Selectivity enhancement in acetylene hydrogenation over diphenyl sulphide-modified Pd/TiO$_2$ catalysts

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ABSTRACT

Pd/TiO$_2$ catalysts have been exposed to diphenyl sulphide to assess the impact of the modifier on the selective removal of acetylene from ethylene rich feeds. The modified catalysts show a significantly reduced rate of ethylene hydrogenation without noticeably impacting on the rate of acetylene hydrogenation. Even after reduction at 393 K, which led to the loss of the phenyl ligands, the sulphur retained by the Pd was still capable of maintaining this enhanced selectivity of the catalyst to ethylene as opposed to ethane. Results are interpreted in terms of a templating effect on the active Pd surface as a result of the original ligand adsorption pattern that creates appropriate ensembles which allow alkyne adsorption and reaction but severely limits adsorption and reaction of the alkene. A potential contribution to this enhanced selectivity by suppression of subsurface hydrogen formation cannot be discounted.

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1. Introduction

The removal of trace quantities of acetylene from the outlet gas stream of a cracker is an essential part of the process which delivers high-purity ethylene for polymerisation purposes. The removal of acetylene, which otherwise acts as a poison for the polymerisation catalyst, is usually achieved by selective hydrogenation that aims to convert acetylene to ethylene and avoid both over hydrogenation to ethane and avoid converting any of the ethylene in the stream through to ethane. The latter, in addition to avoiding loss of a valuable feedstock, is essential to prevent thermal runaway given the exothermic nature of the reaction. An additional undesired reaction is the formation of oligomers or green oil which ultimately leads to catalyst deactivation. Hydrogenation of acetylene–ethylene mixtures is most commonly performed over supported Pd catalysts which are modified by the addition of silver [1] and by the use of CO which acts as a reversible poison [2,3]. The most widely viewed opinion is that CO does not compete effectively with acetylene for adsorption sites but is able to compete effectively with ethylene and hydrogen [1,2,4], minimising surface concentrations of these two reactants and consequently suppressing alkene hydrogenation. Further complexities arise from the ability of Pd under conditions of alkyne/alkene hydrogenation to form both carbides [5–7] and hydrides [8,9], and the role of CO in suppressing the formation of subsurface hydride and carbide phases in this context has been described [5,7,10].

While the contribution of CO to suppressing ethylene hydrogenation is relatively clear, its effect on the oligomerisation process is somewhat less apparent [2,5,10] with some authors indicating that the presence of CO enhances oligomerisation [4] and others indicating reduced oligomers in its presence [10]. The latter has been interpreted in terms of geometric effects with CO reducing the probability of direct alkyne–alkyne interaction [10] while the contradiction in terms of impact of CO depending on relative concentrations has been rationalised in terms of the relative surface concentrations of hydrogen and vinyl intermediate and the different partial orders of the latter leading to products [2]. It is clear that the use of CO as a means to control selectivity in the process is far from ideal and the need to carefully control its concentration against a backdrop of continuing catalyst deactivation is challenging at an industrial level. Current objectives in catalyst design are to minimise the sensitivity of the catalysts in terms of selectivity and activity to the influence of the transient poison (i.e. CO) in the feedstream [11]. An alternative to catalysts modification via e.g. alloying with Ag [1,12] or Ga [13] would be the use of "semi-transient" [11] rather than transient poisons.

The use of sulphidation to improve selectivity in acetylene–ethylene hydrogenation has been proposed although it is mainly limited to patent literature (see Ref. [2]) and with a focus on modifying nickel for use in front-end processes [14]. The use of diphenyl sulphide to induce chemoselective properties has been reported by Mori et al. for liquid-phase reaction [15–17] including those over Pd/C catalysts; however, in this case, its role is to induce selectivity in terms of the different types of reducible functionalities [15,16] or to enhance hydrogenation relative to hydrogenolysis [17]. We have recently reported preliminary results for triphenyl phosphine

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and diphenyl sulphide-modified Pd/TiO$_2$, which appear to offer a means of enhanced selectivity towards ethylene [18]. The original concept [18] was based on the use of ligands to exaggerate steric or electronic effects by careful ligand selection and thereby assess the mode in which selectivity enhancement might be achieved.

In the present study, acetylene hydrogenation from ethylene-rich steams under conditions of excess hydrogen is described over Pd/TiO$_2$ catalysts which have been modified by exposure to diphenyl sulphide. Operation with excess hydrogen permitted a better assessment of the impact of such treatments as these provide more challenging conditions to obtaining good selectivity to ethylene. Such conditions also reduce the propensity to create carbonaceous deposits and formation of "green oil" [2] which might otherwise distort findings related to modifications induced by the ligands. Operation under such conditions would be more akin to conditions experienced by a catalyst in a "front-end acetylene reactor" than a "back-end" hydrogenation unit [11]. Titania was selected as a support to diminish potential contributions due to oligomerisation which are known to occur more readily over a more acidic oxide support such as alumina. Note that commercial Pd catalysts for the purification of alkene streams contain less than 0.05 wt.% Pd, use alpha-alumina as the support, and the active metal exhibits an egg-shell distributions on the carrier.

2. Experimental

The 1% Pd/TiO$_2$ catalyst was synthesised by wet impregnation. The TiO$_2$ (P25) was prewetted with water and then the palladium nitrate solution (0.022 g of Pd(NO$_3$)$_2$ dissolved in 20 cm^3 of de-ionised water) added using a dropping funnel into the continuously stirred aqueous solution containing the support over a period of 1 h. Once the addition of the precursor solution was completed, the solution was left stirring at room temperature for a further hour. The flask was then transferred to a furnace held at 393 K for 24 h after which about half of the water had evaporated. The solution was stirred and added to a round-bottomed flask. This solution was then placed on a rotary evaporator and dried until a fine powder was obtained. The catalyst was stored in a glass vial until calcination was carried out. A second batch of similarly loaded catalyst was prepared by slight method modification which involved extending the period during which the solution and support remained in contact before initiating the drying process and this led to a sample which exhibited a higher dispersion. To distinguish these in text, the samples are denoted Pd(x)/TiO$_2$ where x refers to the Pd particle size as determined by CO chemisorption.

Calcination of the catalysts was carried out in a quartz holder in a flow of air at 100 mL min^{-1}. The temperature was raised to 673 K at a rate of approximately 20 K min^{-1}. The temperature was held at 673 K for 3 h and was subsequently lowered to room temperature.

The diphenyl sulphide (Ph$_2$S) catalysts were made by initially taking 1%Pd/TiO$_2$ (previously calcined) and reducing at 423 K for 1 h in 1:1 H$_2$ to N$_2$ mix. The cooled catalyst was added to a Ph$_2$S in hexane solution at the appropriate concentration (0.039 g of (C$_6$H$_5$)$_2$S in 100 mL hexane to treat 1 g of catalyst) and stirred at 298 K for 30 min. This was stirred on the rotary evaporator for 30 min before applying vacuum. The sample was dried under vacuum until a fine powder was obtained, and the evaporated solvent was collected and analysed by GC-MS to confirm the complete uptake of modifier. Modified samples are denoted Ph$_2$S–Pd(x)/TiO$_2$(y), where x refers to the estimated particle size and y is the reduction temperature in K.

TG experiments were carried out in a Mettler-Toledo TGA/SDTA 851^e LF1600 instrument. The sample was heated in air (50 mL min^{-1}) from room temperature to 973 K. Signals were normalised per gram, and the derivative weight profile was calculated.

Chemisorption experiments were carried out using a TPDRO 1100. All catalysts were reduced in 5% H$_2$/N$_2$ for 1 h and cooled to room temperature in N$_2$ prior to the pulse chemisorption experiments with unmodified catalysts reduced at 393 K and modified samples reduced at either 323 or 393 K. The pulsing experiments were carried out using a 285-µL sample loop filled with diluted CO (19.7% or 8% in He) being injected to the sample which was held at 293 K in a flow of He. The dispersion and particle size were calculated from the CO uptake assuming a Pd/CO stoichiometry of 2:1 [19]. This assumption, rather than a 1:1 ratio, was supported by FTIR spectra of adsorbed CO (see later) which confirm that multiply bound CO make a significant contribution to the compliment of total CO adsorbed. A spherical particle shape was assumed in calculating particle diameter.

FTIR of adsorbed CO was performed using a PE Spectrum 100 FTIR using sample presented as 16-mm-diameter self-supporting discs using approximately 45 mg of catalyst. The discs were then suspended in a quartz holder and placed in the IR cell. The catalysts were first reduced at 323 or 393 K for 1 h in a flow of 50% hydrogen in nitrogen. The sample cell was then evacuated to a pressure of approximately 3 × 10^{-3} mbar. A background spectrum (15 scans, resolution 4 cm^{-1}) was recorded prior to the introduction of CO. Subsequent spectra were recorded following introduction of increasing pressures of CO in the range 0.1–200 Torr with the samples at beam temperature (ca. 298 K).

XPS spectra were acquired using a Kratos Axis 5-channel HSi spectrometer with monochromated AlKα (1486.6 eV) X-rays operated at 150 W with the axis of the energy analyser normal to the plane of the sample surface. The sample analysis chamber of the XPS instrument was maintained at a pressure of ca. 10^{-9} Torr. The spectra were obtained at a pass energy of 80 eV with an energy resolution of 0.7 eV. The resulting spectra were normalised by adjusting to the Ti^{4+} peak at 458.7 eV. Samples analysed were Pd(3.5)/TiO$_2$ after reduction at 393 K and then storage and the same sample after exposure to Ph$_2$S modifier and storage. Samples were outgassed within the XPS chamber but did not undergo in situ reduction treatment.

All catalyst testing was performed using 50 mg of sample using a water-cooled reactor vessel to maintain the temperature at 323 K. Prior to reaction, the catalysts were reduced at 323 or 393 K under a flow of 50% H$_2$ in N$_2$ at 100 mL min^{-1} in a Pyrex reactor fitted with a frit. The temperature was raised at 20 K min^{-1} and was held at the desired temperature for 1 h before cooling in the hydrogen mix to room temperature. The catalyst remained in the flow of hydrogen until transferring to the reactor.

Two types of reaction tests were performed. To study the acetylene hydrogenation reaction under excess hydrogen conditions, 1% C$_2$H$_2$ in 9% C$_2$H$_4$/N$_2$ was used along with 100% H$_2$ to give a H$_2$/C$_2$H$_2$ ratio of 25:1. The objective of operating under these conditions was to attain high conversion of acetylene and determine how selective the catalyst was towards acetylene removal rather than ethylene reduction.

Further insight into the selectivity enhancements induced by the modifiers was obtained by separately studying the hydrogenation rates of acetylene and ethylene. These were performed using 5% of each gas in nitrogen at 150 ml min^{-1} with the addition of hydrogen to give H$_2$/C$_2$ ratio of approximately 3:1. The objective of performing these tests was to independently assess the activity of the catalyst towards each reagent, avoiding full conversion, and therefore permit a comparison of relative activity.

The reactions were compared on the basis of acetylene concentration in parts per million of ethylene and loss or gain of ethylene. The formulae used are shown below.

$$\text{Acetylene conc./ppm} = \frac{[C_2H_2]_{final}}{[C_2H_4]_{final}} \times 1,000,000 \qquad (1)$$

$$\text{Ethylene gain}/\% = \frac{\Delta[C_2H_4]}{[C_2H_4]_{initial}} \times 100 \qquad (2)$$

Using this system, an ideal catalyst would give a result of <5 ppm acetylene and an ethylene gain of +10% due to the fact that if all acetylene was converted to ethylene with no losses, there would be a 10% increase in ethylene concentration. The worst case scenario would provide an ethylene gain of −100% meaning that all the ethylene present at the start of the reaction was hydrogenated to ethane.

A Perkin-Elmer 8410 GC fitted with a flame ionisation detector (FID) was used to analyse the samples using a 2-m 5A molecular sieve packed column for product separation. The carrier flow was set at 15 mL min^{-1}. The run consisted of a 30-min plateau at 473 K followed by a ramp of 30 °C min^{-1} up to 523 K for a further 15 min. Sampling was carried out using an electrically actuated Valco multiposition valve fitted at the reactor exit. The 10 valve positions were fitted with 250-µL stainless steel loops and were set up in a trapping arrangement for subsequent analysis. In order to ascertain whether steady-state behaviour had been reached, sampling was carried out over two time scales, one for the initial period of reaction up to 120 min and one over a longer time range up to 240 min.

3. Results

The two unmodified Pd/TiO$_2$ catalysts were characterised by CO chemisorption to determine metal area, dispersion and estimated particle size. Calculations were based on Pd levels determined by ICP rather than the nominal loadings. Data in Table 1 indicate that the two samples have suitably different CO uptakes and particle size dimensions to allow this parameter to be investigated in terms of modifier behaviour. Ph$_2$S-modified samples will be referred to with reference to the different estimated particle sizes of 1.7 and 3.5 nm.

Fig. 1 shows the weight loss as a function of temperature in air for one of the Ph$_2$S-modified catalysts. The profile can be directly compared with the Pd(3.5)/TiO$_2$ parent and Pd(3.5)/TiO$_2$ treated in hexane. The later sample was prepared to allow differentiation between diphenyl sulphide decomposition and mass loss due to residual solvent removal. These background measurements suggest that the peak appearing between 323 and 400 K (Fig. 1) in the profile of Ph$_2$S–Pd(3.5)/TiO$_2$ can be mainly attributed to loss of water/solvent. This feature, common to all, was then followed by two features that were specific to the Ph$_2$S-modified sample where, beginning at 400 K in the dTGA, a very large desorption signal was evident followed by a second smaller one commencing at ca. 550 K. In the MS profile, the $m/z = 77$ signal developed just above 380 K and had disappeared by 573 K followed by a subsequent loss of CO$_2$ ($m/z = 44$). The MS representing the second desorption at approximately 600 K showed only a relatively small
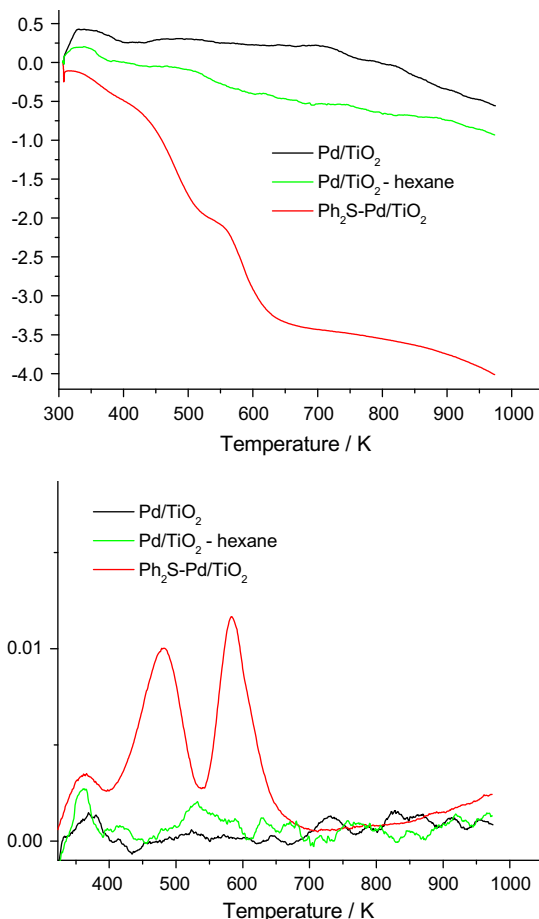
Table 1
Characteristics of Pd and phenyl sulphide-modified Pd catalysts.

Catalyst	CO uptake/ µmol g^{-1}	Metal surface area/m^2 g^{-1} (catalyst)[a]	d/nm[b]
Pd(3.5)/TiO$_2$	13.6	1.28	3.5
Ph$_2$S–Pd(3.5)/TiO$_2$	4.6	0.43	
Ph$_2$S–Pd(3.5)//TiO$_2$ (323)	1.7	0.16	
Ph$_2$S–Pd(3.5)//TiO$_2$ (393)	0.2	0.02	
Pd(1.7)/TiO$_2$	30.5	2.87	1.7
Ph$_2$S–Pd(1.7)/TiO$_2$ (323)	6.6	0.62	
Ph$_2$S–Pd(1.7)/TiO$_2$ (393)	–	–	

[a] Metal surface area/dispersion calculated from pulse CO chemisorption assuming a 2:1 Pd:CO stoichiometry.
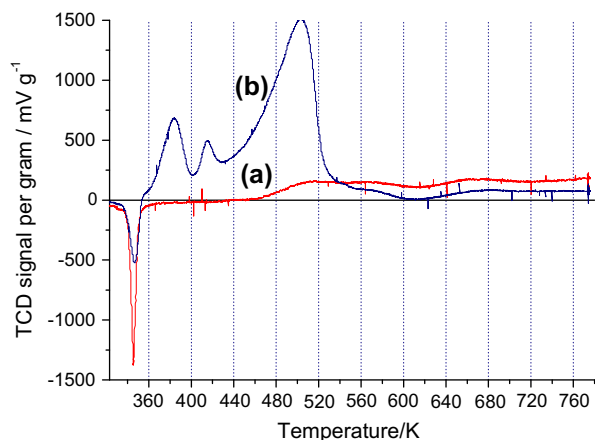[b] Estimation of particle size assuming spherical shape.

Fig. 1. Weight loss (top) and dTGA profiles (bottom) for Pd(3.5)/TiO$_2$, Pd(3.5)/TiO$_2$ – contacted with hexane and Ph$_2$S–Pd(3.5)/TiO$_2$.

contribution due to CO$_2$ and no signals due to benzene but showed a slight rise in the 64 signal suggesting some formation of SO$_2$.

When the sample was treated under temperature-programmed reduction (TPR) conditions using a TCD detector, three prominent features, at 383, 414 and 502 K, indicative of hydrogen consumption were all detected (Fig. 2b) and which were not observed for the unmodified Pd/TiO$_2$ (Fig. 2a). Additionally, the magnitude of the negative feature at 346 K, due to the decomposition of palladium hydride formed by exposure to hydrogen at 298 K [9], was suppressed (ca. 50%) for the sample modified by Ph$_2$S confirming that at least a proportion of the modifier interacted with the metal rather than merely the support component of the catalyst.

To obtain further insight into the importance of pretreatment gas and identify the impact of reduction temperature on the modifier stability and structure, the catalysts were reduced at 393 K and then a TG profile obtained in flowing air (Fig. 3) and compared with an as-prepared, modified sample. The first major weight loss between 323 and 400 K was still present for both samples suggesting moisture readsorbed after prior treatments. The second step, between 420 and 550 K for the as-prepared Ph$_2$S–Pd(3.5)/TiO$_2$, was eradicated following the reduction treatment at 393 K. The overall mass loss on the unreduced catalyst was 4% which compared with 2% on the 393 K reduced sample. The desorption peaks observed in the dTGA profile of the unreduced catalyst were not clear in the reduced case, but the higher temperature peak at 600 K retained some definition although with significantly less intensity. In terms of the observed fragments in the MS, the $m/z = 77$ signal that starts to desorb at 380 K from the unreduced catalyst was not at all evident in the case of the reduced catalyst

Fig. 2. Temperature-programmed reduction profiles for (a) Pd(3.5)/TiO$_2$ and (b) Ph$_2$S–Pd(3.5)/TiO$_2$.

Fig. 4. DRIFTS spectra for the Ph$_2$S–Pd(3.5)/TiO$_2$ catalyst (a) as-prepared (b) after reduction at 323 K and (c) after reduction at 393 K.
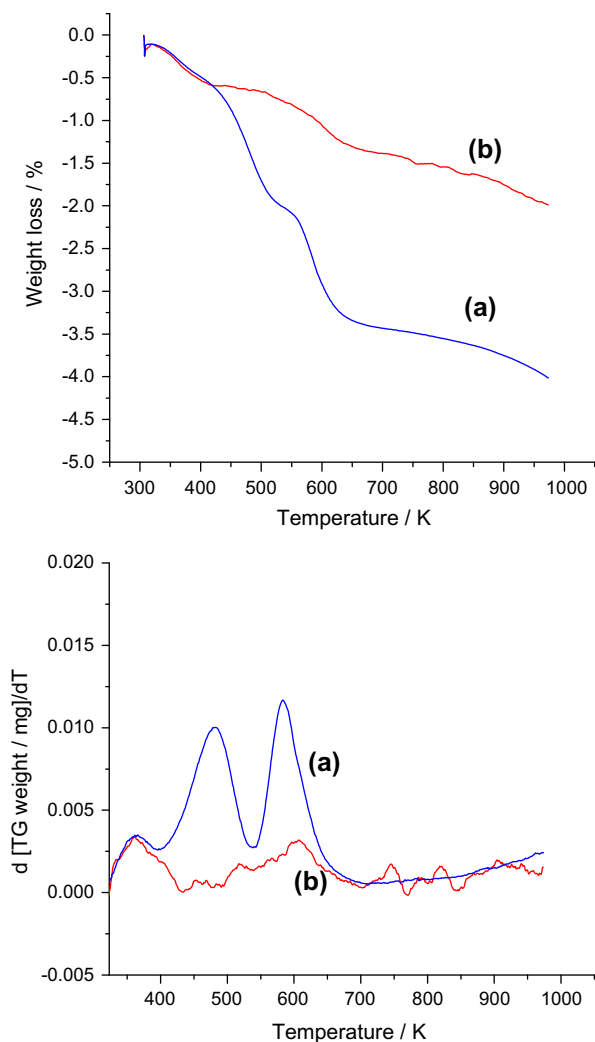

Fig. 3. TG (top) and dTGA (bottom) profiles for Ph$_2$S–Pd(3.5)/TiO$_2$ (a) as-prepared, and (b) after a prereduction treatment at 393 K.

alyst resulting in the lack of any appreciable signals in the dTGA profile.

The impact of reduction at 393 K was investigated by DRIFT spectroscopy and compared a sample which had received no pretreatment and one which had been reduced at 323 K. Spectra of the as-prepared sample show three sharp features at 1580, 1475 and 1440 cm^{-1} due to ring stretching modes of the phenyl rings. Additional broader bands were found at 1630 (water deformation) and 1532 cm^{-1} (Fig. 3a). Reduction in hydrogen at 323 K led to a materials with a spectrum which was not significantly modified compared with the starting material; however, increasing the reduction temperature to 393 K gave a sample with a spectrum with considerably reduced intensity of the three maxima at 1580, 1475 and 1440 cm^{-1} suggesting that the treatment had led to the loss of a large proportion of the aromatic structures. Bands at 1630 and 1532 cm^{-1} were largely unaffected. Results suggest that treatment in hydrogen at 393 K was more effective in decomposition of the modifier and/or that the TGA feature between 323 and 400 K (Fig. 1) also contained a contribution due to loss of ligand.

The extent to which phenyl sulphide interacted with the Pd component was estimated by the use of CO chemisorption. In addition to analysis of the two catalysts in their unmodified state, samples were also analysed after treatment by the modifier and after prereduction at 323 and 393 K. Data are compiled in Table 1. Results show that addition of modifier, irrespective of subsequent post-treatment, led to a significant loss of CO uptake. Treatment at 393 K, which had led to loss of some of the ligand structure, did not result in the recovery of metal sites suggesting retention of a component of the modifier. Note that the use of pulse chemisorption would not discriminate [19] between loss of a sites due to physical blockage of the Pd atom and reduction in uptake due to modification of the site and substantial weakening of the carbon–metal bond. In order to further investigate the nature of the Pd sites which were able to adsorb CO, FTIR spectra were recorded in the presence of this adsorbate under equilibrium conditions rather than the non-equilibrium conditions which exist between pulses which may lead to loss of weakly bound CO [19].

FTIR spectra were recorded of samples after *in situ* reduction at the appropriate temperature (323 or 393 K) and exposed to increasing pressures of CO. For the sake of brevity, the spectra of the unmodified Pd/TiO$_2$ samples are shown only at full coverage (*ca.* 40 Torr) to highlight differences between samples of different dispersion (Fig. 5). In line with the greater CO uptake measured by CO chemisorption, the Pd(1.7)/TiO$_2$ showed the greater combined band envelope due to adsorbed CO; however, it was mainly as a result of a much greater population of bridging sites as the

implying that the phenyl-S bond had already been compromised by the prereduction process. The only mass fragment observed for the modified catalyst was *m/z* 44 corresponding to CO$_2$. The intensity of this signal was much lower than for the unreduced cat-
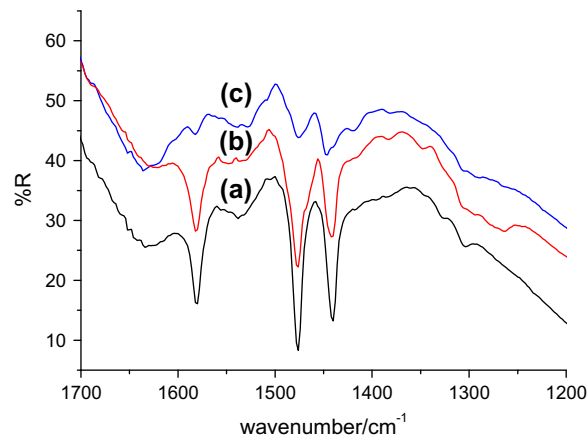
relative area of the absorbance band due to linearly bound CO was almost identical for both samples. Note that the frequency of the band due to twofold bridging carbonyls at *ca.* 1920 cm^{-1} (Fig. 5) is consistent with the attribution to μ_2 – bridge-bonded CO on particle edges (1924 cm^{-1}) rather than CO bridge bound on (1 0 0) type facets (1969 cm^{-1}) as reported by Lennon and co-workers [20], and therefore, entirely consistent with expectation that Pd(1.7)/TiO$_2$ with its higher dispersion and greater CO uptake should exhibit a greater proportion of these sites with respect to Pd(3.5)TiO$_2$.

FTIR of CO adsorbed on the Pd(3.5)TiO$_2$ sample modified by Ph$_2$S and then reduced at 323 K are shown in Fig. 6A with the corresponding spectra for the same sample reduced at 393 K shown in Fig. 6B. Increasing coverage led to a shift in the bridge bound maxima from 1913 to 1946 cm^{-1} (Fig. 6A), while the sample reduced at 393 K gave spectra showing a shift from 1891 to 1927 cm^{-1} (Fig. 6B). The overall band envelope appeared broader for the sample treated at the higher reduction temperature although the absorbance maxima were similar. Higher pressures were required to attain full coverage on the modified samples (*cf.* Figs. 6A and 6B and 5) although, in terms of intensity in the bridging region, bands were more intense for Ph$_2$S-modified samples than untreated Pd(3.5)TiO$_2$. However, when considering the overall integrated intensity, this may have been less for the modified surfaces as
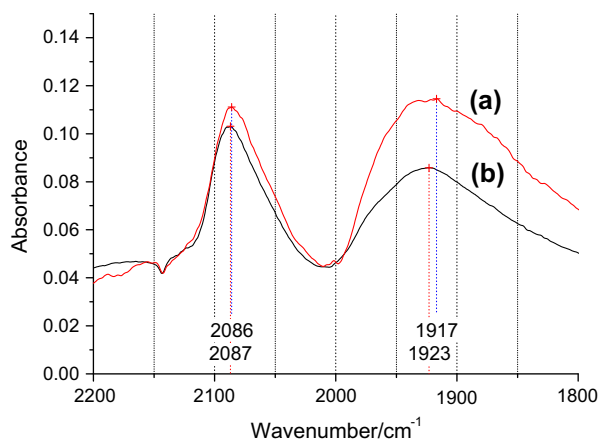

Fig. 5. FTIR spectra of CO adsorbed at 298 K at maximum coverage (40 Torr) on (a) Pd(1.7)/TiO$_2$ and (b) Pd(3.5)/TiO$_2$.
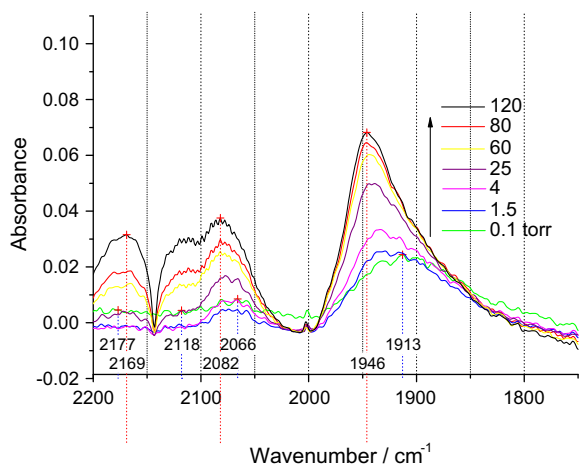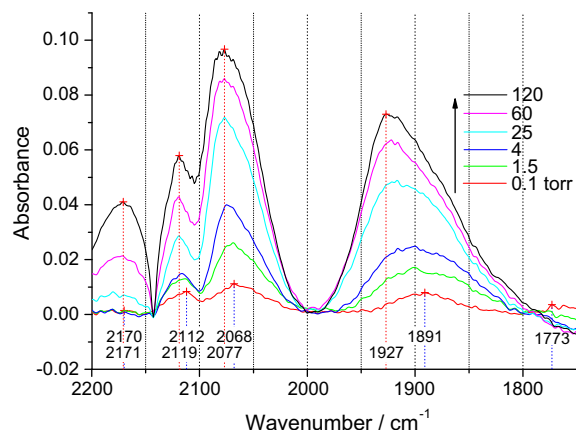

Fig. 6B. FTIR spectra of Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 393 K and exposed to CO at 298 K at increasing pressures up to 120 Torr.

there was a narrowing of the bands and a loss, particularly below 1900 cm^{-1} following modification of the surface. This would suggest loss of access to threefold hollow sites. Ph$_2$S-modified surface after reduction at 323 K (Fig. 6A) showed reduced intensity for the linearly bound feature (2082 cm^{-1}) relative to unmodified surface (Fig. 5); however, this was reversed when the sample was reduced at 393 K (Fig. 6B) further supporting the idea that significant change to the modifier occurred between these two treatment temperatures. Transfer between on-top sites and bridged and fcc sites following ligand decomposition would be analogous with the decomposition of H$_2$S on Pd (1 1 1), where HS and S atoms have a preference for bridge and fcc sites, respectively [21]. Note that bands at 2170 and 2120 cm^{-1} which grow with pressure are due to gaseous CO; however, in the case of the 393 K reduced sample (Fig. 6B), a sharpening and enhancement in intensity of the lower frequency component suggests a feature at *ca.* 2112 cm^{-1} due to an adsorbed mode of CO.

The latter feature at *ca.* 2114 cm^{-1} was also present when the same experiment was conducted by using the better dispersed Pd(1.7)TiO$_2$ sample modified by Ph$_2$S and reducing at 393 K (Fig. 7B). Again, the band due to linearly bound carbonyl species (2076 cm^{-1}) was more intense at full coverage after reducing at 393 (Fig. 7B compared with 323 K (Fig. 7A) and more intense than for unmodified catalyst (Fig. 5). Even though bridge bound carbonyls were more abundant on the unmodified version of the higher

Fig. 6A. FTIR spectra of Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 323 K and exposed to CO at 298 K at increasing pressures up to 120 Torr.
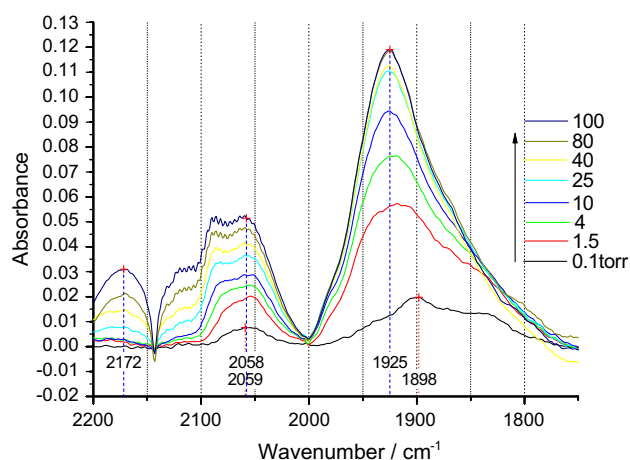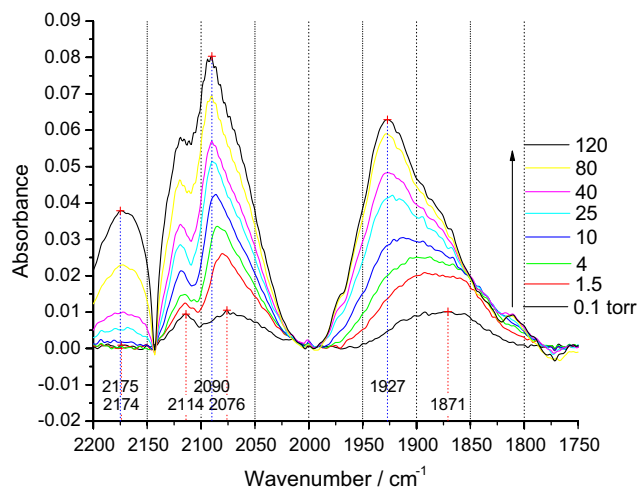

Fig. 7A. FTIR spectra of Ph$_2$S–Pd(1.7)/TiO$_2$ reduced at 323 K and exposed to CO at 298 K at increasing pressures up to 100 Torr.

Fig. 7B. FTIR spectra of Ph$_2$S–Pd(1.7)/TiO$_2$ reduced at 393 K and exposed to CO at increasing pressures up to 120 Torr.

Fig. 8. XPS spectra of the Pd 3d region normalised to Ti^{4+} signal at 458.7 eV for (a) Pd(3.5)/TiO$_2$, reduced at 393 K then stored and (b) Ph$_2$S–Pd (3.5)Pd/TiO$_2$ reduced at 393 K prior to exposure to modifier and stored.

dispersed sample, Ph$_2$S modification still led to yet higher intensity features appearing at full coverage; however, the full integrated intensity was reduced due to lesser intensity at lower frequency of the envelope. Spectra in the 2000–1800 cm^{-1} region for this sample appeared to show two features at low coverage (1898 and 1840 cm^{-1} for 323 K reduction and 1900 and 1850 cm^{-1} for 393 K reduction); however, increasing pressure seemed to enhance intensity mainly of the former band in each case. This would suggest that the threefold hollow sites (1840–50 cm^{-1}) were largely fully occupied at low CO pressure while CO occupying twofold bridging sites (ca. 1900 cm^{-1}) became populated to a greater degree as CO pressure increased in the gas phase.

XPS spectra (Fig. 8) for the Pd(3.5) TiO$_2$-unmodified catalyst gave peaks due to Pd 3d 5/2 corresponding to binding energies of 335.1 and 336.4 eV representing metallic Pd (Pd^0) and PdO (Pd^{2+}), respectively. Note that as samples were not in situ reduced, surface oxidation simply during storage of the samples in air will have taken place and will contribute to Pd^{2+} signals detected in the Pd 3d spectrum. However, if it may be assumed that the extent of re-oxidation by air is similar for both samples, then differences in the observed spectra before and after modifier treatment may be attributed to the interaction with the modifier. The signal resulting from the metallic Pd was detected at a similar binding energy for both modified and unmodified catalyst; however, the signals on the former showed pronounced asymmetry which required deconvolution (not shown) of the shoulders from the main peaks. Six peaks were fitted to the 3d 5/2 and 3/2 signals for phenyl sulphide-modified sample allowing for metallic palladium and two Pd^{2+} complexes. The intensities of the additional features were relatively insignificant compared with the main peak with the weak feature at 334.9 eV indicative of minor amounts of unmodified Pd^0 and suggesting in line with the CO chemisorption data (Table 1) that the sulphur ligand covered a significant part of the metallic surface. The other two contributions were at 337.0 and 339.3 eV. Binding energies between 336.5 and 339.5 eV have previously been assigned [22] to Pd^{2+}—S compounds.

Catalysts were studied to determine the rates of reaction in acetylene hydrogenation and ethylene hydrogenation in separate, non-competitive, reactions. Data are shown in Fig. 9. The effect of particle size in the absence of modifier is observed by comparing data in columns 1 and 5 where it is apparent that both acetylene and ethylene are hydrogenated faster over the catalyst with larger particle size. Increasing dispersion had the greatest effect on acetylene hydrogenation where the rate was reduced by ca. 30%,
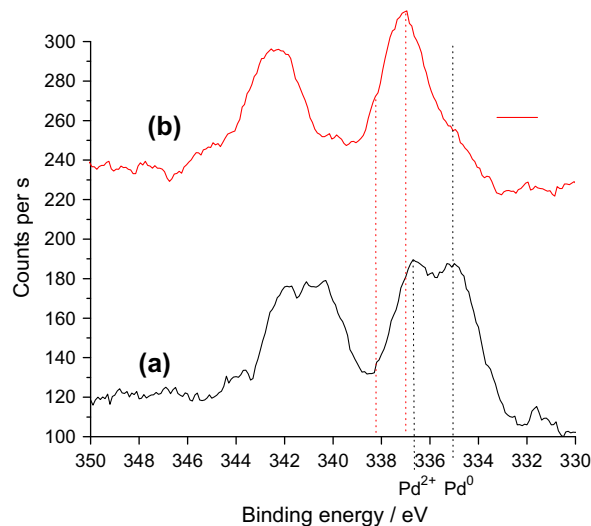
whereas ethylene hydrogenation occurred at a similar rate over both samples suggesting less sensitivity to particle size. The relative sensitivities of the two reactants meant that for the better dispersed catalyst, the rate of ethylene was greater than that of acetylene, whereas on the poorer dispersed sample, it was acetylene which was hydrogenated at the marginally greater rate. For the sample of greater particle size, modification with phenyl sulphide followed by reduction at 323 K had little effect on the rate of acetylene hydrogenation (Fig. 9, column 3) but completely suppressed ethylene hydrogenation and no evidence for ethane was obtained after reaching steady state during a 4-h period on stream. Reduction at 393 K of the phenyl sulphide-modified sample as opposed to 323 K did not have an impact on the rate of acetylene hydrogenation; however, some recovery of the palladium's ability to hydrogenate ethylene was observed giving a rate of 1.4×10^{-6} mol g^{-1} s^{-1} (Fig. 9, column 4). A very similar rate of ethylene hydrogenation was found for Ph$_2$S–Pd(1.7)TiO$_2$ after 393 K reduction (Fig. 9, column 6); however, this catalyst still showed an equivalent ability to hydrogenate acetylene as the

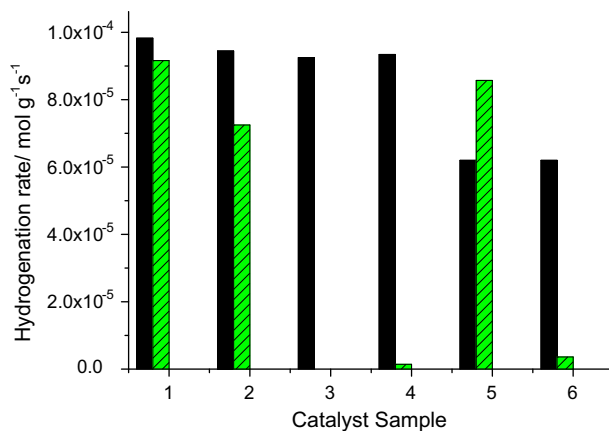**Fig. 9.** Hydrogenation rates of acetylene (solid columns) and ethylene (shaded columns) in separate, non-competitive reactions at 323 K over (1) Pd(3.5)/TiO$_2$ (2) Pd(3.5)/TiO$_2$ with 3 ppm CO in feed (3) Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 323 K (4) Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 393 K, (5) Pd(1.7)/TiO$_2$ and (6) Ph$_2$S–Pd(1.7)/TiO$_2$ reduced at 393 K.

Table 2
Acetylene concentration and conversion and ethylene gain (loss) at 120 min on stream using a mixed ethylene/acetylene feed at 323 K over Pd(3.5)/TiO$_2$, Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 323 K and Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 393 K.

Catalyst	Acetylene conc/ppm	Acetylene conversion/%	Ethylene gain (loss)/%	Rate of C$_2$H$_4$ removal (mol g^{-1} s^{-1})
Pd(3.5)/TiO$_2$	1415	98.6	(−81)	9.6 × 10^{-5}
Pd(3.5)/TiO$_2$, 3 ppm CO				9.7 × 10^{-5}
Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 323 K	571	99.4	3	–
Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 393 K	295	99.7	(−23.5)	2.34 × 10^{-5}
Pd(1.7)/TiO$_2$	0	100	(−93)	9.2 × 10^{-5}

Table 3
By-product formation at 120 min on stream for hydrogenation reaction of acetylene-only, ethylene-only and in a mixed acetylene/ethylene feedstream.

	Oligomers FID signal	Methane FID signal
Ethylene only		
Pd(3.5)/TiO$_2$	170	3445
Pd(3.5)/TiO$_2$ 3 ppm CO	799	3392
Ph$_2$S–Pd/TiO$_2$ reduced at 323 K	118	3155
Ph$_2$S–Pd/TiO$_2$ reduced at 393 K	225	2995
Acetylene only		
Pd(3.5)/TiO$_2$	248,173	61,404
Pd(3.5)/TiO$_2$ 3 ppm CO	296,540	103,000
Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 323 K	273,559	0
Ph$_2$S–Pd(3.5)/TiO$_2$ reduced at 393 K	289,983	0
Mixed acetylene/ethylene reaction		
Pd(3.5)/TiO$_2$	52,415	14,763
Pd(1.7)/TiO$_2$	60,483	14,906
Ph$_2$S–Pd(3.5)/TiO$_2$ reduced 323 K	4510	4425
Ph$_2$S–Pd(3.5)/TiO$_2$ reduced 393 K	10,674	16,195

Fig. 10. Time on stream data for Pt(3.5)/TiO$_2$ at 323 K using a mixed ethylene/acetylene feed.

unmodified catalyst. Not surprisingly, the extent of oligomer formation (mainly C$_4$ and C$_6$ products) was minimal in the case of ethylene-only feedstream, and methane was the main undesired reaction product (Table 3). Neither CO nor the diphenyl sulphide made significant impact on by-product formation. This is surprising given the significant effect which diphenyl sulphide had on the rate of ethylene hydrogenation for ethylene-only feedstreams (Fig. 9). For feedstreams containing acetylene as the reagent, by-product formation (both oligomers and methane) was significantly enhanced compared with ethylene-only feedstreams; however, CO added to the feed marginally enhanced production of both undesired reactions (Table 3). Diphenyl sulphide modification appeared to have negligible impact on the extent of oligomer formation but was able to suppress hydrogenolysis reaction completely, and no methane could be detected after treatment with modifier, after either 323 or 393 K reduction.

Data for competitive reaction using feedstream containing both ethylene and acetylene are shown in Fig. 10 for the first 3 h on stream and a summary of steady-state conversion and selectivity complied in Table 2 at 120 min on stream with by-product distributions shown in Table 3. Unmodified Pd/TiO$_2$ showed a very rapid (<5 min) stabilisation period after which conversion and selectivity remained relatively constant although gradual improvement in selectivity (increase in ethylene and decrease in ethane concentrations) was observed over the 3-h period. Modified samples showed a longer period for attainment of steady-state levels. Data were obtained under conditions that led to high acetylene conversion, and so the data are presented as conversion rather than rate since rates in all cases were similar and approximately
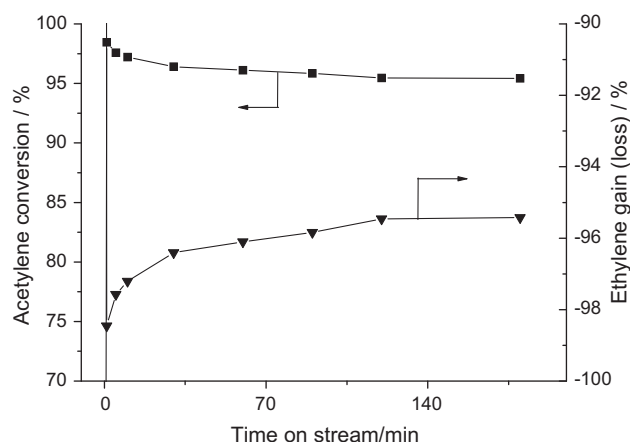
1.09 × 10^{-5} mol g^{-1} s^{-1} in all cases. Ethylene rates, however, are quoted but do not consider the ethylene formed by conversion of acetylene. It can be seen that diphenyl sulphide-modified sample, after 393 K reduction, lowered the rate of ethylene hydrogenation to 25% of the value of the unmodified sample. At steady state, the stream passing over unmodified Pd(3.5)/TiO$_2$ was reduced to 1415 ppm acetylene (98.6% conversion), but the catalyst was largely unselective and also hydrogenated a significant fraction of the ethylene and also yielded large quantities of by-products (methane and C$_4$ + C$_6$ products). Ph$_2$S–Pd(3.5)/TiO$_2$ catalyst reduced at 323 K produced much less by-product, and this catalyst was also able to hydrogenate acetylene giving 99.43% conversion without leading to reduction in ethylene levels in the feedstream (a positive ethylene gain was observed). Reducing the same phenyl sulphide-modified catalyst at 393 rather than 323 K led to improved acetylene conversion (99.7%) but at the expense of loss in selectivity with 23.5% ethylene conversion observed. Unmodified catalyst of higher dispersion was able to completely convert all acetylene but also led to very high ethylene conversion. Differences in dispersion did not appear to significantly affect the amount of undesired by-products, and oligomer and methane formation were equivalent over samples of different particle sizes (Table 3). However, it was noted that the extent of both processes (oligomerisation and hydrogenolysis) were less for mixed feedstreams than for reactions involving acetylene alone. Although there may have been a contribution from the competitive reactions, this is most likely to have originated in the lower acetylene concentration involved in the mixed reagent reactions. Diphenyl sulphide modification followed by 323 K reduction was able to suppress both oligomer and hydrogenolysis reaction rates (Table 3) although this beneficial effect of the ligand was less apparent after reduction of the catalyst at 393 K although some benefit in terms of extent of oligomer formation was still apparent even after this higher temperature reduction was performed (Table 3).

4. Discussion

4.1. Single reagent experiments

A starting point for the interpretation of the role of the ligand modifier on the selective hydrogenation of acetylene within ethylene streams is to look at the relative rates of hydrogenation of the individual components over the various catalysts as summarised in Fig. 9. In the absence of ethylene, acetylene was hydrogenated in a narrow range of rates between 9.3 × 10^{-5} and 11 × 10^{-5} mol g^{-1} s^{-1} over all catalysts based on Pd(3.5)/TiO$_2$. The standard

deviation based on repeat experiments for any one catalyst was marginally less than the range exhibited across the series, and so differences should not be taken as being of considerable significance. However, given the significant variation in CO uptakes across this series (Table 1) as a consequence of ligand modification, the TOF values are expected to show differences of significance. However, given that CO pulse chemisorption showed very low chemisorption capacity after ligand modification (Table 1) at odds with the readily detectable absorbance bands due to CO chemisorption in FTIR (Figs. 6A and 6B), calculation of specific values may provide misleading information. CO pulsing however should provide reliable data for the unmodified samples [19], and therefore, TOFs for the samples of similar loading but different dispersions can be calculated. The calculated values of acetylene TOF for unmodified $Pd(3.5)/TiO_2$ and $Pd(1.7)TiO_2$ are 7.21 and 2.03 s^{-1}, respectively. Gigola et al. [23] report turnover frequencies for Pd/α-Al_2O_3 which encompass this range of values, and furthermore, these authors observed an exponential decrease in TOF as the dispersion was increased. Therefore, the reduced TOF for the $Pd(1.7)TiO_2$ compared with $Pd(3.5)/TiO_2$ is consistent with this data and also with findings [24] that the TOF for acetylene hydrogenation (ethylene-free feed) decreases for Pd particles smaller than 3 nm. More recent studies show that this increase continues until dimensions of ca. 11 nm [25]. Gigola et al. [23] interpreted these observations in terms of changes in the chemisorption strength and/or changes in the availability of absorbed hydrogen as particle size was varied. It was argued that geometric and structural factors could not be used to explain these results because the dependence of turnover number on particle size occurred mainly in the low dispersion range. FTIR spectra of CO adsorbed on the two unmodified catalysts employed in this study show the key difference between higher ($Pd(1.7)TiO_2$) and lower ($Pd(3.5)TiO_2$-dispersed samples to be in the relative abundance of sites which bridge bound CO (Fig. 5). The frequency of this feature (1920 cm^{-1}) suggests bridging across edge atoms rather than on (100) type facets where the expected frequency would be some 50–60 cm^{-1} higher. If these sites are intrinsically less active, then data could be interpreted simply in terms of structure sensitivities. However, given that data were obtained at steady state and that morphology/particle sizes may well play a role in determining both the extent to which subsurface carbon [6,25] and hydrogen [8] may be formed and influence the hydrogenation reaction, judgement will be reserved at this stage until other aspects of the system are discussed.

The non-competitive reactions also allowed determination of the reaction rates (global and per site) for ethylene hydrogenation. Again, the calculation of TOF for the modified samples may contain errors arising from the uncertainties in measuring CO uptake data for such samples. However, TOF values for the different unmodified catalysts were calculated as 2.81 and 6.73 s^{-1} for $Pd(1.7)TiO_2$ and $Pd(3.5)/TiO_2$, respectively. These values lie within the range reported for calculated and experimental values over supported catalysts [26] and for model catalysts and Pd (1 1 1) [27]. However, the trend, as observed for acetylene, that the TOF diminishes as dispersion increases, is inconsistent with the commonly held belief that ethylene hydrogenation is a structure insensitive reaction [1,27] particularly over the range of particle sizes 1.3–6.1 nm which encompasses the dimensions of average particle sizes determined for catalysts employed here (Table 1). Again, further comments at this stage are reserved given the potential impact of dissolved hydrogen [8] and carbon [6] which may be present to different levels on the catalysts at steady state as a consequence of different particle morphologies [25].

The relative rates of acetylene/ethylene hydrogenation in the non-competitive reactions (Fig. 9) indicate that the smaller particles are intrinsically more active for ethylene than acetylene (2.81 vs. 2.03 s^{-1}), while the tendency is reversed for the catalyst with the larger particles (6.73 vs. 7.21 s^{-1}). Again, there may be a temptation to relate this to the relatively higher population of bridged to linear sites available on the better dispersed $Pd(1.7)TiO_2$ and suggest that the edge atom sites capable of bridge bonding CO are relatively more active for ethylene hydrogenation. However, this trend was not observed for the modified surfaces where bridge bound CO was relatively more abundant on the surface reduced at 323 K than on the 393 K reduced surfaces yet ethylene hydrogenation was less on the former than the latter. Care must therefore be taken in using this simple interpretation based on site requirements alone. However, modifiers that selectively act upon such sites might be predicted to enhance the selectivity in reactions in which both acetylene and ethylene are present. Guerrero-Ruiz et al. [28] and Dulaurent et al. [29] have reported that adsorption enthalpies of CO on multibinding sites on Pd are greater than those which singly bond CO. This suggests that the presence of CO in the gas stream might impact selectivity by disfavouring ethylene adsorption on these edge sites that bridge bond CO and where the relative rates of ethylene hydrogenation are greatest. Addition of a second metal to Pd which reduces the proportion of bridge-binding sites present and which also enhances selectivity to ethylene rather than over hydrogenation to ethane [1] would be consistent with this view. Experiments conducted here by the addition of low levels of CO (3 ppm) had little or no effect on acetylene rates but led to a significant reduction in ethylene reaction rate in experiments conducted with individual reactant gases (Fig. 9, column 2). This would provide more support for a model based on the presence of sites of different relative activities for the two reactant molecules [3].

4.2. Experiments using mixed C$_2$ feed

When both reactants were co-fed, it is expected that the rate of acetylene hydrogenation is unaffected [4] while ethylene reaction rates should be diminished. As indicated above, in order to assess the ability to reduce acetylene levels to the minimum values, conversions were consequently high and therefore inappropriate for calculation of rates. To support this, the TOF for $Pd(3.5)/TiO_2$ was 0.8 for acetylene in a mixture containing ethylene but 7.21 s^{-1} in the non-competitive reaction. This low turnover frequency resulting from the high acetylene conversion consequently permitted the ethylene hydrogenation to proceed at a rate of 9.6×10^{-5} mol g^{-1} s^{-1}. This compares with a value of 9.2×10^{-5} mol g^{-1} s^{-1} for the better dispersed catalyst. These values correspond with TOF values of 7.06 and 3.02 s^{-1} for $Pd(3.5)/TiO_2$ and $Pd(1.7)/TiO_2$, respectively. These compare with values of 6.73 and 2.81 s^{-1} for ethylene hydrogenation in the absence of acetylene. (Again note that these calculations omit ethylene formed from acetylene.) The ratio between these values of 1.05 and 1.06 for $Pd(3.5)/TiO_2$ and $Pd(1.7)/TiO_2$, respectively, suggest that both catalysts, irrespective of particle size, respond similarly to the presence of acetylene in the feed in terms of hydrogenation of ethylene. This may be the consequence of the high conversion of acetylene over both catalysts (Table 2) which then fails to suppress significantly the reaction of the alkene, leading to high conversions of the latter (Table 2). Effectively complete suppression of ethylene conversion was attained for sample treated with diphenyl sulphide and then reduced at 323 K resulting in a net gain in ethylene as a result of the selective semi-hydrogenation of acetylene. Note that an ethylene gain of 3% (Table 2) is less than the theoretical maximum of 10% which could be obtained if all acetylene is selectively hydrogenated and no ethylene is converted to ethane. This modifier also diminished the total amount of by-product including oligomer produced (Table 3). The modifier however permitted the hydrogenation of acetylene to proceed and led to a conversion of 99.43% as

opposed to 98.6% in its absence (Table 2) which consequently led to a marginal improvement in the level to which acetylene was removed (571 vs. 1415 ppm). These results might indicate that the diphenyl sulphide is capable of performing a role equivalent to that normally performed by CO but with the additional, significant advantage that is does not have to be co-fed with the reactants with careful monitoring of its concentration. However, as the diphenyl sulphide is omnipresent, but yet permits the hydrogenation of acetylene to proceed at an equivalent rate as in its absence (Fig. 9, Table 2) this casts doubt upon the widely held belief that CO enhances selectivity by occupying sites which would otherwise be available to acetylene [4] (and where selective hydrogenation occurs) and that the presence of CO hinders access of ethylene to the surface when all/most of the acetylene has been consumed. Our data would suggest a model based on different site requirements (potentially including also, availability to hydrogen) for the two hydrocarbons with diphenyl sulphide-covered surfaces preventing access of ethylene to the surface (and/or minimising hydrogen adsorption) but permitting access of acetylene as indicated by the ability to hydrogenate acetylene at the same rate either with or without diphenyl sulphide but to suppress ethylene in the single reactant experiments (Fig. 9, column 1 and 3). The situation would be closer to a scenario whereby selectivity in acetylene hydrogenation is enhanced following the formation of appropriate geometrically distinct adsorption sites created by deposition of immobile carbonaceous layers [3,30,31] or by use of intermetallic compounds which lead to active Pd-site isolation [13].

It should be noted, however, that the presence of any overlayer structure including TiO_x [9], carbonaceous layers [30] or indeed, adsorbed CO [10] is expected to suppress the formation of subsurface hydrogen and this is consistent with the reduced intensity of the negative feature due to hydride decomposition at *ca.* 350 K in the TPR profile for Ph$_2$S-modified Pd (Fig. 2). Integration and calibration of this feature indicate that an H/Pd ratio of 0.32: 1 was reduced to 0.20: 1 by the presence of Ph$_2$S. The presence of such subsurface hydrogen has been shown to promote unselective hydrogenation [7] and thus enhance ethane production from alkyne or alkene [8]. As the formation of an overlayer, either of diphenyl sulphide molecules or carbonaceous material, leads to associated suppression of bulk hydride formation, it is not a simple task to separate and attribute enhanced selectivity to one or the other of these effects.

4.3. Sulphur modification

Under the conditions described in the previous paragraph, the diphenyl sulphide existed in a state where the phenyl ligands remained intact (Figs. 1 and 4), and it is assumed that the molecule was bound to surface Pd atoms *via* sulphur. Comparison of FTIR of adsorbed CO on untreated and diphenyl sulphide-treated samples reduced at 323 K (Figs. 5 and 6A and 7A) would suggest that these modifiers showed a preference to block sites where CO would adsorb in on-top mode. These structures were thermally stable at the reaction temperature of 323 K as evidenced by the characterisation performed (Figs. 1, 2 and 4), and no notable changes in conversion/selectivity as a function of time on stream were detected although the time required for stabilising the catalyst with time on stream was longer than for the unmodified sample (Fig. 10). No leached sulphur was detected for a Pd/C catalyst when a similar modifier was used in liquid-phase hydrogenation [15]. Reactions conducted at 323 K but at 10 Bar pressure over 5 h time on stream gave no indication which might suggest loss of ligands [35]. However, when the samples previously modified with diphenyl sulphide were treated at higher temperatures, TG analysis (Fig. 1) and TPR (Fig. 2) indicate decomposition or reduc-

tion of the complex. FTIR (Fig. 4) and TG analyses (Fig. 3) suggest that reduction at 393 K was sufficient to remove most of the complex; however, the absence of a recovery of CO chemisorption capacity (Table 1) and detection of S by XPS would suggest that a residue was retained by the Pd surface. The latter pieces of evidence would suggest that the complex had been decomposed to yield benzene, with loss of the phenyl ligands and retention of sulphur by the Pd [18]. Note that changes in the relative population of on-top and bridge bound CO (Figs. 6A and 6B and 7A and 7B) for modified surfaces after reduction at 393 K suggest different site occupation by the retained S species compared with the original diphenyl sulphide modifier. This may be viewed as analogous to predictions of H$_2$S adsorption on Pd surfaces where the initially adsorbed molecules shows preference for on-top sites but loss of H to produce HS adsorbed species then preferentially binds to bridging sites [21]. This retained sulphur or HS species was also capable of almost complete suppression of ethylene hydrogenation in noncompetitive hydrogenation reaction (Fig. 9) which led to a selective hydrogenation catalyst in acetylene/ethylene mixed feedstream (Table 2). Loss of the phenyl ligands which accompanied the 393 K reduction led to a slightly more active catalyst, increasing the acetylene conversion from 99.4% to 99.7%. However, this occurred at the expense of a poorer selectivity with greater loss of ethylene. An apparent anomaly here was the ability to almost fully suppress ethylene hydrogenation when fed as a single reagent (Fig. 9) but permit notable levels of ethylene conversion (23.5%) when presented in a mixed feed along with acetylene (Table 2). A hypothesis which was explored was the facilitated removal of surface sulphur when acetylene was present but not ethylene alone. However, mass spectrometer analysis failed to detect any sulphur containing molecules that might have been liberated from the surface.

The sulphur appears to interact strongly with the surface Pd atoms. XPS analysis suggests that the initially reduced surface became oxidised on exposure to diphenyl sulphide. In addition to the feature at 334.9 eV indicative of Pd^0, the other two contributions at 337.0 and 339.3 eV compare with binding energies between 336.5 and 339.5 eV previously assigned to Pd^{2+} sulphide compounds [22]. A binding energy for Pd 3d$_{5/2}$ of 337.9 eV has been attributed to the presence of a covalent Pd—S bond with electron transfer from the Pd [32]. It has been previously noted that at 300 K, a chemisorbed layer of S on Pd(1 1 1) forms a bulk sulphide phase [33]. The presence of exposed Pd cations would be consistent [19] with the appearance of the FTIR feature at *ca.* 2119 cm^{-1} for samples exposed to CO after reduction at 393 K (Figs. 6B and 7B). These would be expected to be less active towards unsaturated hydrocarbon hydrogenation [11]. Analysis of the infrared spectra of adsorbed CO indicates [19] that the available Pd surface still contained zero-valent Pd atoms after exposure to Ph$_2$S as evidenced by the bands at *ca.* 2080, 1930 and 1871 cm^{-1} (Figs. 6 and 7) which equate to equivalent features in the spectra of the reduced, modifier-free Pd/TiO$_2$ samples (Fig. 5). Access to such sites by CO under conditions of the FTIR experiments, but suppression under conditions used for CO pulsing experiments (Table 1) can be rationalised on the basis of weakened adsorption of CO due to the presence of adsorbed S (or HS) or Ph$_2$S which limits uptake under the non-equilibrated conditions of pulsing (weakly adsorbed molecules are removed between pulses) [19]. On Pt surfaces, surface sulphur has been shown to decrease the initial binding energy of CO [34]. This is consistent with the need to employ higher equilibrium pressures of CO to attain maximum coverage in the presence of the modifiers (Figs. 6 and 7) compared with that in their absence (Fig. 5). It might be argued that omnipresence of CO in the gas phase in the FTIR experiments led to a gradual displacement of phenyl sulphide or sulphur with the creation of additional sites for CO adsorption. However, hydrogenation experiments conducted at 10 bar in

the presence of 100 ppm CO indicate that the deposited sulphur was not displaced during extended times on stream and that the beneficial effects of the modifier were not lost [35].

The impact of the adsorbed diphenyl sulphide or its hydrogenation/decomposition product, adsorbed sulphur, after higher temperature treatment resulted in a weakening of the Pd—CO bond as deduced from the differences between CO pulse and CO-FTIR experiments and is consistent with observations based on single crystal studies [34]. One might also interpret enhanced selectivity in acetylene hydrogenation to reduced adsorption strengths of ethylene (and acetylene). DFT calculations suggest that Pd modification by alloying and by carbon deposition (surface and subsurface) improves selectivity by weakening of the chemisorption energy [36]. Attempts to measure this effect through ethylene TPD proved inconclusive due to the broad nature of the desorption signals. A counter argument against a model whereby enhanced selectivity was attained only on the basis of weakening adsorption strengths of ethylene and acetylene is that such a model leads to enhanced selectivity (weaker ethylene adsorption and less reacted to ethane) but at the expense of conversion (weaker acetylene adsorption so lower TOF). Such a scenario is at odds with the data presented in this study. While reduced adsorption enthalpies may exist in the presence of diphenyl sulphide and retained sulphur, the key to enhanced selectivity is the creation of adsorption sites which are able to adsorb acetylene but hinder adsorption of ethylene. The analogue of such sites would be the creation of "A" sites by the deposition of a carbonaceous overlayer which selectively hydrogenate acetylene as described by Borodziski and Bond [3]. However in this case, the creation of such sites is produced by the packing restraints caused by the physical dimensions of the ligands which limit the density of the surface poison. The template created on the surface, which may provide two adjacent Pd atom sites as in the case of the "A" site model [3] is retained even after the ligands are destroyed and as the S atoms becomes embedded in the surface Pd layer. Note that the use of H_2S to create such ensemble sites is challenging given the high sticking coefficient of this molecule which leads to high-surface densities of adsorbed S atoms at 300 K which form $(\sqrt{3} \times \sqrt{3})R30$ overlayers [37,38] and block and occupy the threefold hollow sites [21]. The latter are present here, albeit in diminished quantities, after exposure to diphenyl sulphide and accessible to CO (Figs. 6 and 7).

5. Conclusions

Exposure of Pd/TiO_2 catalysts to phenyl sulphide leads to the suppression of ethylene hydrogenation capability and consequently improvement in the selectivity of acetylene hydrogenation in the presence of excess ethylene. Evidence was found to suggest that partial Pd coverage of the surface leaves ensembles of available active atoms which can accommodate acetylene but not ethylene. Even after thermal treatments which led to decomposition of the adsorbed phenyl sulphide and liberation of benzene, the retained sulphur was still capable of providing enhanced selectivity in mixed acetylene/ethylene feed streams due to suppressed ethylene hydrogenation activity.

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