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Using modifiers to specify stereochemistry and enhance selectivity and activity in palladium-catalysed, liquid phase hydrogenation of alkynes

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ABSTRACT

Enhancing selectivity is a key parameter in green chemistry. In this study, we have examined the liquid phase hydrogenation of alkynes over a palladium catalyst and used modifiers to enhance selectivity and activity. The reactions studied were the hydrogenation of 1-pentyne and 2-pentyne. Five modifiers were used, pentane nitrile and its respective amine, pentyl amine, 3-phenyl propionitrile and its respective amine, 3-phenyl propylamine and trans-cinnamonitrile. These modifiers were not hydrogenated under reaction conditions. It was possible to obtain high (>90%) selectivities to 1-pentene and cis-2-pentene at high conversion. The effect on rate was dependent upon the modifier and the alkyne. The effect of the modifier was the same whether added with or before the reactants. Competitive reactions confirmed that terminal alkynes and internal alkynes are hydrogenated on separate sites and do not interfere and that the modifier influences each separately.

1. Introduction

The selective hydrogenation of alkynes to alkenes is an area of catalysis that has been active for over 100 years and yet our understanding is not complete. Recent results [1–5] have revealed the importance of sub-surface hydrogen and carbon in determining the activity and selectivity of palladium catalysts. While work by Boitiaux et al. [6] showed that a particle size effect was in evidence when highly dispersed catalysts were used. Once having produced the alkene there are issues of isomerisation and subsequent hydrogenation. In some very elegant work Zaera [7] and references therein investigated alkene isomerisation and showed over Pt that the shape of the crystallite, and hence the crystal face, had a significant effect on trans–cis and cis–trans isomerisation such that the rate of each reaction was different depending on the starting isomer.

Modifiers are common in alkyne hydrogenation [8–10]. In ethyne hydrogenation carbon monoxide is typically added to inhibit ethane hydrogenation by what is normally considered a site blocking mechanism with the CO being more strongly bound to the surface than the ethane. Modifiers have also been used in the liquid phase the liquid phase and nitrogen containing modifiers have been reported in the literature [11–13] and in patents [14]. In general they are thought to compete for the surface in the same way as CO in ethyne hydrogenation, inhibiting the secondary reaction of the alkene. However the study by Moulijn and co-workers [13] indicates that on its own this effect did not explain the role of quinoline on alkyne hydrogenation. It has been suggested [12] that donation of the lone pair on the nitrogen to the metal can potentially change the electronic nature of the metal and hence change activity and selectivity, and indeed work by Yu et al. has shown evidence for this [15]. In this study, we have examined the role of nitrile and amine modifiers with both terminal and internal alkynes, looking at their effect on activity and selectivity.

2. Experimental

The catalyst used throughout this study was a 1% w/w Pd/θ-alumina (Johnson Matthey, characterised by a BET area of 97.6 $m^2\,g^{-1}$, a pore volume of 0.49 ml g^{-1}, a metal loading of 1 wt.% and a metal dispersion of 32.5%). All reactants were used without further purification. The reaction was carried out in a 0.5l Buchi stirred autoclave. 0.05 g of catalyst was added to 330 ml of degassed solvent, hexane. Reduction of the catalyst was performed *in situ* by sparging the system with H_2 (300 $cm^3\,min^{-1}$) for 30 min at 313 K while stirring the contents of the autoclave at 800 rpm. After reduction, the autoclave was adjusted to the appropriate reaction temperature of between 298 and 333 K under a nitrogen atmosphere. For both 1-pentyne and 2-pentyne, 1 ml was injected into an unstirred solution, followed by 20 ml of degassed hexane

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Table 1
First order rate constants ($\times 10^{-3}$ min^{-1}) for alkyne hydrogenation.

Alkyne	No mod.	PA	3-PPA	PN	3-PPN	TCN
1-Pentyne	32.9 ± 0.6	42.2 ± 1.1	36.6 ± 0.6	16.9 ± 0.4	14.1 ± 0.2	27.7 ± 0.7
2-Pentyne	18.8 ± 0.3	9.8 ± 0.6	7.5 ± 0.4	16.6 ± 0.2	18.0 ± 0.3	13.5 ± 0.1

Table 2
Selectivity (%) at 20% conversion for 1-pentyne hydrogenation.

	Pentane	Trans-2-pentene	1-pentene	Cis-2-pentene
No modifier	17.1	16.1	60.4	6.4
3PPA	8.4	3.0	87.1	1.4
PA	6.7	5.3	85.8	2.2
3PPN	21.9	18.5	52.0	7.6
PN	27.3	20.3	45.2	7.2
PN[a]	29.9	19.9	43.3	7.0
TCN	0.6	1.6	96.9	0.8

[a] PN added 30 min before 1-pentyne.

to ensure that all the reactant was washed into the reactor. For the competitive reactions, 1 ml of modifier was added with the reactant. The autoclave was then mixed briefly at a stirrer speed of 800 rpm and pressurised to 1 barg with N_2 and a sample was taken. The vessel was depressurised and then pressurised with H_2 to 2 barg. Following this the stirrer was set to a speed of 1000 rpm and samples taken. Liquid samples were analysed by GC using a 50 m CP-Al_2O_3/Na_2SO_4 column. Standard checks were undertaken to confirm that the system was not under mass transport control.

3. Results

The reactions studied were the hydrogenation of 1-pentyne and 2-pentyne. Four modifiers were used, pentane nitrile (PN, valeronitrile) and its respective amine, pentyl amine (PA, amyl amine), and 3-phenyl propionitrile (3-PPN) and its respective amine, 3-phenyl propylamine (3-PPA). These modifiers were not hydrogenated under reaction conditions. The first order rate constants for the reactions are reported in Table 1.

Surprisingly, in 1-pentyne hydrogenation, the amine modifiers enhance the rate of hydrogenation, whereas the nitrile modifiers decrease the rate of hydrogenation. With 2-pentyne the effects are almost reversed with the amine modifiers causing a reduction in hydrogenation rate while the nitriles have much reduced effect. Clearly the dominant functional group in the adsorption is the amine or nitrile whereas the aromatic ring has little effect. To examine the effect of when the modifier was added, PN was added to a reduced catalyst 30 min before 1-pentyne. The rate constant for 1-pentyne hydrogenation was 23.3 ± 0.8.

The effect of the modifiers on selectivity was also examined. A comparison of selectivity at 20% conversion for 1-pentyne is reported in Table 2 and for 2-pentyne in Table 3.

It is also of interest to see the effect of the modifiers on selectivity over the full range of conversion. This is shown in Fig. 1 for 1-pentyne hydrogenation and Fig. 2 for 2-pentyne hydrogenation.

With 1-pentyne the modifiers split into two groups, the amines, which increase selectivity and the nitriles, which decrease selectivity. Trans-cinnamonitrile however is the most effective modifier with selectivity to the alkene >90% at 95% conversion. For 2-pentyne hydrogenation all the modifiers enhance selectivity and enable >90% alkene selectivity to be achieved at high conversion.

Table 3
Selectivity (%) at 20% conversion for 2-pentyne hydrogenation.

	Pentane	Trans-2-pentene	1-pentene	Cis-2-pentene
No modifier	15.5	17.7	1.1	65.7
3PPA	0	3.2	0.3	96.5
PA	0	6.1	0.5	93.4
3PPN	1.7	13.5	1.1	83.8
PN	0	7.5	0.7	91.8
TCN	0.8	3.6	2.1	93.6

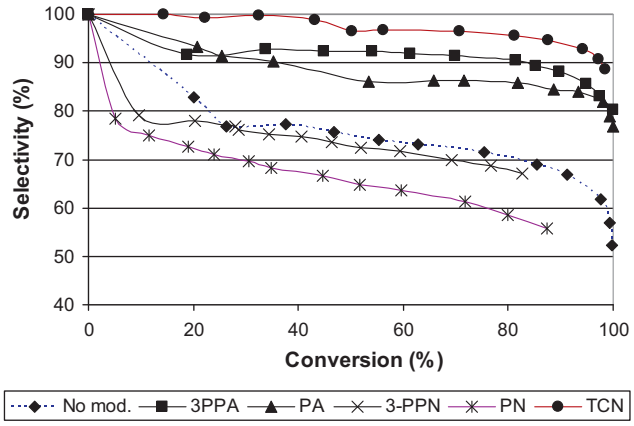

Fig. 1. Selectivity/conversion plot for 1-pentyne hydrogenation.

The competitive reaction between 1-pentyne and 2-pentyne was also examined. The rate constant for 1-pentyne hydrogenation, in the presence of equimolar 2-pentyne, was 32.7 ± 4.8 (c.f. 32.9 ± 0.6 in the absence of 2-pentyne), while the rate constant for 2-pentyne hydrogenation, in the presence of equimolar 1-pentyne, was 17.2 ± 3.2 (c.f. 18.8 ± 0.3 in the absence of 1-pentyne). These results indicate that the rate of hydrogenation of each alkyne is not influenced by the presence of the other.

The competitive reaction between the alkynes was repeated with PN present. PN was chosen because with 1-pentyne it caused a reduction in alkene selectivity whereas with 2-pentyne it enhanced alkene selectivity. To determine whether the PN was affecting the alkene selectivity in the same manner as when each alkyne was present in the absence of the other, the selectivity was measured and compared with a modelled selectivity taken from the individual reactions in the presence of PN at equivalent conversion. The results are shown in Table 4.

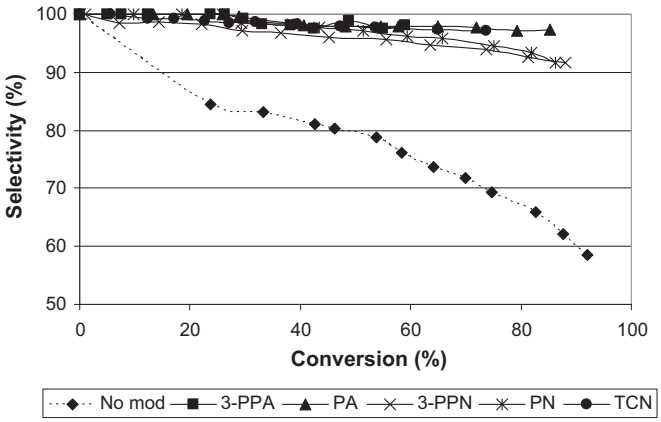

Fig. 2. Selectivity/conversion plot for 2-pentyne hydrogenation.

Table 4
Alkene selectivity (%) during competitive alkyne hydrogenation with and without PN at equivalent conversions.

	Trans-2-pentene	1-pentene	Cis-2-pentene
1-PY/2-PY, no modifier	16.6	30.4	53.0
1-PY/2-PY, modelled from individual runs	19.5	29.5	51
1-PY/2-PY, with PN modifier	22.7	35.8	41.6
1-PY/2-PY, modelled from individual runs with PN	23	33.5	43.5

4. Discussion

The effect of nitrile and amine modifiers in hydrogenation of C5-alkynes has been investigated. It is clear for the results presented that there is a difference in response to the modifier depending on whether the reactant is a terminal or internal alkyne and whether the modifier is an amine or nitrile.

Amines are known to be catalyst poisons and this action relates to the lone pair on nitrogen and its ability to donate to the metal. Hence aromatic amines where the lone pair is conjugated to the aromatic ring are much less deleterious to a reaction than aliphatic amines [16,17]. However, in contrast to this inhibition effect, the rate of reaction of 1-pentyne increases (Table 1) when pentyl amine and 3-phenyl-propyl amine are present. Similar behaviour has been observed with 1-butyne hydrogenation [11] where addition of piperidine resulted in a rate enhancement. The reason for this enhancement can be related to the strength of adsorption of the alkyne. Typically alkynes are strongly adsorbed and show either zero or slightly negative order kinetics. Hence the rational for the enhancement effect of the amine molecules argues that the amine donates electron density to the palladium and so reduces the strength of alkyne adsorption allowing a faster rate of hydrogenation to be achieved. However this argument only appears to hold for primary alkynes (1-butyne and 1-pentyne) and not for internal alkynes, where the effect of the amine modifiers on 2-pentyne hydrogenation is to significantly reduce the rate rather than enhance it. This difference in behaviour can be understood in terms of adsorption characteristics of terminal and internal alkynes. Terminal alkynes have been shown to hydrogenate at low coordination sites such as edge and corner atoms whereas internal alkynes favour terraces [18–20]. The results of the competitive reaction between 1-pentyne and 2-pentyne confirm that they react on different parts of the surface and do not influence each other. As the adsorption of amines is strong one may expect that they would preferentially adsorb at low coordination sites on the catalyst surface; in doing so they affect the reactivity of the terminal alkyne by reducing its strength of adsorption due to electron donation to the Pd hence allowing faster hydrogenation. Because the adsorption takes place on the edges and corners and the flexible modes of adsorption available to the terminal alkyne, we envisage that there is the potential for co-adsorption rather than competitive adsorption. With the internal alkyne, adsorption takes place on terrace and faces. Here we suggest the amine will compete directly with the alkyne and cause the reduction in activity observed.

The nitrile modifier is much less basic than the amine and hence any electron donation will be reduced, however it will still have the potential for strong adsorption due to the unsaturated nature of the C≡N triple bond. Hence the main effect of the nitrile species should be to reduce the activity and this is what is found. The effect is more pronounced with the 1-pentyne. Note that adding the modifier before 1-pentyne does not change the rate of hydrogenation or the alkene selectivity. Indeed the nitriles reduce the rate of 2-alkyne by very little. It is not immediately clear why this should be the case. It is possible that the strength of adsorption of the nitrile on the terraces is significantly less than on the edge and corner sites and so the 2-alkyne competes more effectively. When pentanenitrile was added to a mix of 1-pentyne and 2-pentyne it can be seen from the alkene selectivities (Table 4) that the modifier affects each alkyne independently. Modelling the selectivity values at equal conversion from the single alkyne/modifier reaction gives good agreement with the values found for the co-hydrogenation. This reinforces the separate site nature of the 1-alkyne and 2-alkyne hydrogenation with 1-pentene formed at edge sites and cis-2-pentene formed on the terraces. A recent study of 1-phenyl-1-propyne hydrogenation, another internal alkyne, using variable amounts of 3-PPN showed that, as the concentration of the modifier is reduced the rate constant for the hydrogenation of the internal alkyne increases (Fig. 3) [21] supporting the view that the effect of the nitrile modifier is related to strength of adsorption.

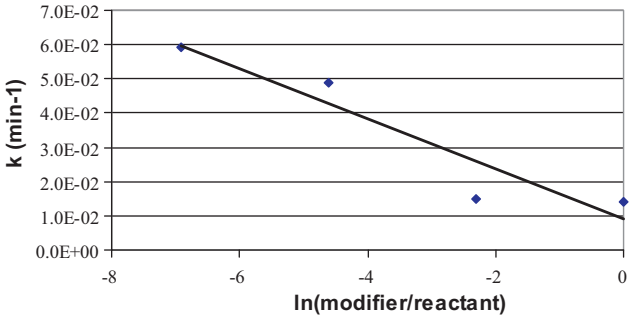

Fig. 3. The relationship between 3-PPN modifier concentration and rate constant for 1-phenyl-1-propyne [21].

Subsequent hydrogenation and isomerisation of the alkenes formed is in general significantly inhibited by the presence of either amine or nitrile and this is expected as re-adsorption of the alkene will be inhibited by the presence of the more strongly bound amine and nitrile. However the nitrile modifiers appear to enhance the conversion of the alkene when used in the presence of 1-pentyne. This is true whether the modifier is added before the alkyne or coincidentally. Separate tests using a 3PPN/1-pentene mix showed that the nitriles inhibited the hydrogenation of 1-pentene. Therefore the enhancement of the rate of alkene hydrogenation must occur before the 1-pentene desorbs from the surface. Note however that the same enhancement is not seen when the primary alkene is the cis-2-alkene suggesting that, like the alkynes there are differences in adsorption/hydrogenation for 1-pentene and cis-2-pentene. This is supported by work by Zaera [7] who found that cis/trans isomerisation is sensitive to surface structure and that certain surfaces favour cis/trans isomerisation whereas other favour trans/cis isomerisation. The effect of the modifiers on cis/trans isomerisation can be seen in Table 3. Even though all the modifiers inhibit alkene hydrogenation, isomerisation is sensitive to the modifier with the amines giving high cis:trans ratios (>15) while the nitriles give low cis:trans ratios ($\leq$ 12). TCN, the conjugated nitrile has cis:trans values closer to the amines.

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