Front. Chem. Sci. Eng. 2015, 9(2): 142–153
DOI 10.1007/s11705-015-1516-4

REVIEW ARTICLE

Recent advances in selective acetylene hydrogenation using palladium containing catalysts

Alan J. McCue (✉)[1], **James A. Anderson** (✉)[1,2]

1 Surface Chemistry and Catalysis Group, Department of Chemistry, University of Aberdeen, Aberdeen, AB24 3UE, UK
2 Materials and Chemical Engineering Group, School of Engineering, University of Aberdeen, Aberdeen, AB24 3UE, UK

Alan J. McCue received his BSc (Hons) degree in Chemistry in 2008 and PhD in Chemistry in 2012 from the University of Aberdeen, UK. His primary interest is in the design and application of supported metal catalysts for selective alkyne hydrogenation. Strategies of particular interest include the addition of a 2nd or 3rd metal to modulate activity and the use of selectivity modifiers to moderate selectivity. To date, he has published 12 scientific papers.

James Anderson holds a Sixth Century Chair in Materials at The University of Aberdeen where he heads the Surface Chemistry and Catalysis Group and also a Chair in Chemical Engineering where he heads the Materials and Chemical Engineering Group. He has previously held the posts of Chairman of the UK SURCAT group (RSC Surface and Reactivity group) and secretary of EFCATS (European Federation of Catalysis Societies). He is author/co-author of over 180 scientific papers. His research interests include: use of vibrational spectroscopy to examine surfaces and interfaces, hydrocarbon (including biomass) activation (reforming and hydroisomerisation), acetylene, alkyne and carbon monoxide hydrogenation and photocatalytic water treatment.

Abstract Recent advances with Pd containing catalysts for the selective hydrogenation of acetylene are described. The overview classifies enhancement of catalytic properties for monometallic and bimetallic Pd catalysts. Activity/selectivity of Pd catalysts can be modified by controlling particle shape/morphology or immobilisation on a support which interacts strongly with Pd particles. In both cases enhanced ethylene selectivity is generally associated with modifying ethylene adsorption strength and/or changes to hydride formation. Inorganic and organic selectivity modifiers (i.e., species adsorbed onto Pd particle surface) have also been shown to enhance ethylene selectivity. Inorganic modifiers such as TiO_2 change Pd ensemble size and modify ethylene adsorption strength whereas organic modifiers such as diphenylsulfide are thought to create a surface template effect which favours acetylene adsorption with respect to ethylene. A number of metals and synthetic approaches have been explored to prepare Pd bimetallic catalysts. Examples where enhanced selectivity is observed are generally associated with decreased Pd ensemble size and/or hindering of the ease with which an unselective hydride phase is formed for Pd. A final class of bimetallic catalysts are discussed where Pd is not thought to be the primary reaction site but merely acts as a site where hydrogen dissociation and spillover occurs onto a second metal (Cu or Au) where the reaction takes place more selectively.

Keywords acetylene, ethylene, selective hydrogenation, palladium, bimetallic

1 Introduction

The selective hydrogenation of acetylene to ethylene remains a challenge of fundamental importance in both academia and industry. In academia, acetylene hydrogenation serves as a model reaction for selective hydrogenation both in terms of practical and theoretical studies. Industrially, selective hydrogenation remains the most appropriate means of purifying ethylene streams produced from naphtha cracking prior to polyethylene production since it yields additional alkene and therefore increases

Received March 31, 2015; accepted May 12, 2015

E-mail: a.mccue@abdn.ac.uk, j.anderson@abdn.ac.uk

profitability and removes undesired alkyne [1]. Selective acetylene hydrogenation has been extensively reviewed elsewhere [2–4] and only a summary of key results are discussed in this section. The reaction scheme can be summarised as shown in Fig. 1. In general, there are two competing reaction pathways: hydrogenation to produce ethylene/ethane and oligomerisation leading to the formation of 1,3-butadiene and larger hydrocarbons. This later pathway is highly relevant given that oligomers are the precursor for the formation of ‘green oil’ which generally results in catalyst deactivation due to hydrocarbon accumulation on the catalyst surface. Therefore, in principle, the ideal catalyst for acetylene hydrogenation would avoid formation of oligomers. However, this seems extremely challenging with Pd based catalysts and instead it is more realistic to look for catalysts which minimise the formation of 1,3-butadiene (small k_3 in Fig. 1) or the build-up of larger oligomers which ultimately lead to deactivation (small k_4 in Fig. 1).

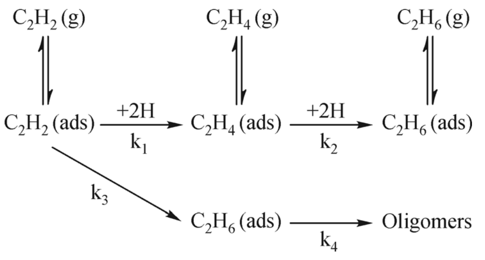


Fig. 1 Reaction network for acetylene hydrogenation

In order for a catalyst to selectively hydrogenate acetylene, it is imperative to maximise the rate of ethylene formation (large k_1 in Fig. 1) whilst minimising over-hydrogenation (k_2 in Fig. 1). Recent literature suggests there are essentially two drivers for alkene selectivity-thermodynamic selectivity and hindering hydride formation [5]. A catalyst which offers thermodynamic selectivity involves one where there is an energy barrier which hinders ethylene adsorption relative to acetylene adsorption meaning that over-hydrogenation is limited. This is not the main driver for palladium based catalysts but is the most controlling factor for moderate-high alkene selectivity over metals such as Cu, Ni, Au and Ag [6–8]. Such metals offer high alkene selectivity but typically require activation/use at elevated temperatures which limit widespread industrial use [7–14]. Selectivity over Pd based catalysts is believed to involve control over hydride formation which results in the formation of reactive sub-surface hydrogen which is prone to hydrogenate ethylene to ethane upon migration back to the surface [15–20]. Recent surface science-studies indicate that the incorporation of C atoms into Pd nanoparticles play a crucial role in controlling the formation/diffusion of sub-surface hydrogen [21–24]. In essence, ethylene selectivity over Pd catalysts is governed by the interplay between hydride and carbide phases and this topic has been discussed elsewhere in significant detail [25]. In order to prepare a selective Pd catalyst for acetylene hydrogenation it is generally accepted that hydride formation should be prevented and this is most readily achieved through alloying with a second metal [26]. Indeed, almost all industrial catalysts are low loaded Pd ($<$ 0.1 wt-%) egg-shell catalysts [1,27] where the active component is alloyed with Ag or Au acting as a structural diluent.

Table 1 Typical feed compositions and reactor conditions for front-end and back-end hydrogenation reactors

Item	Front-end reactor	Back-end reactor
Feed composition /%		
C_2H_2	0.9	1.5
C_2H_4	38.0	75.0
C_2H_4	7.0	22.50
CH_4	35.0	1.00
H_2	19.0	–
CO	0.1	–
Reactor parameter		
Space velocity /h^{-1}	5–8000	1.5–3000
Pressure /bar	15–35	15–35
Temperature /K	343–363	313–393
Regeneration	Rarely	1–4 times per year

Prior to discussing recent advances in Pd catalysts for acetylene hydrogenation it is important to consider the requirements of current industrial reactors since these often differ significantly from laboratory-based studies. Industrially, acetylene reactors can be configured as ‘front-end’ or ‘back-end’ units depending on location with each reactor dealing with different feed compositions/operating conditions (Table 1) [1]. Front-end reactors are situated prior to the removal of C1 cuts and contain a large excess of hydrogen. Under these conditions, selective hydrogenation is more challenging although oligomer formation is less significant. Back-end reactors are positioned after C1 separation and this means that the feed gas is far simpler and the amount of hydrogen used can be added stoichiometrically. This limits over-hydrogenation but promotes oligomer formation meaning that deactivation is more significant. In addition, CO is not present in the feed gas so can be added in trace amounts to moderate alkene selectivity since it competes with ethylene but not acetylene for adsorption sites [1,3]. Addition of CO is complex since it acts as a transient poison and the addition of too large a concentration can reduce catalyst activity and cause acetylene slip. Regardless of whether lab-based studies mimic front-end or back-end hydrogenation there are two common differences from standard industrial practise. Firstly, many studies use simplified gas mixtures, often omitting the large excess of ethylene (non-competitive conditions). This simplifies analysis and allows for more fundamental studies of reaction kinetics and mechanism; however it is important to appreciate that selectivity observed under non-competitive conditions may not always extend to conditions where ethylene is present in the feed. Given that acetylene adsorbs more strongly than ethylene (thermodynamic selectivity), acetylene will preferentially adsorb when present. Towards the end of a catalyst bed where near to full conversion is achieved, ethylene is more likely to find vacant adsorption sites and undergo reaction. Under non-competitive conditions the ethylene concentration is significantly lower and probability of consecutive reaction of any ethylene produced is low. Secondly, the vast majority of lab studies operate under conditions of low pressure (typically 1 bar) while both front and back end hydrogenation units industrially operate between 15 and 35 bar (Table 1). In general, under these conditions it is far easier to achieve high ethylene selectivity. In order to develop catalysts which are industrially relevant it is important to address these shortcomings in coming years. Based on current industrial practise desirable characteristics for Pd containing catalysts are listed below:

- Highly active at temperatures in the range 313–373 K
- Highly selective irrespective of hydrogen : acetylene ratio
- Highly selective at pressures up to 35 bar
- Highly stable and not prone to excess green oil formation
- Readily regenerated without adversely effecting activity/selectivity
- Low sensitivity to CO swings (front-end), selective in the absence of CO (back-end)

In the subsequent sections, new approaches to controlling selectivity in Pd containing catalysts are described. Initially, methods applicable to monometallic Pd catalysts are discussed including the use of new synthetic methods and selectivity moderation using inorganic and organic based surface modifiers. Relevant strategies which have been applied to bimetallic catalysts are then discussed where Pd acts as the active site for hydrogenation and the second metal plays the role of a structural modifier. The final section deals with a new class of catalysts where Pd is used to enhance the activity of an alternative metal by acting as a site for hydrogen dissociation.

2 Monometallic Pd catalysts

2.1 Shaped Pd nanoparticles

Recent decades have seen a remarkable improvement in synthetic methodologies leading to the preparation of well-defined metal nanoparticles using a solution phase approach [28]. A number of different nanoparticle morphologies can readily be prepared which means the effect of exposed crystal face can be studied in greater detail. For example, the preparation of nano sized cubes produces a surface terminated with (100) faces whereas octahedra preferentially expose (111) facets. Given that each crystal face possess subtly different atomic arrangements and different adsorption characteristics, the opportunity to study each in isolation is exceptionally appealing. Prior to discussing specific examples it is important to appreciate that typical synthetic methodologies rely upon the use of additional capping agents which may remain bound to the metal particle surface thereby influencing activity/selectivity. Similarly, it is important to acknowledge that activity may vary with particle size therefore comparing activity of different particle shapes and sizes may, on occasion, lead to misleading results. Yarulin et al. [29] systematically studied the influence of Pd particle shape on acetylene hydrogenation by preparing well defined Pd cubes [(100) faces], cuboctahedra [(100) and (111) faces] and octahedra [(111) faces]. The different morphologies were cleaned using UV light/ozone which has been shown to be an effective way to remove surface residues without altering particle shape [30] — therefore eliminating one potential source of influence from the study. Catalyst testing under non-competitive conditions indicated that particle shape had no impact on selectivity (Fig. 2) at an equivalent degree of conversion [29]. However, results indicated that turnover frequency (TOF) increased in the order cubes < cuboctahedra < octahedra implying that (111) faces are more active than (100) faces (note: different particle size).

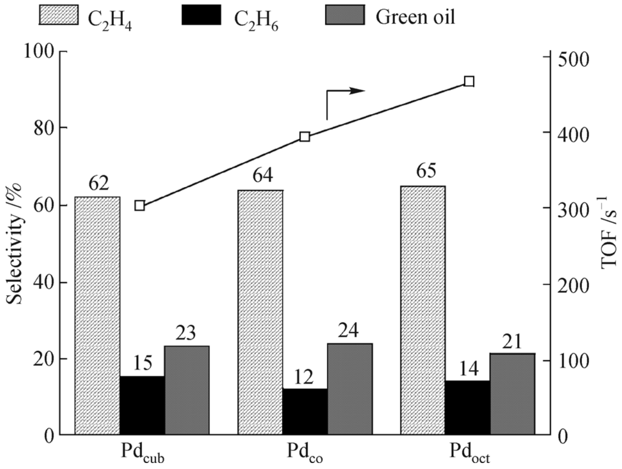


Fig. 2 Product selectivity (bars, left hand Y-axis) and turnover frequency (line, right hand Y-axis) for different Pd particle shapes. Conditions: 13% conversion and 393 K. 'Pd$_{cub}$' denotes cubic shape, 'Pd$_{co}$' denotes cuboctahrdal shape and 'Pd$_{oct}$' denotes octahedral shape. Reproduced from reference [29] with kind permission from Springer Science and Business Media

Kim et al. [31] also studied the effect of particle morphology starting with Pd nanocubes which could be converted into mainly spherical particles [mixture of (100) and (111) faces] by heating to 463 K. Catalyst testing revealed that the TOF for the cubes was higher than the spherical particles, contrary with the earlier report [29]. In this case, it was reported that over-hydrogenation was less significant over the cubes compared with spheres. This was attributed to the influence of hydride formation/decomposition (hydride decomposition occurred at lower temperature on nanocubes) and weaker ethylene adsorption on (100) faces [31]. He et al. [32] explored the differences of Pd cuboctahedron and nanowires towards acetylene hydrogenation prepared by varying the amount of bromide added to the synthesis procedure. High resolution TEM images indicated that nanowires were composed of smaller cuboctahedra connected by different crystal faces. Testing under competitive conditions demonstrated that nanowires were more active than the cuboctahedra although not as selective. The enhanced activity of the nanowires was attributed to a larger number of defect sites associated with the wire being composed of a number of smaller interconnecting cuboctahedra [32].

2.2 Alternative catalyst supports

The majority of research papers exploring selective acetylene hydrogenation tend to use traditional inorganic oxides as catalyst supports such as Al_2O_3, SiO_2 or TiO_2 and generally assume that the support plays relatively little role in controlling catalytic properties. Two recent studies indicate that the choice of support may influence the performance of very small Pd nanoparticles more significantly. Benavidez et al. [33] used solution phase alcohol reduction of $Pd(OAc)_2$ [34] to produce very small Pd nanoparticles (0.5–1.0 nm) and subsequently deposited them onto carbon, alumina and magnesia as supports (Fig. 3). TEM measurements showed narrow particle size distributions using all supports, although the Pd/C support had a particularly narrow distribution with no particles larger than 1.5 nm observed. Catalyst testing performed under competitive conditions demonstrated differences in catalyst activity ($Pd/Al_2O_3 > Pd/MgO > Pd/C$) but significant changes in ethylene selectivity (Fig. 3). Pd supported on alumina or magnesia resulted in unselective acetylene hydrogenation as well as notable ethylene consumption. In contrast Pd/C resulted in an ethylene gain across a wide range of conversion. Based on XANES measurements, the authors suggest that the enhanced selectivity is a result of metal-support interactions between the carbon support and Pd particles [33]. It is also acknowledged that the interaction of Pd and C may influence the ability to form a hydride phase given that the Pd particle size is exceptionally small and this correlates with the report of Boudart and Hwang [35] who reported hydride formation decreases as Pd dispersion approaches 100%.

A second study of note involves the use of silicate based fiberglass as a support [36]. It is suggested that such a support (non-crystalline in nature) can stabilise small Pd particles ($\approx$ 1 nm), although only at low loading (<0.025 wt-%). Catalyst testing under competitive conditions and at 20 bar pressure demonstrated that ethylene selectivity of $>56\%$ could be achieved at 100% conversion (Fig. 4) even under conditions of excess hydrogen (1.5 eq. H_2 : acetylene). Careful characterisation studies suggested that the key Pd sites were contained within the upper layers of the fibreglass support and selectivity was attributed to the way in which acetylene and ethylene interact with the support [36]. In essence, the more polar or more polarizable the molecule the more likely it is to penetrate into the glassy support. It is therefore thought that acetylene will be more readily find the active Pd sites compared with ethylene which allows for less over-hydrogenation.

Riyapan et al. have explored the effect of Ti^{3+} defects

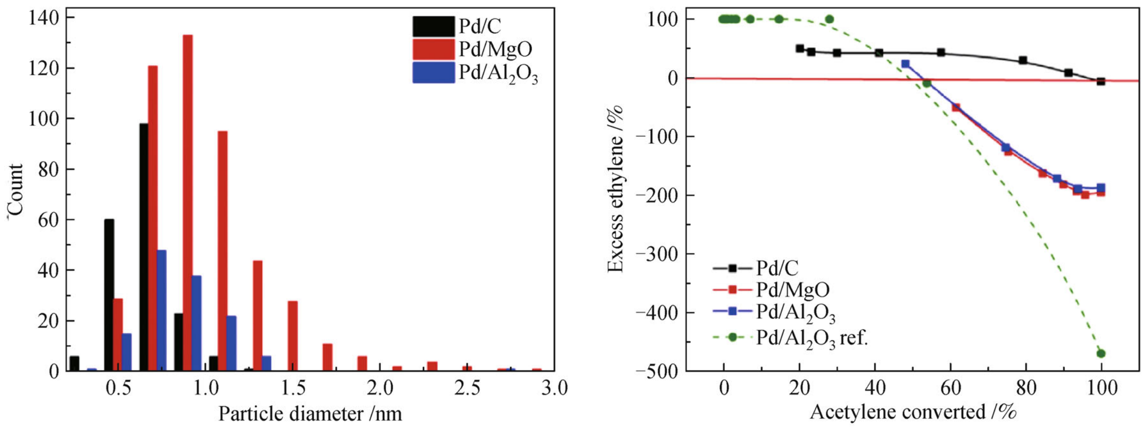


Fig. 3 Particle size distribution (LHS) and excess ethylene *versus* acetylene conversion (RHS) for Pd catalysts immobilised on carbon, magnesia and alumina supports (see legend inset). Reproduced with permission from Elsevier [33]

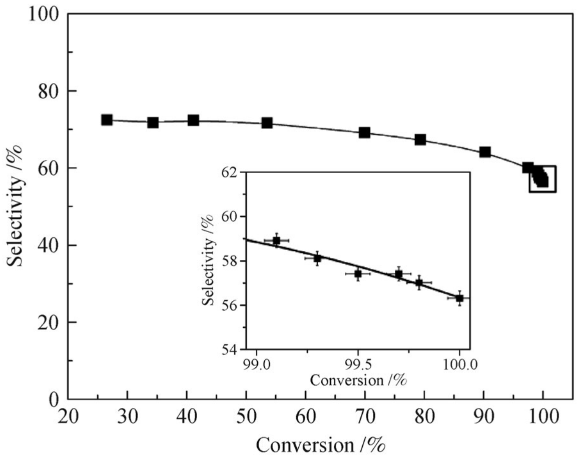


Fig. 4 Ethylene selectivity *versus* acetylene conversion over Pd/Fibreglass catalyst. Outer graph: 330 K, GHSV = 1570–9000 h^{-1}. Inset: 350 K, GHSV = 2210–2840 h^{-1}. Reproduced with permission from Elsevier [36]

created by various thermal pre-treatments to TiO_2 prior to addition of Pd by either impregnation or electroless deposition (metal deposition in the absence of an external current) [37,38]. TiO_2 was prepared by a sol-gel methodology and then treated in hydrogen, nitrogen, oxygen or air at 623 K. In general, the thermal pre-treatment appeared to have relatively little effect on physicochemical properties such as surface area and pore diameter. However, a marked effect on the number of defect sites, as accessed by EPR measurements was observed for samples pre-treated in N_2 or H_2. Materials with more Ti^{3+} defects then resulted in higher Pd dispersion and improved acetylene conversion during catalyst testing [37,38]. On the basis of data presented it is not clear if the enhanced activity is purely as a result of more Pd surface atoms, a particle size effect or whether turnover frequency also increased. Regardless, samples on H_2 or N_2 pre-treated TiO_2 exhibited marked improvement in ethylene selectivity. Most notably, pre-treatment in H_2 resulted in 85%–90% ethylene selectivity at 100% conversion [37]. The authors postulated that higher defect site concentrations resulted in more strong metal support interactions which increased selectivity. However, the role of hydride formation in these samples was not discussed.

2.3 Plasma pre-treatments

From the previous section it would appear that the preparation of a catalyst with exceptionally small Pd particles and with strong metal support interactions is beneficial for achieving high ethylene selectivity. However, this is not readily achievable without the use of a thermal treatment to induce SMSI. Recently, Jang and co-workers [39,40] demonstrated that similar effects may be achieved using radio frequency (RF) plasma treatments. It is thought that the interaction of a Pd precursor deposited onto a TiO_2 support with plasma (hydrogen, nitrogen or oxygen based) can effectively reduce the metal at room temperature. Catalyst testing (after an additional reduction at 473 K) under competitive conditions demonstrated that plasma treated Pd/TiO_2 showed higher conversion compared with the same non-plasma treated sample. A small increase in ethylene selectivity was also apparent for plasma treated samples although once high conversion was achieved, significant ethylene hydrogenation was apparent. Characterisation results suggested that plasma treatment did induce SMSI which in turn affected ethylene adsorption.

2.4 Inorganic selectivity modifiers

Pd catalysts supported on inorganic oxides which offer SMSI have been shown to offer enhanced performance for acetylene hydrogenation. Moon and co-workers have demonstrated that the deposition of small quantities of inorganic species onto Pd containing catalysts can also result in enhanced catalytic properties. In this case, characterisation suggests that the modifier acts more like a surface species and as such is classed as an ‘inorganic selectivity modifier’ in this review. The topic has already been extensively reviewed elsewhere [41] and as such only some pertinent points will be summarised here. Shin et al. [42] demonstrated that the decomposition of SiH_4 on a Pd/SiO_2 catalyst followed by oxidation resulted in the majority of Si being deposited on Pd, likely as SiO_2. Catalyst testing under competitive conditions indicated that the addition of a Si species decreased activity, consistent with a loss of surface Pd sites, but increased selectivity in favour in ethylene. Characterisation data (FTIR of adsorbed CO and ethylene TPD) indicated that Si acts to break up the Pd ensembles and weakens ethylene adsorption which was thought to enhance selectivity [43].

In subsequent studies, TiO_2, La_2O_3 and Nb_2O_5 [41,44,45] were deposited onto Pd/SiO_2 and it was demonstrated that improved catalytic properties could be obtained after reduction at elevated temperature (773 K) (Fig. 5). In general, the selectivity enhancement was largest with La_2O_3 and smallest with Nb_2O_5 [44] and it was thought that reduction at higher temperature was necessary to induce an interaction more akin to an SMSI state. As with Si, the enhanced selectivity was attributed to a combination of geometric and electronic effects (Pd ensemble dilution and change to the strength of ethylene adsorption). It should be noted that the interplay between inorganic selectivity modifiers and palladium hydride formation is not known suggesting scope for further studies. There are two final points which should be highlighted in this section. Firstly, the use of Ti, La, Nb species requires the use of elevated temperatures which means that modification of existing industrial catalysts *in-*

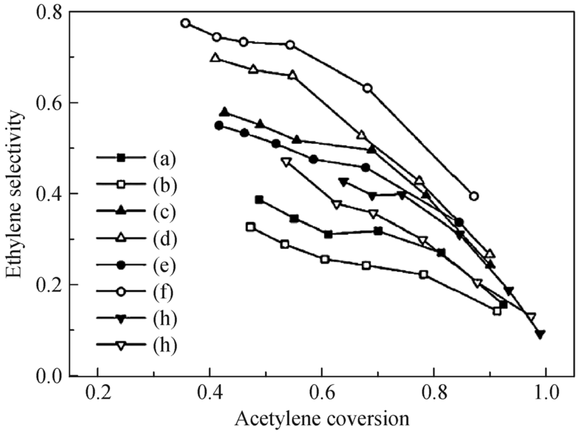


Fig. 5 Ethylene selectivity *versus* acetylene conversion for Pd/SiO_2 catalyst treated with various inorganic selectivity modifiers. Legend inset: (a) Pd/SiO_2 reduced at 573 K, (b) Pd/SiO_2 reduced at 773 K, (c) Pd/SiO_2 + Ti reduced at 573 K, (d) Pd/SiO_2 + Ti reduced at 773 K, (e) Pd/SiO_2 + La reduced at 573 K, (f) Pd/SiO_2 + La reduced at 773 K, (g) Pd/SiO_2 + Nb reduced at 573 K and (h) Pd/SiO_2 + Ni reduced at 773 K. Reproduced with permission from Elsevier [41]

situ would not be feasible (as acknowledged by Kim and Moon [41]). Secondly, the addition of any inorganic species reported to date appears to reduce the formation of green oil/reduce deactivation [41], therefore increasing catalyst stability/lifetime.

2.5 Organic selectivity modifiers

Recent reports indicate that it is also possible to modify the activity/selectivity of Pd based catalysts by adsorbing various organic species onto the metal surface. The group of Anderson investigated the adsorption of organic sulfur [46–49] and phosphorous [48–50] modifiers on acetylene hydrogenation. Diphenylsulfide and triphenylphosphine were adsorbed onto a Pd/TiO_2 catalyst by impregnation from a hexane solution. Characterisation indicated that both modifiers adsorbed in part on Pd as judged by reduced metal surface determined from CO pulse chemisorption with, excess modifier likely adsorbed on the support. Through combined TGA-MS and FTIR experiments it was possible to deduce the thermal stability of the modifiers. It appeared possible to lose triphenylphosphine adsorbed from the support by reduction at 393 K whereas higher temperatures were necessary to remove the modifier from the metal [50]. In the case of diphenylsulfide, reduction at 393 K appeared to result in the loss of the phenyl ligands with the sulfur atom being retained. Catalyst performance was first accessed by measuring the reaction rate of acetylene and ethylene in separate non-competitive reactions [46]. Freshly reduced Pd/TiO_2 hydrogenated both acetylene and ethylene at a similar rate (Fig. 6). This is in contrast to triphenylphosphine treated Pd/TiO_2 where the rate of acetylene hydrogenation was increased and the rate of ethylene hydrogenation decreased by more than 80% [50]. The use of diphenylsulfide resulted in negligible change to the rate at which acetylene was hydrogenated but completely supressed ethylene hydrogenation under non-competitive conditions [46].

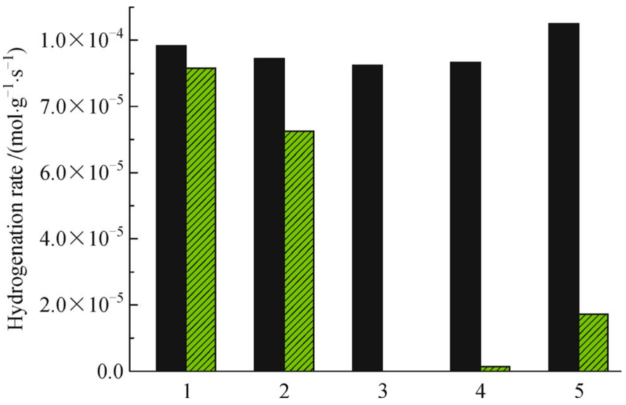


Fig. 6 Hydrogenation rate of acetylene (black) and ethylene (green) from non-competitive reactions at 323 K. (1) Pd/TiO_2, (2) Pd/TiO_2 with 3 ppm CO in the fed, (3) Pd/TiO_2 + diphenylsulfide reduced at 323 K, (4) Pd/TiO_2 + diphenylsulfide reduced at 393 K and (5) Pd/TiO_2 + triphenylphosphine reduced at 393 K. Reproduced with permission from Elsevier [46] and Royal Society of Chemistry [50]

The catalysts were then tested under challenging front-end conditions using a large excess H_2 relative to acetylene (25 : 1) and an excess of ethylene (9 : 1, ethylene : acetylene). Under these conditions the unmodified Pd catalyst was very unselective and resulted 80% of the ethylene initially present in the feed being hydrogenated to ethane. Triphenylphosphine treated sample performed significantly better with only 5% of the feed ethylene being hydrogenated [50]. In agreement with non-competitive reactions, diphenylsulfide acted as a more effective modifier resulting in a net gain in ethylene [46]. Subsequent catalyst testing at moderate pressure indicated that enhanced selectivity could be retained at 10 bar pressure in the presence of CO [49], although tests with triphenylphosphine treated Pd/TiO_2 in the absence of CO fail to show enhanced selectivity [50]. Results were interpreted in terms of the modifiers creating a surface template based on geometric packing on the Pd surface. This was thought to result in the formation of adsorption sites which favoured acetylene adsorption but hindered ethylene adsorption. However, it is interesting to note that the adsorption of diphenylsulfide and triphenylsulfide had an impact of hydride formation on Pd/TiO_2 as judged by temperature programmed reduction measurements (Fig. 7). The size of the negative feature associated with hydride decomposition *ca*. 345 K decreased upon going from untreated Pd/TiO_2 to triphenylphosphine treated to diphenylsulfide treated which correlates with catalyst selectivity. As such, it may be the combination of reduced hydride formation and a surface template effect which is responsible for enhanced selectivity. In addition to enhanced selectivity, samples treated with diphenylsulfide of triphenylphosphine also produced less oligomers hinting at improved stability.

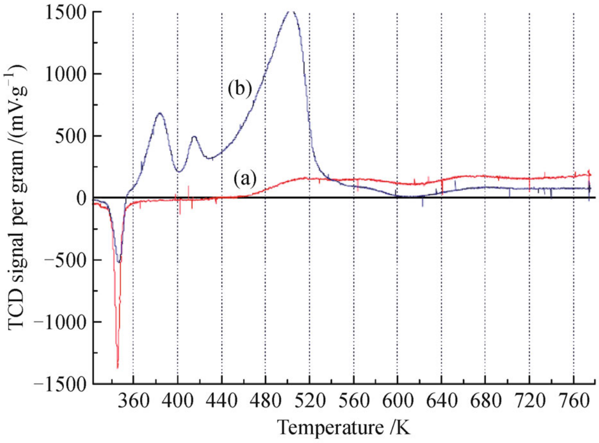


Fig. 7 Temperature programmed reduction profiles for (a) Pd/TiO_2 and (b) Pd/TiO_2 + diphenylsulfide. Reproduced with permission from Elsevier [46]

3 Bimetallic Pd catalysts

3.1 Addition of a second metal

Almost all industrial Pd catalysts used for selective acetylene hydrogenation are bimetallic (typically Pd + Ag or Au) [4,27] with the second metal known to dilute Pd ensemble size and limit hydride formation [26], thereby decreasing over-hydrogenation. A number of recent studies have looked at the choice of second metal as well as the method of introduction. Han et al. [51] reported a novel method for introduction of Ag to Pd/TiO_2 catalysts *via* sequential photo-deposition. Based on FTIR of adsorbed CO it was thought that this resulted in the preferential deposition of Ag onto a Pd core, as opposed to metal mixing. Catalyst testing under competitive back-end type conditions demonstrated that PdAg/TiO_2 prepared by this method resulted in improved selectivity compared with PdAg/TiO_2 prepared *via* impregnation. It was thought that this method shows wider ranging promise since core-shell type structures are not readily prepared by simple synthetic methods. In principle, similar materials were prepared by Zhang et al. [52] using electroless deposition of Ag or Au onto a pre-made Pd/SiO_2 catalyst. Selective chemisorption was used to estimate Ag/Au surface coverage and indicated that higher metal loadings were necessary to achieve high Ag/Au surface coverage suggesting a degree of metal mixing (likely associated with thermal reduction at 473 K). A plot of conversion and ethylene selectivity *versus* Ag and Au surface coverage is shown in Fig. 8.

In general as Ag/Au coverage increases, conversion decreases and selectivity increases. Interestingly, turnover frequency (calculated on the basis of Pd surface atoms) increases to a maximum point as Ag/Au surface coverage approach 0.9. PdAu particle morphology was explored by Ma et al. [53] who prepared bimetallic nanoparticles with octahedral and a ‘nanoflower’ shape (organised agglomerates of the octahedra). Catalytic testing indicated that the unique nanoflower morphology resulted in higher activity, ethylene selectivity and stability when compared with the sample possessing octahedral shape. Similar to the Pd nanowires described earlier [32], enhanced activity was attributed to a higher number of defect sites present in the nanoflowers.

Other metals have also been explored as structural

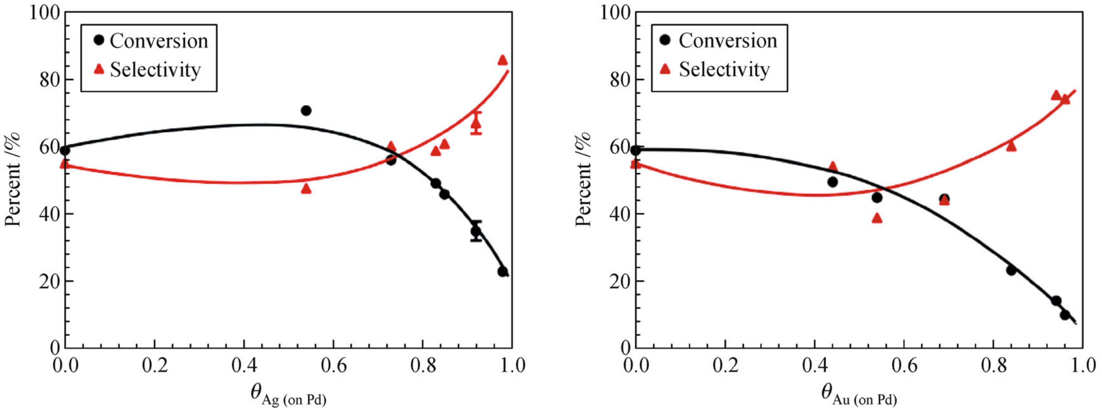


Fig. 8 Conversion (black circles) and ethylene selectivity (red triangles) *versus* Ag surface coverage on Pd (LHS) and Au surface coverage on Pd (RHS). Reproduced with permission from Elsevier [52]

diluents. PdGa intermetallic compounds (defined as having a precisely defined structural order and unique electronic properties compared with either metal [54]) have been prepared, thoroughly characterised [55] and tested in acetylene hydrogenation [56]. Results indicated that PdGa intermetallic compounds offered superior selectivity when compared with intermetallic PdAg intermetallic or a reference Pd/Al_2O_3 catalyst and this was attributed to Pd site isolation and decreased hydride formation. One key point to note is that PdGa catalysts require operation at elevated temperatures (473 K) which may restrict widespread application. Readers are directed towards the review article by Armbrűster et al. for more information [25]. Cu has also been used as the structural diluent for both bulk and supported Pd catalysts. Depending on thermal pre-treatment, compound with a $Cu_{60}Pd_{40}$ composition could possess an ordered or unordered structure [57]. Ethylene selectivity in excess of 90% could be achieved through geometric and electronic effects using the ordered material but again reactions needed to be run at 473 K in order to achieve adequate conversion. Finally, Kim et al. [58] reported that addition of Cu *via* a surface redox approach produced catalysts with enhanced ethylene selectivity (compared with Ag). Note: in the latter two examples Cu acts as a structural modifier and not as the primary active site — this is different from materials discussed in section 3.2 below.

3.2 Use of Pd to enhance activity of other metals

In terms of acetylene hydrogenation almost all industrial catalysts utilise Pd as the active metal since it offers high activity at relatively low temperature. However, the low inherent selectivity of Pd (associated with hydride formation) means that it is necessary to dilute Pd with a second metal. Recent studies have indicated that a number of alternative metals offer superior selectivity to ethylene such as Ni, Cu, Au and Ag but suffer from other drawbacks which limit industrial use. For example hydrogen dissociation is less favourable meaning that elevated temperatures are necessary in order to achieve rates comparable to Pd based catalysts. In addition, metals such as Ni and Cu are prone to forming larger quantities of oligomers leading to more pronounced deactivation unless operated at elevated temperature or very high hydrogen pressures. An alternative approach is to combine the catalytic properties of Pd with a second more selective metal — ideally with Pd acting as a site for hydrogen dissociation and the second metal acting as a site for acetylene hydrogenation *via* hydrogen spillover. Recent surface science reports suggest that by vapour phase deposition of Pd onto a Cu (111) surface, it is possible to prepare a 'single atom alloy' where individual Pd atoms are incorporated into the Cu surface (verified by scanning tunnelling microscopy) [59,60]. The dynamics of hydrogen adsorption/desorption was studied by temperature programmed desorption and indicated that hydrogen dissociation and spillover from Pd to Cu occurs even at very low Pd surface concentrations (≈ 1%) and at temperatures far lower than on a Cu (111) surface (Fig. 9) [61]. The authors then demonstrated that 1% Pd dosed onto a Cu (111) surface could be used for acetylene hydrogenation at low temperature under ultra-high vacuum conditions [60].

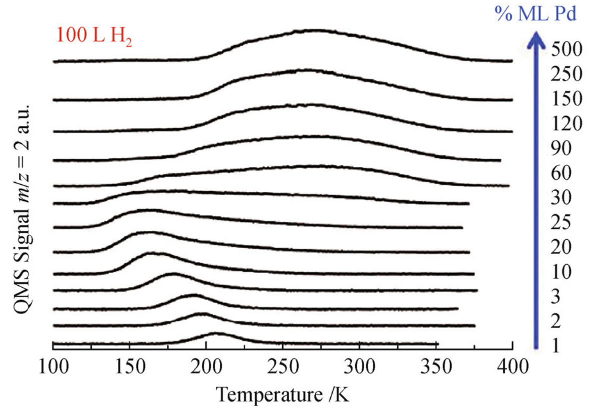
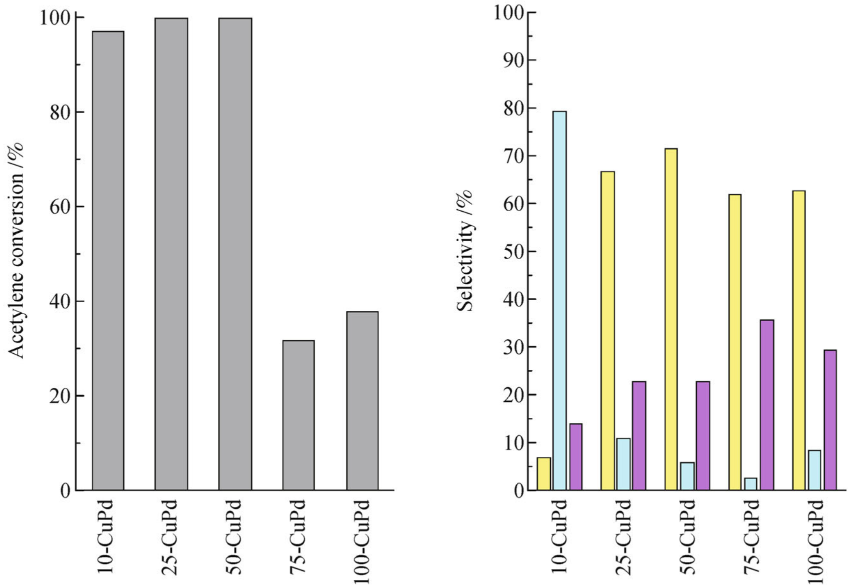


Fig. 9 H_2 desorption from Cu (111) surface with various amounts of Pd deposited ontop (scale on RHS). Reproduced from reference [61] with permission of the Royal Society of Chemistry

A subsequent study by McCue et al. applied this methodology to more traditional powdered catalysts by adding small amounts of Pd (10, 25, 50, 75 and 100 : 1, Cu : Pd atomic ratio) to 10 wt-% Cu/Al_2O_3 using sequential impregnation (i.e., Pd added after Cu) [62]. Catalyst testing was, in the first instance, performed under non-competitive conditions and results indicated that sample with a nominal 50 : 1 Cu : Pd ratio appeared to offer activity/selectivity which combined the desirable features of both monometallic Cu and Pd catalysts. Using a 3 fold excess of H_2 relative to acetylene, full acetylene conversion was achieved at 373 K with ethylene selectivity in excess of 70% and ethane selectivity falling below 10% (Fig. 10). This represented a 50 K decrease in the temperature necessary to achieve full conversion over monometallic Cu under the same conditions suggesting that this catalyst could operate within the temperature range currently used industrially [62]. Interestingly the same catalyst exhibited enhanced activity and selectivity when reaction was performed with 10 equivalents of H_2 relative to acetylene. In this case, close to 100% conversion could be achieved at 353 K with an ethylene selectivity of 80%.

Characterisation data suggested the catalyst possessed a copper rich surface with Pd surface concentration so low that it was difficult to access the nature of the Pd surface species [62]. As such, it was not possible to identify if the Pd site responsible for hydrogen dissociation was

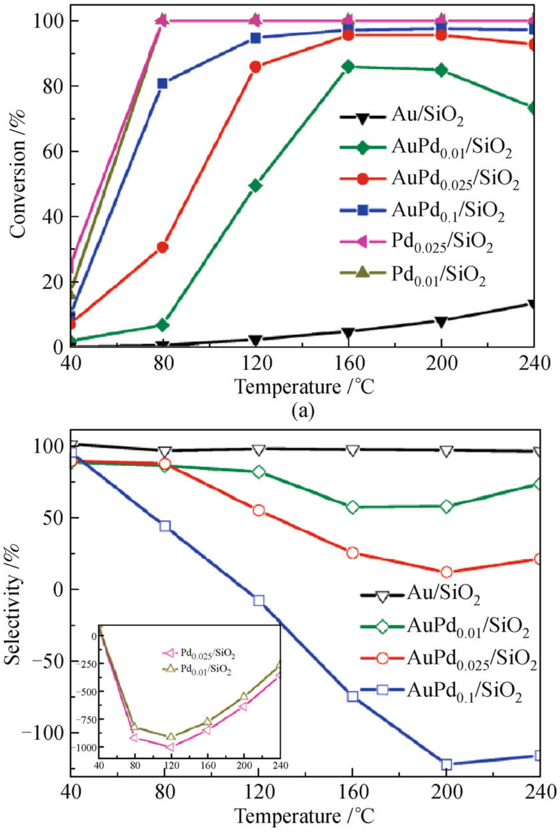


(a) (b)

Fig. 10 (a) Acetylene conversion and (b) Product selectivity (yellow = ethylene, cyan = ethane, pink = oligomers) over CuPd/Al_2O_3 catalysts (number denotes Cu : Pd atomic ratio). Conditions: 0.6% acetylene, 1.8% H_2, balance N_2, 373 K. Reproduced from reference [62]

composed of isolated Pd atoms as reported previously [59]. Based on density functional theory calculations reported by Fu and Luo [63] it appears that Pd clusters which encompass both the surface and near surface layers represent sites where hydrogen dissociation should be more favourable than on monometallic Cu indicating that it may not be necessary to form single atom sites in the alloy before enhanced activity is observed. McCue et al. have more recently explored different preparation methods for CuPd catalysts and found that any preparation route which enhances activity results in decreased ethylene selectivity and as such a balance between activity/selectivity must be reached [64]. Testing of the most selective catalyst (50 : 1, Cu : Pd atomic ratio prepared by sequential impregnation) under more industrially relevant conditions demonstrated that good ethylene selectivity can be achieved under competitive conditions, although ethane selectivity increases when operated at higher pressure [64]. Therefore whilst CuPd catalysts can operate at industrially relevant temperatures it is unlikely that they could be used at the pressures used within current industrial reactors which may limit potential application.

Pei et al. [65] have demonstrated that similar results can be obtained using AuPd/SiO_2 catalysts. Catalyst testing under competitive conditions demonstrated that the addition of Pd resulted in a marked increase in activity compared with monometallic Au (Fig. 11). Again it appears that a balance between activity and selectivity must be struck with a 40 : 1 Au : Pd ratio representing optimum performance. This catalyst composition meant that at 393 K ≈ 85% conversion could be achieved with



(a)

(b)

Fig. 11 (a) acetylene conversion and (b) ethylene selectivity over Au/SiO_2 and Pd doped Au/SiO_2 catalysts (see legend inset). Reproduced from reference [65] with permission of the Royal Society of Chemistry greater than 50% selectivity to ethylene. In comparison, monometallic Au exhibits less than 5% conversion under the same conditions. Characterisation led to the authors postulating that they had prepared an alloy containing single isolated Pd sites. No Pd-Pd distances were extracted from EXAFS data when the Au : Pd was 40 or higher. Similarly DRIFTS spectra after reduction and adsorption of CO indicated the lack of bridge bound CO. However, it is important to appreciate that each characterisation technique has its own inherent limit of detection meaning that small concentrations of Pd-Pd dimers may exist which are not readily detected. Regardless, initial reports indicate that the use of Pd as a site to enhance hydrogen dissociation on a metal which offers high ethylene selectivity is promising and warrants further investigation.

4 Conclusions

A number of strategies have been reviewed which can be applied to monometallic Pd or bimetallic catalyst containing Pd to enhance selectivity for acetylene hydrogenation. Catalytic performance of monometallic Pd catalysts can be influenced to some extent by controlling particle shape/morphology. Inducing a state of SMSI appears to enhance ethylene selectivity but typically requires high temperature before such effects are seen. The use of plasma treatments seems to induce a state of SMSI without the need for high temperature treatments. Both inorganic and organic selectivity modifiers appear effective for enhancing ethylene selectivity. Enhanced selectivity is attributed to modified ethylene adsorption (both electronic and geometric effects). The addition of a second metal can enhance selectivity by diluting Pd ensemble size and reducing the formation of palladium hydride. The use of Pd to enhance the activity of other metals which are inherently selective for acetylene hydrogenation appears viable with examples of both CuPd and AuPd reported to date.

References

1. Tiedtke D B, Cheung T T P, Leger J, Zisman S A, Bergmeister J J, Delzer G A. In: 13th Ethylene Producers Conference, 2001, 10: 1–21
2. Borodziński A, Bond G C. Selective Hydrogenation of ethyne in ethene—rich streams on palladium catalysts. Part 1. Effect of changes to the catalyst during reaction. Catalysis Reviews, 2006, 48 (2): 91–144
3. Borodziński A, Bond G C. Selective hydrogenation of ethyne in ethene—rich streams on palladium catalysts. Part 2: Steady—state kinetics and effects of palladium particle size, carbon monoxide, and promoters. Catalysis Reviews, 2008, 50(3): 379–469
4. Nikolaev S A, Zanaveskin I L N, Smirnov V V, Averyanov V A, Zanaveskin K I. Catalytic hydrogenation of alkyne and alkadiene impurities from alkenes. Practical and theoretical aspects. Russian Chemical Reviews, 2009, 78(3): 231–247
5. García-Mota M, Gómez-Díaz J, Novell-Leruth G, Vargas-Fuentes C, Bellarosa L, Bridier B, Pérez-Ramírez J, López N. A density functional theory study of the “mythic” Lindlar hydrogenation catalyst. Theoretical Chemistry Accounts, 2011, 128(4): 663–673
6. Bridier B, Lopez N, Pérez-Ramírez J. Molecular understanding of alkyne hydrogenation for the design of selective catalysts. Dalton Transactions, 2010, 39(36): 8412–8419
7. Segura Y, López N, Pérez-Ramírez J. Origin of the superior hydrogenation selectivity of gold nanoparticles in alkyne + alkene mixtures: Triple- *versus* double-bond activation. Journal of Catalysis, 2007, 247(2): 383–386
8. Vilé G, Baudouin D, Remediakis I N, Copéret C, López N, Pérez-Ramírez J. Silver nanoparticles for olefin production: New insights into the mechanistic description of propyne hydrogenation. ChemCatChem, 2013, 5(12): 3750–3759
9. Wehrli J T, Thomas D J, Wainwright M S, Trimm D L, Cant N W. Selective hydrogenation of propyne over supported copper catalysts: Influence of support. Applied Catalysis, 1991, 70(1): 253–262
10. Bridier B, López N, Pérez-Ramírez J. Partial hydrogenation of propyne over copper-based catalysts and comparison with nickel-based analogues. Journal of Catalysis, 2010, 269(1): 80–92
11. Abelló S, Verboekend D, Bridier B, Pérez-Ramírez J. Activated takovite catalysts for partial hydrogenation of ethyne, propyne, and propadiene. Journal of Catalysis, 2008, 259(1): 85–95
12. Trimm D L, Liu I O Y, Cant N W. The selective hydrogenation of acetylene over a Ni/SiO_2 catalyst in the presence and absence of carbon monoxide. Applied Catalysis A, General, 2010, 374(1-2): 58–64
13. Trimm D L, Cant N W, Liu I O Y. The selective hydrogenation of acetylene in the presence of carbon monoxide over Ni and Ni-Zn supported on $MgAl_2O_4$. Catalysis Today, 2011, 178(1): 181–186
14. Lopez-Sanchez J A, Lennon D. The use of titania- and iron oxide-supported gold catalysts for the hydrogenation of propyne. Applied Catalysis A, General, 2005, 291(1-2): 230–237
15. García-Mota M, Bridier B, Pérez-Ramírez J, López N. Interplay between carbon monoxide, hydrides, and carbides in selective alkyne hydrogenation on palladium. Journal of Catalysis, 2010, 273 (2): 92–102
16. Yang B, Burch R, Hardacre C, Headdock G, Hu P. Influence of surface structures, subsurface carbon and hydrogen, and surface alloying on the activity and selectivity of acetylene hydrogenation on Pd surfaces: A density functional theory study. Journal of Catalysis, 2013, 305: 264–276
17. Gabasch H, Hayek K, Klötzer B, Knop-Gericke A, Schlögl R. Carbon incorporation in Pd(111) by adsorption and dehydrogenation of ethene. Journal of Physical Chemistry B, 2006, 110(10): 4947–4952
18. Teschner D, Borsodi J, Wootsch A, Révay Z, Hävecker M, Knop-Gericke A, Jackson S D, Schlögl R. The roles of subsurface carbon and hydrogen in palladium-catalyzed alkyne hydrogenation. Science, 2008, 320(5872): 86–89
19. Teschner D, Borsodi J, Kis Z, Szentmiklósi L, Révay Z, Knop-Gericke A, Schlögl R, Torres D, Sautet P. Role of hydrogen species in palladium-catalyzed alkyne hydrogenation. Journal of Physical

Chemistry C, 2010, 114(5): 2293–2299

20. Sá J, Arteaga G D, Daley R A, Bernardi J, Anderson J A. Factors influencing hydride formation in a Pd/TiO_2 catalyst. Journal of Physical Chemistry B, 2006, 110(34): 17090–17095
21. Schauermann S, Nilius N, Shaikhutdinov S, Freund H J. Nanoparticles for heterogeneous catalysis: New mechanistic insights. Accounts of Chemical Research, 2013, 46(8): 1673–1681
22. Ludwig W, Savara A, Madix R J, Schauermann S, Freund H J. Subsurface hydrogen diffusion into Pd nanoparticles: Role of low-coordinated surface sites and facilitation by carbon. Journal of Physical Chemistry C, 2012, 116(5): 3539–3544
23. Ludwig W, Savara A, Dostert K H, Schauermann S. Olefin hydrogenation on Pd model supported catalysts: New mechanistic insights. Journal of Catalysis, 2011, 284(2): 148–156
24. Wilde M, Fukutani K, Ludwig W, Brandt B, Fischer J H, Schauermann S, Freund H J. Influence of carbon deposition on the hydrogen distribution in Pd nanoparticles and their reactivity in olefin hydrogenation. Angewandte Chemie International Edition, 2008, 47(48): 9289–9293
25. Armbrüster M, Behrens M, Cinquini F, Föttinger K, Grin Y, Haghofer A, Klötzer B, Knop-Gericke A, Lorenz H, Ota A, Penner S, Prinz J, Rameshan C, Révay Z, Rosenthal D, Rupprechter G, Teschner D, Torres D, Wagner R, Widmer R, Wowsnick G. How to control the selectivity of palladium-based catalysts in hydrogenation reactions: The role of subsurface chemistry. ChemCatChem, 2012, 4 (8): 1048–1063
26. Khan N A, Shaikhutdinov S, Freund H J. Acetylene and ethylene hydrogenation on alumina supported Pd-Ag model catalysts. Catalysis Letters, 2006, 108(3-4): 159–164
27. Johnson M M, Walker D W, Nowack G P. U S Patent, 4404124A, 1983-09-13
28. Lim B, Jiang M, Tao J, Camargo P H C, Zhu Y, Xia Y. Shape-controlled synthesis of Pd nanocrystals in aqueous solutions. Advanced Functional Materials, 2009, 19(2): 189–200
29. Yarulin A E, Crespo-Quesada R M, Egorova E V, Kiwi-Minsker L L. Structure sensitivity of selective acetylene hydrogenation over the catalysts with shape-controlled palladium nanoparticles. Kinetics and Catalysis, 2012, 53(2): 253–261
30. Crespo-Quesada M, Andanson J M, Yarulin A, Lim B, Xia Y, Kiwi-Minsker L. UV-ozone cleaning of supported poly(vinylpyrrolidone)-stabilized palladium nanocubes: Effect of stabilizer removal on morphology and catalytic behavior. Langmuir, 2011, 27(12): 7909–7916
31. Kim S K, Kim C, Lee J H, Kim J, Lee H, Moon S H. Performance of shape-controlled Pd nanoparticles in the selective hydrogenation of acetylene. Journal of Catalysis, 2013, 306: 146–150
32. He Y F, Feng J T, Du Y Y, Li D Q. Controllable synthesis and acetylene hydrogenation performance of supported pd nanowire and cuboctahedron catalysts. ACS Catalysis, 2012, 2(8): 1703–1710
33. Benavidez A D, Burton P D, Nogales J L, Jenkins A R, Ivanov S A, Miller J T, Karim A M, Datye A K. Improved selectivity of carbon-supported palladium catalysts for the hydrogenaiton of acetylene in excess ethylene. Applied Catalysis A, General, 2014, 482: 108–115
34. Burton P D, Boyle T J, Datye A K. Facile. Surfactant-free synthesis of Pd nanoparticles for heterogeneous catalysts. Journal of Catalysis, 2011, 280(2): 145–149
35. Boudart M, Hwang H S. Solubility of hydrogen in small particles of palladium. Journal of Catalysis, 1975, 39(1): 44–52
36. Gulyaeva Y K, Kaichev V V, Zaikovskii V I, Kovalyov E V, Suknev A P, Bal'zhinimaev B S. Selective hydrogenation of acetylene over novel Pd/fiberglass catalysts. Catalysis Today, 2015, 245: 139–146
37. Riyapan S, Boonyongmaneerat Y, Mekasuwandumrong O, Yoshida H, Fujita S I, Arai M, Panpranot J. Improved catalytic performance of Pd/TiO_2 in the selective hydrogenation of acetylene by using H_2-treated sol-gel TiO_2. Journal of Molecular Catalysis A Chemical, 2014, 383-384: 182–187
38. Riyapan S, Boonyongmaneerat Y, Mekasuwandumrong O, Praserthdam P, Panpranot J. Effect of surface Ti^{3+} on the sol-gel derived TiO_2 in the selective acetylene hydrogenation on Pd/TiO_2 catalysts. Catalysis Today, 2014, 245: 134–138
39. Li Y, Jang B W L. Non-thermal RF plasma effects on surface properties of Pd/TiO_2 catalysts for selective hydrogenation of acetylene. Applied Catalysis A, General, 2011, 392(1-2): 173–179
40. Zhu B, Jang B W L. Insights into surface properties of non-thermal RF plasmas treated Pd/TiO_2 in acetylene hydrogenation. Journal of Molecular Catalysis A, Chemical, 2014, 395: 137–144
41. Kim W J, Moon S H. Modified Pd catalysts for the selective hydrogenation of acetylene. Catalysis Today, 2012, 185(1): 2–16
42. Shin E W, Choi C H, Chang K S, Na Y H, Moon S H. Properties of Si-modified Pd catalyst for selective hydrogenation of acetylene. Catalysis Today, 1998, 44(3): 137–143
43. Shin E W, Kang J H, Kim W J, Park J D, Moon S H. Performance of Si-modified Pd catalyst in acetylene hydrogenation: The origin of the ethylene selectivity improvement. Applied Catalysis A, General, 2002, 223(1-2): 161–172
44. Ahn I Y, Kim W J, Moon S H. Performance of La_2O_3- or Nb_2O_5-added Pd/SiO_2 catalysts in acetylene hydrogenation. Applied Catalysis A, General, 2006, 308: 75–81
45. Kim W J, Ahn I Y, Lee J H, Moon S H. Properties of Pd/SiO2 catalyst doubly promoted with La oxide and Si for acetylene hydrogenation. Catalysis Communications, 2012, 24: 52–55
46. McKenna F M, Anderson J A. Selectivity enhancement in acetylene hydrogenation over diphenyl sulphide-modified Pd/TiO_2 catalysts. Journal of Catalysis, 2011, 281(2): 231–240
47. McCue A J, Anderson J A. Sulfur as a catalyst promoter or selectivity modifier in heterogeneous catalysis. Catalysis Science & Technology, 2014, 4(2): 272–294
48. McKenna F M, Wells R P K, Anderson J A. Enhanced selectivity in acetylene hydrogenation by ligand modified Pd/TiO_2 catalysts. Chemical Communications, 2011, 47(8): 2351–2353
49. McKenna F M, Mantarosie L, Wells R P K, Hardacre C, Anderson J A. Selective hydrogenation of acetylene in ethylene rich feed streams at high pressure over ligand modified Pd/TiO_2. Catalysis Science & Technology, 2012, 2(3): 632–638
50. McCue A J, McKenna F M, Anderson J A. Triphenylphosphine: A ligand for heterogeneous catalysis too? Selectivity enhancement in acetylene hydrogenation over modified Pd/TiO_2 catalyst. Catalysis Science & Technology, 2015, 5(4): 2449–2459
51. Han Y, Peng D, Xu Z, Wan H, Zheng S, Zhu D. TiO_2 supported Pd@Ag as highly selective catalysts for hydrogenation of acetylene

in excess ethylene. Chemical Communications, 2013, 49(75): 8350–8352

52. Zhang Y, Diao W, Williams C T, Monnier J R. Selective hydrogenation of acetylene in excess ethylene using Ag- and Au-Pd/SiO_2 bimetallic catalysts prepared by electroless deposition. Applied Catalysis A, General, 2014, 469: 419–426
53. Ma C, Du Y, Feng J, Cao X, Yang J, Li D. Fabrication of supported PdAu nanoflower catalyst for partial hydrogenation of acetylene. Journal of Catalysis, 2014, 317: 263–271
54. Cherkasov N, Ibhadon A O, McCue A J, Anderson J A, Johnston S K. Palladium-bismuth intermetallic and surface-poisoned catalysts for the semi-hydrogenation of 2-methyl-3-butyn-2-ol. Applied Catalysis A, General, 2015, 497: 22–30
55. Osswald J, Giedigkeit R, Jentoft R E, Armbrüster M, Girgsdies F, Kovnir K, Ressler T, Grin Y, Schlögl R. Palladium-gallium intermetallic compounds for the selective hydrogenation of acetylene Part 1: Preparation and structural investigation under reaction conditions. Journal of Catalysis, 2008, 258(1): 210–218
56. Osswald J, Kovnir K, Armbrüster M, Giedigkeit R, Jentoft R E, Wild U, Grin Y, Schlögl R. Palladium-gallium intermetallic compounds for the selective hydrogenation of acetylene. Part II: Surface characterization and catalytic performance. Journal of Catalysis, 2008, 258(1): 219–227
57. Friedrich M, Villaseca S A, Szentmiklósi L, Teschner D, Armbrüster M. Order-induced selectivity increase of Cu60Pd40 in the semi-hydrogenation of acetylene. Materials, 2013, 6(7): 2958–2977
58. Kim S K, Lee J H, Ahn I Y, Kim W J, Moon S H. Performance of Cu-promoted Pd catalysts prepared by adding Cu using a surface redox method in acetylene hydrogenation. Applied Catalysis A, General, 2011, 401(1-2): 12–19
59. Tierney H L, Baber A E, Kitchin J R, Sykes E C H. Hydrogen dissociation and spillover on individual isolated palladium atoms. Physical Review Letters, 2009, 103(24): 246102–246104
60. Kyriakou G, Boucher M B, Jewell A D, Lewis E A, Lawton T J, Baber A E, Tierney H L, Flytzani-Stephanopoulos M, Sykes E C H. Isolated metal atom geomretries as a strategy for selective heterogeneous hydrogenations. Science, 2012, 335(6073): 1209–1212
61. Boucher M B, Zugic B, Cladaras G, Kammert J, Marcinkowski M D, Lawton T J, Sykes E C H, Flytzani-Stephanopoulos M. Single atom alloy surface analogs in Pd0.18Cu15 nanoparticles for selective hydrogenation reactions. Physical Chemistry Chemical Physics, 2013, 15(29): 12187–12196
62. McCue A J, McRitchie C J, Shepherd A M, Anderson J A. Cu/Al_2O_3 catalysts modified with Pd for selective acetylene hydrogenation. Journal of Catalysis, 2014, 319: 127–135
63. Fu Q, Luo Y. Active sites of Pd-doped flat and stepped Cu(111) surfaces for H_2 dissociation in heterogeneous catalytic hydrogenation. ACS Catalysis, 2013, 3(6): 1245–1252
64. McCue A J, Shepherd A M, Anderson J A. Optimisation of preparation method for Pd coped Cu/Al_2O_3 catalysts for selective acetylene hydrogenation. Catalysis Science & Technology, 2015, 5 (5): 2880–2890
65. Pei G X, Liu X Y, Wang A, Li L, Huang Y, Zhang T, Lee J W, Jang B W L, Mou C Y. Promotional effect of Pd single atoms on Au nanoparticles supported on silica for the selective hydrogenation of acetylene in excess ethylene. New Journal of Chemistry, 2014, 38 (5): 2043–2051