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Selective partial oxidation of light paraffins with hydrogen peroxide on thin-layer supported Nafion-H catalysts

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Thin-layer carbon supported Nafion-H catalysts were found to be active and highly selective ($S > 98\%$) for the partial oxidation of C_1-C_3 alkanes, in a three phase catalytic membrane reactor (3PCMR), under mild conditions and in the presence of H_2O_2. The influences of the catalyst teflon loading and H_2O_2 concentration on the reaction rate have been evaluated. A reaction pathway, based on the electrophilic hydroxylation of the C-H bond of alkanes with protonated hydrogen peroxide ($H_3O_2^+$), is discussed.

Keywords: Light paraffins; partial oxidation; supported Nafion-H; hydrogen peroxide; oxygenates; three phase reactor

1. Introduction

Partial oxidation of light paraffins to useful chemicals and liquid fuels is a topic of great interest to the gas and petroleum industries. The introduction of functional groups into the light paraffins require severe and thus unselective conditions due to their chemical inertness. However, several attempts to achieve selective partial oxidation under mild conditions have been made [1]. In this context the use of H_2O_2 as oxidant has attracted a great deal of interest over the last few years since it has a high active oxygen content, is readily available and because it gives H_2O as secondary product [2]. Indeed, liquid phase activation of alkanes with H_2O_2 in the presence of superacids [3,4], iron complexes [5] and titanium silicalite [6] has been reported. Besides, it has also been demonstrated that CH_4 can be activated via a radical mechanism involving the $OH^{\cdot}$ species generated by the reaction between Fe^{2+} and H_2O_2 synthetized

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Table 1
List of thin layer catalysts

Sample [a]	S.A. (m^2/g)	Catalytic layer [b]	
		Teflon (wt%)	Nafion (wt%)
V3-1	20	30	10
V3-2	10	30	10
V3-3	n.d.	30	18
K1-1	270	10	20
K1-2	253	20	20
K1-3	142	30	20
K1-4	125	40	20

[a] K and V codes refer to Ketjenblack and Vulcan carbons respectively.
[b] Nafion and teflon loadings are calculated on carbon weight basis.

in situ by the electrochemical reduction of O_2 [7]. More recently, Kao et al. [8] have claimed an electrophilic pathway to describe the selective conversion of CH_4 into CH_3OH catalysed by Pd^{2+} ions in a H_2O_2 and trifluoroacetic anhydride solution.

Therefore, in order to bring an original contribution to this topic, here we report on the selective partial oxidation of C_1-C_3 paraffins with H_2O_2 on thin layer carbon supported Nafion-H (perfluororesinsulfonic acid) catalyst in a three phase catalytic membrane reactor (3PCMR).

2. Experimental

The catalysts were prepared by deposition of carbon-teflon paste on carbon paper, activation at 300°C in N_2 atmosphere and subsequent impregnation with an isopropanol solution of Nafion-H (1100 EW product, Dupont, Wilmington, DE). Two types of carbon were used: Ketjenblack (EC 600 Akzo Chemie; S.A., 950 m^2/g) and Vulcan (XC-72, Cabot Corp.; S.A., 250 m^2/g). Several catalysts with different teflon loading (10–40 wt%) have been prepared. The list of the thin layer catalysts is reported in table 1.

Catalysts have been tested in a 3PCMR, elsewhere described [9], suitably designed to prevent the consecutive oxidation of the intermediate products. Experimental runs have been carried out in batch mode with recirculation of both gas and liquid phases, in the range 60–120°C, at 1.4 bar absolute pressure, with 1.4–1.8 g of catalyst (thickness $= 6 \times 10^{-2}$ cm, $S = 50$ cm^2), 17 mmol of alkane and H_2O_2 concentration ranging from 0.44 to 2.2 mol/dm^3. Oxygenated products were trapped at 2°C down-stream of the reactor while the H_2O_2 concentration change was followed by periodical titration with permanganate solution (0.1 mol/dm^3).

3. Results and discussion

In table 2 are presented the reaction rates and the distribution of products measured in the partial oxidation of C_1-C_3 paraffins on catalyst V3-1 at 120°C. As expected the reaction rate depends upon the chain length, while the selectivity to oxygenates remains always very high ($> 98\%$) for all the paraffins. In particular, methane was oxidised selectively to methanol while ethane and propane mainly to acetaldehyde and acetone respectively. In all the experimental conditions the catalysts have been found to be very stable. Indeed, Nafion-H is well anchored on carbon surface denoting both a good resistance to the leaching action exerted by the water and a high chemical stability in the presence of H_2O_2.

The partial oxidation of ethane has been studied in the range 60–120°C on catalyst K1-1. The results presented in fig. 1 notably evidentiate that the selectivity to oxygenates (CH_3CH_2OH and CH_3CHO) does not change with the increase in the reaction rate. The high selectivity ($> 98\%$) experienced well accounts for the peculiar feature of the 3PCMR which allows the continuous removal of the reaction products from the liquid phase by steam stripping, thus avoiding their further oxidation. In fig. 2 is shown the hydrogen peroxide concentration dependence of the ethane conversion rate at 120°C over catalyst K1-1. The reaction order of H_2O_2 results about 0.12. The slight enhancing effect exerted by H_2O_2 on the conversion rate does not alter the distribution of products.

The reactivity of the partially hydrophobic catalysts is strongly controlled by their teflon content [10]. Therefore, in order to asses the influence of this parameter on the performance of our thin layer catalysts we have evaluated the activity of differently teflon loaded catalysts of the series K1 in the ethane partial oxidation at 120°C. The results reported in fig. 3 indicate that the reaction rate decreases almost linearly with the teflon loading. However, although the surface area of the catalysts decreases with the teflon loading likely as consequence of the blockage of the carbon micropores by the microsize particles of teflon attached on the surface of the macropores [10], the different reactivity exhibited by the samples of the series K1 cannot be exclusively related

Table 2
Partial oxidation of light paraffins on catalyst V3-1 at 120°C. Selectivity to oxygenated products

Alkane	Reaction rate of alkane (10^{-8} mol/s·g_{cat})	Selectivity (%)
CH_4	0.31	CH_3OH(100)
C_2H_6	1.80	CH_3CH_2OH(16); CH_3CHO(82)
C_3H_8	4.30	$(CH_3)_2CHOH$(8); C_2H_5CHO(10); CH_3COCH_3(80)

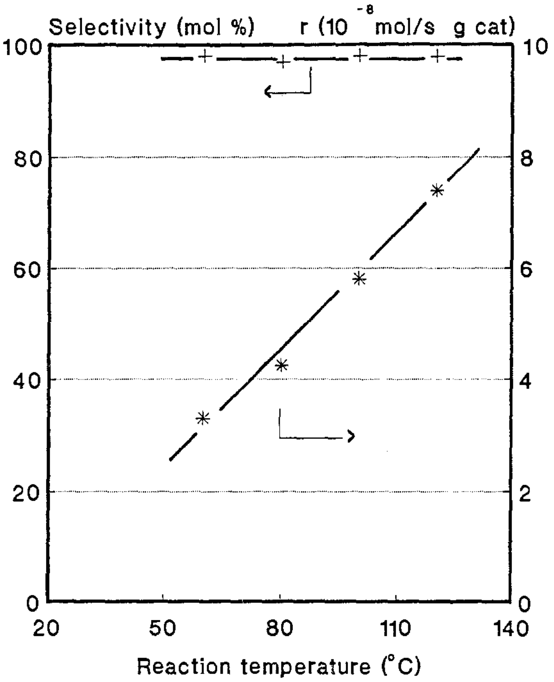

Fig. 1. Partial oxidation of ethane on catalyst K1-1. Influence of reaction temperature on reaction rate and selectivity to oxygenates. $[H_2O_2] = 0.44$ mol/dm^3.

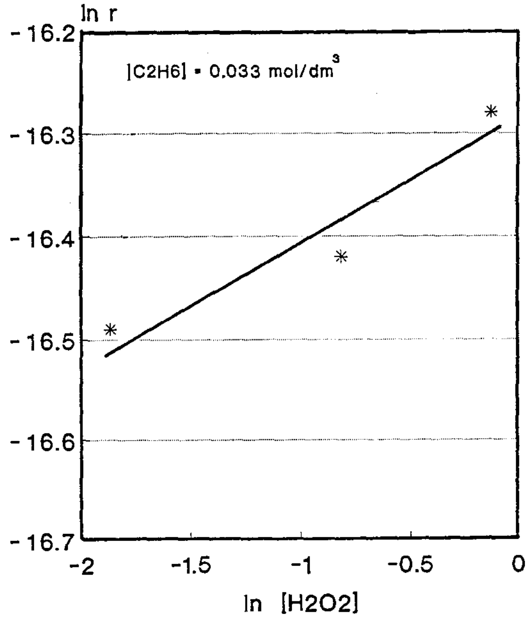

Fig. 2. H_2O_2 concentration dependence of ethane partial oxidation rate on catalyst K1-1. $T_R = 120$°C.

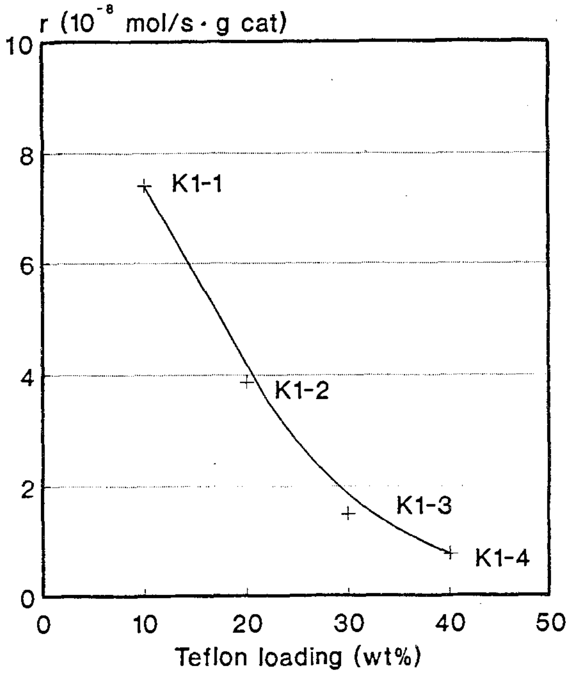

Fig. 3. Reaction rate of ethane partial oxidation versus catalyst teflon loading. $T_R = 120°C$, $[H_2O_2] = 0.44$ mol/dm^3.

to their different surface areas. Indeed, K1-1 and K1-2 samples have similar surface area (see table 1) while the activity of K1-1 is about twice that of K1-2. This leads us to hypothesize that the fraction of partial wetting [9], which decreases with the teflon loading, plays a fundamental role in controlling the reaction rate.

Moreover, the conversion rates of propane partial oxidation on catalyst V3-1 in the range 60–120°C were found to fit the Arrhenius plot, as shown in fig. 4, with an apparent activation energy, E_a, of 7.6 kcal/mol.

To elucidate the role of the catalyst and the nature of the oxidising species, several different experimental runs have been carried out: (i) O_2 in the gas phase and only H_2O in the liquid phase; (ii) $Cr_2O_7^{2-}$ solution instead of H_2O_2; (iii) bare thin layer carbon catalyst in the presence of H_2O_2. As the oxidation reaction takes place only in the presence of Nafion-H and H_2O_2, we infer that the reaction mechanism likely involves the electrophilic hydroxylation of C-H bond of the alkane with hydroperoxonium ion ($H_3O_2^+$) formed from the interaction of Nafion-H with H_2O_2 [4]. In particular, the partial oxidation of ethane should proceed according to the reaction pathway shown in fig. 5. The hydroxycarbenium ion (3) can evolve towards either ethanol (4) or carbenium ion (5) which can react with excess of H_2O_2 giving ethyl-hydroperoxide (6). This complex, by rearrangement and cleavage, rapidly evolves to acetaldehyde (7).

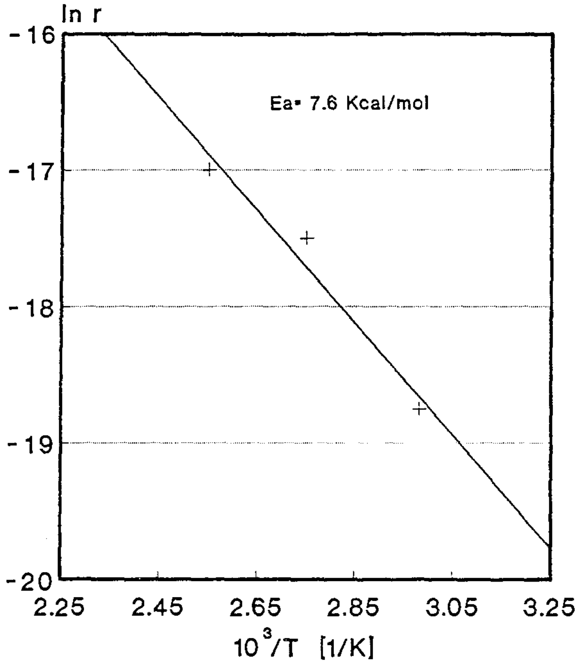

Fig. 4. Arrhenius plot of propane partial oxidation on catalyst V3-1. $[H_2O_2] = 0.44$ mol/dm^3.

Similar electrophilic reaction pathways can be formulated to account for the partial oxidation of methane and propane.

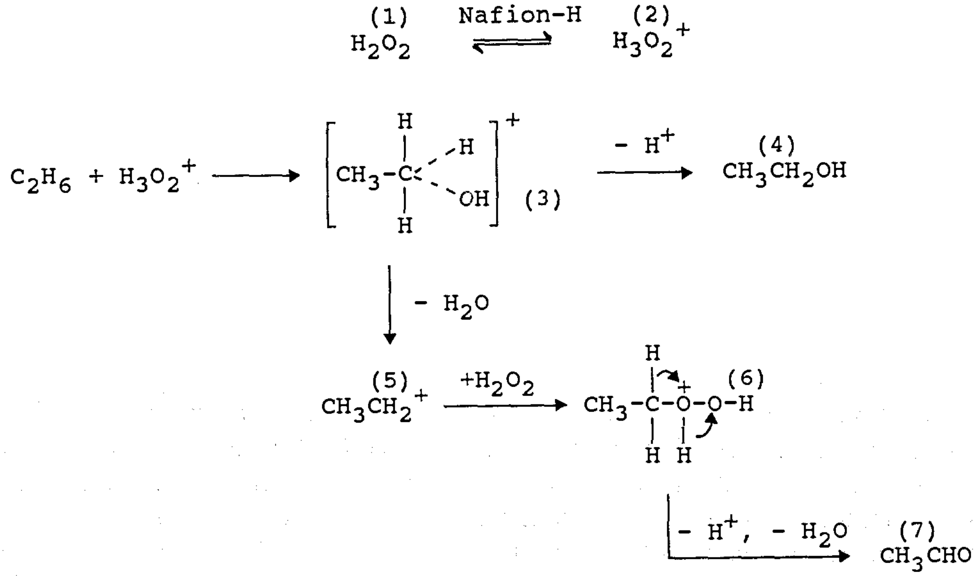

Fig. 5. Reaction pathway for ethane partial oxidation with hydrogen peroxide catalysed by thin-layer supported Nafion-H catalysts.

4. Conclusions

From the bulk of our results it emerges that:

(i) thin layer supported Nafion-H catalysts, mediated by aqueous H_2O_2, are able to activate light paraffins under mild conditions;

(ii) thin layer supported Nafion-H catalyst denote a high chemical stability in the presence of H_2O_2;

(iii) the activation mechanism of C_1-C_3 paraffins likely involves the electrophilic hydroxylation of C-H bond with hydroperoxonium ion ($H_3O_2^+$);

(iv) 3PCMR is a very novel and promising tool to achieve selective partial oxidation of light paraffins under mild conditions.

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