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A wet air oxidation process using a catalytic membrane contactor

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Abstract

A new process for oxidation of toxic compounds in liquids has been demonstrated. The concept is based on the same principles as catalytic wet air oxidation (CWAO), but the metal catalyst is fixed to a ceramic porous membrane in a catalytic membrane reactor of the contactor type (CMR-C). Air is flowing along the surface of the contactor, and the waste liquid is supplied from the other side of the contactor through the porous contactor wall. In this way, the gas and liquid phases are driven to contact in the porous network of the catalytic contactor separating them. Fifty percent of conversion of formic acid model solution (5 g/l) was obtained in initial reactor experiments at 150 °C and 10 bar pressure, but the observed oxidation rate was low: about 0.13 mmol/s per g_{Pt}. TEM and EDS investigations of the contactor showed that 5–10 nm Pt particles were evenly distributed close to the surface of the mesoporous TiO_2 top layer. After the experiments, a 10–50 nm thick aluminium-rich amorphous deposit was observed in the porous structure. The low conversion rate has been attributed to this deposit causing deactivation by encapsulation of the catalyst and plugging of the mesoporous layer of the contactor. The deposits are believed to be caused by chemical instability of α-Al_2O_3 in acidic aqueous environment at elevated temperature. α-Al_2O_3 is present in the coarse-grained membrane support.

Keywords: Catalytic membrane reactor; CMR-C; Wet air oxidation; WAO; Waste treatment

1. Introduction

Elimination of organic pollutants from industrial waste waters may be achieved by several different processes. Dilute waste waters containing non-toxic substances can be treated using biological techniques, whereas incineration is the most appropriate technique to treat concentrated effluents. However, there are few available destruction techniques for the treatment of low to medium chemical oxygen demand (COD) effluents containing non-biodegradable or toxic compounds. Wet air oxidation (WAO) and catalytic wet air oxida-

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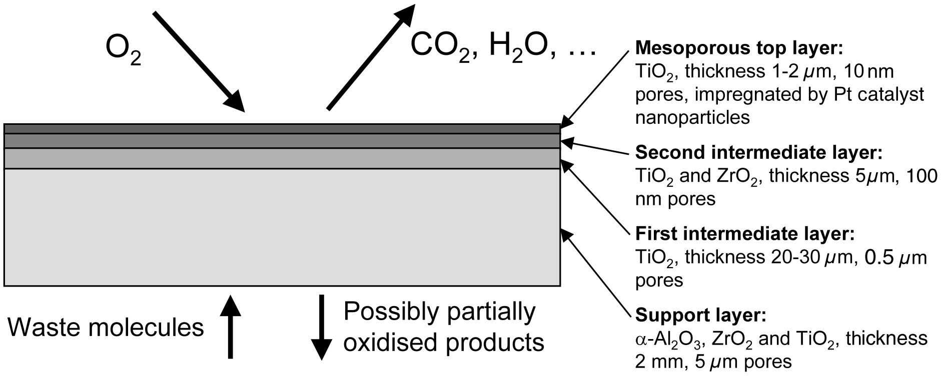

Fig. 1. Schematic illustration of the working principle of the CMR-C for WAO. The illustration shows a cross section of the four-layer catalytic contactor, including the mesoporous top layer that has been impregnated with catalyst particles.

tion (CWAO) [1–3], which involve the oxidation of organic compounds in water in a stirred tank reactor, are sometimes used for treating such effluents. But these techniques require very high temperatures and pressures (up to 300 °C and 200 bars) and are associated with severe corrosion problems, so their practical applications have been limited.

In the present work, we have studied a new process based on a Catalytic Membrane Reactor of the Contactor type (CMR-C) for oxidation of toxic compounds in liquids. Similar processes have been used previously for reduction reactions [4,5] but has not been applied to oxidation until now. The new concept is based on the same principles as CWAO, but the catalyst is fixed to an inorganic porous membrane contactor. Air flows along one side of the CMR-C, and the waste liquid is supplied to the other side of the membrane through its porous wall. In this way, the gas and liquid phases are driven to contact in the porous network of the catalytic membrane separating them. Experiments carried out at low temperature (30–80 °C) and pressure (1 bar) have shown higher initial conversion rates for the CMR-C (0.9 mmol/s per g_{Pt}) than for a similar conventional WAO reactor (0.2 mmol/s per g_{Pt}) [6]. The high initial rate was, however, followed by irreversible deactivation of the catalyst.

In this work, the process has been studied at conditions that provide more energy to the system; i.e. at elevated temperature (150 °C) and pressure

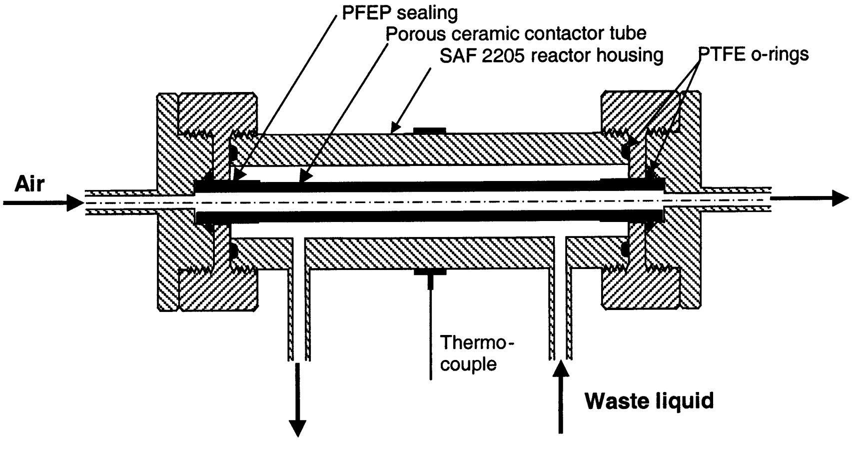

Fig. 2. Schematic cross section of the catalytic oxidation membrane reactor.

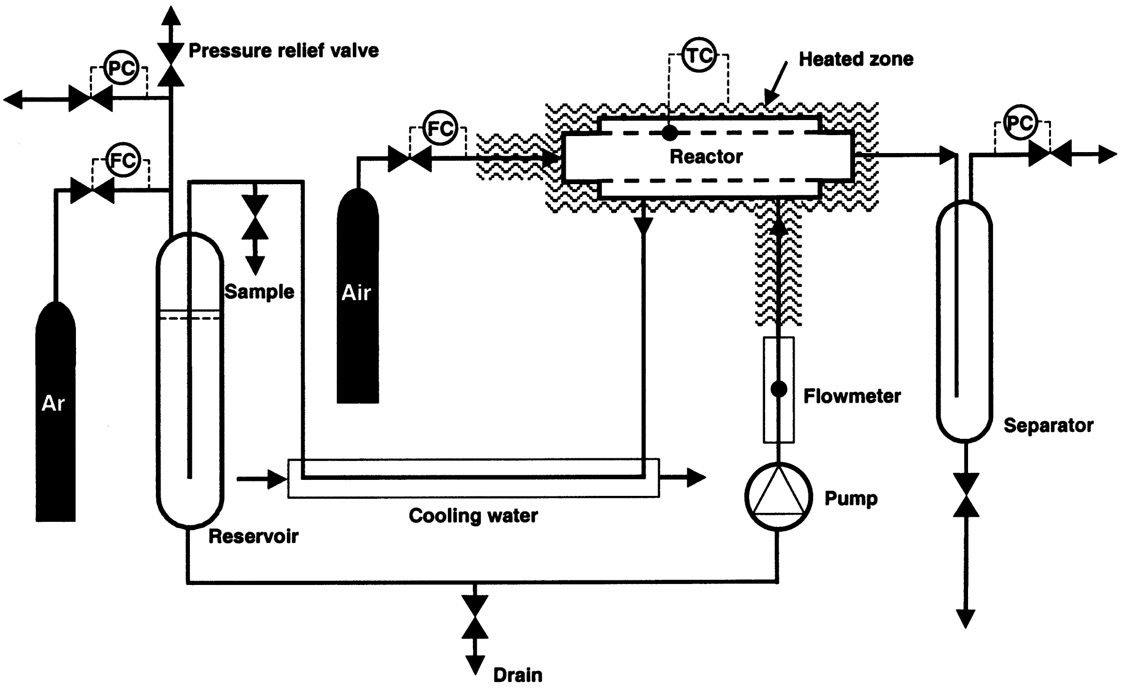

Fig. 3. Laboratory set-up for testing of the new catalytic wet oxidation process at 150 °C and 10 bar pressure.

(10 bar). The reactor concept is shown schematically in Fig. 1.

2. Experimental

The ceramic membrane tubes used in this work were delivered by TAMI Industries SA (France) and were composed of four layers with subsequently finer pores; the layer with the finest pores being on the inner surface of the tubes. The membranes had an internal diameter of 6 mm, an external diameter of 10 mm and a total length of 100 mm. The endings were coated (1.5 cm on each side) with poly(fluoroethlylenepropylene) (PFEP) in order to seal the ends and soften the surface on which the o-ring seals were applied. The length of the membrane permeable active zone was thus 70 mm.

The catalytic layer was prepared by anionic deposition [7] from a precursor solution of hexachloroplatinic acid (H_2PtCl_6 at 0.1 g Pt/l). The membranes were first saturated with deionised water by immersion during 2 h with magnetic stirring, then immersed for 4 h in the Pt precursor solution, and finally dried in ambient air. Finally, they were reduced under hydrogen flow at 200 °C for 12 h. Polished sections of some of the tubes were characterised by transmission electron microscopy (TEM) and electron dispersive spectrometry (EDS) before and after the experiments, using a Phillips CM30T TEM equipped with an EDAX DX4 EDS.

The CMR-C tube to be tested was placed in a reactor housing made of SAF2205 alloy as shown in cross section in Fig. 2, and the reactor was mounted in a laboratory scale reactor system as shown schematically in Fig. 3.

Formic acid (5 g/l) was used as model solution for the experiments. The liquid was pumped at 50 ml/min from a reservoir of either 500 or 1000 ml volume through a heater to obtain 150 °C and then flushed along the outer wall of the membrane tube in the reactor housing. After leaving the reactor, the liquid was passed through a cooler at 10 °C and finally returned to the reservoir. Dry air was preheated to 150 °C and flushed through the membrane tube at 100 ml/min. The pressure in the set-up was maintained at 10 bar by pressurisation of the reservoir with Ar. The transmembrane pressure difference was kept below ±0.1 bar, but in some experiments overpressures up to 0.6 bar occurred occasionally on either side.

Test samples of the liquid (10 ml each) were taken from the exit of the reactor after the cooler and analysed for COD by the Norwegian Institute for Water Research, Oslo (Norway).

3. Results and discussion

TEM micrographs of a catalytic membrane cross section are shown in Fig. 4. Finely dispersed Pt particles, 5–10 nm in diameter, evenly distributed in the outer half of the TiO_2 membrane top layer, are observed. Both the size and location of the catalyst nanoparticles are promising considering that a high catalyst surface area close to the contactor surface is beneficial for the process to operate efficiently.

Fig. 5 shows the conversion of formic acid as a function of time when the reactor was operated in the recycling mode at 150 °C and 10 bar. In one experiment 50% conversion was achieved after 2 days of operation of the reactor unit. The conversion rate was, however, low; about 0.13 mmol/s per g_{Pt}, corresponding to 0.3 mmol/s per m^2 with respect to contactor area. Reference experiments using the same process conditions but a blank contactor without catalyst resulted in zero conversion even after several days of operation.

To investigate the cause of the low conversion rate, the catalytic membrane was examined by TEM and EDS before and after the experiments. A TEM-micrograph of the interface between the top mesoporous layer and the second intermediate layer after an experiment is shown in Fig. 6. A 10–50 nm thick amorphous film is clearly seen in the

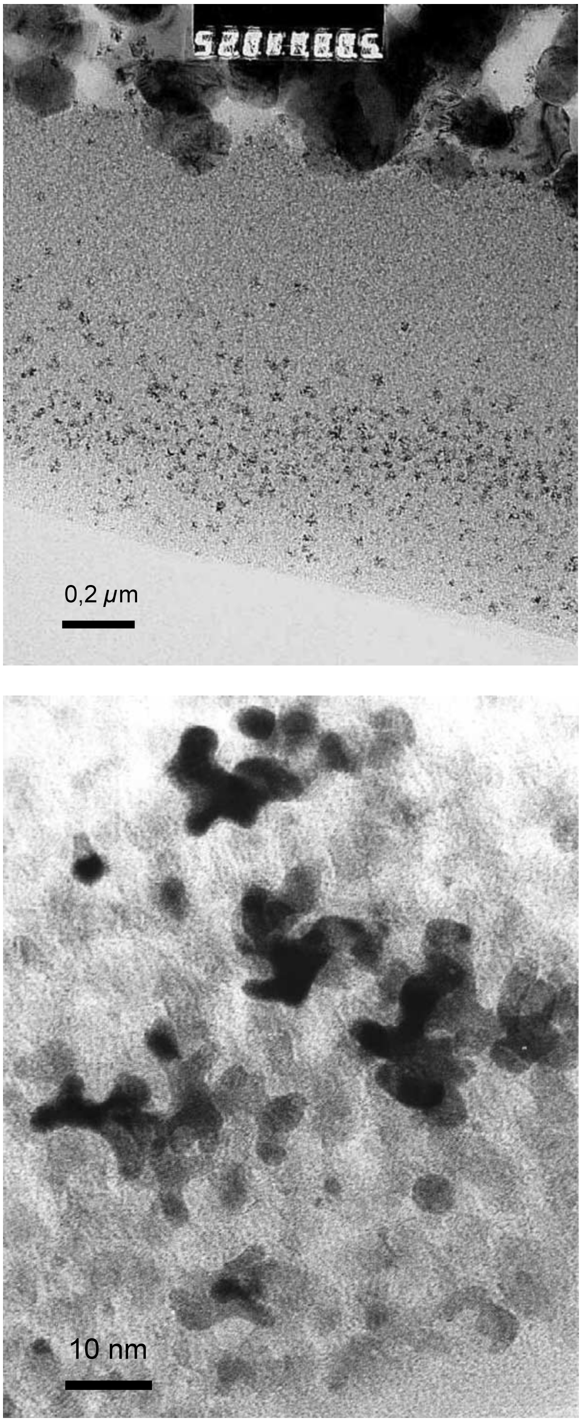

Fig. 4

Fig. 4. TEM micrographs showing cross sections of the mesoporous TiO_2 top layer of the contactor tubes, impregnated by the Pt catalyst. The dark spots are Pt particles 5–10 nm in size, finely dispersed in the outer half the membrane top layer.

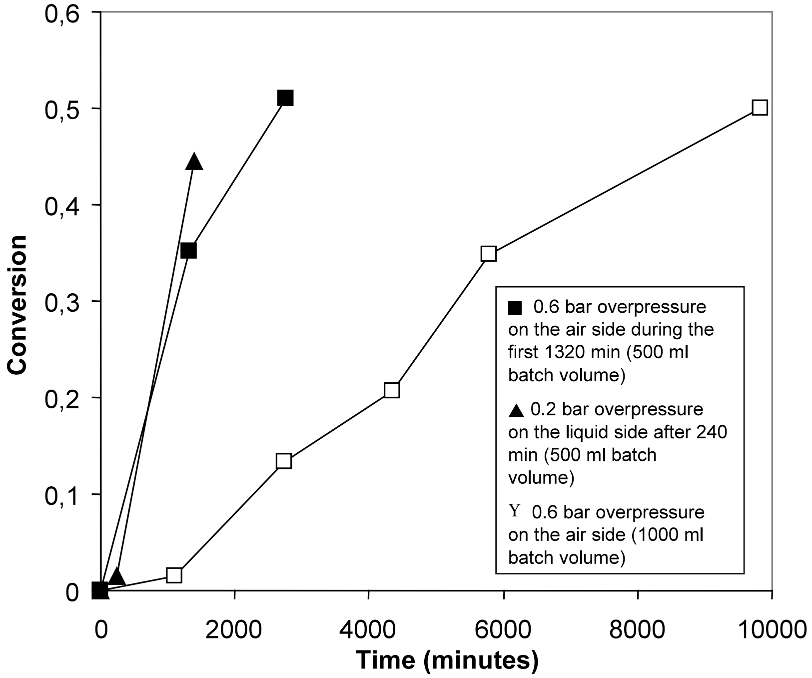

Fig. 5. Oxidation of formic acid model solution (5 g/l) vs. time for three test runs at 150 °C and 10 bar pressure.

porous structure. Such films were not observed when contactors were examined by TEM before the experiments. Fig. 7 shows an EDS spectrum obtained from a narrow spot on the film compared with a spectrum obtained from a much larger area within the mesoporous TiO_2 top layer. A much higher content of aluminium is observed in the amorphous layer. The only major aluminium source in the system is α-Al_2O_3 present in the Al_2O_3–ZrO_2–TiO_2 support. It is known [8] that α-Al_2O_3 has reduced stability in aqueous acidic environment. Small but significant amounts of aluminium species can have been dissolved from the support during the experiments and deposited as an amorphous oxide/hydroxide film in the upper TiO_2 layers of the membrane, causing encapsulation of the platinum catalyst and plugging of the mesoporous top layer. Even very small amounts of deposits may lead to severe and irreversible deactivation. Further experiments are in progress with the Al_2O_3-containing support material replaced by materials known to be stable in the acidic aqueous environment.

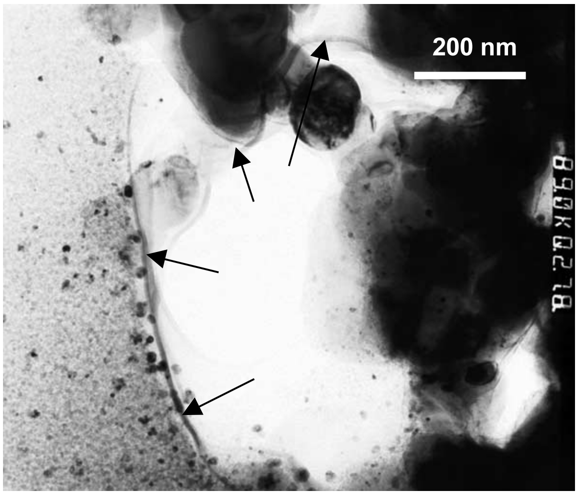

Fig. 6. TEM-micrograph of a section of a catalytic membrane tube after the experiments, showing the interface between the top mesoporous layer and the second intermediate layer. The arrows indicate a 10–50 nm thick amorphous film deposit in the porous structure. EDS spectra of the film are shown in Fig. 7.

The control of the transmembrane pressure is believed to be very important for the proper operation of the process. In order to obtain optimum transport of oxygen to the active sites,

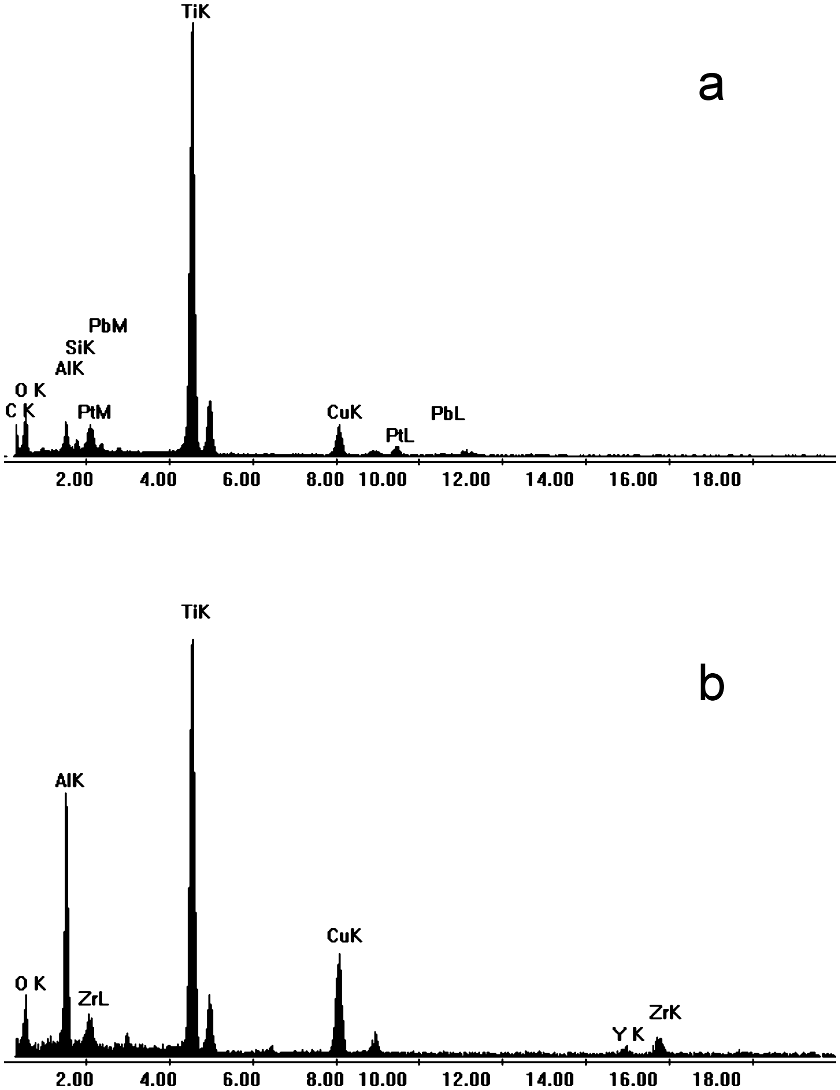

Fig. 7. EDS spectra of a section of a catalytic membrane tube after the experiments. The upper spectrum (a) shows the general composition of the top mesoporous layer (spot size 1 μm), whereas the spectrum below (b) shows the composition of a small area (spot size 20–50 nm) on the amorphous layer indicated by arrows in Fig. 6. The aluminium content is much higher in the amorphous area than in the bulk layer.

the diffusion path for oxygen should be as short as possible. The formation of a liquid film on the surface of the contactor top layer should, therefore, be avoided. If the formation of a liquid film is unavoidable, the film should be as thin as possible. In theory, this can be achieved by applying a slightly higher pressure on the gas side than on the liquid side. For a perfect membrane with a pore size of about 10 nm this will not cause any air intrusion problem in the membrane due to the high capillary forces, but for a real membrane with large-pore defects and possibly other small leaks, gas may enter the membrane and maintain the real gas/liquid interface out of the catalytic zone. Mass transfer studies and possibly numerical modelling of the mass transport of reactants and products will significantly enhance the understanding of the process and facilitate the development of an efficient process based on these principles. Such studies are currently being carried out by the authors.

4. Conclusion

The working principle of the process has been demonstrated at elevated temperature and pressure, although only a low conversion rate has been measured. Characterisation by TEM has shown that the microstructural features of the catalytic contactor are promising considering that a high catalyst surface area close to the contactor surface is beneficial for the process to operate efficiently. The low conversion rate is attributed to catalyst encapsulation and plugging of the mesoporous top layer of the contactor by amorphous aluminium-rich deposits observed by TEM and EDS. The deposits are probably caused by leaching of aluminium from α-Al_2O_3 present in the contactor support due to insufficient chemical stability of α-Al_2O_3 in the aqueous acidic environment. Better control of the transmembrane pressure difference may also lead to better performance. New experiments with contactor materials that are chemically stable in acidic environments and mass transport studies are under way and will increase the understanding of the process at a detailed level. New contactor designs and process layouts are also under consideration by the authors.

Acknowledgements

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