

EXECUTIVE SUMMARY

Rationale

Industrial effluents are routinely polluted with a range of organic materials, many of which are toxic and difficult to remove. Various approaches have been employed to remediate these industrial effluents. Included amongst the methods used are wet air oxidation, electrochemical oxidation, supercritical water oxidation and straight forward incineration. All of these methods are energy intensive and are usually carried out under extreme conditions. A way to overcome the draw-backs of the aforementioned methods is to employ catalytic wet air oxidation. Several catalyst systems have been developed for catalytic wet air oxidation. Unfortunately the known methods still suffer from relatively low activity. We therefore set out to develop alternative catalyst systems with the hope of improving the activity. These systems are based on immobilized metal complexes. Immobilization of the catalysts would also allow us a way of catalyst separation from the reaction mixture.

Aims

The initial aims for the project were:

- The immobilization of salicylaldehyde complexes on siliceous materials such as MCM-41 (mesoporous silica) and Davisil 710 (amorphous silica).
- The immobilization of salicylaldehyde complexes on polypropyleneimine dendrimers.
- The evaluation of the immobilized catalysts in the wet air oxidation of phenol. This is a model reaction for wastewater remediation.
- Preliminary evaluation of new catalysts in remediation of industrial wastewaters via catalytic wet air oxidation.

Approach

The approach followed to achieve the above aims was to take known homogeneous catalysts and to immobilize these on suitable supports. We thus set out to investigate ways to develop immobilized salicylaldehyde metal complexes. The reason for choosing salicylaldehyde metal complexes was because these complexes are known to be active catalysts in a range of chemical reactions. The motivation for immobilizing the catalysts was to have a method to separate the catalysts from the reaction mixture after completion of the reaction. This is not possible when using homogeneous catalysts which are totally soluble in the reaction medium. Two immobilization approaches were employed viz. immobilization on siliceous supports and immobilization on dendrimers (highly branched macromolecules).

Methodology

The anchoring of the metal complexes to the silica support was done by initially synthesizing siloxane functionalized salicylaldehyde complexes followed by the reaction of the siloxane tail of the complex with the surface silanol groups of the silica. In this way the metal complexes are chemically bound to the support and not physically absorbed as is the case for other known heterogeneous catalysts. The second immobilization approach involves the use of dendrimer supports. Dendrimers are macromolecules with three-dimensional architecture. It is increasingly being applied as catalyst carriers. We developed new polypropylene imine dendrimers which we functionalized with salicylaldehyde units on the periphery of the dendrimer to produce multinuclear catalysts. This was then employed as a synthetic scaffold to multinuclear catalysts.

The evaluation of the immobilized catalysts in the oxidation of phenol was carried out in aqueous solutions over a range of pH values. The pH of the reaction medium was varied by using appropriate buffer solutions. This is a model reaction for the oxidative remediation of wastewaters. Oxidation products were analyzed by HPLC.

The efficiency of the immobilized catalysts was compared with that of model homogeneous catalysts. These are discrete mononuclear complexes which are normally soluble in the reaction medium. Once we identified the best catalyst systems, we then employed these in the remediation of wastewaters from four local industries. The catalysts were evaluated in terms of their ability to reduce COD values of the wastewaters.

Results

We have successfully developed a methodology to anchor salicylaldimine complexes of copper, cobalt and nickel onto the surface of both MCM-41 and Davisil 710 supports. The immobilized catalysts were characterized by IR, SEM, XRD and BET surface analysis. From these techniques it can be seen that the metal centres are securely anchored onto the surface.

We also have developed a synthetic methodology to prepare a range of new salicylaldimine modified dendrimers to which we successfully complexed transition metals. Both the dendrimeric ligands and their metal complexes were fully characterized by a range of analytical techniques.

The immobilized catalysts were tested in the wet air oxidation of phenol using H_2O_2 as co-oxidant. All the catalysts tested were found to be active in the oxidation of phenol. The silica immobilized catalysts, especially the MCM-41 systems performed slightly better than the dendrimer based catalysts. In all cases the catalysts based on copper were found to be the most effective giving the highest phenol conversion. The catalysts were also evaluated in terms of their ability to produce both primary and secondary oxidation products. The major primary oxidation products detected were the dihydroxybenzenes, catechol and hydroquinone with catechol being produced at higher levels in all cases. The efficiency of the catalysts is dependent on the pH of the reaction medium with optimum phenol conversion being achieved at moderately acidic values. The MCM-41 catalysts show a different behaviour to that of the other catalysts in terms of the distribution of primary oxidation products. The MCM-41 systems show higher level of hydroquinone production.

In all reactions carried out we also observed the formation of secondary oxidation products. These are largely low molecular weight carboxylic acids. Once again the copper based systems are the most effective on converting phenol to secondary oxidation products. All catalysts produce higher levels of secondary oxidation products at pH 6.

Finally the copper catalysts were evaluated in the catalytic wet air oxidation of wastewaters from four local industries in the Western Cape. Once again it was found that the silica immobilized catalysts performed better than the dendrimer based catalysts with the MCM-41 system being slightly better than the Davisil 710 systems.

Recommendations

It is recommended that the research be extended to optimize the wet air oxidation remediation of wastewaters. Aspects that need further investigation include:

- The effect of performing the oxidation processes at slightly elevated pressures.

- The use of binary catalyst systems, i.e. catalyst systems consisting of more than one type of metal.
- The effect of using modified MCM-41 supports. This would include doping the MCM-41 supports with titania. This could potential assist with the oxidation of the organic pollutants.
- Evaluation of suitable reactor systems for the catalytic processes.