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Partial oxidation of propane on Nafion supported catalytic membranes

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Abstract

Nafion supported catalytic membranes were found to be effective in the partial oxidation of propane to oxygenates with H_2O_2 in the presence of Fe^{2+} under mild conditions. The influence of $[Fe^{2+}]$ and $[H_2O_2]$ on the reaction rate and product distribution in the temperature range 80–110°C has been ascertained. A reaction pathway involving the electrophilic activation of propane on superacid sites and subsequent reaction of the activated propane molecules with OH radicals generated by Fe^{2+}/H_2O_2 Fenton system is discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic membrane; Nafion; Fenton system

1. Introduction

The development of one-step processes for the conversion of light paraffins (C_1–C_3) into liquid products is one of the most crucial topics in heterogeneous catalysis. Indeed, the catalytic activation and/or the functionalisation of the C–H bond generally occurs under very drastic operating conditions (high T_R and high P_R) or in the presence of reactive oxidant. Then the attainment of high selectivity to partial oxidation or oxygenated products is seriously limited owing to their consecutive oxidation reactions.

Apart from the catalytic aspects outlined above, the selective oxidation of light alkanes under mild conditions present 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 by-running reaction systems and the technical development and viability of the liquid phase catalytic approaches.

We have already faced these critical aspects of the selective oxidation of light hydrocarbons 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 system [1–3]. 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.

The aim of this work is to highlight the potential of the 3PCMR in the partial oxidation of propane taken as a reaction model for the selective oxidation of light alkanes under mild conditions, providing basic clues

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Table 1
Physico-chemical properties of the 20 wt.% Nafion/C catalytic membrane

Composition of catalytic layer			Thickness of membrane (mm)	Thickness of catalytic layer (mm)	Average pore size (μm)
Carbon loading	Nafion loading (mg/cm^2)	Teflon loading			
5.1	1.0	1.0	0.56	0.15	0.13

about the functionality of Nafion-based catalysts in the activation of the C–H bond of light alkanes in the presence of the Fe^{2+}–H_2O_2 Fenton system.

2. Experimental

2.1. Catalytic membranes

Membranes were obtained by deposition of the carbon–teflon paste on carbon paper and subsequent activation at 300°C in N_2 atmosphere. Ketjenblack carbon (EC 600 Akzo Chemie, BET SA: 950 m^2/g) was used as support. Nafion-based membranes were obtained by incipient wetness impregnation of the bare membrane with an isopropanol solution of Nafion-H (1100 EW product, Dupont Wilmington, DE) [3]. Some physico-chemical properties of the Nafion-supported catalytic membrane are summarised in Table 1.

2.2. Apparatus and procedure

Catalytic membranes have been tested in the 3PCMR described elsewhere [1]. The membrane was sandwiched between two teflon plates with the catalyst side turned towards the liquid phase. Catalytic measurements have been performed in the range 80–110°C with propane–nitrogen mixture ($P_{C_3H_8}/P_{N_2} = 3.7$) 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 ($[Fe^{2+}]=2\times10^{-5}$–8×10^{-5} mol/l). Oxygenates formed during the reaction were trapped at 2°C downstream 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). Gas phase composition was analysed on-line by automatic sampling with a GC equipped with two-column (Porapak and Molecular Sieves) system and TCD [3].

3. Results and discussion

The selective partial oxidation of propane with H_2O_2 on Nafion membranes in the presence of Fe^{2+} leads to the formation of isopropyl alcohol, propionic aldehyde, *n*-propanol and acetone. No CO_2 has been observed.

The results of typical runs at 80–110°C expressed in terms of cumulative amount of oxygenated products formed in both liquid and gas phases versus the reaction time are reported in Fig. 1. 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. It can be observed that the time (t_c) for the attainment of equilibrium concentration (A, B, C and D) of oxygenated products in liquid phase is inversely related to reaction temperature T_R. Evidently, from the non-permselective nature of the Nafion membrane, the permeation rate of oxygenated products from the liquid to the gas phase is controlled by the reaction temperature.

The influence of the reaction temperature on product distribution is shown in Fig. 2. At 80°C, the selectivity value for isopropyl alcohol, propionic aldehyde, *n*-propanol and acetone results to be 32, 13, 3 and 52, respectively. As the reaction temperature increases, the selectivity to acetone and propionic aldehyde increase, while the selectivity to isopropyl alcohol decreases. Selectivity to *n*-propanol does not seem to be influenced by the reaction temperature. The trend of the selectivity to various reaction products

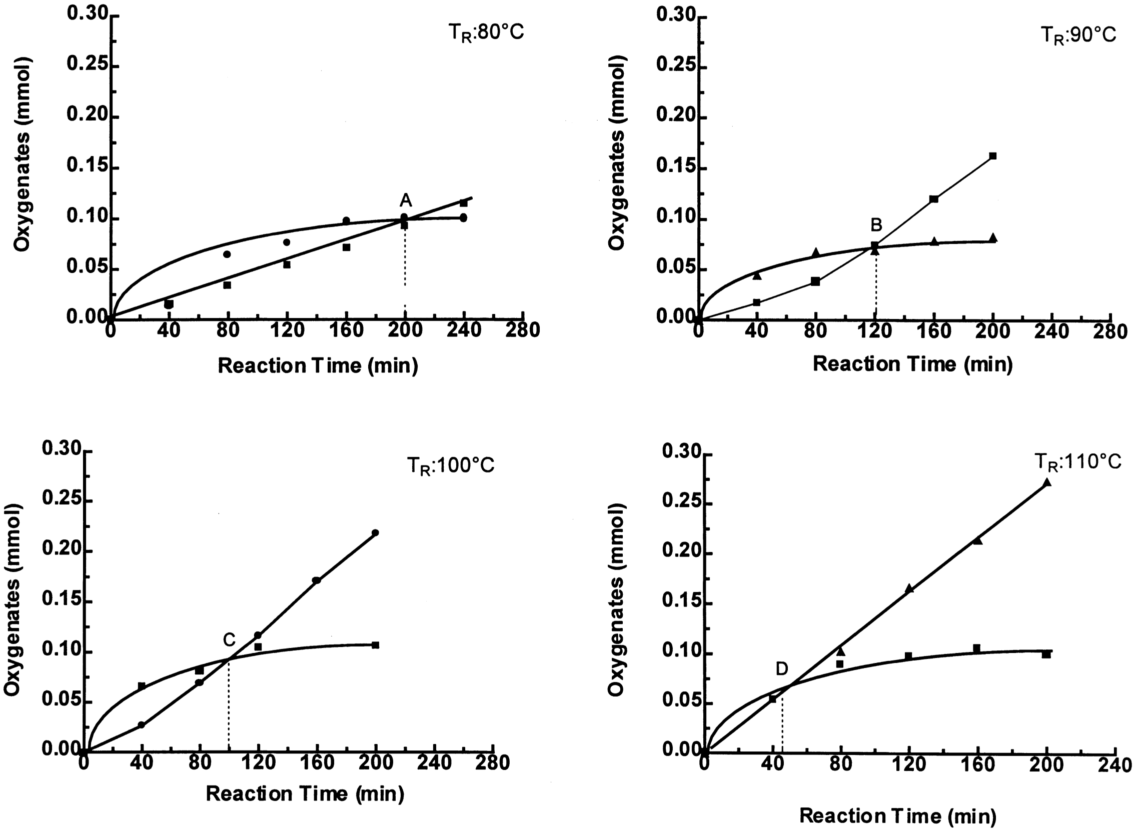


Fig. 1. Selective oxidation of propane on Nafion-based catalytic membrane. Product distribution in the gas and liquid phases vs. reaction time: (▲) gas phase; (■) liquid phase. [Fe^{2+}]=2×10^{-5} mol/l and [H$_2$O$_2$]=0.29 mol/l.

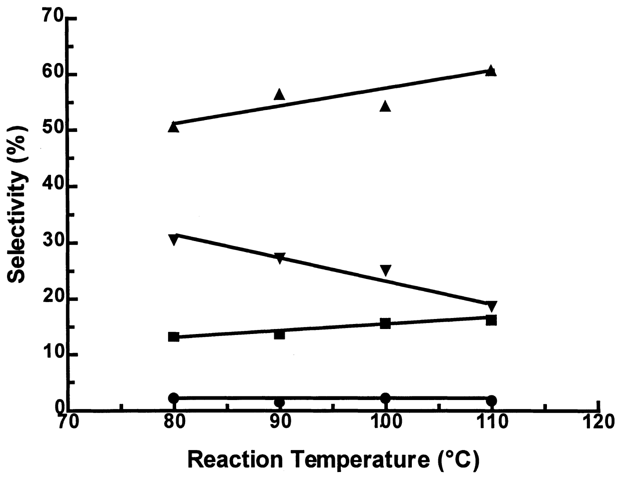


Fig. 2. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of reaction temperature on the selectivity to oxygenated products: (▲) acetone; (■) propionic aldehyde; (▼) isopropyl alcohol; (●) *n*-propanol.

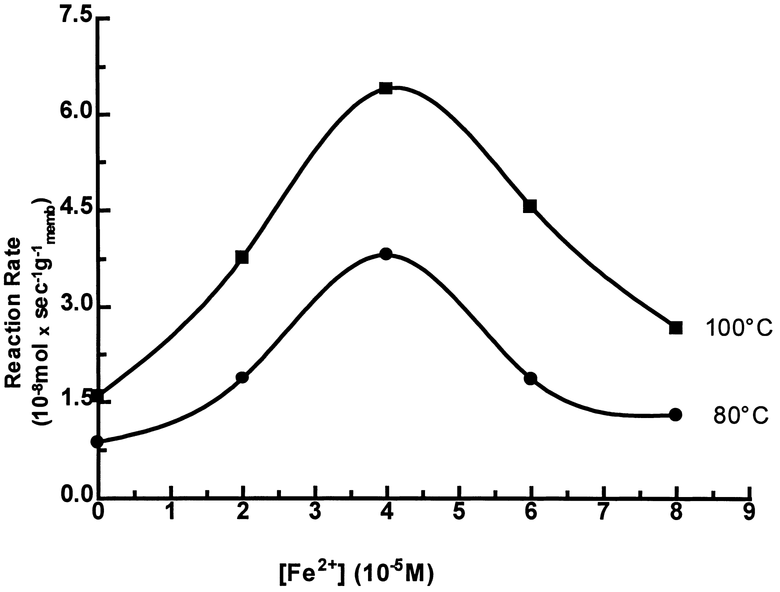


Fig. 3. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of $[Fe^{2+}]$ on the reaction rate at different reaction temperatures.

likely indicates a consecutive reaction path with the isopropyl alcohol being the primary reaction product.

In order to evaluate if the reaction configuration affects the reaction pathway and product distribution, the activity of a Nafion/C catalyst at 80°C has been evaluated in an autoclave system under the same experimental conditions adopted for the catalytic tests in the 3PCMR. In the autoclave system, the selectivity to acetone, always after few minutes of reaction time, was 90%. This finding demonstrates that the use of a catalytic membrane, allowing continuous separation of intermediate products from the liquid phase containing the oxidant, is very effective in preventing further oxidation of intermediate products and thus reaching high yields of partially oxidated light paraffins.

The influence of $[Fe^{2+}]$ on the reaction rate, evaluated at 80 and 100°C, results in a volcano-shaped relationship (Fig. 3) which accounts for the enhancing effect of Fe^{2+} ions on the reaction rate according to a radical mechanism involving the generation of hydroxyl radicals and their subsequent attack to the surface-activated propane molecules [3]. On the other hand, the observed peculiar influence of $[Fe^{2+}]$ on the reaction rate matches well with the Fenton system chemistry. Indeed, at high $[Fe^{2+}]$, OH radicals formed by the reaction $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + OH^\bullet$ further react with Fe^{2+} ($Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^-$) with consequent lowering of both OH radicals concentration and reaction rate.

From the influence of $[H_2O_2]$ on the reaction rate, the results reported in Fig. 4 point out that H_2O_2 concentration up to a value of 1.2 mol/l exerts a positive effect on the reaction rate, while no further enhancing effect is observed at higher $[H_2O_2]$. It can be argued that at high H_2O_2 concentration, OH radicals formed

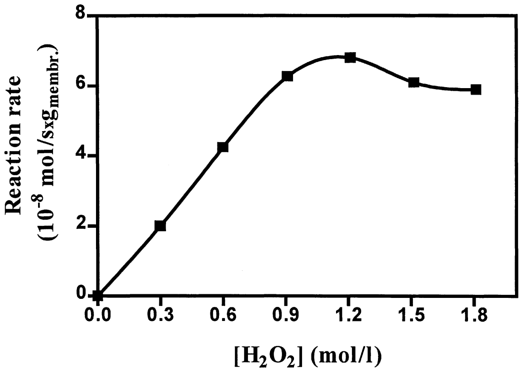


Fig. 4. Selective oxidation of propane on Nafion-based catalytic membrane. Influence of $[H_2O_2]$ on the reaction rate.

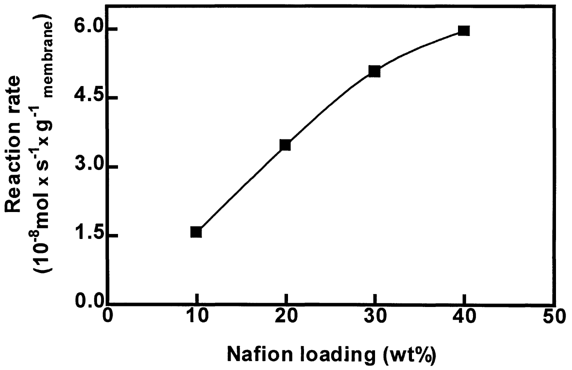
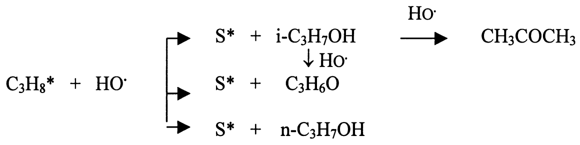


Fig. 5. Selective oxidation of propane on Nafion-based catalytic membrane. Reaction rate at 80°C as a function of Nafion loading.

according to the above Fenton reaction can be consumed by the following side reaction ($HO^{\bullet}+H_2O_2 \rightarrow HO_2{}^{\bullet}+H_2O$) with consequent lowering of the reaction rate.

On the basis of the above results, it can be inferred that the selective oxidation of propane on Nafion-based catalytic membrane proceeds according to a reaction mechanism involving the activation of propane molecules on superacid sites (S*) and the subsequent reaction of activated paraffin with OH radicals generated by the Fe^{2+}/H_2O_2 Fenton system

$$C_3H_8 + S^* \rightarrow C_3H_8{}^*$$



where S* and $C_3H_8{}^*$ refer to superacid active sites and surface-activated C_3H_8 molecules, respectively.

The fundamental role of Nafion as active phase was confirmed by evaluating the influence of Nafion loading on the reactivity of membranes. The reaction rate increases monotonically with the Nafion loading (Fig. 5), in particular, in the range 10–30 wt.% a linear increasing has been observed, while for Nafion loading higher than 30 wt.% the slight increase in the catalytic activity likely accounts for the decreased dispersion and availability of active sites.

In conclusion, from the results reported above it can be inferred that partial oxidation of propane proceeds according to a surface radical mechanism which entails the activation of paraffin on superacid sites and the subsequent reaction of activated paraffins with OH radicals generated according to the Fenton chemistry. The potential of the catalytic membrane reactor as a promising tool for carrying out the selective partial oxidation of propane under mild conditions has been demonstrated.

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