SYNTHESIS AND APPLICATIONS OF FUNCTIONALIZED POLYMERS

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CERTIFICATE

This is to certify that the thesis entitled, "**SYNTHESIS AND APPLICATIONS OF FUNCTIONALIZED POLYMERS**" being submitted by **Ms. Rajinder Kaur Bhatia** to the **Indian Institute of Technology, Delhi**, for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Ms. Rajinder Kaur Bhatia has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results, contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

Functionalized polymers are macromolecules in which functional groups are incorporated chemically in the polymer and they have a wide variety of chemical, biological and technical applications. They are particularly useful as catalysts in organic chemistry as these have the added advantage of easy separation and recycling in comparison to the homogeneous catalysts. Research work in the area of oxidation of organic compounds catalyzed by polymer supported metal complexes is rather limited though it shows a lot of promise.

The polymer anchored vanadium and molybdenum complexes were prepared as they are known to act as efficient oxygen-transfer catalysts for reactions involving organic hydroperoxides as oxidants in the oxidation of sulfides, sulfoxides, amines, alkenes, allylic alcohols etc. in homogeneous medium. The polymer anchored vanadium complexes of three different ligands salicylaldoxime (a), 3-2(thenoyl-1,1,1-trifluoroacetylacetone) (b) and (o-phenylene-bis-salicyl-aldimine) (c) and molybdenum complexes of salicylaldoxime (d) and (o-phenylene-bis-salicylaldimine) (e) were synthesized. These anchored complexes were characterized by infrared spectra, thermogravimetry and chemical analysis. The effectiveness of the anchored complexes for the oxidation of dimethylsulfoxide with tert.-butyl hydroperoxide (TBH) was investigated. The vanadium and molybdenum complexes of different ligands were used to study the effect of metal and ligand on catalytic activity. In the oxidation of dimethylsulfoxide with polymer anchored vanadium complexes, the order of catalytic activity was a $\approx$ b $>$ c. For comparison

the corresponding homogeneous oxidation reactions were also carried out under similar conditions and in this case the order of catalytic activity was found to be b > c > a. The polymeric beads isolated at the end of oxidation reaction were used for successive runs and the catalytic activity was similar during the first three runs. The oxidation of diphenylsulfoxide was also carried out to study the effect of size of substrate. In the oxidation of dimethylsulfoxide with polymer anchored moybdenum complexes, the order of catalytic activity was e > d. The same order of catalytic activity was observed with the non anchored molybdenum catalysts. Lower yields of dimethylsulfone and diphenylsulfone were obtained with molybdenum complexes as compared to the vanadium complexes. The results are discussed on the basis of structural features of the ligands and the reactants.

In heterogeneous catalysis, the choice of support is also an important factor and so to study the effect of support the same vanadium complexes were anchored to alumina and used for the oxidation of sulfoxides. In this case, the order of catalytic activity similar to the organic polymer anchored complexes was observed. An interesting difference between the alumina and organic polymer anchored vanadyl complex catalysts was that as compared with organic polymer supported catalysts, the size of substrate had no effect on the yield of the product with the alumina supported catalysts.

The organic polymer and alumina anchored vanadyl and molybdenyl complexes were used for the oxidation of α-ketol (benzoin) with (TBH) as oxidant. With some of the catalysts only benzil was obtained whereas with others three products benzil, methyl benzoate and benzoic acid were formed. The anchored molybdenum complexes were observed to be better catalysts than anchored vanadium complexes for the oxidation of benzoin. With the organic polymer anchored MoO_2(salphen) catalyst, 89% conversion of benzoin to benzil was observed.

The ligand coordinated to metal ion was found to effect the yields of the oxidation products. In polymer supported metal complex oxidation catalysts, a good catalyst for the oxidation with TBH as oxidant should be a good lewis acid and should have the proper geometry to facilitate the formation of complex with the oxidant. However, the nucleophilicity and size of substrate also affected the reaction yield in some cases.

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