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On the potential of the multifunctional three phase catalytic membrane reactor in the selective oxidation of light alkanes by Fe^{2+}–H_2O_2 Fenton system

C. Espro[a], F. Arena[a], F. Frusteri[b], A. Parmaliana[b,c,*]

[a] *Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università degli Studi di Messina,*
Salita Sperone c.p. 29, I-98166 S. Agata, Messina, Italy
[b] *Istituto CNR-TAE, Via Salita S. Lucia 39, I-98126 S. Lucia, Messina, Italy*
[c] *Dipartimento di Chimica, Università degli Studi "La Sapienza" di Roma, P.le A. Moro 5, I-00185 Rome, Italy*

Abstract

Selective oxidation of light alkanes under mild conditions (T_R, 80–120°C; P_R, 140 kPa) is attained in a multifunctional three phase catalytic membrane reactor (3PCMR).

The functionalisation of C_1–C_3 alkanes to the corresponding oxygenates on superacid catalytic membranes mediated by Fe^{2+}/H_2O_2 Fenton system is achieved. Among the various superacid catalytic agents, Nafion-based ones revealed the best performance. The features of the 3PCMR in enabling simultaneous reaction and product separation are presented. The influence of the operating conditions (T_R, $[H_2O_2]$, $[Fe^{2+}]$ or $[Fe^{3+}]$) on the catalyst activity is outlined. A general reaction pathway accounting for the activation of the C–H bond of the alkane molecule on the superacid sites and the subsequent reaction of the activated alkane with primary reactive intermediates, generated from the Fe^{2+}/H_2O_2 system, is proposed.

Keywords: Membrane reactor; Superacid catalytic membranes; Light alkanes selective oxidation; Oxygenated products

1. Introduction

The selective oxidation of methane and light alkanes (C_2–C_3) to oxygenates , fuels and higher hydrocarbons owing to the challenge to disclose viable processes for the valorisation of the large reserves of natural gas via its conversion into higher added value products, is currently attracting a great research interest. Among the different catalytic approaches, the liquid phase oxidation under mild conditions should allow in principle the attainment of high selectivity to the desired product. However, the activation and functionalisation of C–H and C–C bonds is a hard task, since the low reactivity of alkanes and the occurrence of subsequent reactions of the intermediate products which tend to be more reactive than the alkane itself. The relevance of such research field resulted in the proposition of various original catalytic systems based on the use of quite different reagent/activating agents acting according to different reaction pathways. Indeed, selective electrophilic activation of light alkanes, firstly proposed by Olah [1], based on the protonation of the alkane substrate by superacid agents, in non-nucleophilic media has been widely documented [2–4], while others have attempted to activate the C–H bond by means of various

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[*] Corresponding author. Tel.: +390-90-676-5606;
fax: +390-90-391518.
E-mail address: adolfo.parmaliana@unime.it (A. Parmaliana).

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transition metal electrophiles, of which $Pt(II)Cl_4^{2-}$ has been the most extensively studied [4]. Periana et al. [5] have recently disclosed the extraordinary catalytic action of platinum complexes from the bidiazine ligand family which ensure the attainment of 70% one-pass yield in the direct oxidative conversion of methane to methanol. Sen and his co-workers have proposed various functionalisation reactions of light alkanes based on the use of Pd(II) as catalytic agent, in strongly acidic media or H_2O_2 in anhydride media, to give alkyl esters [6]. Strong solid-acids are largely studied as active species in the catalytic conversion of light alkanes in presence of H_2O_2 [2,7]. Among this class of catalysts, we have reported that Nafion-based catalytic membranes, in presence of the Fe(II)–H_2O_2 Fenton system, catalyse the selective oxidation of methane to methanol [8] and ethane to ethanol and acetaldehyde [9]. The metal/hydroperoxide induced activation of O_2 for the selective oxidation of various hydrocarbon substrates has been recently reconsidered in order to ascertain the reaction pathways, the nature of the active oxygen species and reaction intermediates [10]. It is not definitively assessed if the oxygenated Fenton chemistry for the selective conversion of hydrocarbons involves a classical reaction mechanism or a single free radical mediated chemistry [10]. Lyons and Ellis [11], studying the selective oxidation of light alkanes on phthalocyanine complexes, have found that propane can be selectively oxidised to isopropyl alcohol and acetone at 125°C on a perfluorophthalocyanatoiron(III) azide. However, the selective oxidation of light alkanes under mild conditions bears several critical concerns and drawbacks, mainly linked with the kinetics of the liquid phase reaction as well as the separation of the catalyst from the reaction media and an effective separation and recovery of the reaction products which seriously limit the realisation of continuous running reaction systems and the technical development and viability of such novel catalytic routes. We have already faced these critical aspects by designing and exploiting an original three phase catalytic membrane reactor (3PCMR) which allows to overcome the classical drawbacks of the conventional liquid-phase reaction systems [2,7] enabling simultaneous reaction and product separation. Indeed, the active species is immobilised on the membrane surface, the separation between liquid and gas phases is ensured by the membrane itself, while the reaction products are easily separated and recovered by condensation in the gas-phase of the reaction tool [8,9].

The aim of this paper is to present the features and the potential of the multifunctional 3PCMR in attaining the selective oxidation of light (C_1–C_3) alkanes on superacid catalytic membranes by Fe^{2+}–H_2O_2 system.

2. Experimental

2.1. Catalytic membranes

Catalytic membranes were prepared by two procedures:

1. impregnation of the bare membranes with a solution of the active species;
2. deposition of a paste containing active species and Teflon on a carbon paper acting as physical support.

Bare membranes were obtained by deposition of the carbon–teflon paste on carbon paper and subsequent activation at 300°C in N_2 atmosphere. Ketjenblack (EC 600 Akzo Chemie, BET SA $= 950\,m^2/g$) carbon was used as support.

Nafion-based membranes (samples A-1, A-2, A-3 and A-4) were obtained by incipient wetness impregnation of the bare membrane with an isopropanol solution of Nafion-H (1100 EW product, Dupont Wilmington, DE). Several membranes with different Nafion loading (5–30 wt.%), referred to the weight of the catalytic layer, were prepared. After impregnation, all samples were dried at 80°C under vacuum.

Supported phosphomolybdic acid membranes were prepared by impregnation of bare membrane with an ethanolic solution of phosphomolybdic acid (HPMo). The concentration of the HPMo solution was selected in order to achieve HPMo loadings of 20, 40 and 60 wt.% (samples C-2, C-4 and C-6), respectively. Due to the poor wetting of the carbon substrate of the bare membrane care was taken to maintain a uniform film of the liquid on the carbon layer, whilst ethanol was slowly removed at room temperature, then the samples were dried at 70°C overnight. In addition, a 20 wt.% phosphotungstic acid (HPW) membrane (sample D-2) was prepared by the same preparation procedure adopted for HPMo membranes.

The Cs (CsM) based membrane was prepared by deposition of $H_{0.5}Cs_{2.5}PW_{12}O_{40}$–teflon paste (30 wt.%

Table 1
List of the catalytic membranes

Sample	Active species	Composition of catalytic layer		
		Carbon loading (mg/cm^2)	Active species loading (mg/cm^2)	Active species loading (wt.%)
A-1	Nafion	5.1	0.25	5
A-2	Nafion	5.1	0.51	10
A-3	Nafion	5.1	1.02	20
A-4	Nafion	5.1	1.53	30
C-2	HPMo	5.4	1.02	20
C-4	HPMo	5.4	2.0	40
C-6	HPMo	5.4	3.05	60
D-2	HPW	5.3	2.3	20
CsM	$H_{0.5}Cs_{2.5}PW_{12}O_{40}$	5.2	8.0	–

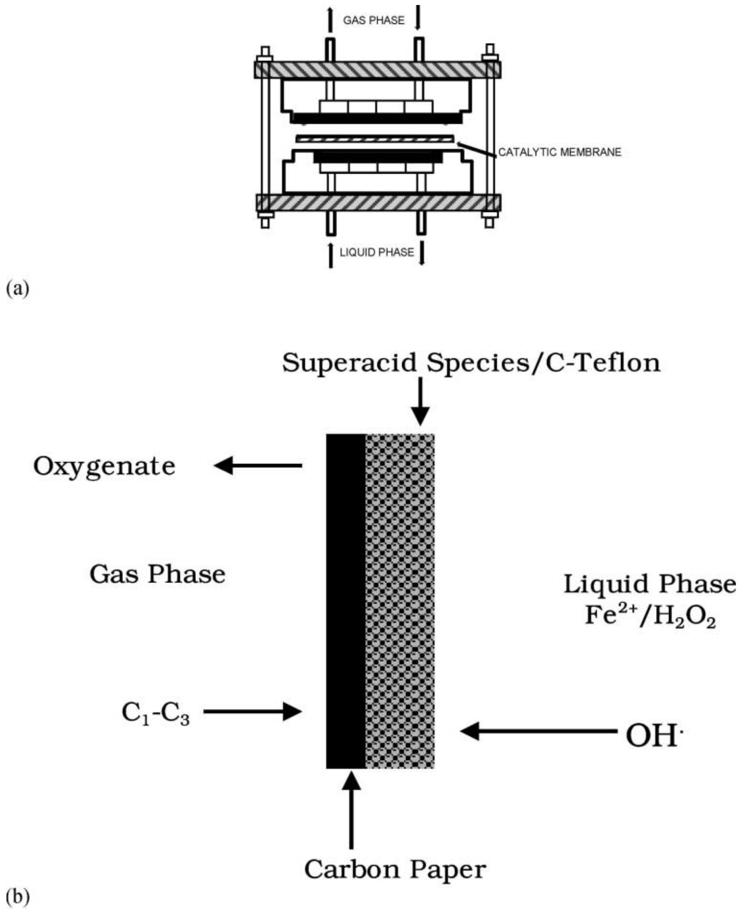


Fig. 1. Three phase catalytic membrane reactor (3PCMR): (a) schematic of 3PMCR; (b) section of the catalytic membrane.

of teflon) on carbon paper and subsequent activation at 300°C in air. $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ was obtained by the titration of $H_3PW_{12}O_{40}$ solution with an aqueous solution of Cs_2CO_3. The precipitated salt was washed and dried at 70°C.

The chemical composition and the sample code of the catalytic membranes are summarised in Table 1.

2.2. Three-phase catalytic membrane reactor (3PCMR) and experimental set-up

Catalytic membranes have been tested in the 3PCMR described elsewhere [12]. The membrane was sandwiched between two Teflon plates with the catalyst side turned towards the liquid phase (Fig. 1). During reaction care was taken to maintain a pressure difference of 3 kPa between the gas and the liquid sides in order to control the filling of the pores in the hydrophobic catalytic layer with gas and to control the physical damage to the membrane.

Catalytic measurements have been performed in the range 80–120°C with alkane–nitrogen on mixture ($P_{\mathrm{hydr}}/P_{\mathrm{N_2}} = 3.7$) at 140 kPa absolute pressure operating in batch mode with separate recirculation of both the gas and the liquid phases. The liquid phase was constituted by a H_2O_2 solution (7.25×10^{-2}–1.17 mol/l) containing Fe^{2+} ions or Fe^{3+} ($[Fe^{n+}] = 1 \times 10^{-6}$–$2.7 \times 10^{-4}$ mol/l).

Oxygenates formed during reaction were trapped at 2°C down-stream of the reactor and analysed by a GC equipped with an FID detector using a Carbopack B 3% SP1500 column ($l = 2.5$ m; i.d. = 2 mm) operating at 50°C. H_2O_2 concentration change was followed by periodical titration with permanganate solution (0.1 mol/l).

2.3. Membrane characterisation

2.3.1. NH_3 adsorption

The acidic properties of the membranes were comparatively evaluated by ammonia chemisorption tests carried out in a Micromeritics 2900 TPR/TPD unit equipped with TCD. Prior to each chemisorption test the samples were outgassed at 120°C for 1 h in He flow, then the temperature was fixed at 45°C. Subsequently, NH_3 pulses were injected into the feed stream up to saturation.

2.3.2. Scanning electron microscopy (SEM–EDX)

In order to evaluate the morphological features and the surface chemical composition of the catalytic layer, Nafion-based membranes were analysed by scanning electron microscopy using a Philips XL20 equipped with EDS micro-probe which allowed to accomplish the surface chemical map.

3. Results and discussion

3.1. Characterisation of catalytic membranes

3.1.1. NH_3 adsorption

In Table 2 are listed the values of NH_3 uptake of several catalytic membranes. By comparing the acidic properties of various membranes with the same surface loading (1 mg/cm^2) of the active species, it comes out that the Nafion-based sample (A-3 sample) is much less acidic than HPMo and HPW ones. For HPMo series, the NH_3 uptake increases with loading increasing from 20 to 40 wt.% (C-2 and C-6 samples) and it levels off for 60 wt.% loaded membrane (C-4 sample). HPW membrane (D-2 sample) shows a similar NH_3 uptake of the same loaded HPMo one (C-2 sample), while the amount of NH_3 adsorbed on CsM membrane (referred to the unity weight of active species), in spite of its high surface loading, is of the same order of magnitude of that of Nafion-based membranes.

3.1.2. Scanning electron microscopy

The surface morphology of the bare system is rather regular, while the surface catalytic layer of Nafion membranes is characterised by the presence of contiguous islands delimited by deep cracks [9]. Such a disgregation of the surface layer could be

Table 2
NH_3 uptake data of various superacid membranes

Sample	Active species loading (mg/cm^2)	NH_3 uptake (μmol/g_{memb})
A-3	1.02	6.01
C-2	1.02	36.2
C-4	2.0	126.7
C-6	3.05	133.6
D-2	1.02	20.7
CsM	8.0	78.4

Table 3
SEM–EDX analysis of carbon-supported Nafion catalytic membranes

Sample	C (mol %)	O (mol %)	F (mol %)	S (mol %)	Cl (mol %)	K (mol %)
Bare-membrane	99.196	0.178	0.597	0.017	0.008	0.001
A-1	97.491	0.296	2.048	0.122	0.010	0.017
A-2	95.593	0.503	3.571	0.251	0.015	0.045
A-3	89.381	1.246	8.599	0.633	0.020	0.100

associated to the change in the volume of catalytic layer occurring during the rapid evaporation of solvent in the drying step of the membranes. The surface morphology of Nafion membranes depends upon the Nafion loading. In addition, the surface chemical composition of Nafion-based membranes has been evaluated by EDX measurements. The data reported in Table 3, in terms of atomic percentage of the various elements, indicate a progressive decrease of C and corresponding increase in O, F, and S with Nafion loading. The increase of S with Nafion loading reflect the increase in the concentration of sulphonic group ($-SO_3H$) which likely controls the acidic properties of the Nafion membranes.

3.2. Selective oxidation of light alkanes

We have previously disclosed that Nafion-based membranes mediated by Fe^{2+}/H_2O_2 Fenton system catalyse the selective oxidation of C_1–C_3 alkanes to the corresponding oxygenates in the 3PCMR [8]. As Nafion membranes likely act according to a similar pattern in activating the C_1–C_3 light alkanes, a general understanding of the features of the 3PCMR as well as of the factors and operating parameters controlling the catalyst performance and reaction pathway has been gained by devising and undertaking several series of experiments using CH_4, C_2H_6 or C_3H_8 as "model" molecule. Namely, the influence of the nature and loading of the superacid species has been evaluated in the selective oxidation of methane, the features of the 3PCMR in allowing product distribution in gas and liquid phase and the consequent continuous product separation are shown in the selective oxidation of ethane, while basic insights for the reaction pathway have been achieved in the selective oxidation of propane.

3.2.1. Selective oxidation of methane

Nafion-based membranes catalyse the selective partial oxidation of methane to methanol with H_2O_2 in the presence of Fe^{2+} ions in the T_R range 80–110°C [8]. The selectivity to CH_3OH is 100% in all the adopted experimental conditions.

In order to evaluate the functionality of the different superacid catalytic systems in the selective oxidation of light paraffins, the activity of the various superacid catalytic membranes has been comparatively determined in the selective oxidation of methane with H_2O_2in the presence of Fe^{2+} at 80°C. The values of reaction rate ($r_1 = 10^{-9}\,\mathrm{mol/s\,g_{memb}}$ and $r_2 = 10^{-9}\,\mathrm{mol/s\,g_{active\,species}}$), shown in Table 4, indicate that the activity of the Nafion-based membrane (sample A-3, $r_1 = 2.6 \times 10^{-9}\,\mathrm{mol/s\,g_{memb}}$) is one order of magnitude higher than that of HPMo, HPW and CsM membrane samples ($r_1 = 0.1$–$1.2 \times 10^{-9}\,\mathrm{mol/s\,g_{memb}}$). Such a different catalytic

Table 4
Selective oxidation of CH_4 to methanol on different carbon-supported catalytic membranes[a]

Sample	Active species	Reaction rate (r_1) ($10^{-9}\,\mathrm{mol/s\,g_{memb}}$)	Reaction rate (r_2) ($10^{-9}\,\mathrm{mol/s\,g_{active\,species}}$)
A-3	Nafion/C	2.60	1.15
C-4	HPMo/C	0.2	0.45
D-2	HPW/C	0.1	0.195
CsM	$H_{0.5}Cs_{2.5}PW_{12}O_{40}$	1.2	0.675

[a] T_R: 80°C; $[H_2O_2] = 0.29\,\mathrm{mol/l}$; $[Fe^{2+}] = 10.8 \times 10^{-5}\,\mathrm{mol/l}$.

behaviour cannot be rationalised in terms of acidic properties of the various systems as probed by NH_3 adsorption. In fact, among the investigated membranes (Table 4), A-3 sample is characterised by the lowest NH_3 uptake whilst it reveals the highest catalytic activity. Then, it can be inferred that the concentration of acidic sites, which can be related with the NH_3 uptake, does not control the catalytic performance of the superacid-based membranes in the selective oxidation of light paraffins. However, neither the acidic strength of the various active species, expressed in terms of Hammett function value (Ho), can be invoked to rationalise the catalytic behaviour of such catalytic membranes. Indeed, on the basis of the Ho values, heteropolyacid-based systems (HPMo, HPW and CsM membranes) should be stronger acids than Nafion [13]. Therefore, the reason for the different catalytic behaviour of our system could lie in their different stability in H_2O_2media. Nafion is a very stable catalyst in the presence of H_2O_2 [13], while heteropolyacid system could react with H_2O_2 to form peroxophosphates ($PW_xO_y{}^{2-}$; $PMo_xO_y{}^{2-}$) which do not enable any catalytic action [13].

Considering the Nafion-based membrane series, the influence of the Nafion loading on the activity of the differently loaded membrane at 80°C has been evaluated. The reaction rate for weight unity of both Nafion and membrane versus the surface Nafion loading is presented in Fig. 2. For Nafion loading higher than 0.51 mg/cm^2 a progressive decrease in the catalytic activity occurs as a consequence of a decreased Nafion dispersion and availability. However, a linear relationship between the reaction rate, referred to the weight unity of the membrane, and the concentration of acidic sites (–SO_3–H) estimated by EDX analysis is found (Fig. 3). This linear trend is diagnostic of the fact that

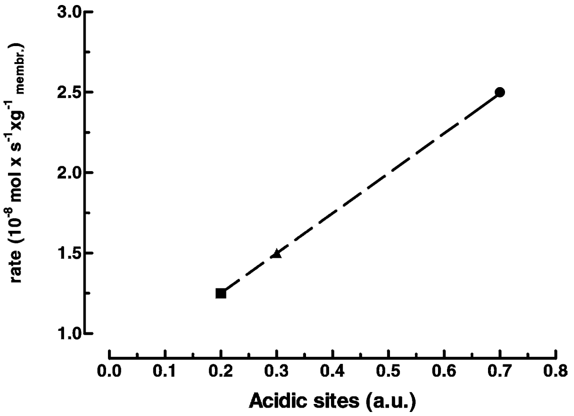


Fig. 3. Selective oxidation of CH_4 to CH_3OH on Nafion-supported catalytic membranes. Reaction rate as function of concentration of acidic sites. (■) Sample A-1 (5% Nafion/C); (●) sample A-2 (10% Nafion/C) and (▲) sample A-4 (30% Nafion/C). $T_R = 80°C$; $[H_2O_2] = 0.29$ mol/l; $[Fe^{2+}] = 10.8 \times 10^{-5}$ mol/l.

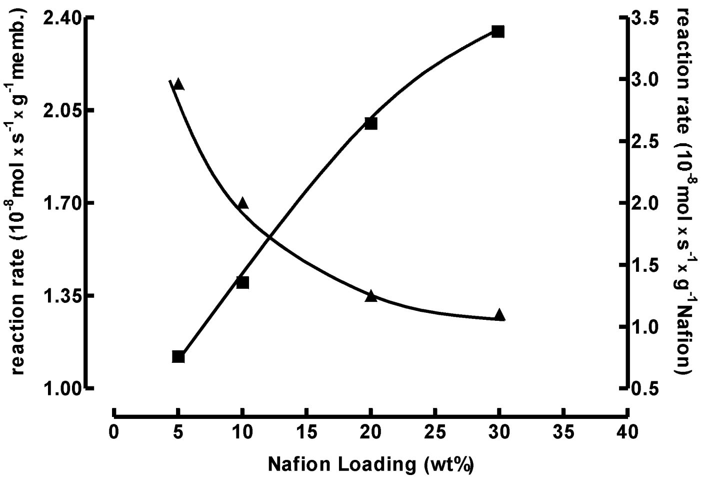


Fig. 2. Selective oxidation of CH_4 to CH_3OH on Nafion-supported catalytic membranes. Influence of Nafion loading on reaction rate. $T_R = 80°C$; $[H_2O_2] = 0.29$ mol/l; $[Fe^{2+}] = 10.8 \times 10^{-5}$ mol/l. (■) Reaction rate referred to the membrane weight; (▲) reaction rate referred to the Nafion weight.

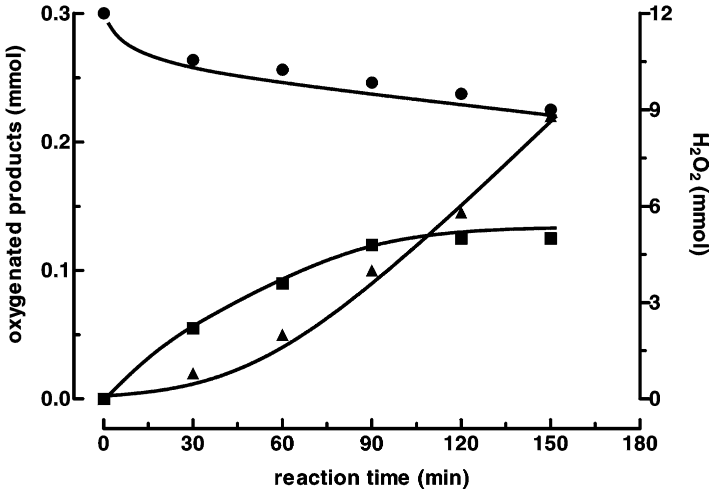


Fig. 4. Partial oxidation of C_2H_6 on 20% Nafion/C catalytic membrane. Product distribution in the gas and liquid phases as a function of reaction time: $T_R = 100°C$; $[Fe^{2+}] = 5.4 \times 10^{-5}$ mol/l; $[H_2O_2] = 0.29$ mol/l. (●) H_2O_2; (■) liquid phase; (▲) gas phase.

the reaction occurs at the exposed surface (liquid side surface) of the membrane and therefore the fraction of active species distributed into the pore structure of the catalytic layer, being inaccessible to the gas reactant, is not catalytically effective.

3.2.2. Selective oxidation of ethane

The selective partial oxidation of ethane with H_2O_2 on Nafion membranes in the presence of Fe^{2+} in the range 80–120°C, leads to the formation of acetaldehyde (C_2H_4O) and ethanol (C_2H_6O). No CO_2 has been observed.

The result of a typical run at 100°C (membrane sample A-3; $[Fe^{2+}] = 5.6 \times 10^{-5}$ mol/l and $[H_2O_2] = 0.29$ mol/l) expressed in terms of cumulative amount of oxygenated products (C_2H_4O and C_2H_6O) formed in both liquid and gas phases and H_2O_2 concentration versus the reaction time is reported in Fig. 4 . The selectivity values to C_2H_4O and C_2H_6O were 88 and 12%, respectively. It can be observed that at the beginning of the reaction the oxygenated products distribute in both gas and liquid phases until their concentration in liquid phase reaches the saturation equilibrium value, afterwards all products formed are continuously collected in gas phase.

No catalytic activity decay has been experienced during the reaction time (150–200 min), besides the stability of the Nafion membrane catalyst has been positively checked performing several reproducibility tests. Thus, on the whole it can be stated that Nafion is well anchored on carbon support and the catalytic performance of Nafion membranes is not affected either by Fe^{2+} or by H_2O_2.

The time of the attainment of saturation equilibrium concentration of oxygenated products in liquid phase (t_c) depends upon the reaction temperature (T_R). Higher the T_R lower is t_c, namely t_c at 80 and 110°C is 150 and 90 min, respectively. This finding could be explained considering that the membranes are not perm-selective, therefore the permeation of reaction products from the liquid phase containing the oxidant is controlled by their boiling points. As a consequence, in the gas phase relevant amount of H_2O (b.p. = 100°C) and negligible amount of H_2O_2 (b.p. = 152.4°C) are collected together with C_2H_4O (b.p. = 20.2°C) and C_2H_6O (b.p. = 78.4°C).

3.2.3. Selective oxidation of propane

The selective oxidation of propane on Nafion catalytic membrane mediated by Fe^{2+}/H_2O_2 Fenton system in the T_R range 80–110°C leads to the formation of isopropanol, *n*-propanol, acetone and propionic aldehyde. No CO_x have been detected. The product selectivity is controlled by reaction temperature, Fe^{2+} and H_2O_2 concentration.

The influence of the reaction temperature on product distribution is shown in Fig. 5. At 80°C the selectivity value to isopropanol, propionic aldehyde, *n*-propanol

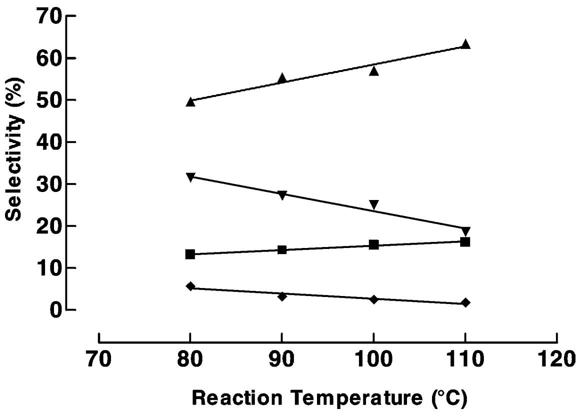


Fig. 5. Selective oxidation of propane on 20% Nafion/C based catalytic membrane. Influence of reaction temperature on the selectivity to oxygenated products: (▲) acetone; (■) propionic aldehyde; (▼) isopropanol, (◆) *n*-propanol. $[Fe^{2+}] = 4 \times 10^{-5}$ mol/l and $[H_2O_2] = 0.3$ mol/l.

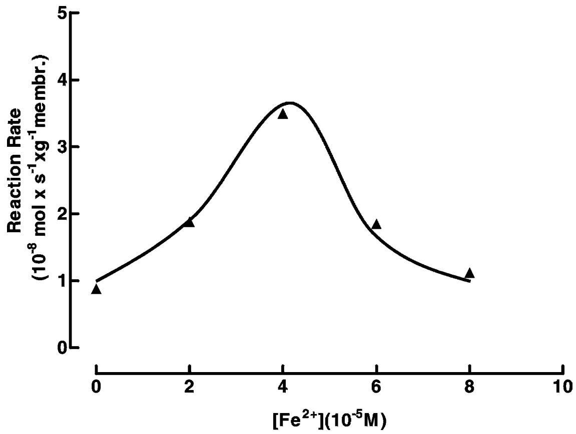
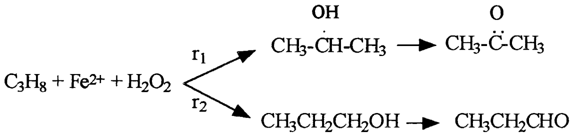


Fig. 6. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of $[Fe^{2+}]$ on reaction rate. $T_R = 80$°C and $[H_2O_2] = 0.3$ mol/l.

and acetone is 32, 13, 3 and 52, respectively. A slight rise in the selectivity to acetone and propionic aldehyde and a concomitant decrease in the selectivity to isopropanol and *n*-propanol with T_R have been experienced. The pattern of the product selectivity likely accounts for a parallel — consecutive reaction scheme



where the path r_1, involving the activation of the secondary C atom and resulting in the formation of isopropanol and acetone, is more effective than that r_2 related to the functionalisation of the terminal C–H bond leading to *n*-propanol and propionic aldehyde. On the whole, in the experimental range investigated, about 75% of the oxygenated products are obtained through the r_1 path.

The influence of Fe^{2+} and H_2O_2 concentration on the reaction rate has been evaluated at 80°C performing two series of experiments at different $[Fe^{2+}]$ and $[H_2O_2]$. The results outlined in Fig. 6 indicate that $[Fe^{2+}]$ enhances the reaction rate according to a volcano-shaped relationship whose maximum corresponds to a $[Fe^{2+}]$ of 4×10^{-5} mol/l. The promoting role of Fe^{2+} is likely associated with the generation of OH radicals or nucleophilic adducts $[Fe^{II}OOH(H_2O)_6{}^{+}–H_3O^{+}]$ via the reaction paths

$$Fe^{II}(H_2O)_6{}^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{III}(H_2O)_6{}^{3+} \quad (1)$$

$$Fe^{II}(H_2O)_6{}^{2+} + H_2O_2 \rightarrow [Fe^{II}OOH(H_2O)_6{}^{+}–H_3O^{+}] \quad (2)$$

which act as primary reactive intermediates [10].

Blank experiments carried out on bare membrane mediated by the Fe^{2+}/H_2O_2 Fenton system have indicated that reaction does not occur, then in our reaction medium a synergetic action between the superacid active species and primary reactive intermediates is the key factor for activating the C_3H_8 molecule. When Fe^{3+} instead of Fe^{2+} is used for activating H_2O_2, a volcano relationship between $[Fe^{3+}]$ and reaction rate is still observed. However, Fe^{3+} ions, in the same operating conditions, enable lower reaction rate values. The difference experienced when Fe^{3+} or Fe^{2+} ions are used likely arises from the different efficiency of the Fe^{3+}/H_2O_2 and Fe^{2+}/H_2O_2 systems in generating active intermediates.

In order to further probe the nature of the reaction, a series of experiments has been performed by adding different amounts of Cl^- ions to the liquid phase during the reaction. The addition of Cl^- ions implies a sudden drop of the reaction rate. As shown in Fig. 7

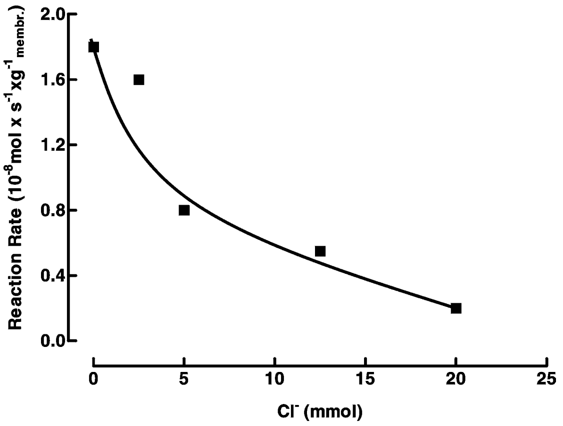


Fig. 7. Selective oxidation of propane on 20% Nafion/C catalytic membrane. Influence of Cl^- ions added to the liquid phase on the reaction rate. $T_R = 80°C$; $[Fe^{2+}] = 4 \times 10^{-5}$ mol/l; $[H_2O_2] = 0.29$ mol/l.

the lowering in reaction rate depends upon the amount of Cl^- added being more significant at the lower Cl^- extent (<10 mmol). Such finding clearly indicates that Cl^- act as scavenger of any radical species present in the reaction media and directly involved in the reaction scheme.

On the basis of such results it can be inferred that the reaction proceeds according to a mechanism which involves the activation of propane on superacid sites (S^*) and the subsequent reaction of activated paraffin with the primary reactive intermediate ($OH^\bullet$ or $Fe^{II}OOH(H_2O)_6{}^+–H_3O^+$)

$$C_3H_8 + S^* \rightarrow C_3H_8{}^* \qquad \text{(a)}$$

$$\begin{aligned} &C_3H_8{}^* + OH^\bullet \text{ or } [Fe^{II}OOH(H_2O)_6{}^+–H_3O^+] \\ &\quad \rightarrow S^* + CH_3CH(OH)CH_3 \\ &\qquad + CH_3CH_2CH_2OH \qquad \text{(b)} \end{aligned}$$

By two series of experiments performed in standard reaction conditions ($T_R = 80°C$; $[H_2O_2] = 0.3$ mol/l; $[Fe^{2+}] = 4 \times 10^{-5}$ mol/l), using isopropanol and *n*-propanol (0.1 mol/l) as reagent in liquid phase it has been ascertained that acetone and propionaldehyde are the products of the further oxidation of isopropanol and *n*-propanol, respectively.

The reaction pathway above proposed for the selective oxidation of propane can be considered as a general reaction model accounting for the activation of light alkanes on superacid catalytic membranes in the 3PCMR. In order to explain the volcano-shaped relationship between reaction rate and Fe^{2+} concentration (Fig. 6), the reaction mechanism of the $Fe^{2+}–H_2O_2$ Fenton system could be invoked [14]:

$$Fe^{2+} + H_2O_2 \rightarrow HO^\bullet + OH^- + Fe^{3+} \qquad (3)$$

$$HO^\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (4)$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2{}^\bullet + H_2O \qquad (5)$$

$$HO_2{}^\bullet + Fe^{2+} \rightarrow OH_2{}^- + Fe^{3+} \qquad (6)$$

$$HO_2{}^\bullet + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+} \qquad (7)$$

From this reaction network it emerges that OH radicals generated in reaction (3) can further react with Fe^{2+} to form OH^- and Fe^{3+} (reaction (4)) and with H_2O_2 to form $HO_2{}^\bullet$ and H_2O (reaction (5)). According to this scheme, it can be assumed that in our reaction system activated paraffin ($C_3H_8{}^*$), Fe^{2+} and H_2O_2 compete for OH radicals. The influence of $[H_2O_2]$ on reaction rate is presented in Fig. 8. The reaction rate rises with H_2O_2 concentration up to a value of 1.2 mol/l, while at higher $[H_2O_2]$ no further enhancing effect is observed. Neither the extent nor the trend of the product distribution is significantly affected by both $[Fe^{2+}]$ and $[H_2O_2]$. However, the H_2O_2 yield is intrinsically limited by the reaction mode. Indeed, only a fraction of the primary reactive intermediate generated in the

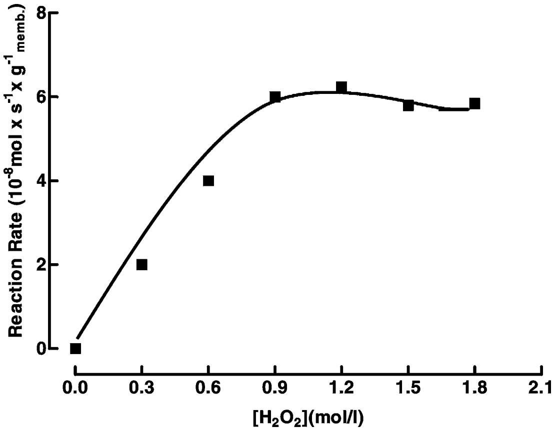


Fig. 8. Selective oxidation of propane on 20% Nafion/C based catalytic membrane. Influence of $[H_2O_2]$ on reaction rate. $T_R = 80°C$ and $[Fe^{2+}] = 4 \times 10^{-5}$ mol/l.

liquid phase reaches the catalyst surface to react with the molecules of activated paraffin ($C_3H_8{}^*$), the majority of (i) OH radicals could further react in the liquid phase with the other components (Fe^{2+}, H_2O_2) of the system according to the above side reactions (4) and (5) or (ii) [$Fe^{II}OOH(H_2O)_6{}^+–H_3O^+$] adducts can react with excess of $Fe^{II}(H_2O)_6{}^{2+}$ according to the following reaction:

$$[Fe^{II}OOH(H_2O)_6{}^{+}–H_3O^{+}] + Fe^{II}(H_2O)_6{}^{2+} \rightarrow 2Fe^{III}(H_2O)_6OH^{2+} + H_2O \qquad (8)$$

The pathway of oxygenated Fenton chemistry in the functionalisation of hydrocarbons in liquid phase systems induced by different metal/hydroperoxide reaction media is still an undecided matter [15]. In fact, controversial insights about both its radical [16,17] or non-radical nature [10,18] have been claimed. No direct experimental evidences and/or clues are at this stage yet available to ascertain the nature of the reaction pathway of the selective oxidation of light paraffins on a Nafion-based membrane in presence of the Fe^{II}/H_2O_2 Fenton system. The work is in progress and the use of other radical scavengers and other ligands of the Fe^{2+} ions should allow to acquire definitive proofs about this peculiar reaction system and to gain insights for the improvement of the efficiency of the three phase catalytic system here proposed for the functionalisation of the light paraffins under mild conditions.

4. Conclusions

- The 3PCMR is a multifunctional reactor device which enables the selective oxidation of light alkanes under mild conditions (T_R, 80–120°C; P_R, 140 kPa).
- The 3PCMR is a peculiar multiphase reactor for light alkanes functionalisation which offers the advantages of the liquid phase oxidation systems along with the continuous product separation and recovery.
- Selective oxidation of C_1–C_3 alkanes to the corresponding oxygenates is attained on Nafion-based catalytic membranes mediated by Fe^{2+}–H_2O_2 Fenton system.

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