Hydrogen in Hydrotreating and Other Catalysts Studied by Inelastic Neutron Scattering -Spillover Hydrogen and H-containing Compounds

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Although some catalytic chemists have exploited the neutron as a spectroscopic probe, others regard the neutron as esoteric. Moreover, since neutrons are not available in one's local laboratory, experiments must be carried out at a central facility equipped with a nuclear reactor or a pulsed neutron source. Nevertheless, neutron scattering has much utility as a spectroscopic technique in catalysis. In this presentation, the application of neutron scattering spectroscopy to studies of catalysts and adsorbed molecules will be reviewed – timely in the light of the development of enhanced neutron scattering facilities in Europe and the United States.

In *incoherent inelastic neutron scattering* (INS), a fraction of incident neutrons loses energy by exciting vibrational modes of the scatterer; the INS spectrum is thus an *energy loss vibrational spectrum*. With recent improvements in instrumentation we can record the INS spectra of solids and liquids at a resolution approaching that of infrared spectroscopy, see Figure 1.

Nuclear interactions are not subject to the selection rules of optical and electronic spectroscopy: all vibrations are, in principle, observable. The scattering intensity is simply proportional to the concentration of the scatterer and its cross section. For the study of hydrogen in catalysts, the neutron is an ideal probe since the scattering cross section for H is much greater (80 barn) than for other element (5 barn).[1] The *ab initio* computational modelling of INS spectra (frequencies and intensities) with, for example, density functional theory, is straightforward.

The following topics, *inter alia*, will be presented.

Hydrogen in metal sulfide hydrotreating catalysts. Identifying S-H and M-H species (where M is, for example, Mo, W, Ru, Co, Ni.).[2]

Thiophene and benzothiophenes on molybdenum disulfide catalysts. Thiophene interacting with the catalyst through the ring or sulfur – or both.[3]

Direct observation of spillover hydrogen with INS. INS as a spectroscopic fingerprint of spillover hydrogen on, e.g., Pt/C, Ru/C and MoS_2/C catalysts.[4,5]

Spectroscopic evidence of the dissociation (or not) of adsorbed H_2. The H_2 rotational transition at 120 cm^{-1} is observable as a strong sharp line in INS spectroscopy.[6] Disappearance of this line (when, for example, a catalyst with adsorbed H_2 is warmed) and the appearance of vibrations of H atoms is direct evidence for the dissociation of H_2 on a catalyst, for example, Mo_2C and MoS_2.

Obervation and characterization of surface vibrational states of dispersed catalyst particles. Adsorbed H atoms move in phase with vibrational displacements of surface atoms. Neutrons are strongly scattered by the H atoms; the surface vibrational modes are thereby amplified and rendered susceptible to study by INS. Their characteristic spectra tell us, for example, which crystallographic plane is preferentially exposed. [5]

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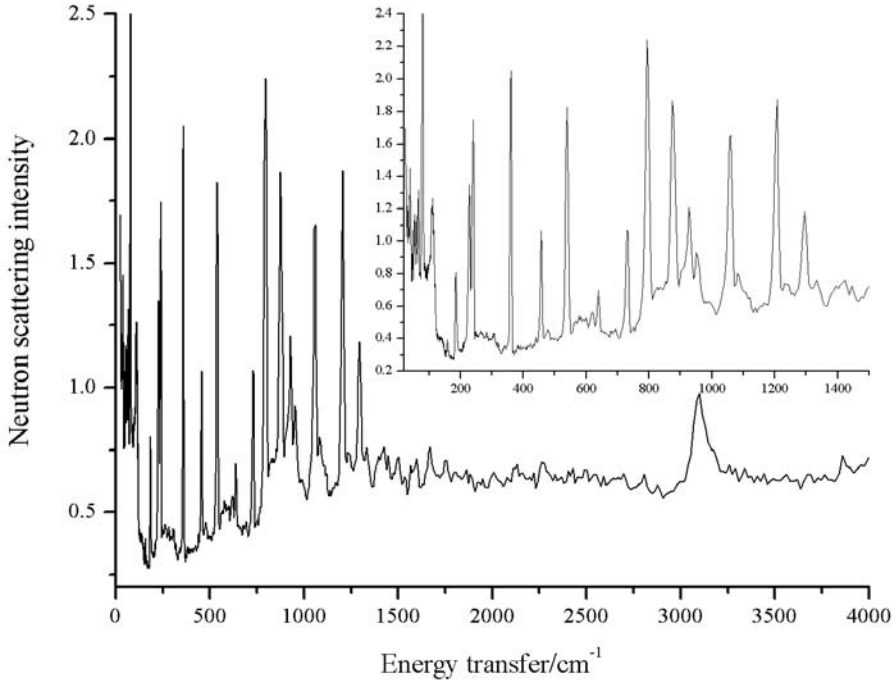

Figure 1. The inelastic neutron scattering spectrum of 2,5-diiodothiophene at 20 K on the TOSCA spectrometer at the ISIS Facility at the Rutherford Appleton Laboratory in the UK. TOSCA covers the range 16 to 4000 cm^{-1} with a resolution of 1-1.5% of the energy transferred. 2,5-Diiodothiophene is used to calibrate the spectrometer. The spectrum of thiophene is similar. The inset is the spectrum below 1500 cm^{-1}.

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