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Comparison of a contactor catalytic membrane reactor with a conventional reactor: example of wet air oxidation

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Abstract

A wet air oxidation reaction was carried out in a gas/liquid catalytic membrane reactor of the contactor type. The oxidation of formic acid was used as a model reaction. The mesoporous top-layer of a ceramic tubular membrane was used as catalyst (Pt) support, and was placed at the interface of the gas (air) and liquid (HCOOH solution) phases.

A similar reaction was carried out in a conventional batch reactor, using a steering rate high enough to avoid gas-diffusion limitations, and exactly identical conditions than for the CMR (amount of catalyst, pressure, etc.). At room temperature, the CMR showed an initial activity three to six times higher than the conventional reactor. This activity increase was attributed to an easier oxygen access to the catalytic sites. Nevertheless, the catalytic membrane gradually deactivated after a few hours of operation. Different deactivation mechanisms are presented.

Keywords: Catalytic membrane reactor; Contactor; Formic acid; Platinum; Wet air oxidation

1. Introduction

Water is present on the globe mainly in the oceans and the ice caps. The amount of fresh water available on Earth add up to less than 1% of this total amount, a fifth underground and the rest in surface waters (lakes and rivers). Therefore, what could be thought as an endless resource some decades ago is now regarded as a precious and short-recycling material. Any pollution from industry, domestic and agricultural use of water must be extracted or degraded, at the lowest energy cost. Some pollutants, as organic acids, present at low concentration (less than 5 g/l), are currently totally oxidised using the process called wet air oxidation. This gas/liquid reaction uses oxygen as oxidant, and produces carbon dioxide and water. It is usually a difficult reaction, and needs high temperature and pressure to obtain complete oxidation.

The use of a heterogeneous catalyst allows to reduce the temperature and pressure conditions from 240–275 °C/50–100 bar down to 200–250 °C/5–90 bar. Nevertheless, the amount of energy needed is still quite high, and there might be some way to soften further these conditions. An analysis of the situation point out the reason of such high pressure and temperature. The main limitation lays in the diffusion of the gas reactant (oxygen) down to the solid catalyst. The conventional answer to this limitation is increased temperature and pressure.

Another way to improve the gas/liquid/solid contact could be the use of a catalytic membrane reactor

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(CMR) of the contactor type. CMRs can be defined as reactors drawing a special advantage from the synergy of the catalyst and the membrane when implemented in the same device.

As conventional catalytic reactors are traditionally classified into different types, such as fixed or fluidised bed, batch reactors and many others, CMRs have been divided in previous papers from our group into three categories. Each set can be characterised according to the physical process the membrane is involved in within the reactor. In the *extractor* type, widely experimented for dehydrogenation reactions, the membrane can be made of palladium or MFI zeolite [1]. It selectively removes hydrogen from the catalyst fixed bed with which it is in contact. This selective extraction brings about the well-known equilibrium shift, which will allow higher conversions than what is limited by thermodynamics in a conventional fixed bed reactor. Another advantage can be the selective extraction of a primary product when successive reactions may occur, with an improved selectivity towards this product [2].

When the membrane is used as a *distributor* [3], the second reactant is introduced through the membrane all along the length of the catalyst bed. In this way, the concentration of the distributed reactant is kept at a low value in the catalyst, while the total amount introduced may be high. This may limit secondary reactions, as was shown in the case of selective oxidations [4]. This also allows the use of reactive mixtures that are forbidden in conventional reactors due to flammability problems [5].

1.1. Contactor CMRs

The third physical process in which the membrane may be involved is the triple contact between two different reactant fluid phases and the catalyst. In conventional reactors, one of the reactant is usually favoured by the fact that the catalyst on its support is dispersed in its phase, allowing an easy contact between the two. Nevertheless, the second phase reactant has to suffer access limitations, due to its diffusion path between the two-phase interface and the catalyst. Moreover, even in an ideal triphasic reactor, the catalyst is usually deposited in dead-end—or at least in a hardly accessible—pore of the support. The chemicals must then migrate into the support particle, down to the catalyst itself, in order to react. This process usually results in some access hindrance for one of the two reactants, as exposed earlier for the gas phase in WAO reactions.

The contactor type CMRs offer an improvement for that unfavoured reactant, with two handling possibilities. The first alternative is the flow-through contactor, in which a solution of the two reactants is forced through the membrane, constraining both reactants to come into the porous network of the membrane, as close as possible to the catalyst particle. As a matter of fact, the catalyst particle is here deposited in a membrane double-ended pore, through which the pumped flux impose the triple contact explained above [6–8].

The second alternative can be called the interfacial contactor. In this case the catalyst particles are also included into the pores of the membrane, but this time each fluid phase is located on a different side of the membrane. The operational conditions allow a proper location of the interface, which is in the catalysed zone of the membrane.

Such a system has been studied thoroughly through the model reaction of nitrobenzene hydrogenation [9]. It was then demonstrated that the reactor design in itself favoured the access of the gas to the catalytic zone. This work applies such an interfacial contactor CMR to WAO of formic acid, and compares the CMR performance to that of a conventional batch reactor.

2. Experimental

2.1. Materials

The tubular membranes used in this work were provided by TAMI Industries (Nyons, France). They are made of four concentric layers, showing an average pore size decreasing from outside. The largest layer is a mixture of α-alumina, zirconia and titania with a 10 μm pore size and a 2 mm thickness. The two subsequent layers are made of titania and titania/zirconia and the top-layer of pure rutile titania (Fig. 1). The membrane is tubular and has an internal diameter of 6 mm, an external diameter of 10 mm, and a total length of 10 cm. Both endings were covered with poly(fluoroelthylenepropylene) (PFEP) on 1 cm, for proper sealing.

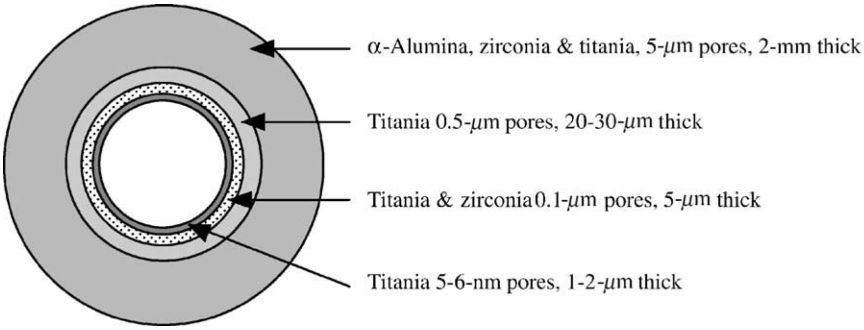

Fig. 1. Schematic cross-section of the membrane showing the four layers, their thickness and pore sizes.

The platinum precursor used to prepare the catalytic membranes was hydrochloric acid (H_2PtCl_6 Aldrich Chemical solution).

The powder support used to prepare catalysts for conventional reactor experiments was titania (TiO_2 Rhône-Poulenc DT51), with a surface area of 92 m^2/g, similar to the material used for the top-layer of the membrane.

2.2. Catalyst preparation and characterisation

The technique used here is inspired by a similar protocol widely practised on powder supported dispersed catalysts, and referred to as anionic impregnation. This method has proved to be efficient in obtaining well-dispersed Pt metal particles [10,11], in order to reach the highest active surface. It was used just so for the powder catalyst, and the application to the membrane was well described elsewhere [12,13].

Full characterisations of the catalytic membrane by titration of the deposited platinum, permeance measurements, and even scanning and transmission electron microscopy can be found elsewhere [12]. Similar procedures were carried out on the powder catalyst, and results similar to well-established literature were obtained [10,11].

Both catalysts showed nanometer-sized particles, with a slightly larger diameter (4–5 nm) in the case of the membrane support. In this last case, a deposited platinum mass of 3 mg was located essentially into the mesoporous top-layer of the membrane tube, on the whole 8 cm active membrane length. The platinum loading of the powder catalyst was 0.27%.

2.3. CMR operation

The tubular membrane described earlier was mounted in a membrane reactor, using a tight sealing separating the liquid feed on the shell side from the gas feed on the tube side. The liquid and gas pressures were maintained slightly above atmospheric pressure, for regulation purposes (120 and 122 kPa, respectively). As a matter of fact, the gas overpressure was carefully controlled using a pressure-difference gauge and a PID regulator, acting on the gas feed through a pneumatic valve. The average gas and liquid flow rates were 40 and 3 ml/min, respectively. The liquid was recycled into the reactor, for a total volume of 300 ml. The initial formic acid concentration was 5 g/l. Temperature and pressure-difference stationary state was reached using nitrogen, before switching to air and start oxidation.

The reactor was immersed into a temperature regulating water bath, after checking no bubbles were leaking through the membrane or the end sealing. The conversion of formic acid was followed by use of a high precision pH-meter (Hanna instrument PH301), regularly calibrated with a total organic carbon analyser (Shimadzu TOC5050A) and regularly controlled with a total organic carbon analyser (Shimadzu TOC5050A).

2.4. Conventional reactor operation

A glass autoclave including a double-wall oil thermal regulation, a water-cooled reflux, a mechanical stirrer, and a tube air feed bubbling in the liquid, was used for conventional wet air oxidation. The amount of liquid and catalyst were identical than for the CMR (300 ml and 3 mg_{Pt} on 1.2 g of TiO_2 support). The experiments were carried out at atmospheric pressure, using a gas flow rate 10 times higher than for the CMR and high rate stirring, as a precaution against any kinetic gas-diffusion limitation. The reactor having been tested in this reaction to reach a plateau in conversion rate when stirred over 1000 rpm, the steering rate was fixed at 1200 rpm.

In the case of the conventional reactor, both TOC and pH-meter were used to follow the conversion of formic acid. They proved to be in good keeping, therefore calibrating the pH-meter.

More details on the experimental conditions can be found in [14].

3. Results

3.1. Conventional reactor

The formic acid conversion as a function of time at three different temperatures is shown in Fig. 2. As one can expect, with increasing temperature, the initial rate increases, and the total conversion is reached earlier.

The actual initial rate, that will be the main parameter of comparison between the two reactors, are 0.2, 1.3 and 4.3 mmol/s/g_{Pt} at 20, 50 and 80 °C, respectively. These values were obtained as the initial slope of the curve of concentration as a function of time, considering a closed system with recirculation.

3.2. Catalytic membrane reactor

The results of experiments carried out at 20 and 80 °C are shown in Fig. 3. The same trend of initial rate increase with temperature is observed, but with actual values much higher than for the conventional reactor. Values of 0.6–0.9 mmol/s/g_{Pt} were achieved at 20 °C, and 22 mmol/s/g_{Pt} at 80 °C.

Nevertheless, a strong phenomenon of deactivation stops the reaction before complete conversion. It has to be noted that the same membrane could be reactivated using high temperature (200 °C) hydrogen treatment.

4. Discussion

4.1. Gain of activity in the CMR

In conditions as similar as possible on both systems, the initial conversion rate of the CMR exceeds by a factor of 3–6 the performance of the conventional reactor. This can be attributed to the fact that the gaseous reactant, oxygen, is given an easier access to the catalytic site. Due to capillary forces, the liquid phase fills up the whole porous network of the ceramic membrane, up to the mesoporous catalytically active layer. In this prospect, a carefully controlled regime is likely to maintain the gas–liquid interface into the mesoporous top-layer, where are located the catalyst particles.

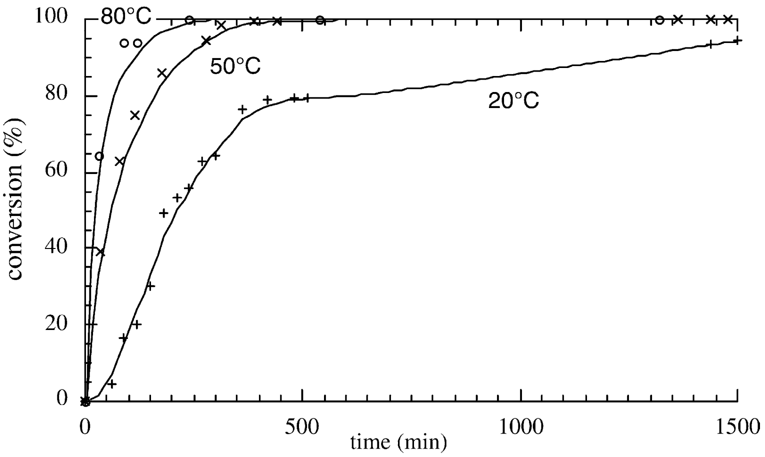

Fig. 2. Formic acid conversion as a function of time in a conventional, ideally stirred autoclave reactor at 20 (+), 50 (×) and 80 °C (○).

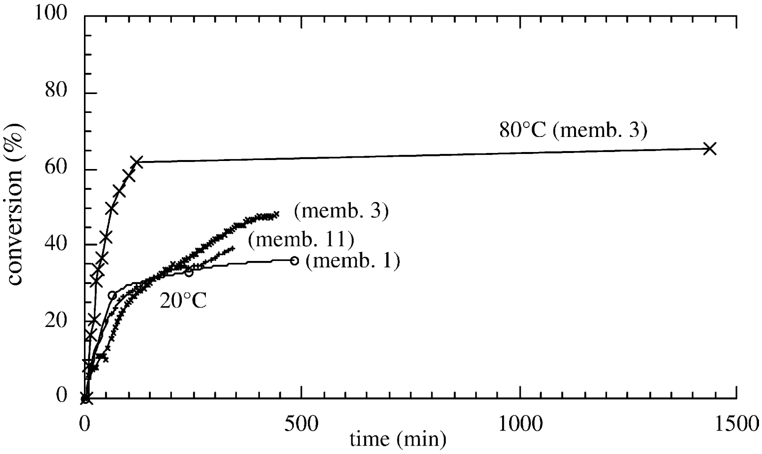

Fig. 3. Formic acid conversion as a function of time in a CMR at 20 and 80 °C. Please note the illustration of discrepancy shown for 20 °C by three similar membrane samples, obtained using the same preparation protocol.

Several benefits can be suggested to explain such a better access of the gas to the catalyst. A peculiar feature of the membrane is the fact that the catalytic pore exhibits two opposite inlets, which is not usually the case in powder mesoporous catalyst supports. This unique configuration may help the diffusion of each reactant from the two opposite sides of the pores, particularly when the pore size is only an order of magnitude larger than the molecular diameter.

Moreover, at the scale of a few micrometers, the boundary between the gas and the liquid phases is fuzzy. Therefore, the solubility of the gas may behave differently than on the macroscopic scale.

As a matter of fact, a conclusion of a previous work on different reactions has to be quoted. One of us [9] demonstrated that in the case of a hydrogenation reaction, the kinetic order of the gas reactant was nil. The main explanation was that the gas took benefit of a higher concentration in the liquid phase confined in mesopores than in macroscopic conditions. This “oversolubility” effect may well take place in this work. It is currently under study using independent means of investigation [15].

All this argument remains valid if, and only if, the gas–liquid interface is actually located in the very thickness of the mesoporous catalytic top-layer of the membrane separating the two phases. Let us see now how this may occur.

The capillary pressure due to the size of the mesopores is, in theory, very high. According to basic calculations, a gas overpressure of more than 10 MPa would be needed to expel the liquid from this layer, back down to the liquid side. In practice, though, the mesoporous top-layer is not a network of infinite length capillaries, but an interconnection of channels made of interstices between the ceramic particles the top-layer is made of. Non-cylindrical tortuous pores are non-ideal, and should limit the real capillary pressure by a big deal. However, another important factor, the presence of unavoidable defect(s) in the membrane, reduces this pressure. It has been observed experimentally that increasing the gas pressure over 10 or 20 kPa drives the conversion to nil, instantly. This is thought to be due to the gas crossing the membrane catalytic top-layer, moving down the gas/liquid interface into layers where no or very few catalyst particles are present.

On the other hand, when a liquid overpressure was applied, a similar loss of activity was observed. This overpressure on the liquid side is likely to produce a liquid film on top of the catalytic layer. This film thickness may be quite large, of the order of a millimeter fraction, preventing an easy gas access to the catalyst.

4.2. Catalytic membrane deactivation

4.2.1. Short-term deactivation

Another result, of this work is the fast deactivation of the catalytic membrane. It is so fast that almost no conversion experiment could be driven to its end, the conversion reaching a plateau, denoting, after a couple of hours, an absence of catalytic activity. An easy calculation based on simple modelling of diffusion phenomena in porous networks [9] excludes a first hypothesis of liquid reactant diffusion limitation. Moreover, the fact that the membrane was not active if re-mounted in the CMR with fresh solution also goes against this idea.

On the opposite, a membrane treated overnight under hydrogen flow at high temperature recovered its initial activity. Therefore, the deactivation was attributed to some poisoning of the catalyst, by species degradable during this kind of thermal treatment. One can think of catalyst superficial oxidation, or poisoning by some by-products of formic acid degradation. On the other hand, platinum-based catalysts are known to be affected by oxygen core absorption poisoning in this type of reaction when high pressure is used [16,17]. Therefore, in a next step, it is planned to use other catalytic phases, and/or optimise the catalyst operating conditions to avoid these phenomena.

4.2.2. *Long-term deactivation*

Another issue is long-term deactivation. The same catalytic membrane, after a couple of hundred hours use could not be reactivated using the hydrogen thermal treatment described earlier. This total loss of activity was reproduced over more than five samples. It was associated with a membrane mass increase (a few milligrams) and a dramatic gas permeance loss (from -20 to -100%). The mesoporous layer, controlling the gas transfer through the membrane was obviously plugged during operation in the CMR. As this plugging material could not be cleaned up using common washing techniques (solvent and acids), it was decided to have a closer look at the mesoporous layer structure after this long-term deactivation. As reported elsewhere [18], the top-layer appeared plugged with an Al-containing material. This material reduced the pore diameter (thus reducing the permeance), covering the Pt particles (thus reducing the catalytic activity).

As the top-layer was not made of alumina, but of titania, it was suggested that this Al species was displaced from an underneath supporting layer. Therefore, the long-term deactivation process could be the following. During CMR operation, a diffusion of formic acid from the bulk up to the catalytic layer occurs, due to its conversion that originates a concentration gradient. During this diffusion, it is proposed that formic acid forms a complex with aluminium species extracted from the larger-pore layers of the membrane, that are made of α-alumina. When this complex comes up to the catalytic site, the formic acid molecule would be oxidised, and the complex would then collapse, resulting in precipitation of the remaining aluminium species. Even if very small amounts of aluminium were transported this way through the membrane, it would be enough to plug the pores of the top-layer, which is three orders of magnitude thinner than the three other alumina-containing layers.

5. Conclusion

The CMR of the contactor type offers a promising approach to improve the gas access to the catalyst in the case of wet air oxidation processes. Initial activities are reported here that offers an increase of 3–6 over the corresponding conventional batch reactor, used in similar conditions.

In order to overcome the two deactivation processes described here, some change of material used in the CMR must be achieved. A chemically resistant support that does not include alumina seems necessary to avoid long-term deactivation. Also, other active phases and operating conditions can be thought of to prevent short-term deactivation.

These first results drove the partners to propose and obtain a European Project, named WaterCatox, currently in application, in order to transfer this lab-scale technology to pilot plant unit operation, using a larger range of pressure and temperature testing ability, with as a final goal industrial application. In case of success, it would be, to our best knowledge one of the first industrial process using a CMR of any type.

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