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Polyaniline Supported Cobalt(II) Catalyst : Oxidation of Alkenes with Molecular Oxygen

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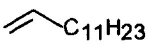
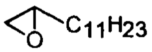
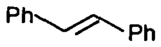
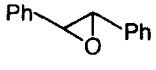
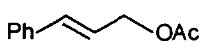
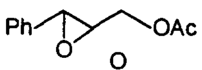
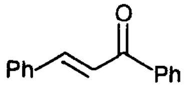
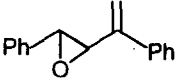
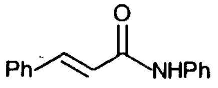
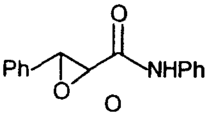
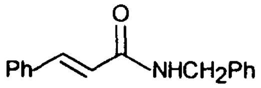
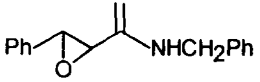
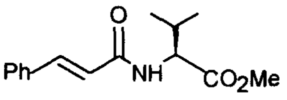
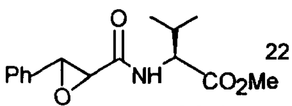
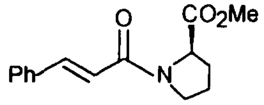
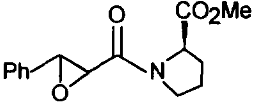
Abstract: Polyaniline supported Co(II) acetate catalyses the oxidation of different alkenes in the presence of 2-methylpropanal under the oxygen atmosphere at ambient temperature. This catalyst can be reused for epoxidations without any decline in its catalytic efficiency. © 1997, Published by Elsevier Science Ltd. All rights reserved.

Metal catalyzed oxidation of organic substrates with oxygen is currently[1] an area of intensive research aimed at developing an efficient catalyst that can replace the conventional mode of oxidation which involves stoichiometric amount of Cr or Mn salts. The requirements for salt free oxidative procedures have now become more or less mandatory mainly due to the stipulation laid down by the environmental agencies. In view of these restrictions there is a constant search for an efficient system comprising of metal catalyst which can promote oxidations of a variety of organic substrates without producing many harmful byproducts. Heterogeneous catalysis has been sought[2] as one of the ways of addressing these problems mainly due to the attractiveness involved in the recycleability of the catalyst. Recent advances in the polymer supported metal catalyst has opened up new avenues for the use of heterogeneous catalysis in organic transformations. We now demonstrate for the first time that polyaniline supported cobalt(II) acetate functions as an efficient catalyst during the oxidation of various alkenes in the presence of 2-methylpropanal and oxygen. Polyaniline supported cobalt(II) acetate catalyst can be made merely by mixing equal amounts (by weight) of polyleucoemeraldine base[3] and cobalt(II) acetate hexahydrate in a 1:1 mixture of acetic acid and acetonitrile at ambient temperature. This is the first synthesis[4] of such a catalyst which can be recycled and is stable in aqueous medium.Polyaniline has the advantage over the other polymer like polystyrene as the nitrogen atom in the former anchors the cobalt through coordination which leads to a stable polyaniline cobalt complex.

The reaction of various alkenes in the presence of polyaniline supported cobalt(II) catalyst is presented[5] in table 1. Thus tridecene & trans-stilbene can be converted to the corresponding epoxides in high yields using a catalytic amount of polyaniline supported cobalt(II) catalyst, 2-methylpropanal under oxygen atmosphere (table 1,entry 1 & 2). Similarly cinnamyl acetate could be transformed to the corresponding epoxide in nearly quantitative yields (table 1, entry 3). The epoxidation of α,β-unsaturated carbonyl compounds is normally carried out by an alkaline hydrogen peroxide procedure and there are a few catalytic

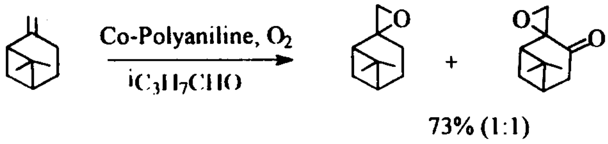
Table1. Polyaniline supported Co(II)catalysed oxidation of alkenes with dioxygen

Entry	Substrates	Product(s)	Time(h)	Yield(%)
1			12	50
2			4	80 72^b
3			8	65
4			13	72
5			18	53
6			17	63 58^b 60^c
7			22	55
8			35	38^d

[a] Isolated Yield. [b]Yield obtained using recovered catalyst. [c]Yield obtained using catalyst recovered from aqueous medium. [d]Determined by HPLC.

methods[6] for performing these epoxidations. Interestingly, polyaniline supported cobalt catalyst can be used to effect the epoxidation of chalcone and α,β-unsaturated amides in a very satisfactory manner. According to this protocol chalcone and cinnamoyl amide could be converted to the corresponding epoxides in good yields by employing polyaniline supported cobalt catalysed reaction (Table 1, entries 4 - 6). *It is interesting to note that this catalyst can be reused by merely filtering and drying as evidenced in the epoxidation of trans-stilbene and benzyl cinnamoyl amide which resulted in the same efficiency when compared to the fresh catalyst (Table1 ,entries 2 & 6).* The epoxidation of benzyl cinnamoyl amide could also be performed by catalyst recovered after treatment with water for 24 h (Table 1, entry 6). The epoxidation of cinnamoyl amide of L-methyl serine and L-methyl proline can also be performed under these conditions to give good to excellent yields of the corresponding epoxy amides (Table 1, entries 7 and 8). The oxidation of cyclic alkenes by this catalytic system results in allylic oxidation. Accordingly, β-pinene underwent oxidation to afford a

1:1 mixture of the corresponding epoxide and epoxy ketone (Eq. 1). The epoxide obtained from β-pinene was



(Eq. 1)

obtained as a mixture of diastereomers and no attempts were made to separate them. In order to ascertain the formation of polyaniline supported cobalt catalyst, we have conducted preliminary UV-Visible studies on the solid obtained by mixing polyaniline and cobalt acetate. Thus, the initial absorption spectrum of polyaniline in N-methyl-2-pyrrolidone changes from 626 nm and 326 nm to 553 nm and 329 nm respectively on treatment with cobalt acetate (Fig. 1a and 1b). The λ_{max} at 553nm is indicative of a cobalt complex with planar geometry[8] as observed earlier by us for cobalt(II) porphyrin complexes. Thus UV-Visible spectrum clearly supports the formation of a polyaniline cobalt (II) acetate complex.

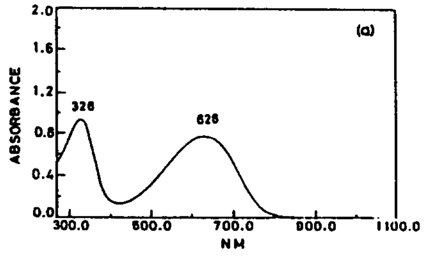


Fig. 1a. UV-Visible spectra of polyaniline in N-methyl-2-pyrrolidone.

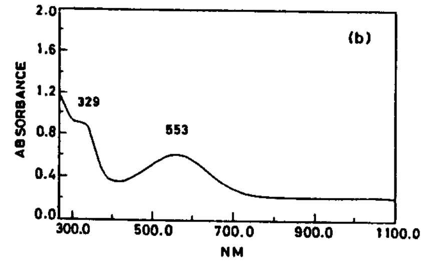


Fig. 1b. UV-Visible spectra of polyaniline supported cobalt(II)acetate in N-methyl-2-pyrrolidone.

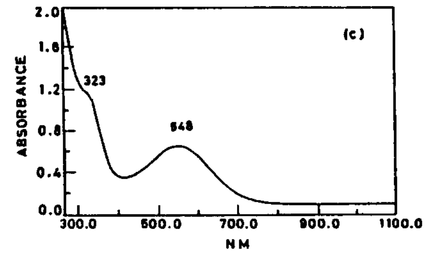


Fig. 1c. UV-Visible spectra of polyaniline supported Co(II)-acetate in N-methyl-2-pyrrolidone after bubbling oxygen for 5 min.

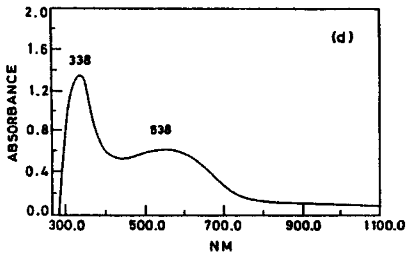


Fig. 1d. UV-Visible spectra of polyaniline supported Co(II)-acetate in N-methyl-2-pyrrolidone after stirring under oxygen for 3h.

The behaviour of this complex in the presence of oxygen is quite interesting as bubbling the latter in N-methyl-2-pyrrolidone solution of polyaniline supported cobalt acetate, a shift in λ_{max} to 548 nm and 323 nm is observed (Fig. 1c). On stirring the solution of this catalyst in N-methyl-2-pyrrolidone in oxygen balloon a further shift in λ_{max} to 538 nm and 338 nm is observed after 3 h (Fig. 1d). The shift in the λ_{max} value for this catalyst on exposure to oxygen indicates the formation of a metal oxygen species like Co(III)-O-O. The presence of the latter species is also confirmed by the solid state EPR (Fig. 2) of the catalyst in the presence of oxygen which exhibits a sharp signal at 3331G (g_{iso}=2.0004) indicative of a cobalt superoxo species. The studies by others and ourselvs[7,9] have already established the presence of a sharp signal in EPR due to the formation of Co(III)-O-O species.

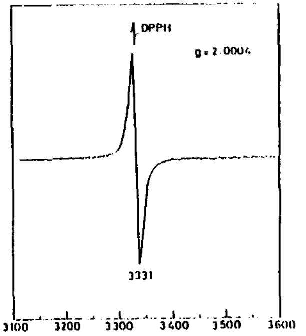


Fig.2 Solid state EPR spectra of polyaniline supported cobalt(II)acetate in presence of oxygen.

In conclusion, polyaniline supported cobalt catalyst promises to be an excellent catalyst in promoting oxidation of different alkenes in high yields under mild conditions. The recycleability of this catalyst makes it a very attractive system for exploration in industrial oxidation processes.

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3. a) Polyaniline in the form of polyleucoemeraldine was prepared according to the reference 3b and used without purification or molecular weight determination. To the best of our knowledge no other analogue of polyaniline supported cobalt complex is known in the literature. b) Hasik, M.; Turek, W.; Stochmal, E.; Lapkowski, M.; Pron, A *J. Catal.* **1994**, 147, 544.

4. Preparation of polyaniline supported cobalt(II) catalyst: A mixture of polyaniline (200 mg) and cobalt acetate (200 mg, 1:1=w/w) was stirred in acetonitrile and acetic acid (1:1=V/V) for 72 h at room temperature. The reaction mixture was filtered and the solid catalyst washed with acetonitrile until the filtrate became colourless. The catalyst was dried at 110 - 120° C.

5. General procedure : A mixture of alkene (5 mmol), 2-methylpropanal (15 mmol) and catalyst (5 mol%) were dissolved in acetonitrile (30 mL) in an oxygen atmosphere at room temperature. After completion of the reaction (monitored by TLC), the catalyst was filtered and the solvent was evaporated and the residue purifed by column chromatography.

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