

# Selective oxidation of propane on a Nafion-based catalytic membrane mediated by Fe<sup>II</sup>–H<sub>2</sub>O<sub>2</sub> Fenton system

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## Abstract

A Nafion-based catalytic membrane was found to be active and highly selective for the partial oxidation of propane to the corresponding C<sub>3</sub> oxygenates under mild conditions ( $T_R$ , 80–110°C;  $P_R$ , 140 kPa) in the presence of the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> Fenton system. A reaction pathway accounting for the electrophilic hydroxylation of the C–H bond on the superacid sites and subsequent reaction of the activated propane molecule with primary reactive intermediates, generated from the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> system, has been proposed. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Membrane reactors; Superacid catalytic membrane; Propane selective oxidation; Oxygenated products

## 1. Introduction

The selective oxidation of methane and light alkanes (C<sub>2</sub>–C<sub>3</sub>) 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 value-added 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 that 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, first proposed by Olah and Schlosberg [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 transition metal electrophiles, of which Pt(II)Cl<sub>4</sub><sup>–</sup> has been the most extensively studied [4]. Periana et al. [5] have

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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 [6] proposed various functionalisation reactions of light alkanes based on the use of Pd(II) as catalytic agent, in strongly acidic media or  $\text{H}_2\text{O}_2$  in anhydride media, to give alkyl esters. Strong solid acids are largely studied as active species in the catalytic conversion of light alkanes in presence of  $\text{H}_2\text{O}_2$  [2,7]. Among this class of catalysts, we have reported that Nafion-based catalytic membranes, in presence of the Fe(II)– $\text{H}_2\text{O}_2$  Fenton system, catalyse the selective oxidation of methane to methanol [8] and ethane to ethanol and acetaldehyde [9]. The metal/hydroperoxide induced activation of  $\text{O}_2$  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) that 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 immobilized 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].

Then, in this letter, we report preliminary results on the selective oxidation of propane to  $\text{C}_3$  oxygenates on a Nafion-based catalytic membrane in the presence of the Fe<sup>II</sup>– $\text{H}_2\text{O}_2$  Fenton system in the 3PCMR.

## 2. Experimental

### 2.1. Nafion-supported catalytic membrane

A 20% Nafion-supported catalytic membrane has been prepared by incipient wetness impregnation of a bare membrane (BET, 219  $\text{m}^2 \text{g}^{-1}$ ), obtained by deposition of a carbon–teflon paste on carbon paper and subsequent activation at 300°C in  $\text{N}_2$  atmosphere, with an isopropanol solution of Nafion-H and subsequent drying at 80°C under vacuum [9]. The surface loading of carbon was 4.86  $\text{mg}/\text{cm}^2$ , while the teflon content on carbon weight basis, was 20%. The Nafion loading (20 wt.%) is referred to the weight of the thin layer constituted by carbon and teflon. The thickness of the catalytic membrane was 0.40 mm.

### 2.2. 3PCMR and procedure

The 20 wt.% Nafion-supported catalytic membrane has been tested in the 3PCMR described elsewhere [8,9,12]. The membrane was sandwiched between two teflon plates with the catalyst side turned towards the liquid phase. 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 prevent the physical dam-

age of the membrane. Catalytic measurements have been performed in the range 80–110°C with propane–nitrogen–helium mixture ( $P_{C_3H_8}/P_{N_2}/P_{He} = 8/0.8/1.2$ ) at 140 kPa absolute pressure operating in batch mode with separate recirculation of both gas and liquid phases. The liquid phase (pH, 3.2) was constituted by a  $H_2O_2$  solution ( $[H_2O_2]$ , 0.3–1.8 mol/l) containing  $Fe^{2+}$  ions ( $[FeSO_4]$ ,  $2-8 \times 10^{-5}$  mol/l). Oxygenates formed during reaction were trapped at 2°C down stream of the reactor and analysed by a GC equipped with a FID detector using a Carbowax 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 ( $[MnO_4^-]$ ,  $1 \times 10^{-2}$  mol/l). Reaction evolution was monitored by GC analysis of  $C_3H_8$  in gas phase and oxygenated products in both liquid phase and condensate withdrawn from the gas phase.

### 3. Results and discussion

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  $CO_x$  has

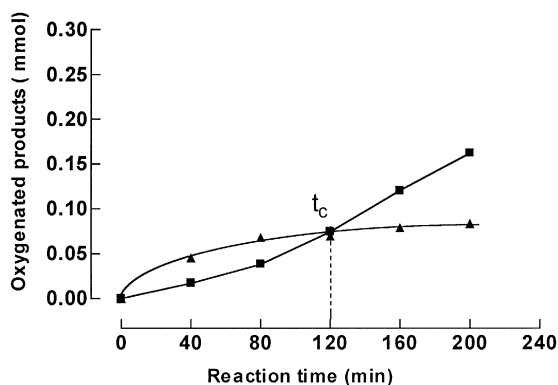


Fig. 1. Selective oxidation of propane on Nafion-based catalytic membrane. Product distribution in the gas and liquid phases vs. reaction time: (▲) liquid phase; (■) gas phase.  $T_R = 90^\circ C$ ;  $[Fe^{2+}] = 4 \times 10^{-5}$  mol/l and  $[H_2O_2] = 0.3$  mol/l.

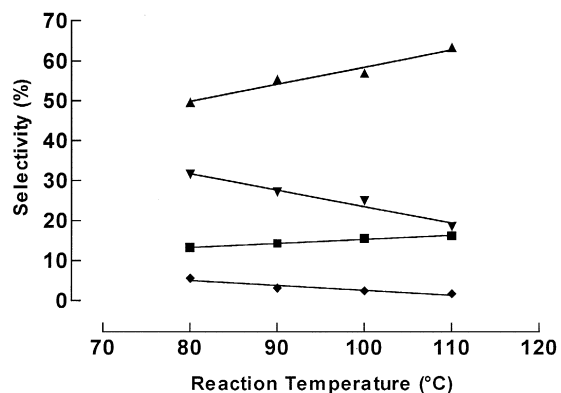
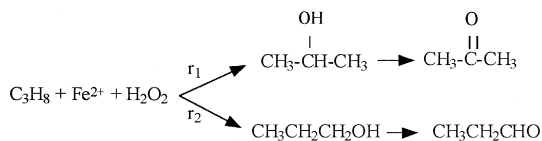


Fig. 2. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of reaction temperature on the selectivity to oxygenated products: (▲) acetone; (■) propionic aldehyde; (▼) isopropanol; (●) *n*-propanol.  $[Fe^{2+}] = 4 \times 10^{-5}$  mol/l and  $[H_2O_2] = 0.3$  mol/l.

been detected. The product selectivity is controlled by reaction temperature,  $Fe^{2+}$  and  $H_2O_2$  concentration. The reaction products once formed on the catalytic membrane are distributed in both liquid and gas phases. The evolution of a typical run at 90°C is depicted in Fig. 1 in terms of cumulative amount of oxygenated products accumulated in liquid phase and extracted from the gas phase as a function of the reaction time. The extent of products in the liquid phase rises until 120 min; afterwards, all the products once formed permeate in the gas phase where they are recovered by condensation. The relative distribution of products in the two phases and the value of the reaction time ( $t_c$ ) at which the maximum amount of products in liquid phase is attained depend upon  $T_R$ . Probatory data on the catalytic functionality of the Nafion membrane have been achieved by evaluating reaction rate and product distribution at reaction times higher than  $t_c$ .

The influence of the reaction temperature on product distribution is shown in Fig. 2. At 80°C, the selectivity value to isopropanol, propionic aldehyde, *n*-propanol 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 the  $r_2$  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  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentration on the reaction rate has been evaluated at  $80^\circ\text{C}$  performing two series of experiments at different  $[\text{Fe}^{2+}]$  and  $[\text{H}_2\text{O}_2]$ . The results outlined in Fig. 3 indicate that  $[\text{Fe}^{2+}]$  enhances the reaction rate according to a volcano-shaped relationship whose maximum corresponds to a  $[\text{Fe}^{2+}]$  of  $4 \times 10^{-5}$  mol/l. The promoting role of  $\text{Fe}^{2+}$  is likely associated with the genera-

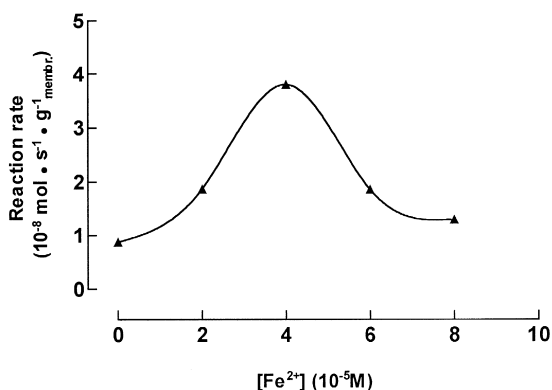
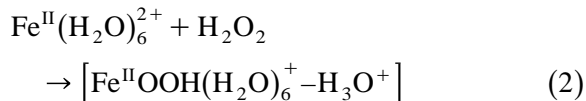
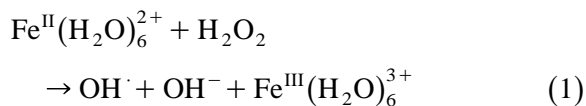


Fig. 3. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of  $[\text{Fe}^{2+}]$  on reaction rate.  $T_{\text{R}} = 80^\circ\text{C}$  and  $[\text{H}_2\text{O}_2] = 0.3$  mol/l.

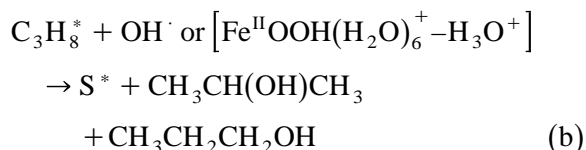
tion of OH radicals or nucleophilic adducts  $[\text{Fe}^{\text{II}}\text{OOH}(\text{H}_2\text{O})_6^+ - \text{H}_3\text{O}^+]$  via the reaction paths



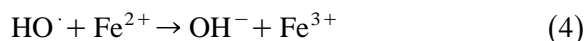
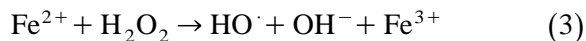
which act as primary reactive intermediates [10].

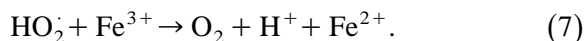
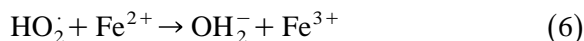
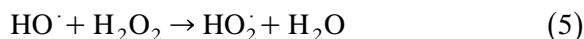
Blank experiments carried out on bare membrane mediated by the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  Fenton system have indicated that reaction does not occur, then in our reaction medium, a synergetic action between the superacid active species and primary reactive intermediates is the key factor for activating the  $\text{C}_3\text{H}_8$  molecule.

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 ( $\text{S}^*$ ) and the subsequent reaction of activated paraffin with the primary reactive intermediate ( $\text{OH}^\cdot$  or  $[\text{Fe}^{\text{II}}\text{OOH}(\text{H}_2\text{O})_6^+ - \text{H}_3\text{O}^+]$ )

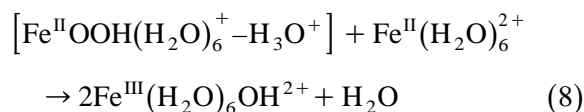


By two series of experiments performed in standard reaction conditions ( $T_{\text{R}} = 80^\circ\text{C}$ ;  $[\text{H}_2\text{O}_2] = 0.3$  mol/l;  $[\text{Fe}^{2+}] = 4 \times 10^{-5}$  mol/l), using isopropanol and *n*-propanol (0.1 mol/l) as reagent in liquid phase, it has been ascertained that acetone and propionaldehyde are the products of the further oxidation of isopropanol and *n*-propanol, respectively. In order to explain the volcano-shaped relationship between reaction rate and  $\text{Fe}^{2+}$  concentration (Fig. 3), the reaction mechanism of the  $\text{Fe}^{2+} - \text{H}_2\text{O}_2$  Fenton system could be invoked [13]





From this reaction network, it emerges that OH radicals generated in reaction (3) can further react with  $\text{Fe}^{2+}$  to form  $\text{OH}^-$  and  $\text{Fe}^{3+}$  (reaction (4)) and with  $\text{H}_2\text{O}_2$  to form  $\text{HO}_2\cdot$  and  $\text{H}_2\text{O}$  (reaction (5)). According to this scheme, it can be assumed that in our reaction system activated paraffin ( $\text{C}_3\text{H}_8^*$ ),  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  compete for OH radicals. The influence of  $[\text{H}_2\text{O}_2]$  on reaction rate is presented in Fig. 4. The reaction rate rises with  $\text{H}_2\text{O}_2$  concentration up to a value of 1.2 mol/l, while at higher  $[\text{H}_2\text{O}_2]$ , no further enhancing effect is observed. Neither the extent nor the trend of the product distribution is significantly affected by both  $[\text{Fe}^{2+}]$  and  $[\text{H}_2\text{O}_2]$ . However, the  $\text{H}_2\text{O}_2$  yield is intrinsically limited by the reaction mode. Indeed, only a fraction of the primary reactive intermediate generated in the liquid phase reaches the catalyst surface to react with the molecules of activated paraffin ( $\text{C}_3\text{H}_8^*$ ), the majority of (i) OH radicals could further react in the liquid phase with the other components ( $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ ) of the system according to the above side reactions (4) and (5), or (ii)  $[\text{Fe}^{\text{II}}\text{OOH}(\text{H}_2\text{O})_6^+ - \text{H}_3\text{O}^+]$  adducts can react with excess of  $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$  according to the following reaction



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 [14]. In fact, controversial insights about both its radical [15,16] or non-radical nature [10,17] 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

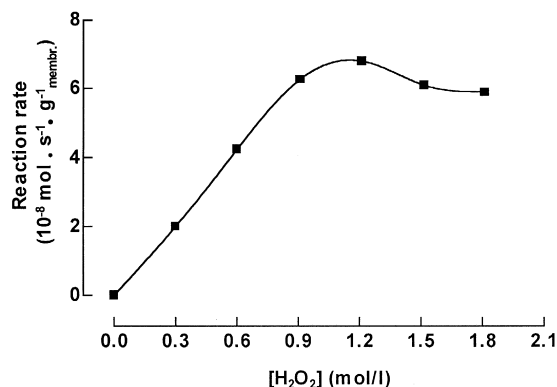


Fig. 4. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of  $[\text{H}_2\text{O}_2]$  on reaction rate.  $T_R = 80^\circ\text{C}$  and  $[\text{Fe}^{2+}] = 4 \times 10^{-5} \text{ mol/l}$ .

light paraffins on a Nafion-based membrane in presence of the  $\text{Fe}^{\text{II}}/\text{H}_2\text{O}_2$  Fenton system. The work is in progress, and the use of both radical scavengers and other ligands of the  $\text{Fe}^{2+}$  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 proposed here for the functionalisation of the light paraffins under mild conditions.

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