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Propyne and 1,3-Butadiene Adsorption and Co-Adsorption Over Palladium Catalysts[1]

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Abstract—The adsorption of propyne, 1,3-butadiene and the co-adsorption of propyne and 1,3-butadiene has been studied over a series of palladium catalysts. The adsorption of propyne shows a "secondary" adsorption region typical of hydrocarbon adsorption over supported metal catalysts. Hydrogenation occurs via the hydrogen associated with the β-palladium hydride formed during reduction. A support effect is seen with the titania support reducing the stability of the palladium hydride resulting in a lower hydrogen concentration in the titania supported hydrides. The behaviour of 1,3-butadiene is similar to that found with propyne. The catalyst with the lowest dispersion, as measured by carbon monoxide adsorption, has the highest butadiene adsorption and *vice versa*, whereas propyne adsorption followed the same trend as carbon monoxide. This behaviour is linked to the mode of adsorption and site requirements. Sequential adsorption revealed that the catalysts had sites that were specific to each adsorbate. Co-adsorption revealed a reduction in adsorption for both gases but with a larger reduction for 1,3-butadiene due to site requirements.

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The adsorption of hydrocarbons on catalyst surfaces has long been examined by a range of techniques including IR spectroscopy [1, 2], scanning tunnelling microscopy [3], low energy electron diffraction (LEED) [4], and X-ray adsorption spectroscopy (XAS) [5]. Many of these studies are reported in Somorjai's book [6], which is an excellent reference of adsorption studies under ultra-high vacuum (UHV) conditions. These studies have significantly advanced the understanding of the mode of adsorption of hydrocarbons, in many cases defining both structure and bonding of the adsorbed molecule on the catalyst surface. For example, 1,3-butadiene, one of the molecules used in this study, has been studied by Jugnet and co-workers [7] and its adsorption has been shown to be through di-π-interactions with the carbon backbone parallel to the surface. However many of these techniques rely on adsorption under UHV conditions, on single crystals. Recently it has been shown that hydrogenation of alkenes over single crystals may not be a good model for supported metal catalysts [8] and so there remains a place for the measurement and study of adsorption of hydrocarbons under more realistic conditions of pressure and temperature over supported metal catalysts.

In this study we have investigated the adsorption of propyne and 1,3-butadiene over palladium catalysts. The adsorption propyne has been studied however there is not a vast literature. The adsorption of propyne on a Pt(111) surface was studied using LEED [9] where at room temperature the alkylidyne species was detected. In a reflection adsorption IR spectroscopy (RAIRS) study the di-σ/di-π surface species formed at low temperature was shown to be stable up to room temperature on both Ni(111) and Cu(110) surfaces [10]. Similar results were found for low temperature propyne adsorption on Pd(100) [11]. High temperature adsorption (573 K) of propyne was studied over Pt/Al_2O_3 and Ni/SiO_2 [12] and Ni/Al_2O_3 [13]. The effect of hydrogen retained from the reduction process was noted on the platinum system and significant differences were found when co-adsorption with carbon monoxide was examined. The adsorption of 1,3-butadiene has also been studied over single crystal surfaces. The adsorption of 1,3-butadiene on Pt(111) and Pd(111) was studied by near edge X-ray absorption fine structure [7]. It was found that at 300 K, 1,3-butadiene adsorption differs depending on the substrate. A di-π-bonding was observed on Pd(111) while on Pt(111), a di-σ-interaction, keeping one central carbon-carbon double bond, was proposed. The low temperature (90 K) adsorption structure of 1,3-butadiene chemisorbed on Pd(110) has been studied by high resolution electron energy loss spectroscopy (HREELS), near edge X-ray absorption fine structure (NEXAFS), and scanning tunnelling microscopy (STM) [14]. The HREELS and NEXAFS results revealed that 1,3-butadiene was adsorbed by its π-bond and the molecular plane was parallel to the surface.

In this study we will contrast and compare the adsorption properties of the propyne and 1,3-butadiene. We will also examine the competitive adsorption

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[1] The article is published in the original.

Table 1. Carbon monoxide adsorption

Catalyst	CO adsorbed, μmol/g	Dispersion, %	Average metal particle size, nm
$Pd(N)/TiO_2$	2.1	9.1	12.0
$Pd(N)/ZrO_2$	7.8	32.9	3.3
$Pd(Cl)/TiO_2$	7.1	29.9	3.7
$Pd(Cl)/ZrO_2$	6.9	29.0	3.8

between the two gases as this may give us useful insights into transhydrogenation reactions.

EXPERIMENTAL

Four catalysts were prepared by impregnation using two palladium salts ($PdCl_2$ and $Pd(NO_3)_2$) and two supports (titania and zirconia). Sufficient palladium nitrate (Johnson Matthey) solution, to produce a 1% by weight catalyst, was added to titania (Degussa, Surface Area $S = 35$ m^2/g) and zirconia (Degussa, $S = 35$ m^2/g). The catalysts were dried at 358 K for 24 h before calcination at 723 K for 3 h. For the catalysts prepared from palladium chloride the methodology was altered slightly. The palladium chloride (Johnson Matthey) was initially dissolved in hydrochloric acid (BDH Aristar) before addition to both supports. All other aspects were identical. The catalysts have been designated $Pd(N)/TiO_2$, $Pd(N)/ZrO_2$, $Pd(Cl)/TiO_2$, and $Pd(Cl)/ZrO_2$ to reflect the different preparations.

Chemisorption studies were performed in a dynamic mode using a pulse-flow microreactor system in which the catalyst sample was placed on a sintered glass disc in a vertical tube (8 mm id, down flow) inside a furnace. The reactant pulses were introduced into the gas stream immediately above the catalyst bed using a sample loop of identical dimensions to the reactor. Using this system the catalysts (typically 0.5 g) were reduced in situ in a flow of dihydrogen (40 cm^3/min) by heating to 473 K at a rate of 8 K/min. The catalyst was held at this temperature for 30 min. The catalyst was cooled in flowing dihydrogen and maintained in a flow of helium (40 cm^3/min). The adsorbate gases were admitted by injecting pulses of known size (typically 24 μmol) into the helium carrier-gas stream and hence onto the catalyst. In all cases the whole pulse was analysed by on-line GC-MS. The amount of gas adsorbed, from any pulse, was determined from the difference between a calibration peak area and the peak area obtained following the injection of pulses of comparable size onto the catalyst. The detection limit for adsorption was 0.3 μmol/g. Adsorption was followed using a gas chromatograph fitted with a thermal conductivity detector and Porapak Q column coupled to a mass spectrometer (ESS GeneSys Quadstar 422).

Both the helium (BOC, 99.997%) and the dihydrogen (BOC, 99.999%) were further purified by passing through Chrompack Gas-Clean Oxygen filter to remove any oxygen impurity, and a bed of Chrompack Gas-Clean Moisture filter to remove any water impurity. The carbon monoxide (99.99% Research Grade), propyne (99.5%), and 1,3-butadiene (99%) were all used as received.

RESULTS

The adsorption of carbon monoxide, propyne and butadiene was examined over the titania and zirconia supports. Both supports were reduced as per the catalyst samples. No adsorption of carbon monoxide was detected over either support. Propyne adsorbed on both supports (2.9 μmol/g on zirconia and 6.04 μmol/g on titania). Butadiene did not adsorb on the titania support, however an adsorption of 1.28 μmol/g was measured over the zirconia support. Neither support produced hydrogenated C3/C4 products, nor was any adsorption observed when a second gas was pulsed over a surface that had previously been exposed to propyne or butadiene.

Immediately after reduction each catalyst was subjected to pulses of carbon monoxide at 293 K. The results are shown in Table 1. The dispersion of each catalyst was calculated using the carbon monoxide data, assuming a CO : Pd ratio of 1 : 2. The calculated dispersions were then used to determine the average palladium particle size.

The adsorption of propyne was examined over each freshly reduced catalyst at 293 K. The results are shown in Table 2 and Fig. 1. Table 2 shows the results on a pulse-by-pulse basis, while Fig. 1 shows the cumulative uptake. Clearly even after pulse 1 the uptake was in excess of monolayer coverage as described by CO chemisorption. All four catalysts produce propene while only the $Pd(Cl)/ZrO_2$ catalyst does not produce propane.

The adsorption of butadiene was examined over each freshly reduced catalyst at 293 K. The results are shown in Table 3 and Fig. 2. Table 3 shows the results on a pulse-by-pulse basis, while Fig. 2 shows the cumulative uptake. Once again, even after pulse 1, the uptake was in excess of monolayer coverage as described by CO chemisorption. All of the catalysts produce butene and butane (the butene isomers were not separated).

The co-adsorption of a 1 : 1 propyne : butadiene mix was studied over each catalyst immediately after reduction at 293 K. The results are shown in Table 4 and Fig. 3. Table 4 shows the results on a pulse-by-pulse basis, while Fig. 3 shows the cumulative uptake.

The sequential adsorption of propyne and butadiene was also investigated. After a catalyst had six pulses of propyne passed over it, three pulses of butadiene were passed over the sample. The cumulative adsorption is shown in Fig. 4. No butene or butane was

Table 2. Propyne adsorption*

Catalyst	Pulse no.	Propyne adsorbed	Propene produced	Propane produced
		μmol/g		
Pd(N)/TiO_2	1	24.5	3.1	1.9
	2	23.5	1.9	0.0
	3	25.2	0.6	0.0
	4	18.0	0.0	0.0
	5	17.2	0.0	0.0
	6	17.1	0.0	0.0
Pd(N)/ZrO_2	1	41.3	1.3	5.1
	2	37.9	1.9	1.9
	3	31.2	1.3	1.3
	4	28.5	0.6	0.6
	5	28.2	0.0	0.0
	6	25.6	0.0	0.0
Pd(Cl)/TiO_2	1	35.0	1.2	0.0
	2	31.9	0.6	0.0
	3	28.2	0.5	0.0
	4	25.8	0.0	0.0
	5	22.2	0.0	0.0
	6	21.0	0.0	0.0
Pd(Cl)/ZrO_2	1	38.1	3.1	3.1
	2	31.5	2.5	2.5
	3	28.1	1.9	1.2
	4	26.0	0.6	0.6
	5	23.3	0.0	0.6
	6	20.0	0.0	0.0

* Inlet pulse 24 μmol.

formed. A similar process was investigated with six pulses of butadiene being adsorbed followed by pulses of propyne. The cumulative adsorption results are shown in Fig. 5. No propene or propane was formed. In neither case was any of the initially adsorbed species desorbed by the second gas.

DISCUSSION

In the literature no adsorption studies of propyne over supported Pd catalysts could be found. Although the adsorption of methane, ethane, ethene, ethyne, propane, propene and cyclopropane [15] have all been studied over palladium catalysts, propyne was not examined. The same is also true for the other precious metals [16]; ethene and ethyne have been exhaustively studied but not the C-3 alkyne. The data from these studies suggests that the majority of the adsorption should not take the form of a classical Langmuir isotherm, but should have a "primary" and "secondary" adsorption regions [15, 16]. These two distinct regions are characterised by a steep "primary" region which, from related ^{14}C carbon monoxide adsorption [15–17], was considered to represent monolayer coverage of the metal by hydrocarbon, and a subsequent linear adsorption region which was thought to be associated with the support. The adsorption data was plotted in a form similar to that found in [15–17] (Fig. 6) and linear plots were obtained for each catalyst indicating that the adsorption is consistent with previous hydrocarbon adsorption over palladium catalysts.

When palladium has been treated at high temperature in hydrogen and subsequently cooled in hydrogen palladium hydride can be formed. Palladium hydride is catalytically active for hydrogenation reaction of ethyne, ethene and propene [18–20] and although we can find no specific reference for propyne we would expect similar behaviour. Alkyne hydrogenation over palladium catalysts is usually highly selective to the alkene [21]; when the selectivity is defined as [alkene]/([alkene]+[alkane]) values approaching unity are often obtained. However in the hydrogenation of

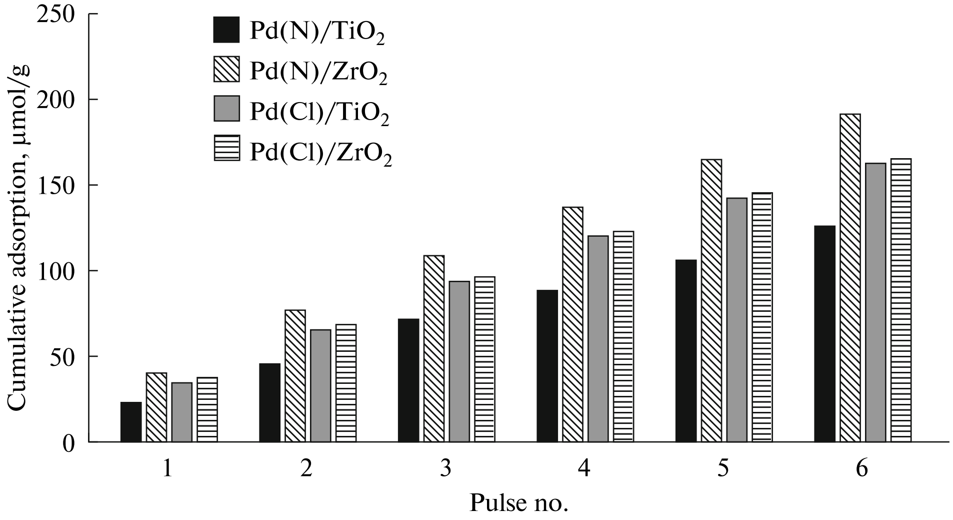

Fig. 1. Cumulative adsorption of propyne over the catalysts.

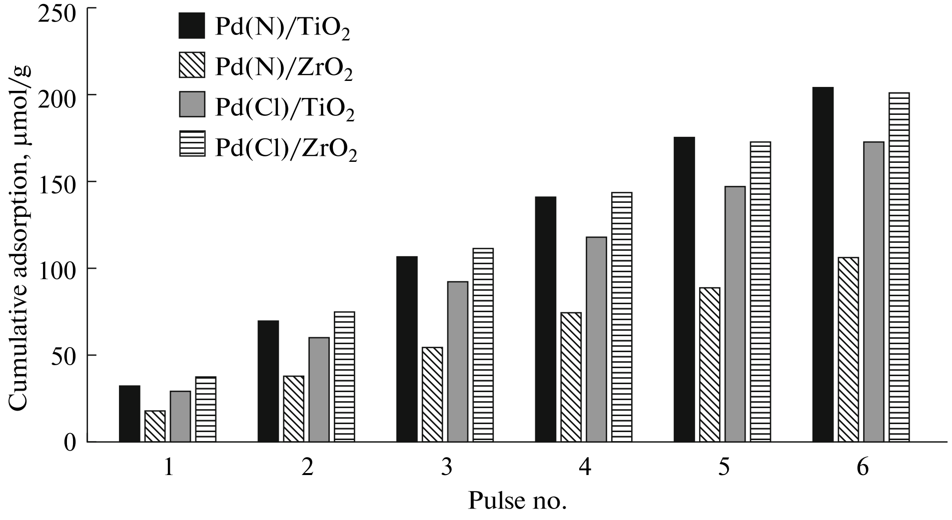

Fig. 2. Cumulative adsorption of 1,3-butadiene over the catalysts.

ethyne, palladium hydride was found to be less selective than Pd metal, producing more ethane. In hydrogenation of propyne over Pd catalysts very high and very low propene selectivities have been observed [22] and these have been shown to relate to the levels of subsurface H and surface H [23], where subsurface hydrogen gives rise to the alkane while surface H produces the alkene. Assuming that we have formed a palladium hydride we can expect the system to have both types of hydrogen and hence have a poor selectivity. This is indeed the case, with only the Pd(Cl)/TiO_2 selective to propene. All the other catalysts show selectivities of between 20 and 62%. When the extent of propyne hydrogenation to propene and propane is examined in detail (Table 2), it can be seen that there is a support effect, with the zirconia-supported catalysts having a much greater propensity for hydrogenation than the titania supported samples. Interestingly the support effect overrules any potential metal crystallite size effect. Support effects have been observed in hydrocarbon adsorption [24] with alumina giving significantly different behaviour to silica. Adsorption of propyne directly onto the support, in total, is less than 25% of the adsorption from the first pulse over titania and less than 10% over zirconia. Therefore either the support effect is electronic or involves the support defining, to some extent, some property of metal crystallites. If we consider that the hydrogen used in the hydrogenation comes solely from the palladium hydride then a measure of the H content can be

Table 3. Butadiene adsorption*

Catalyst	Pulse no.	Butadiene adsorbed	Butene produced	Butane produced
		μmol/g		
Pd(N)/TiO_2	1	35.8	7.2	3.2
	2	37.0	2.4	0.8
	3	36.8	1.6	0.8
	4	33.5	1.6	0.8
	5	32.9	0.8	0.0
	6	30.0	0.0	0.0
Pd(N)/ZrO_2	1	20.7	1.7	0.9
	2	19.9	1.7	0.9
	3	18.2	1.7	0.9
	4	18.9	1.7	0.0
	5	15.2	0.0	0.0
	6	15.2	0.0	0.0
Pd(Cl)/TiO_2	1	31.7	1.6	0.8
	2	32.4	0.0	0.0
	3	29.3	0.0	0.0
	4	27.8	0.0	0.0
	5	27.1	0.0	0.0
	6	26.6	0.0	0.0
Pd(Cl)/ZrO_2	1	39.3	2.9	2.2
	2	37.5	1.4	1.4
	3	36.6	0.0	0.0
	4	32.9	0.0	0.0
	5	29.3	0.0	0.0
	6	27.8	0.0	0.0

* Inlet pulse 24 μmol.

obtained. Making this assumption, values of x for PdH_x can be calculated giving, 0.4 for Pd(N)/ZrO_2, 0.4 for Pd(Cl)/ZrO_2, 0.2 for Pd(N)/TiO_2, and 0.1 for Pd(Cl)/TiO_2. These values are typical for β-PdH and suggest that the support is influencing the extent of hydrogen sorption in the palladium. In a recent paper on PdH stability [25] it was found that the degree of contact between the Pd and the support had a significant influence on the stability of palladium hydride. As the interaction between palladium and the support increased the concentration of hydrogen in the hydride decreased, which would indicate that there is a stronger metal–support interaction between palladium and titania than there is between palladium and zirconia. Titania has been shown to reduce easily in hydrogen when a precious metal is present and was the support where the term strong metal support interaction (SMSI) was first coined [26]. Hence it is no surprise to find that it has the most significant effect on palladium hydride stability.

In contrast to propyne there is literature available on the adsorption of 1,3-butadiene on palladium surfaces. A study by Jugnet and co-workers [7] of 1,3-butadiene adsorption on Pd (111) revealed that the adsorbed state at 300 K was di-π-bonded with the carbon chain parallel to the surface. No re-hybridisation of the carbon atoms was detected (in contrast to Pt(111)) indicating that no hydrogenation or partial hydrogenation had occurred. In a recent study [8] it was shown that single crystal surfaces do not perform hydrogenation in contrast with supported crystallites and that this was related to the presence of subsurface hydrogen. In our system subsurface hydrogen is present and hydrogenation is observed. The behaviour of 1,3-butadiene is similar to that found with propyne. Linear "secondary isotherm" plots were obtained (Fig. 7) and the selectivity obtained in the hydrogenation is low. Analysing the amount of hydrogen required to produce the hydrogenated products and assuming that all comes from the hydride then a measure of the H content can be obtained. Making this assumption, values of x for

Table 4. Co-adsorption of propyne and butadiene*

Catalyst	Pulse no.	Propyne adsorbed	Propene produced	Propane produced	Butadiene adsorbed	Butene produced	Butane produced
		µmol/g					
Pd(N)/TiO_2	1	21.3	0.6	0.6	18.0	1.7	1.5
	2	21.6	0.3	0.0	17.1	0.8	0.8
	3	20.4	0.3	0.0	16.4		
	4	20.0			14.9		
	5	18.3			11.6		
	6	11.3			5.6		
Pd(N)/ZrO_2	1	26.6	2.8	1.6	7.9	7.9	
	2	25.7	0.8	0.0	11.8	0	
	3	24.8	0.4	0.0	14.2		
	4	24.0	0.4		17.3		
	5	23.3			18.9		
	6	22.5			18.9		
Pd(Cl)/TiO_2	1	26.9	0.9	0.0	2.8	2.2	1.1
	2	26.1	0.6	0.0	14.0	0.0	1.1
	3	25.3	0.3	0.0	17.9		0.6
	4	24.4			12.9		
	5	23.6			13.4		
	6	22.9			13.4		
Pd(Cl)/ZrO_2	1	27.9	1.5	1.2	8.4	0.0	2.4
	2	26.9	1.2	0.0	12.0	0.0	1.2
	3	26.0	0.8	0.0	14.4		
	4	25.1	0.4		15.6		
	5	24.3			16.8		
	6	23.5			16.8		

* Inlet pulse 24 µmol.

PdH_x can be calculated giving, 0.3 for Pd(N)/ZrO_2, 0.3 for Pd(Cl)/ZrO_2, 0.5 for Pd(N)/TiO_2, and 0.1 for Pd(Cl)/TiO_2. Although the absolute values are slightly different from those calculated from propyne hydrogenation the trend is comparable with Pd(Cl)/TiO_2 giving the lowest value and the zirconia supported samples giving similar values. Any difference in absolute value may be related to whether any self-hydrogenation takes place and the fact that the rate of 1,3-butadiene hydrogenation is crystal face dependent [27].

When the adsorption of propyne is considered, it can be seen (Fig. 1) that the extent of adsorption follows the same profile as that of carbon monoxide. Hence the Pd(N)/TiO_2 sample adsorbs the least, Pd(N)/ZrO_2 the most, while the chloride derived samples adsorb very similar amounts intermediate between the nitrate samples. However when butadiene adsorption is examined (Fig. 2), a significantly different pattern is observed. The catalyst with the lowest dispersion, as measured by carbon monoxide adsorption, has the highest butadiene adsorption and *vice versa*. This is a surprising result and throws into sharp contrast the differences in adsorption site requirements between alkyne and alkadiene. Given this, it is unsurprising that there are different sensitivities to the surface properties of the catalysts as noted above. The adsorption of 1,3-butadiene has been shown to be through di-π-interactions with the carbon backbone parallel to the surface [7]. Such a mode of adsorption will require an ensemble of metal atoms and would be in keeping with greater adsorption on larger crystallites that have extended terraces. It is interesting to note that 1,3-butadiene hydrogenation shows an antipathetic particle size effect [28, 29] in keeping with the trend observed in the adsorption study. Although this is has been shown now to be related to crystal face dependence rather particle size per se [27]. In contrast, propyne adsorption can have a variety of different modes available, with both vertical and horizontal positioning having been identified [11, 30].

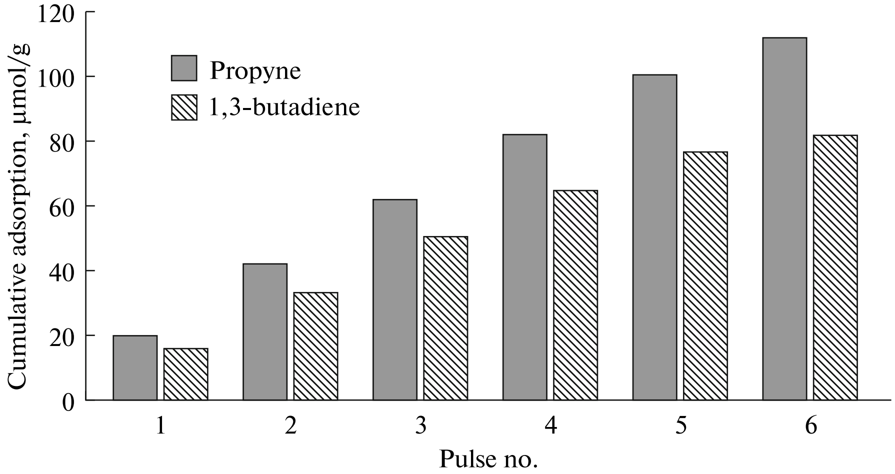

Fig. 3. Cumulative co-adsorption of propyne and 1,3-butadiene.

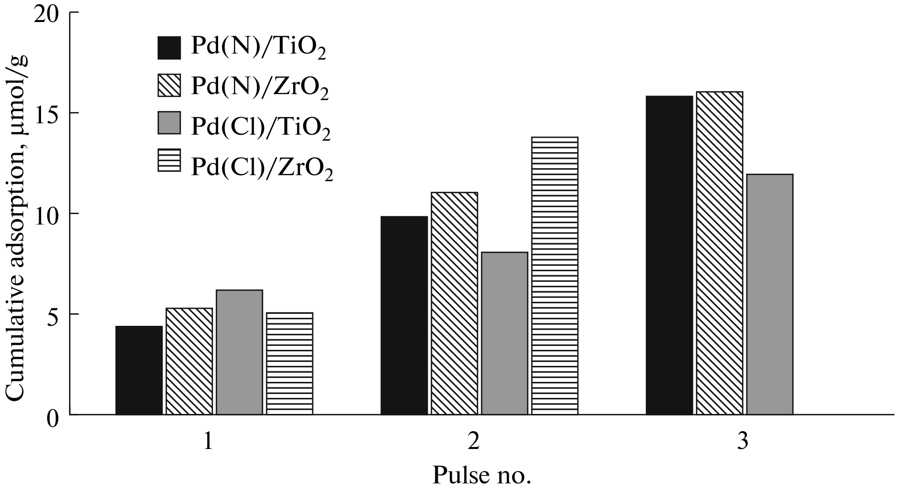

Fig. 4. Cumulative adsorption of 1,3-butadiene after 6 pulses of propyne.

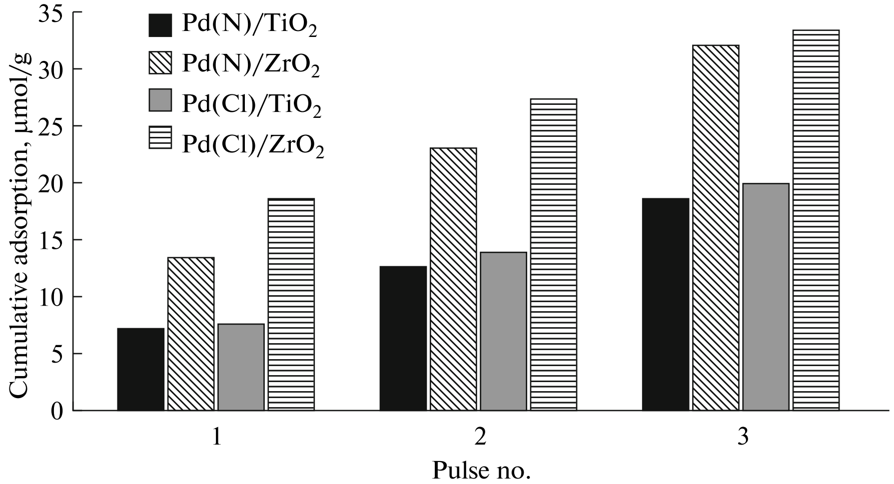

Fig. 5. Cumulative adsorption of propyne after 6 pulses of 1,3-butadiene.

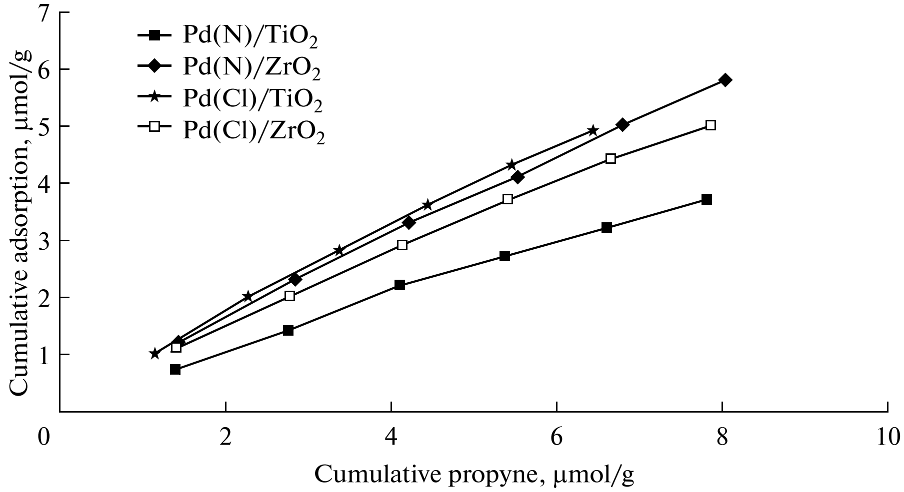

Fig. 6. Adsorption isotherms for propyne adsorption showing linear "secondary" adsorption behaviour.

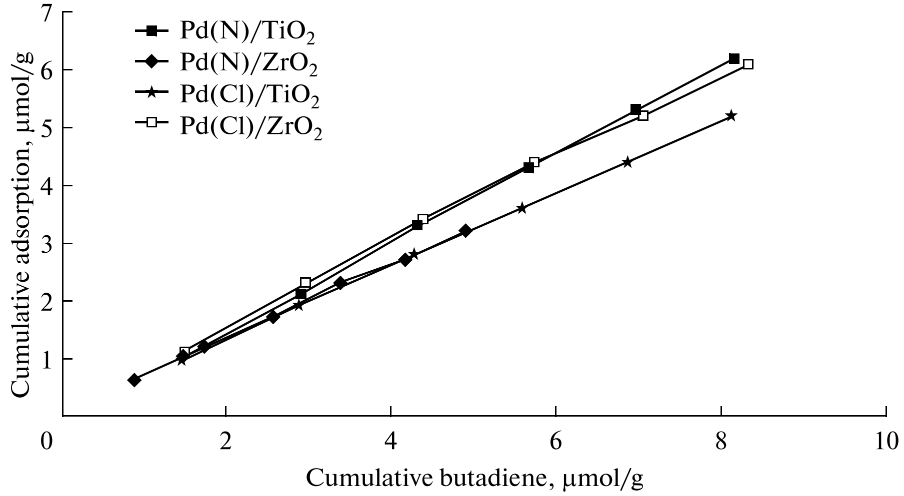

Fig. 7. Adsorption isotherms for 1,3-butadiene adsorption showing linear "secondary" adsorption behaviour.

Following on to consider sequential adsorption, we note that adsorption of the second gas does take place even though there is no displacement of the primary adsorbed gas. The extent of adsorption is small, but nevertheless indicates that different sites are available for each species. The lack of desorption could be taken to indicate that the strength of adsorption for each species was similar but it is more likely that with dissociative adsorption of the initially adsorbed species, there is no route for desorption. The absence of a hydrogenated product for the second gas adsorption is in keeping with the view that there is no self-hydrogenation and that the source and cause of the hydrogenated products is the hydride hydrogen.

When the co-adsorption behaviour is examined (Table 4), as expected the extent of adsorption of each gas is reduced (Table 5). However the extent of reduction is revealing. The maximum reduction of the propyne adsorption is 24% (Pd(N)/ZrO_2) while all the others are reduced by ~10%. Whereas the 1,3-butadiene adsorption is reduced by ~60% except for Pd(N)/ZrO_2 where the adsorption is reduced by only 18%. Therefore the 1,3-butadiene adsorption, which has the larger site requirement, is the more affected adsorbate, except on the most highly dispersed catalyst. Each adsorbate undergoes some hydrogenation although in general the extent of hydrogenation is less than found with the single adsorbate. The total amount of hydrogen need for hydrogenation over each catalyst however is comparable to the total removed by either propyne or 1,3-butadiene in non-competitive hydrogenation.

The extent of adsorption, for both propyne and butadiene, is vastly in excess of the notional site den-

Table 5. Extent of reduction of adsorption during co-adsorption

Catalyst	Reduction in first pulse compared to single adsorption, %		Reduction after 6 pulses compared to single adsorption, %	
	propyne	1,3-butadiene	propyne	1,3-butadiene
Pd(N)/TiO_2	13	50	10	59
Pd(N)/ZrO_2	36	62	24	18
Pd(Cl)/TiO_2	23	91	9	58
Pd(Cl)/ZrO_2	27	79	8	59

sity as measured by carbon monoxide. However the extent of propyne adsorption over the catalysts follows the same pattern as the carbon monoxide, i.e. the extent of adsorption is proportional to metal surface area (Fig. 1). By pulse 6 the amount of propyne adsorbed is typically 20× the amount of carbon monoxide adsorbed. Whereas 1,3-butadiene adsorption shows the reverse trend (Fig. 2), but even here the extent of adsorption is in considerable excess over the carbon monoxide value (~25 times). This behaviour was expected. The adsorption studies by Thomson, Webb and co-workers [17, 31] and references therein also observed this phenomenon. The "secondary region" in their isotherms usually represented adsorption greater than monolayer coverage. Both adsorption on the supports and multilayer adsorption were proposed to interpret the excess, however no mechanism for the multilayer adsorption was proposed. In this study direct adsorption is observed on the supports, but at a low level. Nevertheless it confirms that the supports have the potential to adsorb and hence a spillover mechanism from the metal to the support is possible. However to interpret the results for both gases the mechanism would require that the extent of spillover was proportional to the metal surface area for propyne and an inversely proportional for 1,3-butadiene. Given the different site requirements of propyne and 1,3-butadiene this is a possible interpretation of the adsorption over and above monolayer coverage. Another interpretation is that multilayers are formed on the surface of the metal. Multilayer adsorption is usually associated with physisorption and as such would be weak and unsustainable in a flow system. Oligomerisation is also possible. However, it has been shown that large multilayer structures can be produced from organic molecules with π-systems through π-π-stacking and that these systems can influence hydrogenation in multilayers [32]. We cannot definitively confirm the mechanism of enhanced adsorption especially as it should be noted that the proposals outlined above are not exclusive, but given the linear nature of the increase and the maintenance of the relationship with the initial adsorption we are minded to favour either the π-π stacking mechanism or spillover to the support.

So, the adsorptions of propyne and 1,3-butadiene, over a series of palladium catalysts, show a "secondary" adsorption region typical of other hydrocarbon adsorption. The hydrogen associated with the palladium hydride facilitates hydrogenation for both adsorbates producing both alkene and alkane. Changes in degree of hydrogenation were related to support effects modifying the stability of the palladium hydride and hence the hydrogen content. The difference in the mode of adsorption of propyne and 1,3-butadiene is seen in that the catalyst with the lowest dispersion, as measured by carbon monoxide adsorption, has the highest butadiene adsorption and *vice versa*, whereas propyne adsorption followed the same trend as carbon monoxide. The absolute amount of hydrocarbon adsorption is much larger than metal monolayer capacity and we suggest that this is due to π-π-stacking or spillover. Sequential adsorption revealed that sites specific to each gas were extant on the catalyst surface and that no adsorbed species was displaced due to the adsorption of the second gas. Co-adsorption revealed a reduction in adsorption for both gases but with a larger reduction for 1,3-butadiene due to site requirements. The extent of hydrogenation was also reduced for each species but the total quantity of hydrogen used matched the hydrogen availability from the hydride.

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