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C-5 alkene hydrogenation: Effect of competitive reactions on activity and selectivity

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Abstract

The hydrogenation of 1-pentene, *cis*-2-pentene and *trans*-2-pentene was studied over a 1% Pd/alumina catalyst. The rate of hydrogenation was *cis*-2-pentene > 1-pentene > *trans*-2-pentene. As the system moved towards thermodynamic equilibrium in pentene isomers the rate constant changed to that of the *trans*-isomer in a competitive environment. In competitive hydrogenation between the alkenes the hydrogenation rate of 1-pentene and *trans*-2-pentene are enhanced while that of *cis*-2-pentene is decreased. In a competitive system between alkene and alkyne, the rate of 1-pentene hydrogenation is increased 20-fold, even after all the pentyne is reacted. Enhanced hydrogen transfer through a modified hydrocarbonaceous deposit is believed to be the cause. The results also support the concept of separate sites for alkyne and alkene in a competitive environment.

Keywords: Hydrogenation; 1-Pentene; Selectivity; Palladium; Alkenes; Competitive reactions

1. Introduction

Selective hydrogenation of alkynes and alkenes still remains an important topical issue in modern heterogeneous catalysis. Much of the early work in this area concentrated on low molecular weight species such as ethylene and acetylene and is reviewed in the following references [1–3]. However, more recently research interest has focused on the hydrogenation of higher molecular weight molecules.

Studies into the mechanism of higher alkyne hydrogenation have revealed that an extrapolation of the classical hydrogenation theories derived from ethyne studies is not applicable to higher alkyne systems [4]. To gain further insight into these systems, competing reactions can provide vital information on the role of the products and intermediates on reaction activity and selectivity, as well as giving an idea on the active sites of the catalyst.

A number of recent studies have investigated competitive hydrogenation reactions, such as phenyl acetylene and styrene on Pd/C [5], benzonitrile on higher alkynes [6], 1-pentyne and 2-pentyne [7,8] and competitive reactions of C6 and C8 species over palladium and platinum catalysts [9]. Various effects have been demonstrated in these studies, from rate depression of one or more of the competing reactants, to a rate enhancement of both reacting species.

This study aims to provide a comprehensive investigation of the C5 system, studying competitive reactions between the pentene isomers; 1-pentene, *trans*-2-pentene and *cis*-2-pentene. The effect of 1-pentyne and 2-pentyne additions on these systems will also be studied. The study has been designed to investigate the effect on activity and selectivity in a competing environment between alkynes and alkenes, internal and terminal bonds and the reaction between stereoisomers.

2. Experimental

The catalyst used throughout this study was a 1% w/w palladium on alumina supplied by Johnson Matthey. The support consisted of θ-alumina trilobes (S.A. $\sim 100\ m^2\ g^{-1}$) and the catalyst was sized to <250 μm for all catalytic studies. The alkenes and alkynes (all Aldrich, >99%) were used without further purification. No significant impurities were detected by GC. The gases (BOC, >99.99%) were used as received.

The reaction was carried out in a 0.5 l Buchi stirred autoclave equipped with an oil jacket and a hydrogen-on-

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demand delivery system. About 0.05 g of 1% Pd/Al_2O_3 was added to 330 ml of degassed solvent, 2,2,4-trimethylpentane. Reduction of the catalyst was performed in situ by sparging the solution with H_2 (300 $cm^3 min^{-1}$) for 30 min at 313 K at a stirring speed of 800 rpm. After reduction, the autoclave was adjusted to the appropriate reaction temperature of between 298 and 333 K under a nitrogen atmosphere. For the single reactants, 1 ml of 1-pentene, *cis*-2-pentene, *trans*-2-pentene, 1-pentyne or 2-pentyne was injected into an unstirred solution, followed by 20 ml of degassed 2,2,4-trimethylpentane. For the competitive reactions, 1 ml of each reactant was added prior to solvent injection. The autoclave was then mixed briefly at a stirrer speed of 800 rpm and pressurised to 1 barg with nitrogen and a sample was taken. The vessel was then depressurised and then pressurised with hydrogen to 2 barg. Following this the stirrer was set to a speed of 1000 rpm and samples were taken via a sample valve at defined time intervals. The liquid samples were analysed by gas chromatography on a Agilent 6890 Series. The column used was a 50 m Chrompack CP-Al_2O_3/Na_2SO_4.

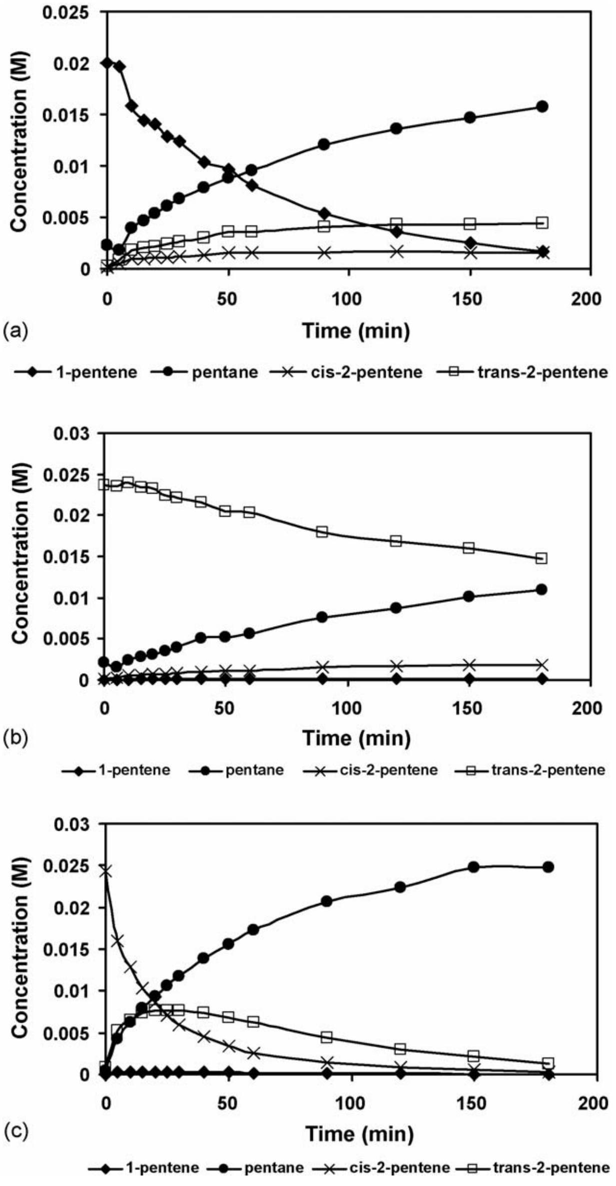

Fig. 1. (a) Reaction profile for 1-pentene hydrogenation; (b) reaction profile for *trans*-2-pentene hydrogenation; (c) reaction profile for *cis*-2-pentene hydrogenation.

3. Results

3.1. Competitive pentene reactions

Three alkene competitive hydrogenation reactions were investigated, 1-pentene/*cis*-2-pentene, 1-pentene/*trans*-2-pentene and *cis*-2-pentene/*trans*-2-pentene. The single systems were also studied as references. Fig. 1 shows the reaction profile

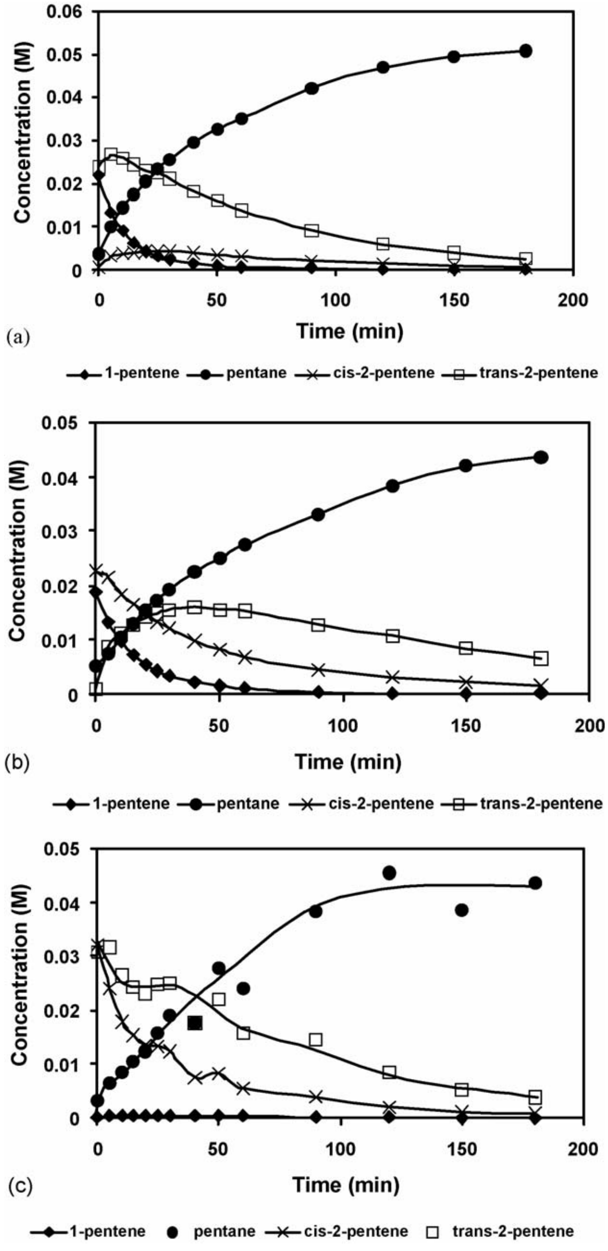

Fig. 2. (a) Reaction profile for 1-pentene/*trans*-2-pentene hydrogenation; (b) reaction profile for 1-pentene/*cis*-2-pentene hydrogenation; (c) reaction profile for *cis*-2-pentene/*trans*-2-pentene hydrogenation.

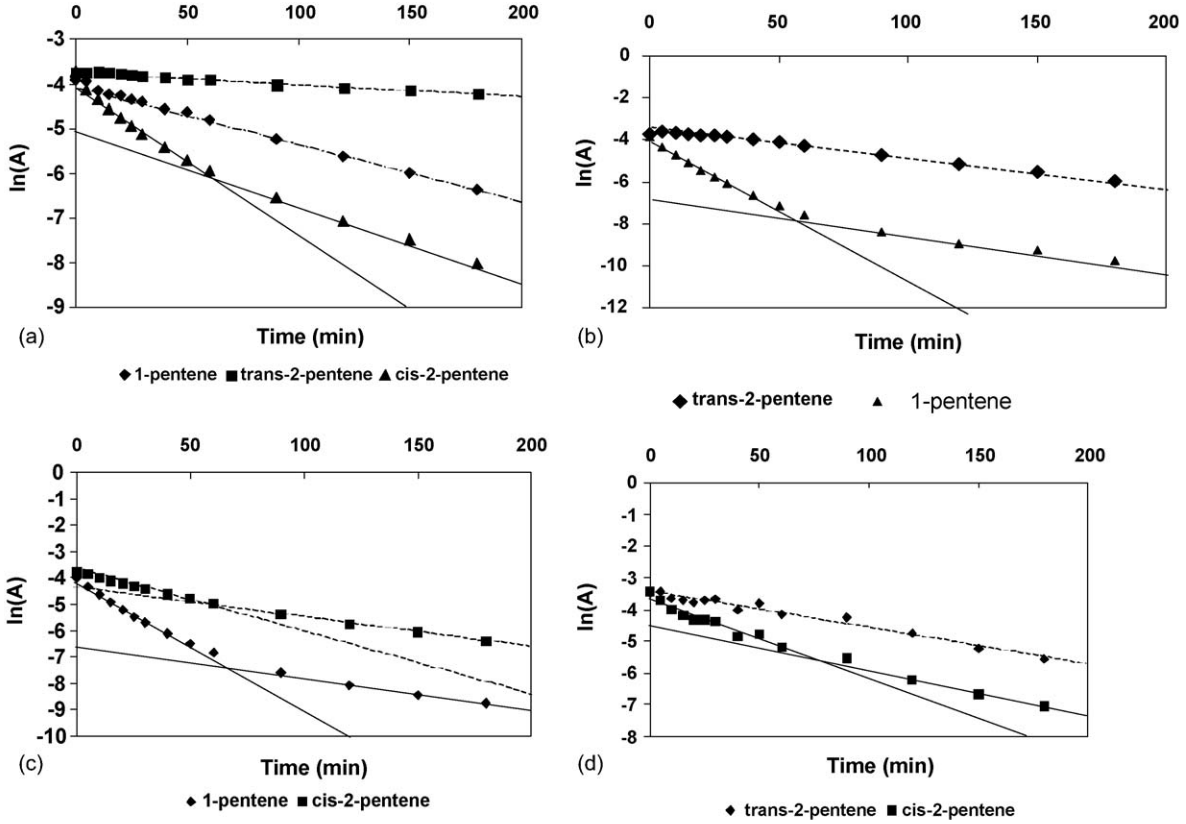

Fig. 3. (a) Plot of $\ln(A) = -kt + \ln(A)_0$ for 1-pentene, *cis*-2-pentene and *trans*-2-pentene hydrogenation reactions; (b) plot of $\ln(A) = -kt + \ln(A)_0$ for 1-pentene/*trans*-2-pentene competitive hydrogenation reaction; (c) plot of $\ln(A) = -kt + \ln(A)_0$ for 1-pentene/*cis*-2-pentene competitive hydrogenation reaction; (d) plot of $\ln(A) = -kt + \ln(A)_0$ for *cis*-2-pentene/*trans*-2-pentene competitive hydrogenation reaction.

for the single hydrogenation systems. Fig. 1a shows the hydrogenation profile for 1-pentene and it can be seen that along with hydrogenation to pentane there is isomerisation to *cis*-2-pentene and *trans*-2-pentene. It can also be seen that while there is the formation of these isomers, they have not themselves begun to hydrogenate by 180 min. Fig. 1b displays the reaction profile for *trans*-2-pentene hydrogenation, it can be seen that the rate of the reaction is considerably slower than for 1-pentene hydrogenation, while for *cis*-2-pentene hydrogenation (Fig. 1c) the hydrogenation is faster than both the 1-pentene and *trans*-2-pentene systems. During *cis*-2-pentene hydrogenation the *trans*-2-pentene formed through isomerisation begins to hydrogenate after 30 min. It is interesting to note that for both the internal alkenes the isomerisation to 1-pentene is very minimal, while the 1-pentene system isomerises readily to the internal pentene isomers. Fig. 2 presents the reaction profiles for the competitive hydrogenation systems.

All of the hydrogenation reactions of the alkenes in both singular and competitive systems were fitted against the standard equation for first order, $\ln(A) = -kt + \ln(A)_0$, kinetics for the loss of each reactant. Fig. 3a shows the first order plot for the singular reactant systems. 1-Pentene and *trans*-2-pentene show a straight line relationship fits of greater than 0.99. However, *cis*-2-pentene does not show a linear relationship for

Table 1
Reaction rate constants for the individual and competitive pentene hydrogenation systems

Reactant	Rate constants (min^{-1})	Rate trend	Conversion at break (%, ~60 min)
1-Pentene	0.014		59
cis-2-Pentene	0.035/0.017		89
trans-2-Pentene	0.003		3
1-Pentene/*cis*-2-pentene	0.047/0.015	↑	94
1-Pentene/*trans*-2-pentene	0.062/0.017	↑	97
cis-2-Pentene/1-pentene	0.020/0.012	↓	70
cis-2-Pentene/*trans*-2-pentene	0.026/0.016	↓	82
trans-2-Pentene/1-pentene	0.013	↑	46
trans-2-Pentene/*cis*-2-pentene	0.011	↑	46

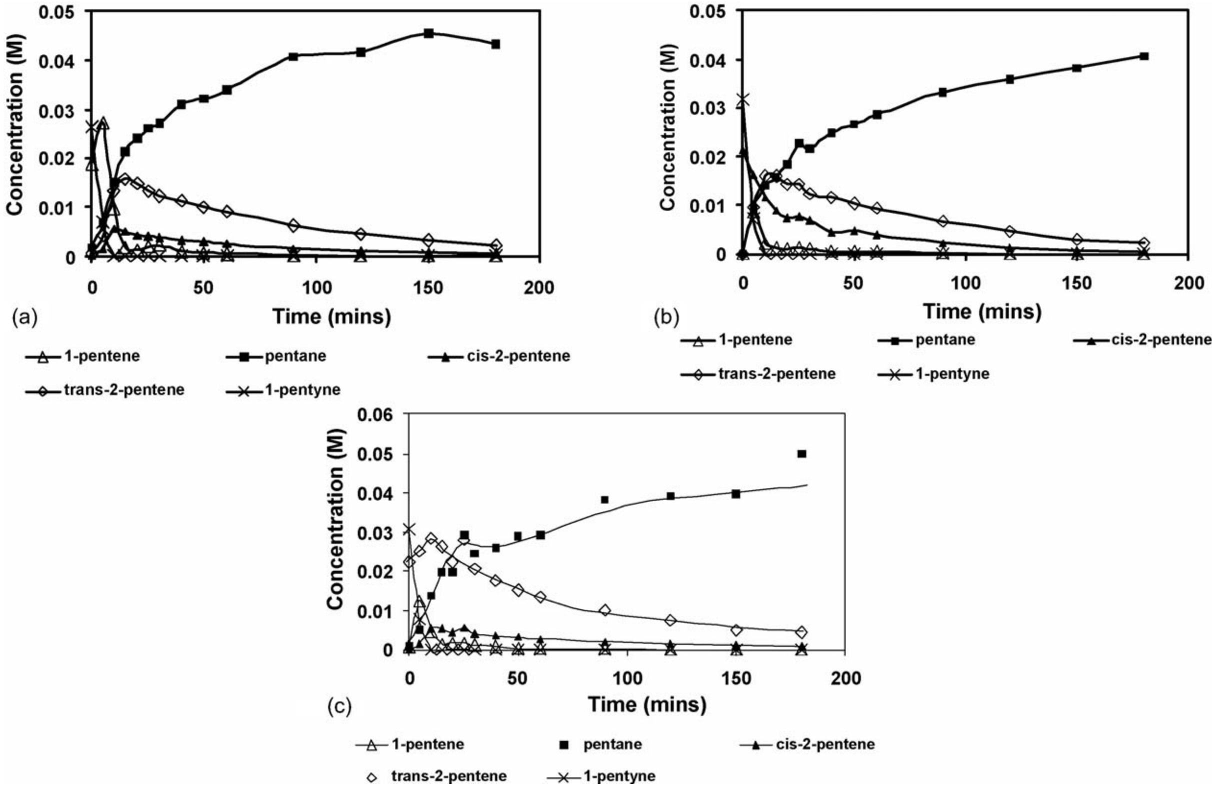

Fig. 4. (a) Reaction profile for 1-pentene/1-pentyne hydrogenation; (b) reaction profile for *cis*-2-pentene/1-pentyne hydrogenation; (c) reaction profile for *trans*-2-pentene/1-pentyne hydrogenation.

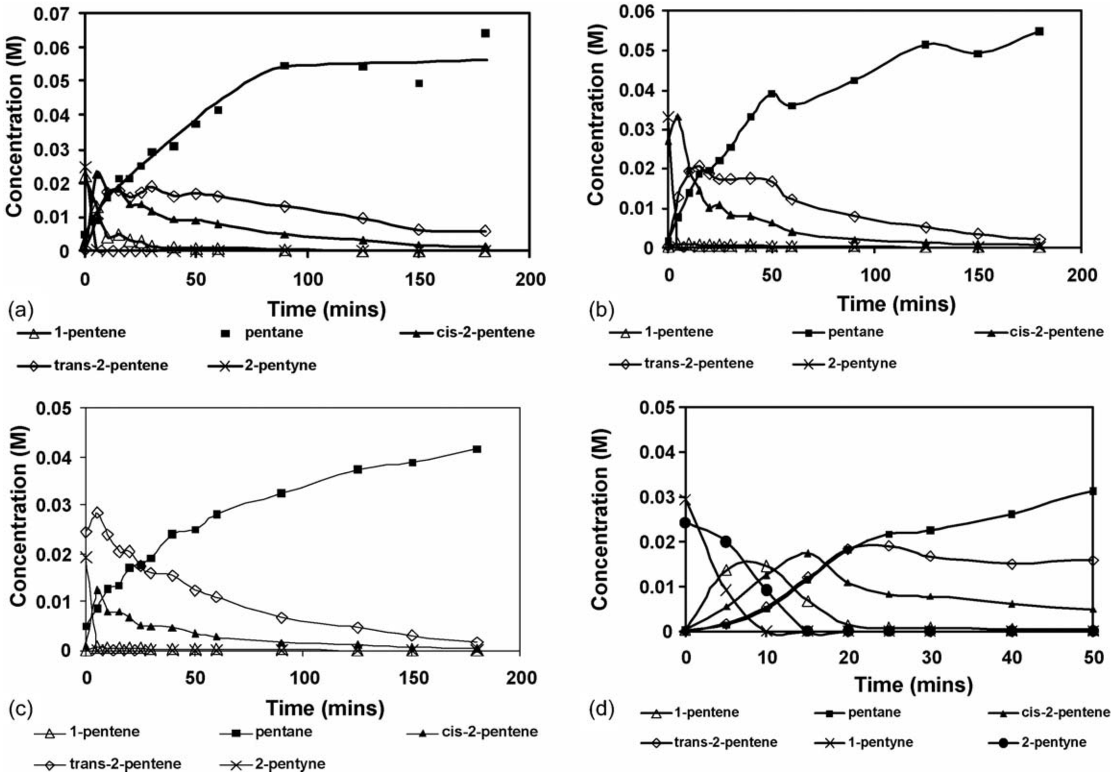

Fig. 5. (a) Reaction profile for 1-pentene/2-pentyne hydrogenation; (b) reaction profile for *cis*-2-pentene/2-pentyne hydrogenation; (c) reaction profile for *trans*-2-pentene/2-pentyne hydrogenation; (d) reaction profile for 1-pentyne/2-pentyne hydrogenation.

Table 2
Reaction rate constants for the competitive pentyne hydrogenation systems, showing additional reaction characteristics

Competing reaction	Rate constant for pentenes (min^{-1})	Reaction characteristics
1-Pentene/1-pentyne	0.27	90% conversion in 15 min
1-Pentene/2-pentyne	0.08	90% conversion in 25 min
cis-2-Pentene/1-pentyne	0.037/0.017	78% conversion at break; 30 min
cis-2-Pentene/2-pentyne	0.046/0.019	70% conversion at break; 50 min
trans-2-Pentene/1-pentyne	0.011	79% conversion at 180 min
trans-2-Pentene/2-pentyne	0.015	93% conversion at 180 min

the 180 min, but does when the first order kinetic plot is divided into two time periods. The break is observed after 89% of the *cis*-2-pentene has been converted to products.

Fig. 3b–d show the first order plots for the various competitive reactions of the pentene isomers. From these plots it can be seen that when the *trans* isomer reacts it shows a linear relationship over the 180-min time period studied, while both the *cis*-2-pentene and 1-pentene show a break in the first order kinetic plot. Table 1 presents reaction rates constants for the singular and competitive systems along with percentage conversion at the break in the first order plots. It can be seen that in a single component system *cis*-2-pentene has the fastest rate of reaction with an initial rate constant of 0.035 min^{-1}. Whereas 1-pentene has a rate constant of 0.014 min^{-1} and *trans*-2-pentene, which reacts very slowly, a rate constant of only 0.003 min^{-1}. As expected the trend of these rate constants falls in line with the percentage conversion of each reactant after 60 min, 89, 3, and 59% for *cis*-2, *trans*-2 and 1-pentene, respectively.

3.2. Effect of pentynes on pentene hydrogenation

The effect of pentyne addition was also investigated for the competitive hydrogenation of the pentene systems. 1-Pentyne and 2-pentyne were added with each of the pentene isomers and the reaction profiles observed are shown in Figs. 4 and 5. As a comparison, the competitive hydrogenation of 1-pentyne and 2-pentyne was also investigated and is shown in Fig. 5d. Although this reaction was performed over 180 min, the first 50 min are displayed to illustrate the complexity in the initial stages of the reaction. Due to the rapid hydrogenation of the pentynes (in most cases they were fully reacted within the first 5 min), under competing conditions, calculation of reaction rate constants was impossible. The reaction rate constants however could be calculated for the pentenes and are shown in Table 2.

4. Discussion

4.1. Single systems

The results show that for single component systems the order in the rates of hydrogenation derived from rate constants over the 1% Pd/Al_2O_3 catalyst is *cis*-2-pentene > 1-pentene ≫ *trans*-2-pentene. The reason for the sluggish hydrogenation activity of *trans*-2-pentene may result from it being the thermodynamically more stable isomer (thermodynamic mixture: 81, 17.5, and 1.5% for *trans*-2, *cis*-2 and 1-pentene, respectively) [10] and thus more reluctant to isomerise or hydrogenate when it reaches this preferred state. Bond and Winterbottom [11] observed a similar trend for *n*-butene hydrogenation over alumina-supported palladium, where the hydrogenation activity of the *trans*-isomer was significantly slower than *cis*-2-butene and 1-butene [11]. The *cis*-2-pentene first order plot shows evidence of two first order rate constants with change in gradient at approximately 60 min. At this point the *trans* isomer is now the dominant species in solution. An inspection of the relative amounts of the three isomers in the reaction mixture reveals a ratio of 69:29:2 for *trans*-2-pentene:*cis*-2-pentene:1-pentene, respectively (Table 3). Therefore, the behaviour of the system is now dependent on the *trans* isomer and not the original reactant, *cis*-2-pentene. For 1-pentene and *trans*-2-pentene, at the 60-min time interval both are still the dominant species in their corresponding single component system (Table 3). For the *cis*-2-pentene system the high level of isomerisation to the *trans* isomer is most likely a result of the system heading towards equilibrium and a slow hydrogenation rate of the *trans*-2-pentene that is formed. For both the internal pentenes there is no significant isomerisation to the 1-pentene isomer, while 1-pentene freely isomerizes to a mixture of the *cis* and *trans* isomers. It is likely that this behaviour is due to thermodynamic considerations given that the thermodynamic ratio of pentenes is 81, 17.5, and 1.5% for *trans*-2, *cis*-2 and 1-pentene, respectively. An examination of the initial rates of isomerisation (Table 4), which represents a period where the reaction is well removed from equilibrium, confirms this previous observation as the isomerisation of both 2-pentenes to 1-pentene show negligible activity, exhibiting initial isomerisation reaction rates of 3×10^{-6} moles min^{-1}. This observation is verified in a study of liquid phase hydrogenation of pentenes by Bond and Rank [10], who found that *cis*-2-pentene isomerises to give chiefly *trans*-2-pentene and a kinetically inaccessible quantity of 1-pentene [10]. This high isomerisation activity of *cis*-2-pentene is also observed when selectivity is compared at equal conversion (Table 5).

Table 3
Ratio of pentene isomers after 60 min of reaction for the single hydrogenation systems

Reactant	Ratio of isomers (%)		
	trans-2-Pentene	*cis*-2-Pentene	1-Pentene
1-Pentene	27.0	11.5	61.5
cis-2-Pentene	68.9	29.0	2.1
trans-2-Pentene	93.9	5.4	0.7

Table 4
Initial rates of hydrogenation and isomerisation for the single pentene hydrogenation reactions

Reactant	Initial rate of hydrogenation (moles min^{-1}) × 10^{-5}	Isomer formed	Rate of isomerisation (moles min^{-1}) × 10^{-5}
1-Pentene	23	*trans*-2-Pentene	8.5
		cis-2-Pentene	3.8
cis-2-Pentene	34	1-Pentene	0.3
		trans-2-Pentene	16
trans-2-Pentene	4.7	1-Pentene	0.3
		cis-2-Pentene	2.7

In the literature there are two main mechanisms proposed for alkene isomerisation, the addition–abstraction mechanism, via adsorbed alkyl species or through the abstraction–addition mechanism involving π-allylic surface intermediates [1]. The degree of isomerisation over metal catalysts generally decreases in the order: Pd > Ni > Rh > Os ≈ Ir ≈ Pt and the extensive double bond isomerisation often observed for palladium and nickel catalysts has been attributed to the formation of the adsorbed π-allyl species [12]. However, a number of recent studies have strongly favoured the addition–abstraction mechanism, via adsorbed alkyl species [13–15]. The intermediates in this mechanism, which was in vogue before the proposal of a π-allyl intermediate [11], have all been identified and it must now be taken as the correct description.

4.2. Competitive pentene hydrogenations

For the competitive hydrogenation reactions between the three pentene isomers several points are apparent. Firstly, the terminal alkene, 1-pentene, in a competing system exhibits a dramatic increase in reaction rate in the presence of *cis*- or *trans*-2-pentene. Similarly the *trans*-2-pentene rate constant, 0.0028 min^{-1}, is greatly enhanced in the presence of either of the other competing isomers. Contrary to this the most active isomer, *cis*-2-pentene, undergoes a reduction in reaction rate. Rate enhancement has previously been attributed to an increase in the capacity for hydrogen transfer through an adsorbed competing reagent [16]. In a recent study, Doyle et al. [17] showed that hydrogenation of pentenes only took place when subsurface hydrogen was present. In light of this increasing the concentration of subsurface hydrogen and/or more effective transfer of sub-surface hydrogen to the reactant could achieve rate enhancement. Whether one or both of these options is occurring cannot be determined from this study, however either would explain the enhancement in rate for 1-pentene in a competitive system. The rate of *trans*-2-pentene hydrogenation, in a single component system, is very slow, however in the presence of another C5 species its hydrogenation rate is increased up to five-fold. It is possible that the factors outlined above play a role but another aspect should also be considered. The lack of activity for the *trans* isomer may be a result of its thermodynamic stability, however the presence of second adsorbing isomer, such as 1-pentene, the *trans*-2-pentene strength of adsorption may be weakened and hence allow a faster rate of hydrogenation. The more difficult result to interpret is that the individual hydrogenation rate of *cis*-2-pentene decreases in a competitive environment although the other reactant exhibits a rate increase. Given that only one of the reactants exhibits a decrease in rate it is unlikely that there has been a reduction in hydrogen flux. Also *cis*-2-pentene must adsorb sufficiently to perturb the other alkene. It can also be seen that 1-pentene has the most significant effect of the rate. After 5 min the conversion of *cis*-2-pentene as a single reactant is 34%, whereas in the presence of 1-pentene the *cis*-2-pentene conversion is reduced to only 6% (*trans*-2-pentene reduces the *cis*-2-pentene conversion to 24%). It seems likely that the competing alkene is reducing the concentration of *cis*-2-pentene on the surface and hence reducing the rate.

Examining Table 1, shows that the rate constants for *cis*-2-pentene and 1-pentene in all competing cases undergo a change similar to that observed during *cis*-2-pentene hydrogenation in the single component system. Analysis of the ratio of species in solution at the change in reaction rate constant, shown in Table 6, reveals that, at the break point in the linear first order plots (Fig. 3), *trans*-2-pentene is the dominant species and the reaction rate constant is now dependent on this species under competing conditions. It can be seen that the rate constants for *trans*-2-pentene, under all competing circumstances, are approximately constant at 0.011–0.017 min^{-1}. As the reactions proceed each system strives to reach isomeric equilibrium, as it gets closer to this point the system reaches a constant reaction rate which is a result of the dominant *trans*-2-pentene in solution.

Table 5
Selectivity to products at 20% conversion for the pentene isomers in the single hydrogenation systems

Reactant	% Selectivity to products at 20% conversion			
	Pentane	1-Pentene	*cis*-2-Pentene	*trans*-2-Pentene
1-Pentene	79.0	–	2.0	19.0
cis-2-Pentene	39.1	2.9	–	57.9
trans-2-Pentene	82.0	1.7	16.3	–

Table 6
Percentage of each pentene isomers at the point of change of rate constant for the pentene competitive systems

Competing reagents	Percentage of isomers at break in 1st order *k*		
	trans-2-Pentene	*cis*-2-Pentene	1-Pentene
1-Pentene/*cis*-2-pentene	65.4	30.0	4.6
1-Pentene/*trans*-2-pentene	79.7	17.4	2.9
trans-2-Pentene/*cis*-2-pentene	72.9	25.5	1.6

Table 7
Percentage conversion after 5 min for the pentyne isomers in the competitive pentyne/pentene couple reactions

	Percentage conversion after 5 min				
	Single system	1-Pentene	*cis*-2-Pentene	*trans*-2-Pentene	Other pentyne
2-Pentyne	100	98.4	100	100	17.6
1-Pentyne	74.8	73.4	77.4	74.6	68.9

4.3. *Effect of pentynes on pentene hydrogenation*

The competitive reactions between alkynes and alkenes show differing behaviour in the literature and it has been shown that the behaviour of a given alkyne/alkene couple is not necessarily predictable from other alkyne/alkene systems [4]. The rate enhancement of 1-pentene in the presence of 1-pentyne shows a remarkable 20-fold increase with 90% of 1-pentene reacted by 15 min, whereas in the single component system 90% conversion was not reached until 180 min. Classical theory suggests that the alkene will not react until all of the alkyne has first reacted and an examination of Fig. 5 appears to confirm this view. However, as with a previous study of a 1-pentene/1-pentyne competitive reaction [4], it was observed that the existence of each species still has a positive effect on the rate of hydrogenation of the other even after one has been fully hydrogenated. For example, once 1-pentyne has fully reacted and is not detectable in the system, 1-pentene still reacts 20-fold faster than on a fresh catalyst. This rate enhancement has been previously proposed to be a result of the formation of a hydrocarbonaceous residue that increases the rate of hydrogen transfer to the competing species [4]. This concept has been strengthened by a recent study [14] that has shown that there can be considerable quantities of carbonaceous material retained by a palladium catalyst and that the nature of the deposit affects the activity of the catalyst. A rate enhancement was also observed for 1-pentene in the presence of 2-pentyne with a six-fold increase in the rate constant. There is no increase in *cis*-2-pentene rate in a competitive situation with 1-pentyne, while in the presence of 2-pentyne the rate is increased only slightly from 0.035 to 0.046 min^{-1}. *Trans*-2-pentene does increase in rate with the pentyne isomers, but no more than it does in any competitive situation. It therefore seems that the terminal 1-pentene species, most likely due to its ability to bond perpendicular to the surface, benefits the most from a residue formed from the pentyne species and that hydrogen transfer to a terminal alkene group must be much more efficient than to an internal alkene. The small benefit of rate enhancement for *cis*-2-pentene species with 2-pentyne and not 1-pentyne may result from the presence of different active sites, one for terminal groups, i.e. perpendicular binding and the other for internal groups, i.e. parallel binding. Jackson and Kelly proposed such active sites for a similar hydrogenation system [4]. The same behaviour can be observed in the *trans*-2-pentene system, with a greater enhancement of initial rate in the 2-pentyne competitive reaction over the 1-pentyne system.

Although it is problematic to obtain rate constants or even initial rates of reaction for the individual pentyne systems, some indication of the speed of reaction can be taken from the conversion after 5 min, which is the first sample point. Table 7, compares the effect of conversion over the different competitive systems, including, the individual systems and the 1-pentyne/2-pentyne reaction. There is no significant difference in the amount of pentyne reacted in the single component system compared to a system with a competing pentene. However, the 1-pentyne/2-pentyne system surprisingly shows a massive decrease in 2-pentyne activity along with a small depression in 1-pentyne activity. This indicates that there is competitive hydrogenation occurring on the same sites and 1-pentyne hydrogenation is favoured over 2-pentyne hydrogenation. Taken with the results from the alkene/alkyne competitive systems we can propose that there are different sites responsible for alkene and alkyne hydrogenation, which accounts for the rates of alkyne not being affected in an alkene/alkyne system. This is consistent with work by Al-Ammar and Webb who using isotopic labelling invoked a multiple site model for ethyne and ethene hydrogenation [18,19].

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