the gas phase (along with a smaller concentration of CO) such that at 270 K the gas phase pressure in the isolated 60-cm^3 sample cell is > 1000 Torr. It is clear that at higher temperatures adsorbed H is strongly perturbed by the adsorbed CO. Additional evidence for this temperature/pressure dependent interaction is seen in Fig. 2. The hydrogen spectrum (solid points) represents the scattering due to saturation coverage at 273 K. The solid curve represents the scattering observed following subsequent CO adsorption at 80 K and equilibration of the H + CO sample at 273 K (without removal of gas phase species). Since the background subtraction procedure

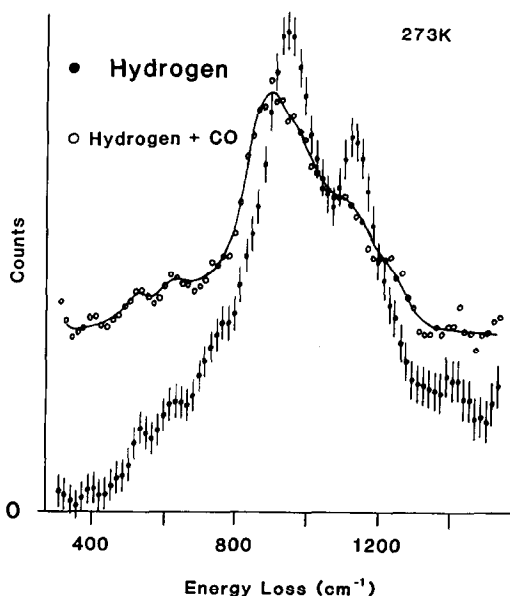


Fig. 2. NIS intensity as a function of energy loss recorded at 80 K. The solid points indicate the spectrum of adsorbed hydrogen. The solid line (open points) indicates the spectrum following the introduction of CO at 80 K and subsequent warming to room temperature without evacuation of desorbed gases.

described earlier was used to establish the baseline for adsorbate scattering, and as the thermal processing was performed *in situ* on the spectrometer, the observed alteration in scattering intensity is a direct result of changes in the chemical binding of hydrogen. Thus, the spectral shifts near 1000 cm^{-1} and the large increase of scattering intensity at low energy indicate the generation of new hydrogenous species on the surface as a result of this thermal processing.

Reactions. We have also investigated the interaction of adsorbed H and CO at 300 and at 450 K in a flowing 7:1 H_2/CO reactant gas mixture at 1 atm pressure. The NIS sample cell served as the reactor and was enclosed in an oven with a reactant gas preheater (copper). The reactant gases were ultrahigh grade purity which were further purified by passing through molecular sieve traps, and in the case of CO by passing through a trap containing hot copper fillings

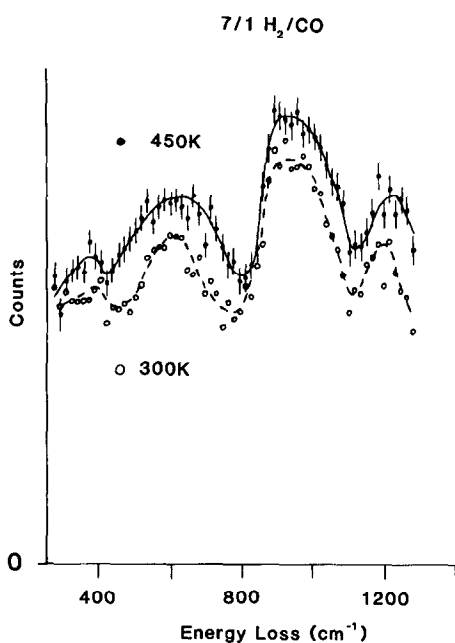


FIG. 3. NIS intensity as a function of energy loss recorded at 80 K. The broken line indicates the spectrum observed from a sample held at 300 K while flowing H₂/CO = 7, no conversion of CO to hydrocarbons was observed. Solid line indicates spectrum after flowing the same gas mix, but with the sample held at 450 K where 50% of the CO was converted to hydrocarbons.

to remove carbonyls (9). The reaction experiments were initiated by flowing pure H₂ at 300 K and gradually introducing CO into the reactant gas until the 7 : 1 ratio was established. The temperature was then slowly increased to the desired value. The gas exiting the reactor was passed through the sample injection loop of a flame ionization gas chromatograph equipped to measure low-molecular-weight hydrocarbons as well as CO and CO₂ with the detection sensitivity of CH₄.

These initial reaction spectroscopy studies were not conducted *in situ* in the neutron spectrometer. 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. 3 for reaction temperatures of 300 and 450 K. The total quantity of gas phase molecules in the sample cell, even at 1 atm pressure, represents less than 10% of the molecules adsorbed on the catalyst surface. Thus, the NIS spectra are dominated by surface species in these stopped flow experiments. In addition, the turnover number for methane production (CH₄ molecules per surface site per second) at 450 K is approximately 10⁻⁴ and strongly temperature dependent (11). This low turnover number suggests that the surface layer measured under these stopped flow conditions provides a good representation of the surface species present at the reaction temperature.

At 300 K no products were detected in the exit gas stream (CH₄ detection sensitivity was greater than 1 part in 10⁷). To insure steady state conditions, the Raney nickel sample was exposed to the H₂/CO gas for a period of 12 h before the cell was isolated in preparation for the NIS measurement. At 450 K the reaction products were CH₄, C₂, C₃, and C₄ hydrocarbons, water, and a small quantity of CO₂. The olefin to alkane ratio (C₂-C₄) was approximately 1 : 100. The quantity and distribution of these products was unchanged over a period of 24 h, indicating a constant reaction rate in which approximately 50% of the reactant CO was converted to products.

The striking feature of Fig. 3 is the similarity in the spectra. At 300 K no products are formed and only small differences are discerned when compared to the 450 K data where 50% of the CO is converted to products. This similarity of the spectra in the presence and absence of hydrocarbon products demonstrates that the observed signal cannot be due to the readsorption of reaction products upon cooling. Furthermore, since the amount of hydrogen trapped in the cell under the stopped flow conditions of these experiments is less than 10% of the adsorbed hydrogen coverage in Fig. 1, and since the integrated signal for all hydrogenous species in Fig. 3 is comparable to the

integrated signal for adsorbed hydrogen in Fig. 1, the major source of the signal in Fig. 3 must be the adsorbed hydrogenous species which are present under flow conditions. While there are quantitative differences between the two spectra (e.g., somewhat higher overall intensity at 450 K), 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 threefold nickel sites and a relative increase in the low energy region, including a distinct band centered at $\sim 650\text{ cm}^{-1}$ and a second feature around 400 cm^{-1} . In contrast, the chemisorbed H spectrum in Fig. 1 shows a broad shoulder at $\sim 600\text{ cm}^{-1}$, and little intensity at lower energies. The peaks at 945 and 1200 cm^{-1} in Fig. 3 indicate the presence of H in threefold sites. Comparison with the results of spectra measured under identical H_2 flow conditions *without* CO, suggests that the chemisorbed H associated with the threefold sites, represents 30% or less of the available threefold sites, and that significant new intensity is present at low energy.

Previous work with neutron scattering of hydrogen chemisorbed on a carbided Raney nickel surface (2) and a recent work on the adsorption of C_2H_2 and C_2H_4 at 300 K on Raney nickel (10) show that carbon-hydrogen fragments contribute vibrational peaks at low energies ($<500\text{ cm}^{-1}$). Therefore, the feature near 400 cm^{-1} (and possibly at 650 cm^{-1}) in Fig. 3 strongly indicates the existence of carbon-hydrogen fragments on the surface at both 300 and 450 K. In order to completely resolve the question of the relative contributions from readsorbed hydrogen, *in situ* NIS studies of this catalytic system must be performed.

SUMMARY AND CONCLUSIONS

In summary, these experiments have shown the coexistence of equal quantities of H and CO surface species on a nickel surface at 80 K with remarkably little interaction. The dominant H species remains

virtually unperturbed in its original threefold site in spite of coadsorbed CO. Warming the Raney nickel to 300 K, however, results in significant changes in the NIS spectra indicating strongly perturbed H or new hydrogenous species on the surface. Preliminary NIS experiments have been conducted for the first time in H_2/CO gas mixtures under catalytic reaction conditions. The results indicate that the hydrogenous surface species include hydrogen atoms bound in threefold nickel sites along with a significant concentration of hydrocarbon fragments, following nonreactive conditions (300 K) and after conditions of substantial conversion of CO to hydrocarbons (50% conversion at 450 K). Future *in situ* experiments are planned under varying reaction conditions and at lower vibrational energies to better characterize the surface spectroscopy of this catalytic reaction.

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