Inelastic Neutron Scattering Studies of Hydrogen Uptake by a Model Hydrodesulphurization Catalyst at High Pressure

Sukumaran Vasudevan,[a] John M. Thomas,*[a] Christopher J. Wright,*[b] and Christopher Sampson[b]

[a] *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*
[b] *Materials Physics Division, A.E.R.E. Harwell, Oxfordshire OX22 0RA, U.K.*

Inelastic neutron scattering reveals the existence of two sites at which hydrogen may be sorbed on MoS_2.

MoS_2 supported on γ-Al_2O_3 is a widely used hydrodesulphurization catalyst in the petroleum industry. We have studied the hydrogen sorption on MoS_2 by inelastic neutron scattering (I.N.S.) spectroscopy using a stainless steel sample cell capable of operating under typical industrial conditions (473 to 673 K and hydrogen pressures between 30 and 60 atm). Previous work[1] had identified a site where S–H bonds are formed.

Poorly crystalline samples of MoS_2 were prepared by non-aqueous metathesis reactions.[2] Isobar measurements of hydrogen sorption showed that sorption occurred in two stages. 60% of the final volume is sorbed below 423 K whilst near this temperature there was a rapid increase in the uptake suggesting that there were at least two sites for hydrogen sorption. It was possible to measure the change in enthalpy associated with the increased uptake at 423 K using a differential scanning calorimeter. Only a single exotherm was observed between 300 and 573 K up to hydrogen pressures of 70 atm. The variation of ΔH with pressure resembled a type I isotherm with saturation occurring at *ca.* 50 atm.

I.N.S. spectra of MoS_2 equilibrated with 1 atm of hydrogen at 300 and 433 K were recorded using a Be-filter spectrometer at AERE, Harwell and ILL, Grenoble. Both spectra showed excitations at 622 and 872 cm^{-1}. The first of these had previously been assigned to S–H deformation-vibrations. The excitation at 872 cm^{-1} could be due to either Mo–H or Mo–OH (owing to possible surface contamination) deformation modes. The spectra at 433 K showed that although the intensity of excitations at 662 cm^{-1} and 872 cm^{-1} remained constant the intensity of the scattering at 400 cm^{-1} increased with increasing pressure. (At 45 atm and 433 K the sorption of hydrogen by stainless steel is negligible and the scattering at 400 cm^{-1} can in no way be associated with the stainless steel cell.) It was also observed that the intensity of the *ca.* 470 cm^{-1} A_{2u}, B_{2g} lattice modes of MoS_2 increased on going to higher pressure. Further confirmation of this was obtained using a time-of-flight spectrometer which showed an increase in the intensity of the scattering at 400 cm^{-1}.

The I.N.S. data suggest that hydrogen sorbs at two sites on MoS_2, the first of which (identifiable by the scattering at

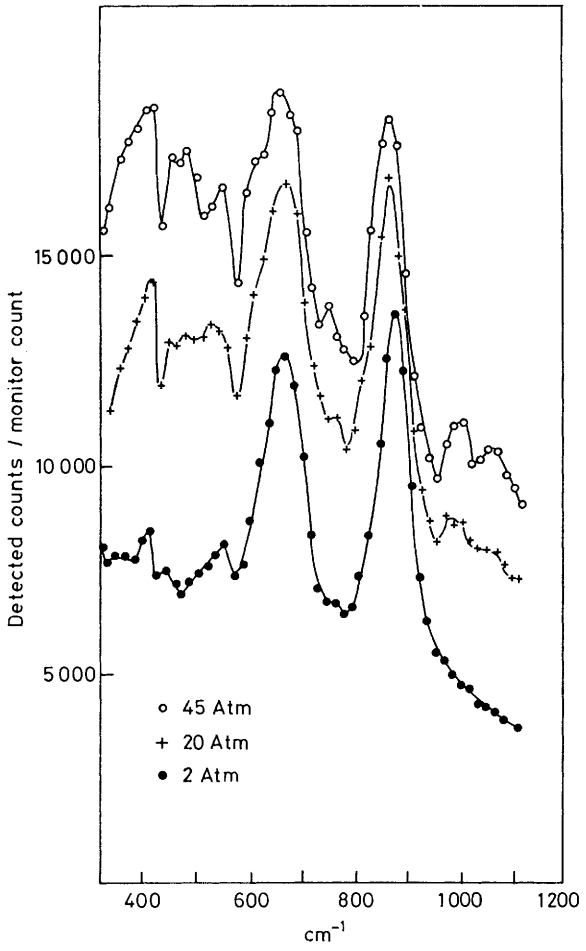

Figure 1. Inelastic neutron scattering spectra of hydrogen sorbed on MoS_2 at 2, 20, and 45 atm (after subtraction of scattering from the stainless steel cell).

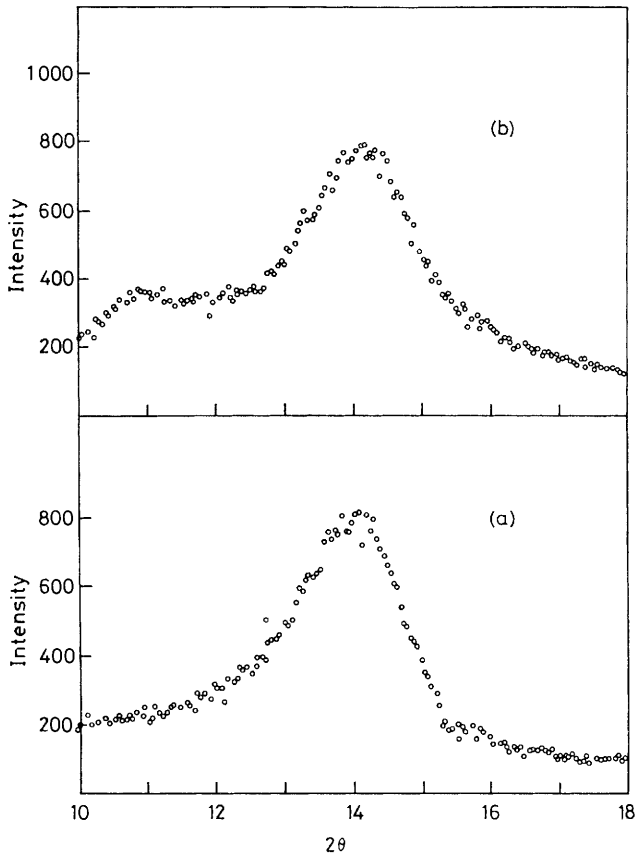

Figure 2. *X*-Ray diffraction traces for MoS_2 before (a) and after (b) heating at 433 K in 1 atm of hydrogen.

662 cm^{-1}) is saturated at pressures of less than 1 atm. Sorption on the second site takes place only at higher temperatures and is saturated at pressures of *ca.* 50 atm.

Preliminary *X*-ray investigations of MoS_2 in the presence of hydrogen at 300 and 433 K show the emergence of a Bragg peak at a 2θ value of 10.8° (Cu-K_α) at higher temperatures (Figure 2). If the new structure is isomorphous with the parent structure it would correspond to a *c*-axis lattice spacing of 15.6 Å as compared to 12.6 Å for the parent structure. We estimate, on the basis of the known covalent and van der Waals radii of sulphur and hydrogen, that the *c*-spacing would increase by *ca.* 2.2 Å if hydrogen atoms were bonded to the sulphur such that the S–H link is perpendicular to the layers. At 1 atm it appears that only part of the material is converted and the resultant material is biphasic.

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