Applications of neutron scattering to heterogeneous catalysis

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Abstract. Historically, most studies of heterogeneous catalysts that have used neutron vibrational spectroscopy have employed indirect geometry instruments with a low (\(<40\) cm\(^{-1}\)) final energy. In this paper we examine the reasons why this has been the case and highlight the advantages and disadvantages of this approach. We then show how some of these may be overcome by the use of direct geometry spectrometers. We illustrate the use of direct geometry spectrometers with examples from reforming of methane to synthesis gas (CO + H\(_2\)) over Ni/Al\(_2\)O\(_3\) catalysts and an operando study of CO oxidation. We conclude with a proposal for a unique instrument that combines both indirect and direct geometry spectrometers.

1. Indirect and direct geometry spectrometers

The first reported example of an adsorbed species (water on silica and alumina [1]) studied by neutron vibrational spectroscopy (inelastic neutron scattering, INS) used a direct geometry spectrometer [2]. However, since then almost all INS studies of catalysts (see [3] and [4] for reviews) have used indirect geometry spectrometers. It is useful to understand why this is the case and also what are the limitations of this approach.

In an INS experiment the aim is to measure the energy transfer \(E_T\) (cm\(^{-1}\)):

\[E_T = E_i - E_f\]

where the subscripts \(i\) and \(f\) refer to the incident and final states respectively. The associated momentum transfer \(Q\) (\(\text{Å}^{-1}\)) is given by:

\[Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos \theta\]

where \(k\) is the wavevector (\(k = 2\pi/\lambda\)), \(\lambda\) is the neutron wavelength (Å) and \(\theta\) is the scattering angle. Indirect geometry spectrometers for INS spectroscopy all use a small final energy, typically \(<30\) cm\(^{-1}\). Consequently \(k_f >> k_i\) and equation (2) reduces to:

\[Q^2 \approx k_i^2\]

Energy and wavevector are related (\(m_n\) is the mass of the neutron) by:

\[E = \frac{\hbar^2 |k|^2}{2m_n} = 16.7 |k|^2\]

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Combining equations (3) and (4):

\[ E_T = 16.7 Q^2 \]  \hspace{1cm} (5)

Equation (5) has several important consequences. It states that there is a single momentum transfer value at each energy transfer, thus the instruments have an approximately parabolic trajectory through \((Q,E_T)\) space. This means that the resulting spectra resemble vibrational spectra recorded by conventional methods as may be seen in the left part of figure 1, which compares the spectra of LiOH.H2O \[6\] (a model compound for adsorbed water on oxide surfaces) recorded by TOSCA (an indirect geometry INS spectrometer \[5\]), infrared and Raman spectroscopies. Note the excellent resolution in the TOSCA spectrum; the linewidths are comparable to those in the infrared and Raman spectra and this is a major advantage of this type of instrument. For catalysts the region below 2000 cm\(^{-1}\) is often difficult to access spectroscopically by conventional means, whether through absorption of the incident radiation by the support for oxide or carbon supported catalysts or few modes being allowed by the surface selection rule for metals. The highly penetrating nature of neutrons and the absence of selection rules make both factors irrelevant for INS spectroscopy. In addition, as there are few options for the user, indirect geometry spectrometers are generally relatively easy to use.

However, there are disadvantages to indirect geometry spectrometers. A major problem is availability: worldwide there are only six operating low final energy indirect geometry spectrometers, whereas there are 10 direct geometry spectrometers \[7\]. This trend will continue at the European Spallation Source (ESS): four direct geometry spectrometers are planned, whereas there will only be one indirect geometry spectrometer.

![Figure 1. Vibrational spectra of LiOH.H2O. (a), (a') INS, recorded with TOSCA \((a') = (a) \times 5\) ordinate expansion, (b), (b') infrared, (c), (c') FT-Raman, 1064 nm excitation, \((c') = (c) \times 3\) ordinate expansion, (d) INS, recorded with HET, \(E_i = 2420\) cm\(^{-1}\) and (e) INS, recorded with HET, \(E_i = 6850\) cm\(^{-1}\). The assignments for regions 1 – 9 are given in table 1.](image-url)
Table 1. Assignment of the vibrational spectra of LiOH.H₂O.

| Region cm⁻¹ | Description                      |
|-------------|----------------------------------|
| 1 0 - 570   | Translations                     |
| 2 570 - 740 | OH librations                    |
| 3 740 - 1160| H₂O librations                   |
| 4 1160 - 1500| 1ˢᵗ overtone of OH⁻ librations  |
| 5 1500 - 1840| H–O–H scissors                    |
| 6 1840 - 2510| Overtones and combinations of H₂O librations |
| 7 2510 - 3350| H₂O O–H stretch modes            |
| 8 3350 - 3900| O–H⁻ stretch modes               |
| 9 3900 - 4800| Combination O–H⁻ stretch + OH⁻ librations |

Historically, indirect geometry spectrometers have also been relatively insensitive owing to small detector areas, usually <1 m², in contrast to state-of-art direct geometry spectrometers that have >10 m² of detector area. This is a problem that is becoming less serious for the current generation of spectrometers with high m-number neutron guides (VISION [8] at SNS, TOSCA [5] at ISIS) and/or optimised collection systems (IN1-Lagrange [9] at ILL).

The largest disadvantage of indirect geometry spectrometers is illustrated in the right hand side of figure 1 in the region above 2000 cm⁻¹. While the O–H stretch modes of the water and hydroxyls are clearly seen in the infrared and Raman spectra, figure 1b,c, the TOSCA spectrum is essentially featureless, figure 1a. The reason for this lies in equation (5): large energy transfer means large momentum transfer; at 2830 cm⁻¹ (the maximum in the O–H stretch in the Raman spectrum, figure 1c), Q ~ 13 Å⁻¹. This is a problem because the INS intensity of a mode is given by:

\[ S(Q,n\omega_i) \propto \left(\frac{QU_i}{n!}\right)^n \exp\left(-\left(\frac{QU_{\text{Tot}}}{n!}\right)^2\right) \sigma \]

where \( \omega_i \) is the \( i \)th mode at transition energy \( \omega, n = 1 \) for a fundamental, 2 for a first overtone or binary combination, 3 for a second overtone or ternary combination etc..., \( U_\omega \) is the root mean square displacement of the atoms in the mode at \( \omega \) cm⁻¹, \( \sigma \) is the inelastic scattering cross section of the atom and the exponential term is a Debye-Waller factor, \( U_{\text{Tot}} \) is the total root mean square displacement of all the atoms in all the modes, (both internal and external), and its magnitude is in part determined by thermal motion. (This can be reduced by cooling the sample and so spectra are typically recorded below 30 K). Thus, large \( Q \) has two detrimental effects: it suppresses the total intensity via the Debye-Waller factor and, worse, the intensity of the overtones and combinations is proportional to \( Q^4, Q^6 \)… for \( n = 2, 3 \ldots \) and their intensity relative to the fundamental makes the latter unobservable.

Direct geometry spectrometers provide a solution to this problem. Figure 2 shows the \( S(Q,E_T) \) map of LiOH.H₂O recorded on HET [10]. HET had a low angle (i.e. small \( Q \)) detector bank at 3 – 29° and a high angle (large \( Q \)) at 110 – 140°, (state-of-the art instruments e.g. MAPS [11] have continuous \( Q \) range, rather than the discrete coverage of HET). By only using the low \( Q \) detectors, it is possible to observe the water bend and O–H stretch regions, figure 1d,e. Figure 2 also shows the \( (Q,E_T) \) trajectories of TOSCA, which are typical of low final energy indirect geometry instruments. It can be seen that for any energy transfer, a direct geometry spectrometer can always access lower \( Q \) than an indirect geometry spectrometer.
2. Benefits of access to small $Q$

For molecular spectroscopy in general, and catalysis in particular, access to small $Q$ has three major uses: observation of the C–H/N–H/O–H stretch region, quantification of surface species and the study of *operando* reactions. In the next three sections we describe these in more detail.

![Figure 2](image)

**Figure 2.** $S(Q,E_r)$ map of LiOH·H$_2$O recorded on HET [10] with $E_r = 2420$ cm$^{-1}$ and 6850 cm$^{-1}$. The black lines are the trajectories for an indirect geometry spectrometer with scattering angles $\theta = 45^\circ$ (left) and $135^\circ$ (right).

2.1. Observation of the C–H/N–H/O–H stretch region

Hydrogen is a vital component in the production of very large scale commodity chemicals such as ammonia, methanol and the Fischer-Tröpsch synthesis of hydrocarbons. Hydrogen is typically produced *via* reforming of methane to synthesis gas (syngas, CO + H$_2$). Industrially this is done using steam as the oxidant (steam reforming):

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$$

(7)

An alternative method is to use CO$_2$ as the oxidant (dry reforming):

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2$$

(8)

Apart from the obvious environmental advantage of CO$_2$ utilisation, dry reforming is well-suited to hydrogen production from biomass gasification and as the feedstock for Fischer-Tröpsch synthesis. Both methane reforming processes may use a high metal loading Ni/Al$_2$O$_3$ catalyst; however, a major problem is catalyst deactivation by coke formation. The nature of the coke is poorly understood and, in particular, the degree of hydrogen incorporation was unknown.

Figure 3 shows INS spectra in the C–H/O–H stretch region recorded with the direct geometry spectrometer MAPS [11] at ISIS for both dry (figure 3a,b) [12],[13] and steam (figure 3c) [14] reforming over Ni/Al$_2$O$_3$ catalysts. It can be seen that the spectra are markedly different. Transmission electron microscopy shows physical differences between the overlayers; amorphous carbon in the case of figure 3a and filamentous (graphitic) carbon in the case of figure 3b,c. While the catalysts that were used for dry reforming in figure 3a,b are broadly similar, the $\alpha$-Al$_2$O$_3$ support was obtained from different sources and the calcination conditions were different. In figure 3a, a significant quantity of hydroxyls are present (broad, intense peak at 3335 cm$^{-1}$) while there is a complete absence of...
hydroxyls in figure 3b. The hydrocarbonaceous overlayers are also very different: in figure 1a, the overlayer is largely aliphatic sp$^3$ carbon, as shown by the C–H stretch at 2950 cm$^{-1}$, while in figure 3b, it is largely aromatic sp$^2$ carbon, as shown by the C–H stretch at 3040 cm$^{-1}$. For steam reforming, figure 3c, the catalyst was prepared in the same way as that used for figure 3b, in this case the overlayer is again aromatic (C–H stretch at 3045 cm$^{-1}$). In this case there is also a small amount of hydroxyls present, which is not surprising in view of the reaction conditions. Thus, ready access to the C–H/O–H stretch region, with reasonable resolution and good sensitivity, enables clear distinctions between the catalysts and shows the dramatic differences that a change of preparation methods or reaction conditions can engender.

2.2. Quantification of surface species

Characterisation of surface species is vital in order to understand a catalytic process, however, being able to quantify the amount of material present is also invaluable and is often difficult. In the case of the hydrocarbonaceous overlayers shown in figure 3, quantification of the amount of carbon present is straightforward by temperature programmed oxidation (TPO: the catalyst is heated in an oxygen-containing gas stream and the amount of CO$_2$ produced is measured). Qualitatively, it is apparent that the amount of hydrogen present in the spectra in figure 3 is (a) >> (b) >> (c) (note the different scale bars) but quantitative data would be very useful. However, hydrogen at low levels is very difficult to quantify and INS spectroscopy provides a useful capability in this regard.

In the harmonic approximation the term $U_\omega$ in equation (6) is given by:

$$(U_\omega)^2 = \frac{\hbar}{2\mu \omega}$$

where $\mu$ is the reduced mass. Since hydrogen is the lightest element we can approximate $\mu$ as a diatomic, e.g. C–H or O–H. Hence $U_\omega$ is independent of the nature of the species and all hydrocarbons with a C–H stretch mode at $\omega$ cm$^{-1}$ will have the same intensity per C–H oscillator and similarly for hydroxyls. This means that a calibration is transferable. A calibration made with known masses of an appropriate material, in our case we used polystyrene and brucite (Mg(OH)$_2$) for the C–H and O–H regions respectively[12], can be used to quantify the amount of hydrogen present on the surface. The use of a direct geometry is essential for two reasons: the stretch region is relatively clear from interference from other modes and we measure at small $Q$, in order to minimise the effect of the Debye–Waller term.

![Figure 3. INS spectra of surface species on Ni/Al$_2$O$_3$ catalysts after methane reforming recorded on MAPS [11] with $E_i = 4840$ cm$^{-1}$. (a) Amorphous hydrocarbonaceous overlayer from dry reforming over Ni(45%)/α-Al$_2$O$_3$ [12]. (b) Filamentous hydrocarbonaceous overlayer from dry reforming over Ni(26%)/α-Al$_2$O$_3$ [13]. (c) Filamentous hydrocarbonaceous overlayer from steam reforming over Ni(26%)/α-Al$_2$O$_3$ [14].](image-url)
By curvefitting the data (as shown in figure 1a), and using the calibration factor the amount of hydrogen can be determined. For the reforming catalysts the amount of carbon-bound hydrogen is very small <100 μmol H (g cat)^-1. This can be combined with the carbon content derived from TPO to obtain a C:H ratio and these are given in table 2.

From figure 3 and table 2 it can be seen that the nature and quantity of hydrocarbonaceous overlayer is dependent on both the catalyst preparation and the reaction conditions. It is also apparent that the catalyst is very efficient at cycling hydrogen and much less efficient for carbon and it is this that leads to the carbon build-up that results in deactivation.

### Table 2. Quantification of hydrocarbonaceous overlayers on Ni/α-Al2O3 methane reforming catalysts.

| Process                        | C:H  |
|--------------------------------|------|
| Dry reforming (figure 1a)      | 160:1|
| Dry reforming (figure 1b)      | 2550:1|
| Steam reforming (figure 1c)    | 11690:1|

2.3. Operando studies

The current trend in studies of catalytic systems is to study a reacting system under realistic conditions of temperature and pressure while simultaneously maximising the amount of information obtained, so-called operando studies. In practice, for gas-solid systems, this means running a reaction with at least one spectroscopic method and with concurrent analysis of the reaction products by gas chromatography or mass spectrometry. Such studies are commonplace at synchrotrons e.g. [15] but not at neutron sources and particularly not for INS studies. The reasons are twofold: firstly, the flux is generally insufficient to be able to record data of sufficient quality on the timescale of the reaction and secondly, the need to minimise the Debye-Waller factor (equation (1)) means that the measurements are made at < 30 K. Thus the samples for the work on methane reforming discussed in the previous sub-sections were prepared offline at temperatures of 900 – 1200 K but measured at ~10 K.

With current instrumentation, low flux is becoming less of a limitation due to higher power sources such as SNS and J-PARC and improvements in neutron guides that provide more efficient transport of neutrons. The difficulty caused by the Debye-Waller factor cannot be addressed by indirect geometry instruments, but with a direct geometry instrument, by using only small Q data, the effect of the Debye-Waller factor can be mitigated. This compounds the problem with flux because much of the data is discarded but in favourable cases it is possible to study a system by INS adopting operando methods.

The oxidation of CO to CO₂ is a crucial reaction in an automotive catalytic converter. This is accomplished by the Pd component of the three-way (Pt/Pd/Rh) converter. A model system for this component of the three-way converter is hydrous palladium oxide, PdO.H₂O. This consists of ~18 Å diameter particles of nanocrystalline PdO with a monolayer or so of hydroxyls capped by 4-7 layers of water [16]. PdO.H₂O has the very useful property that it oxidises CO to CO₂ at room temperature at a rate that is convenient for INS studies. Figure 4a,b show the INS spectra recorded on MAPS together with simultaneous gas analysis by mass spectrometry, respectively.

From figure 4b, it can be seen that the catalyst is initially very effective: there is immediate, almost complete, consumption of CO and concomitant production of CO₂ as soon as the feed (100 cm³ min⁻¹ of He/CO(4%)/O₂(4%)) is switched to the catalyst at time 0 (the flows were set-up using a bypass loop). The heat of reaction results in an increased rate that decreases to an approximately steady-state after an hour or so. This is maintained until ~ 5 hours of elapsed time when CO₂ formation abruptly ends. The reason for this can be seen in the INS spectra recorded on MAPS; (which shows the Pd–O–H bending mode of the surface hydroxyls [16],[17]), as the reaction proceeds there is progressive decrease of the hydroxyls until they are completely consumed. The reason for this is that
there are two reactions occurring simultaneously, a catalytic reaction, equation (9), and a direct reaction, equation (10):

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \]  
\[ \text{Pd(II)O} + \text{CO} \rightarrow \text{Pd(0)} + \text{CO}_2 \]  

Both reactions require the presence of hydroxyls and we have shown elsewhere [17] that the direct reaction, equation (10), requires two hydroxyls:

\[ \text{CO} + 2\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  

At room temperature Pd(0) cannot be re-oxidised to Pd(II) and when all of the surface Pd(II) has been reduced, the reaction stops.

\[ \text{Figure 4.} \quad \text{(a) INS spectra recorded on MAPS with } E_i = 2420 \text{ cm}^{-1} \text{ of the reaction of } 100 \text{ cm}^3 \text{ min}^{-1} \text{ of He/CO(4%)/O}_2(2%) \text{ over hydrous palladium oxide at 300 K. The spectra are difference spectra, the spectrum recorded at 24 hours elapsed time has been subtracted from the data. The thick black line is the initial spectrum, the upper series of spectra were recorded over 00:00 to 03:29 elapsed time, the lower three were recorded at 09:45, 12:03 and 14:13 elapsed time. (b) Exit gas analysis by mass spectrometry recorded simultaneously with the INS spectra. The signals from the reactants, CO and O}_2, \text{ and the products, CO}_2 \text{ and H}_2\text{O}, \text{ have been ratioed to that of the He carrier gas. The reaction temperature (dashed line) is also shown.} \]
3. Disadvantages of direct geometry spectrometers and the way forward

It is clear that the use of direct geometry spectrometers offers significant advantages for studies of molecular systems and of catalysts. Nonetheless, there are disadvantages to the instruments. The first is that they are complex to operate because there are many possible options regarding flux, spectral range and resolution [11]. The correct choice is not always obvious and even experienced users may require several iterations to arrive at the optimum configuration for a given experiment.

The second disadvantage is that the resolution at \(<2000\, \text{cm}^{-1}\) is generally inferior to that of the best direct geometry instruments, TOSCA and VISION. This is because the resolution is a % of \(E_i\), with the best resolution at \(E_i \approx E_i\) and worsening with decreasing \(E_i\). Thus to obtain the best resolution possible across the entire spectral range requires multiple scans (and hence increased beamtime) and merging the scans is not simple.

It is apparent that both direct and indirect geometry spectrometers have significant advantages for studies of catalysts and both are often needed to provide a more complete understanding of a system. Using two different spectrometers often involves delays due to the need to apply for beamtime and repeat the sample preparation. An outline of an instrument, Cerberus [18] figure 5, has been described that offers the capabilities of both direct and indirect geometry instruments. The instrument would operate in a sequential mode; with the Fermi chopper out of the beam, an indirect geometry spectrum would be recorded using the indirect geometry modules. These would utilise the focussing analysers developed on VISION to maximise the collection area, while retaining a short secondary flightpath for the best possible energy resolution. On completion of data acquisition, the Fermi chopper would be moved into the incident beam and a direct geometry spectrum recorded. This would usually be at high energy (\(E_i \sim 4000\, \text{cm}^{-1}\)) to observe the C–H/N–H/X–H stretch region. However, the access to small Q means that time resolved studies at ‘catalytically interesting’ temperatures up to 473 K would also be feasible with any desired incident energy. Note that in the indirect mode, the detector in forward scattering used for the direct geometry data, would function as a low resolution diffraction detector. While this is not ideal for conventional powder diffraction, it would work well for total scattering studies involving hydrogen, thus providing a complementary structural capability. Cerberus would undoubtedly find much use in the fields of molecular spectroscopy and catalysis.

![Figure 5. The key components of Cerberus [18] showing the indirect geometry detectors in backscattering (blue) and the area detector in forward scattering for direct geometry and diffraction.](image-url)
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