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Selective oxidation of ethylene over carbon-supported Pd and Pt catalytic membranes

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A three-phase catalytic membrane reactor (3PCMR), designed for the evaluation of catalytic membranes, was successfully applied to carry out selective oxidation of ethylene to acetaldehyde under mild conditions. The reaction was performed over carbon-supported Pd and Pt partial hydrophobic catalytic membranes by using different redox couples as reaction medium. Results have shown that reaction proceeds with relevant rate and high acetaldehyde selectivity (> 97%). As expected, the Pd membrane was found to be more active and selective than the Pt membrane. 3PCMR allows continuous separation of acetaldehyde while the reaction proceeds, therefore its employment could offer an original alternative to overcome several engineering problems of the conventional Wacker process. A reaction model adequate to describe the reaction system is proposed.

Keywords: ethylene, selective oxidation, catalytic membrane, membrane reactor

1. Introduction

Many industrial liquid-phase catalysed reactions are carried out in stirred tanks or bubble column reactors. As it is well known, these types of reactor sometimes impose engineering problems such as low conversion due to back-mixing in the liquid phase, reactor corrosion and separation of the catalyst from the reaction mixture. Referring to the oxidation of ethylene to acetaldehyde (EO) by the Wacker process, many efforts to overcome these problems have been made. In particular, Smidt et al. [1] developed an industrial Wacker process based on the use of a supported liquid-phase (SLP) catalyst with dioxygen as oxidant. Komiyama and Inoue [2,3] documented that the limited stability of the SLP is due to the loss of solvent by vaporisation. However, though the saturation of the reaction mixture (C_2H_4–O_2) reduces such a negative effect, it causes an increase in the diffusive resistance by liquid filling the pore system of the SLP catalysts [3]. The influence of the textural properties of the support and the role of the Pd/Cu ratio liquid loading on the performance of the SLP catalysts have been also reported [4]. The silica-supported $PdCl_2/CuCl_2$ molten salt Wacker (SMS) catalysts, which differ from the SLP catalysts since the aqueous solvent is replaced with an eutectic melt of KCl and CuCl, have been found to be very stable, active and selective in the EO reaction at 468 K and 0.16 MPa [5]. In the continuous search for the heterogenisation of the Wacker process, Espell et al. [6] have pointed out that Pd–Cu-exchanged Y-zeolites catalyse the partial oxidation of ethylene to acetaldehyde with O_2 at 100°C with a reaction mechanism identical to that of the homogeneous process. Van der Heide et al. [7] have reported that the Wacker oxidation of low alkanes proceeds under mild conditions over heterogenized catalysts consisting of $PdCl_4$ adsorbed on γ-Al_2O_3 or TiO_2 precovered with a monolayer of V_2O_5; the reaction mixture was composed by an alkene, water and oxygen, even if the reaction can be carried out also in absence of oxygen in the feed [7]. Recently, Pd salts of heteropolyacids (PdHPAs) of the Keggin series supported on silica have been used as gas-phase Wacker catalysts [8,9]; however, the slow reoxidation of the reduced PdHPA under the reaction conditions and the rapid initial deactivation limit the performance of such catalysts. Otsuka et al. [10] suggested to solve the engineering problems associated with the Wacker process by using a fuel cell system which allows the cogeneration of electricity and acetaldehyde.

In gas–liquid–solid reactions the resistance to mass transfer at gas–liquid and liquid–solid interfaces often controls the overall reaction rate. Thus in order to reduce this effect the use of water-repellent catalysts has been proposed [11,12]. In particular, Hatziantonlou et al. [13] claimed the peculiar features of hydrophobic thin catalytic plates in enhancing the mass transfer of gas and liquid and in increasing the effectiveness factor in liquid-phase hydrogenation. We have also contributed to this topic reporting preliminary data on the suitability of a three-phase catalytic membrane reactor (3PCMR) in both the selective oxidation of ethylene to acetaldehyde [14] and the partial oxidation of light alkanes [15].

The aim of this work is to assess the validity of an ori-

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Table 1
Physico-chemical characteristics of partially hydrophobic catalytic membranes

Sample	BET (m^2/g)	Pore volume (cm^3/g)	Mean pore radius		PTFE (wt%)	Thickness (mm)	Metal loading	
			$< 4\mu$	$> 4\mu$			(mg/cm^2)	(wt/%)
$E_{30\text{-}A}$	134	0.16	–	–	30	0.6	1.0	2.28
$E_{30\text{-}B}$	130	0.175	0.16	2.18	30	0.6	1.05	2.40

ginal approach to carry out the Wacker oxidation of light hydrocarbons in the 3PCMR. The selective oxidation of ethylene to acetaldehyde has been selected as a model reaction and the performance of carbon-supported noble-metal (Pd and Pt) partially hydrophobic catalytic membranes mediated by various redox couples acting as oxidising agents and the related reaction pathway have been described.

2. Experimental

2.1. Catalytic membrane

The catalytic membranes were prepared according to the following procedure: carbon-supported noble-metal catalysts (10 wt% Pt/C; 10 wt% Pd/C) were ultrasonically dispersed in H_2O. By adding teflon (PTFE) and isopropanol a paste is formed. This paste is spread on a carbon paper (Stackpole PC 206) previously wetproofed with a poly-tetrafluoroethylene–propylene solution. The membrane so obtained was pressed, dried in air at 373 K and activated at 573 K in N_2 flow. Physicochemical characteristics of the partially hydrophobic catalytic membranes prepared according to the above procedure are listed in table 1.

2.2. Apparatus and procedure

The 3PCMR reactor used in this study is schematically represented in figure 1. The catalytic membrane (thickness = 0.6 mm; $d = 90$ mm) is mounted between two stainless-steel plates provided with turbulence nets. Care was taken to maintain a pressure difference of 3 kPa ($\Delta P = P_g - P_\ell$) between the gas and liquid sides of the membrane in order to control: (i) the filling of the pores in the hydrophobic catalytic layer with gas; (ii) the liquid and gas leakages; (iii) the occurrence of physical damage to the membrane. In practice, the membrane reactor is used in a horizontal rather than vertical position. It is felt that this arrangement leads to a better mode of transport of gaseous and liquid components through the membrane.

Catalytic measurements in the EO reaction have been performed by the experimental equipment shown in figure 2. The system is provided with liquid and gas recycle pumps which allow operations in batch, semibatch and continuous modes. Catalytic measurements have been performed in the range 323–393 K with an ethylene–nitrogen mixture $P_{C_2H_4}/P_{N_2} = 3.7$ at 140 kPa absolute pressure operating in batch mode with separate recirculation of both the gas and the liquid phases. The liquid phase was a sulphuric acid solution of Fe^{3+}

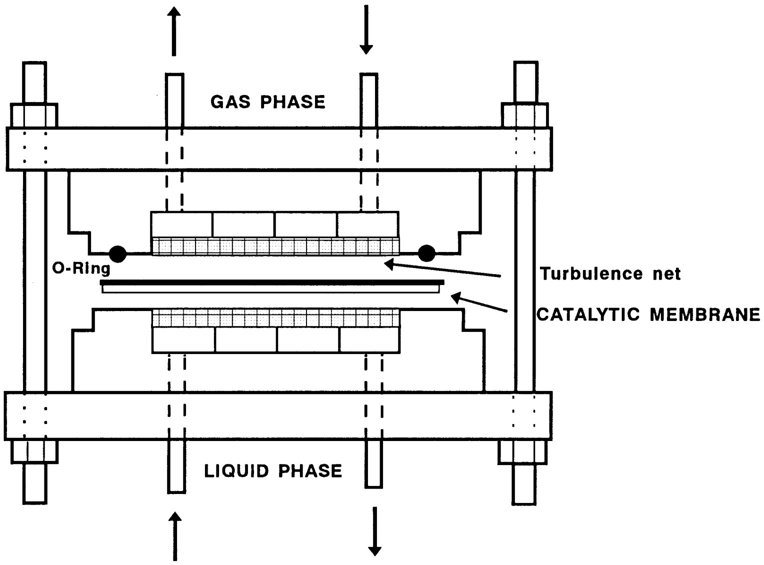

Figure 1. Three-phase catalytic membrane reactor.

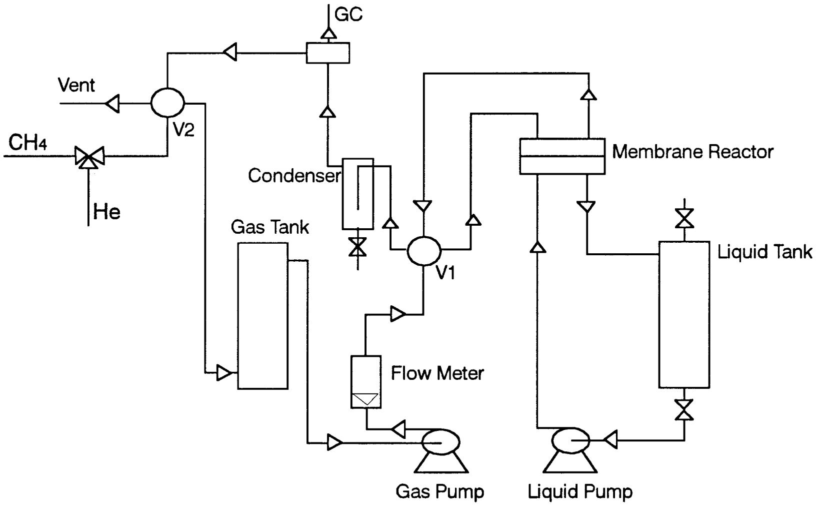

Figure 2. Schematic diagram of the experimental equipment.

($[Fe^{3+}] = 0.1$–1.0 mol/dm^3, pH = 1), an aqueous solution of ClO_3^- ($[ClO_3^-] = 0.37$ mol/dm^3) and an aqueous solution of $Cr_2O_7^{2-}$ ($[Cr_2O_7^{2-}] = 0.37$ mol/dm^3). The volume of gas and liquid phase was 0.5 and 0.1 dm^3 respectively. Acetaldehyde formed during reaction was trapped at 273 K down-stream of the reactor.

The evolution of catalytic activity has been followed by: (i) continuous potentiometric measurement; (ii) volumetric titration of Fe^{2+} formed; (iii) gas-chromatographic analysis of liquid and gas phases. GC analysis of the gaseous component of the reaction mixture N_2, O_2, CO_2, C_2H_4 and H_2O was carried out using a two-column system (A - Porapak QS, $l = 2.5$ m, i.d. = 2 mm; B - Molecular Sieve 5A, $l = 3$ m, i.d. = 2 mm) operating at 353 K, and a thermal conductivity detector (TCD), while a Carbopack B-3% SP 1500 column ($l = 2.5$ m; i.d. = 2 mm) operating at 363 K coupled with a flame ionisation detector (FID) for the analysis of oxygenated products was used.

3. Results and discussion

3.1. Catalytic activity

In order to assess the reliability of the reaction system a series of preliminary runs has been performed. The oxygenated products, formed at the gas–liquid–solid interphase, are distributed 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 and then trapped down-stream of the reactor.

The results of a typical run, expressed in terms of C_2H_4 molar conversion (as measured by GC analysis), concentration of Fe^{2+} formed during reaction and potential change ΔE ($\Delta E = E_t - E_0$ where E_t and E_0 are, the cell potential at reaction time t and $t_0 = 0$ respectively) versus the reaction time are reported in figure 3. These data indicate that the monitored change in potential correlates well with ethylene conversion. Therefore, potentiometry can be used as a tool for instantaneous kinetic measurements.

A comparison in terms of C_2H_4 conversion, CH_3CHO selectivity and reaction rate in the range 323–393 K between Pt- and Pd-based membranes is reported in table 2. Such results clearly indicate that the Pd catalyst is more active and selective than the Pt one. Furthermore, on the Pt membrane the selectivity to acetaldehyde (S_{HCHO}) is significantly affected by reaction temperature, decreasing from 72% at 353 K to 56% at 393 K, while on the Pd membrane such effect is negligible since the S_{HCHO} is almost constant (97–98%) in the T_R range 323–393 K. In addition, it is important to underline that the reaction rate referred to the volume of membrane (2.5×10^{-3} mol/(ℓ_{cat} s)) obtained by using the Pd catalyst (see table 2) is very close to that calculated for the SMC (5.4×10^{-3} mol/(ℓ_{cat} s); T_R, 373 K) [5] and about two orders of magnitude higher than that found

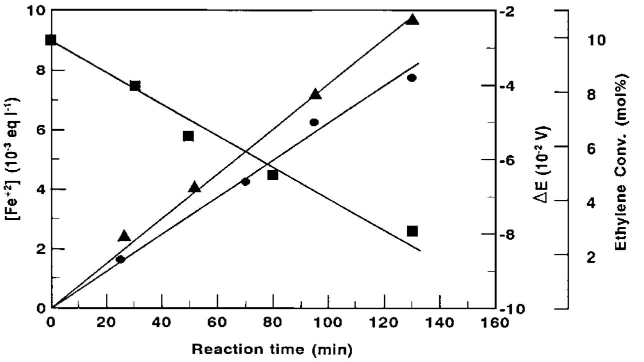

Figure 3. Ethylene conversion versus reaction time on the $E_{30\text{-}A}$ catalytic membrane: $T_R = 373$ K. (Δ) $[Fe^{2+}]$; (□) $E_t - E_0$ potential change; (○) C_2H_4 conversion.

Table 2
Partial oxidation of ethylene. Catalytic activity of Pt and Pd partially hydrophobic membranes

Catalyst	Noble metal	T_R (K)	C_2H_4 conv. [a] (mol%)	S_{CH_3CHO} (%)	S_{CO_2} (%)	Rate (10^{-3} mol/(ℓ_{cat} s))
$E_{30\text{-}A}$	Pd	323	9.2	98	2.0	1.0
		343	21.0	98	2.9	1.8
		373	27.0	97	3.0	2.5
		393	30.1	96.7	3.3	3.1
$E_{30\text{-}B}$	Pt	353	3.8	72	28	0.16
		373	7.0	67	33	0.31
		393	13	56	44	0.52

[a] Conversion at 100 min.

for the SLP catalyst (7×10^{-5} mol/(ℓ_{cat} s); T_R, 353 K) [3].

The influence of Fe^{3+} concentration on the activity and selectivity to acetaldehyde of the $E_{30\text{-}A}$ sample at 373 K is shown in figure 4. From these data it can be seen that the Fe^{3+} concentration, in the range 0.1–1.0 eq/dm^3, slightly enhances the reaction rate while it does not affect significantly the CH_3CHO selectivity.

The evolution of the reaction at various reaction temperatures in terms of C_2H_4 conversion versus reaction time is reported in figure 5. It can be seen that, notwithstanding in all experiments we operate with ethylene conversion lower than 30%, in all reaction conditions the reaction rate decreases with reaction time. Such decreasing of reaction rate, more evident at low reaction temperature, could be associated with the strong but reversible poisoning adsorption of acetaldehyde dissolved in liquid phase on the active sites of the Pd catalyst. This hypothesis is well supported by the fact that such inhibition effect is more important at the lower reaction temperatures where the acetaldehyde solubility in the liquid phase is higher.

The role of the oxidising agent on the reaction pattern has been evaluated by performing several experiments with a ClO_3^- (pH = 3) or CrO_4^{2-} (pH = 3) solution as reaction medium. The values of reaction rate and acetaldehyde selectivity obtained on the $E_{30\text{-}B}$ sample at 373 K using equimolar solutions of Fe^{3+}, Cr^{6+} and ClO_3^- are comparatively presented in figure 6. It can be observed that both reaction rate and selectivity are not substantially affected by the nature of the oxidant. Then, since the selectivity to CH_3CHO does not change by using various oxidising agents, characterised by different oxidative strengths ($P_{Cr^{6+}/Cr^{3+}} = 1.33$ V, $P_{ClO^{3-}/Cl^-} = 0.71$ V, $P_{Fe^{3+}/Fe^{2+}} = 0.77$ V [15]), it can be excluded that acetaldehyde may be further oxidised in the adopted reaction media. Such data allow inferring that the redox couple, as for the homogeneous Wacker process, is mainly involved in the Pd^0 reoxidation step [1].

3.2. Reaction kinetics

On the basis of the well known Wacker mechanism [1] we hypothesize that in our case reaction evolves according to the following pathway:

$$2Fe^{3+} + Pd^0 \rightarrow 2Fe^{2+} + Pd^{2+} \quad (1)$$

$$Pd^{2+} + H_2O \rightleftharpoons Pd^{2+}{*}H_2O \quad (2)$$

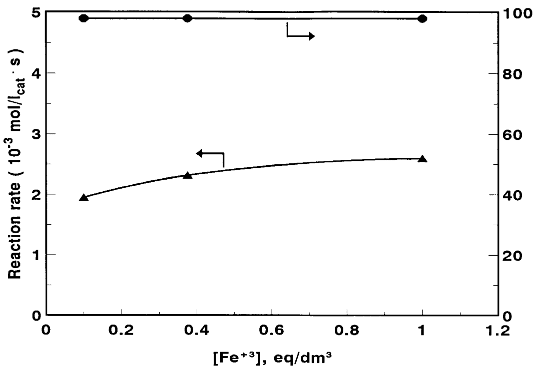

Figure 4. Influence of Fe^{3+} concentration on reaction rate and selectivity to acetaldehyde in the selective oxidation of ethylene on the $E_{30\text{-}A}$ catalytic membrane at 373 K.

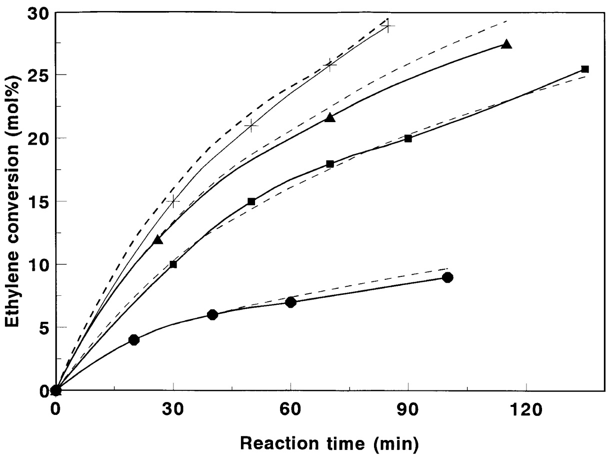

Figure 5. Ethylene conversion versus reaction time at different temperatures (solid line): (●) 323 K; (■) 343 K; (▲) 373 K; (×) 393 K, $E_{30\text{-}A}$ catalytic membrane.

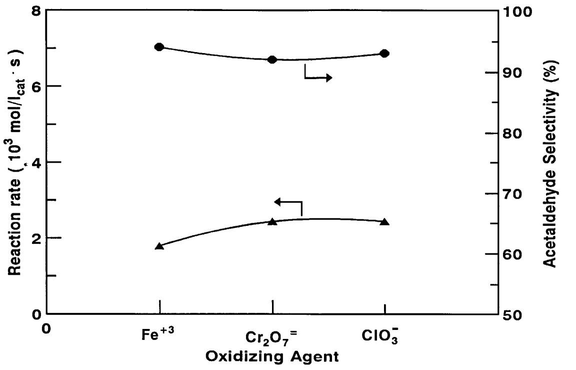

Figure 6. Influence of different oxidizing agents on the reaction rate and selectivity to acetaldehyde: $T_R = 373$ K, $E_{30\text{-}B}$ catalytic membrane.

$$Pd^{2+}{*}H_2O + C_2H_4 \rightleftharpoons Pd^{2+}{*}H_2O{*}C_2H_4 \tag{3}$$

$$Pd^{2+}{*}H_2O{*}C_2H_4 \rightleftharpoons Pd^{+}{*}C_2H_4OH + H^+ \tag{4}$$

$$Pd^{+}{*}C_2H_4OH \rightarrow Pd^{0}{*}C_2H_4O + H^+ \tag{5}$$

$$Pd^{0}{*}C_2H_4O \rightleftharpoons Pd^{0} + C_2H_4O \tag{6}$$

The reaction rate for each step can be written as follows:

$$r_1 = K_1 C_F^2 \Theta_O\,,$$

$$r_2 = K_2 C_W \Theta_2 - K_{-2}\Theta_W\,,$$

$$r_3 = K_3 C_E \Theta_W - K_{-3}\Theta_E\,,$$

$$r_4 = K_4 \Theta_E - K_{-4} C_H \Theta_C\,,$$

$$r_5 = K_5 \Theta_C\,,$$

$$r_6 = K_6 \Theta_A - K_{-6} C_A \Theta_O\,,$$

where Θ_i is the surface intermediate concentration of the species i ($\sum \Theta_i = 1$).

Then, we infer that C_2H_4 is activated on Pd^{2+} generated by the oxidation of supported Pd^0 with the Fe^{3+} present in the liquid phase. Thus we argue that H_2O, which is a σ-donor ligand, activated by supported Pd^{2+} (step (2)), reacts with ethylene to give a Pd^{2+}–ethylene complex (step (3)) which loses H^+ to give rise to the formation of a Pd^+–ethanol complex (step (4)). Step (5) accounts for the reduction of Pd^+ to Pd^0 with formation of acetaldehyde, while step (6) refers to Pd^0–acetaldehyde interaction which lowers the reaction rate mainly at low reaction temperatures. In the Wacker process such inhibition is not observed, but in our case it takes place probably due to the presence of well dispersed Pd^0 on which the adsorption of acetaldehyde may be expected to occur with a concomitant drop of the reaction rate.

Assuming that the equilibrium of steps (2), (3), (4) and (6) is attained and hypothesizing that under quasi-steady-state conditions $r_1 = r_5$, the reaction rate equation can be written as follows:

$$-\frac{dC_E}{dt} = \frac{V_c}{V_g} K_5 b_W C_W \frac{b_E C_E}{b_H C_H}\left\{1 + b_W C_H\left[1 + b_E C_E + \frac{b_E C_E}{b_H C_H}\left(1 + \frac{1}{K_1 C_F^2} + \frac{K_5 b_A C_A}{K_1 C_F^2}\right)\right]\right\}^{-1}, \tag{7}$$

where: (i) V_c and V_g refer to the volume of catalyst and gas respectively; (ii) C_E, C_A and C_F are ethylene, acetaldehyde and Fe^{3+} concentrations respectively; (iii) b_W, b_A, b_H and b_E are the adsorption equilibrium constants of H_2O, acetaldehyde, H^+ and ethylene respectively.

Considering that in our reaction condition $b_W C_W$ is almost constant and $b_A C_A \gg 1$, eq. (7) can be simplified as:

$$-\frac{dC_E}{dt} = \frac{V_c}{V_g} K_5 \frac{b_E C_E}{b_H C_H} \times \left(1 + b_E C_E + \frac{K_5}{K_1 C_F^2}\frac{b_E C_E}{b_H C_H} b_A C_A\right)^{-1}. \tag{8}$$

Setting $b_1 = b_E/b_H$, $b_2 = K_5 b_A/K_1$ and considering that $b_E C_E \ll 1$ eq. (8) can be further rearranged as follows:

$$\frac{dx}{dt} = \frac{V_c}{V_g} K_5 (1 - x)\left(\frac{C_H}{b_1} + \frac{b_2 C_E C_A}{C_F^2}\right)^{-1}. \tag{9}$$

The values of ethylene conversion calculated by such a model (dashed lines) at different reaction temperatures are shown in figure 5 together with the experimental values (dashed line) already considered to describe the evolution of reaction. A good agreement between experimental and calculated values has been obtained independently for the reaction temperatures investigated, therefore the proposed model seems to be adequate to describe the evolution of the reaction.

The values of reaction rate, adsorption equilibrium constants, activation energy and heat of adsorption have been also calculated and are summarised in table 3. Apparent activation energy E_5, evaluated in the T range 323–373 K, results to be 15 kcal/mol. Such value is in good agreement with the values of 14.7 and 13.7 kcal/mol reported by other authors [3,4].

4. Conclusions

The feasibility of the three-phase catalytic membrane reactor has been successfully demonstrated for ethylene oxidation to acetaldehyde on carbon-supported noble-metal partially hydrophobic catalytic membranes, using redox couples as reaction medium. On the Pd-based membrane reaction proceeds with reasonable rate and high selectivity to acetaldehyde. Acetaldehyde selectivity seems not to be affected by redox couple employed.

Table 3
Kinetic parameters

Reaction rate and adsorption equilibrium constant at 343 K		Activation energy and heat of adsorption (kcal/mol)	
K	0.52–0.04	$E = E_5 - Q_e - Q_H$	2 ± 0.3
b	39–3.0	$Q = Q_a + E_1 - E_1$	30 ± 2
K_5	2.6–0.2	E_5	15 ± 0.5
b_1	0.20–0.02	$Q_1 = Q_e - Q_H$	4 ± 0.5
b_2	150–10	$Q_2 = Q_a + E_1 - E_5$	28 ± 2.0

Due to the unique ability to transfer in gas phase the acetaldehyde formed during the reaction, the proposed three-phase catalytic membrane reactor (3PCMR) appears to be a very good alternative to overcome the engineering problems linked to the Wacker process.

The reaction model proposed appears adequate to describe the reaction system investigated. A good correlation between experimental and calculated values was obtained in all the T ranges investigated. The apparent activation energy was measured to be 15 ± 0.5 kcal/mol which is in good agreement with the value reported by other authors.

The overall results reported here clearly indicate that the novel experimental approach proposed (3PCMR) could open new perspectives on carrying out hydrocarbon partial oxidation under mild conditions.

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