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Polymer-Supported Pd(II) Wacker-Type Catalysts
II. Application in the Oxidation of Dec-1-ene

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Seven polymer-supported Pd(II) catalysts have been prepared employing polymers carrying nitrile (cyanomethyl) ligands. Five of these involve polybenzimidazole backbones, one a polystyrene skeleton and the last a polyacrylonitrile backbone. The supported complexes have been used with $CuCl_2$ co-catalyst to oxidise dec-1-ene primarily to methyl ketone under normal Wacker oxidation conditions. In some instances the supported complexes are more active than the $(CH_3CN)_2PdCl_2$ model. The most active species is a highly rigid *N*-cyanomethylated polybenzimidazole and at least some of these metal centres may be coordinatively unsaturated. The effect of solvent, temperature, and co-catalyst ratio have been examined and discussed. The polymer-supported species remain very active at high temperature (~120°C) and require the addition of no hydrochloric acid to avoid irreversible precipitation of Pd(0) species. This is in complete contrast to homogeneous $PdCl_2$, which is rapidly deactivated under similar conditions with copious Pd black formation. Pd(0) complexes immobilised on the polymer seem to be "site isolated" and unable to aggregate. Reoxidation therefore remains facile. The polymer-supported species have been recycled seven times. An initial fall in activity levels takes place after three cycles and thereafter they remain essentially constant. Appreciable Pd leaching also occurs in the first reaction but is rapidly arrested. After ~6 cycles Pd loss is only ~1 ppm per cycle. Following the use of $CuCl_2$ co-catalyst in the first cycle, no additional Cu(II) needs to be added; sufficient co-catalyst appears to be carried through with the isolated polymer-supported Pd(II) species.

INTRODUCTION

In 1960 chemists at Wacker Chemie in Germany developed the Wacker process (*1–4*) in which ethylene and oxygen are passed into a solution of Pd(II) chloride and Cu(II) chloride in dilute hydrochloric acid. This leads to the oxidation of ethylene to acetaldehyde. Extension of the Wacker method to propene and higher terminal alkene yielding mainly methyl ketones (Scheme 1) would also be very attractive. However, it is unfortunate that the oxidation rate decreases as the carbon chain length and degree of substitution of the alkene increase (*5*). Also, by-products are sometimes formed due to various halogenation reactions, as well as to isomerization of the double bond (*6–12*). Higher temperature would in principle increase the reaction rate, but this also tends to cause Pd(0) precipitation. In the Wacker industrial process hydrochloric acid is used to prevent the irreversible precipitation of Pd(0). However, the presence of Cl^- not only offers the prospect of chloride by-products, but also can retard the oxidation reaction. In fact, the Wacker reaction can be terminated in high concentrations of hydrochloric acid, and hence some chloride-free catalytic systems have been reported (*13*). There are also a number of physical or engineering problems. The higher alkenes and their oxidation products generally have high boiling points. As a result, the separation of the expensive catalyst from the products by distillation can be difficult. Hence, in principle, it would be very attractive to develop a new type of heterogeneous catalytic system which could be used at higher temperature without using

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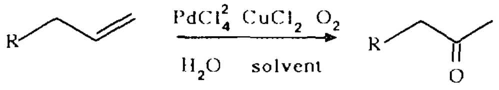


SCHEME 1. Wacker-type oxidation of terminal alkenes.

hydrochloric acid and simultaneously to prevent Pd(0) precipitation. Such a catalyst might also be readily separated from the products and reactants. One way of achieving this might be to attach an active Pd(II) Wacker-type catalyst to a thermooxidatively stable polymer support, and to use the polymeric system as a heterogeneous catalyst. Two earlier reports (*14, 15*) do exist of polymer-supported Pd(II) species being employed in Wacker oxidation of ethylene, and in 1985 Cum *et al* (*16*) reported on a system used for pent-1-ene and dec-1-ene oxidation. In this case the support was an oligo-*p*-phenyleneterephthalamide and was "impregnated" with $Pd(OAc)_2$. The resulting species was then heat treated to 950°C before being used as a catalyst in ethanol/water containing 70% $HClO_4$. It is not clear what the final form of supported catalyst was but at 950°C even aromatic polyamides are likely to be heavily if not totally degraded.

We have chosen to use a structurally better defined thermooxidatively stable polymer support and have already reported (*17*) the preparation and characterisation of this cyanomethylated polybenzimidazole (PBI-CH_2CN) supported Pd(II) complex which might function as a Wacker-type catalyst. We believe that this is a coordinatively unsaturated complex. In this paper we report the detailed behaviour of this heterogeneous species as a catalyst in the Wacker-type oxidation of higher alkenes.

EXPERIMENTAL

Materials

Pd(II) chloride was supplied by Johnson Matthey Chemicals Ltd. Dec-1-ene was obtained from Koch–Light Laboratories Ltd. Polybenzimidazole (PBI) beads were kindly donated by the Hoechst Celanese Co. All other chemicals were supplied by the Aldrich Chemical Co.

Catalysts

These were prepared and characterised in-house, full experimental details have been published elsewhere (*17*).

Catal-1. This was prepared from a cyanomethylated polybenzimidazole *powder*, the structure is indicated in Scheme 2. The Pd content is 1.7 mmol g^{-1} measured by atomic absorption spectrophotomeric (AAS) methods.

Catal-2. This was prepared from a carboxymethylated polybenzimidazole *powder* (Scheme 2); Pd content is 2.7 mmol g^{-1}.

Catal-3a. This was prepared from a polybenzimidazole *powder* grafted with short polyacrylonitrile chains (Scheme 2); the Pd content is 1.6 mmol g^{-1}.

Catal-3b. This was prepared from polybenzimidazole *beads* (diameter ~250 μm, surface area ~30 m^2g^{-1}) grafted with short polyacrylonitrile chains (Scheme 2); the Pd content is 1.5 mmol g^{-1}.

Catal-4. This was prepared by loading $Pd(II)Cl_2$ directly on to unmodified polybenzimidazole *beads* (Scheme 2); the Pd content is ~0.7 mmol g^{-1}.

Catal-5. This was prepared from cyanomethylated crosslinked macroporous polystyrene resin *beads* (diameter ~250 μm, surface area ~60 m^2g^{-1}) (Scheme 2); the Pd loading is 0.3 mmol g^{-1}.

Catal-6. This was prepared from macroporous crosslinked polyacrylonitrile resin *beads* (diameter ~250 μm, surface area ~120 m^2g^{-1}) (Scheme 2); the Pd loading is 0.6 mmol g^{-1}.

Instrumentation

Gas-liquid chromatographic (glc) analyses were performed on a Fractovap 2150 (Carlo Erba) with an FID detector employing a 3-m glass column packed with Apiezon-L (5%) on Chromosorb-W. The temperature programme was isothermal at 140°C for 8 min and then 20°C/min up to

200°C. The gas flow rates were H_2, 70 ml/min; air, 70 ml/min; N_2 carrier, 100 ml/min. The peak areas were computed on a JCL 6000 chromatography data system (Jones Chromatography Ltd.). Pd analyses were performed on a Philips PU9100X atomic absorption spectrophotometer.

RESULTS

Wacker-type Oxidations

A typical reaction was performed as follows. The reactor was a 40-ml two-necked glass flask fitted with a water jacket. A water bath was used to control the temperature, warm water being continuously pumped through the jacket. The reactor, equipped with a magnetic stirrer, a condenser, and an air inlet, was charged with a mixture of polymer-supported Pd(II) catalyst (e.g., Catal-1, 50 mg containing 0.085 mmol Pd) and Cu(II) chloride (about 200 mg, 2 mmol) in ethanol (15 ml) and water (5 ml). The catalyst was suspended in the solution. The mixture was stirred at 50°C with air bubbled (about 120–150 ml/min) through the solution for 30 min. Then dec-1-ene (1.50 ml, 7.9 mmol) was added by pipette. The oxidation reaction was monitored by quantitative gas–liquid chromatography (glc). The reaction was generally completed in several hours depending on the catalyst.

Samples were removed from the reaction solution using a glass dropper (50–100 μl) and placed in a test tube. The sample was then centrifuged to sediment the polymer-supported catalyst. The upper clear layer of liquid was then sampled (1 μl) for glc injection. The area of the product peaks increases with time while the area of the alkene peaks decreases. The yield (%) of product was calculated from the expression

$$\text{product yield} = \frac{(\Sigma F_{\text{prod}} \times A_{\text{prod}}) \times 100\%}{F_{\text{alk}} \times A_{\text{alk}} + (\Sigma F_{\text{prod}} \times A_{\text{prod}})}$$

where F_x = glc response factor (product and alkene) and A_x = glc peak area (product and alkene). For comparing the activities of the various catalysts the turnover number (TON) was chosen as the parameter. It must be emphasized that the turnover number was calculated based on the weight of oxidation product. In these polymer-supported catalytic reactions, however, the nonoxidized by-products were small and could be neglected. Hence the conversion of alkene and the yield of oxidation products were essentially equal. TON data were calculated using the expression

$$\text{TON} = \frac{V_{\text{alk}} \times d_{\text{alk}} \times \text{product yield}}{W_{\text{cat}} \times \text{Pd} \times t} \quad \text{g product g}^{-1}\ \text{Pd hr}^{-1},$$

where V_{alk} = volume of alkene (cm^3); d_{alk} = density of alkene (g cm^{-3}); W_{cat} = weight of polymer catalyst (g); Pd = weight % of metal on polymer; t = time (hr). A summary of the results using the various catalysts is shown in Table 1.

Effect of Solvent

Reactions were carried out in various solvent mixtures with water as described above using as catalyst Catal-1 in each case. Typical conversion curves are shown in Fig. 1 and the calculated TON data are shown in Table 2.

Temperature Effects

The rate of a Wacker-type reaction was expected to show a normal Arrhenius temperature dependence. However, it was felt that the solvent might also be of importance in this respect. Reactions were therefore carried out as before at temperatures 30, 50, and 70°C with solvents methanol, ethanol, and DMF. In each case Catal-1 was the catalyst. The results are shown graphically in Fig. 2, where the TON was calculated after 8 hours.

Since precipitation of Pd(0) is a known potential problem with these reactions a "high temperature" test was also carried out in order to encourage Pd(0) precipitation. The reaction was carried out as before using Catal-1 and with methoxyethanol as the or-

TABLE 1

Activities of Various Catalysts in Wacker-Type Oxidation of Dec-1-ene in Ethanol/Water (3/1)

Catalyst	Weight of catalyst (g)	Yield[a] (%)	TON	
			(g/g-Pd hr)	(mmol/g-Pd hr)
Catal-1	0.05	~100	15	107
Catal-2	0.05	41	3	21
Catal-3a	0.05	37	4	31
Catal-3b	0.10	34	2	15
Catal-4	0.10	10[b]	0.9	7
Catal-5	0.10	70	13	94
Catal-6	0.10	98	13	94
$PdCl_2$	0.011	38	8	56
$(MeCN)_2PdCl_2$	0.016	55	12	84
PBI[c] + $CuCl_2$	0.10	<5[b]	—	—

[a] 1.5 ml dec-1-ene, 50°C, 11 hrs.

[b] Reaction time 8 hr.

[c] PBI = polybenzimidazole powder with no Pd loaded.

ganic solvent at 120°C. After 8 hr *no Pd(0) was precipitated*, although a control reaction under identical conditions using $PdCl_2$ as the catalyst showed little reaction and precipitation of Pd black along with a Pd mirror on the flask wall.

Catal-6 was used similarly with *no formation of a Pd(0) precipitate*. See Table 3 for data.

Promotion Effect of Water

Water is a reactant in Wacker oxidations and it was expected that the water content of the reaction medium might influence the TON. Reactions were therefore carried out as before using Catal-1 at 50°C with various ratios of ethanol and water as the reaction medium. The results are shown in Table 4.

Level of Co-catalyst, Cu(II)

Reactions were carried out as before in ethanol/water using a fixed level of Catal-1 (50 mg, 0.085 mmol Pd) but with Catal-1/$CuCl_2$ weight ratios of 1/1, 1/5, and 1/20. The results are shown graphically in Fig. 3.

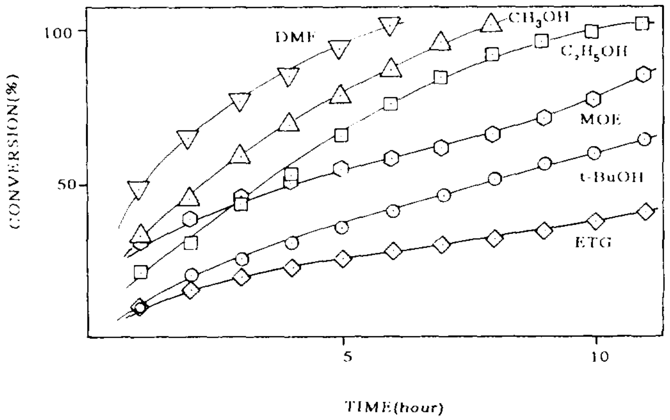


FIG. 1. Time–conversion curves for Wacker oxidation of dec-1-ene with Catal-1 in various solvents (see Experimental for conditions).

TABLE 2

Solvent Effect on the Oxidation of Dec-1-ene Under Wacker-Type Conditions[a]

	Time (hr)	Yield (%)	TON	
			(mmol/g-Pd hr)	(g/g-Pd hr)
MeOH	8	~100	147	21
EtOH	11	~100	107	15
t-BuOH	8	55	81	11
DMF[b]	6	~100	196	28
Ether	8	< 5	—	—
Acetone	8	< 5	—	—
ETG[b]	8	30	44	6
MOE[b]	8	65	96	14

[a] Catal-1, 50°C.

[b] DMF = dimethylformamide; ETG = ethylene glycol; MOE = methoxyethanol.

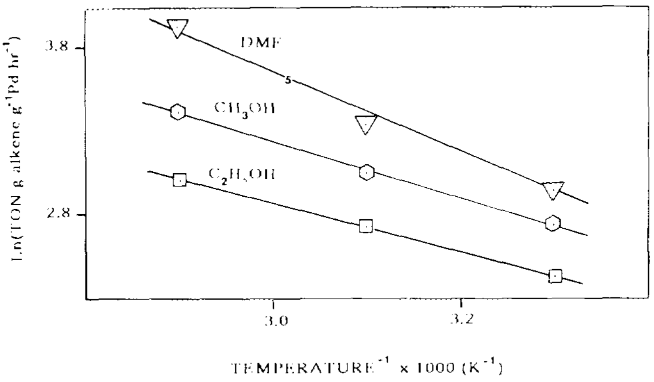


FIG. 2. Temperature dependence of TON for Wacker oxidation of dec-1-ene using Catal-1 in various solvents (see Experimental for conditions).

TABLE 3

Wacker-Type Oxidation of Dec-1-ene at 120°C in 2-Methoxyethanol

Catalyst	Weight of catalyst (g)	Time (hr)	Yield (%)	TON	
				(g/g-Pd hr)	(mmol/g-Pd hr)
Catal-1	0.05	7.5	~100	22	157
Catal-6	0.1	8	~100	18	130
$PdCl_2$	0.01	Pd ↓	—	—	—

TABLE 4

Promotion Effect of Water in Wacker-Type Oxidation of Dec-1-ene[a]

Water (ml)	0.75	1.5	3.0	4.5	6.0
EtOH (ml)	14.3	13.5	12.0	10.5	9.0
[water] (mol/l)	2.8	5.6	11.1	16.7	22.2
Conversion (%)	50	55	60	75	90
TON (g/g-Pd hr)	10.3	11.4	12.4	15.5	18.6

[a] Catal-1 (50 mg), 50°C, reaction time 8 hr.

Recycling of Polymer-Support Catalysts

To offer any technological advantage supported catalysts should be reusable. To check this a reaction was run as before using Catal-1 in ethanol/water at 50°C. After 11 hr the reaction mixture was cooled to room temperature and left to stand overnight. The catalyst powder (Catal-1) (or beads (Catal-7)) was collected by filtration, washed with ethanol, and then used as before in another reaction. Successive reactions were treated in an identical manner. The supernatant solution from each reaction was analysed for Pd using an AAS method. The results using Catal-1 are shown in Fig. 4, and for Catal-7 in Fig. 5.

DISCUSSION

Catalyst Activity

Although no details are presented in this paper, in fact the reaction with dec-1-ene (and other higher alkenes) is highly complex. Rapid isomerisation occurs concurrently with oxidation, with the result that although the methyl ketone is the major product, other ketones are also formed. This effect is well documented (e.g., Ref. (*10*)) and we will report separately on our own findings in this context. For the sake of this report, however, which focuses primarily on catalytic activity and recycling, no distinction is made between the reaction products; they are regarded simply as "the ketone product." The results in Table 1 show that the polymer-support Pd(II) complexes are indeed active Wacker oxidation catalysts, and in favourable cases are at least as active as $PdCl_2$ itself.

Superficially the TON data indicate an order of activity Catal-1 > Catal-5 ≈ Catal-6 > Catal-3a > Catal-2 > Catal-3b > Catal-4. The control reactions show that there is no activity from a polybenzimidazole poly-

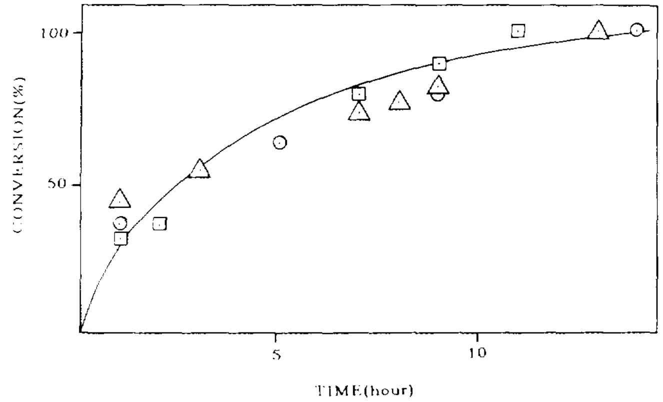


FIG. 3. Variation of conversion/time data with level of Cu(II) co-catalyst in Wacker-oxidation of dec-1-ene using Catal-1, Catal-1/$CuCl_2$: ○, 1/1; □, 1/5; △, 1/20 w/w (see Experimental for further details).

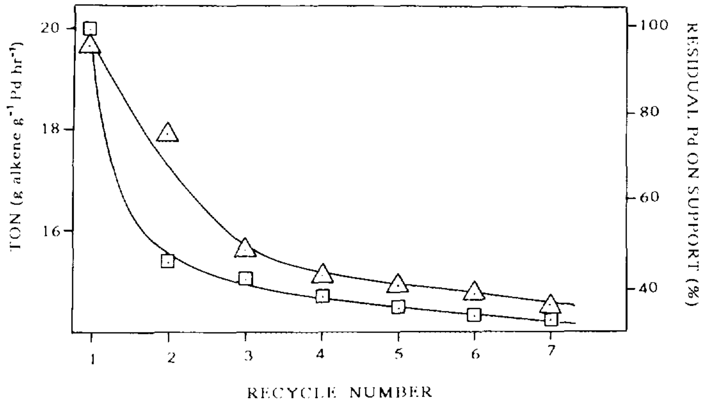


FIG. 4. Activity of Catal-1 and leaching of Pd(II) during recycling in Wacker oxidation of dec-1-ene: △, TON; □ Residual Pd(%).

mer (PBI) carrying no Pd(II) (last entry), and that the homogeneous complex $(MeCN)_2PdCl_2$, which is a reasonably close model for the most likely structures on the polymers (except for Catal-2), is about as active as Catal-5 and Catal-6. Though Catal-1 is measurably more active than Catal-5 and Catal-6 the former is a powder (particle diameter ~1 μm). Unfortunately no surface area data are available for these particular powder samples, but from results on very similar species we do not anticipate the surface area to be significantly larger than ~50 m^2g^{-1}. Catal-5 and Catal-6 in contrast are resin beads (particle diameter ~250 μm). Despite the fact that these do have a discrete pore structure (surface areas ~60 and 120 m^2g^{-1} respectively), the larger physical form may impose some mass transfer limitation on some Pd(II) sites, and this physical effect may be responsible for the difference in activity. Such effects have been reported for other systems (*18*). In practice, however, we can only speculate about the proportion of immobilised Pd(II) which is active in each catalyst and if this is less than 100%, then Catal-1 in particular is indeed significantly more active than $(MeCN)_2PdCl_2$.

In addition to the above factor, however, there appears to be a significant effect of the

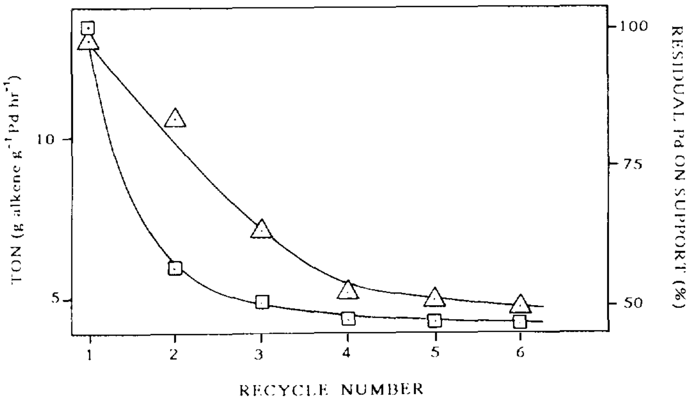


FIG. 5. Activity of Catal-6 and leaching of Pd(II) during recycling in Wacker oxidation of dec-1-ene: △, TON; □ Residual Pd(%).

ligand in these catalysts. The imidazole ring in PBI polymers is itself a potentially convenient ligand, and has been reported as such for PBI-supported Pd(0) alkene hydrogenation catalysts (*19*). Unfortunately, however, amine n-donors generally yield Pd(II) complexes which are poor Wacker catalysts, and this most probably explains the poor activity of Catal-4. In contrast, acetonitrile is known to be a ligand which yields active Pd(II) species, and indeed this influenced the original choice of polymer-bound ligands. Catal-1 indeed contains a cyanomethyl residue and this catalyst is more active than $(CH_3CN)PdCl_2$. One possible explanation for this is that at least some of the Pd(II) centres in Catal-1 may be coordinatively unsaturated (see Scheme 2). The arguments and experimental evidence for such a structure have already been reported in detail (*17*). It is well known that during the Wacker reaction the alkene reacts with the metal catalyst to form a π-complex (*12*). For the formation of this either a ligand on the metal centre needs to be replaced by an alkene π-ligand, or a vacant site is required at the metal centre. Acetonitrile is a good ligand because it complexes strongly and yet is very easy to displace with alkene to form the π-complex (*20*). However, with a coordinatively unsaturated complex, a vacant site is already available for the formation of π-complex, and such a complex is likely to be very active. In the homogeneous case, it is difficult to form and retain a coordinatively unsaturated complex since the vacant site is so readily filled by e.g. ligand sharing. However, because of the "polymer-support effect," i.e., "site–site separation", it is possible to understand how such coordinatively unsaturated complexes might be formed and retained in immobilised species.

PBI is a particularly rigid macromolecule and hence presents the maximum opportunity for "site isolation" of ligands. Polystyrene is somewhat less rigid, and polyacrylonitrile even less so, and as a result effective site isolation is less likely with Catal-5 and Catal-6. However, it is unlikely that these supported complexes are entirely structurally uniform and lower levels of unsaturated sites may occur in these two catalysts, as well. The prospects for site isolation in Catal-3a and 3b are even lower, because although these are PBI-based species, short, highly flexible chains of polyacrylonitrile have been grafted to the rigid main chain of the PBI. This structure would be expected to offer two nitrile ligands to each Pd(II) centre with little difficulty (Scheme 2), and this probably explains the lower activity of these catalysts.

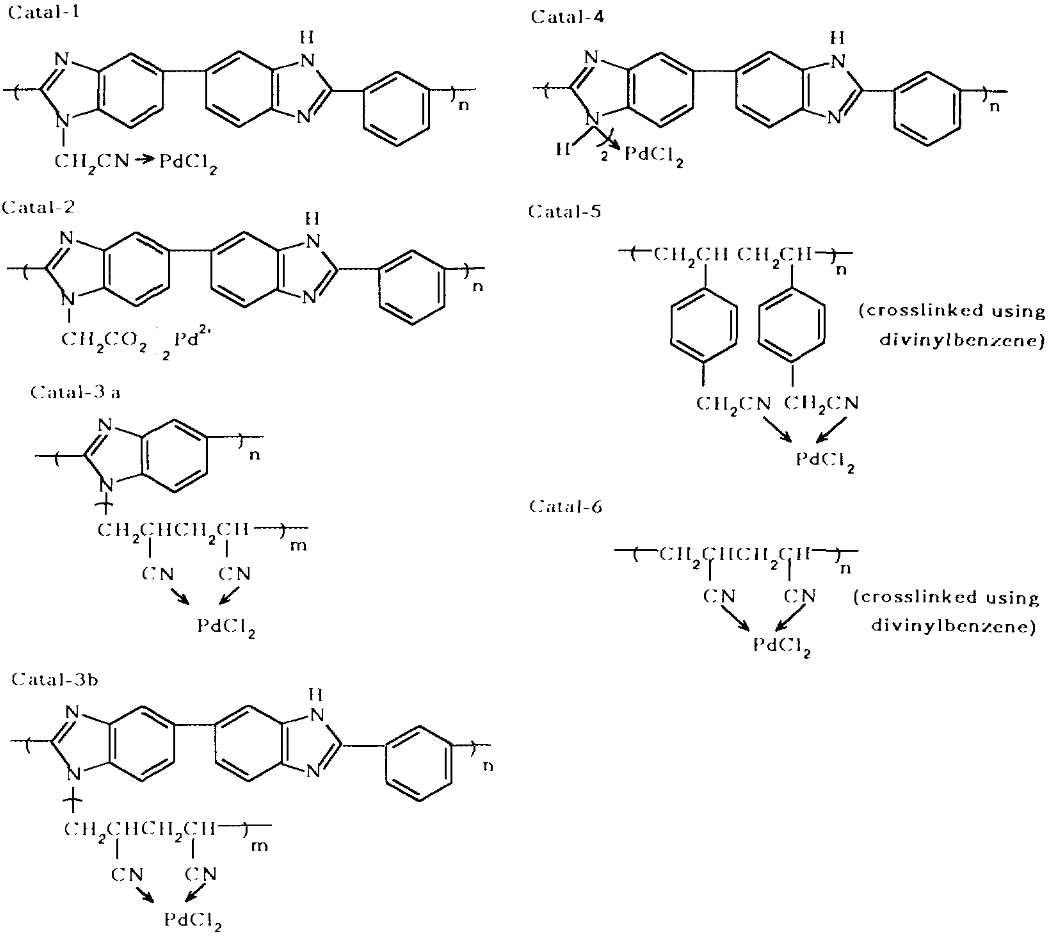
Catal-2 differs substantially from the other species because it has a carboxylate ligand. Acetate anion is also known to be a good ligand for a Wacker-type catalyst. There are several reports on the use of homogeneous Pd(II) acetate as a catalyst. Despite this the caboxymethylated PBI-supported Pd(II) (Catal-2) proved to have rather low activity. The reason might be that Catal-2 was prepared via a ligand exchange reaction in methanol, which seemed to proceed rather slowly (72 hr). During this period some Pd(II) might have been reduced to Pd(O), and reoxidation to Pd(II) is impossible in the absence of $CuCl_2$. Over this period nonactive Pd(O) could have precipitated within the polymer. Although the nominal Pd loading looks high, the loading of active Pd(II) may well have been rather low.

In the more detailed studies which follow Catal-1 was chosen for further investigation because of its optimum activity.

Solvent Effect

Water is an essential reactant in Wacker oxidations although it remains unclear whether attack of hydroxide on coordinated ethene occurs within the Pd coordination sphere, or can be from outside (*21–23*). The promotion effect (Table 4) observed with increasing levels of water in EtOH presumably arises because it is a reactant. The effect clearly overrides any decrease in solubility of the alkene as the water content is increased.

It has also been shown that the rate con-



SCHEME 2. Structures of polymer-supported Pd(II) Wacker catalysts.

trolling step in the Wacker industrial process is the mass transfer of ethylene and oxygen (*24*). In Wacker-type reactions involving higher alkenes it is also likely that the rate controlling step is alkene mass transfer. Hence an organic solvent is generally required to improve the solubility of the alkene in the water-containing reaction medium and at the same time to improve the mass transfer situation. Not surprisingly, the reaction rate is known to vary with the solvent used. Hence hydrophilic organic solvents tend to increase the solubility of the alkene in water and thus to increase the rate and yield of the reaction. In the polymer-supported catalytic reaction, the solvent is not only likely to influence the catalytic process and the solubility of the alkene, but it might also influence the configuration and flexibility of the polymer support (via solvation) and hence indirectly influence the catalyst behaviour. In the homogeneous ($PdCl_2$) catalytic system, the reaction rate in various solvents is in the order MeOH > EtOH > DMF (*25*). In the present work with Catal-1, the reaction rate is in the order DMF > MeOH > EtOH (Fig. 1). DMF is likely to be a much better plasticizer of PBI than MeOH and EtOH, and indeed the PBI support may even swell in DMF. These factors would tend to favour the reaction. It is well known that the homogeneous Wacker-type reaction is a sterically selective one (*26–28*). The reaction rate in *t*-BuOH is much lower than that in MeOH and EtOH because of the bulkiness of this solvent. The reaction rate tends to fall with increasing chain length of primary monohydric alcohol solvent or increasing substitution of the alcohol. The same effect is seen here with *t*-BuOH. Ethylene glycol (ETG) was expected to have a favourable influence on the reaction because of its polarity and its miscibility with water and alk-1-ene. However, it also has a high viscosity and is likely to be a poor plasticizer of the PBI backbone. Hence the reaction rate is lower than in MeOH, EtOH. The reaction rate in methoxy ethanol (MOE) compares favourably with that in other primary alcohols. This high boiling solvent was therefore a good candidate for our high temperature test.

Temperature Effects

The influence of temperature on the TON for Catal-1 is shown in Fig. 2. As expected, the TON increases with increasing temperature and the effect is almost identical in the two alcohol solvents. With DMF the temperature dependence is a little stronger, and this itself is perhaps indicative of the large number of factors contained within these overall experimental dependences. Clearly there is the Arrhenius factor associated with each step in the reaction mechanism, along with other considerations such as the temperature variation of solvation of both the catalytic centres and the macromolecular support.

One of the attractive features of PBI-supported catalysts is there potentially very high thermal stability. Thus possible applications are more likely to be limited by decomposition of the metal complex rather than problems associated with polymer degradation. The present work has shown that both Catal-1 and Catal-6 can be operated very successfully at 120°C in 2-methoxyethanol as the organic solvent, with the water component largely in the vapour phase. Even more remarkable is that even after 8 hr at this temperature, and in the reactions run at 50°C, the polymer catalysts remained brown/green in colour, and there was *no visual evidence for Pd(0) precipitation*. In contrast, the control reaction using soluble $PdCl_2$ yielded Pd black along with a Pd mirror on the reactor wall very quickly at this temperature, and the oxidation reaction essentially stopped. It must also be emphasised that *no hydrochloric acid was required* to prevent Pd(0) formation in the use of Catal-1 and Catal-6. Complexed Pd(0) is an essential feature of Wacker oxidations, with Cu(II) functioning to reoxidise this to Pd(II) and the so-formed Cu(I) itself being re-oxidized by the O_2 in the air feed. At high temperature it seems that molecular Pd(0) complexes rapidly aggregate to form larger Pd(0) particles and finally precipitate as Pd black. Use of hydrochloric acid prevents aggregation and precipitation. With the present polymer-supported catalysts it is clear that similar redox cycles must be involved. However, when molecular Pd(0) complexes are formed, immobilised on polymer chains, they seem to be site isolated and inhibited from migrating to initiate Pd(0) particle formation. Reoxidation to Pd(II) therefore remains efficient and the catalysts are stable and long-lived even at high temperature.

Another advantage of the polymer-supported catalytic system arises by eliminating the need for HCl. The rate expression for Wacker-type homogeneous reactions using aqueous $PdCl_4^{2-}$ is shown in Scheme 3 (*29*). From this it is clear that the rate decreases with an increase in the concentration of hydrogen ions and chloride ions in the reaction medium; i.e., HCl retards the reaction. The polymer-support Pd(II) catalytic system requires no HCl, and hence this retardation is eliminated. In addition, no chloride by-products are possible beyond the level which might arise from hydrolysis of the $CuCl_2$ co-catalyst. The latter could be significant in first cycles, but not in recycles nor in continuous use.

$$PdCl_4^{2} + C_nH_{2n} + H_2O \longrightarrow Pd(0) + C_nH_{2n}O + 2HCl + 2Cl^-$$

$$\text{reaction rate} = \frac{K\,[PdCl_4^{2}][\text{alkene}]}{[H^+][Cl^-]^2}$$

SCHEME 3. Kinetic equation for Wacker oxidation involving $PdCl_4^-$.

Cu(II) Co-catalyst

In the present work $CuCl_2$ was used as the co-catalyst to reoxidize Pd(0) in the usual way, and we have no evidence that the catalysts are active without Cu(II). The $CuCl_2$ was added homogeneously and within the range of Catal-1/$CuCl_2$ ratios examined (1/1–1/20) the level of Cu(II) did not influence the catalytic activity (Fig. 3). The reoxidation step is therefore not rate limiting. In the case of the PBI-supported systems (Catal-1, 3a, b; and 4) it is possible that Cu(II) could become anchored to the polymer via the large number of nitrogen donor centres along the backbone; i.e., the PBI polymers might be able to coordinate both Pd(II) and Cu(II). In practice the occurrence of such an immobilised bimetallic catalyst was not demonstrated directly. In a typical reaction $CuCl_2$ and the immobilised Pd(II) complex were stirred in solvent for 30 min before the alkene was added to start the reaction. However, in one instance the premixing process was continued for 72 hr to deliberately allow Cu(II) complexation with the PBI and/or Cu(II)/Pd(II) exchange. Strangely the activity of the resultant system was very low. This approach was therefore not pursued further, but it does show perhaps that the interaction of the two metal centres is not straightforward. For example, if all the Cu(II) were immobilised and the Pd(II) were free, e.g., by complete metal ion exchange, then it might be that catalytic activity is lost. This could arise, for example, if migration of the Pd complexes and/or O_2 into the polymer were inhibited. The role of Cu(II) in the recycling experiments is also intriguing.

Recycling of Catalysts

One of the most attractive potential advantages of polymer-supported catalysts is that they might be recycled several times or used continuously. In the present work, Catal-1 and Catal-5 were chosen for use in recycling experiments because of their relatively high activity. The data in Figs. 4 and 5 show clearly that both supported catalysts remain active over many cycles. However, in both cases the TON falls rapidly over the first three cycles and thereafter stabilises at essentially level values. The data in the figures also show that Pd is leached from the support rapidly in the first cycle, but thereafter Pd loss is arrested. Indeed, entry 7 for Catal-1 (Fig. 4) and entries 5 and 6 for Catal-6 (Fig. 5) correspond to a Pd loss of only ~1 ppm in the respective cycle. Hence apart from the first reaction with each catalyst, the amount of free Pd present in any single reaction is rather low. Furthermore, the TON data correlate rather well with the level of Pd residing on the support, and very poorly with that in solution. Clearly, therefore, the major catalytically active Pd species is that on the support. The initial rapid loss of Pd may arise because some metal centres are rather weakly bound, whereas the residual species may be some relatively tightly bound catalytically active entity. Alternatively the relatively high ligand/Pd ratio generated after initial leaching may simply inhibit further leaching by a mass action effect.

It is also important to emphasise that in these recycling experiments *no additional $CuCl_2$ was required* to be added in each cycle. Either the level of Cu(II) ion exchanged or coordinated onto the support in the first reaction, or the level of insoluble $CuCl_2$ recovered at the end of each cycle, is sufficient to act as an effective co-catalyst in all the subsequent reactions. While these recycling results are very encouraging, they do raise a number of questions, and our investigation of these systems continues in order to try to answer these.

CONCLUSIONS

Pd(II) has been immobilised on a number of polymer supports carrying cyanomethyl ligands. These polymer-supported catalysts are active in Wacker-type oxidation of dec-1-ene, some being more active than $PdCl_2$ itself. $CuCl_2$ added homogeneously functions as an effective co-catalyst. The most active Pd(II) species is one immobilised on a highly rigid cyanomethylated polybenzimidazole and at least some of these metal centres may be coordinatively unsaturated (*14*). Whereas the lower alcohols are the most useful solvents for the homogeneous catalyst systems, dimethylformamide is the best of the solvents examined with the polymer-supported species, probably because this solvates the polybenzimidazole most effectively. The supported catalyst readily functions at ~120°C without formation of Pd(0) black and without the need for addition of hydrochloric acid. In contrast, under the same conditions, $PdCl_2$ is rapidly deactivated as insoluble Pd(0). Recycling of the supported catalysts is very effective. Some drop in catalyst activity is observed initially along with leaching of Pd. However, catalysts become stable after three cycles and Pd loss drops rapidly to the ppm level. During recycling no additional Cu(II) co-catalyst needs to be added.

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