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Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of ethyne hydrogenation on Pd/Al_2O_3

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Abstract

Preliminary characterisation studies are reported regarding a flow switching experiment combined with DRIFTS monitoring, which has been applied for the first time to the study of adsorption and hydrogenation of ethyne and ethene over: (1) a 0.02 wt.% Pd/αAl_2O_3 catalyst and (2) a 2 wt.% Pd/γAl_2O_3 catalyst (Johnson Matthey). The catalysts were pre-reduced under a flow of hydrogen, followed by flushing under helium at 120 °C or 200 °C. During adsorption of ethyne, a carbonaceous layer was formed on the catalyst in the early stages of the exposure of the catalyst to ethyne, but carbonaceous deposits were not observed during ethene adsorption under identical conditions of freshly reduced catalyst. From the infrared spectra, octane was tentatively identified as being present in the carbonaceous layer. Upon exposing the catalyst to five 5 cm^3 'pulses' of ethyne, sequential hydrogenation to ethene and ethane occurred during the first two pulses applied even in the absence of gas phase hydrogen, but decreased significantly in the three subsequent pulses. Possible sources of hydrogen for the reaction were retention by the catalyst during the pre-reduction or transfer from the carbonaceous layer. Upon heating the 2 wt.% catalyst to 200 °C in a flow of helium to remove residual hydrogen from the pre-reduction, then exposing it to ethyne, hydrogenation still occurred with an increased selectivity towards ethane, suggesting that the carbonaceous layer was the more likely source of hydrogen. Less ethane was formed over the 0.02 wt.% Pd/α-Al_2O_3 catalyst compared with the 2 wt.% Pd/γ-Al_2O_3, as the former catalyst is designed to prevent hydrogenation to the alkane through its low metal loading, optimal pore structure and Pd dispersion. The technique gives insights in to the reaction pathways and could potentially be used to derive kinetic and transport parameters for the reaction system.

Keywords: Ethyne; Hydrogen; Palladium; DRIFTS; Adsorption; Coke

1. Introduction

1.1. Ethyne hydrogenation

The hydrogenation of ethyne on Pd/Al_2O_3 catalysts is a well-studied reaction of industrial importance, since it is used to remove ethyne impurities from ethene. Approximately, 50–60% of ethene production is used in manufacture of polyethene. The production of ethene in the thermal steam cracking process leads to the production of small amounts of ethyne as a side product. Ethyne impurities (~0.35 wt.%) must be removed to a level of 5 ppm if ethene is to be used for polymerisation to polyethene [1], as ethyne would poison the homogeneous polymerisation catalysts. An obvious objective is to remove ethyne by hydrogenation to ethene without further hydrogenation of ethene to ethane.

Key to the understanding of the selectivity issues in ethyne hydrogenation are the modes of adsorption of ethyne and ethene upon the catalyst. Arafa and Webb [2] suggested that three types of active site exist on the catalyst surface, as follows:

1. Type I sites are active for ethyne hydrogenation to ethene.
2. Type II sites are active for direct hydrogenation of ethyne to ethane.
3. Type III sites are active for hydrogenation of ethene to ethane.

A number of studies reported the mechanisms of the reaction, incorporating different hydrogenation and oligomerisation routes [3,4]. These schemes typically consist of: (1) the

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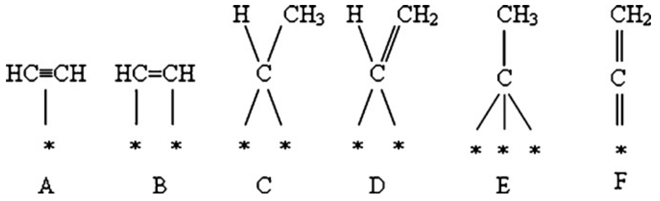

Fig. 1. Illustration of the possible modes of adsorption of ethyne according to Bos and Westerterp [10]. (A) π-Complex; (B) di-σ-adsorbed; (C) ethylidene; (D) vinyl; (E) ethylidyne; (F) vinylidene.

direct hydrogenation of ethyne to ethane via strongly adsorbed species, e.g. ethylidyne, (2) the hydrogenation of ethyne to ethene via associatively adsorbed ethyne and (3) oligomerisation via a dissociatively adsorbed ethyne.

A more recent and comprehensive analysis was provided by Borodziński and Cybulski [5]. Their model allowed for ethyne hydrogenation on a surface on which some carbonaceous deposits already exist. They assumed that there are three types of active sites (A_1, A_2 and E sites), created on the palladium surface by carbonaceous deposits. Their model was novel in the consideration of the role in the kinetic analysis of (1) carbonaceous deposits in creating a heterogeneous surface, and (2) the transfer of hydrogen atoms from the carbon to hydrogenate ethyne.

Fig. 1 shows the various modes in which ethyne can adsorb upon the metal sites of a catalyst. Ethyne can mainly adsorb on a catalyst surface as a di-σ bonded species, as a di-π-bound, associated species or as ethylidyne. Ethene can also form di-σ, ethylidene, π, or di-σ/π bonds. Under industrial hydrogenation conditions, where the concentration of ethyne is relatively low, the strongly adsorbed di-σ species competes with ethene for adsorption sites.

The formation of ethylidyne involves the dissociation of the ethyne, supplying hydrogen atoms to the catalyst surface. The hydrogen on the catalyst surface further reacts with ethyne as it adsorbs to form more ethylidyne. Ethylidyne is involved in the direct formation of ethane via a series of adsorbed components by the following sequential hydrogenation process: ethylidyne ≫ ethylidene ≫ ethyl ≫ ethane. Ethylidyne formation is favoured when three adjacent adsorption sites are available on the catalyst surface. Control of the different forms of adsorbed ethyne can be used to regulate the selectivity of the hydrogenation reaction. One way that this is achieved industrially is by adding a small amount of CO to the reactant gas, which blocks the sites that are responsible for the formation of ethane.

For ethene, there are a number of different adsorption modes, including both associative and dissociative adsorption. These include the π-complex, di-σ-adsorbed, ethylidene, vinyl and ethylidyne modes of adsorption. There is a possibility that a carbonaceous layer builds up on the catalyst surface. The species that participate in the hydrogenation reaction may not be adsorbed directly on the metal, but on a carbonaceous overlayer [6–8,3]. It has also been generally accepted that the adsorption of ethyne on Pd is much stronger than that of ethene, whilst ethane adsorbs only very weakly. Thermodynamic interpretations of this effect have been able to explain some, but not all of the observed selectivity phenomena [9].

1.2. Coking of ethyne hydrogenation catalysts

Al-Ammar et al. [10,6–7] and Berndt et al. [11] showed that for an ethyne hydrogenation catalyst that had been run long enough to achieve steady state activity, the metal was effectively covered with an overlayer of hydrocarbonaceous residues. Moses et al. [1] and Al-Ammar and Webb [6,7] suggested that a third mode of ethyne adsorption involves a C_2H_x species, where x is less than 2, and for a Pd/Al_2O_3 catalyst was found that $x = 1.4$ [6,7]. This species was thought to be responsible for the formation of C_4^+ oligomers and carbonaceous deposits on the catalyst surface. Thompson and Webb [12] proposed that it exists in a primary adsorption layer and acts as a transfer medium, supplying hydrogen for hydrogenations to the associatively adsorbed species within a secondary adsorbed layer.

During ethyne hydrogenation a number of surface polymers may be formed [13], as well as butene and benzene [14,15]. Green oil is a known side product of ethyne hydrogenation [16] which has composition including alkanes and alkenes of high molecular weight. The green oil can poison or block access to the ethyne hydrogenation sites of the catalyst, but the product distribution (selectivity) is not significantly affected by its presence.

Sárkány [17] studied the formation of C_4 oligomers during ethyne hydrogenation of alumina supported palladium and found that significant carbon poisoning appears to be a necessary requisite for selective formation of ethene. During the initial stage of the reaction, PdH on the catalyst surface behaves as a reactant, supplying hydrogen to react with ethyne, leading to the eventual formation of ethane. Subsequently, the retained hydrocarbons poison PdH and the catalyst state transforms to a hydrogen deficient Pd–C_xH_y state. Poisoning reduces the amount of hydrogen available on the catalyst surface and the amount of ethane formed decreases. Borodzinski [18] found that the carbonaceous deposits on Pd/SiO_2 play a key role in transferring hydrogen to the reacting ethyne molecules. The addition of Au to the catalyst decreased the carbon coverage and improved the ethene selectivity.

1.3. FTIR studies

Infrared spectroscopy has been applied quite extensively to the study of adsorption of ethyne [e.g. [15]] and ethene [19,20] on supported metal catalysts and single crystals [21,22], though most of the above studies were conducted at low temperatures, sometimes under special conditions such as high pressures or ultrahigh vacuum [15]. The use of low temperatures enabled the spectral features of the different modes of ethene adsorption to be more easily distinguished than at elevated temperatures. For example between 129 K and 180 K, the spectra of adsorbed ethene were mainly due to π- and di-σ bonded species, whilst between 206 K and 294 K adsorption bands due to ethylidyne could be observed [19]. Stacchiola et al. [15] studied the pathways for ethyne trimerisation and hydrogenation over a Pd

(111) surface. They found that benzene is formed on a clean Pd (111) surface, but catalytic cyclotrimerisation proceeds in the presence of a carbonaceous layer. Ethene was found to be di-σ-bonded on a clean Pd (111), but formed a π-bonded species on a hydrogen pre-covered surface, where the transformation was induced by sub-surface hydrogen.

Relatively few studies of ethene adsorption have been carried out under conditions of realistic catalytic processes upon real catalysts, although Jackson et al. [23] attempted to replicate more realistic industrial process conditions in their experiments. They studied the high-temperature adsorption of ethene, propene, propyne and carbon monoxide over Pt/alumina and Pt/silica catalysts. Their FTIR experimental set up consisted of a heated gas cell, with the catalyst loaded into the reactor as a pressed disc. The catalyst was mounted on a glass sample holder so that it was not in the path of the infrared beam, and therefore the signal came from the gas phase. The Pt catalyst was found to retain hydrogen from the reduction process, this hydrogen being released by ethene adsorption at 573 K. In fact, sub-surface hydrogen was thought to be released by the adsorption of ethene on Pt, which subsequently reacts with ethene. The adsorption of propene did not liberate hydrogen from the catalyst in the same way, whilst adsorption of propyne led to greater carbon laydown on the surface. Jackson and Casey [24] studied the hydrogenation of propyne over palladium catalysts. A non-steady state regime was observed during start up, during which there was significant carbon laydown. Only once the initial layer of carbon was deposited did the catalyst achieve steady state operation. Other studies of hydrocarbon hydrogenation using FTIR have used higher molecular weight compounds. Maetz et al. [25] studied the hydrogenation of but-1-yne on Pt/silica catalysts using dynamic in-situ infrared.

In this paper, a study of adsorption and hydrogenation of ethene and ethyne observed using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is reported. The experiments were carried out at temperatures of 100 °C over two supported palladium catalysts, firstly a 0.02 wt.% Pd/α-Al_2O_3 industrial ethyne hydrogenation catalyst (Johnson Matthey) and secondly a 2 wt.% Pd/γ-Al_2O_3 catalyst (Johnson Matthey). The aim of the experiment was to apply FTIR monitoring to observe the reaction products, possible intermediates and deposits retained by the catalyst surface during the adsorption and hydrogenation experiments. Using a pulse adsorption of ethyne technique, the effect of the catalyst preparation procedure upon the ability of the catalyst to retain hydrogen was studied. This revealed the extent to which palladium hydride on the catalyst surface leads to hydrogenation of the alkyne in the absence of gas phase hydrogen. FTIR spectra of the deposits retained by the catalyst following the adsorption experiments showed the extent of carbon deposition following each pulse of ethene or ethyne. This gave information about the reaction time at which carbon deposition commences, as well as the chemical nature of carbon deposited. Time profiles of the integrated peak areas corresponding to ethyne, ethene and ethane gave insights in to the kinetics and pathways of the reaction.

2. Experimental

2.1. FTIR set up

Fig. 2 shows the experimental flow set up of the reaction cell, which is housed within the sample compartment of a Tensor 37 FTIR spectrometer (Bruker Optics) equipped with a medium band liquid nitrogen cooled HgCdTe (MCT) detector and running under OPUS/IR software. The reaction cell itself is comprised of an environmental chamber (ThermoNicolet), which fits on to the Collector diffuse reflectance accessory, hereafter referred to as a ‘reaction cell’. The reaction cell allows the exposure of the sample to reactant gases at high temperature and pressure (maximum 900 °C, 1500 psi = 103.42 bar). The cell consists of a heated catalyst holder covered by a dome fitted with zinc selenide windows. The catalyst holder is comprised of a ceramic/alumina cup, which held 0.052 g catalyst/KBr mixture. KBr is commonly used as an inert diluent in FTIR studies, as well as for the manufacture of transmission disks and spectrometer windows. The sample holder contains a heating element and a thermocouple within the catalyst holder such that the sample temperature is closely regulated. Cooling water is circulated through a coil surrounding the base of the dome to facilitate temperature regulation and rapid cooling of the cell after the set-point is adjusted.

To test whether it was completely inert, a sample of KBr was exposed to ethyne at a flow rate of 5 $cm^3\ min^{-1}$ for a duration of 20 min, followed by flushing with helium. The spectra recorded over KBr were also used to subtract the IR bands arising from the gas phase from the spectra recorded over a catalyst, in order to highlight features resulting from species adsorbed on the catalyst surface. FTIR spectra were recorded with a resolution of 4 cm^{-1} with a scanner velocity of 20 kHz. The data were recorded in the range 4000–550 cm^{-1} and 150 scans were co-added to produce each spectrum. The results were presented in absorbance mode.

2.2. Gas-dosing system

The gas-dosing system is controlled by three mass flow controllers (Brooks Instrument) that regulate the flow of hydrogen (0–10 ml min^{-1}), ethene (0–5 ml min^{-1}) and ethyne (0–5 ml min^{-1}). For experiments in which gas blends are required, a mixing chamber of volume approximately 79 cm^3 is fitted in the gas inlet line after the mixing point where the three gas lines intersect. When gas blending is not required, ethyne is supplied to the cell via a by-pass line around the mixing chamber, during which time the mixing chamber is isolated. The ethyne mass flow controller is fitted with an electronic batch controller and secondary solenoid valve, such that accurately measured pulses of ethyne can be supplied to the reaction cell, using the by-pass line to avoid the dead volume of the mixing chamber introducing an unnecessary increase in residence time to the flow. The flow of helium or hydrogen to the reaction cell is via the mixing chamber.

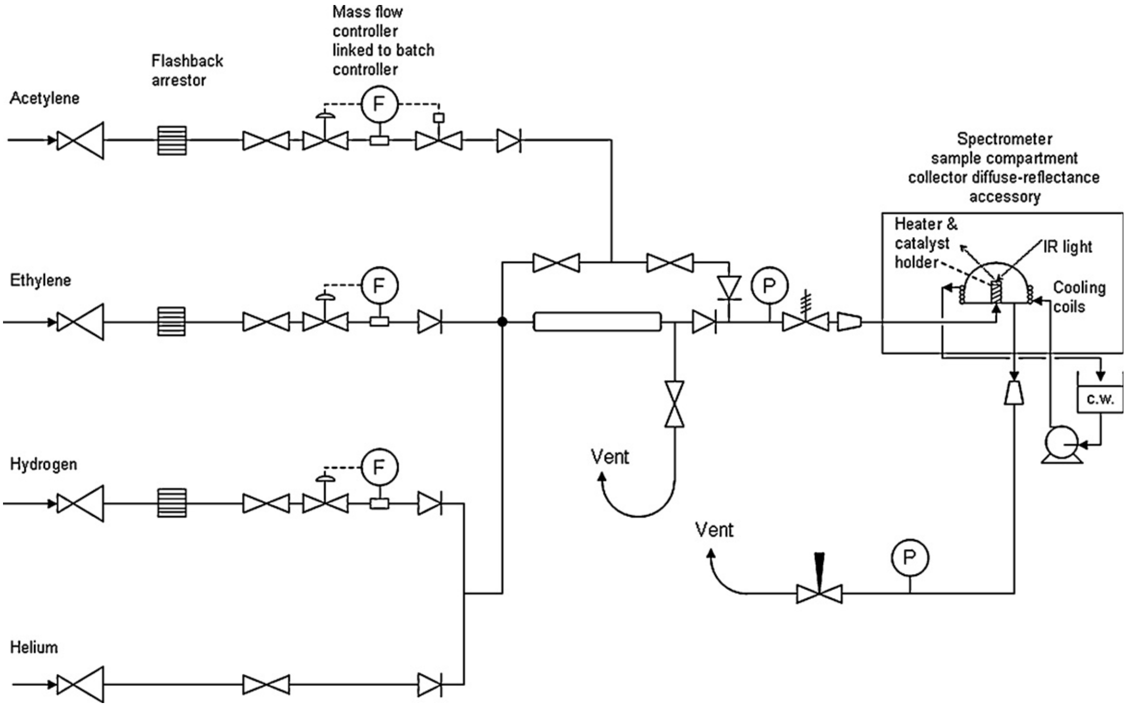

Fig. 2. Flow diagram of the high-temperature high-pressure in-situ FTIR reaction cell, gas supply, mixing chamber (volume 79 cm^3) and exhaust system. The four-way connector is indicated by a black dot.

2.3. Catalyst preparation

Catalysts selected for the experiments were 2 wt.% Pd/γ-Al_2O_3 and an ethyne hydrogenation catalyst comprised of 0.02 wt.% Pd/α-Al_2O_3. The former catalyst was used because it was thought that the high metal loading might have led to sufficient adsorption for surface intermediates and adsorbed components to be detected by FTIR. Additionally, it was intended to compare the selectivity of the real ethyne hydrogenation catalyst of low metal loading with the other sample of higher loading. Catalyst samples were prepared for IR measurements by crushing with a pestle and mortar to produce a very fine powder and mixing in the ratio 20% catalyst: 80% KBr reference compound, then further grinding. The particle size of the primary KBr particles was determined by microscopy (Leica ×4 magnification) to be ∼10 μm and the same batches of KBr and each catalyst were used for all experiments. The samples were dried at 120 °C to remove some of the residual moisture, carefully loaded in to the sample holder of reaction cell before levelling the top surface using a spatula and replacing the dome of the cell.

The catalysts were pre-treated by flushing helium over them for a few minutes at room temperature, followed by reduction in hydrogen for 1 h at 120 °C. Further purging in helium was carried out at 120 °C as standard, and at 200 °C in one selected experiment to ensure that hydrogen was removed from the catalyst surface. Using temperature programmed desorption, it has been shown that all hydrogen has been desorbed from the surface at a temperature of 127 °C (400 K) [26].

2.4. Pulse adsorption experiments

In the adsorption and reaction experiments, high purity (99.9%) ethyne and ethene (BOC gases) were used. In this work, the catalysts were exposed to a constant flow of analysis gas (ethyne), followed by switching to helium and observing the changes in infrared spectra that occurred after the switch took place. Therefore, the experiment differed in nature from a traditional ‘injection’ experiment in which microlitres of analysis gas are typically injected in to a flow of carrier gas. The pulse volumes of ethyne used in this work were 5 ml, 50 ml and 100 ml. Pulses of ethyne were introduced to the reaction cell by opening the solenoid valve for a timed period, during which a flow of 5 ml min^{-1} of ethyne was maintained. The adsorption experiment was carried out at temperatures of 26 °C and 100 °C. Prior to commencing the adsorption experiments over the catalyst, an experiment was carried out by pulsing 100 ml ethyne over KBr powder at a temperature of 100 °C at a rate of 5 ml min^{-1}, in order to examine the profile of ethyne peak area versus time in the absence of a catalyst.

The smaller pulse volume of 5 ml was applied repeatedly to probe gradual changes in the development of the carbonaceous layer on the catalyst, and selectivity of the hydrogenation reaction as it is exposed to progressive amount of hydrocarbon gas. This experiment was performed separately over both the 2 wt.% Pd/γ-Al_2O_3 and 0.02 wt.% Pd/α-Al_2O_3 catalysts. Both catalysts were pre-treated as detailed above and ethyne pulses were introduced to the cell at a flow rate of 5 ml min^{-1} using the batch controller. Subsequently, the flow was switched to helium carrier gas for between 12 min and 40 min, until the gas phase ethyne signal had decayed to the baseline, before repeating the pulse of ethyne and again switching to helium thereafter. The pulses of ethyne were repeated up to five times during the experiment.

The larger pulses of 50 ml or 100 ml ethyne were used to ensure a strong signal from the hydrocarbon gas in the reaction cell, and to deposit sufficient carbonaceous material on the catalyst to obtain a spectrum from the surface layer. In the adsorption experiment, a total of 50 ml or 100 ml ethyne was dosed on to the catalyst using the batch controller at a flow rate of 5 ml min^{-1}, for 10 min or 20 min, respectively. The flow was then switched to helium carrier gas, which swept the gas phase ethyne out of the cell to exhaust. The helium flow was continued for 2.5 h until all gas phase contributions to the spectra were eliminated by flushing the cell through. In order to remove gas phase contributions to the spectra, 'blank' experiments were also carried out by repeating the usual procedure of the adsorption experiment using a KBr reference sample without any catalyst mixed with it. The cell was purged for a further 30 min in flowing He.

2.5. Hydrogenation reactions

The same catalyst was then used to perform a hydrogenation reaction. Another background measurement was taken in order to remove the spectral contributions from any deposits left on the catalyst from the adsorption experiment. In the reaction experiment, 100 ml ethyne was dosed on to the catalyst at a flow of 5 ml min^{-1}, followed by 2.5 h of hydrogen flow at 10 ml min^{-1}. This pulse volume was used to ensure a sufficient carbonaceous deposit on the catalyst surface to observe by DRIFTS. The experiments described above for ethyne were repeated with the same flow rates of ethene, in order to observe the differences in behaviour of the alkene compared with the alkyne. The temperature used in the experiment was 100 °C.

3. Results and discussion

In Fig. 3, spectra A and B display the main gas phase peaks of ethyne. The band assignments are as follows: at 3308 cm^{-1} and 3263 cm^{-1} are the R ($\delta J = +1$) and P ($\delta J = -1$) vibration rotation branches of the CH stretch fundamental (ν_3), at 1351 cm^{-1} and 1302 cm^{-1} are the R and P branches of the combination band of the two CH bend fundamentals ($\nu_4 + \nu_5$) and at 716–752 cm^{-1} the IR active CH bend (ν_5), which also shows a sharp central Q branch peak ($\delta J = 0$) at 729 cm^{-1}. In Fig. 3 spectrum A (2 wt.% Pd/γ-Al_2O_3 catalyst was mixed with KBr), but not spectrum B (KBr only), a peak at 1707 cm^{-1} is observed that may be associated with a carbonyl (C=O) stretch, such as a ketone. The carbonyl peak occurs over the Pd catalyst and alumina, but not KBr. The carbonyl peak could result from interaction of ethyne with alumina, such as formation of a carbonate species or less likely interaction with the lattice oxygen of the support. Alternatively, if an impurity such as acetone is present in the gas stream it is only detected after desorption on alumina as no carbonyl peak was observed when KBr was exposed to ethyne. Fig. 3, spectrum C was recorded after exposing KBr to a cumulative flow of 100 cm^3 ethyne, followed by flushing with helium to remove the gas phase contribution to the spectrum, and is essentially free of peaks, indicating that after the gas phase ethyne is flushed away from the KBr powder no evidence of residual bands corresponding to adsorbed components and carbonaceous deposits is observed. This therefore suggests that KBr is inert, as expected. Spectrum subtraction (Fig. 3, spectrum D) was carried out to try to observe peaks of adsorbed components following the removal of the gas phase contribution. However, spectrum D displays only the peak at 1707 cm^{-1}, which corresponds to the carbonyl stretch discussed already, and some artefacts resulting from imperfections in the spectrum subtraction. Therefore it is not possible to distinguish between different modes of ethyne adsorption from these spectra. The di-σ and π-bonded species have been previously observed at low temperatures, such as 150 K [20], and therefore their absence at the temperature of 299 K used in this experiment is not surprising.

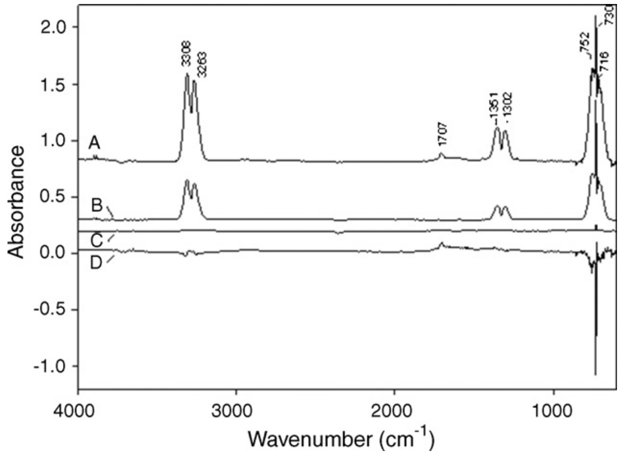

Fig. 3. Spectra showing (A) ethyne over 2 wt.% Pd/γ-Al_2O_3 catalyst mixed with KBr (20 wt.% catalyst:80 wt.% KBr); (B) ethyne over KBr powder; (C) KBr powder after exposure to ethyne followed by flushing with helium for 40 min; (D) ethyne recorded over the 2 wt.% Pd/γ-Al_2O_3 catalyst with the gas phase contribution subtracted using the spectrum subtraction facility of the OPUS software (spectrum A −2.26 × spectrum B). The spectra were recorded at a temperature of 100 °C.

Fig. 4 displays the spectra recorded during the application of a pulse of ethyne followed by purging with helium. After 30 min since first exposure to ethyne, the peaks displayed correspond to the gas phase ethyne, and the assignments are the same as those of Fig. 3, spectrum A. It is observed that the peaks due to gas phase ethyne decrease as a function of time and disappear after about 60 min helium purge and the peaks in the range 3050–2850 cm^{-1} start to become visible at 30 min, and continue to become more intense as time progresses. Peaks corresponding to CH_3 asymmetric stretch (2962 cm^{-1}), CH_2 asymmetric stretch (2928 cm^{-1}), CH_3 symmetric stretch (2863 cm^{-1}) and CH_2 symmetric stretch (2856 cm^{-1}) are observed, which will be further discussed in the context of Fig. 6, which is presented on an enlarged scale. Collectively, these peaks could correspond to a straight chain hydrocarbon of high molecular weight, although some C_2 molecular species may also remain on the catalyst derived from ethyne. This suggests that a layer of alkane hydrocarbon forms on the

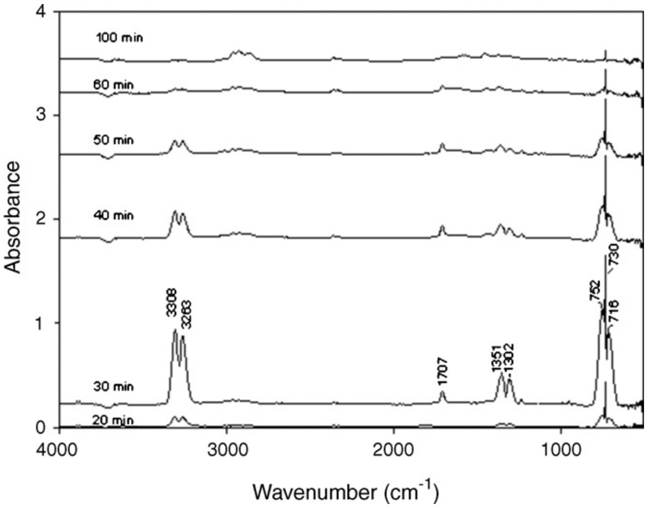

Fig. 4. DRIFTS spectra recorded during a 100 cm^3 pulse of ethyne at 5 ml min^{-1}, 26 °C over a 2 wt.% Pd/γ-Al_2O_3 catalyst, followed after 20 min by purging with helium. Unless otherwise stated, catalysts were pre-treated by reduction in hydrogen for 1 h at 120 °C, and further flushing in helium for 1 h at 120 °C to purge off the hydrogen.

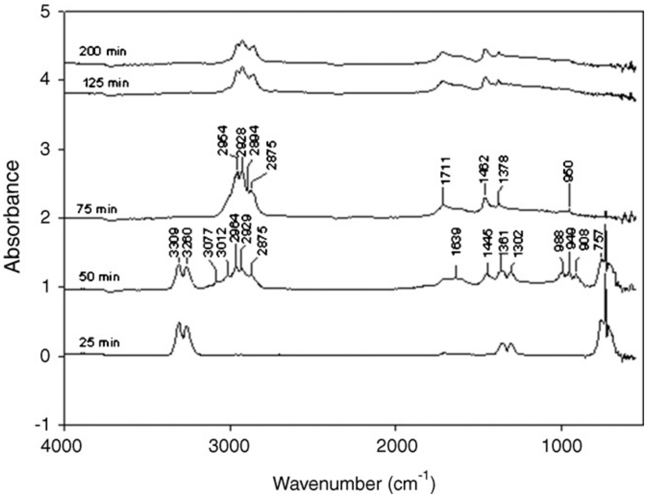

Fig. 5. Absorbance spectra recorded during ethyne hydrogenation over a 2 wt.% Pd/γ-Al_2O_3 catalyst at 100 °C. A 100 ml pulse of ethyne was introduced at a rate of 5 ml min^{-1}, followed after 20 min by flushing with hydrogen.

catalyst in the presence of ethyne, even before hydrogenation commences, which could be the precursor to coke and green oil formation in the hydrogenation reaction.

Further peaks in the region 1700–1000 cm^{-1} are difficult to assign as they occur in the fingerprint region. In the region 1800–1400 cm^{-1}, residual artefact water vapour lines occur, resulting from moisture in the atmosphere outside of the reaction cell, through which the IR beam passes. At around 2360 cm^{-1}, a further peak occurs due to atmospheric CO_2. Spectral features due to atmospheric gases can be observed if the absorptions of water vapour and carbon dioxide change between the sample measurement and the background. This can happen if the concentration of water vapour and carbon dioxide change between the two measurements. Although these peaks could be removed by purging the sample compartment with nitrogen, or using an automatic atmospheric compensation facility software feature being introduced by modern spectrometer manufacturers, this was not considered essential as the atmospheric peaks did not significantly overlap with those of the hydrocarbon gases of interest.

Fig. 5 shows spectra recorded during the hydrogenation of ethyne at 100 °C over the 2 wt.% Pd/γ-Al_2O_3 catalyst. It is observed that the spectrum recorded after 25 min corresponds to ethyne, with bands in the same ranges noted in Fig. 3. After 50 min and 75 min, the spectra show some additional features resulting from ethene. For ethene, the expected features are a strong absorption band in the region 800–1100 cm^{-1} corresponding to the CH_2 wag fundamental (ν_7), the CH_2 scissors fundamental (ν_{12}) in the range 1400–1500 cm^{-1}, the overtone of the CH_2 wag ($2\nu_7$) in the range 1800–1912 cm^{-1}, the Q branch of the CH_2 symmetric stretch fundamental (ν_{11}) at 2988 cm^{-1} and absorption in the region 3050–3200 cm^{-1} due to the CH_2 asymmetric stretch (ν_9). Features of ethane are the CH_3 rocking fundamental (ν_{12}) at 822 cm^{-1}, two CH_3 deformation modes (ν_6 and ν_{11}) at 1360–1580 cm^{-1} and two CH_3 stretch fundamentals (ν_5 and ν_{10}) at 2895 and 2985 cm^{-1}. Finally, at 125 min and 200 min, the peaks of the spectra correspond to surface deposits retained by the catalyst. The last five spectra have been added together and are shown in Fig. 6, in order to enhance the features of the end deposit spectra. The peaks at 2955 cm^{-1}, 2926 cm^{-1}, 2863 cm^{-1} and a small peak at 2856 cm^{-1} correspond to CH_3 asymmetric stretch, CH_2 asymmetric stretch, CH_3 symmetric stretch and CH_2 symmetric stretch The associated peaks at 1461 cm^{-1} are CH_2 def., CH_3 asymmetric def. and at 1378 cm^{-1} is attributed to CH_3 asymmetric def. As for the spectra recorded during ethyne adsorption, these peaks could correspond to a straight chain hydrocarbon of high molecular weight, and a small contribution of CH alkene stretch, as seen by the small shoulder at 3012 cm^{-1} due to the =C–H stretch, which could result from some residual alkenes on the catalyst surface. The deposit spectra of Fig. 6 show a remarkable similarity to the library

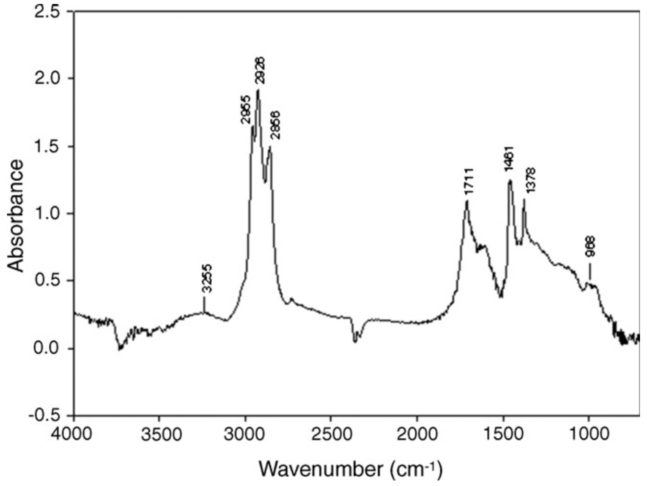

Fig. 6. Spectrum formed by addition of the last five successive spectra recorded during ethyne hydrogenation over a 2 wt.% Pd/γ-Al_2O_3 at 100 °C, highlighting the features of the carbonaceous deposits.

spectrum of octane [27], particularly the ratio of CH_3 and CH_2 stretching peaks. It is therefore tentatively suggested that the hydrocarbon formed on the catalyst was mainly octane, or straight chain hydrocarbons of close carbon number. Again the peaks in the fingerprint region 1700–1000 cm^{-1} are difficult to assign. Residual artefact water vapour lines occur at 1800–1400 cm^{-1}, and CO_2 gives rise to a peak at 2360 cm^{-1}. Green oil could be formed from oligomers adsorbed on the catalyst, and consists of C_4 hydrocarbons to alkanes and alkenes of higher molecular weight [17]. The strong peaks of alkane compounds observed in this work, weak alkene peak and presence of carbonyl (1711 cm^{-1}) were consistent with those obtained for the upper phase of green oil, after settling in to two immiscible layers [17]. Similar results were observed by Teschner et al. [28] during pentyne hydrogenation over 1% Pd/θ-Al_2O_3 in which a palladium–carbon surface layer built up in the early stages of the reaction. The current study validates that the findings of Teschner et al. [28] apply to alkyne hydrogenation in general and not just to C5 alkynes. As ethyne adsorbs upon the surface, the liberation of ethene and ethane leaves the carbonaceous surface deposits poor in hydrogen. Although the deposit spectra described suggest that C8 species form such as octane adsorbed at the outside surface, adjacent to the Pd particles it is possible that a C-rich PdC layer forms, as also reported by Teschner et al. [28]. The same authors also reported that carbon may dissolve in to the palladium particle to form subsurface carbon.

It is noted that in this study the catalysts were operated for a relatively short amount of time of around 3 h per reaction, so any green oil or 'coke' produced corresponds to initial coke, or coke precursor. Operation of the catalyst for longer amounts of time may lead to the production of longer chain molecules, and possibly aromatic compounds, however further studies of longer reaction times are needed to confirm this.

In order to ascertain that the deposits observed did not result from impurities in the gas supply, spectra were recorded over alumina containing no Pd. Fig. 7 displays a spectra for ethyne recorded after 30 min exposure to an alumina sample containing no Pd and over 2 wt.%Pd/γ-Al_2O_3 mixed with KBr. It is noted that in the region 2800–3000 cm^{-1} features corresponding to deposition of higher hydrocarbons are already visible for the catalyst sample as highlighted in the enlarged figure insert, whilst there is no trace of peaks in the same range over the sample containing only alumina. This suggests that the higher hydrocarbons were formed as the carbonaceous over layer was laid down during adsorption of ethyne upon Pd, and were not a result of gas phase impurities. The carbonyl peak at 1710 cm^{-1} does occur over both samples, indicating the possible interaction of ethyne with oxygen of the alumina lattice or formation of an adsorbed carbonate species, regardless of whether Pd is present on the alumina surface.

Fig. 8 shows selected spectra recorded during the adsorption of ethene upon the 2 wt.% Pd/γ-Al_2O_3 catalyst. The features of ethene are most evident in the spectrum recorded after 12 min, with the adsorption bands assigned as for ethene observed in Fig. 5. Fig. 8 also shows the spectrum recorded at both 0 min and 70 min, where features of the ethene spectrum are not visible and only some small inverted peaks occur in the range 2800–3200 cm^{-1}. It is possible that these peaks may have resulted from a trace of ethane left in the cell during the background measurement, giving rise to a negative signal after further flushing with helium.

In order to further investigate the adsorption behaviour of ethyne, the pulse adsorption experiment was performed. Fig. 9 shows the spectra during the application of a 5 cm^3 pulse of ethyne at 100 °C, from which it is observed that similar features occur in the spectra at 50 min, corresponding to deposits on the catalyst surface. This suggests that the carbonaceous deposits formed at 100 °C are quite similar to those formed at room temperature. As noted earlier, the same deposits were not formed over KBr in the absence of the catalyst.

It was found that by integrating selected peaks characteristic of particular reactants and products, their appearance or disappearance as a function of time could be monitored, and

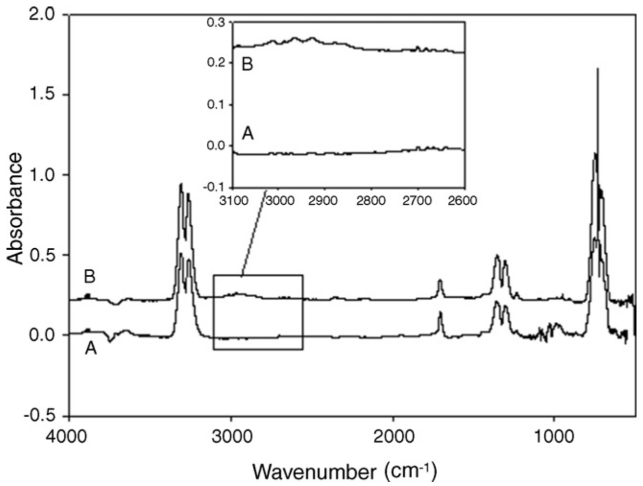

Fig. 7. DRIFTS spectra recorded 30 min after exposure of ethyne to (A) a sample of alumina and (B) a sample of 2 wt.% Pd/γ-Al_2O_3 mixed with KBr at 100 °C.

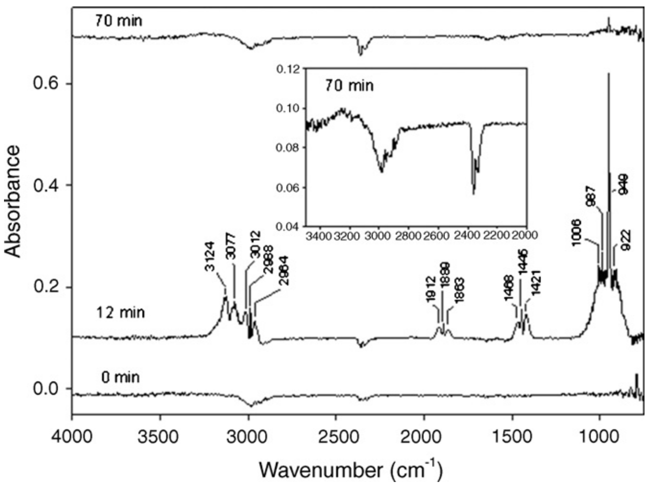

Fig. 8. DRIFTS spectra recorded during a 100 cm^3 pulse of ethene at 5 ml min^{-1} at 100 °C, over a 2 wt.% Pd/γ-Al_2O_3 catalyst, followed by purging with helium.

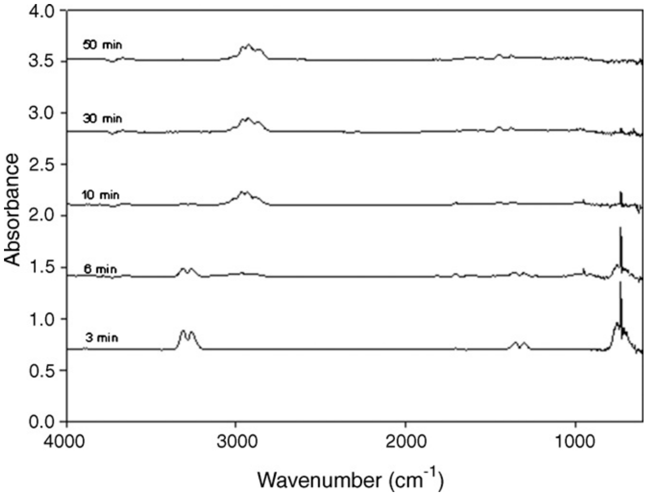

Fig. 9. DRIFTS spectra recorded during a 5 cm^3 pulse of ethyne at 5 ml min^{-1}, at 100 °C over a 2 wt.% Pd/γ-Al_2O_3 catalyst, followed by purging with helium.

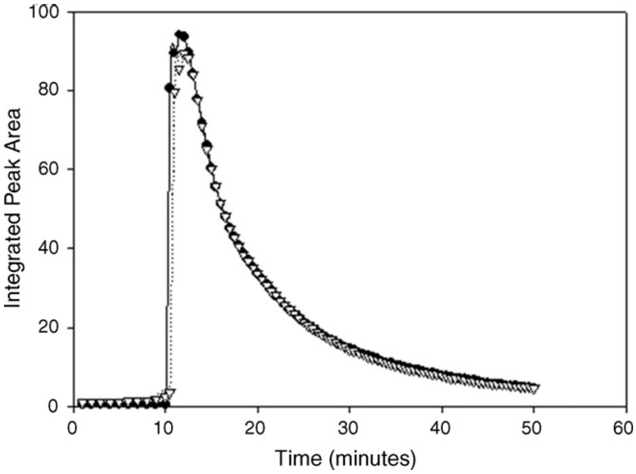

Fig. 11. Integrated peak area of ethyne as a function of time during a 50 ml pulse of ethyne followed by flushing with helium at 100 °C during two repeat experiments over KBr.

potentially a wealth of information regarding the dynamics of adsorption and reaction could be extracted from the data. The peaks obtained were integrated using an OPUS macro for the separate components ethyne using the ranges of wavenumbers shown in Fig. 10. Although the peak selected to represent ethane occurs in a region where there are also ethene absorptions, a distinct peak can be observed as indicated which is attributable to ethane. The integration was carried out by including only the area shown in Fig. 10, and not the whole region between the curve and the axis, therefore representing the contribution from ethane only. Fig. 10 also illustrates the peak areas used to integrate the contributions for ethene and ethyne. Fig. 11 shows the integrated ethyne peak area as a function of time during a 50 ml pulse of ethyne followed by flushing with helium. The curves of two successive peaks have been plotted on the same scale to illustrate that the data are reproducible. During the first 10 min very little ethyne appears, thereafter the helium flow started which flushed ethyne through to the cell. Fig. 12 shows the integrated peak area during a 100 ml pulse of ethyne over the 2 wt.% Pd/γ-Al_2O_3 catalyst mixed with KBr and KBr only. In Fig. 12 it is observed that the peak for KBr without catalyst displays an earlier maximum than the curve for the catalyst mixed with KBr, and that the tail decreases gradually over a longer period compared with the curve recorded over the sample containing catalyst. For the catalyst sample, the more rapid decrease in peak area of ethyne following the maximum value occurs because ethyne is consumed by the hydrogenation reactions occurring. For the non-reacting case of KBr, ethyne spends longer in the cell before being flushed through to exhaust by the helium flow.

Fig. 13 shows the trace of ethyne, ethene and ethane integrated peak areas over the 2 wt.% Pd/γ-Al_2O_3 catalyst for the 5 ml pulses of ethyne. The first two peaks for ethyne are sharp, with only a minor tail following the main peak, whilst the subsequent pulses of ethyne give rise to a sharp peak followed by a second broad peak, which forms part of the tail of the first.

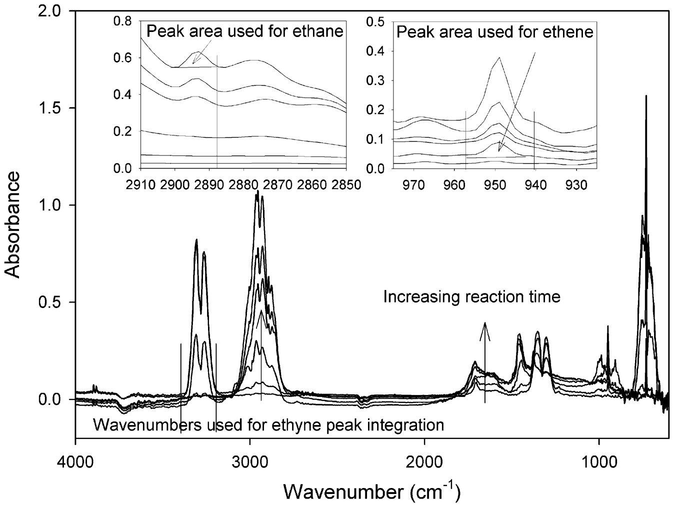

Fig. 10. DRIFTS spectra recorded during hydrogenation of ethyne over a 2 wt.% Pd/γ-Al_2O_3 catalyst at 100 °C, showing ranges of wavenumbers used for the peak integration: ethyne (3360–3200 cm^{-1}), ethene (957–942 cm^{-1}) and ethane (2901–2888 cm^{-1}).

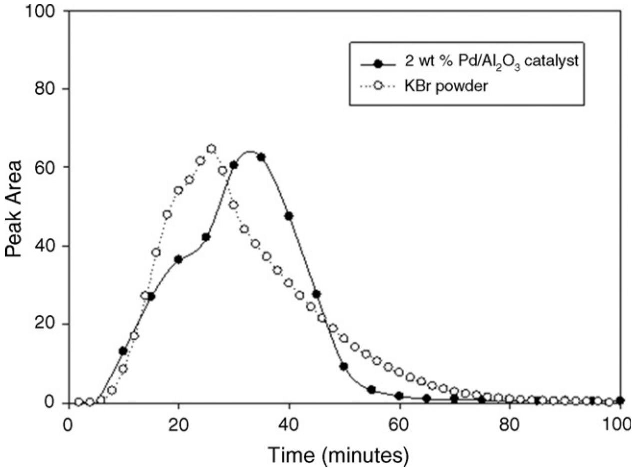

Fig. 12. Integrated peak area of ethyne as a function of time during 100 ml pulse ethyne followed by flushing with helium at 100 °C over 2 wt.% Pd/γ-Al_2O_3 mixed with KBr and KBr only.

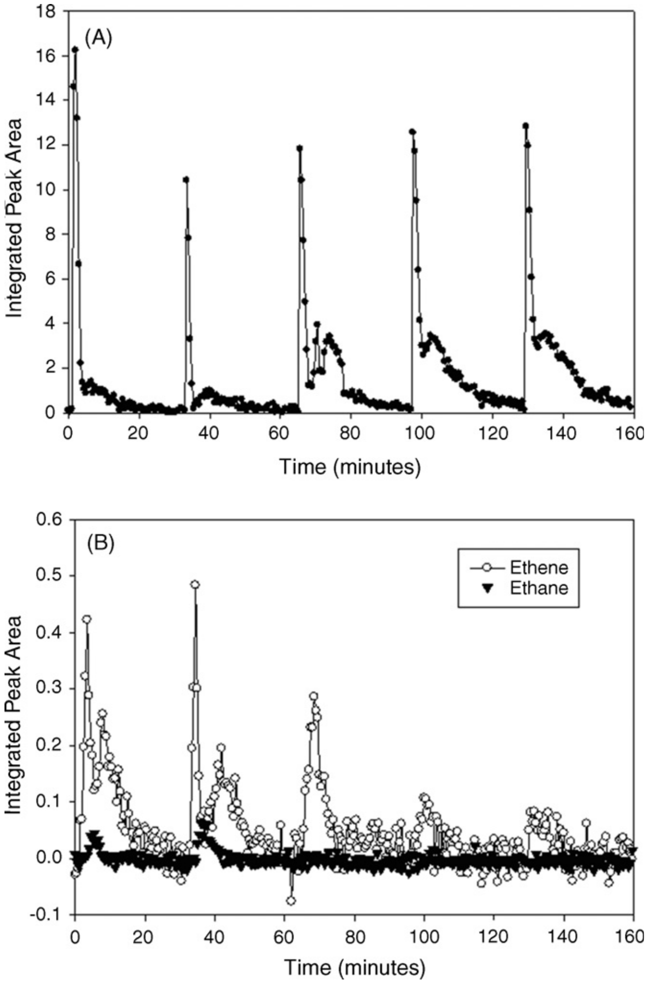

Fig. 13. Integrated peak area for (A) ethyne, (B) ethene and ethane introduced in 5 cm^3 pulses at 35 min intervals with a flow of 5 ml min^{-1}, 100 °C over a over a 2 wt.% Pd/γ-Al_2O_3 catalyst. Between ethyne pulses the reaction cell was purged with helium.

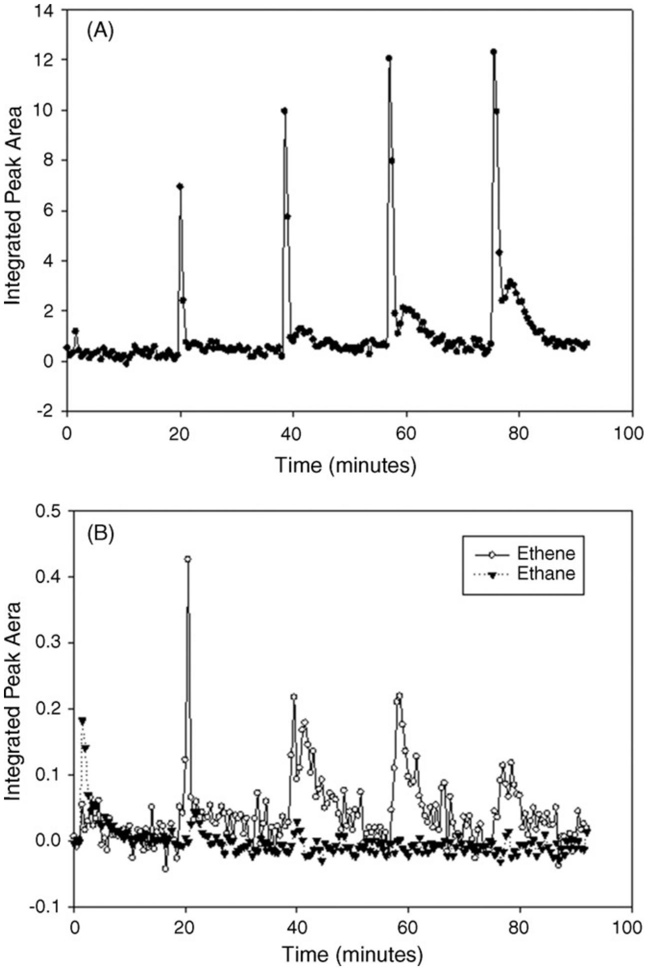

Fig. 14. Integrated peak areas for (A) ethyne, (B) ethene and ethane. Ethyne introduced in 5 cm^3 pulses at 35 min intervals with a flow of 5 ml min^{-1}, 100 °C over a over a 2 wt.% Pd/γ-Al_2O_3 catalyst. Between ethyne pulses the reaction cell was purged with helium. In contrast with other reported experiments, in order to remove surface hydrogen prior to introducing ethyne, after reducing in hydrogen as usual, the catalyst was heated to 200 °C and held for 2 h in a flow of helium.

Ethene is mainly produced in the first three pulses of ethyne, with a much smaller amount being formed in the fourth and fifth pulses. Ethane is only produced in very small quantities during the first and second pulses.

The above results show that ethyne is hydrogenated during the early stages of adsorption upon the 2 wt.% Pd/γ-Al_2O_3 catalyst, even in the absence of molecular hydrogen gas. The question arises as to the origin of the hydrogen. The catalyst preparation involves the reduction of the catalyst in a stream of hydrogen gas, followed by purging for 1 h in helium at 120 °C. However, it is possible that palladium hydride may form during the reduction, which is not removed by the helium purge under such conditions. Also hydrogen may be present as surface hydrogen on the support, which has spilled over from the metal, and as subsurface hydrogen within the support. In order to remove adsorbed hydrogen from the surface of the catalyst, a further experiment was performed, in which the catalyst was heated to 200 °C for an hour in helium following hydrogen reduction. Khan et al. [26] presented TPD profiles for the H_2/Pd system, which showed that hydrogen may persist on the catalyst surface up to around 127 °C (400 K). Therefore, at a temperature of 200 °C the catalyst surface should be free of adsorbed hydrogen. The integrated peak areas are shown in Fig. 14 for ethyne, ethene and ethane. The remarkable feature of the ethyne trace is that the first peak is extremely small relative to the others possibly through adsorbed hydrogen removal promoting ethyne adsorption, and during the first pulse a relatively large amount of ethane is formed. Pulses 2–4 show a significant production of ethene, with less production of ethane. The ethyne trace in pulses 4 and 5 shows evidence of a shoulder after the sharper peak. The evidence of hydrogenation occurring after purging the catalyst at 200 °C suggest that some hydrogenation still occurs even if adsorbed hydrogen and palladium hydride has been removed from the surface. This indicates the possibility of self-hydrogenation of ethyne, possibly through removal of hydrogen from the carbonaceous layer. Alter et al. [29] reported the possibility of self-hydrogenation of alkynes, and Al-Ammar and Webb [7] proposed that the carbonaceous layer acts as a hydrogen transfer medium. In order for this to be the case, the carbonaceous layer must participate in a trans-hydrogenation reaction, in which C=C bonds are formed in the carbonaceous material from alkanes in order to release hydrogen to react with the triple bond of ethyne.

The differences observed between pre-treatment methods suggest that during the first pulse, ethyne adsorbs and reacts to form oligomers to a greater extent on a ‘clean’ catalyst where hydrogen has been removed, due to the smaller first gas phase ethyne peak observed. The selectivity towards ethane also appears to be higher on a ‘clean’ catalyst. This result is slightly surprising, since more hydrogen is obviously required for the production of ethane than ethene. However, on a clean catalyst it would be expected that there exists a larger number of larger Pd sites available for adsorption, consistent with the ‘E’ sites mentioned by Borodziński and Cybulski [5]. These larger sites may be able to retain an ethene molecule for further hydrogenation, with less competition for the adsorption site from ethyne compared with a catalyst which already has pre-adsorbed hydrogen or coke on its surface. Hydrogen must be released from neighbouring sites on which coke is forming. From Fig. 14, it is observed that during the second pulse, the amount of ethane formed is negligible whilst the ethene formation greatly increases. This suggests that as the carbonaceous layer develops on the catalyst the number of available ‘E’ sites decreases, such that ethane formation is suppressed.

Under both sets of pulse-adsorption conditions, the fourth, fifth, and sometimes the third peaks for ethyne show the second broad peak or shoulder, which is thought to correspond to ethyne adsorbed on the catalyst before it desorbs and is eventually flushed out of the chamber. The first and second pulses of ethyne tend to lead to the greater production of ethene and ethane with less of a tail on the ethyne peak. From these experiments it appears that during the coke formation process, the coke is able to release hydrogen, which reacts with ethyne, but after three or four pulses the coke is more stable, probably deficient of hydrogen, and less able to release hydrogen for the reaction.

Fig. 15 shows the pulse adsorption of ethyne over the 0.02 wt.% Pd/α-Al_2O_3 catalyst. In this experiment the first peak of ethyne is of similar magnitude to the subsequent ones, suggesting that less ethyne is converted to coke over the 0.02 wt.% Pd/α-Al_2O_3 catalyst compared with the 2 wt.% Pd/γ-Al_2O_3 catalyst. Some ethene was observed, especially during the first pulse, but negligible ethane was formed. As expected, the 0.02 wt.% Pd/α-Al_2O_3 catalyst shows better selectivity to ethene compared with the 2 wt.% Pd/γ-Al_2O_3, since pore size distribution, the loading and dispersion of metal has been specifically designed for the ethyne hydrogenation reaction. It is suggested that the formation of ethylidyne is inhibited upon the 0.02 wt.% Pd/α-Al_2O_3 compared with the 2 wt.% Pd/γ-Al_2O_3, which reduces amount of ethane formed directly from ethyne. The second pulse of ethyne leads to less ethene formation than the first pulse, and the subsequent pulses produce negligible ethene. The first peak of ethyne does not have a shoulder; the subsequent ones do have a shoulder which is though to result from adsorbed ethyne.

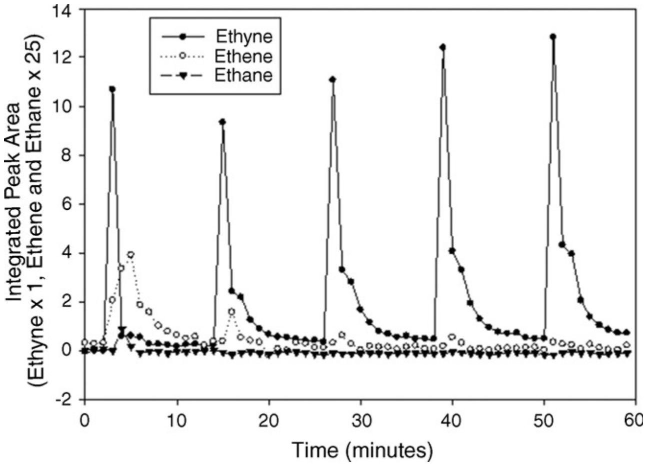

Fig. 15. Integrated peak areas for ethyne, ethene and ethane, whilst introducing 5 cm^3 pulses of ethyne to the cell over a 0.02 wt.% Pd/α-Al_2O_3 catalyst at 100 °C. Pulses introduced to the cell at 12 min intervals, with helium purge between pulses.

4. Conclusions

Adsorption and hydrogenation of both ethyne and ethene has been studied in-situ over two Pd/Al_2O_3 catalysts. For the first time a pulse-adsorption technique combined with on-line monitoring using DRIFTS has been used to observe both the spectra and reaction profiles of ethyne and the products ethene and ethane. The technique is rich in information concerning the conditions under which the carbonaceous layer forms on the catalyst and its chemical nature, as well as the mechanism and kinetics of the hydrogenation reaction. In this paper a qualitative analysis of the spectra and reaction profiles has led to the following conclusions:

- Ethyne adsorption and hydrogenation on both catalysts leads to the formation of a carbonaceous layer on the catalyst surface, whilst neither adsorption nor hydrogenation of ethene leaves such deposits. The carbonaceous layer has spectral features characteristic of octane or longer straight chain alkanes, with some weaker alkene character also, and displays similar spectral features to the upper phase of green oil.
- Surface hydrogen retained on the catalyst initially makes possible the hydrogenation of associatively adsorbed ethyne, which tends to form ethene rather than ethane.
- Removal of hydrogen from the catalyst surface by heating to 200 °C prior to conducting a pulse adsorption experiment leads to significantly more ethane production in the first pulse of ethyne on the 2 wt.% catalyst than the case where palladium hydride remains on the surface. This may be due to the dissociative adsorption of ethyne as ethylidyne on a completely clean catalyst with high metal loading, subsequently leading to direct hydrogenation to ethane. Hydrogen is likely to be supplied from the carbonaceous layer as ethyne dissociatively adsorbs and polymerises. Selectivity of the catalyst towards ethene improves during the second pulse, as the carbonaceous layer reduces the number of clean adjacent palladium sites available for adsorption of ethylidyne.

- Following the first two pulses, the production of ethene and ethane decreases as the carbonaceous layer becomes hydrogen deficient. The third or fourth and fifth pulses therefore tend to show a shoulder after the sharp peak, corresponding to ethyne adsorption on the catalyst.
- The pulse adsorption on the 0.02 wt.% catalyst shows similar behaviour to the 2 wt.% catalyst, except ethane formation is negligible.

The traces of integrated peak profiles have tremendous potential for providing quantitative kinetic and transport information, which will be further investigated and reported upon in future work.

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