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Polarisation enhanced ^{13}C magnetic resonance studies of the hydrogenation of pentene over Pd/Al_2O_3 catalysts

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Abstract

This paper reports the first demonstration of ^{13}C distortionless enhancement by polarisation transfer (DEPT) NMR spectroscopy at natural abundance to study the hydrogenation and isomerisation of pentenes over a 1 wt% Pd/Al_2O_3 catalyst. Single component C5 hydrocarbons and binary mixtures of hydrocarbon and hydrogen have been adsorbed on both a pure alumina support and the Pd/Al_2O_3 catalyst derived from it. The pentene species studied were 1-, *cis*-2- and *trans*-2-pentene. No isomerisation or hydrogenation was observed when single component pentene isomers or binary mixtures of 1-pentene and hydrogen, and *cis*-2-pentene and hydrogen were adsorbed onto the pure alumina support. However, when *trans*-2-pentene and hydrogen were both adsorbed onto the support, partial hydrogenation to *n*-pentane was observed in addition to the presence of both *cis*-2- and *trans*-2-pentenes. All pentene isomers hydrogenate over the Pd/Al_2O_3 catalyst to give predominantly *n*-pentane and a small amount of the *trans*-2-pentene isomer. For the parameters chosen here these studies show that *trans*-2-pentene appears to be the active isomer for hydrogenation over the pure support alone.

Keywords: Hydrogenation; Pentene; NMR; DEPT

1. Introduction

The selective hydrogenation of unsaturated hydrocarbons using precious metal catalysts is of particular importance in the petroleum refining and fine chemicals industries [1,2]. For example, the hydrogenation and subsequent reaction of C5 streams, obtained from fluid catalytic cracking, is used in the production of *tertiary*-amyl-methyl-ether, which is used as an additive to petrol to increase its octane number. Whilst the theoretical reaction mechanism of hydrogenation over well defined precious metal surfaces was first proposed as long ago as 1934 by Horiuti and Polanyi [3] there has been little work to our knowledge using in situ spectroscopic studies to probe the reaction mechanism of C5 hydrogenation over commercial palladium catalysts. The long-term aim of this work is to use spectroscopic and reactor studies to investigate the extent to which we can identify key steps in the mechanism of pentene hydrogenation as we scale up from model to industrial catalyst. Hence, we hope to evaluate the extent to which hydrogenation studies performed over model catalysts represent the operation of real industrial catalysts and, further, to explore the extent to which we can manufacture real industrial catalysts with the catalytic properties of model catalysts [4–8].

In a study related to the work presented in this paper, Doyle et al. [4] have reported the use of temperature programmed desorption (TPD) to study the low pressure hydrogenation of *trans*-2-pentene over both single crystal Pd(1 1 1) and Pd nano-particles deposited on thin films of alumina. TPD spectra for *trans*-2-pentene adsorbed, initially at 100 K, on Pd(1 1 1) and the Pd nano-particle system showed that some of the *trans*-2-pentene desorbs intact, up to temperatures of 280 K. Multiple desorption peaks in the TPD traces from 100 K to 280 K were assigned to a condensed pentene phase at 130 K, a π-bonded pentene species at 170 K and a σ-bonded pentene species at 260 K. Upon further heating of the system, dehydrogenation occurred on both systems, but the onset of dehydrogenation for the Pd nano-particles occurred at a temperature some 100 K lower than that on the Pd(1 1 1) surface leading to the conclusion that alkene dehydrogenation proceeds more rapidly on the Pd nano-particles. When *trans*-2-pentene was exposed to a Pd(1 1 1) surface at 100 K, which was pretreated at 200 K with D_2, H atoms and D-hydrogenated pentyl species were

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observed in the TPD data indicating H–D exchange with pre-adsorbed D atoms and also *trans*-2-pentene half-hydrogenation. Interestingly, no products associated with pentane were observed leading the authors to conclude that pentene hydrogenation to pentane does not occur on Pd(1 1 1). In contrast to Pd(1 1 1), pentane was detected in the TPD spectra recorded for adsorption on the Pd nano-particles. In order to explain these results, Doyle et al. [4,5] considered the existence of subsurface hydrogen on both Pd(1 1 1) and Pd nano-particles as a requirement for hydrogenation. Careful examination of the TPD traces for the desorption of D_2 from both systems led the authors to conclude that weakly bound subsurface hydrogen was vital for the hydrogenation reaction to occur, the accessibility of the hydrogen being enhanced on the Pd nano-particles. Further studies on the Pd nano-particle model catalysts [8] addressed the effects of Pd particle size on *trans*-2-pentene hydrogenation. The results showed that the reactions of *trans*-2-pentene exhibited site-specific behaviour, which were assigned to reaction occurring separately on facets and on low coordination sites. A strong dependence on Pd particle size was also observed for the hydrogenation of *trans*-2-pentene, leading the authors to conclude that the hydrogenation proceeds via a di-σ-bonded pentene intermediate. The aim of the NMR study presented here is to investigate the hydrogenation of pentene isomers over an industrial Al_2O_3 support and Pd/Al_2O_3 catalyst to compare the behaviour of *trans*-2-pentene with 1- and *cis*-2-pentene.

Multinuclear magnetic resonance techniques have long been applied to the study of in situ catalysis, and recent reviews of these and other spectroscopic modalities may be found elsewhere [9,10]. Most commonly, ^{13}C solid state NMR techniques are used in preference to ^{1}H NMR because of the greater chemical shift range of the ^{13}C nucleus. However, by moving from ^{1}H to ^{13}C observation there is a loss in achievable signal intensity of ~3 orders of magnitude, arising from the low natural abundance and inherent insensitivity of the ^{13}C nucleus. To overcome this loss of signal, in situ NMR spectroscopy experiments are usually performed using isotopically enriched ^{13}C reactants. In the present study we exploit ^{13}C distortionless enhancement by polarisation transfer (DEPT) NMR [11] so that the reactions may be studied without isotopic enrichment. Whilst ^{13}C DEPT NMR has been used in studies of homogeneous catalysis [12–14] it does not appear to have been used in in situ studies of heterogeneous catalysis. This paper illustrates the potential of using ^{13}C DEPT NMR in such applications. In related studies we are also using the ^{13}C DEPT NMR technique integrated into a magnetic resonance imaging (MRI) pulse sequence so that spatial variations in alkene isomerisation and hydrogenation within a fixed bed of Pd/Al_2O_3 catalyst operating under continuous flow conditions can be studied [15]. To perform such an experiment using isotopically enriched ^{13}C reactant species would be prohibitively expensive. An initial report of ^{13}C DEPT MRI in application to a continuous fixed bed process has recently been reported by Akpa et al. [16] who studied the competing etherification and hydration of 2-methyl-2-butene to *tertiary*-amyl-methyl-ether and *tertiary*-amyl-methyl-alcohol over a packed bed of Amberlyst 15 catalyst particles.

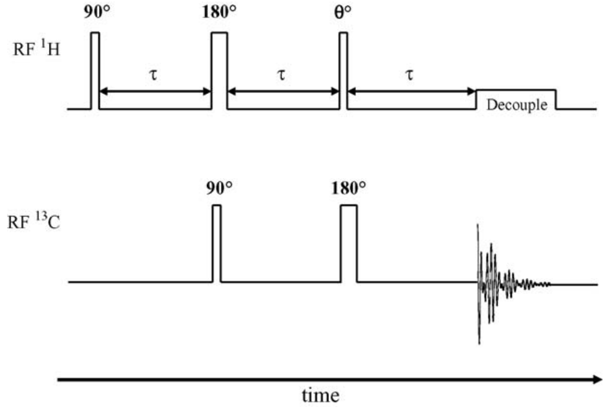

Fig. 1. Schematic of the ^{13}C DEPT pulse sequence used for spectral acquisition. The final ^{1}H pulse angle θ is chosen as 45° so that all CH_n (n = 1, 2 and 3) moieties are detected.

This paper reports the first direct polarisation enhanced, natural abundance ^{13}C NMR study of the hydrogenation and isomerisation of pentenes over an industrial Pd/Al_2O_3 catalyst. The ^{13}C DEPT technique (see Fig. 1) is used because it overcomes a number of problems associated with both traditional ^{13}C and ^{1}H NMR spectroscopies as follows:

(i) ^{13}C DEPT NMR uses the much greater polarisation of the ^{1}H nuclei (compared to ^{13}C) bonded to ^{13}C nuclei within the CH_n (n = 1, 2 or 3) groups of organic molecules to enhance the ^{13}C signal by up to a factor of 4.
(ii) ^{13}C DEPT NMR eliminates broad overlapping ^{13}C background signals from the materials making up the NMR probe because of the much shorter spin–spin relaxation (T_2) values associated with these resonances (see Fig. 2).
(iii) The lower limit on the time between successive signal averages is dependent upon the ^{1}H spin–lattice relaxation (T_1) time and not the ^{13}C spin–lattice relaxation time, which is typically three to five times longer. Thus, data acquisition times can be significantly faster to obtain the same signal-to-noise in a ^{13}C DEPT NMR experiment compared to a standard ^{13}C pulse-acquire sequence.

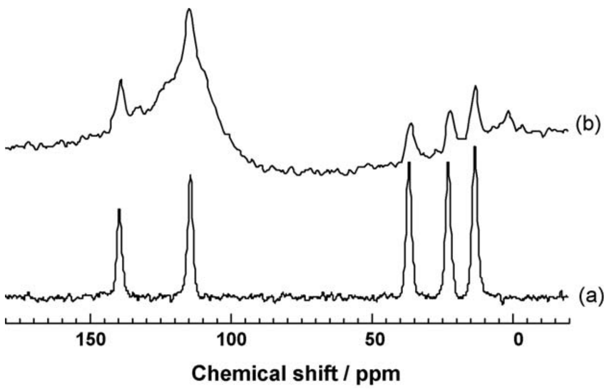

Fig. 2. Comparison of (a) a ^{13}C DEPT-45 spectrum of 1-pentene adsorbed on Al_2O_3 with (b) a standard ^{13}C NMR pulse-acquire acquisition. Note the broadened line widths in the olefinic region and the significant background, which leads to the rolling baseline in (b).

(iv) The greater chemical shift range of the ^{13}C nucleus compared to that of the ^{1}H nucleus, along with a decrease in the number of spectral resonances from ^{13}C observation, facilitates the unambiguous chemical assignment of ^{13}C resonance peaks.

2. Experimental

2.1. NMR methods

All ^{13}C and ^{1}H experiments were performed on a Bruker Biospin AV 400 spectrometer operating at ^{13}C and ^{1}H frequencies of 100.06 MHz and 400.23 MHz, respectively. A 25 mm dual resonance birdcage radio frequency (rf) coil, attached to a Bruker micro 2.5 probe was used. The ^{13}C and ^{1}H 90° pulses were of duration 50 μs and 2048 time domain data points were acquired. In order to maximize the ^{13}C signal-to-noise ratio, two separate sets of ^{13}C spectra were acquired: one with the ^{13}C pulse frequency offset set to the center of the aliphatic region (~20 ppm) of the ^{13}C NMR spectrum and the other with the frequency offset set to the center of the olefinic region (~130 ppm) of the ^{13}C NMR spectrum. This ensures that the DEPT experiment operates at maximum efficiency. The two spectra from the different regions are then simply merged to produce a single spectrum. The DEPT-45 rf sequence (see Fig. 1) was used in all experiments as this particular form of the sequence ensures that a ^{13}C NMR signal is observed from all the CH_n chemical groups (where $n = 1$, 2 or 3) following a single application of the rf pulse sequence. Broadband proton decoupling was employed during the acquisition of the ^{13}C signal. A recycle time of 1.0 s was used and typically 1024 scans were acquired. The value of τ was chosen to be $1/2J$, where J is a typical value of the spin–spin coupling constant, which for a ^{13}C–^{1}H group is approximately 145 Hz thus making $\tau = 3.45$ ms. The time domain data were Fourier transformed with an exponential line-broadening function of 50 Hz. A spectral width of 25 kHz was used for all ^{13}C spectral acquisition. Broadband proton radio frequency decoupling was applied during ^{13}C signal detection to ensure that the ^{13}C spectra were free from any heteronuclear spin–spin coupling fine structure; this also improves the signal-to-noise ratio and facilitates unambiguous ^{13}C resonance assignment. Variable temperature NMR experiments were achieved using a Bruker digital BVT 3000 temperature control unit in conjunction with a Bruker low temperature accessory. The temperature was monitored via a PT 100 thermocouple located at the base of the 25 mm rf coil. All temperatures are accurate to ±0.5 K. All ^{13}C chemical shifts are given relative to the ^{13}C resonance in tetramethylsilane (TMS), and have a typical error of ±1 ppm.

2.2. Sample preparation

Approximately 4 g of Al_2O_3 trilobes or 1 wt% Pd/Al_2O_3 trilobe eggshell catalysts (Johnson Matthey Catalysts plc) were loaded into an NMR sample tube which was subsequently attached to a Pyrex glass vacuum manifold. The trilobes were of diameter 1.0 mm and length 6 ± 2 mm. The support/catalyst was then reduced in flowing hydrogen (99.99%, Messer U.K.) at 473 ± 2 K for 2 h. The hydrogen flow rate was 1.25 ml s^{-1}. The sample was then evacuated at 298 K to a pressure of 10^{-3} mbar after which it was loaded with single-component hydrocarbon or a binary mixture of hydrocarbon and hydrogen. All hydrocarbons were purified by exposing them to three freeze–pump–thaw cycles prior to dosing. The purified hydrocarbon was then admitted as a vapour to the sample using J. Young's valves and the dosing pressure monitored using a Pirani gauge (Edwards plc). The pressures quoted are accurate to 0.1 mbar. For the case of single-component adsorption the sample was then frozen at 77 K and flame sealed. If a binary mixture was to be studied, following freezing of the hydrocarbon at 77 K, a controlled pressure of hydrogen was also admitted to the sample tube and the tube was then flame sealed. After flame sealing, all samples were stored at 195 K prior to commencing the NMR experiment. When NMR data were to be acquired at 298 K, the sample was warmed to room temperature for at least 20 min prior to spectral acquisition. For variable temperature NMR studies the samples were stored at 195 K and then transferred directly to the NMR spectrometer for immediate spectral acquisition. Transfer to the NMR spectrometer took ~10 s. For the variable temperature studies, spectra were acquired in the temperature range 243–268 K. The heating rate was 5 K min^{-1} and samples were equilibrated at each temperature for which spectra were acquired for 15 min prior to data acquisition.

3. Results and discussion

3.1. Adsorption onto pure alumina supports

Fig. 3 shows the ^{13}C DEPT-45 spectrum for the adsorption of 1-pentene onto the Al_2O_3 support material. Five peaks in the spectra are evident which can be grouped into two regions: (i) the olefinic peaks of the 1-pentene are located at approximately 114 ppm and 141 ppm and correspond to the $H_2C^*{=}CH{-}CH_2{-}$

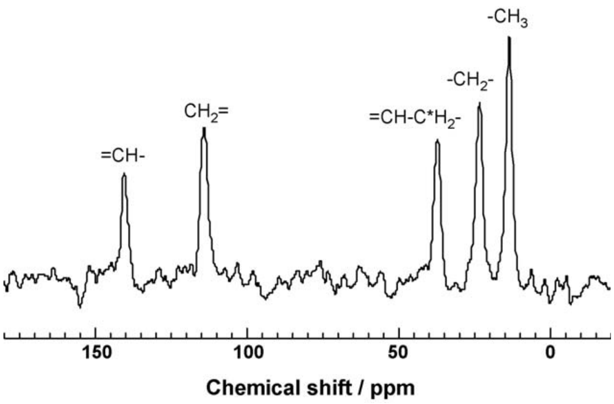

Fig. 3. ^{13}C DEPT-45 spectrum acquired at 298 K for the adsorption of 1.0 mmol of 1-pentene on the pure Al_2O_3 support material. The assignments of the various peaks, which are indicated in the figure, are grouped into two distinct regions: the olefinic region has two peaks centered at 114 ppm and 141 ppm and the aliphatic region has three peaks centered at 13 ppm, 23 ppm and 38 ppm. All chemical shifts are quoted relative to the ^{13}C methyl resonance in tetramethylsilane.

CH_2–CH_3 and the H_2C=C^*H–CH_2–CH_2–CH_3 carbons, respectively, where '*' denotes the nucleus in question, and (ii) the aliphatic peaks at 13 ppm, 23 ppm and 38 ppm which are assigned to the H_2C=CH–CH_2–CH_2–C^*H_3, H_2C=CH–CH_2–C^*H_2–CH_3 and H_2C=CH–C^*H_2–CH_2–CH_3 resonances of 1-pentene, respectively. The chemical shift assignment of these peaks is in good agreement with database [17] ^{13}C spectra of pure liquid 1-pentene. It may be expected from standard NMR theory that the ratio of the intensities/areas of each of the ^{13}C peaks in the whole spectrum should be 1:1:1:1:1. However, this is not the case because of the non-linear nature of the ^1H to ^{13}C magnetization polarisation transfer. Instead the intensity of the carbon peaks in a ^{13}C DEPT NMR spectrum is described [18] by Eq. (1).

$$\text{Intensity}(C^*H_n) = n \sin\theta \cos^{n-1}\theta \quad (1)$$

where n = 1, 2 or 3 and θ is the pulse angle of the final ^1H pulse in the DEPT sequence, which in this study was 45°. Therefore, the relative intensities of CH:CH_2:CH_3 in an ideal DEPT-45 experiment should be 0.71:1.00:1.06, respectively. A detailed discussion regarding this behaviour is beyond the scope of this paper and the reader is referred to reference [18] for a more detailed discussion. Fig. 4 shows the DEPT-45 ^{13}C spectra recorded at 298 K for single component adsorption of *trans*-2- and *cis*-2-pentene onto the Al_2O_3 support. The ^{13}C spectrum for *trans*-2-pentene again shows five resonance lines. The two resonances in the olefinic region at 124 ppm and 134 ppm are attributed to the H_3C–HC^*=CH–H_2–CH_2–CH_3 and H_3C–HC=C^*H–H_2–CH_2–CH_3 carbons, respectively. The three peaks in the aliphatic region at approximately 14 ppm, 18 ppm and 26 ppm are attributed to the H_2C=CH–CH_2–CH_2–C^*H_3, H_2C=CH–CH_2–C^*H_2–CH_3 and H_2C=CH–C^*H_2–CH_2–CH_3, respectively. The ^{13}C spectrum for *cis*-2-pentene shows four resonance lines, two in the olefinic region at 124 ppm and 134 ppm, which are attributed to the H_3C–HC^*=CH–H_2–CH_2–CH_3 and H_3C–HC=C^*H–H_2–CH_2–CH_3 carbons, respectively. The peak at approximately 21 ppm is attributed to the H_3C–CH=CH_2–C^*H_2–CH_3 resonance. The other peak, centered at around 13 ppm, is the unresolved peak from the two terminal methyl resonances H_3C^*–CH=CH_2–CH_2–C^*H_3. A comparison of Figs. 3 and 4 shows that the 1-, *cis*-2- and *trans*-2-pentene isomers are readily distinguishable with the largest difference being apparent in the olefinic region. Fig. 5 shows ^{13}C DEPT-45 spectra recorded following the co-adsorption of 1-, *cis*-2- and *trans*-2-pentene/hydrogen on Al_2O_3. The assignments for 1-pentene/hydrogen (aliphatic peaks at 13 ppm, 23 ppm and 38 ppm and olefinic peaks at 114 ppm and 141 ppm) and *cis*-2-pentene/hydrogen (aliphatic peaks at 13 ppm and 21 ppm and olefinic peaks at 124 ppm and 134 ppm) show that no transformation of the hydrocarbon has occurred. However, the ^{13}C spectrum for *trans*-2-pentene/hydrogen adsorbed on Al_2O_3 shows, in addition to the expected *trans*-2-pentene peaks, additional peaks at approximately 35 ppm and 23 ppm which are assigned to the hydrogenation product, *n*-pentane. These chemical shift values agree well with the ^{13}C spectral database values for pure liquid pentane which includes a peak at 14 ppm coincident

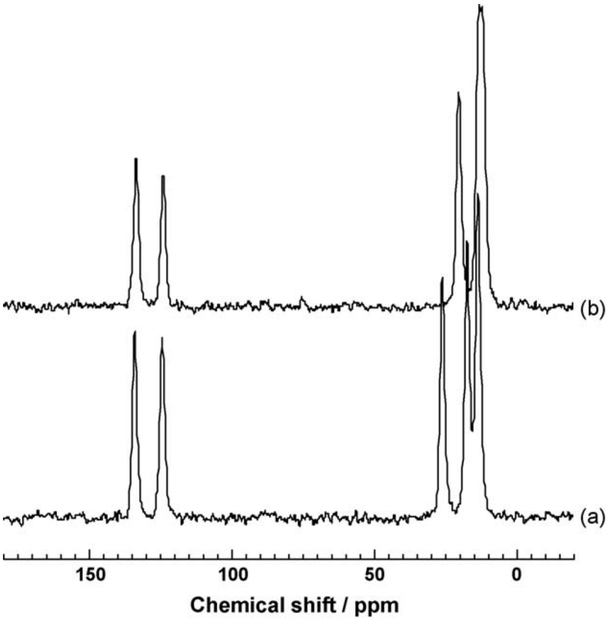

Fig. 4. ^{13}C DEPT-45 spectra of single-component C5 adsorption on Al_2O_3. Data were acquired at 298 K. (a) Adsorption of 2.1 mmol of *trans*-2-pentene. Five resonance lines, two in the olefinic region at 124 ppm and 134 ppm and three in the aliphatic region at 14 ppm, 18 ppm and 26 ppm, are evident. (b) Adsorption of 1.8 mmol of *cis*-2-pentene. Four resonance lines, two in the olefinic region at 124 ppm and 134 ppm and two in the aliphatic region at 13 ppm and 21 ppm, are evident. The peak centered on 13 ppm comprises two peaks, which are not resolved.

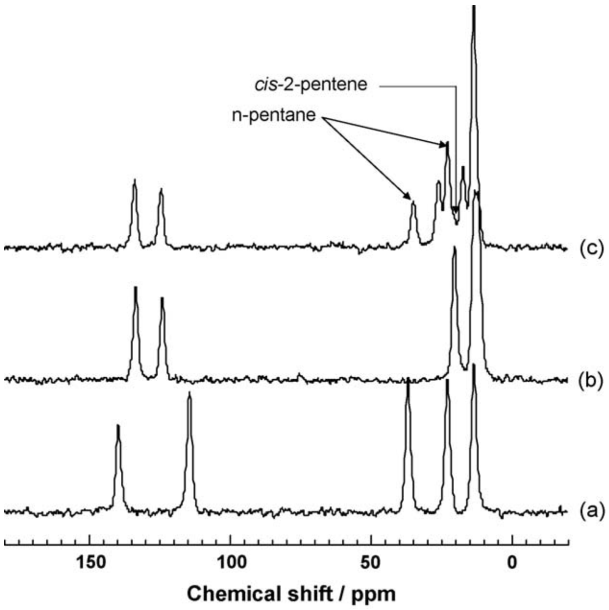

Fig. 5. ^{13}C DEPT-45 spectra of co-adsorption of C5 hydrocarbon and hydrogen on Al_2O_3. Data were acquired at 298 K. (a) 1-pentene and hydrogen adsorbed in a molar ratio 2.6:1 at a hydrogen pressure of 2.4 bar. (b) *cis*-2-pentene and hydrogen adsorbed in a molar ratio of 2.0:1 at a hydrogen pressure of 3.0 bar. (c) *trans*-2-pentene and hydrogen adsorbed in a molar ratio of 2.7:1 at a hydrogen pressure of 2.8 bar; also shows the appearance of peaks associated with *n*-pentane and *cis*-2-pentene as indicated in the figure.

with one of the methyl resonances of both *cis*-2- and *trans*-2-penetene. Moreover, the intensity of the peak assigned to *n*-pentane at 35 ppm is relatively strong indicating that most, if not all, of the available hydrogen has been used up in the formation of *n*-pentane. It is worth emphasising that whilst pure *n*-pentane and 1-pentene both have aliphatic peaks centered around 35 ppm and 38 ppm, respectively, the assignment of the peak at 35 ppm to *n*-pentane, and not to 1-pentene, is unambiguous because we would expect to see peaks at 141 ppm and 114 ppm (corresponding to the olefinic resonances of 1-pentene) if 1-pentene were present. In addition to the presence of *n*-pentane, there is also evidence of a shoulder at approximately 21 ppm for the *trans*-2-pentene/hydrogen sample indicating the presence of *cis*-2-pentene. Collectively, the results presented in Figs. 3–5 show that only *trans*-2-pentene, in the presence of hydrogen, will hydrogenate to *n*-pentane in the presence of pure Al_2O_3 at 298 K. This is indeed a surprising result and to our knowledge represents the first direct in situ spectroscopic evidence of the conversion of *trans*-2-pentene to *n*-pentane over Al_2O_3.

3.2. Adsorption onto Pd/alumina catalysts

Fig. 6 shows the ^{13}C DEPT-45 spectrum for the adsorption of pure 1-pentene onto the Pd/Al_2O_3 catalyst at 298 K. Five major peaks are again visible in the spectra, and a comparison of these with those shown in Figs. 3 and 4 indicates that all of the 1-pentene has isomerised, predominantly to *trans*-2-pentene. Fig. 6 also shows a distinct shoulder at 21 ppm which is attributed to a small amount of *cis*-2-pentene present in the system. Fig. 7 shows the ^{13}C DEPT-45 spectra for the co-adsorption of 1-pentene and hydrogen, respectively, on Pd/Al_2O_3 at 298 K. It is immediately obvious that most of the pentene has hydrogenated to *n*-pentane as evidenced by the intense aliphatic peaks centered at 14 ppm, 23 ppm and 35 ppm. However, unreacted *trans*-2-pentene is also present in the system as shown by the weaker olefinic peaks at 124 ppm and 134 ppm as well as weak shoulders in the aliphatic region at 18 ppm and 26 ppm. Fig. 8 shows that a similar behaviour is seen for samples of *cis*-2- and *trans*-2-pentene/hydrogen on Pd/Al_2O_3 at 298 K; both show *n*-pentane formation and *trans*-2-pentene as the dominant unreacted isomer.

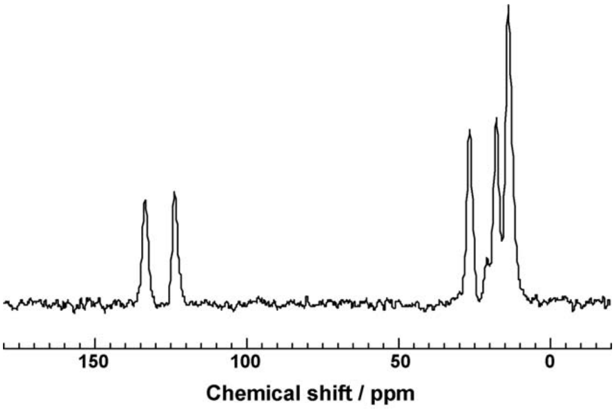

Fig. 6. ^{13}C DEPT-45 spectrum of 2.2 mmol of 1-pentene adsorbed on a Pd/Al_2O_3 catalyst. Data were acquired at 298 K. Complete isomerisation, mainly to *trans*-2-pentene, is evident with a small amount of *cis*-2-pentene also present.

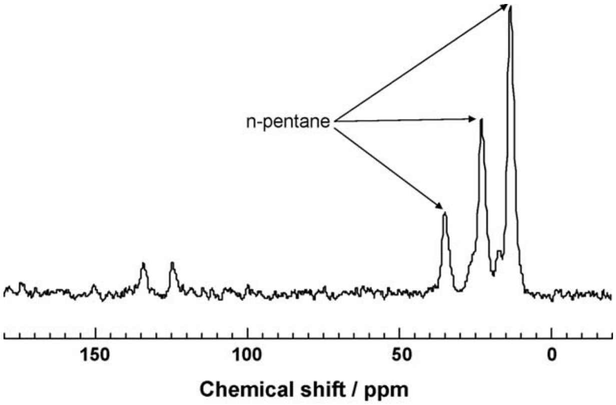

Fig. 7. ^{13}C DEPT-45 spectrum of 1-pentene and hydrogen co-adsorbed on the Pd/Al_2O_3 catalyst. 1-Pentene and hydrogen were loaded in a molar ratio of 1.6:1 at a hydrogen pressure of 3.6 bar. Data were acquired at 298 K. Formation of a large amount of *n*-pentane is observed along with a small amount of *trans*-2-pentene.

In order to further investigate the interplay between isomerisation and reaction behaviour of 1-pentene/hydrogen on Pd/Al_2O_3 a variable temperature study was performed. Fig. 9 shows ^{13}C DEPT NMR spectra in the temperature range $243\ K < T < 288\ K$. At 243 K the ^{13}C spectra show complete isomerisation of 1- to *trans*-2-pentene. Upon further heating to 288 K there is tentative evidence for hydrogenation of *trans*-2-pentene to *n*-pentane with a peak appearing at 35 ppm. These data confirm that it is the presence of *trans*-2-pentene isomer that is favoured at 243 K and that this isomer exists on the catalyst up to a temperature of 288 K at which hydrogenation also occurs. These observations may be consistent with the

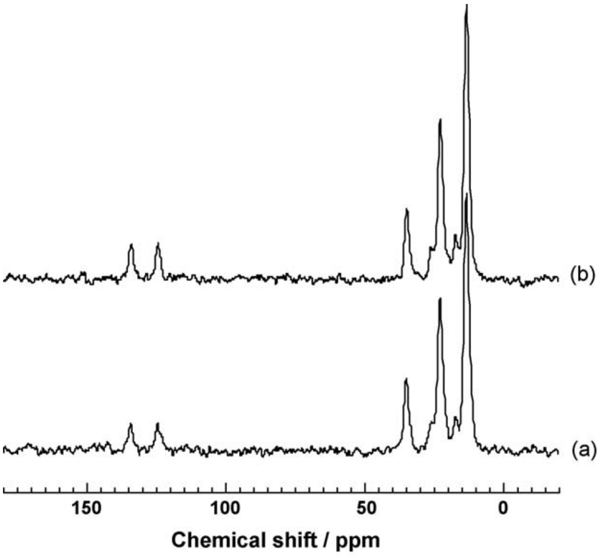

Fig. 8. ^{13}C DEPT-45 spectra of co-adsorbed C5 and hydrogen mixtures on the Pd/Al_2O_3 catalyst. (a) *cis*-2-pentene and hydrogen adsorbed in a molar ratio of 1.7:1 at a hydrogen pressure of 3.5 bar. (b) *trans*-2-pentene and hydrogen adsorbed in a molar ratio of 1.5:1 at a hydrogen pressure of 3.7 bar. Both samples show a predominance of *n*-pentane with small amounts of *trans*-2-pentene present. Data were acquired at 298 K.

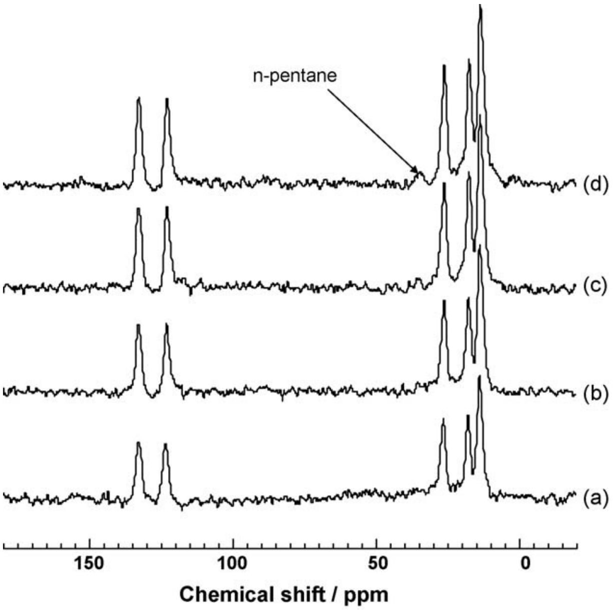

Fig. 9. ^{13}C DEPT-45 spectra of 1-pentene and hydrogen co-adsorbed in a molar ratio of 22:1 at a hydrogen partial pressure of 0.9 bar. Spectra are recorded at increasing temperatures: (a) 243 K, (b) 268 K, (c) 273 K and (d) 288 K. Full isomerisation to *trans*-2-pentene has already taken place 243 K and there is evidence for *n*-pentane formation in the spectrum recorded at 288 K.

conclusions of Doyle et al. [5] who showed that *trans*-2-pentene adsorbed on Pd(1 1 1) and Pd nano-particles dispersed on thin alumina films hydrogenated through to *n*-pentane via the di-σ bonded adsorbed state. Further work in our group is extending variable temperature NMR studies, the role of subsurface hydrogen [4,5] and a comparison of *cis*-2- and *trans*-2-pentene behaviour on this catalyst, to give additional insights into the mechanism of isomerisation and hydrogenation of pentenes over Pd/Al_2O_3 catalysts.

4. Conclusions

We have shown for the first time the applicability of standard ^{13}C DEPT NMR spectroscopy, at natural abundance, to probe the isomerisation and hydrogenation of pentenes over Al_2O_3 support material and the related Pd/Al_2O_3 catalyst. The enhanced signal and clarity of the ^{13}C peaks resulting from the ^{13}C DEPT-45 NMR pulse sequence allows the unambiguous assignment of all ^{13}C peaks associated with the reactants and products of the reaction. The results show that the pure Al_2O_3 support is inert to all single component C5 adsorption and to co-adsorption of 1- and *cis*-2-pentene/hydrogen at 298 K. However, co-adsorption of *trans*-2-pentene and hydrogen causes hydrogenation through to *n*-pentane. The adsorption of single-component pentene isomers on the Pd/Al_2O_3 catalyst shows rapid isomerisation to predominantly *trans*-2-pentene. Additionally the co-adsorption of pentenes and hydrogen shows the formation of *n*-pentane in all cases. Initial variable temperature studies of co-adsorbed 1-pentene/hydrogen on the Pd/Al_2O_3 catalyst shows rapid isomerisation of the 1- to *trans*-2-pentene at 243 K, which subsequently reacts at 288 K to yield *n*-pentane.

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