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Pd catalysed hexyne hydrogenation modified by Bi and by Pb

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ABSTRACT

Two Pd/Al_2O_3 catalysts of different loadings and dispersions were modified by the addition of various amounts of Bi and studied in the hydrogenation of 1-hexyne and 2-hexyne and in the consecutive reactions of the products formed. Catalyst behaviour was compared with a commercial Lindlar catalyst and Pb-free Pd/$CaCO_3$. Results are consistent with a preference of Bi to occupy step and edge sites while leaving the terraces and extended facets relatively unaffected. Results show that while Bi had little effect on the rate of the 1-hexyne hydrogenation, the rate of subsequent reactions of the 1-hexene formed were suppressed. In this context, Bi was a more effective modifier than Pb. This situation was reversed when reactions were performed using 2-hexyne. Results are discussed in terms of the reaction mechanism and key intermediates in the process and the roles of bismuth, relative to lead, in creating an appropriate ensemble of surface Pd atoms to permit control of selectivity.

1. Introduction

Improved selectivity in industrial catalytic processes is key in terms of reducing waste and improving performance. Supported metals are widely used in hydrogenation and other reactions although they are not intrinsically highly selective. Selectivity is often improved by the use of modifiers which, in general can be separated into two groups; reversible adsorbates and irreversible adsorbates. The later grouping, in terms of their mechanism of operation might also include alloying and surface bimetallics since, in the main, they operate by modifying the size of the available surface metal atom ensemble and thus promote reactions which can be accommodated by the restricted size/shape of the available metal atom array. Although it might be inferred that selectivity is enhanced by geometric/ensemble effects, it is often difficult to separate these factors from the electronic influence of the secondary atoms. Well-known examples here include Pt catalysts with Sn, Ge or Re/S for the reforming of Naphtha [1]. The use of S in directing selectivity where multiple functionalities are present, e.g. in unsaturated aldehydes is also known and would be an example of an irreversible adsorbate induced selectivity. It might be argued that they are more widely used in cases where concurrent (parallel) reactions pathways are to be controlled. Reversible adsorbates are often added to avoid consecutive reactions and in particular, operate well under circumstances where the reaction product, whose subsequent reactions are to be suppressed, have a lesser adsorption enthalpy than the starting reagent. Reversible adsorbates with intermediate adsorption strengths may then be used to suppress secondary reactions without impacting on the primary (desired) reaction. A good example of this scenario would be selective hydrogenation of alkynes where the alkene is the desired product and over-hydrogenation to the alkane is to be avoided. For example, CO is introduced into ethylene streams contaminated by acetylene where it is desirable to remove the latter before contact is made with the polymerisation catalyst. In the liquid phase, the Lindlar catalyst exploits a similar property of quinoline, to deactivate the catalyst for secondary reactions thereby permitting high selectivity to be retained to high conversion of the alkyne [2]. This catalyst is rather unique in the context of the description regarding categorisation of modifiers in that in addition to the use of the reversible/competitive adsorbate, it also makes use of Pb as an irreversible dopant to steer reactions involving the stereoselective reduction of the alkyne function to *cis*-alkene with low accompanying yields of *trans*-alkene and alkane. Environmental concern regarding the use of soluble lead compounds in synthesis is such that an alternative catalyst not involving use of lead would be welcomed. In the work outlined here, the use of bismuth as a potential lead substitute is assessed.

Selective gas phase alkyne hydrogenation has been widely studied mainly as a consequence of the industrial relevance to understanding how ethyne can be eliminated from ethene feedstreams [3–5]. However these reactions simultaneously deposit carbonaceous residues on the catalyst surface and there is evidence that this carbon containing overlayer and/or subsurface carbon, may influence selectivity [6]. Therefore, extrapolating findings to the three-phase liquid hydrogenation system where carbon deposition is much less significant, should be done with caution and in par-

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ticular, the use of findings relevant to structure sensitivity. There is limited available data concerning any potential structure sensitivity for three-phase alkyne hydrogenation [7,8] although experiments conducted using Pd particles in the range 6 to 14 nm using 1-hexyne [7] and comparing behaviour of Pd (111) and (110) for 2-hexyne hydrogenation [9] suggest some degree of sensitivity which could be exploited through selective deposition of modifier.

Several studies have dealt with Bi as a potential surface modifier. Attard et al. [10] studied S and Bi on Pt/graphite and determined their effect on catalyst morphology on the basis of cyclic voltammetry (CV) measurements by comparison with CVs of Pt single crystals [11]. It was concluded that sulphur occupied terrace sites and at $\vartheta = 0.26$, bismuth occupied only $(111) \times (111)$ and $(100) \times (111)$ step/kink sites with a slight occupation of the (100) terrace sites and no occupation of the (111) terrace sites. These results are entirely consistent with studies of Bi deposition on Pt(775) stepped crystal [12]. A study which prepared Bi doped Pd/SnO_2 by introducing Bi into solution and allowing equilibration in the presence of hydrogen, did not, unambiguously determine the nature or location of the added Bi although it was suggested that these decorated lower-coordinated Pd atoms in high index planes [13]. Bi is often combined with Pd-based catalyst for improved performance in selective oxidation [14,15]. Keresszegi et al. [15,16] deposited Bi mainly as adatoms onto the supported Pd particles. Most of the Bi atoms (73%) were located on the Pd and were more dispersed than the Pd itself. The remaining 27% of Bi was presumed to be present as $Bi_2O_3{\cdot}xH_2O$ on the Al_2O_3 support. They concluded that the geometric blocking of a fraction of active sites was consistent with results obtained in the oxidation of 1-phenylethanol rather than models which relied upon partially or completely oxidised forms of the promoter [16]. The latter interpretation was used to explain improved performance of Pt/Bi/C catalysts in selective oxidation of glyceric to hydoxypyruvic acid [17]. Other interpretations include a role of Bi in maintaining high Pd dispersion and controlling the valency state of Pd [14]. In the present study, the use of Bi as a modifier of supported Pd catalysts was investigated in order to better understand whether hydrogenation reactions of internal and terminal alkynes could be manipulated by the use of such modifiers.

2. Experimental

Pd/Al_2O_3 catalysts with nominal loadings of 1 and 5% were prepared using $Pd(NO_3)_2$ (Johnson Matthey $Pd(NO_3)_2{\cdot}5H_2O$, 45.3% Assay) and γ-Al_2O_3 Degussa-C. These were calcined at 300 °C for 1 h and reduced at 150 °C for 1 h before any characterisation was carried out or before exposure to Bi. Addition of the later involved a solution of $Bi(NO_3)_3{\cdot}5H_2O$ (Aldrich 98% $Bi(NO_3)_3{\cdot}5H_2O$) that had been dissolved in 2% acetic acid and which was added to the catalyst via a dropping funnel into a round bottom flask under acidic (pH 3.0), reducing conditions. The amount of Bi deposited was controlled by varying the contact time (between 5 and 75 min) between the Pd/Al_2O_3 and the Bi containing solution. Sample notation involved the weight loading of Pd and *x*mBi where *x* refers to the contact time in minutes between catalyst and Bi solution used in preparing the modified catalyst. Commercial samples of Lindlar catalyst (5% $PdCaCO_3$/Pb) and 5% Pd/$CaCO_3$ (both Alfa Aeser) were used as reference materials. Note that throughout this work the Pb-modified Pd/$CaCO_3$ catalyst is referred to as Lindlar catalysts but was used as received without the addition of quinoline, as used in the original study by Lindlar [18].

Bi content of the samples were obtained by difference by measuring the Bi remaining in solution after exposure to the Pd/Al_2O_3. AAS was performed on a Varian Spectra AA-10 using a Bi hollow cathode lamp. The signal intensity from the lamp was optimised before a 5 point calibration curve was obtained. The samples were analysed three times to ensure reproducibility.

A CE Instruments TPDRO 1100 was used for CO chemisorption and uptake data used to determine dispersion and loss of surface available Pd atoms resulting from Bi deposition. Samples were placed in a reactor tube and purged using N_2 gas. 5% H_2/N_2 was then introduced while the temperature was increased at 20 K min^{-1} to 150 °C and then held at this temperature for 1 h. The sample was held at this temperature for a further 30 min in a flow of oxygen-free N_2 (20 $ml\,min^{-1}$). The temperature was maintained at 20 °C whilst CO was pulsed (loop volume was 0.452 ml) into a stream of He at 10 min intervals.

FTIR spectra of CO adsorbed on reduced catalysts surface were recorded on a Perkin Elmer 1720X spectrometer at 4.0 cm^{-1} resolution averaging 25 scans to obtain the desired s/n ratio. Pressed powder sample discs were placed in a quartz holder and moved up to the furnace, at 150 °C. Heated cable was employed to prevent water condensation within the system. H_2 gas was passed over the sample at atmospheric pressure at 50 $cm^3\,min^{-1}$ for 1 h after which time the cell was evacuated for 30 min at reduction temperature. An IR spectrum was recorded of the sample at beam temperature before exposure to the adsorbate. Equilibrium CO pressures were recorded on an Edwards active strain gauge.

Catalyst (0.05 g) was *ex situ* reduced at 150 °C and then transferred to a round-bottomed flask where toluene (40 g) was added before flowing hydrogen at 1 atm pressure. The reaction was initiated when 0.5 g hexyne (1-hexyne Aldrich 97%) was added (0.12 $mol\,dm^{-3}$). This provides reactant:surface Pd ratios in the range 1730–5240. Unless otherwise stated, all reactions were conducted at 25 °C with constant stirring at 1100 rpm. Stirring speeds were periodically checked using an external stroboscope. Experiments conducted at different stirring speeds and using a range of catalyst masses, confirm that under conditions of reaction, the rates were not mass transfer limited. Aliquots (0.2 cm^3) were removed at routine intervals for analysis. The latter was conducted using a Varian 3400 GC fitted with autosampler and an Al_2O_3 MAPD capillary column.

3. Results

Characteristics of the samples are compiled in Table 1. The two Bi-free Pd catalysts gave CO uptakes of 15.76 and 29.59 $\mu mol\,g_{cat}^{-1}$ for the 1 and 5 wt% loaded samples suggesting dispersions of 33.5 and 12.6% respectively using an assumed CO:Pd ratio of 1:2 [19]. These equate to average particle sizes of approximately 3.4 and 8 nm, respectively. These figures were consistent with TEM analysis which also confirmed that the procedures involved in the addition of Bi did not modify Pd particle size. Increasing the contact time between Pd catalyst and Bi solution increased the amount of residual deposited Bi although the amount retained by the cata-

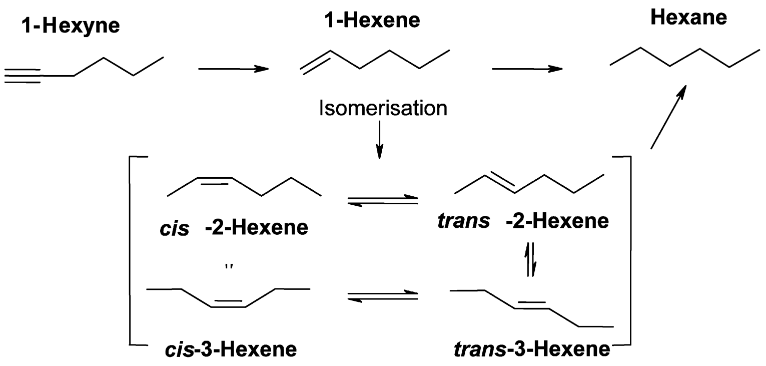
Table 1
Characteristics of Pd/Al_2O_3 and Bi modified catalysts.

Sample	CO uptake[a]	Dispersion (%)	$\mu mol\,Bi\,g_{cat}^{-1}$[b]	Bi:Pd[c]
1% Pd/Al_2O_3	15.76	33.5	0	–
1% Pd/$Al_2O_3$5mBi	15.34		0.6	0.02:1
1% Pd/$Al_2O_3$15mBi	11.61		27.8	0.88:1
5% Pd/Al_2O_3	29.59	12.6	0	–
5% Pd/$Al_2O_3$15mBi	29.38		14.2	0.24:1
5% Pd/$Al_2O_3$75mBi	17.97		19.4	0.54:1
Lindlar	30.98	13.2	0	–
5% Pd/$CaCO_3$	35.15	15.0	0	–

[a] $\mu mol\,g_{cat}^{-1}$.

[b] Moles of Bi on catalyst on the basis of calculated Bi remaining in preparation solution from AAS analysis.

[c] Surface atomic ratios calculated assuming a 2:1 Pd:CO ratio and assuming all Bi is deposited on Pd surface.



Scheme 1. Routes to potential products following the hydrogenation of 1-hexyne.

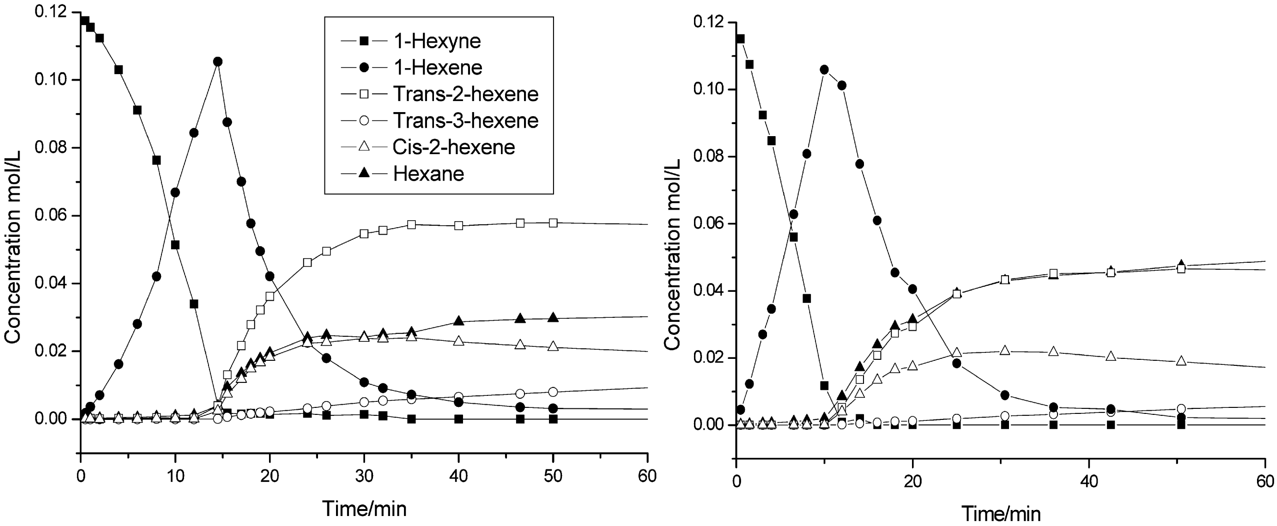


Fig. 1. Reaction profiles for the hydrogenation of 1-hexyne at 298 K over (left) 1% Pd/Al_2O_3 and (right) 5% Pd/Al_2O_3.

lyst showed particle size/loading/dispersion dependence (Table 1). For an equivalent exposure time (15 min) the higher dispersed, 1% Pd/Al_2O_3 retained a greater amount of Bi (2.78×10^{-5} compared with 1.42×10^{-5} $\text{mol}\,g_{\text{cat}}^{-1}$) compared to the higher loaded catalyst resulting in a greater Bi:exposed Pd atom ratio (Table 1). While this may suggest site specific uptake of Bi, it should be noted that some differences between the data calculated on the basis of moles Bi consumed, and the predicted number of sites blocked and leading to reduced CO chemisorption volumes indicate that some of the Bi may have been deposited on the support.

Fig. 1 shows the reaction profiles of 1-hexyne hydrogenation conducted over unmodified Pd catalysts of 1 and 5% loading. While the higher loaded sample shows a straight line consistent with zero order kinetics up to high (ca. 95%) conversion, the 1% loaded sample shows a plot shape indicative that reaction rate increased as 1-hexyne was consumed and consistent with a profile where inhibition due to strong reactant adsorption exists. Subsequently, a direct comparison of rate for the two catalysts loadings is complicated. However, if an instantaneous rate at 50% is chosen for comparative purposes, the rate for the 1% sample can be calculated as 12 $\text{mmol}\,\text{min}^{-1}\,\text{g}^{-1}$ which equates to a turn-over frequency (TOF) of 6.3 s^{-1}. This compares with a value of 3.2 s^{-1} for the 5% loaded sample. In both cases, 1-hexyne is almost completely reacted to produce 1-hexene before the consecutive reaction products (Scheme 1) from reaction of 1-hexene are detected (Fig. 1). This leads to similar maximum yields of 88% to 1-hexene for both catalysts at the point where all hexyne has been hydrogenated. Beyond this point where all hexyne is removed, a number of products were formed (Fig. 1), consistent with the details shown in Scheme 1 and these include *cis*- and *trans*-2-hexene and hexane and *trans*-3-hexene. The first 3 of these appeared simultaneously whereas the latter was produced at a significantly lower rate and appeared to be formed as a product of reaction of one (or both) of the 2-hexenes. Formation rate of hexane was greater on the 5% catalyst than the lower loaded sample and after ca. 40 min of reaction, when little 1-hexene remained, this was the dominant product along with *trans*-2-hexene for that catalyst (Fig. 1). The hexane concentration at this stage was noticeably lower for the 1% catalyst and this was compensated for, to some extent by the greater quantity of *trans*-2-hexene formed.

To ascertain as to whether plateaux emerging after 35 min reaction time (Fig. 1) were the result of slow intrinsic reaction rates of the components of the system or whether deactivation resulting from site blocking accompanied earlier stage conversion, an experiment was performed where a further quantity of 1-hexyne was added after 30 min reaction. As shown in Fig. 2, this led to an instant cessation of reaction involving the hexene isomers and 1-hexyne was reacted exclusively and at a similar rate to the reaction over fresh catalyst. After hydrogenation of hexyne was complete, the 1-hexene was converted with similar selectivities as observed over fresh catalyst (Fig. 2).

Fig. 3 shows profiles over the 1% $Pd/Al_2O_3$15mBi catalysts as representative of the impact of treating the 1% loaded catalyst with Bi. On comparing the profiles with those of the Bi-free 1% Pd/Al_2O_3 (Fig. 1) it can be seen that the hexyne removal still gave a profile which showed an accelerating rate with conversion although the instantaneous rate at 50% conversion had dropped from 12.0 to 8.7 $\text{mmol}\,\text{min}^{-1}\,\text{g}^{-1}$. However, if the loss of Pd sites by

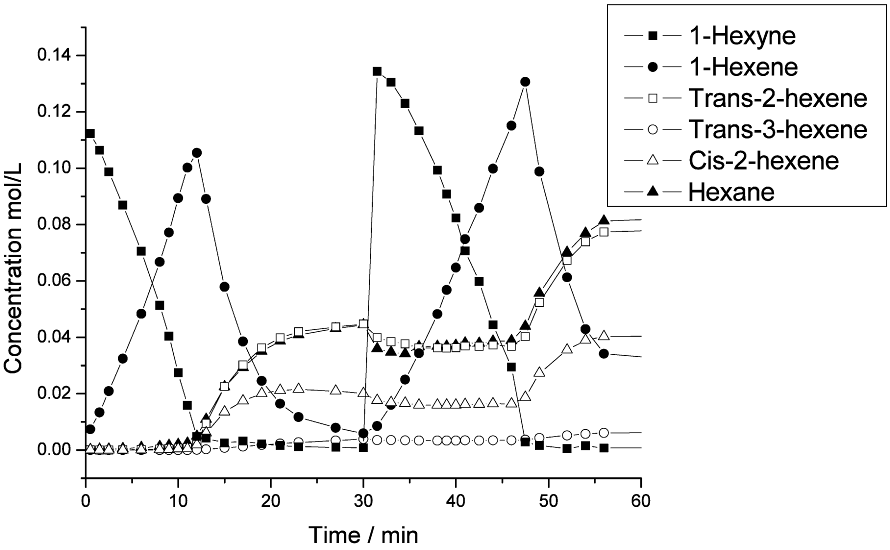


Fig. 2. Reaction profiles for 1-hexyne hydrogenation at 298 K over 5% Pd/Al_2O_3 where a second aliquot of reagent was added after 30 min.

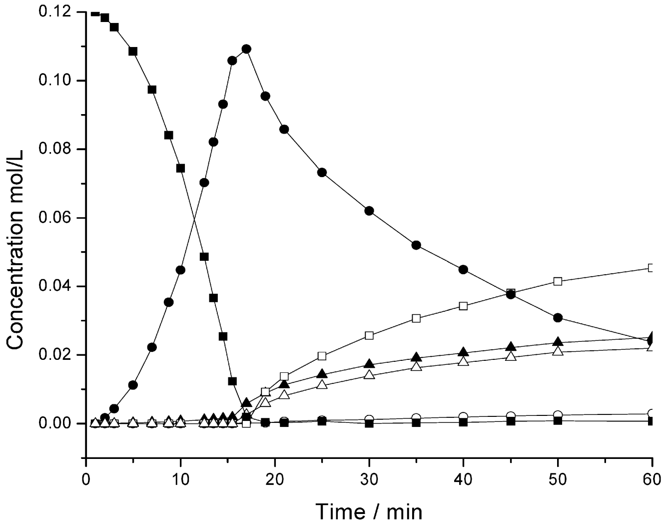


Fig. 3. Reaction profiles of 1-hexyne at 298 K over 1% Pd/$Al_2O_3$15mBi (symbols as in Figs. 1 and 2).

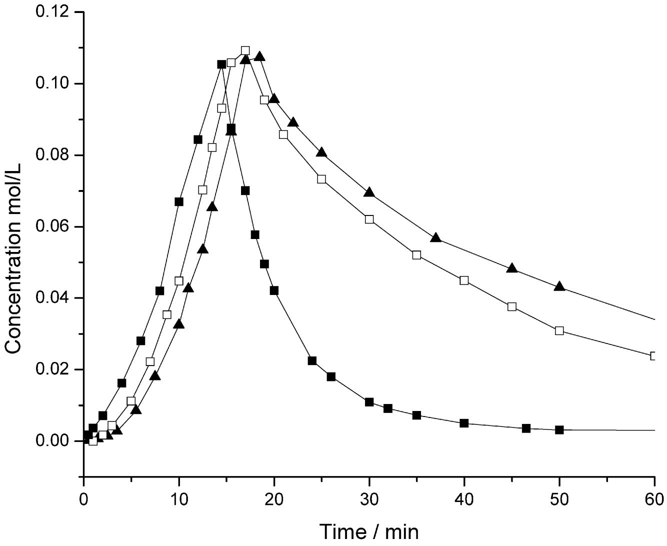


Fig. 4. Plot of formation and subsequent conversion of 1-hexene at 298 K over 1% Pd/Al_2O_3 (filled squares), 1%Pd/$Al_2O_3$5mBi (open squares) and 1% Pd/$Al_2O_3$15mBi (filled triangles).

Bi blocking is considered (CO chemisorption data, Table 1), then the rate of reaction per exposed Pd site (at 50% conversion) becomes 6.2 compared with 6.3 s^{-1} for the Bi-free sample. However, the TOF for the subsequent reaction of 1-hexene, calculated from the instantaneous rate when the concentration was 0.08 mol dm^{-3} dropped from 5.4 to 1.7 s^{-1}. The suppression of the rate of removal of 1-hexene and the rate of formation of the subsequent products is also clear from the fact that at 35 min reaction time, the concentrations of the products had not entered the plateau range observed for the Bi-free sample at this point, and that the conversion of 1-hexene was only roughly 50%.

An alternative method of comparing Bi and Bi free-samples, was to isolate the 1-hexene data alone since the profiles for this single intermediate contain the relative rates of removal of hexyne and the subsequent rate data for the removal of the intermediate. As shown in Fig. 4, although there was a slight displacement in the time-axis, the curve shapes reflecting the rates of 1-hexene formation (≈ rate of hydrogenation of hexyne) could be effectively superimposed, indicating that the addition of Bi had little impact on the initial reaction. However, the tailing of the plot with increasing Bi deposition time (Fig. 4) is clear evidence for the suppression of secondary reactions. The move from the Bi-free catalyst which shows a symmetrical profile to the asymmetrical profiles for the Bi containing samples, can also be expressed in terms of the relative turn over frequencies at fixed concentration. Again using the arbitrary value of 0.08 mol dm^{-3} as before, the relative TOF ratios (1-hexene formation ≈ 1-hexyne hydrogenation/1-hexene removal) were calculated as 1.2, 2.5 and 3.6 for 1% Pd/Al_2O_3, 1% Pd/$Al_2O_3$5mBi and 1% Pd/$Al_2O_3$15mBi, respectively.

In order to derive additional information regarding the location of deposited Bi, FTIR spectra of adsorbed CO were recorded at increasing pressures after *in situ* reduction of the samples. Both samples showed 3 main features with two appearing below 2000 cm^{-1} due to multiply bound CO and one above 2000 cm^{-1} due to on-top or linearly bound adsorbate [19,20]. The latter appeared at ca. 2076 cm^{-1} for both samples at the maximum CO pressures used (Fig. 5). Bands shifted to higher frequencies as a function of CO pressure consistent with expectations for coverage dependant CO coupling effects. Spectra of samples which had been exposed to Bi showed less intense features than Bi-free samples (compare *y*-axis scales) consistent with expectation on the basis

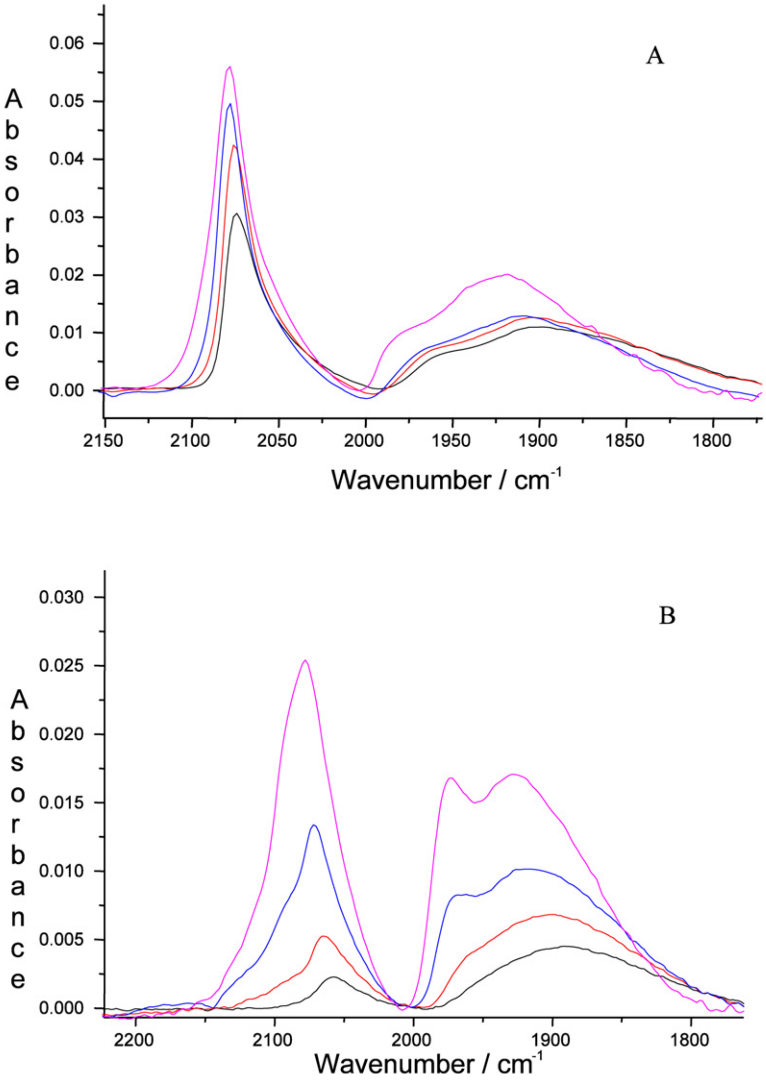


Fig. 5. FTIR spectra of (A) 1% Pd/Al_2O_3, and (B) 1% $Pd/Al_2O_3$15mBi after exposure to pressures of 0.1, 2, 10 and 20 Torr CO at 298 K.

of reduction of uptake indicated by pulse chemisorption data (Table 1). In particular, the band due to linearly adsorbed CO was ca. half the intensity. The overall integrated intensity may not, however, have been reduced by half as, in the presence of Bi, the band was considerably broader, as reflected by the asymmetry towards higher frequencies resulting from the presence of an additional, unresolved linear feature. An additional observation was that the bands due to the multiply bound states showed a much greater pressure dependence for Bi treated surfaces (Fig. 5B) and at the maximum pressure of CO the features at 1973 and 1927 cm^{-1} were of equivalent intensity whereas their counterparts (at 1978 and 1921 cm^{-1}) showed a preference for the lower frequency component.

In order to determine whether Pb and Bi might have equivalent roles in surface Pd modification, 1-hexyne reaction was studied over commercial Lindlar (Pb modified $Pd/CaCO_3$) and lead-free $Pd/CaCO_3$. Samples had the same loading as our 5% Pd/Al_2O_3 sample and pulse chemisorption measurements indicate that samples were of a similar dispersion (Table 1). Reaction profiles (Fig. 6) are also similar to those shown by the 5% Pd/Al_2O_3 in terms of the ca. zero order removal of 1-hexyne and symmetrical profile of the 1-hexene formation/conversion. The Pb-free $Pd/CaCO_3$ (Fig. 6) and 5% Pd/Al_2O_3 (Fig. 1) show a greater degree of similarity in terms of the relative amounts and formation rates of hexane and *trans*-2-hexene in that in both cases, the profiles for these products were almost completely superimposed. The Lindlar catalyst showed greater selectivity to *trans*-2-hexene than to hexane (Fig. 6). However, the fairly similar behaviour of both samples for this reaction suggests that the addition of Pb did not yield the benefits which were gained by addition of Bi to Pd catalyst in terms of reducing the rate of 1-hexene conversion without suppressing its rate of formation as exemplified in Fig. 4. Only when reaction was performed in the presence of quinoline at half the molar equivalent of 1-hexyne, could the conversion rate of 1-hexene be significantly suppressed (with no impact of 1-hexyne hydrogenation rates) and in such a case, no differences between Pb-free $Pd/CaCO_3$ and Lindlar catalyst could be observed [21].

Significant discrimination between the Pb-free $Pd/CaCO_3$ and Lindlar could be observed when 2-hexyne was used as substrate (Fig. 7) rather than 1-hexyne (Fig. 6). Both samples show equivalent zero order behaviour with similar rates of conversion of the initial 2-hexyne. However, in the case of the Pb treated Pd (Lindlar), virtually zero 2-hexene was converted until all of the 2-hexyne was hydrogenated, leading to a maximum ca. 100% selectivity (and 100% yield) to the *cis*-alkene (Fig. 7). In the case of the Pb-free $Pd/CaCO_3$ a maximum yield to *cis*-hexene of ca. 84% was obtained largely as a consequence of the formation of *trans*-2-hexene. Note that the latter appeared to result from isomerisation of the *cis*-hexene rather than as a primary product of hexyne hydrogenation as extrapolation to zero concentration did not coincide

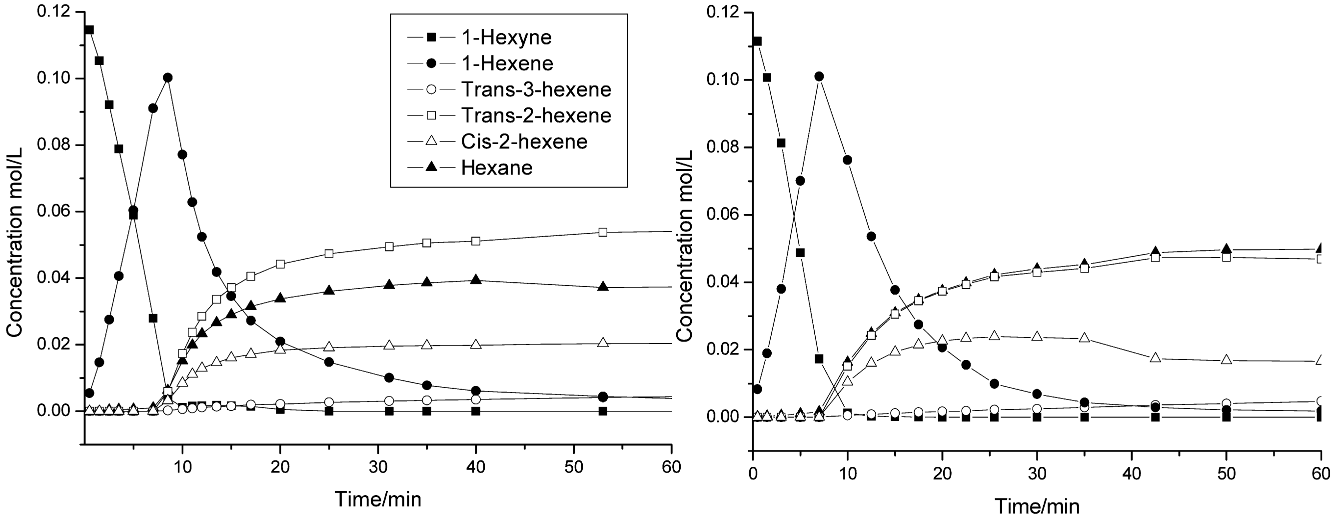


Fig. 6. Reaction profiles for the hydrogenation of 1-hexyne at 298 K over (left) Lindlar catalysts and (right) 5% Pd/$CaCO_3$.

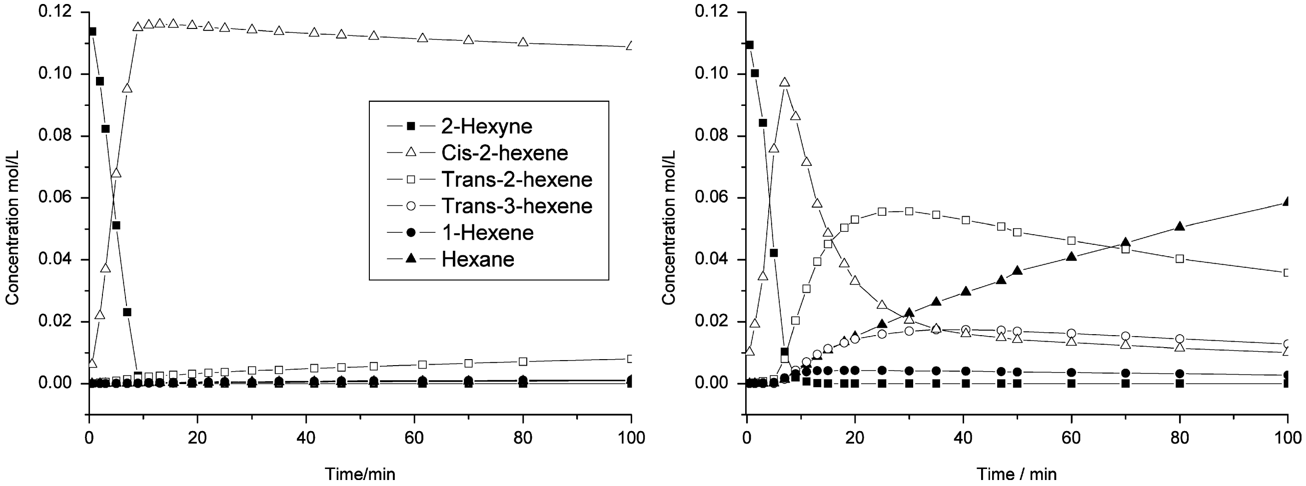


Fig. 7. Reaction profiles for the hydrogenation of 2-hexyne at 323 K over (left) Lindlar catalysts and (right) 5% Pd/$CaCO_3$.

with the origin. The significant role played by lead in preventing consecutive reactions of the *cis*-hexene is illustrated by the fact that after 100 min of reaction, this product represented 95% of the total C_6 hydrocarbons, whereas the same product represented only 12% of the C_6 hydrocarbons in the system containing the Pb-free catalysts at the same stage.

The 2-hexyne reaction was performed, at 298 K over the two unmodified Pd/Al_2O_3 samples to determine any influence of dispersion. Profiles show that rates of 2-hexyne hydrogenation (Fig. 8) are less than the rate of 1-hexyne hydrogenation (Fig. 1). However, of greater significance is that fact that once formed, the *cis*-2-hexene is very unreactive over the better dispersed 1% Pd/Al_2O_3 but undergoes more rapid transformation over the poorer dispersed 5% Pd/Al_2O_3. The main product of the transformation was *trans*-2-hexene showing that isomerisation, rather than hydrogenation to hexane was the key reaction which was more facile on the 5% catalyst than on the 1% sample.

Given that the rate of *cis*-hexene reaction was greater over the 5% Pd/Al_2O_3 than 1% Pd/Al_2O_3, the former sample was selected in order to determine whether addition of Bi to such a sample would influence the rate at which *cis*-hexene, formed by 2-hexyne hydrogenation, underwent reaction. The reaction was conducted at 323 rather than 298 K in this instance to allow a higher conversion to be attained over a similar time period and thus allow greater scope to observe any impact of Bi on the overall reaction pathways. Under these conditions, 5% Pd/Al_2O_3 (Fig. 9) performs similarly to 5% Pd/$CaCO_3$ (Fig. 7) and the behaviour is not significantly modified by the addition of Bi (Fig. 9). A slight reduction in the rate of 2-hexene conversion was noted and this appears to result from a suppression of the rate of hydrogenation to hexane.

4. Discussion

4.1. Structure sensitivity

As indicated recently by Semagina et al. [7] there is a deficiency in data concerning potential structure sensitivity for three-phase alkyne hydrogenation although their own study noted that initial TOF for 1-hexyne hydrogenation was low and constant for particle sizes up to 11 nm and then increased for particles above this size. Selectivity towards 1-hexene however, was not influenced by particle size. Results here for 1 and 5% loaded Pd/Al_2O_3 catalysts (Fig. 1) with average particles sizes of 3.4 and 8 nm, respectively, show differences, both in terms of profile shape (i.e., reaction order) and TOF. The linear, zero order profiles found for 5% Pd/Al_2O_3 are consistent with profiles for a similarly loaded Pd/Al_2O_3 used for 3-hexyne and di-*tert*-butylacetylene hydrogenation [2] for 2% Pd on silica monolith for hydrogenation of 3-methyl-1-pentyn-3-ol [22] and for phenylacetylene half-hydrogenation over ca. 1% Pd using vitreous supports [23]. However, Silvestre-Alvero et al. [24] re-

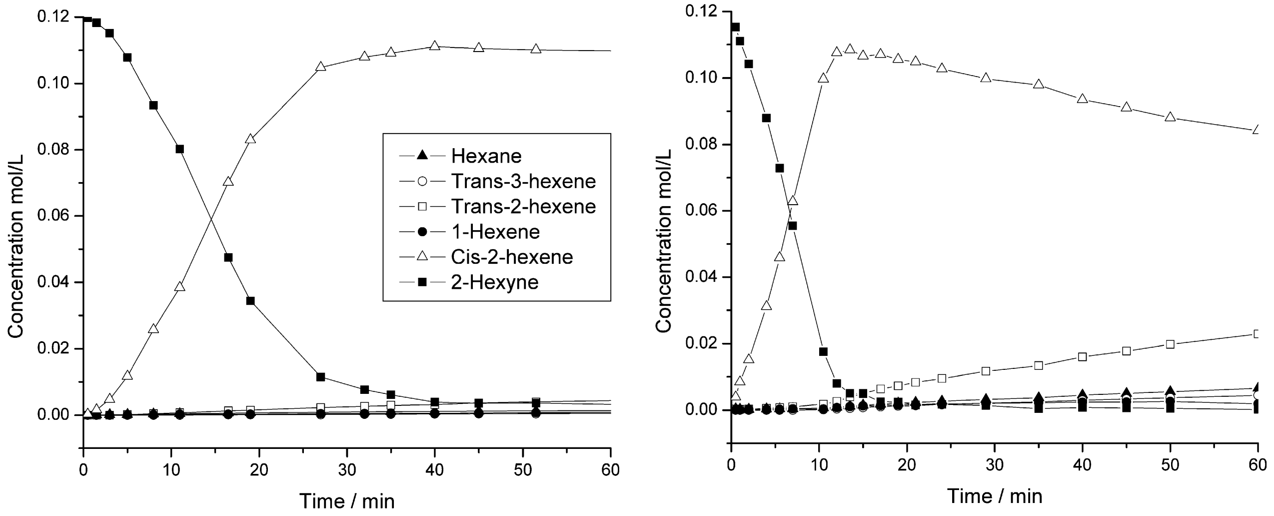


Fig. 8. Reaction profiles for the hydrogenation of 2-hexyne at 298 K over (left) 1% Pd/Al_2O_3 and (right) 5% Pd/Al_2O_3.

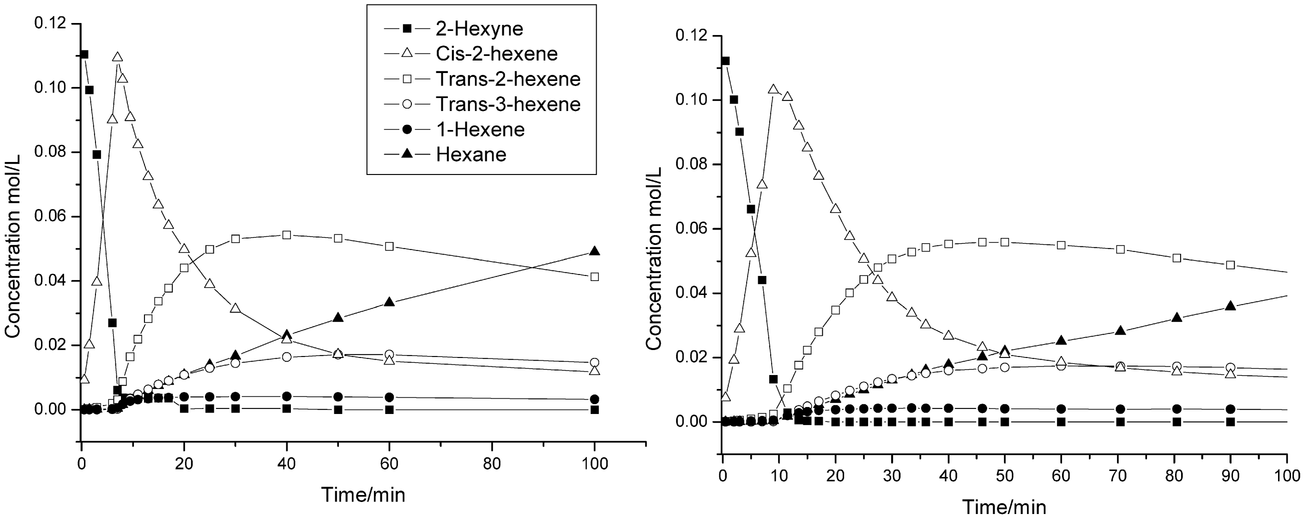


Fig. 9. Reaction profiles for the hydrogenation of 2-hexyne at 323 K over (left) 5% Pd/Al_2O_3 and (right) 5% $Pd/Al_2O_3$75mBi.

port variation in profile shape in 1,3-butadiene hydrogenation as a function of particle size and only when the model catalyst particle size reached ca. 7.7 nm in diameter, did the reaction show near zero order kinetics. Deviation from this behaviour (resulting in concave type conversion *vs* time plots as shown for 1% catalyst here (Fig. 1)) was attributed to strong butadiene adsorption which inhibited adsorption of hydrogen. Note that when a test reaction was conducted at 3 rather than 1 atm, the hydrogenation of 1-hexyne showed a zero order, linear plot and the rate increased by a factor of 1.73 [21]. It is apparent therefore that strong 1-hexyne adsorption is responsible for suppressing the initial rate of 1-hexyne hydrogenation over the 1% Pd/Al_2O_3 catalyst here although when compared at ca. 50% conversion or a solution concentration of 0.06 $\text{mol}\,\text{dm}^{-3}$ (Fig. 1) the rate (TOF) was greater than over the 5% loaded sample. The apparently conflicting trend obtained by Semagina et al. [7] arises due to these authors selecting initial TOF using a relatively high solution concentration (0.5 $\text{mol}\,\text{dm}^{-3}$) to compare the effect of particle size which would place their conditions in the "adsorption/desorption-limited regime" rather than the "kinetic regime" [24]. Results here clearly demonstrate that under appropriate reaction conditions, samples with higher dispersion show intrinsically faster reaction rate. Note that in the semihydrogenation of phenylacetylene and 4-octyne, Mastalir et al. [8] report that the catalytic activity of supported Pd particles diminished for particles of diameters above 4 nm. Note that tests performed here (Fig. 2) indicate that no appreciable deactivation due to coke laydown took place. This is of particular concern [7] for gas-phase reactions where structure-sensitive coke deposition can occur with the creation of sites which are active for carbon triple bond carbon hydrogenation [6,25].

The greater rate of 1-hexyne hydrogenation reaction over smaller particles was not, apparently a function of sites specific to the smaller particles but rather an intrinsic value of the smaller particles. Addition of Bi to the 1% Pd/Al_2O_3 catalyst led to diminished CO uptakes (Table 1) and reduced FTIR band intensities for adsorbed CO (Fig. 5) which confirms that some of the Bi blocked Pd sites which would otherwise have been available for reaction. Although the global reaction rate was reduced slightly by Bi addition (Fig. 3) the TOF when compared at 50% conversion, showed the rate per site of 1-hexyne hydrogenation to be nearly identical (6.3 vs. 6.2) in the absence or presence of Bi. These observations suggest that the reaction is structure insensitive but size-dependent. We would therefore disagree with the findings of Semagina et al. [7] and argue that an "electronic effect" is significant in 1-hexyne hydrogenation for small Pd nanoparticles.

4.2. Site selective addition of Bi

It might be argued that retention of overall TOF for a structure insensitive 1-hexyne hydrogenation despite the loss of sites blocked by Bi addition may result from random coverage of the surface by the modifier. However, there are key observations which indicate that deposition of Bi was site selective which leads to improved behaviour in 1-hexyne hydrogenation (by suppression of subsequent reactions of the 1-hexene formed). These key observations were:

(a) Bi added to Pd suppresses reactions of 1-hexene formed after 1-hexyne hydrogenation. Pb on Pd does not show this effect.
(b) FTIR spectroscopy shows that Bi appears to selectively titrate sites which would otherwise adsorb CO in the on-top mode.
(c) Bi is a poor modifier for the 2-hexyne reaction and fails to suppress reactions of *cis*-2-hexene. Pb on the other hand, has a significant impact in terms of suppressing reactions of *cis*-2-hexene.

Data shown in Fig. 4, illustrate that, despite addition of Bi to Pd/Al_2O_3, the rate of formation of 1-hexene although displaced in the time axis, remains effectively constant, reflecting the structure insensitive nature of the 1-hexyne hydrogenation. The yield to 1-hexene was not affected by Bi addition and similarly was not affected by Pd loading (Fig. 1) or by varying Pd particle size [7]. However, addition of progressively increasing amounts of Bi (Table 1) to Pd catalyst had the effect of progressively reducing the rate at which 1-hexene underwent reaction (Fig. 4). By comparing data for Bi-free 1% Pd/Al_2O_3 (Fig. 1) and 1% Pd/$Al_2O_3$15mBi (Fig. 3), it is clear that the key reaction undergone by 1-hexene by the former catalyst is double-bond shift isomerisation leading to *trans*-2-hexene which becomes the dominant product. While Bi containing catalyst appears to suppress the initial rates of formation of all secondary products, suggesting that alkene re-adsorption is impeded, it is the extent to which *trans*-2-hexene is formed which makes the most significant impact on final selectivity. For example, after 60 min reaction, selectivity to the fully hydrogenated product hexane was 25% over 1% Pd/Al_2O_3 and 21% over 1% Pd/$Al_2O_3$15mBi. However, selectivity to *trans*-2-hexene dropped from 48 to 38% when 1% Pd/Al_2O_3 was compared with 1% Pd/$Al_2O_3$15mBi. To determine which sites exhibited greater double bond-shift isomerisation activity relative to hydrogenation activity and thus were suppressed by addition of Bi, selectivities can be compared over the Bi-free samples of different dispersion. After 60 min of reaction, conversion of 1-hexene had reached ca. 98% in both cases. Selectivity to *trans*-2-hexene was 48 and 38% over the 1 and 5% Pd catalysts, respectively while hexane selectivities were 25 and 41% over these samples (Fig. 1). The greater hydrogenation activity over the poorer dispersed 5% Pd sample is consistent with the lower hexene/hexane ratio as a function of increasing particle size reported by Semagina et al. [7] and suggests that this reaction is facilitated over flat extended, Pd facets. Conversely, the double-bond shift isomerisation rate appears to proceed faster over the lower loaded catalyst containing smaller particles, and it could be argued, featured a greater proportion of step and edge sites. As it is this reaction which is less facilitated over the 5% Pd catalyst with more extended terraces and which is also most suppressed by addition of Bi, the data would be consistent with a model where the majority of the Bi which was present over the palladium surface, was located at step and edge sites which then force 1-hexene to react over the remaining flat terrace sites and give rise to the selectivity effects described. Note that these findings, in terms of preferential population of step and edge sites by Bi, are entirely consistent with studies of Bi doping of Pt single crystal surfaces by Attard and co-workers [10,11] and Herrero et al. [12]. Note also that Pd single crystal studies by Ulan et al. [9] suggest on the basis of steric effects that alkynes are equally well accommodated on either flat surface or terraces, whereas the resulting alkenes suffer more steric hindrance on the terrace sites. Blockage of step and edge sites by Bi would be expected to have little impact on TOF for hexyne hydrogenation but would reduce TOF for subsequent alkene reaction, consistent with our findings (Fig. 4). Further elaboration of this steric model [9], along with knowledge of localised hydrogen availabilities, might explain the relative rates at which isomerisation and hydrogenation reactions proceed.

If Bi selectively blocks step and edge sites on Pd/Al_2O_3 catalyst, and thus enhances behaviour in the selective hydrogenation of 1-hexyne, one might predict similar results for Pb doping of Pd/$CaCO_3$ since in the Lindlar catalyst, it is thought that the addition of Pb enhances selectivity by blocking certain active sites [26] and that these sites are thought to be steps and kink sites [27]. The enhanced selectivity has been explained in terms of an increase in terrace type sites at the expense of stepped and kink sites [27]. However, reaction profiles for the hydrogenation of 1-hexyne at 298 K over Lindlar catalysts and 5% Pd/$CaCO_3$ show considerable similarity (Fig. 6) albeit that the Pb-free sample gives very similar selectivity to *trans*-2-hexene and hexane while the Pb-doped Lindlar shows slightly greater *trans*-2-hexene selectivity at the expense of hexane selectivity. It is clear that although Bi has a much greater impact on selectivity, its effect is not similar to that of Pb and that both modifiers cannot be blocking the same type of surface Pd site.

Some insight into the location of Bi atoms on the Pd/Al_2O_3 catalysts used here was provided by FTIR analysis of spectra of adsorbed CO (Fig. 5). Spectra show some loss of intensity after samples were exposed to Bi although one might not predict this loss to correspond directly to the 27% difference between samples calculated by CO pulse chemisorption (Table 1) given that a linear correlation between total integrated intensity and number of adsorbate molecules (i.e., a constant absorption coefficient) is not expected. However, when the areas under bands representing the multiple bonded carbonyls (2000–1800 cm^{-1}) were integrated, values of 2.04 and 2.08 for Bi-free and Bi modified samples, respectively were obtained, suggesting that the number of sites represented by these carbonyl bands, are not significantly affected by the modifier. These bands are thought to arise mainly from CO adsorption on (100) and (111) type facets on small Pd crystallites [19,28]. On the other hand, when the integrated area representing linearly bound carbonyls (2150–2000 cm^{-1}) was calculated, values of 1.965 and 1.404 were obtained for Bi-free and Bi modified samples. This represents 28.5% loss of band intensity following addition of Bi and is very close to the 27% loss calculated from CO pulse chemisorption values (Table 1). Although such correlation is perhaps unexpected given that the effective molecular absorption coefficient for adsorbed CO should decrease as the number of interacting (coupled) molecules increased [29,30], studies showing the invariability of this function exist [31]. The key observation is the apparent selective loss of sites which would otherwise adsorb CO in linear mode when Bi is present. Although Pd (111) surfaces and model catalyst adsorb CO in this mode, giving a band at ca. 2110 cm^{-1} [28], this is limited to conditions which lead to compressed adsorption structures which exist at low temperatures and such a feature is not normally observed on these surfaces at room temperature [28]. TPD and SSIMS study of Pd particles with mean diameters in the range below and above 0.5 nm show that edge sites on particles adsorb CO in the linear mode [32] consistent with the impact expected on such sites by increasing the reduction temperature for supported Pd catalysts [20]. Evidence therefore indicates that the loss of intensity of the band due to linearly bound CO reflects blocking of step and edge sites by the Bi modifier. Such a finding for Bi modified supported Pd catalysts is consistent with single crystal studies of Bi modified Pt [10–12]. However, differences found between the impact of Bi (Fig. 4) and Pb (Fig. 6) infers that Pb is not preferentially located at step and edge sites, in direct conflict with previous [27] assumptions.

4.3. *Role of Pb vs. Bi*

The use of 1-hexyne as a test reaction did not discriminate between Pb-containing Lindlar and Pb-free Pd/$CaCO_3$ (Fig. 6) while there is a stark contrast in behaviour between these two samples when the internal alkyne, 2-hexyne is selected as test reagent (Fig. 7). This reaction, when compared in reaction profiles for 1% Pd/Al_2O_3 and 5% Pd/Al_2O_3 (Fig. 8) show that the poorer dispersed 5% loaded sample showed less desirable behaviour in that the rate of conversion of *cis*-2-hexene to *trans*-2-hexane was relatively high (when compared to the better dispersed 1% sample). Addition of Bi to the 5% loaded Pd/Al_2O_3 did not suppress the reaction rate of the intermediate 2-hexene (Fig. 9). Given the evidence above that Bi preferentially locates at step and edge sites and that rate of 2-hexene was not suppressed by this modifier and that the rate of this reaction was greater over Pd catalysts with lower dispersion, it could be concluded that *cis*–*trans* isomerisation which was responsible for the loss of *cis*-2-hexene, is favoured over flat, open terrace like facets rather than at steps and edges. Further evidence for this proposal was found when the 1% Pd/Al_2O_3 was reduced at 350 rather than 150 °C to induce [33] a flattening of the particle morphology and an increase in the proportion of terrace to step/edge type sites. Results show that such a treatment led to an increase in the relative rate of *cis*–*trans* isomerisation of 2-hexene [21]. It is clear from this body of evidence that in order to suppress the latter reaction, a modifier can only do so by preferentially locating at the open terrace sites where the rate of this reaction appears to be greatest. It would appear, despite opinions to the contrary [27], that this is where lead is preferentially located in the commercial Lindlar catalyst and which leads to the dramatic selectivity enhancement in 2-hexyne reaction when compared with 5% Pd/$CaCO_3$ (Fig. 7).

Addition of either Bi (1-hexyne) or Pb (2-hexyne) to Pd catalysts lead to improved behaviour in selective hydrogenation by suppressing undesired isomerisation reactions of the primary products (1-hexene or *cis*-2-hexene, respectively). 1-hexene undergoes further reaction via double bond migration whereas *cis*-2-hexene isomerises via *cis*–*trans* isomerisation. The former reaction exhibits isotope effects while the latter does not [34] so it is not surprising that these reactions proceed at different rates over sites of differing geometries.

5. Conclusion

Selectivities in hexyne hydrogenation reactions have been improved by exploiting knowledge obtained of the structure sensitivities of the different hexenes formed as primary products of the hydrogenation reactions. Terminal alkenes undergo rapid double-bond shift reaction at step and edge sites and these can be suppressed by deposition of Bi as catalysts modifier. Internal alkenes undergo rapid *cis*–*trans* isomerisation over extended flat terrace sites and these may be suppressed by modifiers such as Pb in the Lindlar catalyst. The rates of the initial hexyne hydrogenations are relatively unperturbed by either modifier. Bi and Pb each modify selectivity in Pd-catalysed hexyne hydrogenation but their effects are not the same.

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