Catalysis Science & Technology

Triphenylphosphine: a ligand for heterogeneous catalysis too?

Selectivity enhancement in acetylene hydrogenation over modified Pd/TiO_2 catalyts.

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Abstract

Pd/TiO_2 catalysts were modified by exposure to triphenylphosphine to assess the impact of the presence of the ligand on the selective removal of acetylene from ethylene rich feeds. The ligand modified metal created a catalyst which showed significantly improved selectivity as a result of a decrease in the extent of over-hydrogenation of ethylene to ethane. The physical presence of the ligand modifier is thought to create sites which permit adsorption of acetylene but hinder access of ethylene to metal sites. In addition, the rate of acetylene hydrogenation appeared to be enhanced in the presence of the modifier consistent with a promotional effect. A potential contribution to enhanced selectivity due to suppression of sub-surface hydrogen formation/diffusion cannot be discounted.

Keywords

Acetylene, ethylene, selective hydrogenation, triphenylphosphine

Introduction

The removal of trace acetylene from C2 streams produced from naphtha crackers is a key step in producing high purity ethylene. If not removed, acetylene will act as a poison for downstream polymerisation catalysts. Industrially, the preferred method of removal is selective catalytic hydrogenation using a Pd based catalyst.[1,2] However, avoiding over-hydrogenation and loss of ethylene is a challenge with recent studies indicating that the formation of Pd carbides[3,4,5] and hydrides[6,7] play an important role in controlling selectivity with sub-surface hydrogen often associated with over-hydrogenation.[5,6,8,9] Industrially, selectivity is enhanced by alloying with Ag or

Au,[1,2,10,11] although this still requires CO to be co-fed to act as a transient poison which competes with ethylene but not acetylene for adsorption sites.[12,13] Whilst this works in practice, it is not an ideal methodology as the quantity of CO added needs to be regulated in real-time to avoid acetylene slip (i.e. less than 100% acetylene conversion). In addition, to acting as a competitive adsorbate, some studies indicate that CO may enhance the formation of green oil[3,14] (acetylene oligomers) which can block active sites and eventually result in catalyst deactivation, although other studies suggest green oil formation to be supressed.[15] Enhanced selectivity can also be achieved by alloying with non-pgm metals such as Ga,[16,17] although there are also numerous reports of 'Pd-free' catalysts which offer moderate to high selectivity to alkenes. Examples include monometallic Cu,[18] Ag,[19] Au,[20] bimetallic Cu-Al hydrotalcite,[21] tri-metallic Cu-Ni-Fe[22] and metal free CeO_2.[23,24] Whilst Pd-free catalysts can offer high alkene selectivity it is generally necessary to operate at higher temperatures than currently used in industrial reactors, perhaps limiting use. Finally, recent studies indicate that the combination of Pd and Cu at the appropriate atomic ratio can result in a system which is selective to ethylene but can operate at reduced temperature.[25,26] In this case, Pd acts as a site for hydrogen dissociation with Cu appearing as the active site for hydrogenation.

An alternative approach involves the adsorption of a selectivity modifier onto a Pd surface to manipulate selectivity in hydrogenation reactions. The use of a nitrogen containing modifier has been reported to enhance alkene selectivity in liquid phase alkyne hydrogenation[27,28] and the catalyst formulation has been commercialised by BASF.[29] Even before this more recent advance, the so called 'Lindlar' catalyst (Pb poisoned $Pd/CaCO_3$ with quinolone as selectivity modifier) has been used as the standard catalyst for selective liquid phase alkyne hydrogenation.[30,31,32] Although, a recent theoretical report suggests that whilst Pb and quinolone are both necessary, Pb has a more significant effect than the organic modifier.[33] Similar effects have also been reported for liquid phase hydrogenation of 4-octyne using octylamine as a ligand modifier for Pt and CoPt catalysts.[34] Mori *et al*.[35,36,37] have shown that diphenylsulfide can be used to modify chemoselectivity for a Pd/C catalyst and these results and others involving sulfur as a selectivity modifier have been recently reviewed.[38] It has also been shown that the same modifier can greatly reduce the ability of Pd to hydrogenate ethylene.[39,40,41] Results were interpreted in terms of a surface template effect where the arrangement of adsorbed phenyl ligands creates Pd ensembles which favour acetylene adsorption in the same manner as Ag or Au. It was also shown that the phenyl ligands of diphenylsulfide could be decomposed at moderate temperature which increased the ability of the catalyst to adsorb and hydrogenate ethylene.[40] Such an observation is in agreement with the ligands acting as a surface template. More recently Altmann *et al*.[42] have demonstrated that dodecylamine adsorbed on Pt/SiO_2 and $PtSn/SiO_2$ also enhanced ethylene selectivity and their results were attributed to the same surface template effect.

To further explore how adsorbed ligands affect selectivity, different modifier structures have been investigated and preliminary results suggest a similar effect may be obtained with triphenylphosphine.[41] However, these results were obtained in presence of CO as co-modifier and therefore experiments which differentiate between the effects of CO and triphenylphosphine under high pressure are necessary.[41] Despite the fact that triphenylphosphine is one of the most commonly employed ligands in homogeneous catalysis,[43] reports of its use in heterogeneous systems is rare[44] beyond cases where it forms part of an anchored complex.[45,46,47] In this paper we report characterisation for triphenylphosphine modified Pd/TiO_2 as well as evaluating catalytic performance at atmospheric pressure (as commonly reported in academic literature). In addition, catalyst performance and stability under high pressure conditions (as applied in industry) is investigated for longer periods on stream than previously reported, and in the absence of CO.

Experimental

Pd/TiO_2 (1 wt%) was prepared from $Pd(NO_3)_2$ and P25 TiO_2 by wetness impregnation as described previously[40] and subjected to calcination in a 100 ml min^{-1} flow at 673 K for 3 h. The base catalyst was modified with triphenylphosphine (PPh_3) by reducing 1 g of Pd/TiO_2 at 423 K for 1 h in a 1:1 H_2:N_2 mix (100 ml min^{-1}) and adding the reduced catalyst to a solution of PPh_3 dissolved in hexane (100 ml). The resulting mixture was stirred on a rotary evaporator for 30 min before applying vacuum to yield a fine, dry powder. Analysis of the evaporated solvent by GC-MS confirmed complete uptake of the modifier. Catalysts were prepared with a 0.02, 2.5, 5 and 10:1 molar ratio of PPh_3 relative to total Pd content (note: 0.02 eq. PPh_3 corresponds to a 1:4 ratio relative to surface atoms). The PPh_3 catalysts are denoted as 'PPh_3 X Pd/TiO_2' where X denotes the ratio of PPh_3 to bulk Pd.

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

Chemisorption experiments were carried out using a TPDRO 1100 instrument. All samples were reduced at 393 K in 5% H_2/N_2 for 1 h and cooled to room temperature in N_2. Pulse experiments were carried out using a 285 µL sample loop filled with diluted CO (8 or 19.7% in He) being injected into a flow of He passing over the sample with the latter held at 293 K. Metal dispersion and particle size were calculated from the CO uptake assuming a spherical particle shape and a Pd:CO stoichiometry of 2:1.[48] This latter assumption was supported by FTIR spectra of adsorbed CO (see later) which confirm that multiply bound CO made a significant contribution to the compliment of total CO adsorbed. Temperature programmed reduction (TPR) experiments were performed on the same instrument using a heating rate of 5 K min^{-1}. Results are presented per gram of sample and hydrogen consumption quantified based on a response factor determined by using a CuO standard.

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 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 x 10^{-3} mbar. A background spectrum (15 scans, resolution 4 cm^{-1}) was recorded prior to introduction of CO. Subsequent spectra were recorded following introduction of increasing pressures of CO in the range 0.1 to 200 Torr.

Three types of catalytic tests were performed. The first two types of tests were conducted at 1 bar using 50 mg catalyst supported in a water cooled reactor vessel to maintain temperature at 323 K. Prior to reaction, the catalysts were reduced for 1 h at 393 K under a 100 ml min^{-1} 1:1 H_2:N_2 flow in a pyrex reactor fitted with a frit. After reduction, the catalyst was cooled under the same gas flow and transferred to the catalytic reactor immediately. The first type of test reaction was performed with a mixture of 5% acetylene or ethylene in N_2, a 3:1 ratio of H_2:C_2 and a total flow of 150 ml min^{-1}. This type of test allowed for an evaluation of catalyst activity with/without PPh_3 by operating at moderate conversion of the C_2 species.

The second type of test reaction was performed with a mixture of 1% acetylene, 9% ethylene/balance N_2, a 25:1 H_2:acetylene ratio and a total flow of 95 ml min^{-1}. This type of test meant that high acetylene conversion could be achieved and the selectivity of the catalyst towards acetylene removal and not ethylene reduction could be evaluated. Analysis was performed using a Perkin-Elmer 8410 GC fitted with a flame ionisation detector (FID) and 2 m 5 A molecular sieve packed column. Sampling was carried out using an electrically actuated Valco 10 position valve fitted with 250 µL stainless steel loops. This allowed for product analysis for up to 4 hour on stream (TOS). The third type of test conducted was performed at 10 bar pressure in a Microactivity reference reactor (PID Eng & Tech, supplied by Micromeritics) using 100 mg catalyst pre-mixed with 400 mg SiC (200-450 mesh) supported in a 9 mm stainless steel reactor. Reactions were also performed with a mixture of 1% acetylene, 9% ethylene/balance N_2 and a 25:1 H_2:acetylene ratio but with a gas hourly space velocity of 6000 h^{-1} over a 16 h period. The effluent gas exiting the reactor was split and analysis was performed with a combination of a Perkin-Elmer Clarus 580 GC fitted with an FID and a 30 m x 0.53 mm elite alumina capillary column and a MKS instruments Cirrus quadruple mass spectrometer (QMS).

The competitive acetylene/ethylene reactions were compared on the basis of acetylene concentration in parts per million (ppm) and loss/gain of ethylene based on the formulae shown below:

Equation 1:

$$Acetylene \quad conc./\,ppm = \frac{[C_2H_2]_{final}}{[C_2H_4]_{final}} \times 1000000$$

Equation 2:

$$Ethylene \quad gain\,/\,\% = \frac{\Delta[C_2H_4]}{[C_2H_4]_{initial}} \times 100$$

Using this system, an ideal catalyst would give a result of < 5 ppm acetylene (i.e., >99.95% conversion) and an ethylene gain of +10% if all acetylene was converted to ethylene and none of the ethylene originally present in the gas stream was hydrogenated to ethane. The worst case scenario would be an ethylene gain of -100% meaning that all of the ethylene present at the start of the reaction was hydrogenated to ethane.

Results

The unmodified Pd/TiO_2 catalyst was characterised by CO pulse chemisorption to determine the CO uptake, metal surface area and particle diameter (Table 1). Sample previously exposed to triphenylphosphine showed a decrease in the available metal surface as judged by CO uptake. This confirms that at least part of the modifier was adsorbed directly onto the metal surface with any remainder likely on the TiO_2 support. A correlation between the quantity of PPh_3 adsorbed and CO uptake can be observed with only a small decrease in metal surface area when 0.02 equivalents of modifier was adsorbed, whereas a larger decrease is apparent for higher ratios. Based on the available metal surface area alone for high modifier:Pd ratios, a notable decrease in activity should be expected if no promotional effect occurs due to the adsorbed ligand.

The weight loss and derivative weight loss profiles for Pd/TiO_2 and PPh_3 modified catalysts are shown in Figure 1. The unmodified catalyst shows no weight loss beyond that expected for adsorbed water. Analysis of a sample treated with hexane used for PPh_3 treatments showed almost no change in weight loss following drying and therefore all additional weight loss following PPh_3 treatments can be attributed to the removal of the modifier. There is a clear peak centred at 600 K in the dTGA profile for PPh_3 2.5 Pd/TiO_2 which suggests the modifier should be thermally stable at the temperatures used for catalytic reactions (323 K). Use of mass spectrometry showed that no mass fragments associated with the intact (m/z = 277 or 278) or partially decomposed ligand (m/z = 77) were apparent. Instead, the only mass fragment produced was attributed to CO_2 (m/z = 44) indicative of complete oxidation. These findings would suggest that the ligand cannot be decomposed to leave phosphorous intact on the surface. This is in contrast to previous work with diphenylsulfide where it was shown that reduction at 393 K led to the loss of the phenyl ligands while sulfur was retained by the surface.[39,40] The effect of a reduction step at 393 K on the PPh_3 modified catalysts is shown in Figure 2 and Figure 3. The TGA profile (Figure 2) shows that less weight loss is observed after reduction whereas the DRIFT spectra (Figure 3) shows no significant change to the bands due to the aromatic ring vibrations associated with adsorbed PPh_3. Most notably, the band at *ca.* 1440 cm^{-1} which is associated with the P-Ph bond[49] does not change, implying PPh_3 remains intact on the surface. It is therefore suggested that reduction at 393 K results in the loss of weakly adsorbed PPh_3, most likely from the support. This interpretation is supported by catalytic results (discussed later) which show that the modified catalysts display vastly different behaviour from the unmodified catalysts, even following a reduction step.

The TPR profile for Pd/TiO_2 (Figure 4) shows a large negative feature centred at 345 K which is assigned to the decomposition of palladium hydride formed by exposure to hydrogen at room temperature.[7] When the same TPR experiment was performed with PPh_3 2.5 Pd/TiO_2 sample, the same palladium hydride peak was apparent, although with reduced intensity which may be significant given that sub-surface hydrogen formation is associated with alkyne over-hydrogenation.[5,6,8,9] Calculation of the H_2:Pd molar ratio based on quantification of the hydride peak area gives values of 0.16 and 0.15 for Pd/TiO_2 and PPh_3 2.5 Pd/TiO_2, respectively. Sample modified with triphenylphosphine also displays TPR features at 411 and 442 K which are likely associated with reduction of the organic modifier but at higher temperatures than used for catalytic measurements (see later).

Pulse chemisorption (Table 1) confirmed that the addition of the modifier reduced the quantity of CO adsorbed, however this techniques gives no information as to the nature of the sites lost. In order to understand how PPh_3 interacts with the Pd surface, FTIR spectra were recorded of the samples after reduction at 393 K (i.e., after loss of any weakly bound modifier) and in the presence of increasing overpressures of CO. Firstly, the spectrum of the unmodified catalyst at full coverage (40 torr) shows bands at 2087 and 1923 cm^{-1} (Figure 5). The two modes are assigned to linearly adsorbed CO (2087 cm^{-1}) and bridging CO on edge sites (1923 cm^{-1}) as opposed to bridging on (1 0 0) type facets.[50] When the same experiment was performed with PPh_3 2.5 Pd/TiO_2 (Figure 6) higher overpressures of CO were necessary to achieve full coverage (150 torr), indicating that the strength of adsorption is weaker in the presence of the modifier. Increasing surface coverage by increasing CO pressure resulted in a shift of the band due to the bridge bound mode from 1899 to 1934 cm^{-1} and a small shift for the band due to the linear mode from *ca.* 2070 to 2082 cm^{-1}. The appearance of a band at *ca.* 2100 cm^{-1} at low CO overpressure is indicative of the presence of exposed Pd cations[48] but this band was hidden as the bands due to gas phase CO (2170 and 2120 cm^{-1}) become more prominent at higher pressures. A comparison of samples before and after addition of PPh_3 shows little difference with regards to linearly adsorbed CO, however, there is a notable increase in the intensity (band height) of the bridge bound mode in the presence of the modifier. This is reflected in the apparent increased bridging : linear CO ratio calculated based on the integrated band envelopes (Table 1). In addition, the modified catalyst demonstrates a much narrower band for the bridge bound species, indicative of a decrease in the availability of 3 fold hollow sites.

In order to access the impact of modification with PPh_3, reactions were performed under non-competitive conditions with either acetylene or ethylene as reagent alone (Figure 7). Column 1 shows that both reagents have similar rates of hydrogenation over the unmodified catalyst. Addition of 3 ppm CO had little impact on the hydrogenation rate of acetylene but diminished the rate of ethylene removal (Figure 7 - column 2). Modification of the catalyst with 2.5 equivalents of PPh_3 resulted in a clear decrease in the rate of hydrogenation of ethylene (Figure 7 - column 3). Unexpectedly, the PPh_3 2.5 Pd/TiO_2 catalyst shows a slightly higher rate of hydrogenation of acetylene following modification with triphenylphosphine. In order for a higher rate of conversion to be achieved, a promotional effect must occur given the significant loss in the overall number of available surface Pd sites (Table 1).

The unmodified and modified catalysts were tested under competitive conditions (Table 2), more akin to those found in industry (i.e., presence of both acetylene and ethylene in the feed gas). Under conditions of excess hydrogen, high acetylene conversion was observed for Pd/TiO_2. In addition, reaction over the unmodified catalyst resulted in the consumption of most of the ethylene present in the feed. Following PPh_3 modification, all catalysts (irrespective of PPh_3: Pd ratio) exhibited a higher degree of acetylene conversion consistent with the non-competitive reactions and again indicative of a promotional effect in the presence of the ligand since the modifier blocks a fraction of the Pd surface (CO uptake - Table 1). Whilst all modified catalysts still show that ethylene was consumed during the reaction, the ethylene loss was reduced with respect to the unmodified. The largest improvement was for PPh_3 2.5 Pd/TiO_2 which produced an ethylene loss of only 5%

compared with 81% loss for the equivalent unmodified catalyst. This catalyst showed stable conversion and selectivity for the first 180 min time on stream following a brief stabilisation period (Figure 8).

As well as improved selectivity, the PPh_3 modified catalysts showed a marked decrease in the formation of gas-phase by-products under competitive conditions (Table 3). Comparing Pd/TiO_2 with/without modifier shows that the addition of PPh_3 results in an approximately 10 fold decrease in the quantity of oligomers formed. A comparison of the quantity of oligomers produced under non-competitive conditions highlights that formation is related to acetylene coupling and is enhanced by reducing the H_2:C_2 ratio. In contrast to results obtained under competitive conditions, more oligomers are formed over PPh_3 2.5 Pd/TiO_2 than Pd/TiO_2 when catalyst is exposed to acetylene in the absence of ethylene. However, the modified catalyst shows no formation of methane, suggesting hydrogenolysis is suppressed. When taking this into account, both Pd/TiO_2 and PPh_3 2.5 Pd/TiO_2 produce a similar quantity of by-products.

During industrial application, CO is used as a transient poison to control the extent of over-hydrogenation. Consequently experiments were performed with unmodified Pd/TiO_2 in the presence of CO to make a comparison. Under non-competitive conditions the addition of 3 ppm CO had a marginal effect on the rate of acetylene conversion but a more significant impact on the rate of ethylene consumption (Figure 7 – column 2) in agreement with expectations based on literature.[12,13] The magnitude of the effect observed with CO was less than that observed with triphenylphosphine, suggesting the later might be considered a more effective modifier under the conditions employed. It should be noted that under the hydrogen rich conditions employed in this study, the quantity of CO industrially used may be almost 100 fold higher.[51] With respect to by-product formation, the presence of CO in the feed increased oligomer formation for competitive and non-competitive reactions. On the other hand, modification with PPh_3 resulted in a decrease in by-product formation for mixed acetylene/ethylene reactions, providing further support for the statement that it can be considered as a more effective modifier than CO under these conditions.

As the PPh_3 2.5 Pd/TiO_2 catalyst performed well in reactions of mixed feed at 1 bar, tests were performed under high pressure (10 bar) but still in a large excess of hydrogen. Under these industrially relevant conditions, high selectivity is expected to be difficult to achieve and is therefore an effective test of the catalysts under extreme conditions. A reaction performed using modified catalyst in the absence of CO (Figure 9-A) resulted in high acetylene conversion but an ethylene loss of almost 100%. This test highlights that whilst triphenylphosphine may be an effective modifier at low pressure, its effects are not equivalent under high pressure conditions. When the reaction was performed under similar conditions but with 46 ppm CO added (Figure 10-A) a very different reaction profile was observed. The catalyst initially performed badly with respect to avoiding over hydrogenation of ethylene but this improved with time on stream with a final ethylene loss of 45%. The stability of the modifier was monitored during the full reaction cycle (reduction, bypass, reaction) by coupling the reactor outlet to a quadruple mass spectrometer. All masses associated with the feed gas, hydrogenation products, by-products and possible fragmentation of PPh_3 were monitored but only those masses which showed any change during a reaction cycle are shown in Figure 8-B and Figure 9-B. During the reduction step (1:1 H_2;N_2) there was a small increase in m/z = 34 signal which is attributed to release of PH_3. It has already been shown that a small weight loss occurs during a reduction step (Figure 2) which was assigned to the loss of weakly bound PPh_3 but with no detectable change to the catalyst surface based on DRIFT spectra (Figure 3). It is this same weakly bound PPh_3 which is thought to give rise to the m/z = 34 signal. During the reaction period there was a rise in the m/z = 31 signal which could be attributed to the lost of P. However, given that there is no corresponding rise in signals attributed to PH, PH_2, PH_3 or larger mass fragments associated with triphenylphosphine, it is thought that the signal is related to the fragmentation of one of the reaction by-products. Based on the MS data, the change in selectivity as a function of time on stream under high pressure in the presence of CO is not thought to be related to the loss of the modifier.

Discussion

Reaction testing at low pressure

Under non-competitive conditions the unmodified Pd/TiO_2 catalyst shows fairly similar rates for the hydrogenation of acetylene (9.86×10^{-5} mol g^{-1} s^{-1}) and ethylene (9.17×10^{-5} mol g^{-1} s^{-1}). It is therefore not surprising that under competitive conditions with excess hydrogen (25:1 H_2:acetylene) that the catalyst is inherently unselective. Indeed, at >98% acetylene conversion 81% of ethylene present in the gas feed is lost due to over-hydrogenation to ethane. This catalyst does however act as an effective standard sample to judge the effect of modification with triphenylphosphine. Characterisation of PPh_3 2.5 Pd/TiO_2 following modifier adsorption shows an increase in weight loss from TGA (Figure 1) and the appearance of bands in DRIFT spectra associated with the aromatic rings of PPh_3 (Figure 3). The decrease in metal surface area (Table 1) confirms that at least a fraction of the modifier resides on the metal surface although it is believed that excess modifier occurs in a more weakly adsorbed form on the support. Evidence of this can be seen from characterisation following a reduction step which shows a decrease in TGA weight loss consistent with the loss of a weakly bound species (Figure 2). However, this is not accompanied by change to the DRIFTS spectra suggesting that some of the modifier resides intact on the metal surface after heating to 393 K (Figure 3). This is in contrast to diphenylsulfide as a modifier which partially decomposed at 393 K resulting in the loss of the phenyl groups.[39,40] Following addition of the modifier there was a notable increase in the bridged : linear CO species ratio. This was accompanied by a narrowing of the band between 2000-1800 cm^{-1} at lower wavenumber suggesting a loss of 3 fold hollow sites and an ordering of the CO on the surface. Both of these changes suggest that the modifier blocks sites associated with CO adsorption on the more open facets of Pd which makes sense given the bulky nature of PPh_3. Note that the overall intensity of the FTIR bands of CO (Figure 5) are not diminished to the extent expected as judged by the pulsed CO uptakes (Table 1). This may be rationalised on the basis that the static FTIR measurements permit higher coverage to be achieved than in the dynamic pulse method where only the stronger adsorption sites retain CO and also that the absorption coefficients of the CO on the modified surface are altered due to the weakening of the CO bonding in the presence of the PPh_3 and due to the ordering of the CO induced by the PPh_3 over the surface.

Under non-competitive conditions, Pd/TiO_2 showed a rate of acetylene hydrogenation of $9.86x10^{-5}$ mol g^{-1} s^{-1}. Treatment with 2.5 equivalents of PPh_3 relative to bulk Pd resulted in a small increase in the rate of hydrogenation of acetylene ($1.05x10^{-4}$ mol g^{-1} s^{-1}), although within experimental error this is equivalent to the rate observed in the absence of the modifier. In contrast the modified catalyst showed greater than a 4 fold decrease in the rate of hydrogenation of ethylene ($1.72x10^{-5}$ mol g^{-1} s^{-1} with modifier *vs* $9.17x10^{-5}$ without modifier). On the basis of these results triphenylphosphine has little impact upon acetylene hydrogenation but a significant effect on ethylene hydrogenation. The observed effect is also considerably more noticeable than the effect of CO which is commonly added in industrial reactors to compete with ethylene for adsorption sites to limit over-hydrogenation (Figure 7). Whilst evaluation of individual global reaction rates is useful for interpretation, it is also helpful to consider turnover frequencies (TOF) calculated based on surface Pd atoms (as determined from CO uptake – Table 1). On this basis, Pd/TiO_2 and PPh_3 2.5 Pd/TiO_2 exhibit acetylene TOF's of 3.68 and 21.00 s^{-1} suggesting that not all of the original surface of clean Pd is active, and ethylene TOF's of 3.42 and 3.44 s^{-1}, respectively, suggesting a surface insensitive reaction consistent with commonly held belief.[52] The trend depicted by the TOF's is clear, although the magnitude of the effect may not be totally accurate. For example, CO-FTIR adsorption experiments on the unmodified catalyst required a CO overpressure of only 40 torr to achieve surface saturation whereas the modified catalysts needed pressures or 150 torr. This information suggests that the strength of adsorption of CO on Pd is decreased in the presence of PPh_3 which will have an effect on the quantity of CO adsorbed by pulse chemisorption, given that weakly adsorbed CO is desorbed between pulses.[48] Regardless, these values imply that the modifier may act as a promoter for acetylene hydrogenation (or selectively poisons inactive sites) whilst removing sites which would otherwise be active for ethylene hydrogenation (although as discussed later, the ability of ethylene to adsorb is distorted by the modifier).

For all modified catalysts, the improved performance extended to competitive conditions, although the size of the effect varied with the quantity of modifier adsorbed (Table 2). The use of 0.02 equivalents of PPh_3 to bulk Pd (1:4 PPh_3: surface Pd atoms) showed little impact on acetylene hydrogenation and a small decrease in over-hydrogenation of ethylene (70% loss of ethylene). Increasing the quantity of modifier to 2.5 equivalents relative to bulk Pd increased acetylene conversion and greatly reduced over-hydrogenation of ethylene (5% loss of ethylene). The enhanced acetylene conversion observed in competitive reactions again suggests that the modifier hinders access to sites which are active for ethylene but does not minimise the availability of sites active for acetylene. No change in catalyst performance was observed during 3 h on stream at 1 bar pressure suggesting that neither changes to modifier concentration/arrangement or significant deposition of oligomers occurred under these conditions (Figure 8). The absence of evidence for significant surface bound oligomers was consistent with the gas phase analysis which showed that the presence of triphenylphosphine reduced the quantity of acetylene based oligomers produced by over an order of magnitude (Table 3). This represents a significant benefit when compared with CO which enhanced oligomer formation.[3,14,15]

Reaction testing at high pressure

Industrially this reaction is performed at high pressure and since it is more challenging to achieve high selectivity at high pressure, such a test is imperative. Preliminary results at 10 bar in the presence of 100 ppm CO have been reported where PPh_3 2.5 Pd/TiO_2 demonstrated moderately high selectivity to ethylene at moderate acetylene conversion (≈70-80%), which decreased as a function of time on stream.[41] Questions remain therefore regarding the stability of the modifier and how it would perform in the absence of CO. As such, two key further high pressure tests are reported here. Firstly, mass spectrometry was used to analyse the effluent gas exiting the catalyst bed for evidence of modifier decomposition and secondly, a test in the absence of CO was conducted to differentiate between the effect of PPh_3 and CO on selectivity (Figure 9 and Figure 10). MS analysis suggested that some of the modifier was lost during a pre-treatment (reduction) step (Figure 9-B and Figure 10-B zone i) which is consistent with TGA characterisation already discussed. During the catalytic cycle there was no evidence of further loss of the modifier which suggests any changes in selectivity previously observed[41] are not related to the loss of the modifier but more likely to be associated with a change in coverage of the metal surface by carbonaceous deposits. In the presence of CO the modified catalyst exhibited a mild ability to avoid over-hydrogenation which increased as a function of time on stream. FTIR results of adsorbed CO suggest that the strength of adsorption on Pd in the presence of the modifier is decreased. Since the modifier is not lost under reaction conditions and improved selectivity is not observed with time on stream in the absence of CO it is tentatively suggested that the surface arrangement of modifier undergoes a change in the presence of CO as a function of time on stream. The change in selectivity is speculatively attributed to a re-arrangement which allows CO to adsorb more strongly limiting ethylene hydrogenation. The poorer selectivity observed is this work is primarily attributed to the levels of conversion attained (≈90% here and 70-80% elsewhere).[41] The modified catalyst demonstrated no ability to prevent over-hydrogenation under high pressure in the absence of CO which contrasts with findings observed under low pressure. This highlights the need to perform catalyst testing under appropriate relevant conditions rather than extrapolate from standard lab conditions.

Triphenylphosphine *vs* other ligand based modifiers

In previous work with diphenylsulfide as a selectivity modifier, enhanced selectivity for acetylene/ethylene hydrogenation was attributed to the geometric arrangement of the ligand on the metal surface which is largely controlled by molecular dimensions.[39,40,41] The orientation of the modifier was thought to break up larger Pd ensembles and create sites which favour acetylene adsorption and hinder ethylene adsorption in a similar manner to how carbonaceous overlayers[13] or Ag/Au[1,10] are thought to modify Pd catalysts. A similar interpretation of results has been reported for Pt and PtSn modified with dodecylamine.[42] Based on characterisation and catalytic results presented here, it is believed that an equivalent effect occurs with triphenylphosphine. FTIR of CO adsorption suggests that the modifier is adsorbed on open Pd facets since there is a loss in the contribution from CO adsorbed in 3 fold hollow sites. As the quantity of PPh_3 is increased, changes in selectivity become more pronounced which is consistent with a simple surface templating effect. The tendency for the modified catalyst to produce less oligomers can also be rationalised on the same basis since two acetylene molecules must adsorb in close proximity to each other for coupling to occur and sites which are too small for ethylene adsorption are also unlikely to facilitate oligomersation. The increase in rate of acetylene hydrogenation despite a loss in the overall number of available sites suggest that not all of the clean Pd surface is active and that in the presence of modifier, changes in adsorption strength of acetylene occur which enhance the rate and which would be consistent with changes to the strength of adsorption of CO. This is due to a change in the electronic nature of the Pd atoms in close proximity to the phosphorous atom with electron density transferred from the metal to the ligand. A comparison of catalysts modified with triphenylphosphine and diphenylsulfide shows that the latter is more effective with a complete suppression of ethylene hydrogenation for single reagent experiments.[39,40] The same trend occurs under competitive reactions conditions with triphenylphosphine resulting in 5% loss of ethylene and diphenylsulfide a 3% gain of ethylene.[39,40] The improved performance with diphenylsulfide is most likely associated with a more effective surface arrangement creating less sites for ethylene adsorption due to the closer packing of the smaller modifier.

Recent work from Ludwig *et al*[8] highlights that edge and corner sites in Pd nanoclusters play a significant role in replenishing subsurface hydrogen which is increasingly acknowledged as a cause of over-hydrogenation.[5,6,8,9] Given that FTIR spectra of adsorbed CO provides evidence for the presence of free edge sites in the presence of modifier, it is possible that a route exists for both the formation of subsurface hydrogen and its subsequent replenishment which would be most apparent when using low modifier : metal ratios. TPR measurements (Figure 4) confirm that both the unmodified and PPh_3 treated catalysts can form a hydride phase, although to a lesser extent for ligand modified sample. As such, it is possible that the higher selectivity observed for higher modifier concentrations may also be related to a decrease in the ease of formation of subsurface hydrogen or its hindered diffusion through to the surface in the presence of a dense ligand over-layer. It should be noted that TPR indicates hydride capacity, whereas it may be the dynamics of H transfer which is more significant. However, given that diphenylsulfide modified samples show less hydride formation than samples exposed to triphenylphosphine and are more selective, there does appear to be a correlation between hydride formation and selectivity. Differentiating between the significance of a ligand template effect and sub-surface hydrogen would require a detailed theoretical study out with the scope of this manuscript.

Conclusions

Modification of Pd/TiO_2 with triphenylphosphine limits over-hydrogenation of ethylene to ethane under low pressure conditions for acetylene/ethylene mixed feeds. The effect is interpreted in terms of a surface template effect created by the manner in which the ligand is adsorbed on Pd. This results in a catalyst surface where acetylene can readily adsorb whereas ethylene adsorption is hindered. In addition, adsorbed triphenylphosphine appears to act as a promoter for acetylene hydrogenation whilst also decreasing the quantity of oligomer species produced by more than an order magnitude. The ligand is stable under both low and high pressure conditions but the addition of CO as a co-modifier is necessary under high pressure reaction conditions to retain enhanced selectivity.

Acknowledgements

We thank SABIC for funding a studentship (F. M. M.) and permission to publish this work and Dr. A. M. Ward (SABIC) and Dr R. P. K. Wells (University of Aberdeen) for useful discussions and contributions. We are also grateful to Prof. C. Hardacre and Ms. L. Mantarosie, Queen's University Belfast, for performing preliminary high pressure testing on these catalysts. We also thank MKS instruments for the loan of the Cirrus QMS instrument.

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Tables and Figs

Table 1 – Characteristics of Pd/TiO_2 and triphenylphosphine modified Pd/TiO_2 catalysts.

Catalyst	**CO uptake / µmol g^{-1}**	**Metal surface area [a]/ m^2 g^{-1}**	**Particle diameter [b]/ nm**	**Bridged/linear CO species ratio[c]**
Pd/TiO_2	13.4	1.26	3.5	1.24
PPh_3 0.02 Pd/TiO_2	11.1	1.04	3.5	-
PPh_3 2.5 Pd/TiO_2	2.5	0.24	3.5	2.27
PPh_3 10 Pd/TiO_2	0.4	0.04	3.5	-

[a] Metal surface area calculated from pulse chemisorption assuming 2:1 Pd:CO stoichiometry

[b] Estimation of particle size assuming spherical particle shape. It is assumed that addition of modifier does not influence particle size

[c] Determined from integrated peak areas in FTIR spectroscopy at 200 torr CO pressure

Table 2 - Acetylene concentration and conversion and ethylene gain(loss) at 120 min on stream using a mixed ethylene/acetylene feed at 323 K and 1 bar pressure.

Catalyst	**Residual acetylene conc. / ppm**	**Acetylene conversion / %**	**Ethylene gain (loss) / %**
Pd/TiO_2	1415	98.6	(-81)
PPh_3 0.02 Pd/TiO_2	1376	98.6	(-70)
PPh_3 2.5 Pd/TiO_2	57	99.9	(-5)

Table 3 – By-product formation at 120 min on stream for hydrogenation reactions of acetylene only, ethylene only and mixed acetylene/ethylene reactions at 323 K and 1 bar pressure.

	Oligomers / FID signal	Methane / FID signal
Acetylene only		
Pd/TiO_2	248173	61404
Pd/TiO_2 + 3 ppm CO	296540	103000
PPh_3 2.5 Pd/TiO_2	315656	-
Ethylene only		
Pd/TiO_2	170	3445
Pd/TiO_2 + 3 ppm CO	799	3392
PPh_3 2.5 Pd/TiO_2	290	3100
Mixed acetylene/ethylene reaction		
Pd/TiO_2	52415	14763
Pd/TiO_2 + 3 ppm CO	174911	-
PPh_3 2.5 Pd/TiO_2	4969	9393
PPh_3 10 Pd/TiO_2	4332	6262

Figures

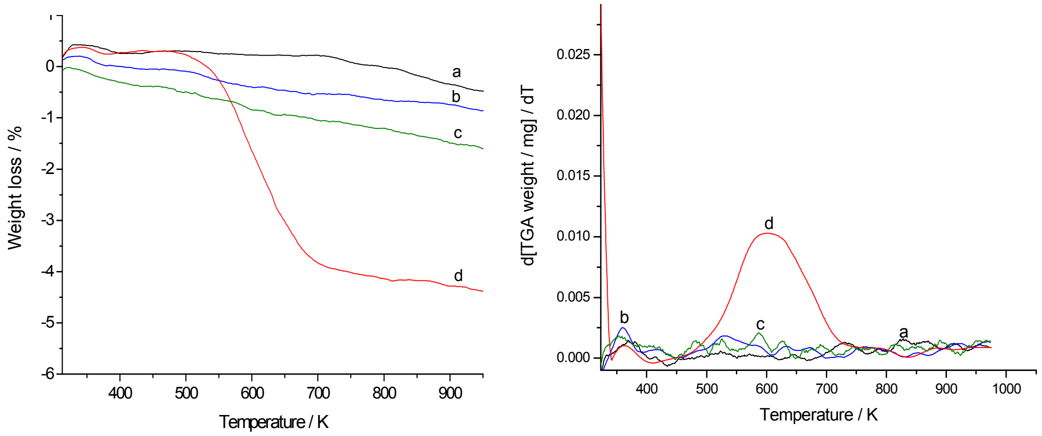


Figure 1 – Weight loss (left) and dTGA profiles (right) for (a) Pd/TiO_2, (b) Pd/TiO_2 contacted with hexane, (c) PPh_3 0.02 Pd/TiO_2 and (d) PPh_3 2.5 Pd/TiO_2.

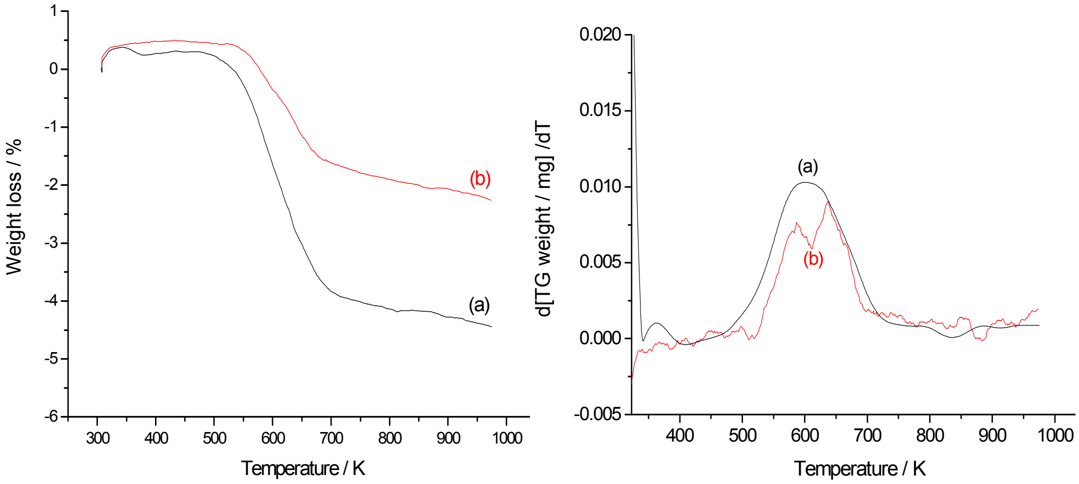


Figure 2 – Weight loss (left) and dTGA profiles (right) for (a) PPh_3 2.5 Pd/TiO_2 and (b) pre-reduced PPh_3 2.5 Pd/TiO_2 (b).

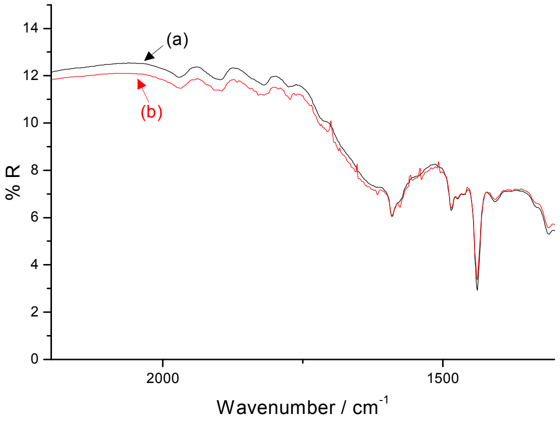


Figure 3 - DRIFTS spectra for (a) PPh_3 2.5 Pd/TiO_2 and (b) pre-reduced (393 K) PPh_3 2.5 Pd/TiO_2.

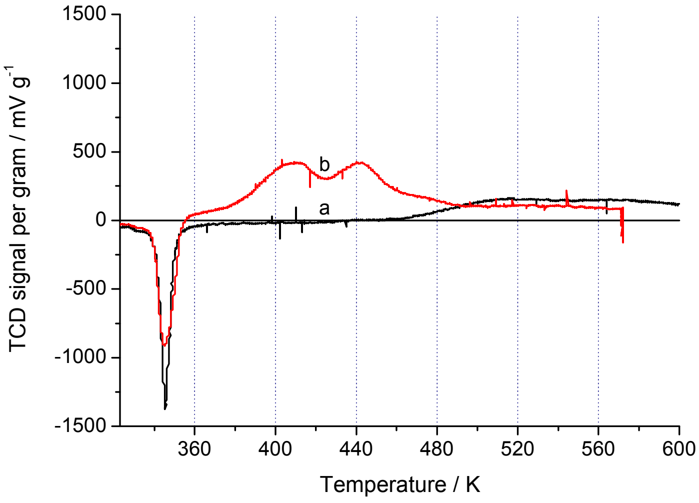


Figure 4 – Temperature programmed reduction profile for (a) Pd/TiO_2 and (b) PPh_3 2.5 Pd/TiO_2.

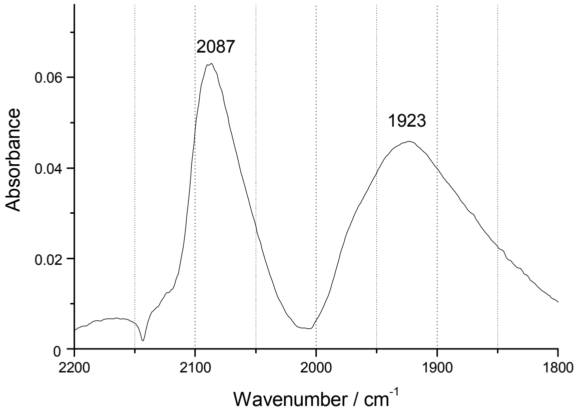


Figure 5 – FTIR spectrum of adsorbed CO on Pd/TiO_2 at 40 Torr.

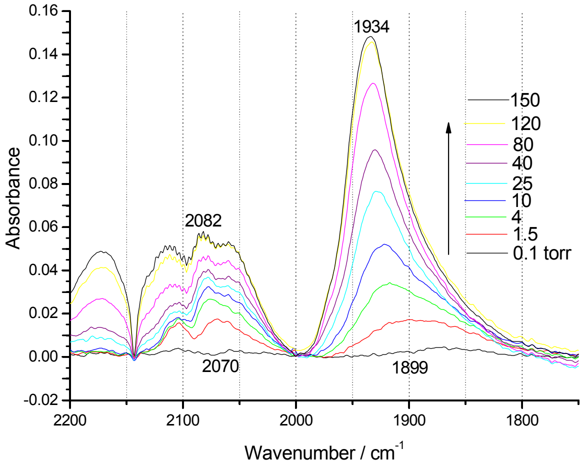


Figure 6 – FTIR spectra of PPh_3 2.5 Pd/TiO_2 reduced at 393 K and exposed to CO at 298 K at increasing pressures up to 150 Torr.

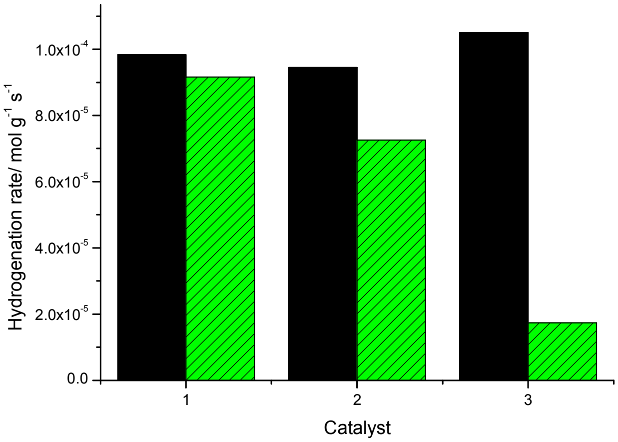


Figure 7 – Hydrogenation rate of acetylene (black) and ethylene (green, shaded) in separate, non-competitive reactions at 323 K , 3:1 H_2:C_2 over (1) Pd/TiO_2, (2) Pd/TiO_2 with 3 ppm CO in feed, (3) PPh_3 2.5 Pd/TiO_2.

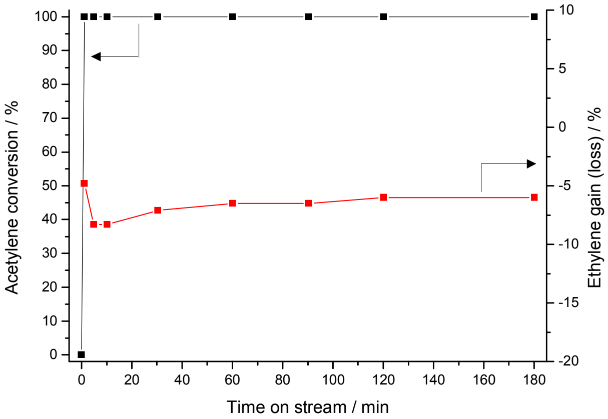


Figure 8 – Acetylene conversion (%) and ethylene gain (loss) over PPh_3 2.5 Pd/TiO_2 as a function of time on stream. Reaction performed at 323 K and 1 bar in the absence of CO.

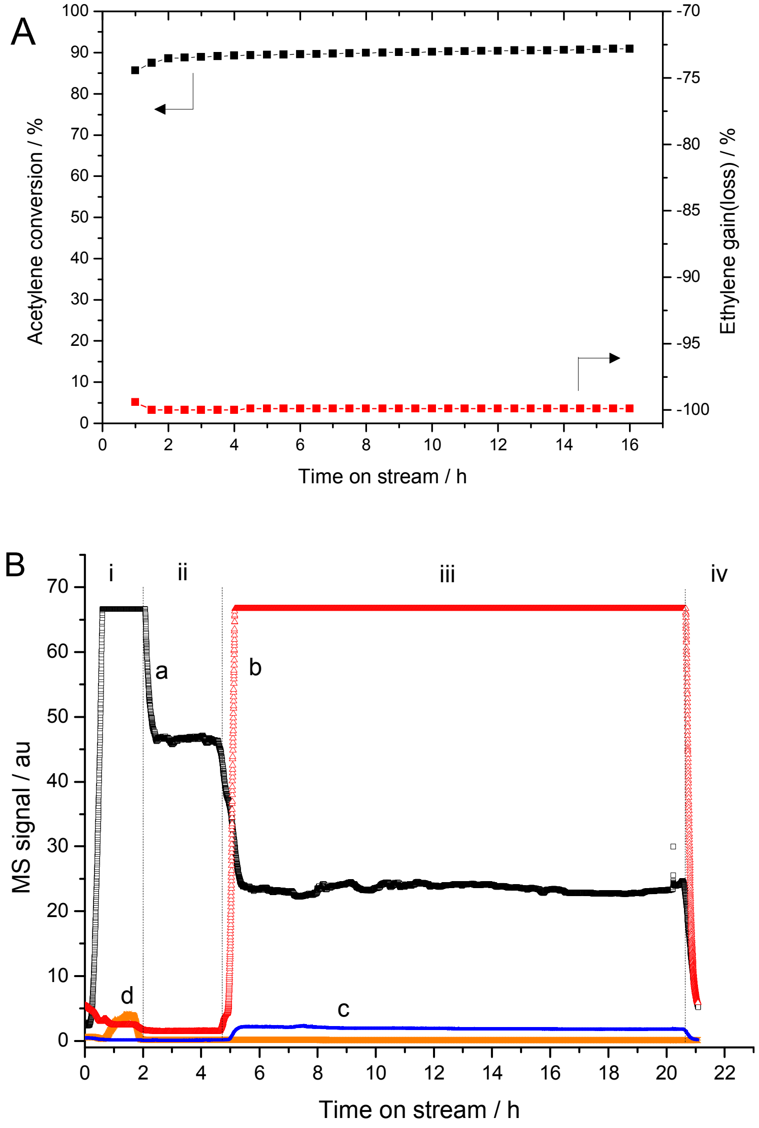


Figure 9 – A: Acetylene conversion (%) and ethylene gain(loss) (%)) over PPh_3 2.5 Pd/TiO_2 as a function of time on stream at 10 bar in the absence of CO. B: MS signals from specific m/z ratios monitored at the reactor outlet – (a) m/z = 2 (hydrogen), (b) m/z = 30 (ethane), (c) m/z = 34 (PH_3) and (d) m/z = 31. i) reduction period, ii) reactor in bypass mode, iii) reaction phase – also shown in A, iv) end of reaction.

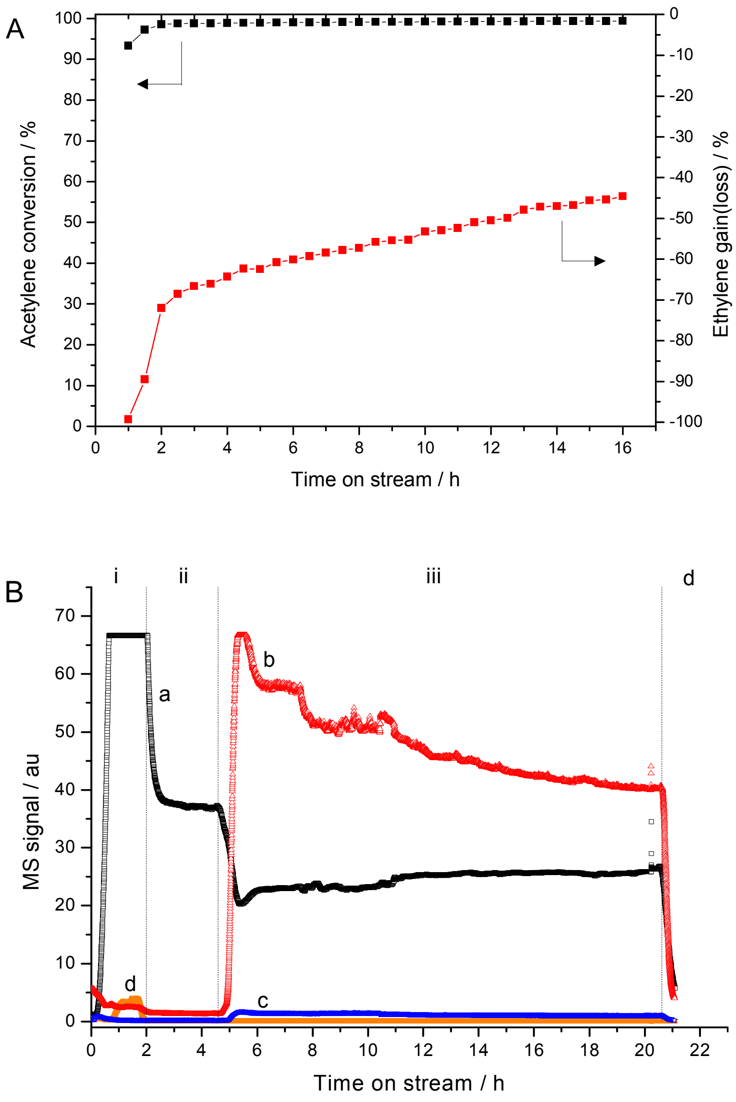
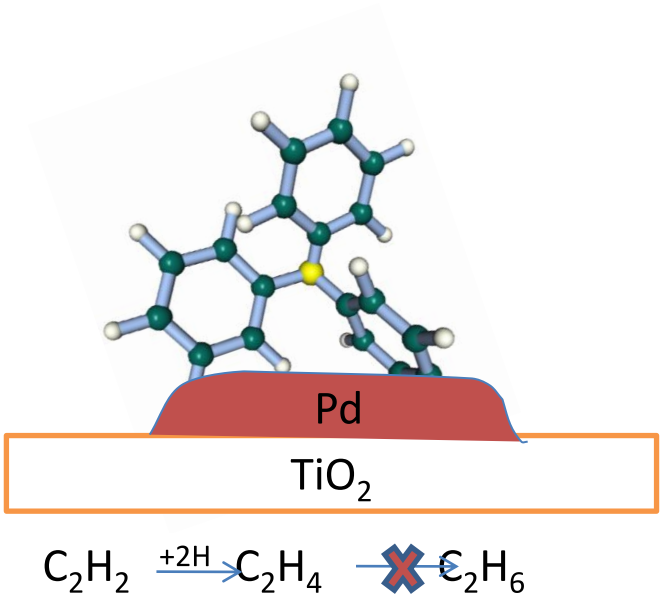


Figure 10 - A: Acetylene conversion (%) and ethylene gain(loss) (%)) over PPh_3 2.5 Pd/TiO_2 as a function of time on stream at 10 bar in the presence of 46 ppm CO. B: MS signals from specific m/z ratios monitored at the reactor outlet – (a) m/z = 2 (hydrogen), (b) m/z = 30 (ethane), (c) m/z = 34 (PH_3) and (d) m/z = 31. i) reduction period, ii) reactor in bypass mode, iii) reaction phase – also shown in A, iv) end of reaction.



Triphenyl phosphine was found to modify the properties of Pd/TiO_2 catalysts leading to enhanced selectivity in acetylene hydrogenation in the presence of ethylene.