Partial oxidation of ethane by in situ generated H_2O_2

F. Frusteri [a,1], E.N. Savinov [b], A. Parmaliana [c], E.R. Savinova [b],
V.N. Parmon [b] and N. Giordano [a]

[a] *Istituto CNR-TAE, Via S. Lucia 39, 98126 S. Lucia, Messina, Italy*
[b] *Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5,*
630090 Novosibirsk, Russia
[c] *Dipartimento di Chimica Industriale, Università degli Studi di Messina,*
CP 29, 98166 S. Agata, Messina, Italy

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Selective partial oxidation of ethane to ethanol and acetaldehyde by in situ generated H_2O_2 has been achieved under cathodic current passing through a carbon supported Nafion-H catalytic membrane. A correlation between H_2O_2 generation rate and reaction rate has been found.

Keywords: H_2O_2; partial oxidation; oxygenates; catalytic membrane

1. Introduction

Functionalisation of light paraffins into their oxygenated compounds is of substantial interest in both industrial and fundamental catalysis. Recently, a large number of low-temperature procedures have been suggested to maximise the selectivity towards liquid intermediates. In particular, the use of H_2O_2 as oxidant has attracted much attention since it contains a high percentage of active oxygen and yields H_2O as a secondary product. The activation of H_2O_2 in superacid media [1,2] by transition metals [3,4] and in the presence of Fe complexes, as well as Fe^{2+} ions [5,6], has been documented. Otsuka and Yamanaka [7] have recently reported that H_2O_2, generated at the cathode of an O_2/H_2 fuel cell, is effective in the selective partial oxidation of benzene and cyclohexane at ambient temperature.

On this account, we have recently studied the selective partial oxidation of light paraffins with H_2O_2 on permeable carbon supported superacid membranes in a three-phase catalytic membrane reactor (3PCMR) [8,9].

The aim of this paper is to propose an original approach for selective oxidation of light paraffins to oxygenated products on carbon supported Nafion superacid membranes with H_2O_2 generated "in situ" by electrochemical reduction of O_2.

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[1] To whom correspondence should be addressed.

2. Experimental

Carbon supported Nafion-H catalytic membrane (sample A) was prepared by deposition of carbon teflon paste on carbon paper and subsequent impregnation with an isopropanol solution of Nafion-H (1100 EW product, Dupont, Wilmington, DE) [8]. Carbon, Ketjenblack EC 600 Akzo Chemie (SA = 950 m^2/g) was used as support. The loading of both Nafion and teflon, calculated with respect to the carbon weight, was 20 wt%. In order to assess the role of the superacid catalyst a bare carbon membrane was also prepared (sample B). In addition, a Fe^{2+} doped carbon supported Nafion-H catalytic membrane (sample C) was obtained by impregnation of the sample A with an acid solution of $FeSO_4$ and subsequent drying at 110°C.

Catalytic membranes were tested in the 3PCMR depicted in fig. 1. The 3PCMR is provided with liquid and gas recycle pumps which allow operations in batch, semi-batch and continuous mode [8]. Oxygenated products were collected in the gas phase and trapped in a cooler ($T = 2°C$) inserted downstream of the reactor. A stabilised voltage battery supplied the current through the membrane. A platinum electrode, introduced directly into the solution near the catalyst, served as

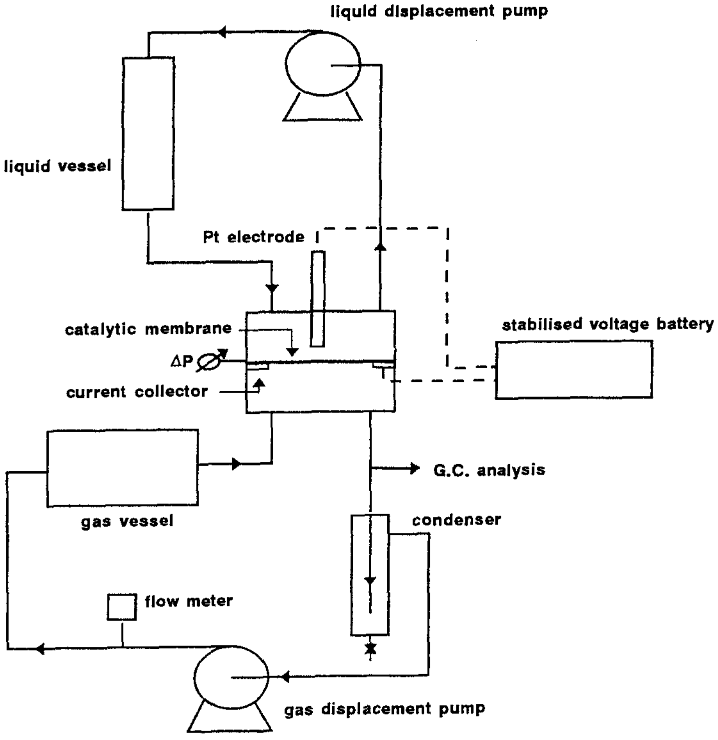


Fig. 1. Schematic diagram of the experimental set-up.

the counter electrode. The gas phase consisted of 12.2 mmol of C_2H_6 and 6.4 mmol of O_2, while the liquid phase was an aqueous solution of sulphuric acid (pH = 3). Typical experiments were carried out at 80°C and 1.2 bar absolute pressure in batch mode with separate recirculation of both gas and liquid phases. The catalyst weight (Nafion/C) was 0.015 g, while the exposed membrane surface was 3 cm^2. The H_2O_2 concentration change was followed by periodic titration with permanganate solution (0.01 mol dm^{-3}).

3. Results and discussion

In order to evaluate the influence of the current density on the rate of H_2O_2 generation, a series of experiments has been performed at 80°C on carbon supported Nafion-H catalytic membrane with a current density ranging between 3.3 and 16.6 $\mathrm{mA/cm}^2$ using O_2 in the gas phase. The results, presented in fig. 2, indicate that the rate of H_2O_2 generation is markedly affected by the current density according to a volcano-shape relationship whose maximum corresponds to a current density of 13.3 $\mathrm{mA/cm}^2$. This finding can be explained taking into account that the H_2O_2, generated by O_2 reduction on the catalyst surface via a two-electron reaction pathway [10] $O_2 + 2H^+ + 2e \rightarrow H_2O_2$ ($E_0 = 0.67$ V) can be also reduced to H_2O

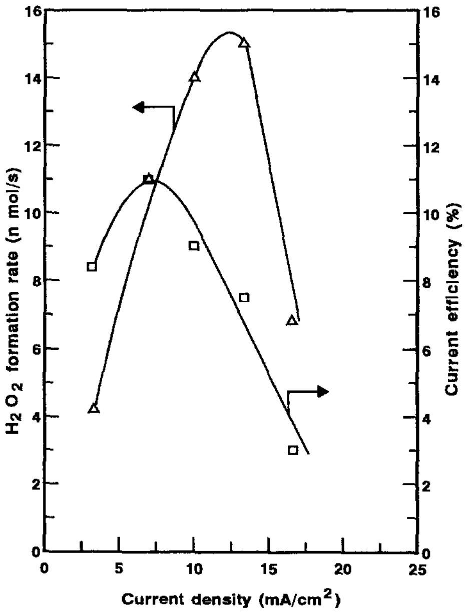


Fig. 2. Effect of current density on the H_2O_2 formation rate and current efficiency. Carbon supported Nafion-H catalytic membrane (sample A): $T = 80$°C; $P_{O_2} = 1.2$ bar; liquid phase, aqueous solution of H_2SO_4 (pH = 3).

according to the following reaction: $H_2O_2 + 2e + 2H^+ \rightarrow 2H_2O$ ($E_0 = 1.78$ V) [11]. A similar volcano shape relationship between current efficiency and current density has been also found even if in this case the highest current efficiency (11%) was observed at a current density of 6.6 mA/cm^2. As similar rates of H_2O_2 generation have been obtained on bare carbon membrane, it can be argued that the process of H_2O_2 formation occurs on the carbon surface and it is unaffected by the Nafion.

Catalytic experiments of partial oxidation of ethane at 80°C have been carried out for 3–4 h, at 1.2 bar absolute pressure, with a reaction mixture constituted by 12.2 mmol of C_2H_6 and 6.4 mmol of O_2. The influence of both current density and addition of H_2O_2 to the liquid phase on the reaction rate and products distribution has been evaluated. For each experiment, in the initial stages the oxygenated products were distributed in both gas and liquid phases, after 1 h of reaction the concentration of oxygenated products in the liquid phase reached the equilibrium value, then all products formed were collected in gas phase and trapped in the cooler down stream of the reactor. No CO_2 has been detected in the gas phase, then the selectivity to oxygenated products was equal to 100%. The main experimental results are summarised in table 1. For sake of comparison the activity data of bare carbon membrane (sample B) and Fe-doped Nafion carbon supported catalytic membrane (sample C) are also included. It is evident that in absence of H_2O_2 in the liquid phase the reaction proceeds only under current, while in presence of H_2O_2 in the liquid phase the reaction occurs also without current even if in this case the rate is greatly enhanced under current. Besides, it can be noted that on bare carbon membrane the reaction occurs with a rate significantly lower than that obtained with Nafion catalytic membrane. This result leads to state that the Nafion exerts a determining role on the reactivity of such membrane catalysts either by activating the C_2H_6 molecules or by generating active species via its interaction with H_2O_2 [1,2]. In fig. 3 are reported the rates of C_2H_6 partial oxidation and products (CH_3CHO and C_2H_5OH) formation as function of the current density. The volcano-shape

Table 1
Partial oxidation of ethane over carbon supported Nafion-H catalytic membranes at 80°C [a]

Run	Sample	H_2O_2 (mmol)	Current density (mA/cm^2)	Reaction rate (10^{-9} mol/s cm^2)	Selectivity (%)	
					CH_3CHO	CH_3CH_2OH
1	A	0	0	0	–	–
2	A	0	3.3	0.37	58.4	41.6
3	A	0	13.3	0.80	67.0	33.0
4	A	24	0	1.3	75.0	25.0
5	A	24	3.3	4.2	80.0	20.0
6	B	0	13.3	0.05	54.0	46.0
7	C	24	0	2.2	75.0	25.0

[a] Gas phase: 12.2 mmol of C_2H_6 and 6.4 mmol of O_2. Liquid phase: aqueous solution of H_2SO_4 (pH = 3).

relationship between reaction rate and current density reflects the similar dependence of the H_2O_2 formation rate on current density (fig. 2) indicating then that the rate of C_2H_6 partial oxidation is directly controlled by the rate of H_2O_2 generation.

In order to better elucidate the reaction, several experiments have been carried out in the presence of H_2O_2 in the liquid phase with Fe^{2+}-Nafion-H carbon supported catalytic membrane (sample C). In this condition (see run 7, table 1) the reaction proceeds with a rate which is twice that obtained under current conditions on Nafion carbon supported catalytic membrane (see run 4, table 1) and a similar products distribution. Therefore, it can be inferred that either on Fe doped or undoped Nafion catalytic membrane the reaction proceeds via a similar reaction pathway. Effectively, the application of current results not only in cathode generation of H_2O_2 but also in its electrochemical activation. On this account, the likely active species could be OH-radicals formed via the reaction: $H_2O_2 + e^- \rightarrow \dot{O}H + OH^-$. Also in the presence of Fe^{2+}, the catalytic activation of H_2O_2 gives rise to OH radicals according to the following reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \dot{O}H + OH^-$.

OH radicals could react with C_2H_6 to form ethyl radicals which subsequently in presence of water likely evolve towards the observed condensed species [6]. However, experiment performed on bare carbon membrane (run 6) shows that even in

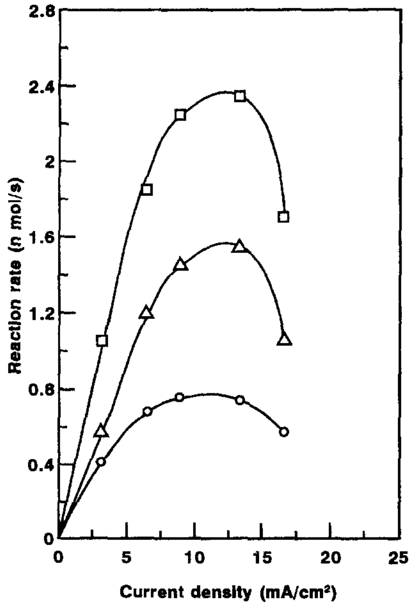
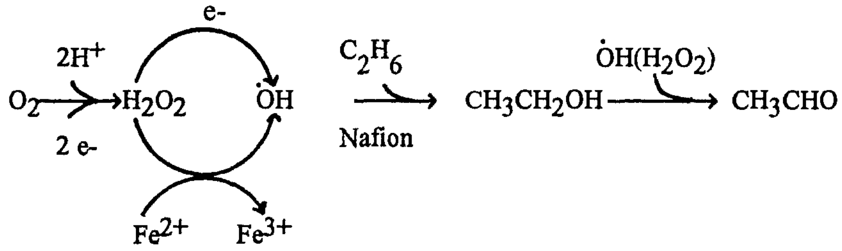


Fig. 3. Effect of current density on the rate of C_2H_6 partial oxidation and product formation ((△) CH_3CHO; (○) C_2H_5OH; (□) total oxygenates) on carbon supported Nafion-H catalytic membrane: $T = 80°C$, $P_{O_2} = 0.4$ bar and $P_{C_2H_6} = 0.8$ bar, liquid phase, aqueous solution of H_2SO_4 (pH = 3).

the presence of OH radicals the reaction occurs with a negligible rate. This signals that OH radicals alone are not active enough to react with paraffin in the absence of the superacid. Furthermore, taking into account that the higher values of selectivity to acetaldehyde have been observed when H_2O_2 is added to the liquid phase (runs 4 and 5), it could be assumed that CH_3CHO is formed via a consecutive reaction of H_2O_2 or OH radicals with ethanol.

According to our observations, the occurrence of C_2H_6 oxidation on Nafion carbon supported catalytic membrane (sample A, run 4) without current and in the presence of H_2O_2 in the liquid phase can be attributed to the fact that a small amount of Fe (0.01 wt%) is present on carbon as an impurity.

In summary, the following reaction scheme for C_2H_6 partial oxidation by O_2 under current can be hypothesised:



In conclusion, electrochemical conditions have been identified for "in situ" generation of H_2O_2 which can be directly used for partial oxidation of ethane to ethanol and acetaldehyde.

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