RESEARCH PAPER

www.rsc.org/pccp

The hydrogenation of 1,3-pentadiene over an alumina-supported palladium catalyst: an FTIR study[†]

Elaine Opara,^a David T. Lundie,^a Timothy Lear,^a Iain W. Sutherland,^a Stewart F. Parker^b and David Lennon^{*a}

^a Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, UK G12 8QQ. E-mail: d.lennon@chem.gla.ac.uk; Fax: (44)-(0)-141-330-4888; Tel: (44)-(0)-141-330-4372

^b ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK OX11 0QX

Received 26th August 2004, Accepted 28th October 2004 First published as an Advance Article on the web 11th November 2004

The hydrogenation of a mixture of *cis*- and *trans*-1,3-pentadiene over a 1% Pd/Al₂O₃ catalyst at 303 K has been studied using infrared spectroscopy to monitor the changes in the composition of the gas phase over the catalyst as a function of time. The reaction is seen to occur as a consecutive process, with the terminal double bond hydrogenated in advance of the internal double bond. Vibrational assignments have been confirmed through ancillary calculations for a number of C₅ molecules. The reaction profile is consistent with the catalyst presenting two distinct reaction sites: hydrogenation of the terminal double bond occurs at Site α , whilst Site β is responsible for hydrogenation of the internal double bond. *Trans*-pent-2-ene is identified as the only reaction intermediate. From comparative studies of the hydrogenation of pentenes over the catalyst, the absence of any *cis*-pent-2-ene in the reaction mixture is tentatively attributed to *cis*-1,3-pentadiene isomerising at Site α to form *trans*-1,3-pentadiene. The effect of toluene-d₈ to act as a chemical modifier was also investigated and shown to selectively poison Site β , Site α being unperturbed.

1. Introduction

Olefin chemistry on the industrial scale is closely linked with increased refinery capacity and covers a wide range of chemical processes.1a C2-C4 olefins dominate although higher olefins (C5-ca. C18) are also industrially significant, with an increasing interest in unbranched olefins due to the latter's linearity linked to products with favourable advantages such as biodegradability.^{1b} A crucial descriptor for the performance of unbranched higher olefins is whether the double bond is positioned at the end of the molecule (terminal) or is internal to the molecule. The market for terminal olefins is greater, with a world manufacturing capacity in 1994 of 2.2 Mtonne.^{1c} Diolefins, or dienes, are also industrially significant, with C4 and C5 1,3dienes featuring strongly. Here, the double bonds are conjugated and the molecules are more reactive than their monoene counterparts.^{1d} 1,3-Butadiene dominates this market and consequently a number of studies have investigated the reaction characteristics of this molecule. For example, the hydrogenation properties have been comprehensively studied by Wells and co-workers²⁻⁵ and the general topic has been reviewed by Webb.⁶ More recently, Souza et al. have examined geometric effects active in butadiene hydrogenation over Pd supported systems⁷ and Moyes *et al.* have examined electronic effects in butadiene hydrogenation catalysed by transition metals.⁸

Of the higher homologues, Wells and Wilson investigated the hydrogenation of *cis*- and *trans*-1,3-pentadiene catalysed by Co, Ni, Cu, Pd and Pt catalysts, with the general features of the gas phase hydrogenation closely resembling those of 1,3-butadiene.9 Reactant isomerization was slow over Pd catalysts and, on the basis of *n*-pentene distributions, it was concluded that 3,4- addition of hydrogen was more important than 1,2addition.⁹ Additionally, pentane yields were shown to be low, with the catalysts exhibiting a high selectivity for the partial hydrogenation products. Vasquez and Madix examined the reactivity of unsaturated linear C₆ hydrocarbons on Pd(111) surfaces and showed 1,3-hexadiene to hydrogenate to hexene but, in a similar manner to that reported by Wells and Wilson,⁹ further hydrogenation to hexane was not observed.¹⁰ H-D exchange into the adsorbed alkene was reported, which was proposed to occur via reversible C-H bond formation in a halfhydrogenated intermediate.¹⁰ Subsequent work by Jackson et al. used FTIR spectroscopy to investigate the hydrogenation of 1,3-hexadiene over a silica-supported Pd catalyst in the presence and absence of toluene-d₈, acting as chemical modifier.¹¹ Depending on the order in which the modifier was added to the reaction system, the toluene-d8 could act as either a promoter or a poison. Furthermore, with respect to the relative reactivity of the two olefin groupings, that study revealed differences in the reaction characteristics of 1,3-hexadiene compared to 1,3-pentadiene. Vasquez and Madix suggest that the central double bond of 1,3-hexadiene to be hydrogenated before the terminal double bond,¹⁰ however, the infrared evidence for the Pd/SiO2 catalyst clearly indicated that the terminal double bond was hydrogenated in advance of the internal double bond.¹¹ Additionally, full hydrogenation of 1,3-hexadiene was reasonably facile over the Pd/SiO2 catalyst,¹¹ whilst this pathway was not accessible for the same molecule on the Pd single crystal.¹⁰

Regarding selective reduction of dienes, usually it is the least hindered double bond that is preferentially hydrogenated and, when steric hindrance effects are approximately equal, the most strained bond will be hydrogenated first.¹² Selectivity characteristics are known to be metal dependent,^{12,13} which is thought

5588

[†] Electronic supplementary information (ESI) available: Comparison of the inelastic neutron scattering spectrum of pentane (solid line) with that calculated by DFT (B3LYP/6-31G*(d,p)) (dashed line) (Fig. S1); comparison of observed and calculated positions and intensities of *cis*and *trans*-1,3-pentadiene (Tables S1 and S2). See http://www.rsc.org/ suppdata/cp/b4/b413178a/

to reflect the relative tendencies of metals to induce conjugation through double bond migration.¹² Additionally, for reductions of dienes to monoenes, it is often practical to stop hydrogen consumption at the stoichiometric point, as few reactions will stop spontaneously and will continue on to form the fully saturated product.¹²

Against this background, it was decided to investigate the hydrogenation of 1,3-pentadiene over an alumina-supported Pd catalyst, to determine the relative sensitivity of the two olefin functionalities to hydrogenation, and to evaluate the potential for toluene-d₈ to act as a selective modifier for this reaction. Following on with the approach adopted for the 1,3hexadiene study over a supported palladium catalyst,¹¹ FTIR was selected to monitor the gas phase reaction as distinct vibrations of the reacting molecules can be used to follow the course of the reaction sequence. Additionally, by using deuterated toluene, any incorporation of hydrogen from the modifier to the product can be readily identified, providing information on hydrogen exchange processes present at the catalyst surface. It is noted that the separation of 1,3-pentadiene from the C₅ cracking fraction is very involved, $1^{1c,e}$ with the 1,3-pentadiene existing as a mixture of cis- and transisomers. To mimic the likely industrial feed, this study has investigated a mixture of cis- and trans-1,3-pentadiene. Hydrogenation of C₅ monoenes was also considered to gauge the effect of conjugation on the hydrogenation activity. Vibrational assignments have been confirmed through ancillary calculations for a number of C_5 molecules.

This study shows that the reaction proceeds as a consecutive process, with the terminal double bond hydrogenated in advance of the internal double bond. The reaction profile is consistent with the catalyst presenting two distinct reaction sites: hydrogenation of the terminal double bond is thought to occur at Site α , whilst Site β is responsible for hydrogenation of the internal double bond. Whereas previous work reports little or no isomerisation for 1,3-pentadiene hydrogenation over Pd-based catalysts,⁹ *cis* to *trans* isomerisation is shown to be facile over this catalyst and is tentatively associated with Site α . The effect of toluene-d₈ to act as a chemical modifier is noted to be different to that observed in the 1,3-hexadiene study¹¹ and, moreover, is seen to selectively poison Site β , leaving Site α unperturbed.

2. Experimental

2.1 Catalyst preparation and characterisation

The 1% w/w Pd/Al₂O₃ catalyst was prepared from anhydrous palladium chloride (Fluka Chemicals) by wet impregnation. The support material was γ -alumina (Degussa Aluminium Oxid C, BET surface area 102 m² g⁻¹). Dropwise addition of HCl was added to a mixed slurry prepared in water to ensure complete dissolution of the PdCl₂. The mixture was transferred to a rotary evaporator where the water was slowly removed by maintaining the sample at 353 K under a nitrogen atmosphere to produce a free-flowing powder. The resulting catalyst was then dried for 12 h at 373 K.

Atomic absorption measurements were performed using a Perkin Elmer 1100B spectrophotometer, which revealed the actual Pd loading of the catalyst to be 0.91%. Carbon monoxide pulse chemisorption was used to evaluate palladium dispersion. Saturation corresponded to a CO coverage of $19.5 \pm 1.4 \mu mol CO g_{(cat)}^{-1}$, with the error representing ± 2 standard deviations in triplicate measurements. This coverage corresponds to 2.35×10^{19} surface Pd atoms g⁻¹, assuming a Pd : CO surface stoichiometry of $2 : 1, ^{14}$ which represents a metal dispersion of 45.6%. Assuming the metal particles are spheres of equal diameter, the chemisorption result equates to a mean particle size of 2.4 nm. The catalyst was examined by transmission electron microscopy using a JOEL 1200 FX

microscope but, unfortunately, it was not possible to precisely identify metal particles against the presence of the support material. This observation is reasonably consistent with the chemisorption data, in that at 2.4 nm the metal particles are too small to be detected by this instrument with a support material that offers poor contrast to metal particles of these dimensions. Temperature programmed reduction studies confirmed that reduction of the palladium occurred below room temperature.

2.2 Apparatus and reaction testing

The reactor was based around a modified Graseby-Specac 5661 heated gas cell fitted with KBr windows and a 20140 automatic temperature controller. Two Brooks 5850E mass flow controllers controlled the flow of hydrogen (BOC, 99.995% purity) and helium (BOC, 99.999% purity) *via* an in-line purifier (Messer Grieshiem Oxisorb) into a 50 cm³ stainless steel mixing vessel packed with glass beads before entering into the reaction cell. A back pressure regulator (Norgen) and isolation valves allowed the cell to be isolated and the pressure monitored. The reactor was housed within a Nicolet Avatar FTIR spectrometer and fitted *via* rubber sleeves to the spectrometer internal gas purge facility (Peak Scientific) to minimise atmospheric contributions to the spectra. The reactor was additionally fitted with an injection septum, through which reagents could be added to the reaction system.

The catalyst was loaded into the reactor as a pressed disc. For all the studies presented in this study, the catalyst was mounted on a glass sample holder so that the catalyst was not in the path of the infrared beam. In this way, all spectra presented arise from the composition of the gaseous phase, with no contribution from the catalyst or the catalyst surface. This simplifies the analysis considerably. Subsequent studies have examined the infrared spectrum when the catalyst disc is mounted in the beam but that work will be presented elsewhere. The catalyst mass was selected to yield a full hydrogenation profile in a time that was sufficiently long (ca. 30 min) so that infrared spectra of sufficient signal/noise ratio could be repeatedly recorded during that interval, so as to define a representative reaction profile. In this manner, 1 part of the 1% Pd/Al₂O₃ catalyst was diluted with 9 parts of the support material (γ -alumina), ground in a pestle and mortar, then *ca*. 20 mg of this mixture pressed into a thin disc using a Perkin Elmer hydraulic press. The catalyst disc was loaded into the reactor and reduced in the following manner. The cell temperature was maintained at 303 K and a mixture of 6.3% H₂-93.7% He was passed through the reactor at a flow rate of 20 ml min⁻¹ for 25 min, then the hydrogen composition was increased to yield an equimolar mixture of hydrogen and helium at the same flow rate. After 5 min the reactor was isolated at a pressure of 1672 torr (0.223 MPa). Hydrocarbons were injected into the cell via the septum. 9 µl of 1,3-pentadiene (piperylene) were used and 5 µl of toluene-d₈. Scanning commenced as soon as the injection of the hydrocarbon was complete. This combination of reagents results in a hydrogen: pentadiene ratio of 49 : 1 and a pentadiene : Pd(s) ratio of 1160 : 1, *i.e.* hydrogen is in excess of the hydrocarbon and the hydrocarbon is in excess of palladium surface atoms. Thus, the infrared cell is acting as a batch reactor under conditions where reasonable conversions represent multiple turnovers, unhindered by the availability of hydrogen. Infrared spectra were recorded at a resolution of 4 cm⁻¹, co-adding 8 scans and requiring an acquisition time of 10 s. The reaction temperature was maintained at 303 K for all the reactions studied. Experiments on an alumina disc showed no conversion of 1,3pentadiene. The toluene- d_8 (Aldrich) had a minimum purity of 99.95% D. The 1,3-pentadiene used was technical grade (Aldrich, >90% purity) and comprised a mixture of cis- and trans-isomers. The sample was analysed by gas liquid chromatography and ¹H NMR spectroscopy, which showed the 1,3-pentadiene isomeric distribution to be comprised of 36% of the *cis*-isomer and 64% of the *trans*-isomer. Reflecting the industrial scenario, ^{1c,e} a small quantity of cyclopentene was also present. This comprised <4% of the mixture and therefore represents a minor contaminant. Infrared spectroscopy of the 1,3-pentadiene in the vapour phase confirmed the mixture of isomers.¹⁵ Pent-1-ene (>99% purity, Aldrich) and *cis*-pent-2-ene (>98% purity, Aldrich) were analysed and found to contain no cyclopentene.

3. Computational studies

Perhaps surprisingly, there have been very few studies of the vibrational spectra of C_5 molecules. Pentane¹⁶ and *cis*- and *trans*-1,3-pentadiene¹⁷ have been studied but there are no studies of the isomeric pentenes to our knowledge. Unambiguous assignment of the modes of the molecules investigated here is essential to their correct identification under catalytic conditions. Density functional theory (DFT) provides frequencies that are accurate to a few per cent for small molecules.¹⁸ To provide the necessary vibrational data we have carried out DFT calculations using the B3LYP functional with the 6-311*g(d,p) basis set as implemented in GAUSSIAN03.¹⁹ Comparison with the literature values for cis- and trans-1,3-pentadiene¹⁷ gave generally good agreement, as shown in Tables S1 and S2.[†] The few disagreements occur for modes that are weak in both the infrared and Raman spectra, so are less certain. A stringent test of any calculation of the vibrational spectrum is comparison with the inelastic neutron scattering (INS) spectrum, since this only depends on the atomic displacements in the modes.²⁰ The INS spectrum of pentane is available from www.insdatabase.rl.ac.uk and the comparison is shown in Fig. S1.[†] The excellent agreement is strong evidence that the DFT calculations provide a rigorous basis for the assignment of the spectra.

4. Results

The hydrogenation of 1,3-pentadiene was studied under three reaction environments. Firstly, the diene was added to the reactor that was pre-charged with an excess of hydrogen gas. Secondly, the hydrogen charged catalyst was pre-treated with a potential modifier, toluene- d_8 , before introduction of the diene. Thirdly, the order of addition of the reagents was further shuffled so that the modifier was added prior to the diene and the hydrogen. Finally, in order to evaluate the relative rates and performance of the monoene options, the hydrogenation of pentene over a hydrogen charged catalyst was also examined.

4.1. $H_2 + 1,3$ -pentadiene

Post-catalyst reduction, the diene was injected into the reactor with an overpressure of hydrogen of 836 torr present over the catalyst and the infrared spectrum of the gas phase continuously monitored. The various reacting entities exhibit a range of vibrational modes that are characteristic of their molecular arrangements, which thereby permit the reaction profile for the hydrogenation reaction to be determined. For 1,3-pentadiene, the anti-symmetric =CH stretch at 3096 cm⁻¹, the overtone of the = CH_2 wag at 1807 cm⁻¹ and the fundamental of the = CH_2 wag at 900 cm⁻¹ represent diagnostic regions of the vibrational spectrum.¹⁷ Partial hydrogenation converts the diene to a monoene with, for example in the case of transpent-2-ene, the symmetric -CH = stretch at 3024 cm⁻¹ and the trans-CH=CH wag at 969 cm⁻¹ providing distinct vibrational signatures.²¹ Full hydrogenation yields pentane. The intensity of the aliphatic modes reflects conversion but, additionally, the anti-symmetric methyl deformation exhibits a slightly higher frequency (1462 cm⁻¹) than its unsaturated counterparts.^{15,21}



Fig. 1 The infrared spectrum in the $3150-2770 \text{ cm}^{-1}$ region as a function of time for Pd/Al₂O₃ + H₂ + 1,3-pentadiene: (a) 0, (b) 8, (c) 12, (d) 23 and (e) 27 min. t = 0 represents the time when the injection of the diene into the reactor is complete.

Collectively, these modes can be used to examine the reaction coordinate and investigate the principal stages of the hydrogenation process.

Fig. 1 presents the infrared spectrum in the $3150-2770 \text{ cm}^{-1}$ region as a function of time, with t = 0 representing the time when the injection of the diene into the reactor is complete. At this time two bands at 3096 and 3024 cm⁻¹ represent unsaturated functionalities. The anti-symmetric =CH₂ stretch at 3096 cm^{-1} is uniquely associated with the terminal olefinic group and reduces to zero intensity between 8-12 min. The symmetric -CH= stretch at 3020 cm⁻¹ has residual intensity at 12 min but is absent in the 27 min spectrum. This feature is associated with the presence of an olefinic functionality and, therefore, it appears that the terminal double bond is hydrogenated before the internal double bond. The formation of saturated species can be represented by the intensity of the antisymmetric C-H stretch about 2976 cm^{-1,21} This is seen to increase dramatically within the first 8 min of reaction. The proportionally greater band intensity of the saturated analogue is thought to partially reflect the distribution of material within the reactor. Unsaturated species will favour binding to the catalyst, reducing their gas phase concentration. Upon formation of the saturated product, these molecules are released to the gas phase, where a noticeable increase in intensity is observed.

Fig. 2 presents the infrared spectrum in the 1880–1730 cm⁻¹ region as a function of time. At t = 0, a sharp band is seen at 1810 cm⁻¹, which is assigned to the overtone of the =CH₂ wag of 1,3-pentadiene.¹⁷ On increasing time, the intensity of this band progressively decreases up to 12 min, when no signal is detected. This mode is specifically associated with the terminal



Fig. 2 The infrared spectrum in the $1880-1730 \text{ cm}^{-1}$ region as a function of time for $Pd/Al_2O_3 + H_2 + 1,3$ -pentadiene: (a) 0, (b) 5, (c) 8 and (d) 12 min.



Fig. 3 The infrared spectrum in the $1125-790 \text{ cm}^{-1}$ region as a function of time for $Pd/Al_2O_3 + H_2 + 1,3$ -pentadiene: (a) 0, (b) 8, (c) 12, (d) 23 and (e) 27 min.

double bond of the diene and indicates hydrogenation to be occurring at this centre. The intensity profile for the 1810 cm^{-1} band matches that of the anti-symmetric =CH₂ stretch at 3096 cm⁻¹ seen in Fig. 1, confirming the initial loss of the terminal olefinic unit.

The spectrum in the $1125-790 \text{ cm}^{-1}$ region is shown in Fig. 3. The t = 0 spectrum (Fig. 3a) is characterised by the *trans*-CH =CH wag (=CH out-of-plane deformation) at 1002 cm⁻¹ which represents the diene functionality, and the fundamental of the = CH₂ wag at 900 cm⁻¹,¹⁷ which is uniquely associated with the terminal olefinic group. At 8 min the trans-CH=CH wag appears to shift to 969 cm^{-1} , then to progressively decrease in intensity up to 23 min, where no significant intensity is seen. Although no such shift is apparent with the =CH₂ wag, the intensity of this feature drops dramatically in the first 8 min but then remains constant up to 27 min. The residual intensity at 910 cm⁻¹ beyond 8 min is attributed to saturated product¹⁵ and the rapid decrease up to that time is associated with consumption of the terminal olefinic group. This analysis is consistent with the rate behaviour of the antisymmetric =C–H stretch (3096 cm⁻¹, Fig. 1) and the overtone of =CH₂ wag (1807 cm⁻¹, Fig. 2). The shift of the 1,3-pentadiene *trans*-CH=CH wag at 1002 cm⁻¹ to 969 cm⁻¹ is indicative of the transition from diene to monene, with the resulting loss of conjugation causing a shift of this mode to lower frequency.²² Comparing candidate monoenes,^{15,23,24} va-



Fig. 4 Reaction profile for the hydrogenation of 1,3-pentadiene over a 1% Pd/Al₂O₃ catalyst at 303 K. The vibrational modes used to define the relative concentration/time dependence of the reacting species are presented in parentheses: 1,3-pentadiene (=CH₂ wag at 904 cm⁻¹), *trans*-pent-2-ene (*trans*-CH=CH wag at 969 cm⁻¹) and pentane (anti-symmetric C–H deformation at 1463 cm⁻¹).

pour phase infrared measurements showed pent-1-ene to be characterised by two strong features in this region at 1005 (*trans*-CH wag) and 920 cm⁻¹ (CH₂ wag),²¹ whereas *cis*-pent-2-ene exhibits a band at 940 cm⁻¹. Calculations show that this mode is the out of phase C_1 - C_2 and C_4 - C_5 stretch. None of these bands coincide with the 969 cm⁻¹ feature present in Fig. 3. Rather, this band more closely corresponds to that of the *trans*-CH=CH wag of *trans*-pent-2-ene,^{15,21} to which this feature is assigned. Thus, this analysis reveals that *trans*-pent-2-ene is formed as a reaction intermediate and there is no evidence for production of other pentenes. The absence of pent-1-ene confirms the selective hydrogenation of the terminal double bond in advance of the internal double bond hydrogenation.

The richness of the vibrational spectrum can then be used to map out a reaction profile for the series of events occurring within the reactor upon addition of the diene to the hydrogencharged catalyst. This is presented in Fig. 4. The terminal double bond of 1,3-pentadiene is hydrogenated within a period of 10 ± 2 min to form uniquely *trans*-2-pentene. This species is then hydrogenated further to produce pentane. That process occurs within 25 ± 2 min. The errors represent the range observed in duplicate measurements and the data is collated in Table 1. No other reaction products were identified during the course of the reaction sequence. The absence of pent-1-ene in the spectrum eliminates the possibility that the reaction follows a concurrent pathway and therefore the reaction is shown to occur *via* a step-wise (consecutive) process.

The 1,3-pentadiene mixture contains a small quantity of cyclopentene (<4%). Cyclopentene can be distinguished from *cis*- and *trans*-1,3-pentadiene and the resulting hydrogenation products by strong bands about 713 and 1067 cm⁻¹. The former is a *cis*-C–H wag, whereas the latter is an out of plane ring deformation. Neither of these features are observable when the 1,3-pentadiene mixture is injected into the reaction cell. This could reflect the low concentration of the cyclopentene is adsorbed on the catalyst surface. Whichever, this entity is thought to play no significant part in the observed chemistry. This matter is considered further in Section 5.1.

4.2. $H_2 + toluene-d_8 + 1,3$ -pentadiene

The second series of diene hydrogenation reactions involved introducing a potential chemical modifier, toluene-d₈, to the hydrogen charged catalyst in advance of the diene. Whereas the anti-symmetric =CH₂ stretch at 3096 cm⁻¹ was removed between 9 and 10 min, in a comparable manner to that seen previously, the symmetric -CH= stretch at 3024 cm⁻¹ was still present at 77 min. This latter mode represents the presence of an olefinic grouping and the time taken for the loss of olefinic

Table 1 Time for the complete hydrogenation of the terminal and internal double bonds within the C_5 framework for the five reactions studied. The errors quoted represent the range from duplicate measurements

Reaction No.	Reaction	t _{terminal} /min	t _{internal} /min
1	$H_2 + 1,3$ -pentadiene.	10 ± 2	25 ± 2
2	$H_2 + toluene-d_8 + 1$,	10 ± 2	ca. 100
	3-pentadiene.		
3	Toluene-d ₈ +1,3-pentadiene	12 ± 2	43-164
	$+ H_2.$		
4	$H_2 + cis$ -pent-2-ene.		25–27
5	$H_2 + pent-1-ene.$	11-14	
6	$H_2 + 1,3$ -pentadiene after	17–19	27-30
	3 repeat 1,3-pentadiene		
	hydrogenation cycles.		



Fig. 5 The infrared spectrum in the $1100-800 \text{ cm}^{-1}$ region as a function of time for $Pd/Al_2O_3 + H_2 + \text{toluene-}d_8 + 1,3\text{-pentadiene:}$ (a) 0, (b) 9, (c) 12, (d) 77 and (e) 100 min.

character is considerably longer than in the absence of a modifier. This increased reaction time relates specifically to consumption of the internal double bond.

The 1100–800 cm⁻¹ region is shown in Fig. 5 and confirms the reduced rate of reaction for the second stage hydrogenation reaction under these conditions. The =CH₂ wag of 1,3-pentadiene at 904 cm⁻¹ is lost between 9 and 12 min. The loss of conjugation again attenuates the 1,3-pentadiene *trans*-CH= CH wag at 1002 cm⁻¹. The resulting presence of *trans*-pent-2ene is signified by the *trans*-CH==CH wag of this entity at 969 cm⁻¹. This band has minimal intensity at 100 min, indicating that the *trans*-pent-2-ene has been fully hydrogenated about this time.

From duplicate measurements, the complete loss of the terminal bond requires 10 ± 2 min, which indicates the modifier to have negligible effect on the first stage hydrogenation process. In contrast, hydrogenation of the internal double bond requires ca. 100 min, 4 times longer than when no modifier was present (Table 1). Clearly, the modifier is acting as a selective poison for the second stage hydrogenation reaction. It is noted that this modification to reaction rate has not affected the selectivity profile. Additionally, if the Datoms associated with the toluene-d8 were incorporated into the pentane product, there would be a growth in intensity of the aliphatic C-D stretching modes around the region of 2100 cm⁻¹.¹¹ No modes were observed around this region at any stage in the hydrogenation process and the modes associated with the non-deuterated aliphatic were observed to increase in intensity throughout the reaction. Therefore, deuterium was not incorporated into the product(s).

4.3. Toluene- $d_8 + 1$,3-pentadiene + H_2

The final series of diene hydrogenation reactions involved introducing the potential modifier before the diene and the hydrogen gas. The anti-symmetric =CH₂ stretch at 3096 cm⁻¹ was removed between 12 and 43 min and the symmetric -CH=stretch at 3024 cm⁻¹ was still present at 43 min but completely removed by 164 min. Fig. 6 presents the infrared spectrum in the 1100–800 cm⁻¹ region as a function of time. The =CH₂ wag at 904 cm⁻¹ is lost between 12 and 43 min. The *trans*-CH =CH wag shifts to 969 cm⁻¹, indicating formation of *trans*pent-2-ene, and disappears between 43 and 164 min. The rate of loss of the terminal double bond is noted at 12 ± 2 min, which is within general agreement for the loss of this entity in reactions 1 and 2 (Table 1). The loss of the internal double bond is, however, reported as 43–164 min, which is broadly consistent with that seen for reaction 2. Once again, as in



Fig. 6 The infrared spectrum in the $1100-800 \text{ cm}^{-1}$ region as a function of time for Pd/Al_2O_3 + toluene- d_8 + 1,3-pentadiene + H₂: (a) 0, (b) 4, (c) 7, (d) 12, (e) 43 and (f) 164 min.

reaction 2, no incorporation of deuterium was observed in the pentane product.

4.4. Pentene hydrogenation

Previous work from this laboratory on hydrogenation reactions over supported Pd catalysts has shown that certain catalysts can present a substantial barrier to alkene hydrogenation.²⁵ In order to check that no such problems existed with this catalyst and to ensure that the catalyst was capable of hydrogenating a terminal and an internal double bond in the absence of any other olefinic functionality, hydrogenation of the monoenes pent-1-ene and cis-pent-2-ene was investigated. Fig. 7 presents the infrared spectrum in the 1050-875 cm⁻ region for the hydrogenation of *cis*-pent-2-ene as a function of reaction time. The t = 0 plot (Fig. 7a) shows the band at 933 cm^{-1} (out of phase C₁–C₂ and C₄–C₅ stretch of *cis*-pent-2-ene) to shift to 969 cm^{-1} , which is characteristic of the *trans*-CH= CH wag.²¹ The 969 cm⁻¹ feature then decreases in intensity on increasing reaction time up to 27 min, when no signal is apparent. This sequence indicates that, in the presence of the catalyst, the cis-pent-2-ene isomerises to trans-pent-2-ene, which is then hydrogenated to form pentane. The residual signal at 915 cm⁻¹ in Fig. 7e, initially evident at 16 min, is associated with the formation of pentane.15

Pent-1-ene hydrogenation was shown to be facile over this catalyst and the times for the complete hydrogenation of the terminal and internal double bonds within the C_5 framework are presented in Table 1. Concentrating on reactions 1 and 5, it is seen that the time taken for the hydrogenation of pent-1-ene



Fig. 7 The infrared spectrum in the 1050–875 cm⁻¹ region as a function of time for Pd/Al₂O₃ + H₂ + *cis*-2-pent-2-ene: (a) 0, (b) 7, (c) 11, (d) 16 and (e) 27 min.

is comparable to that observed for the terminal double bond of the diene, performed in the absence of the modifier. In a similar fashion, comparing reactions 1 and 4, the hydrogenation rate for *cis*-pent-2-ene is comparable to that observed for the internal double bond of the diene. In the following section, these results are considered along with the preceding reactions to consider the mechanistic implications for the reaction of 1,3pentadiene and unsaturated C_5 molecules with hydrogen over this Pd/Al₂O₃ catalyst.

5. Discussion

5.1 Mechanistic implications

With reference to Table 1, the similarity between the time taken for complete hydrogenation of the terminal and internal double bonds in 1,3-pentadiene and that observed for cispent-2-ene (internal double bond) and pent-1-ene (terminal double bond) is strongly suggestive of a two-site model. The data are consistent with two distinct active sites: terminal double bonds are hydrogenated at Site α , with a reaction time of ca. 12 min; and internal double bonds are hydrogenated at Site β , with a reaction time of *ca*. 26 min under the conditions studied. It is possible that steric or stereo-chemical effects could confer two rates of reaction at the same site, however, this situation would be expected to be sensitive to cooperative effects, i.e. rates sensitive to the presence of a co-reactant, and yet the conversion rates for the monoenes match those for their diene counterparts. Another possibility is that 2 sites could be operating simultaneously. This appears not to be the case, as this scenario would lead to the formation of pent-1-ene from the hydrogenation of the terminal double bond in 1,3pentadiene, which is not observed. Furthermore, the absence of pent-1-ene in the 1,3-pentadiene hydrogenation profile has already discounted the possibility of concurrent reactions originating from a single site (see section 4.1). The 2-site model remains consistent with a consecutive process. Recent work by Borodzinski invoking steric arguments has proposed two site regimes as being active for ethyne hydrogenation over supported Pd catalysts.^{26,27} In Borodzinski's model, the active sites are defined by the metal sites accessible within a hydrocarbonaceous overlayer that forms during an initial conditioning process. These sites are termed Site A and Site E. Site A affords a smaller Pd footprint and is associated with ethyne hydrogenation but excludes ethene adsorption and is therefore inactive for ethene hydrogenation. All reagents adsorb at the larger Site E, which is responsible for the hydrogenation of ethene to ethane.²⁷ Recent work from these laboratories has shown a similar 2-site model to also provide a comprehensive description for propyne hydrogenation over supported metal catalysts.^{14,25} In that work, Type I sites were assigned as being responsible for full hydrogenation of propyne to propane, whereas partial hydrogenation of propyne to propene occurs at Type II sites.^{14,25} It is possible that similar distributions of sites are active on this catalyst under the reaction conditions presented here, with Sites α and β differentiating between terminal and internal double bonds on steric grounds. Regretfully, at this time, it is not possible to interrogate these sites directly and therefore it is not possible to determine if Sites A and E^{27} or Sites I and II^{14,15} equate to Sites α and β . However, similar characteristics are indeed observed and the comparisons appear to indicate that conventional catalyst preparations lead to a distribution of reaction sites under steady state operation, which can confer specific selectivity characteristics in multi-stage hydrogenation reactions.

A major difference in the preceding FTIR study of 1,3hexadiene hydrogenation over a Pd/SiO₂ catalyst¹¹ compared to the work performed on a Pd single crystal¹⁰ was that the latter study suggested that the internal double bond was hydrogenated in advance of the terminal double bond. This work on 1,3-pentadiene hydrogenation over a Pd/Al₂O₃ catalyst clearly identifies the terminal double bond to react first and is consistent with the early work of Dobson et al.,²⁸ who identified hydrogenation to occur on multifunctional molecules in clear cut stages, with hydrogenation over a Pd/C catalyst occurring first at the terminal double bond then at the internal double bond. Such an analysis suggests caution is required in extrapolation of results from metal single crystals to finely divided supported metal catalysts. This topic has recently been addressed by Freund and co-workers, who have shown this matter is not just an issue of a 'pressure gap'. Their work on pentene hydrogenation over model Pd/Al_2O_3 catalysts^{29,30} shows that full hydrogenation is possible on the Pd/Al₂O₃ model catalysts but is not accessible on a hydrogen treated Pd(111) surface. These studies demonstrate the crucial aspect of hydrogen supply in hydrogenation reactions,³¹ with metal particles providing hydrogen that is not available on the extended structures of the metal single crystal. However, morphological effects are also expected to contribute to the overall catalytic performance and it is noted that in the study of 1,3-pentadiene hydrogenation by Wells and Wilson that pentane yields over supported Pd catalysts were low.⁹ In fact, these authors suggest that alkane formation may require a distinct surface site which, presumably, is absent or ineffective on their catalysts. In the presence of a generous hydrogen supply, the fully saturated product is readily attained in this work. Furthermore, the earlier study of 1,3-pentadiene on supported metal catalysts showed the presence of pent-1-ene, cis- and trans-pent-2-ene in the product distribution,⁹ which contrasts markedly with that seen in this study. In fact, their results are consistent with a concurrent process, rather than the consecutive series of hydrogenation steps seen in this work. Such a discrepancy suggests that the active site distributions and overall performance of the two catalysts are fundamentally different. Assuming that the initial formation of hydrocarbonaceous overlayers is responsible for the catalyst selectivity characteristics,^{14,32,33} it is tentatively assumed that the catalyst conditioning process is different in both cases and leads to catalysts with different geometric constraints on the active sites³³ and different hydrogen exchange characteristics at these sites. Linkage of the active site distribution with catalyst preparative conditions is highly desirable and would constitute a major advance in heterogeneous catalysis.

It is possible that the small presence of the cyclopentene impurity in the 1,3-pentadiene sample is perturbing the pentadiene hydrogenation characteristics. With reference to Table 1, this possibility is discounted because *cis*-pent-2-ene and pent-1ene give essentially the same reaction times as that identified for the related units of the 1,3-pentadiene molecule. The pentene samples are pure and contain no cyclopentene, indicating that reaction times are unaffected by the presence of cyclopentene in such small quantities. Rather, the absence of any cyclopentene feature in the gas phase is consistent with this minority species being rapidly hydrogenated to cyclopentane, where it takes no further part in the reaction chemistry.

5.2 The effect of the modifier

Table 1 illustrates how the addition of the chemical modifier, toluene- d_8 , can affect the relative hydrogenation characteristics of the reaction system. Interestingly, reactions 2 and 3 show Site α to be unaffected by toluene- d_8 addition, however, the modifier has a pronounced effect on Site β . Adding toluene- d_8 before the diene (reaction 2), leads to a 4-fold increase in the time taken to hydrogenate the internal double bond (at Site β). Changing the order in which the modifier is presented to the catalyst (reaction 3) does not seem to unduly alter this hydrogenation rate. Thus, it appears that the modifier has no effect on Site α but it does retard the hydrogenation rate at Site β , with no apparent sensitivity to the order of the addition process. In this way, toluene- d_8 is behaving as a selective poison, in that its presence preferentially retards hydrogenation of the internal double bond, which occurs at Site β .

The modifier is clearly inducing different characteristics in the Pd/Al₂O₃/H₂/1,3-pentadiene system to that seen for Pd/ SiO₂/H₂/1,3-hexadiene.¹¹ Crucially, all of the spectra in the former show no evidence of D incorporation into the products (spectra not shown). The implication of this is that the toluened₈ is molecularly, not dissociatively, adsorbed. This will then prevent any H/D exchange occurring on the Pd surface and then, ultimately, transferring into the C₅ molecular unit. Alternatively, if any dissociation of the toluene was occurring, presumably centred about the methyl group,^{11,34–36} it occurs to such a small extent that it is below the detection limits of the spectral acquisition conditions used here.

5.3 Catalyst deactivation issues

In order to evaluate if catalyst deactivation might disproportionally affect the hydrogenation kinetics, reaction 6 was performed where the hydrogenation rates for 1,3-pentadiene were monitored after a fresh, activated catalyst had undergone 3 complete diene hydrogenation cycles. The results for the fourth hydrogenation reaction are presented in Table 1, which shows a modest increase in hydrogenation times for both sites, consistent with the reacting system exhibiting a degree of catalyst deactivation, presumably as a result of a small degree of additional hydrocarbonaceous laydown on increasing reaction time.^{14,37} The terminal double bond is hydrogenated within 18 min which represents an increase in reaction time of ca. 50% compared to a mean reaction time of ca. 12 min seen for the fresh catalyst. However, a smaller increase of only 10% is seen with the internal double bond, which requires 28.5 min compared to the 26 min seen when a fresh catalyst is used. Although the increase in reaction times is relatively minor, these results suggest that catalyst deactivation is preferentially affecting Site α , yielding a relatively larger attenuation of hydrogenation rate at this site. A similar link between carbon deposits and catalytic activity and selectivity has been noted by

Bond.³³ Inspection of product selectivities for alkane hydrogenolysis over supported Pt catalysts^{38–42} demonstrated that carbon retention interfered with only a certain class of site on the catalyst surface, while other sites remained active.³³ The fact that Site α appears to be preferentially attenuated *via* a 'traditional' deactivation route and yet this site remains unperturbed by the presence of a chemical modifier, further indicates the subtleties of selective adsorption that exists in competitive adsorption on surfaces offering a variety of sites.

5.4 Stereochemical implications

The reactivity of cis-pent-2-ene has been particularly informative regarding guidance as to how the C5 entities are reacting on this surface. Fig. 7 shows that the catalyst efficiently isomerizes the cis-pent-2-ene to trans-pent-2-ene, which then goes on to react further to form pentane. Additionally, no cispent-2-ene was observed in the 1,3-pentadiene hydrogenation studies, despite the diene being a mixture of cis- and transstereoisomers. Direct hydrogenation of cis-1,3-pentadiene would be expected to produce cis-pent-2-ene.9 It is possible that this stereoisomer is actually selectively retained by the catalyst and it is only the trans-1,3-pentadiene that goes on to react. However, the more likely explanation is thought to be that the catalyst rapidly isomerises the cis-1,3-pentadiene into trans-1,3-pentadiene, which then goes on to form trans-pent-2ene and ultimately pentane. A postulated reaction mechanism is presented in Fig. 8. The mechanism assumes the well established Horiti-Polanyi stepwise hydrogen addition process, with half-hydrogenated states^{10,43} and specifically identifies two sites as being responsible for the partial and full hydrogenation reactions.

Upon examination of Fig. 8 it is intriguing to consider which of the two active sites is responsible for the isomerisation process. Reaction 2 provides some insight into this matter. With prior addition of toluene-d₈, Fig. 5 shows *trans*-pent-2ene to be formed at the same rate as observed for the unmodified catalyst, *i.e.* Site α is unperturbed. However, the modifier has selectively poisoned Site β (see Table 1). If Site β



Fig. 8 A postulated reaction scheme for the surface interactions that correspond to the gas phase reaction profile (Fig. 4) for the hydrogenation of 1,3-pentadiene over a Pd/Al_2O_3 catalyst. The asterisk (*) refers to surface Pd atoms.

were responsible for the isomerisation step, a retardation in the production of trans-pent-2-ene would be expected. The fact that this does not occur suggests that Site α is in fact responsible for the isomerisation reactions (cis-1,3-pentadiene \rightarrow *trans*-1,3-pentadiene and *cis*-pent-2-ene \rightarrow *trans*-pent-2-ene), in addition to hydrogenation of the terminal double bond.

Conclusions 6.

Infrared spectroscopy has been used to study the hydrogenation of a mixture of cis- and trans-1,3-pentadiene over a Pd/ Al₂O₃ catalyst operating under batch conditions. The main findings can be summarised as follows:

(i) The reaction is seen to occur as a consecutive process, with the terminal double bond hydrogenated in advance of the internal double bond.

(ii) The reaction profile is consistent with the catalyst presenting two distinct reaction sites: hydrogenation of the terminal double bond occurs at Site α , whilst Site β is responsible for hydrogenation of the internal double bond.

(iii) trans-Pent-2-ene is identified as the only reaction intermediate. cis-Pent-2-ene is seen to isomerise to trans-pent-2-ene before going on to be hydrogenated to pentane.

(iv) The effect of toluene-d₈ to act as a chemical modifier was also investigated and shown to selectively poison Site β , Site α being unperturbed.

(v) On the basis that modifier studies do not inhibit the formation of *trans*-pent-2-ene, Site α is tentatively identified as the site active for the $cis \rightarrow trans$ -isomerisation process.

(vi) Repeat hydrogenation studies cause a modest drop in hydrogenation rates, indicating a small progressive hydrocarbonaceous laydown on increased reaction time, with Site α demonstrating a greater degree of sensitivity than Site β .

Acknowledgements

ICI are thanked for the award of a Lectureship in Heterogeneous Catalysis (DL). The EPSRC, ICI Chemicals and Polymers Ltd and INEOS Chlor Ltd. are thanked for the awards of Industrial CASE studentships (DTL and IWS). Synetix and the University of Glasgow are thanked for the award of a studentship (TL) and assistance with equipment provision. Rutherford Appleton laboratories are thanked for the provision of neutron beamtime and for access to computational facilities.

References

- (a) K. Weissermel and H.-J. Arpe, in Industrial Organic Chemistry, VCH, Weinheim, 3rd edn., 1997, 59; (b) K. Weissermel and H.-J. Arpe, in Industrial Organic Chemistry, VCH, Weinheim, 3rd edn., 1997, 74; (c) K. Weissermel and H.-J. Arpe, in Industrial Organic Chemistry, VCH, Weinheim, 3rd edn., 1997, 75; (d) K. Weissermel and H.-J. Arpe, in Industrial Organic Chemistry, VCH, Weinheim, 3rd edn., 1997, 105; (e) K. Weissermel and H.-J. Arpe, in Industrial Organic Chemistry, VCH, Weinheim, 3rd edn., 1997, 116.
- B. J. Joice, J. J. Rooney, P. B. Wells and G. R. Wilson, Discuss. Faraday Soc., 1966, 41, 223.
- P. B. Wells and A. J. Bates, J. Chem. Soc. A, 1968, 3064.
- J. J. Philipson, P. B. Wells and G. R. Wilson, J. Chem. Soc. A, 4 1969, 1351.
- 5 A. J. Bates, Z. K. Leszeynski, J. J. Philipson and P. B. Wells, J. Chem. Soc. A, 1970, 2453.
- 6 G. Webb, in Catalysis, Specialist Periodical Reports, ed. C. Kemball and D. A. Dowden, The Chemical Society, London, vol. 2, 1978, p. 155.
- P. R. N. Souza, M. M. Pereira, O. A. C. Antunes, D. A. G. Aranda and J. W. M. Carneiro, Braz. J. Chem. Eng., 2002, 19, 187.
- R. B. Moyes, P. B. Wells, J. Grant and N. Y. Salman, Appl. Catal. A: Gen., 2002, 229, 251.

- 9 P. B. Wells and G. R. Wilson, J. Chem. Soc. A, 1970, 2442.
- N. Vasquez and R. J. Madix, J. Catal., 1998, 178, 234. 10
- 11 S. D. Jackson, S. Munro, P. Colman and D. Lennon, Langmuir, 2000, 16, 6519.
- 12 P. N. Rylander, in Hydrogenation Methods, Academic Press, Orlando FL, 1985, p. 36.
- 13 G. C. Bond and J. C. Rank, Proc. 3rd Intl. Cong. Catal., 1965, 2, 1225.
- 14 D. R. Kennedy, G. Webb, S. D. Jackson and D. Lennon, Appl. Catal. A: Gen., 2004, 259, 109.
- C. J. Pouchert, in The Aldrich Library of FT-IR Spectra, 15 Aldrich Chemical Company, Milwaukee, WI, 1st edn., 1985, vol. 1.
- 16 N. G. Mirkin and S. Krimm, J. Phys. Chem., 1993, 97, 13887.
- D. A. C. Compton, W. O. George and W. F. Maddams, J. Chem. 17 Soc., Perkin 2, 1977, 1311.
- 18 A. P. Scott and L. Radom, J. Phys. Chem., 1996, 100, 16502.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. 19 Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, GAUSSIAN 03W, (Version 6.0), Gaussian, Inc., Pittsburgh PA, 2003.
- 20 P. C. H. Mitchell, S. F. Parker, A. J. Ramirez-Cuesta and J. Tomkinson, in Vibrational Spectroscopy with Neutrons with Applications in Chemistry, Biology, Materials Science and Catalysis, World Scientific, Singapore, 2004.
- N. B. Colthup, L. H. Daly and S. E. Wiberley, in Introduction to 21 Infrared and Raman Spectroscopy, Academic Press, New York, 2nd edn., 1975.
- 22 L. J. Bellamy, in Advances in Infrared Group Frequencies, Methuen, London, 1968, p. 42.
- 23 D. Dolphin and A. Wick, Tabulation of Infrared Spectral Data, Wiley, New York, 1977.
- N. Sheppard and D. M. Simpson, Q. Rev., 1952, 1. 24
- 25 R. Marshall, G. Webb, S. D. Jackson and D. Lennon, J. Mol. Catal. A: Chem., in press.
- A. Borodzinski and A. Golebiowski, Langmuir, 1997, 13, 883. 26
- 27 A. Borodzinski, Catal. Lett., 1999, 63, 35.
- N. A. Dobson, G. Erlinton, M. Krishnamurti, R. A. Raphael and 28 R. G. Willis, Tetrahedron, 1961, 16, 16.
- A. M. Doyle, Sh. K. Shaikhutdinov, S. D. Jackson and H. J. 29 Freund, Angew. Chem. Int. Ed., 2003, 42, 5240.
- 30 A. M. Doyle, Sh. K. Shaikhutdinov and H. J. Freund, J. Catal., 2004. 223. 444.
- D. Lennon, R. Marshall, G. Webb and S. D. Jackson, Stud. 31 Surface Sci. Catal., 2000, 130, 245.
- G. Webb, Catal. Today, 1990, 7, 139. 32
- 33
- G. C. Bond, *Appl. Catal. A: Gen.*, 1997, **149**, 3. J. M. Orozco and G. Webb, *Appl. Catal.*, 1983, **6**, 67. 34
- 35 A. M. Coats, E. Cooper and R. Raval, Surf. Sci., 1994, 307-309, 89
- X.-C. Guo and R. J. Madix, J. Catal., 1995, 155, 336. 36
- 37 D. Lennon, D. R. Kennedy, G. Webb and S. D. Jackson, Stud. Surf. Sci. Catal., 1999, 126, 341.
- 38 G. C. Bond and M. R. Gelsthorpe, J. Chem. Soc., Faraday Trans. 1. 1989. 85. 3767.
- 39 G. C. Bond and L. Hui, J. Catal., 1993, 142, 512.
- 40 G. C. Bond and M. R. Gelsthorpe, Catal. Lett., 1989, 3, 359.
- 41 G. C. Bond and J. C. Slaa, J. Mol. Catal. A: Chem., 1995, 101, 243.
- 42 G. C. Bond and R. H. Cunningham, J. Catal., 1996, 163, 328.
- M. Boudart and G. Djéga-Mariadasson, in Kinetics of Hetero-43 geneous Catalytic Reactions, Princeton University Press, Princeton, 1984, p. 184.