

Characterisation of hydrocarbonaceous overlayers important in metal-catalysed selective hydrogenation reactions



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Dedicated to Dr. John Tomkinson and Dr. Jerry Mayers on the occasion of their retirement.

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ABSTRACT

The hydrogenation of alkynes to alkenes over supported metal catalysts is an important industrial process and it has been shown that hydrocarbonaceous overlayers are important in controlling selectivity profiles of metal-catalysed hydrogenation reactions. As a model system, we have selected propyne hydrogenation over a commercial Pd(5%)/Al₂O₃ catalyst. Inelastic neutron scattering studies show that the C–H stretching mode ranges from 2850 to 3063 cm^{−1}, indicating the mostly aliphatic nature of the overlayer and this is supported by the quantification of the carbon and hydrogen on the surface. There is also a population of strongly hydrogen-bonded hydroxyls, their presence would indicate that the overlayer probably contains some oxygen functionality. There is little evidence for any olefinic or aromatic species. This is distinctly different from the hydrogen-poor overlayers that are deposited on Ni/Al₂O₃ catalysts during methane reforming.

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1. Introduction

The hydrogenation of alkynes to alkenes over supported metal catalysts is an important industrial process [1], e.g. in polyethylene manufacture where it is essential to remove the trace levels of ethyne present in the ethene feedstock to prevent runaway reactions [2]. Ethyne to ethene hydrogenation has been extensively studied and it has been shown that hydrocarbonaceous overlayers are important in controlling selectivity profiles of metal-catalysed hydrogenation reactions [3–5]. However, it has been suggested that ethyne is a special case rather than the norm [6].

The hydrogenation of higher alkynes has been much less studied, although it is clear that hydrocarbonaceous overlayers are also implicated in these cases as well [6–8]. While it is possible to quantify the carbon content by temperature programmed oxidation (TPO), the form and quantity of the hydrogen present is generally unknown, as the overlayer is invariably impervious to investigation by infrared spectroscopy. These lacunae were partly overcome in work from the Fritz Haber Institute on alkene hydrogenation over supported Pd nanoparticles [9]. The authors associate activity with adsorption states of hydrogen that are modified by carbonaceous deposits and have used ¹H-(¹⁵N,αγ)¹²C nuclear reaction analysis (NRA) for hydrogen depth profiling in order to monitor the adsorbed hydrogen. The work establishes a role for hydrogen retention within the carbonaceous overlayer. Although this meth-

odology can detect and quantify hydrogen retention, it is unable to define how the hydrogen is bound.

We have recently shown that vibrational spectroscopy with neutrons (inelastic neutron scattering, INS) is able to detect, speciate and quantify hydrogen in carbon deposited on nickel–alumina catalysts during methane reforming [10–12]. In the present paper we extend the methodology to investigate whether it is possible to better characterise the form of the hydrogen present in the hydrocarbonaceous overlayer that is an integral part of alkyne hydrogenation using supported metal catalysts.

2. Experimental

The catalyst samples were prepared at ISIS [13] in a gas rig developed [14] for the preparation of the large (10–20 g) samples required for INS spectroscopy. 10 g of a Pd(5%)/Al₂O₃ catalyst (Alfa Aesar) was loaded into an Inconel cell. The catalyst was activated by heating at 393 K in flowing He/H₂(10%) mixture. Propyne has a low vapour pressure at room temperature so was introduced into the gas manifold by entraining the vapour in a second helium stream. This was then mixed with the He/H₂(10%) stream and admitted to the reaction cell, which was maintained at 333 K. The reaction was continuously monitored by an on-line quadrupole mass spectrometer (MS, Spectra Microvision plus). The reaction was carried out for two to six hours and then stopped. The sample was then transferred in an argon glovebox ([O₂], [H₂O] < 1 ppm) to an indium sealed thin-walled aluminium can, thus the sample has not been exposed to either oxygen or water

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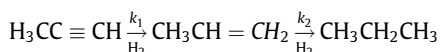
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vapour. The INS spectra were then recorded with various incident energies, E_i , using either MAPS [15] or MERLIN [16] at ISIS [13]. A sample that was activated but not reacted was used as the reference.

Post-reaction the carbon content was determined by temperature programmed oxidation (TPO). The studies were performed using a custom built reaction test rig consisting of 1/8 inch Swagelok tubing. Gas flows are controlled by Hastings Mass Flow controllers and are monitored by mass spectrometry using a Hiden HPR20 mass spectrometer. Samples were inserted into a quartz tube (4 mm internal diameter) and attached to the experimental rig using Cajun Ultra-Torr fittings. Sample heating was provided by a Eurotherm 3508 Microreactor oven. Approximately 40 mg of sample was heated to 1173 K at 5 K min⁻¹ under a flow of O₂ (5% O₂ in He, BOC Ltd, >99%, 70 sccm). The resultant gases were measured by mass spectrometry analysing for the following masses; m/z = 2, 4, 15, 18, 28, 32 and 44. Once the temperature ramp had completed, the sample was cooled under a flow of He (BOC Ltd, >99%, 70 sccm).

3. Results and discussion

As a model system we have selected propyne hydrogenation over a commercial Pd(5%)/Al₂O₃ catalyst:



The reaction conforms to a consecutive process, with partial hydrogenation to propene (k_1) preceding full hydrogenation to propane (k_2) [7,8,17–19]. Fig. 1 shows the on-line mass spectrometer output for the reaction. The immediate production of propene and propane demonstrates that this is a working catalyst. In addition to the expected hydrogenation products, propene and propane, there is also a significant production of the hydrogenolysis product ethene. This is not seen in microreactor studies [17–19] but probably arises because the space velocity in the large gas rig is only ~10% of that in the microreactor, so the residence time is much longer.

The INS spectrum (2500–4000 cm⁻¹) recorded using the MAPS spectrometer is shown in Fig. 2. A feature assigned to hydroxyls on the alumina [11,12] is apparent, however, there is only a barely

discernible feature (signal-to-noise ratio ~2) at 2970 cm⁻¹ in the region where a hydrocarbon signature would occur.

The spectrum shown in Fig. 2 is disappointing, particularly in view of the fact that the catalysis was clearly occurring as seen in Fig. 1. However, direct geometry instruments offer possibilities for trading between flux and resolution in a way that the more commonly used (for catalysis) indirect geometry instruments do not [15]. To increase the signal-to-noise ratio a threefold approach was adopted: (i) the reaction was run for six hours rather than two, (ii) MERLIN was used as the spectrometer since it is more sensitive than MAPS by virtue of a much larger solid angle of collection and the use of a guide on the incident beam [16] and (iii) a low resolution but high flux slit package was used in the Fermi chopper for energy selection. Overall, the changes were expected to result in at least an order of magnitude improvement in sensitivity, albeit at significantly inferior resolution.

Comparison of Figs. 2 and 3 shows that these expectations have been met. The hydroxyl peak in Fig. 2 has a full width at half maximum of ~360 cm⁻¹ whereas that in Fig. 3a and b is ~400 cm⁻¹, since the peak is so broad the resolution would not be expected to change the width significantly. However, the sub-structure apparent in Fig. 2, maxima at 3590 and 3700 cm⁻¹ which can be assigned to hydrogen bonded and isolated hydroxyls, respectively, has disappeared and a single, asymmetric peak at 3600 cm⁻¹ is observed. The spectra in Fig. 3a and b are normalised to the same mass of catalyst, thus it is apparent that ~50% of the hydroxyls have ‘disappeared’. Using Fig. 3a as a reference spectrum, the remaining hydroxyls were subtracted from Fig. 3b to give the scaled difference spectrum, 3c, (note that it is 4× ordinate expanded relative to (a) and (b)). This may be curve resolved to show a feature at 2950 cm⁻¹ and a very broad feature at 3260 cm⁻¹.

The major difference between Figs. 2 and 3 is that the signal-to-noise ratio is now ~10 for the peak at 2970 cm⁻¹ and it is now obviously present. The peak is apparently asymmetric to the low energy side, but this is a consequence of the overlap with the very broad peak at 3260 cm⁻¹. The transition energy indicates that it is largely aliphatic in origin, consistent with the weak feature seen in Fig. 2. This is supported by the observation of two peaks at 1365 and 1465 cm⁻¹ in Fig. 4 that can be assigned to unresolved CH₂ twist and wag modes and CH₂ scissors, respectively and to a peak at 750 cm⁻¹ in Fig. 5 that can be assigned to the CH₂ rock [20]. We note that the spectrum is markedly different from that of solid

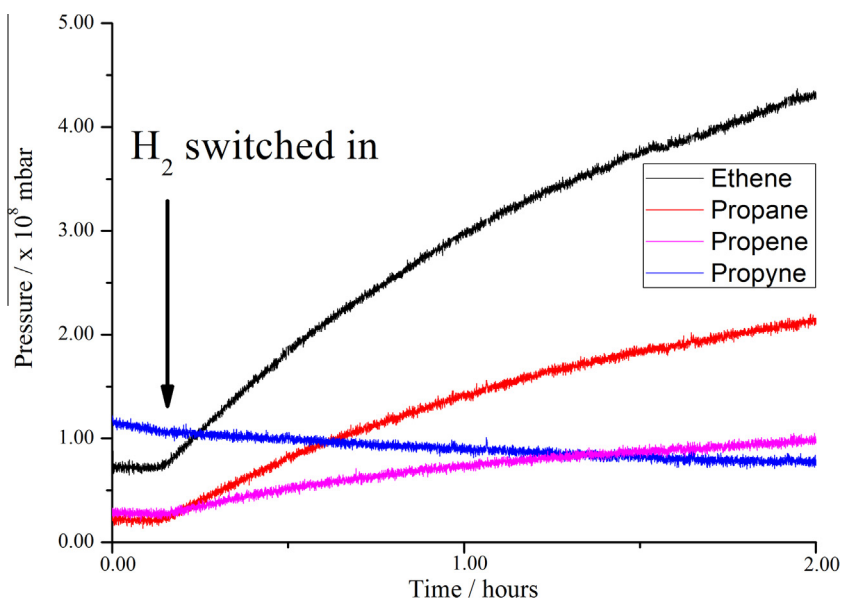


Fig. 1. On-line mass spectrometer output for the hydrogenation of propyne over Pd(5%)/Al₂O₃.

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