

# CONTINUOUS SELECTIVE OXIDATION IN SUPERCRITICAL WATER

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## INTRODUCTION

Improved catalysis and the replacement of conventional organic solvents are key steps towards realistic solutions to the many environmental issues, which have to be addressed by the chemical industry worldwide.

Water is a good candidate because it is abundant, cheap, non-toxic and neither combustible nor explosive. Under supercritical conditions ( $T_c = 374^\circ\text{C}$ ,  $P_c = 221$  bar),  $\text{H}_2\text{O}$  is organic-like and miscible with gases thereby overcoming mass transfer limitations which could occur between phase boundaries. Its physical and chemical properties [1] are unique and easily tunable with temperature and pressure. Also, because of the increase in its ionic product,  $\text{scH}_2\text{O}$  can act as a basic or acid catalyst. Its catalytic effect has been exploited for many reactions [2,3].

$\text{scH}_2\text{O}$  is well known as a solvent for the destruction of organic waste by total oxidation but  $\text{scH}_2\text{O}$  is also an excellent reaction medium offering many opportunities for selective organic synthesis.

Homogeneously catalysed selective oxidations of diverse alkylaromatics (xylenes and polymethylbenzenes) have been investigated by our group using a continuous flow reactor [4-6]. This process offers a potentially cleaner route to the production of bulk chemicals such as terephthalic acid compared to the traditional method which generates lots of wastes and requires big amounts of acetic acid as organic solvent.

## I - MATERIALS AND METHODS

We have demonstrated that different methylaromatic compounds [1,4-dimethylbenzene (*p*-xylene), 1,3-dimethylbenzene (*m*-xylene), 1,2-dimethylbenzene (*o*-xylene), 1,3,5-trimethylbenzene (mesitylene) and 1,2,4-trimethylbenzene (pseudocumene)] can be aerobically oxidized in  $\text{scH}_2\text{O}$  using manganese(II) bromide as homogeneous catalyst and  $\text{H}_2\text{O}_2$  as source of  $\text{O}_2$  to give corresponding carboxylic acids in the continuous mode over a sustained period of time in good yield [4,5]. No partially oxidized intermediates (i.e., toluic acid and benzaldehydes) are detected for the dimethylbenzenes and mesitylene reactions. By fine-tuning pressure and temperature,  $\text{scH}_2\text{O}$  becomes a solvent with physical properties suitable for single-phase oxidation since both organic substrate and oxygen are soluble in  $\text{scH}_2\text{O}$ .

Aromatic acids produced by the loss of one methyl group occurs in all of these reactions, i.e., 3-6% benzoic acid formed during the oxidation of the dimethylbenzenes. Part of this loss is thought to be due to thermal decarboxylation. The thermal decarboxylation can be controlled and monitored *via* Raman spectroscopy.

Despite the differences in reactivity of the xylene isomers in conventional oxidation, a mixture of xylenes ( $\text{C}_8$  refinery mixture) can also be simultaneously oxidised in  $\text{scH}_2\text{O}$  to a

mixture of the corresponding carboxylic acids in high combined yield [6]. The single-phase environment in scH<sub>2</sub>O together with the effect of higher temperatures increases the reaction rate for each of these oxidation reactions and thus reduces the reactivity differences between the components of the xylenes mixture. Such a process should lead to a considerable reduction in the overall energy input for the oxidation of xylenes. The process in scH<sub>2</sub>O described here could simplify the downstream purification processes to a simple crystallization process. This is commercially important, because the purification process can be as expensive as the reaction producing the product. Furthermore, the oxidation of mixed xylenes could avoid the need not only for downstream purification, but also for the upstream separation of the xylene isomers.

There is a strong structural similarity of metal/bromide coordination compounds in the active oxidation solvents (acetic acid and scH<sub>2</sub>O) which does not exist in the much less active H<sub>2</sub>O at lower temperatures [5,7]. This may account for the successful catalysis of the reactions presented.

## CONCLUSION

scH<sub>2</sub>O is an effective solvent and provides for homogeneous catalytic oxidations of alkylaromatics compounds: 1) chemical advantages (high selectivity by fine tuning of solvent properties); 2) environmental advantage through avoiding the use of organic solvents (acetic acid) and reducing subsequent waste (unwanted oxidation and production of CO<sub>2</sub>); 3) economic advantages resulting from more selective and faster reactions; also operating at higher temperature allows for more efficient energy recovery from the exothermic reactions; 4) process intensification (reduction of the size of the reactor and the residence time).

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