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# Selective oxidation of propane on Nafion/PEEK-WC catalytic membranes in a multifunctional reaction system

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## Abstract

A comparative testing of flat and hollow fiber Nafion/PEEK-WC catalytic membranes in the partial oxidation of propane to oxygenates (*n*-propanol, isopropanol, propionic aldehyde and acetone) with $Fe^{2+}$–$H_2O_2$ Fenton system in a multifunctional three-phase reactor (3PCMR) under mild conditions ($T_R$, 70–120 °C; $P_R$, 140 kPa) has been accomplished. The features of the multifunctional 3PCMR that enables reaction along with product separation and recovery are discussed. The influence of the membrane geometry on selectivity and distribution of reaction products in gas and liquid phases is outlined. Hollow fiber systems ensure higher productivity per unit of reactor volume, higher selectivity to primary oxidation products (*n*-propanol and isopropanol) and a more effective product recovery.

*Keywords:* Catalytic membranes; Hollow fiber; Nafion

## 1. Introduction

The development of novel, clean, selective and direct catalytic routes for the conversion of light alkanes into higher added value products still remains a challenging research area, which could imply a significant impact on the framework of the gas and oil industries. Among the various strategies so far proposed, the direct selective oxidation of methane is considered as the most challenging research topic and a sought after technological breakthrough [1]. An extraordinary research effort has been addressed to disclose original catalyst formulations, effective oxidation systems and novel operating strategies for attaining yield values suitable for exploiting the feasibility of the process [1–5]. Recently, Williams et al. [6] evaluated the performance of a bimetallic palladium and copper (II) chloride catalyst in the selective oxidation of methane to methanol derivative at 85 °C and $8.3 \times 10^3$ kPa in a liquid phase copper (II) reaction system containing trifluoroacetic acid (TFA). Despite the promising initial reaction rate, the catalyst deactivation limits the obtainable yield to less than 2%. Nazaki et al. [7] achieved 10% one-pass methanol yield in the selective oxidation of methane at 25 °C and 100 kPa in a microscale non-equilibrium plasma reactor. Several authors have attempted to activate the C–H bond using catalysts which mimic enzymes, like methane monoxygenase or cytochrome P450, in hydroxylating light alkanes. In this regard, Lyons and Ellis [8] studied the oxidation of propane to isopropanol and acetone at 398 K and 40 bar with air over homogeneous metalloporphyrin catalysts. Raja and Ratnasamy [9] reported high yields in the direct aerobic oxidation of propane at ambient conditions to a mixture of isopropanol and acetone over substituted phtalocyanines of Cu, Co and Fe encapsulated in X and Y zeolites. Seki et al. [10,11] claimed that Keggin-type vanadium containing $H_4PVMo_{11}O_{40}$ heteropolyacid is an active catalyst precursor for selective oxidation of methane with hydrogen peroxide. However, all these approaches are limited by hurdles and drawbacks, such as drastic operating conditions, catalyst instability, difficult product separation and recovery from the reaction medium as well as low selectivity and yield. A real breakthrough in this field requires tuned reaction engineering strategies along with effective catalysts. Multifunctional catalytic membrane reaction systems appear to be the most suitable tools for

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overcoming both intrinsic reaction limitations and low yields of the selective oxidation of hydrocarbons, since they allow simultaneously reaction under mild conditions, product separation and recovery. We have recently found that selective oxidation of light alkanes to higher added value oxygenated products can be efficiently performed on Nafion/C-based membranes mediated by the $Fe^{2+}$–$H_2O_2$ Fenton system in a three-phase reactor (3PCMR) [12–16]. Despite their promising performance [15,16], the high thickness, the low mechanical stability, the presence of transition metal impurities in the C support and the multi-step preparation procedure of such Nafion/C-based catalytic membranes limit their further exploitation. The use of polymeric membranes as support of the Nafion active species could overcome the above hurdles. However, the anchoring of catalytic active species to polymeric substrates has so far received a limited attention.

Among the various polymeric materials, PEEK-WC [poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylenoxa-*p*-phenylenoxy-*p*-phenylene)] denotes excellent characteristics in terms of chemical, thermal and mechanical stability. In order to highlight the features and potential of polymeric membrane-based systems as innovative reaction tools for attaining the selective oxidation of light alkanes under mild conditions, this work outlines the performance of several flat and hollow fiber Nafion/PEEK-WC-based membranes in the selective oxidation of propane to oxygenates (*n*-propanol, isopropanol, propionic aldehyde and acetone), taken as reaction model, mediated by $Fe^{2+}$–$H_2O_2$ Fenton system in the multifunctional three-phase catalytic membrane reactor (3PCMR).

## 2. Experimental

### 2.1. Preparation of Nafion/PEEK-WC membranes

*Flat PEEK-WC membranes* were prepared by the wet phase inversion technique. PEEK-WC powder, supplied by the Chanchung Institute of Applied Chemistry (Academia Sinica, China), was dissolved in dimethylformamide (DMF) by magnetically stirring overnight to allow complete solution at room temperature. A thin film of the polymer solution was cast on a glass plate using a casting knife (Braive Instruments) set at 250 μm, then the membrane was immersed in a coagulation bath after exposure for a fixed time to the air until complete evaporation of the solvent. After complete coagulation, the membrane was transferred into a pure water bath, frequently refreshed in order to remove the traces of solvent and to promote the release of the polymeric film. The resulting membrane was soaked in a 20% aqueous glycerol solution for 24 h in order to ensure the wetting of the membrane and to prevent pore collapse or change of transport properties upon drying, and finally dried under vacuum at 70 °C for 24 h.

*Hollow fiber PEEK-WC membranes* were prepared by the spinning technique [17]. PEEK-WC powder was dissolved in a 65/35 (wt/wt) mixture of *N*,*N*-dimethylacetamide (Fluka, Buchs, Switzerland) and tetrahydrofuran (Carlo Erba Reagenti, Italy), respectively by slow addition of the polymer to the solvent under continuous mechanical stirring. The solution containing 18 wt% of PEEK-WC was stirred for 3 h and was left standing for 2 h to remove air bubbles, then it was loaded in a thermostated vessel kept at 30 °C. The polymer solution was spun according to the well-known dry–wet spinning process, using the spinning apparatus (supplied by Stantech GmbH, Hamburg, Germany) elsewhere described [17]. The dope was forced through the spinneret by an $N_2$ overpressure and the flow rate was checked gravimetrically. The bore fluid was washed with bidistilled water and it was fed to the spinneret by a metering pump. The flow rate of the dope and bore fluid was 12 and 15 g/min, respectively. The dope was filtered in line before entering the spinneret. The spinneret had a 2-mm hole and a needle for the bore fluid with an external diameter of 1 mm. The polymer solution leaving the spinneret entered an air gap of 30 cm before dipping into the rotating coagulation bath where the hollow fibers were collected and washed at the end of the spinning test. The spun fibers were cut in pieces of about 30 cm and kept in a fresh water bath for at least 24 h for the complete removal of the solvent. Then, they were soaked in a 20 wt% aqueous glycerol solution for 24 h and finally dried at room temperature for at least 2 days.

*Nafion/PEEK-WC catalytic membranes* were prepared by deposition of an isopropanol solution of Nafion–H on both flat and hollow fiber PEEK-WC membranes using the ultrafiltration technique. The concentration of Nafion–H solution was designed in order to achieve a Nafion surface loading of 1 mg/cm$^2$.

The characteristics and the sample code of flat and hollow fiber catalytic membranes are reported in Table 1.

## 3. Apparatus and procedure

Catalytic membranes were tested in the 3PCMR setup schematically shown in Fig. 1. The system is provided with liquid and gas recycle pumps which allow operations in batch,

Table 1
Characteristics of flat and hollow fiber Nafion/PEEK-WC membranes

| Sample code | Number of hollow fibers | Water permeability (l/h m$^2$ bar) | i.d. (μm) | o.d. (μm) | Pore size (μm) | Thickness (μm) | Membrane surface (cm$^2$) | Membrane weight (g) | Nafion[a] content (mg) |
|---|---|---|---|---|---|---|---|---|---|
| FM | – | 0.04 | – | – | n.d. | 87 | 20 | 0.081 | 20 |
| BHF[b] | 15 | 0.4 | 889 | 1364 | 0.4 | 237 | 50 | 1.020 | – |
| HF2 | 2 | 0.4 | 889 | 1364 | 0.4 | 237 | 10 | 0.170 | 10 |
| HF15 | 15 | 0.4 | 889 | 1364 | 0.4 | 237 | 50 | 0.935 | 50 |

[a] The Nafion surface loading of all the membranes was 1 mg/cm$^2$.
[b] Bare membrane.

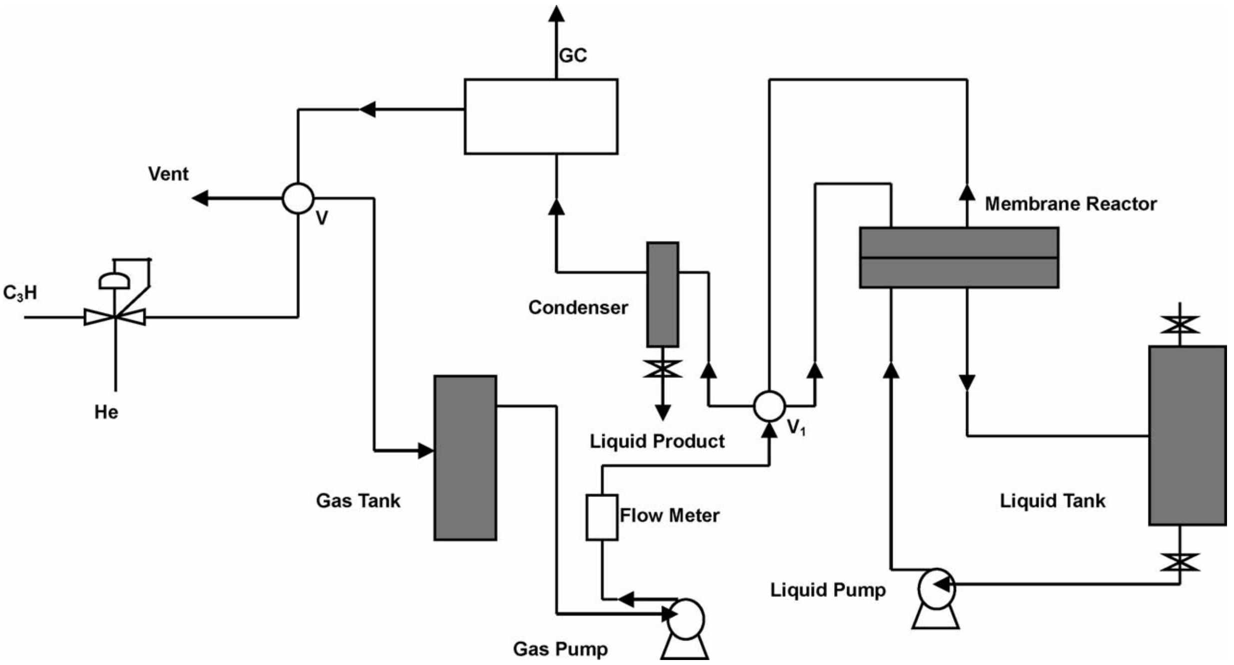

Fig. 1. Schematic diagram of the 3PCMR setup.

semi-batch and continuous mode. A flat catalytic membrane was sandwiched between two Teflon plates provided with turbulence nets, while hollow fiber membranes were collected as a multitubular reactor in a quartz tube ($\phi_{\mathrm{int}}$, 14 mm; $\phi_{\mathrm{est}}$, 18 mm; length, 200 mm). The volume of the reactor in flat and multitubular configuration was 98 and 30 $cm^3$, respectively. During reaction, care was taken to maintain a pressure difference of 3 kPa ($\Delta P = P_g - P_l$) between the gas and the liquid sides in order to ensure adequate mass transfer conditions through the membrane. Catalytic measurements were performed in batch mode with separate recirculation of both the gas (flow rate, 3 $dm^3$/min) and the liquid phases (flow rate, 0.5 $dm^3$/min). Catalytic tests in the selective oxidation of propane were carried out in the $T$ range 70–120 °C and at 140 kPa absolute pressure. The gas phase was constituted of a propane–helium mixture ($P_{C_3H_8}/P_{He} = 3.7/1$) while the liquid phase was a $H_2O_2$ solution ([$H_2O_2$], 0.30 mol/l) containing $Fe^{2+}$ ions ([$Fe^{2+}$], $4 \times 10^{-5}$ mol/l). Oxygenated products formed during reaction were trapped in the gas phase rig at 2 °C downstream of the membrane reactor and analyzed by a GC equipped with an FID detector using a CP Porabond Q column ($l$, 25 m; i.d., 0.53 mm) operating at 90 °C. $H_2O_2$ concentration change was followed by periodical titration with permanganate solution ([$MnO_4^-$], $1 \times 10^{-1}$ mol/l).

## 4. Results and discussion

Since, we have previously outlined the potential of Nafion/C catalytic membranes in the selective oxidation of light alkanes under mild conditions [12–16] evidencing the

Table 2
Activity data of flat and hollow fiber Nafion/PEEK-WC catalytic membranes in the selective oxidation of propane

| Sample code | $T_R$ (°C) | [a]Conversion (mol%) | [a]Reaction rate ($10^{-2}$ µmol $g_{\mathrm{membr}}^{-1}$ $s^{-1}$) | [a]Specific activity (µmol $g_{\mathrm{Nafion}}^{-1}$ $s^{-1}$) | [a]Productivity (µmol$_{\mathrm{oxygenates}}$ $h^{-1}$ $cm_{\mathrm{rv}}^{-3}$) |
|---|---|---|---|---|---|
| BHF | 80 | 0.11 | 0.20 | – | 0.24 |
| BHF | 100 | 0.12 | 0.22 | – | 0.27 |
| BHF | 110 | 0.13 | 0.25 | – | 0.30 |
| FM | 80 | 0.43 | 4.1 | 0.24 | 0.12 |
| FM | 95 | 0.60 | 7.9 | 0.48 | 0.24 |
| FM | 110 | 0.70 | 8.1 | 0.52 | 0.25 |
| HF2 | 70 | 0.31 | 1.9 | 0.20 | 0.36 |
| HF2 | 80 | 0.50 | 2.6 | 0.27 | 0.50 |
| HF15 | 80 | 1.3 | 1.3 | 0.25 | 1.44 |
| HF15 | 100 | 2.1 | 2.2 | 0.40 | 2.45 |
| HF15 | 110 | 2.3 | 2.4 | 0.47 | 2.67 |
| HF15 | 120 | 2.6 | 2.6 | 0.50 | 2.91 |

[a] Conversion, reaction rate, specific activity and productivity values at reaction time of 180 min.

direct involvement of the acidic functionality of the sulfonic group of Nafion species in the reaction pathway, in the present study, we attempt to evaluate: (i) the suitability of PEEK-WC membranes as support of the Nafion active species and (ii) the influence of the geometry on the performance of Nafion/PEEK-WC membranes. The selective oxidation of propane on Nafion/PEEK-WC catalytic membranes in the $T_R$ range 70–120 °C leads to the formation of isopropanol, *n*-propanol, propionic aldehyde and acetone. No $CO_2$ has been detected. A general overview of the performance of flat (FM) and hollow fiber (BHF, HF2 and HF15) membranes at reaction time of 180 min, in terms of $C_3H_8$ conversion, reaction rate, specific activity and oxygenates productivity, is given in Table 2. The specific activity of such Nafion/PEEK-WC catalytic membranes rises with $T_R$, irrespective of the membrane geometry, going from ca. 0.20 to 0.50 $\mu mol\ g_{Nafion}^{-1}\ s^{-1}$ in the $T_R$ range 70–120 °C. The reaction rate values, referred to the unit of membrane weight, account for the different Nafion loading of the investigated samples. Since, the reaction rate value of the bare hollow fiber membrane system (BHF) is more than one order of magnitude lower than that of the Nafion loaded ones, it can be argued that any specific functionality of the Nafion moieties plays a direct catalytic action in the reaction pathway. The similar values of reaction rate for bare BHF membrane in the $T_R$ range 80–110 °C, further confirm the catalytic action of Nafion species in the investigated reaction system. Indeed, the rather low rate ($0.2 \times 10^{-2}\ \mu mol\ g_{membr}^{-1}\ s^{-1}$) likely results from a radical reaction pathway promoted by the $Fe^{2+}/H_2O_2$ Fenton system. The low activation energy value (ca. 25 kJ/mol) of Nafion/PEEK-WC membranes, calculated from the activity data reported in Table 2, indicates that the kinetics is controlled by mass transfer limitations induced by the intrinsic features of both the multiphase reaction tool and membrane system. It is noteworthy that the oxygenates productivity values per unit of reactor volume (0.36–2.91 $\mu mol_{oxyg}\ cm_{rv}^{-3}\ s^{-1}$) of multi-tubular hollow fiber membranes are one order of magnitude higher than those obtained with flat ones. This parameter is of fundamental importance for the selection of membrane geometry as well as for reactor scaling up. Product selectivity data presented in Table 3 account for the influence of reaction temperature as well as for the geometry and textural properties of the membrane samples which likely control their diffusion-permeability pattern [17,18]. The extent of the primary oxidation products, *n*-propanol and isopropanol, slightly decreases with $T_R$. However, in the investigated $T_R$ hollow fiber systems ensure selectivity to alcohols of 60–70%, while this value does not exceed 50% for flat FM sample. For bare BHF membrane, even if the extent of selectivity to alcohols (~70%) is analogous to that of Nafion based hollow fiber systems, a different *n*-propanol/isopropanol ratio is observed. The stability of Nafion/PEEK-WC hollow fiber membranes in the reaction medium was checked by performing a series of reproducibility tests of HF15 sample at 80 °C. The results depicted in Fig. 2, in terms of $C_3H_8$ conversion versus reaction time, are diagnostic of the good stability of the studied Nafion/PEEK-WC membranes. The activity pattern of both flat and hollow fiber Nafion/PEEK-WC membranes at 80 °C is depicted in Fig. 3.

Table 3
Product selectivity of flat and hollow fiber Nafion/PEEK-WC catalytic membranes in the selective oxidation of propane

| Catalytic membrane | $T_R$ (°C) | [a]Product selectivity (mol%) | | | |
|---|---|---|---|---|---|
| | | $n$-$C_3H_8O$ | $i$-$C_3H_8O$ | $CH_3COCH_3$ | $CH_3CH_2CHO$ |
| BHF | 80 | 48.2 | 23.1 | 22.8 | 5.9 |
| BHF | 100 | 46.0 | 22.0 | 23.0 | 9.0 |
| BHF | 110 | 40.0 | 27.8 | 28.5 | 3.7 |
| FM | 80 | 27.8 | 23.8 | 36.8 | 11.6 |
| FM | 95 | 20.4 | 27.3 | 39.1 | 13.2 |
| FM | 110 | 19.1 | 24.7 | 41.0 | 15.2 |
| HF2 | 70 | 11.6 | 50.4 | 31.7 | 6.3 |
| HF2 | 80 | 20.2 | 52.0 | 22.8 | 5.0 |
| HF15 | 80 | 18.9 | 50.8 | 25.5 | 4.8 |
| HF15 | 100 | 23.9 | 49.0 | 20.7 | 6.3 |
| HF15 | 110 | 30.1 | 29.4 | 31.9 | 8.6 |
| HF15 | 120 | 21.6 | 45.1 | 24.4 | 5.1 |

[a] Selectivity values at reaction time of 180 min.

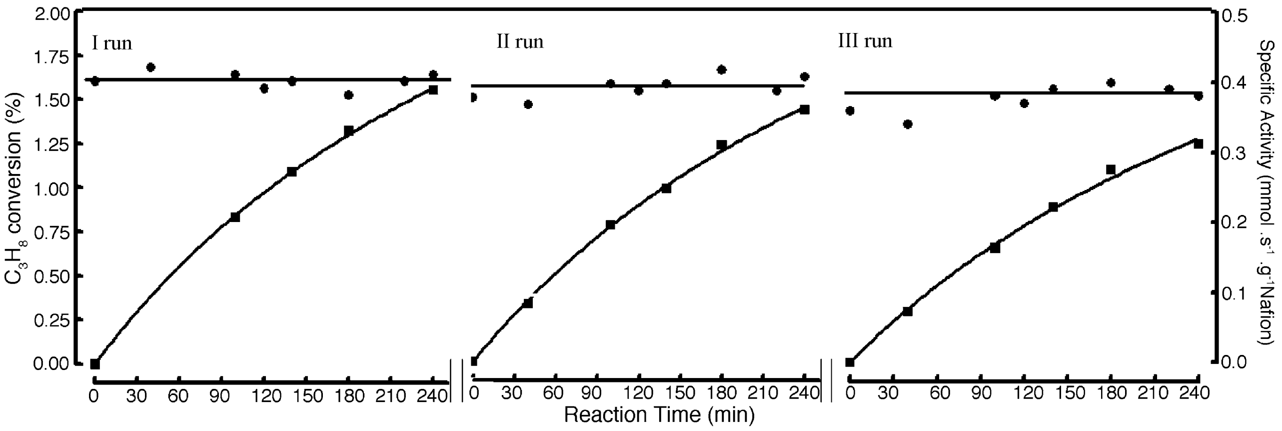

Fig. 2. Selective oxidation of propane on hollow fiber Nafion/PEEK-WC catalytic membrane (HF15). Reproducibility tests: (■) $C_3H_8$ conversion and (●) specific activity vs. reaction time ($T_R$, 80 °C; [$H_2O_2$], 0.3 mol/l; [$Fe^{2+}$], $4 \times 10^{-5}$ mol/l).

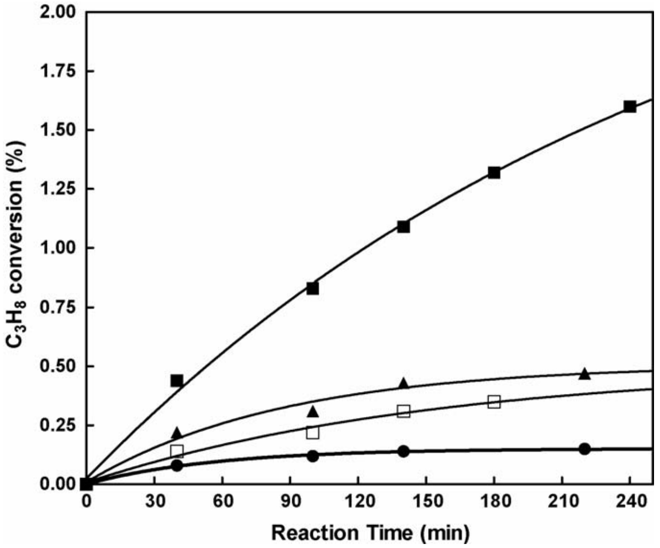

Fig. 3. Selective oxidation of propane on flat and hollow fiber Nafion/PEEK-WC catalytic membranes. $C_3H_8$ conversion vs. reaction time: (■) HF15; (□) HF2; (▲) FM; (●) BHF ($T_R$, 80 °C; [$H_2O_2$], 0.3 mol/l; [$Fe^{2+}$], $4 \times 10^{-5}$ mol/l).

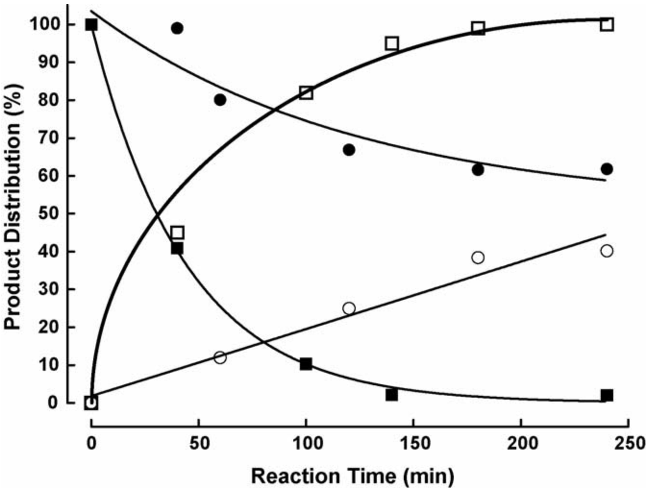

Fig. 5. Selective oxidation of propane on flat and hollow fiber Nafion/PEEK-WC catalytic membranes. Product distribution in (○, □) gas and (●, ■) liquid phases vs. reaction time. (○, ●) FM and (□, ■) HF15 catalytic membranes ($T_R$, 80 °C; [$H_2O_2$], 0.3 mol/l; [$Fe^{2+}$], $4 \times 10^{-5}$ mol/l).

The level of $C_3H_8$ conversion at any reaction time mirrors the relative extent of the active surface of the membrane systems. These findings further support the direct involvement of the Nafion active species, dispersed on the membrane surface, in driving the selective oxidation of propane. The selectivity values to primary (*n*-propanol and isopropanol) and secondary (propionic aldehyde and acetone) oxidation products with reaction time for HF2 and FM membranes at 80 °C are reported in Fig. 4. The hollow fiber configuration enables higher selectivity (~70%) to alcohols which does not vary during the catalytic test, while for flat membrane (FM), a lower initial selectivity to alcohols (~35%) which decreases with reaction time, is recorded. Since, in the multifunctional 3PCMR unit the reaction products are recovered by condensation from the gas phase rig, their dynamic distribution into gas and liquid phases during reaction time is an important issue for evaluating the suitability of any membrane system. Then, the product distribution, expressed as a cumulative amount of oxygenates in gas and liquid phases, of flat (FM) and hollow fiber (HF15) membranes at 80 °C with reaction time is comparatively shown in Fig. 5. For flat (FM) membrane, a progressive decrease of the extent of products in the liquid phase and a consequent increase in the gas phase are observed. The trend in the product distribution of hollow fiber HF15 is similar to that of the FM system. However, a steeper decrease of the extent of products in the liquid phase can be noted along with a concomitant rapid rise in the gas phase. Indeed, after the reaction time of 100 min, all the products permeate through the membrane towards the gas phase. However, the intrinsic physical properties of hollow fiber HF15 membrane imply a diffusion-permeation pattern which favour the transport of reaction products from the liquid to the gas rigs. This feature, besides ensuring a higher selectivity to *n*-propanol and isopropanol, preventing their further oxidation according to a consecutive reaction pathway [12], enables an easier and complete recovery of reaction products by condensation from the gas phase. The above findings support the better suitability of hollow fiber Nafion/PEEK-WC catalytic membranes with respect to the flat ones in the selective oxidation of light alkanes in the 3PCMR tool.

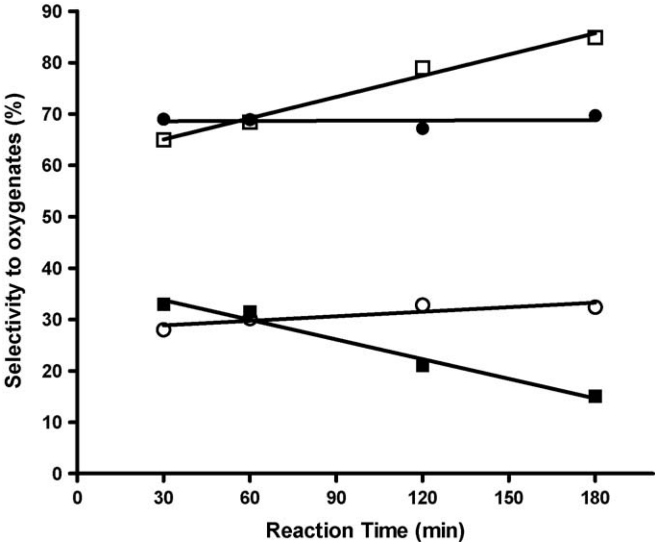

Fig. 4. Selective oxidation of propane on flat and hollow fiber Nafion/PEEK-WC catalytic membranes. Selectivity to (■, ●) primary (*n*-propanol and isopropanol) and secondary (□, ○) reaction products (propionic aldehyde and acetone) vs. reaction time. (■, □) FM and (●, ○) HF2 catalytic membranes ($T_R$, 80 °C; [$H_2O_2$], 0.3 mol/l; [$Fe^{2+}$], $4 \times 10^{-5}$ mol/l).

## 5. Conclusion

Nafion/PEEK-WC catalytic membranes denote a good performance in the selective oxidation of propane to oxygenates with $Fe^{2+}$–$H_2O_2$ Fenton system under mild conditions ($T_R$, 70–120 °C; $P_R$, 140 kPa). From a comparative performance evaluation, it results that hollow fiber Nafion/PEEK-WC membranes are more suitable than the corresponding flat ones in terms of both higher selectivity to more valuable primary oxidation products (*n*-propanol and isopropanol) and easier and complete product recovery by condensation from the gas phase rig. The better performance of multitubular hollow fiber membranes could be attributed to their intrinsic physical characteristics, which allow more adequate reaction regime and diffusion-permeation pattern.

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