A dramatic shift from multiple to simple exchange in the cyclopentane / D_2 probe reaction on palladium catalysts

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Electron deficient active sites in Pd catalysts, either as films or on supports, are deliberately generated by calcining in O_2 at high temperature followed by the mildest possible reduction (with the reaction mixture itself), and are manifested by a marked shift from multiple to simple exchange in the cyclopentane / D_2 probe reaction.

Keywords: cyclopentane / D_2 exchange, Pd catalysts, novel supports and pretreatments, falling initial distributions of deuterioisomers

1. Introduction

The cyclopentane / D_2 exchange reaction is now recognised as an excellent sensitive probe of the active sites in noble metal catalysts [1]. A general consensus has emerged that two major mechanistic variables govern the shapes of the initial distributions of the deuterioisomers; one of these is the relative rate of cyclopentyl reversal to adsorbed cyclopentene, eq. (1), and the other is the relative rate of rollover of the latter, i.e. from cyclopentene to cyclopentene*, eq. (2) ($X = H$ or D):

$$\text{cyclopentane (g)} \underset{+X}{\overset{-X}{\rightleftharpoons}} \text{cyclopentyl (a)} \underset{+X}{\overset{-X}{\rightleftharpoons}} \text{cyclopentene (a)} \qquad (1)$$

$$\text{cyclopentyl (a)} \underset{+X}{\overset{-X}{\rightleftharpoons}} \text{cyclopentene (a)} \rightleftharpoons \text{cyclopentene}^* \text{ (a)} \underset{-X}{\overset{+X}{\rightleftharpoons}} \text{cyclopentyl}^* \text{ (a)} \qquad (2)$$

When cyclopentyl reversal is strong with repeated rollover, multiple initial exchange affording the D_{10}-isomer in abundance is found. At the other extreme a falling initial distribution with mostly the D_1-isomer should be observed if the cyclopentyl reversal is weak. Intermediate behaviour with strong cyclopentyl reversal, but limited rollover of cyclopentene (a), should lead to a large maximum in the D_5-isomer with little of the more heavily deuterated isomers. In practice all three types of behaviour may be noted simultaneously on noble metals with multiple exchange most pronounced on Pd, and a combined distribution, manifesting itself by a double U-shape (maxima at D_1, D_5 and D_{10}), found when using Pt. Obviously more than one type of active centre is responsible and these are believed [1] to be coordinatively highly unsaturated metal atoms.

We report here novel results which not only confirm this general mechanistic picture but also shed new light on the nature of the active sites involved.

2. Experimental

The TiO_2 used in this study was prepared by hydrolysis of $TiCl_4$ using aqueous NH_4OH solution, followed by calcination of the hydroxide in air at 873 K. Tungsten oxide doped titania was prepared using ammonium paratungstate followed by drying and calcining at 873 K. γ-Al_2O_3 (BDH), γ-Al_2O_3 (Laporte) and boehmite (Merck) were used as supplied. All supports were impregnated using $PdCl_2$ aqueous solution, the materials dried overnight at 373 K and then reduced in flowing H_2 at 623 K. Samples (200 mg) were then transferred to a silica reactor, calcined in O_2 at 703 K, evacuated and cooled to 273 K. The reaction mixture, cyclopentane (7.5 Torr) and D_2 (80 Torr) was then introduced at the reaction temperature (273–343 K). For runs A there was a prior reduction in D_2 (80 Torr) at 573 K whereas for runs B in situ reduction by the reaction mixture was used. The reactions were followed by mass spectrometry and the rates and initial deuterioisomer distributions determined as previously described [2].

The EXAFS data was obtained at the SRS in Daresbury, UK, Wiggler station 9.2. Experiments were carried out on the Pd K and W L_{III} edges in fluorescence

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mode under ambient conditions in flowing H_2 using a specially built gas tight cell with Kapton windows in order to simulate the reducing atmosphere present under reaction conditions. Reduced catalysts were transferred via a glove box. Background subtraction of the EXAFS spectra was carried out using EXCALIB and EXBROOK programs, available on the Daresbury Convex system. The spectra were fitted using the EXCURV92 program [3] also on the Convex. Phase shifts used for all the analyses were those calculated when fitting the Pd foil data. The average particle size, as determined by the EXAFS is between 10 and 40 Å [4]. The maximum errors in the co-ordination number and first shell bond distances are estimated to be ±0.3 and ±0.005 Å respectively.

3. Results and discussion

Using various Pd supported catalysts, cyclopentane/D_2 exchange has been performed and the results are shown in table 1. In table 1, the multiplicity is defined by $M = (\sum i\mathrm{D}_i)/100$ ($i = 1$–10), and k_0 is the rate of consumption of the D_0 isomer.

The results indicate that there are two ways of drastically reducing the multiplicity of initial exchange while simultaneously maintaining high activity. The first is general and consists of calcining the catalyst in O_2 at 703 K followed by evacuation, cooling, and immediate admission of the reaction mixture. Generally, reduction at 573 K (entries A , table 1) versus in situ reduction using the reaction mixture at the reaction temperature (entries B , table 1) leads to a marked change in the distribution obtained as shown in figure 1. In the case of Pd films a significant induction period after introduction of the reaction mixture is observed before the exchange proceeds. Quite clearly partial reduction of the surface metal oxide is all that is required to induce high activity, so the active sites consist of electron deficient metal atoms, in contact with surface oxide and/or hydroxide ions. The term electron deficiency does not necessarily imply the presence of cationic Pd, but rather that the active sites are present as highly dispersed metal, or in the case of Pd films, as very rough surfaces induced by the pre-treatment.

The second method of reducing the multiplicity, M, such that falling initial distributions are obtained is exemplified by a comparison of TiO_2 and TiO_2/WO_3 supports. Here the incorporation of WO_3 into the TiO_2 keeps the values of M low even after the calcined catalysts have been reduced by D_2 at 573 K prior to admission of the reaction mixture. The substantial increase in the rate without increasing M when the %WO_3 is increased from 0 to 10 is noteworthy because it shows that the active sites only come into abundance under quite severe reduction conditions.

It has been shown previously [2] that using MgO as a support for the noble metals, multiple initial exchange is greatly enhanced. This is attributed [2,5] to electron donation from the basic oxide to the reduced metal such that formation and rollover of the π-bonded cyclopentene is favoured. It therefore seems reasonable that the converse may be true, i.e. the use of an acid support may lead to electron donation from the reduced metal to the support with a consequent significant reduction in the formation and rollover of the cyclopentene (a), thus leading to much reduced values of M. However, boehmite (table 1), which is an extreme for the three aluminas tested, shows similar behaviour to that of the TiO_2/WO_3 supports, even though it is a basic material. Since boehmite has a higher O/Al ratio than γ-Al_2O_3 produced by dehydration at higher temperatures, O^{2-} and/or OH^- ion contacts to the metal may be the most important factor in producing electron deficient sites. The EXAFS

Table 1
Initial distributions and rates for cyclopentane/D_2 exchange over various Pd catalysts

Catalyst	Run	T (K)	k_0 (% min^{-1} g^{-1} Pd)	% Deuterioisomer										M
				D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	
Pd film	A	323	170	27.7	0.6	0.7	1.6	47.1	2.2	3.1	1.2	4.5	11.3	4.7
	B	333	95	31.3	11.1	14.2	15.9	14.2	9.6	1.8	1.9	0.0	0.0	3.8
5% Pd/γ-Al_2O_3	A	345	81	23.8	1.6	0.4	1.7	3.9	0.7	4.4	10.1	21.0	32.4	6.5
	B	343	147	18.9	25.2	8.7	14.8	25.2	2.0	1.8	1.0	1.4	1	3.4
5% Pd/boehmite	A	273	322	30.0	21	11.4	14.5	17.9	4.6	0.3	0.3	0.0	0.0	2.6
	B	293	21	41.6	24.9	15.1	9.1	5.0	2.0	1.4	0.9	0.0	0.0	1.9
5% Pd/γ-Al_2O_3	A	318	625	29.1	14.3	10.3	20.0	21.6	3.3	0.5	0.0	0.0	0.0	3.0
(Laporte)	B	313	115	33.4	25.1	16.8	9.5	5.5	3.7	2.3	1.6	0.7	0.5	3.0
0.5% Pd/TiO_2	A	273	350	25.6	25.6	11.9	14.5	20.4	0.4	0.5	0.6	0.3	0.2	2.4
	B	273	2425	59.1	23.2	7.7	4.6	3.9	0.7	0.3	0.2	0.2	0.1	1.8
0.5% Pd/TiO_2/1% WO_3	A	273	1410	32.8	27.7	12.6	10.4	9.8	4.4	0.9	0.6	0.4	0.4	2.2
	B	273	906	62.7	26.3	4.4	3.4	2.8	0.3	0.1	0.0	0.0	0.0	1.6
0.5% Pd/TiO_2/10% WO_3	A	273	1447	59.2	28.7	4.7	3.4	2.4	0.4	0.3	0.3	0.3	0.3	1.7
	B	293	144	57.4	24.4	9.6	3.7	3.0	0.8	0.4	0.3	0.3	0.4	1.6

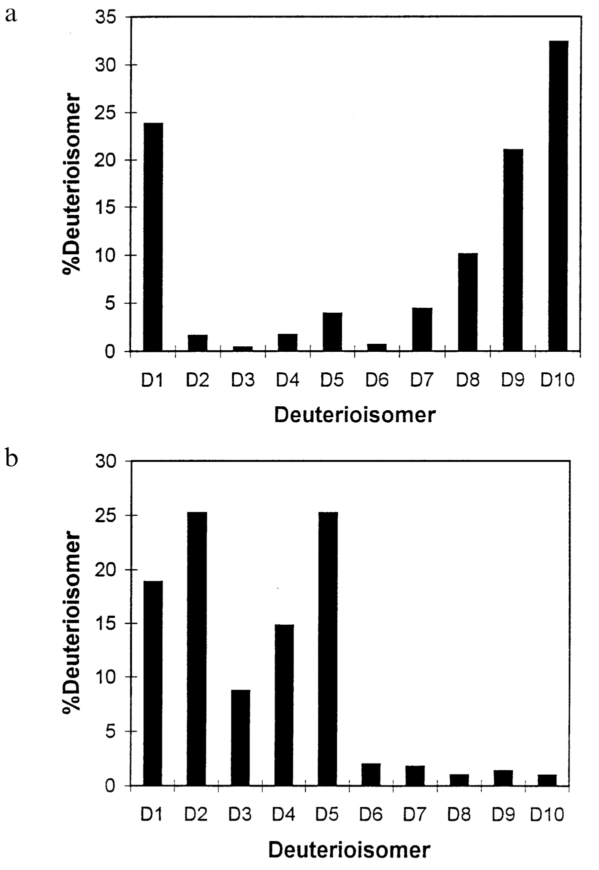

Figure 1. Initial distributions for cyclopentane/D_2 exchange over 5% Pd/γ-Al_2O_3. (a) and (b) correspond to reduction at 573 and 343 K respectively.

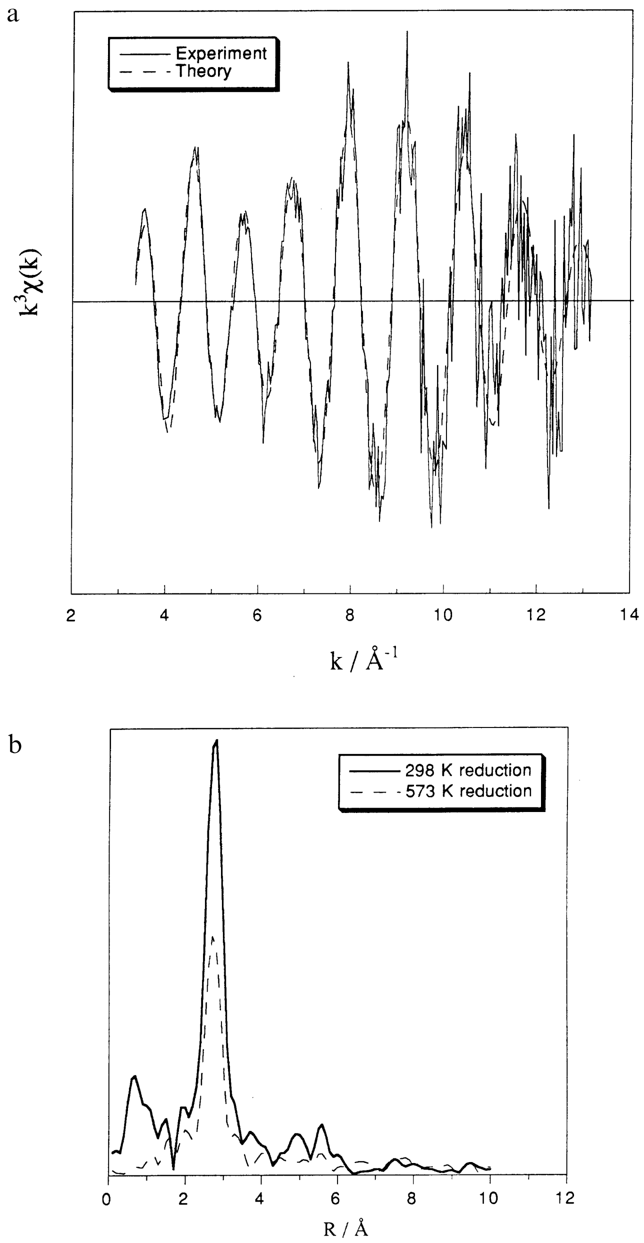

Figure 2. (a) Fitted EXAFS spectra of 0.5% Pd/TiO_2/10% WO_3 following reduction at 573 K in H_2. (b) Comparison of the pseudo-radial distribution functions of 0.5% Pd/TiO_2/10% WO_3 following reduction at 298 and 573 K in H_2 showing decrease in co-ordination number in the first Pd shell.

analysis (figure 2 and table 2) indicates this theory is consistent with the results from Pd/TiO_2 and WO_3 doped catalysts.

In all Pd/TiO_2 catalysts reduction of PdO, formed by prior calcination, occurs at, or below 298 K, as shown by the XANES. This is in agreement with temperature-programmed reduction (TPR) studies on these catalysts which showed only reduction of the oxide support, reduction of the Pd having taken place at room temperature. The increase in the Pd–Pd distance relative to the Pd foil is $\sim$ 2.8% and indicates hydrogen dissolution into the particles. It is in this state that the catalyst is active. This has been observed previously [6] following reduction of Pd; however, in this case the dissolution also takes place at room temperature.

The EXAFS data indicates that the observed distributions and reactivities cannot solely be explained by particle size changes. Large variations in the rate are observed for both the 0.5% Pd/TiO_2 and 0.5% Pd/TiO_2/10% WO_3 catalysts following reduction at 573 K whereas it is only in the latter system that a significant change in co-ordination number occurs, in this case from $N = 8.3$ to 6.0. The decrease observed is probably due to increased wetting of the metal on the support and therefore should lead to an increase in the number of active sites. This is consistent with the reactivity data which shows approximately ten-fold increase in the reaction rate following reduction at 573 K and also with the first shell bond distance decreasing from 2.83 to 2.80 Å indicating a morphological change. It should be noted that the suppression of the anatase to rutile phase change, which occurs on addition of WO_3 to TiO_2, cannot explain the reactivity data. Experiments performed on both anatase and rutile supports afford very similar results. The small increase in Pd particle size following reduction at 573 K of the 0.5% Pd/TiO_2 catalyst is unli-

Table 2
Structural parameters from the fitted EXAFS spectra of Pd/TiO_2 and WO_3 doped Pd/TiO_2 following reduction at 298 and 573 K in H_2

Catalyst	Reduction temperature (K)	First-shell Pd–Pd distance (Å)	Co-ordination No. N	Debye–Waller factor (Å^2)	Fit factor R
Pd foil		2.74	12	0.011	15.7
0.5% Pd/TiO_2	298	2.83	7.5	0.019	31.0
	573	2.83	8.3	0.015	28.1
0.5% Pd/TiO_2/1% WO_3	298	2.83	8.6	0.017	33.0
	573	2.83	9.1	0.015	26.0
0.5% Pd/TiO_2/10% WO_3	298	2.83	8.3	0.016	27.0
	573	2.80	6.0	0.021	31.6

kely to explain the seven-fold decrease in rate. Spillover of oxide over the Pd will result in loss of active metal surface area and may explain the large rate change observed with the apparent small variation in co-ordination number. This type of process may also be used to explain the variation in distribution.

As previously postulated, variations in metal contact with *surface* oxygen/hydroxyl may lead to a change in the distribution of deuterioisomers with an increase in this interaction resulting in a falling versus double U-shaped distribution. Oxide spillover will reduce the metal contact with surface oxygen/hydroxyl and hence favour the latter distribution on reduction as is observed following the 573 K reduction treatment of the 0.5% Pd/TiO_2 catalyst. In the case of the WO_3 doped systems, increases in reduction temperature appear just to change the reactivity not the distribution. Using EXAFS, the doping with 10% WO_3 on TiO_2 has been shown to lead to surface WO_4 and WO_5 and is in agreement with our own findings [7]. This study also indicated that monolayer saturation occurred at doping levels $< 10\%$ with the species terminating in oxygen or hydroxyl. In this case the surface Pd will *only* be in contact with WO_x species and hence modification of the metal by the surface oxygen/hydroxyl leads to the observed falling distribution. Little change in the interaction is expected on reduction at 573 K [7], the reduction inducing wetting of the oxide support only, and hence the distribution does not alter. In the case of 1% WO_3 there are sites available on both TiO_2 and WO_3 and thus whilst the TiO_2 sites dominate the reactivity at low reduction temperatures, leading to a falling distribution, at high reduction temperatures the doped sites dominate, again resulting in the falling distribution. This switch in reactivity with reduction temperature is evident if the rates of the 0.5% Pd/TiO_2/10% WO_3 doped system after reduction at 273 K and 0.5% Pd/TiO_2 after reduction at 573 K are compared – both are low.

The results also show that rollover is most sensitive to the change in the nature of the active sites since D_6–D_{10} isomers often largely disappear while the D_5 isomer is still very abundant. Finally, alkyl reversal also greatly diminishes and the exchange tends to the simple variety only ($M \rightarrow 1.0$), so the ability to form π-bonded alkene and the lifetime of the latter in excess H_2 (reactions (1) and (2)) both decrease as the sites become more electron deficient. This idea is in accord with recent developments in designing homogeneous mononuclear Pd complexes for the polymerization of alk-1-enes [8] where electron deficiency is deliberately induced by hard ligands at the Pd^{2+} cation in order to disfavour alkyl reversal and encourage alkene/alkyl insertion and polymer chain growth. The fact that early transition metal ions polymerize ethene but group VIII ions normally only dimerize the alkene is a further aspect of this important theme of electron deficient centres [9].

In the exchange reaction, if the cyclopentene (a) is the cycloalkene π-bonded to one metal atom, rollover involves rupture of the π-bond with possible reversible spillover of the cycloalkene onto the support. It should be possible therefore to achieve classical dual functional catalysis [10] even at ambient temperatures (exchange range) using Pt or Pd on super-acid oxide supports. Accordingly , a ZrO_2/H_2SO_4 support was prepared [11] and was shown to have very strong Brønsted acidity, using the specific indicator 1,1-diphenylethene [12]. With Pt dispersed on this support, methylcyclopentane and *n*-pentane isomerize readily and selectively in excess H_2, even at room temperature, to cyclohexane and 2-methylbutane, respectively. Furthermore, neopentane, which cannot form an olefin, only isomerizes to isopentane, with concomitant cracking etc., at the usual temperature, $\geqslant 150°C$, required for direct 1,2-bond shift reactions on the metal [1]. The $\alpha\beta$ di-adsorbed species involved is therefore most likely to be the π-bonded alkene [13] and not the corresponding classical di-σ-bonded species since the latter is unlikely to lead to such dual functional behaviour (eq. (3); olefin† is the rearranged form of the initial olefin):

$$\text{paraffin} \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} \text{olefin} \rightleftharpoons \text{olefin}^\dagger \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} \text{paraffin}^\dagger \qquad (3)$$

The same argument concerning the adsorbed cyclopentenes (eqs. (1) and (2)) must therefore apply to the exchange reactions which also occur at ambient temperatures.

We have also found that Pt on various supports ZrO_2/WO_3, ZrO_2/MoO_3, ZrO_2/H_2SO_4, SiO_2/H_2SO_4, boehmite etc. also afford results for cyclopentane/D_2 exchange similar to those described for Pd. These results which contain further novel interesting features will be reported in detail elsewhere. Hitherto falling distributions have only been observed for Pt dispersed in zeolites but not for Pd [14]. The falling distributions were attributed to alkyl intermediates only (individual isolated electron deficient Pt atoms/ions) and the multiple exchange to the di-σ-bonded species at contiguous Pt atoms in reduced metal clusters. However, we are convinced that the present interpretation based on alkene π-bonded to individual metal atoms/ions is more realistic [15]. Variable co-ordination unsaturation and electron deficiency then explain why U-shaped initial distributions are widely found for exchange reactions on Pt, even on single crystals [16].

In conclusion it would appear that the 1,2-di-σ-bonded intermediate in the classical Horiuti–Polanyi mechanism does not play an important role in these exchange reactions. This is in accord with the direct spectroscopic evidence of Somorjai and co-workers [17] that during hydrogenation of ethene on a Pt catalyst, the 1,2-di-π-bonded species is abundant on the surface, but is relatively inert, and it is the π-bonded species, present on only 4% of the exposed metal atoms, which is responsible for the reaction. However, there is evidence that the 1,2-di-σ-bonded species is sometime simultaneously active and important in exchange reactions. In figure 1b there is a significant maximum in the D_2-isomer comparable with the D_5-isomer. This feature is well known for exchange of cyclopentane and *n*-alkanes with D_2 on Rh catalysts, and there is proof that it is due to discrete formation of the 1,2-D_2-isomer [18]. This feature is also known for Pd but has not hitherto been reported for Pt catalysts, e.g. supported on MgO or Al_2O_3 [2,12,19] but is observed for the various Pt/ZrO_2 preparations reported here.

The π-bonded species should readily propagate the exchange reaction around the C_5-ring leading to the D_5-isomer on isolated individual apical metal atoms. However, if the contiguous pair of metal atoms generating the 1,2-di-σ-bonded species are isolated from other active atoms it is essential that each σ-bonded cyclopentyl rotates through 180° around the metal–carbon σ-bond in order that the exchange reaction propagates away from C_1 and C_2. If this rotation is hindered and slow relative to the rate of cyclopentyl elimination off the surface the initial exchange reaction is largely confined to the production of the 1,2-D_2-isomer by this mechanism. This argument resolves a long standing paradox. Previous ideas about the Horiuti–Polanyi mechanism were sometimes based on one species with two processes, one concerted and the other non-concerted, on separate sites. Now two distinct types of intermediates are considered, but both processes are non-concerted, i.e. only one H/D is eliminated/added in each reaction step.

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