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PHOTOELECTRON SPECTROSCOPY (XPS) STUDIES ON SOME PALLADIUM CATALYSTS

JOICE P. MATHEW and M. SRINIVASAN*
Department of Chemistry, Indian Institute of Technology, Madras 600036, India

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Abstract—Several Palladium chloride ($PdCl_2$) and Palladium acetate [$Pd(OAC)_2$] complexes of polymer coated silica have been developed for use as recyclable hydrogenation catalysts. The polymers used are polyacrylamides, polyvinyl pyridine, polyvinyl imidazole and copolyacrylamide methacrylic acid. These catalysts have excellent activity over several cycles of hydrogenation without any significant loss of metal or activity. These catalysts were examined by XPS to identify the oxidation states of Pd and N. The studies indicated that the more active form of the catalyst is the one, which contained Pd(O) or a mixture of Pd (II) and Pd(O). XPS studies on nitrogen (N) showed the presence of both co-ordinated and unco-ordinated N in the support.

INTRODUCTION

Polymer bound transition metal complexes have been extensively studied for academic and industrial purposes [1]. The principle disadvantage of polymer supports are their lack of stability—both thermal and mechanical, especially in reactions where high temperature and mechanical agitation are required [2]. The major advantages of inorganic supports are their better mechanical and thermal stabilities coupled with reasonable heat transfer properties. Although the polymer will still decompose at higher temperatures, a blend of inorganic support with polymer coating with coordinating functionalities at least gives a mechanically more stable catalyst. Also, the diffusion problems associated with the polymer bound transition metal catalysts can probably be minimised by coating the polymer onto a ceramic of large surface area [3, 4]. The ceramic, silica gel in this case, is only a mechanical support and the pores and the available surface area is of consideration, only for providing the host site for reactions to occur. Hence, to ensure that surface area does not decrease significantly to provide optimal adsorption and hence reaction sites, the polymer coating has to be produced while the polymer is forming. Experimental conditions are such as to ensure the availability of a reasonable surface area in the silica gel and the same was monitored both before and after the polymerisation reaction, in the presence of silica gel. The most important point to keep in mind is that the inorganic support, functions as the host site for reaction and the catalyst is the metal co-ordinated to the polymer ligand.

While diffusion problems may be reduced by coating due to possible diminished porosity, the true catalytic species—Pd ion is actually outside the matrix. The purpose of silica gel is thus one of providing a rigid backbone mechanically stronger than the polymer. With these objectives we have designed several silica supported polymer palladium catalysts and proved them to be very efficient hydrogenation catalysts [5, 6]. The influence of the oxidation state of the active metal and the coexistance of several valence states of metal after pre-reduction of the catalysts are well documented [7, 8]. This paper describes a systematic study on the characterisation and catalytic properties of the mixed valence states of materials anchored onto the polymer coated silica supports, through XPS studies, as well as the effect of the ligands binding the metal with respect to the stability of the catalysts.

EXPERIMENTAL

The silica polymer composite supports were prepared by the bulk polymerisation of the monomers in the presence of silica gel as reported earlier from this laboratory [5(a), (b), 6, 9, 10]. The polymer supports with various chelating groups are shown in Scheme 1.

BDH column grade silica gel (particle size distribution 60–120 mesh or 250–125 microns) of surface area 600 m^2 g (as determined by Porous material INC BET Sarphtometer [9]), was used in the preparation of the polymer silica gel matrix.

Silica gel (10 g, 50 wt%) was added to a solution of 4-vinylpyridine (9.8 g, 49 wt%), divinylbenzene (DVB) (0.1 g, 1 wt%) and benzoylperoxide (0.1 g) in diethyl ether. It was stirred for 30 min under N_2. Ether was removed and heated to 80°C under N_2 for 10 hr, to obtain polyvinylpyridine coated silica (19.5 g) (P-1) which was washed well with methanol, acetone, water and then dried. The powdered mass was used for the estimation of Pd content, surface area and for all other studies. Similarly P-2 was obtained from acrylamide (14.7 g, 49 wt%) DVB (0.3 g, 1 wt%) and silica gel (15 g). P-3 was prepared from acrylamide (7.2 g, 24 wt%) methacrylic acid (7.5 g, 25 wt%) DVB (0.3 g, 1 wt%) and silica gel (15 g). P-4 was based on 1-vinylimidazole (14.7 g, 49 wt%) DVB (0.3, 1 wt%) and

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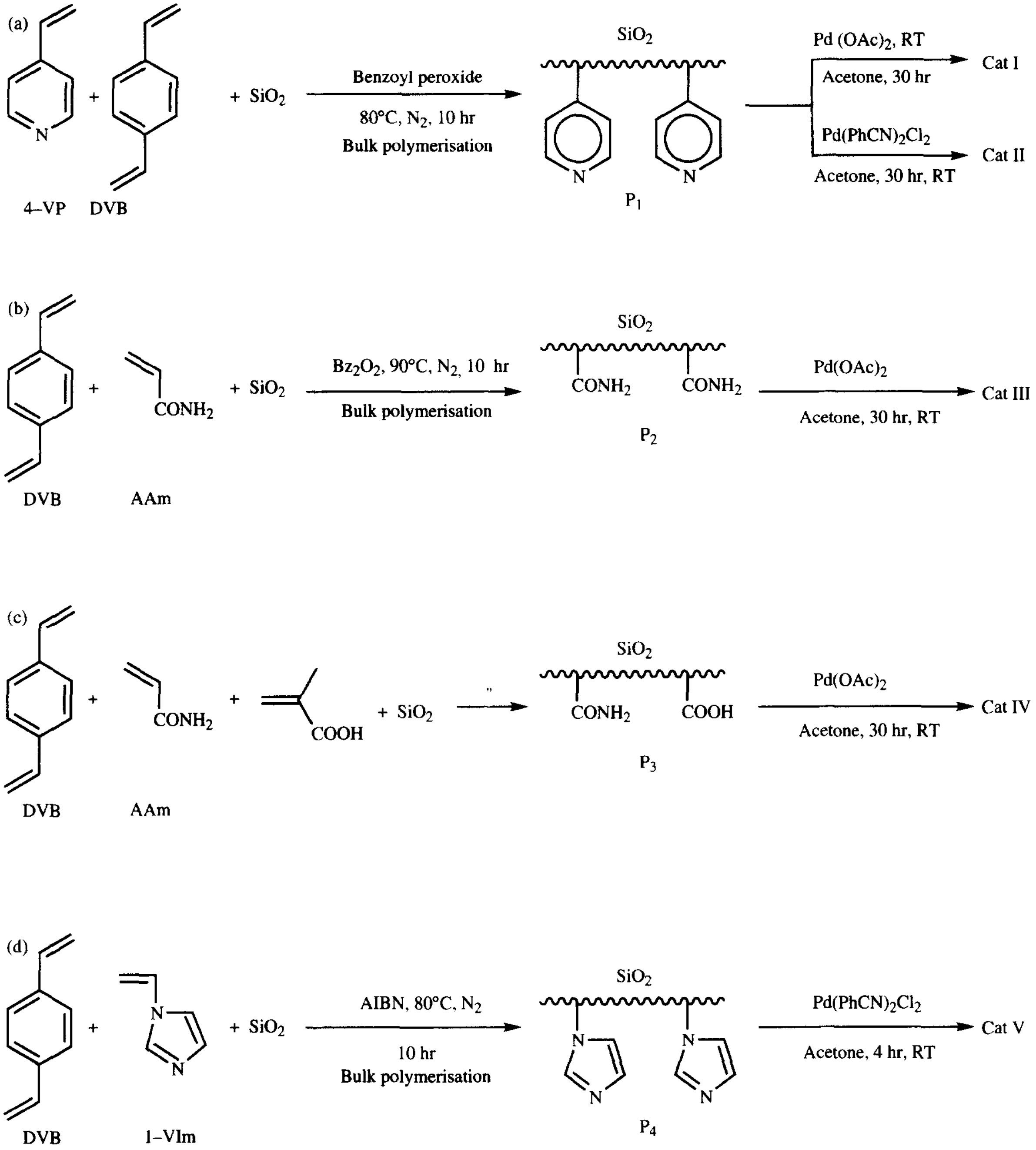
*To whom all correspondence should be addressed to at: Dr Bharat Ram Research and Development Centre, SRF Ltd, Manali, Madras 600 068, India.



Scheme 1. Preparation of catalysts.

silica gel (15 g, 50 wt%). Azobisisobutyronitrile (AIBN, 100 mg) was used as polymerisation initiator while all other conditions were the same as used for P-1, P-2 and P-3.

The catalysts were prepared from 'Analar' grade Palladium acetate $Pd(OAC)_2$ and Palladium chloride ($PdCl_2$) as obtained from Johnson Matthey. Briefly, the catalyst was obtained as below.

The polymer support (5 g) (polymer 1, 2 or 3) was stirred as a suspension in a solution of $Pd(OAC)_2$ (0.65 g, 2.8 mmol) in acetone (100 ml) for 3 h, under N_2 at room temperature to obtain catalysts I, III or IV as a yellow brown mass.

Catalysts II and V were obtained using polymer supports 1 or 4 (5 g) and bisbenzonitrilodichloro Palladium (II) $Pd(PhCN)_2Cl_2$ (1 g, 2.6 mmol) as above.

Then the hydrogenation studies and the XPS studies were carried out with these catalysts. Hydrogenation studies were performed using a constant pressure hydrogenation apparatus as described in Refs [5(b), 6, 10], under an ambient pressure of H_2 in methanol as solvent at room temperature [5(b), 6, 9]. The products were analysed by GC and NMR.

RESULTS AND DISCUSSION

The catalyst obtained by stirring the support with the $Pd(OAC)_2$ solution (Cat I) for 5 hr, showed in the XPS, the presence of only Pd(II), whereas the XPS taken after a stirring period of 30 hr indicated the

Table 1. XPS studies on Cat I

Catalyst	Pd 3d$_{5/2}$ B. E. value	Rate of hydrogenation for acrylonitrile (mol l^1/sec^1)
P1-Pd(OAC)$_2$ after 5 hr	337.50	
P1-Pd(OAC)$_2$ (fresh) after 30 hr	337.75 and 336.75	32.51
P1-Pd(OAC)$_2$ reduced with NaBH$_4$	335.80	33.51
1-Pd(OAC)$_2$ reduced with NH$_2$NH$_2$	336.20 and 337.75	33.14
P1-Pd(OAC)$_2$ recovered or H$_2$ reduced	336.5 and 335.80	33.60

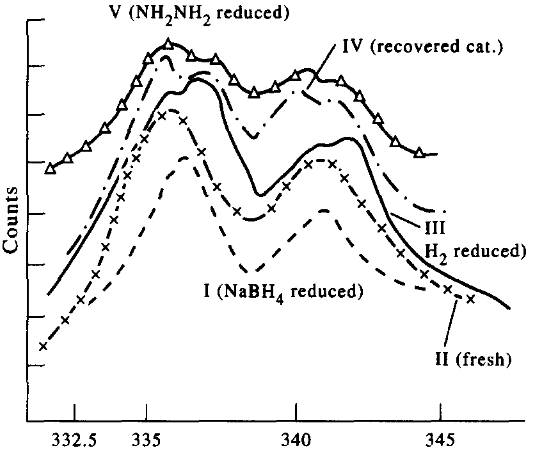


Fig. 1. XPS spectra of Cat I. Fresh, reduced (NaBH$_4$, H$_2$, NH$_2$NH$_2$) and recovered.

presence of two energy states at 336.7 and 337.7 eV (Table 1). The additional XPS peak observed at 336.7 eV which lies between Pd(O) and Pd(II) can be due to Pd(I) as reported by Zharmaambetova [11].

Figure 1 gives the XPS spectra of the Cat I which was reduced by various reducing agents such as molecular H$_2$, sodium borohydride and hydrazene hydrate. It can be seen from the XPS data in Table 1 that when the catalyst was reduced with H$_2$, the Pd(O) content increased thereby decreasing the Pd(II) content. While the action of strong reducing agents like borohydride (BH^{-1}) led only to Pd(O), the catalyst reduced by a weak reagent like hydrazene hydrate, had a mixture of valence states of Pd. it was also observed that the catalysts containing a mixture of valence states of Pd(II) and Pd(O) alone are more active than Pd(II) catalysts.

Ping Lin Ho *et al.*, [8, 12] have reported a similar enhancement of the activity for catalyst containing mixed valence states of Pd by an extensive study on a few polymer -Pd catalysts using ESR and XPS. They also feel that Pd(I) (XPS signal at 336.7 eV) can be present in the catalyst even though it is unstable. Pd(O) also has an XPS signal at this region, but palladium oxide cannot be present since the catalyst has not been subjected to oxidation for a temperature range of 400°C or more.

Mani *et al.* [5(c), 13] observed that in Pd catalysts which are anchored to a polymer support but not through a silica base, Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ binding energies are seen in the region of 338.6–338.1 and 343.5–343.2 before and after activation. The catalyst in this case was derived from PdCl$_2$.

The XPS studies using the other catalysts Cat II, IV and V (Table 2) indicate PdCl$_2$ anchored to support P1 (Cat II) had only Pd(II+) in the fresh catalyst. The recovered catalyst after a hydrogenation reaction (i.e. H$_2$ reduced) contained both Pd(II) and Pd(O) and NaBH$_4$ reduced catalyst indicated the presence of only Pd(O), while the NaBH$_4$ reduced Cat V showed the presence of Pd(O) as well as a small amount of Pd(II). Cat IV also exhibited a spectra similar to Cat I.

Table 2. XPS data for Cat III, IV and V

Catalyst	Binding energy (eV)				
	Pd 3d$_{5/2}$	Pd 3d$_{3/2}$	N1s	O1s	Si$_{2p}$
Cat III					
P1-PdCl$_2$					
Fresh	337.75	342.75	—	533.5	104.0
Recovered	335.75 and 337.75	341.05 and 342.75	—	532.75	103.7
Reduced with NaBH$_4$	335.75	341.0	—	532.75	103.7
Cat IV					
P3-Pd(OAC)$_2$					
Fresh	336.2 and 337.5	341.6 342.7	— —	— —	— —
Cat V					
P4-PdCl$_2$					
Fresh	338.0	343.0	399.75 and 402.0	533.8	104.0
Recovered	337.50 and 336.20	342.75 and 341.60	400.25 and 401.25	532.7	103.2
NaBH$_4$	337.5 and 336.2	342.75 and 341.6	400.25 and 401.25	532.5	101.7

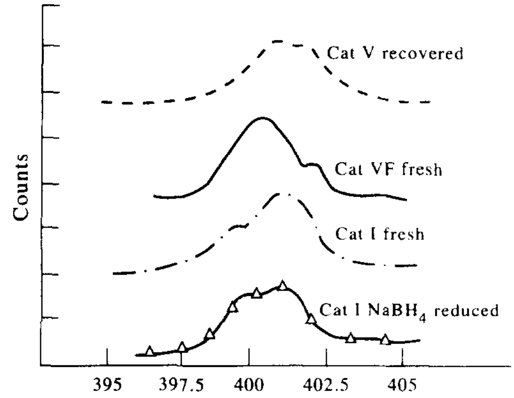


Fig. 2. XPS spectra for N in Cat I and V.

The XPS studies for nitrogen (Fig. 2) was carried out for two of the catalysts (Cat II and V). Pyridyl N in fresh Cat I exhibited two energy states at 398.5 and 400 eV. As in Ref. [11], in free polyvinylpyridine, the nitrogen exhibited a binding energy value of N1s = 398.5 eV, while an additional higher binding energy value has been documented for the co-ordinated N on the PVP–Pd complex catalyst. Hence, in the present case the additional binding energy value at 400 eV for N is asigned to the co-ordinated nitrogen of the catalyst. XPS spectra of nitrogen in the NaBH$_4$ reduced Cat I indicated a decrease in the content of co-ordinated nitrogen and an increase in the intensity of peak due to free nitrogen. This may be due to the partial breakage of the N → Pd bond which can give rise to free pyridine groups [11]. As the catalyst is found to posses good recycling efficiency and hence stability, this reduced Pd species is assumed to be stabilised within the polymer matrix. With Cat V, where Pd(PhCN)$_2$Cl$_2$ is anchored by imidazole ligands, the XPS of the N showed two binding energy values at 399.75 and 402.0 eV. The values are assigned to the free N of the imidazole group and the co-ordinated N. An enhancement of free N content was observed on NaBH$_4$ reduction of the catalyst.

Hydrogenation studies

The analytical data for the catalysts are tabulated in Table 3. Five batches of each of the catalysts were prepared starting from silica gel, through polymer coating to anchoring the metal to establish consistency (Table 5). The catalysts were also used repeatedly and Table 5 lists the batch to batch and recycle consistency of the study through one of the systems, *viz.* Cat I. The initial rates of hydrogenation of a few olefines with the five catalysts are tabulated in Table 4. In order to compare the activity of these catalysts with a silica free polymer-Pd catalyst, the data for such a catalyst reported earlier from our laboratory [9] are also given. It can be seen that the present catalysts are far more active than the conventional polymer bound catalysts. The higher activity is attributed to the relatively large surface area of the catalysts. Comparing the activity of the present five catalysts, it can be seen that the order of activity is Cat I > Cat II > Cat IV > Cat III > Cat V. A large surface area and high metal content of Cat I may be the reason for its highest activity. This was proved by comparing the activity of Cat I and II which are based on the same support, but different surface area. Cat V which has the largest surface area and a comparatively good metal content was the least reactive, showing thereby that the nature of the support also affects the activity significantly. Probably, the high complexing ability of imidazole leads to a very strong bonding making Cat V least active. A second reason may be the N/Pd ratio.

Jiang *et al.* [14] who have studied the variation of rate of hydrogenation with N/Pd ratio reported that maximum activity was observed at a N/Pd ratio between 9 and 18, while low activity was observed for catalysts having N/Pd ratio between 2 and 5. Hence, in the present case, it is possible that the lower N/Pd ratio causes a low reactivity for Cat V in spite of its

Table 3. Analytical data for the catalysts

Catalyst	N (%)	Pd (%)	N/Pd ratio	Surface area	Particle size (microns)
Cat I	6.21	6.01	7.8	220.30	28
Cat II	6.21	5.21	9.2	166.94	37
Cat III	6.50	3.25	15.2	132.08	41
Cat IV	3.09	3.55	6.6	107.05	--
Cat V	2.26	5.55	3.1	325.50	24

Table 4. Hydrogenation studies

	Turn over number (TON)*					
Substrate	I	II	Catalyst III	IV	V	P-PdCl$_2$
Styrene	2225	1644	790	1156	737	144
Acrylonitrile	1967	1511	624	1269	617	167
Cyclohexane	427	361	210	108	122	13
Norbornene	3992	1926	1844	1806	1233	115
1-Octene	1711	1019	316	578	277	—
Dicyclo pentadiene	2995	1879	952	1380	865	678

$$*\text{TON} = \frac{\text{Initial rate} \times 3600}{[\text{Catalyst}]}\ \text{mol/g atm Pd/hr.}$$

= Number of moles of substrate reduced per g atom palladium in 1 hr (3600 sec).

Table 5. Recycling efficiency and batch to batch consistency of the catalysts

Catalyst	Catalyst* (conc. mol l^{-1})	Initial rate of hydrogenation ($\times 10^5$mol l^{-S} cycle) I	II	IV	VI	X	XV
Cat I	2.25	46.7	46.8	45.9	46.5	41.5	40.5
Cat II	1.9	31.50	31.84	31.84	30.16	28.5	—
Cat III	1.50	20.78	20.11	21.11	18.77	14.30	—
Cat IV	1.60	21.78	21.45	22.79	19.44	10.72	—
Cat V	2.10	16.75	17.09	15.08	16.08	13.50	—

Substrate: acrylonitrile (0.05 mol l^{-1}).

Cat I (fresh)†	Rate	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Conc. = 2.25	—	46.7	46.8	46.1	46.4	46.7

*Since Cat I–V are solids, concentration means the number of gram atoms of palladium present in the weight of (g) catalyst (I–V) taken $\times 1000/V$ where V is the reaction volume.

†Batches 2–5 were made only on a small pilot monitoring scale to establish reproducibility.

large surface area compared to even Cat IV which showed a reasonable activity in spite of its small surface with lower metal content.

CONCLUSION

From the XPS data, it is clear that a mixed valence state or Pd(O) with a reasonable high N/Pd ratio, make the catalysts more active.

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