

Catalytic effects of poly(methyl methacrylate)-supported β -diketone-linked palladium complexes in olefin oxidation

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MS received 18 February 2002; revised 18 June 2002

Abstract. Poly(methyl methacrylate)-supported β -diketone-linked palladium complexes on refluxing with olefins at 70°C in methanol–water medium for 10 h afforded carbonyl compounds. The course of the reaction was found to be influenced by the degree of cross-linking of the polymer matrix and the structural environment of the ligand. The reaction is assumed to proceed through a hydroxy palladation intermediate. A suitable mechanism is also suggested.

Keywords. Palladium complexes; poly(methyl methacrylate) support; olefin oxidation; β -diketone-linked complexes.

1. Introduction

Functionalised polymers can be used to promote a wide range of organic transformations and serve as effective purification media^{1–3}. Polymer–metal complexes with good catalytic activity, selectivity and reproducibility have been prepared from such linear and cross-linked organic polymers^{4,5}. The synthetic reactions that they promote and mediate can be monitored using simple analytical techniques such as thin layer chromatography. Cross-linked organic macromolecular species have found wide applications in recent years because of the ease with which the work-up of the reaction mixture can be carried out and also because of their reusability^{6–8}.

The oxidation of olefins to carbonyl compounds in the presence of metal salts has been investigated and stereochemical studies suggest that the reaction takes place by the *trans* attack of the water outside the coordination sphere of the metal^{9–15}. The present paper highlights the role and mechanism of poly(methyl methacrylate)-supported β -diketone-linked palladium complexes in the oxidation of olefins. Incorporation of the metal complex onto the polymer support has been done to exploit the advantages of heterogeneous catalysis, easy work-up of the reaction mixture and reusability^{16–19}.

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2. Experimental

2.1 Materials, methods and instruments

The monomers (Aldrich) were purified by low pressure distillation. Solvents were of reagent grade and were purified by standard procedures. Metal salt solutions were prepared in doubly distilled water. Functional group capacities and metal intake capacities were determined by standard volumetric methods. Electronic spectra were recorded on a Varian Cary 2390 UV-VIS-NIR spectrophotometer and infrared spectra on a Perkin-Elmer 397 spectrophotometer. The NMR spectra were recorded on a Bruker 300 MHz spectrometer. Thermal analyses of the complexes were done on a Dupont 2000 TGA V5 thermobalance.

2.2 Preparation of methyl methacrylate-divinylbenzene copolymer support

The monomers, methyl methacrylate and divinyl benzene, were washed with sodium hydroxide solution (1%, 3 times) and water to remove the inhibitors. The cross-linked polymers were prepared by the suspension polymerization technique. Poly(vinyl pyrrolidine) (150 mg) was dissolved in distilled water (100 ml) and heated to 80°C. Methyl methacrylate (20 ml) and divinyl benzene (1.1 ml) for 2% cross-linked resin and benzoyl peroxide (200 mg) as initiator were added to the hot solution with vigorous stirring. The mixture was heated at 80°C with stirring for 12 h. The polymer so obtained was washed with hot water, carbon tetrachloride, benzene and ethanol and dried at 60°C in vacuum. Yield: 16 g. Polymers with cross-link densities of 5, 10 and 15 were prepared by varying the monomer ratios.

2.3 Preparation of poly(methyl methacrylate)-bound β -diketones

The 2% DVB cross-linked poly(methyl methacrylate) resin (10 g) preswollen in acetonitrile (20 ml) was refluxed with 4'-methylacetophenone (25 ml) and sodium ethoxide (5 g) at refluxing temperature for 12 h. Finally the reaction mixture was cooled in an ice-bath, acidified with sulphuric acid (2N, 20 ml) solution. The product resin was collected by filtration, washed with water, ethanol and acetone and dried in vacuum to constant weight. Yield: 14.5 g.

IR (KBr, pellet): 3000 (C-H str., aromatic), 2950 (C-H str., aliphatic), 1710 (C=O str.), 1620 (C=O...H str.), 1540 (C-C str., aromatic), 1250 (C-C str., aliphatic).

^{13}C -NMR (solid state): 13.4, 16.1, 24.3, 28.6, 32.5, 33.8, 45.6, 51.6 (sp^3 carbon atoms), 94.9 (sp^2 carbon atom) 127.7, 128.2, 136.6, 137.4 (aromatic carbon atoms), 177.2 (carbonyl carbon). CHN analysis, Anal. Calcd.: C, 83.13, H, 7.23%; Found: C, 83.07, H, 7.16%.

Polymer supports with different cross-linking densities were functionalised similarly with various 4'-substituted acetophenones.

2.4 Preparation of poly(methyl methacrylate)-supported β -diketone-linked palladium complexes

Solution of palladium(II) (0.02 M, 40 ml) was shaken on a mechanical shaker with 500 mg each of the poly(methyl methacrylate)-supported β -diketone. The palladium

intake capacity for 2, 5, 10 and 15% of cross-linking were 0.52, 0.49, 0.31 and 0.18 milliequivalents/g respectively.

UV (solid state) cm^{-1} : 14560 [${}^1A_{1g} \rightarrow {}^1A_{2g}$], 19350 [${}^1A_{1g} \rightarrow {}^1B_{1g}$], 23540 [${}^1A_{1g} \rightarrow {}^1E_g$].

IR (KBr, pellet) cm^{-1} : 3020 (C–H str., aromatic), 2950 (C–H str., aliphatic), 1710 (C=O str.), 1620 (C=O...H str.), 1530 (C–C str., aromatic), 1260 (C–C str., aliphatic).

${}^{13}\text{C}$ -NMR (solid state): 13.6, 16.3, 24.7, 28.9, 32.7, 34.1, 45.9, 51.8 (sp^3 carbon atoms), 95.3 (sp^2 carbon atom) 127.9, 128.6, 137.0, 137.8 (aromatic carbon atoms), 178.5 (carbonyl carbon).

ESR and magnetic moment: Complex is diamagnetic.

Thermogravimetric data: First stage decomposition – 6.2% (temperature range: 100–280°C). Second stage decomposition – 88.1% (temperature range: 290–395°C) Residue – 5.7%.

2.5 Oxidation of olefins – General procedure

Olefins (0.01 moles) were refluxed at 70°C in the presence of poly(methyl methacrylate)-supported palladium complexes (metal concentration, 0.1 milliequivalents), H_2O (20 ml) and methanol (20 ml) for 10 h. CuCl_2 (0.01 moles) was added to the reaction mixture as a co-oxidant. The reaction was followed by thin layer chromatography. After the completion of the reaction, the reaction mixture was concentrated, washed several times with chloroform and water, and the product extracted into the organic medium. The combined extract was then concentrated and the product was isolated, dried in vacuum and weighed. The products were characterized by FT-IR and ${}^1\text{H}$ -NMR and also by comparing their physical constants with that of the authentic samples. The influence of degree of cross-linking and the structural environment of the ligand on the catalytic efficiency was investigated by carrying out the reactions under similar conditions.

3. Results and discussion

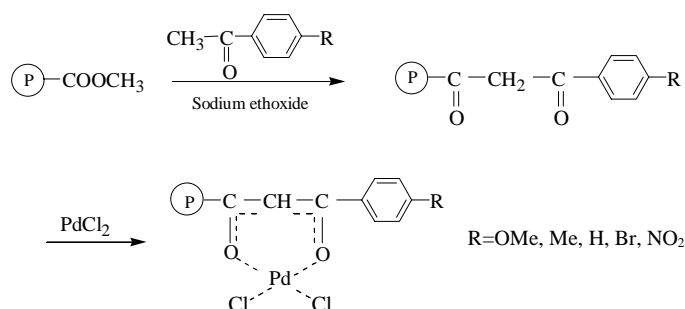
Poly(methyl methacrylate)-supported palladium complexes with different degrees of cross-linking, viz. 2, 5, 10 and 15 were prepared by varying the monomer ratios and employed for the oxidation of olefins (table 1). Maximum yields were obtained with 2% cross-linking. Highly cross-linked resins are unable to expand appreciably on interaction with the solvent. In the case of low degree of cross-linking, sufficient swelling occurs to allow the network to be penetrated by the low molecular weight species and gain accessibility to the reactive sites. The solvent-swollen polymer network provides sufficient channels for the diffusion of solvents and low molecular weight species. A high degree of swelling makes all the active species available for the substrate as in homogeneous reactions.

The effect of structural characteristics of the ligand β -diketone on the activity of poly(methyl methacrylate)-supported metal complexes was established by employing poly(methyl methacrylate)-supported β -diketone containing $-\text{C}_6\text{H}_5$, $-\text{C}_6\text{H}_4\text{Me}$, $-\text{C}_6\text{H}_4\text{OMe}$, $-\text{C}_6\text{H}_4\text{Br}$, $-\text{C}_6\text{H}_4\text{NO}_2$ groups (scheme 1). Oxidation reactions employing these catalysts led to the conclusion that as the electron-donating nature of the ligand increases, catalytic efficiency also increases (table 1). The electron-donating methoxy and methyl groups increase the electron charge density over the ligand function thereby increasing the electron availability at the co-ordination sites. The increase in basicity of the chelating ring thus enhances the π -bond formation between the metal and the olefin

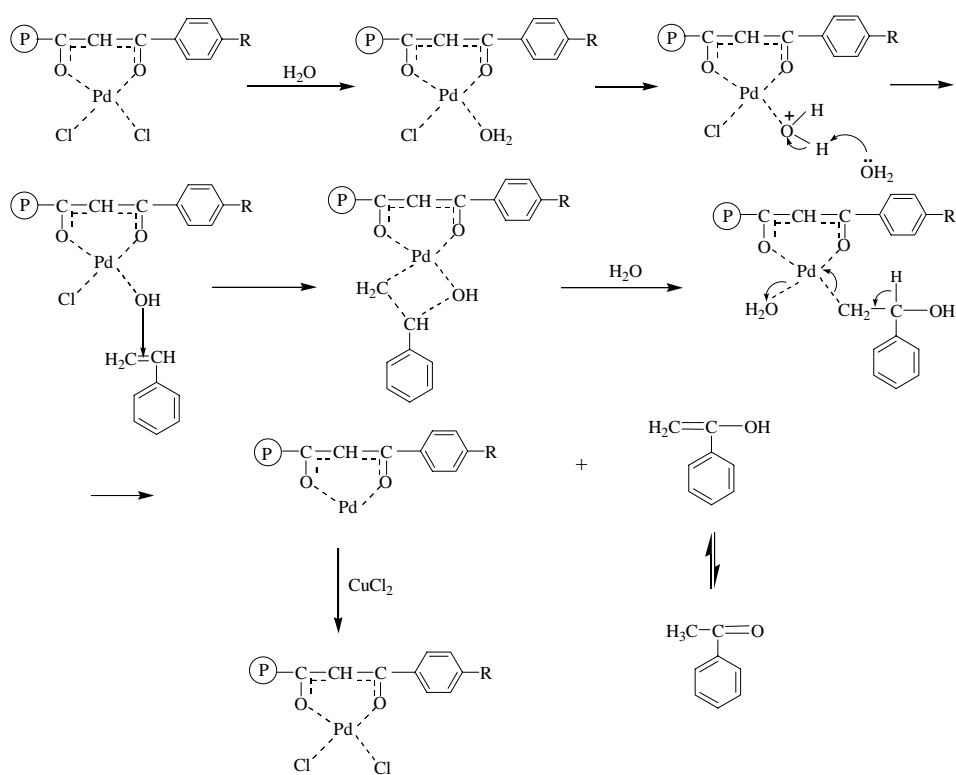
Table 1. Influence of poly(methyl methacrylate)-supported β -diketone-linked palladium catalysts in oxidation of olefins.

Substrate	Product	Degree of cross-linking (%)						Yield (%)					
		2	5	10	15	OMe	Me	H	Br	NO ₂	Recyclability (No. of cycles)		
Styrene	Acetophenone	88.3	85.1	80.9	76.4	89.8	88.3	85.4	80.8	80.3	88.1	87.9	87.6
2-Methyl styrene	2-Methyl acetophenone	90.4	87.5	82.3	78.6	92.0	90.4	87.6	83.0	82.5	90.2	89.9	89.6
Cyclopentene	Cyclopentanone	83.8	80.6	76.7	72.3	85.2	83.8	80.9	76.2	75.8	83.5	83.3	83.0
Cyclohexene	Cyclohexanone	86.7	83.2	79.5	75.2	88.2	86.7	83.5	79.1	78.9	86.5	86.2	85.9

[Substrate], 1×10^{-2} M; catalyst (R = CH₃), metal concentration, 0.1 meq; [CuCl₂], 1×10^{-2} M; H₂O, 20 ml; CH₃OH, 20 ml; temperature, 70°C; time, 10 h



Scheme 1.



Scheme 2.

by electron transfer from the $d\pi$ orbital of the metal to the π^* antibonding orbital of the olefin. On the other hand, bromo and nitro groups, which are electron-withdrawing in nature, decrease the electron density at the co-ordination sites, and hence the basicity, with resultant decrease in the catalytic efficiency. Polymer-supported β -diketone-linked palladium complexes can be removed by simple filtration and can be employed for further reactions without any loss of activity (table 1).

The oxidation of olefins is assumed to take place by the formation of hydroxy-palladation intermediate which occurs by the insertion of the olefin moiety into a Pd–OH bond. The reaction proceeds through a concerted four-centre adduct. The Pd(II) is reduced to Pd(0) during the reaction. The co-oxidant CuCl₂ reoxidises Pd(0) to Pd(II). CuCl₂ is reduced to Cu(I), which is reoxidised to Cu(II) by air so that it is the atmospheric oxygen that is being used up. A detailed mechanism is depicted in scheme 2.

References

1. Ford W T 1986 *Polymeric reagents and catalysts*. ACS Symposium Series, vol. 308 (Washington DC: ACS)
2. Hodge P and Sherrington D C 1988 *Synthesis and separation using functionalised polymers* (New York: Wiley)
3. Sherrington D C 1998 *Chem. Commun.* 2275
4. Akelah A and Sherrington D C 1981 *Chem. Rev.* **81** 577
5. Shuttleworth S J, Allin S M, Wilson R D and Nasturica D 2000 *Synthesis* **8** 1035
6. Allum K G, Hancock R D, Howell I V, Pitkethly R C and Robinson P J 1976 *J. Catal.* **43** 322
7. Ford W T 1997 *React. Funct. Polym.* **33** 147
8. Tonks L and Williams J M J 1997 *Contemp. Org. Synth.* **4** 353
9. Bayon J C, Claver C and Masdeu-Bulto C 1999 *Co-ord. Chem. Rev.* **193** 73
10. Hamaida Z F, Barbier Jr. J, Labruquere S and Duprez D 2001 *Appl. Catal.* **B29** 195
11. Henry P M 1966 *J. Am. Chem. Soc.* **88** 1595
12. Moiseev I I, Levanda O G and Vargaftik M N 1974 *J. Am. Chem. Soc.* **96** 1003
13. Gragor N and Henry P M 1981 *J. Am. Chem. Soc.* **103** 681
14. Henry P M 1965 *J. Am. Chem. Soc.* **87** 990
15. Stille J K and Divakarumi R 1979 *J. Organomet. Chem.* **169** 239
16. Saito S, Murase M and Yamamoto H 1999 *Synlett* 57
17. Kobayashi S and Nagayama S 1998 *J. Am. Chem. Soc.* **120** 2985
18. Zhang T Y and Allen M J 1999 *Tetrahedron Lett.* **40** 5813
19. Nagayama S, Massahiro E and Kobayashi S 1998 *J. Org. Chem.* **63** 6094