Thin-layer Supported Nafion Catalysts for the Partial Oxidation of Light Alkanes

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Thin-layer carbon supported Nafion-H catalysts were found to be active and highly selective for the partial oxidation of C_1–C_3 alkanes under mild conditions and in the presence of aqueous H_2O_2. A three phase catalytic membrane reactor (3PCMR) has been used.

The catalytic partial oxidation of light alkanes is one of the most intriguing and potentially important research fields in both industrial and fundamental catalysis. The introduction of functional groups into the light paraffins requires severe and thus unselective conditions due to their chemical inertness. However, in this context several approaches to achieve selective partial oxidation under mild conditions have been documented.[1] Among these, the liquid phase activation of alkanes in superacid media has received a great deal of attention over the past few years especially in the isomerisation and alkylation reactions.[2] Even if these reactions proceed with all alkanes, it has been shown that the lighter ones (particularly methane) react only under high pressure and in concentrated superacid mixtures.[3] Alkane activation mediated by superacids has also been disclosed using ozone and hydrogen peroxide as oxidising agents.[4,5] Hydrogen peroxide has been used recently for the partial oxidation of alkanes in the presence of iron complexes[6] and on titanium silicalite catalysts.[7]

This paper reports preliminary results on the partial oxidation of the C_1–C_3 alkanes on partially hydrophobic thin-layer carbon-supported Nafion-H catalysts, at low temperatures (80–120 °C) and at atmospheric pressure, in the presence of hydrogen peroxide.

The catalysts were prepared by deposition of carbon–Teflon paste on carbon paper and subsequent impregnation with an propan-2-ol solution of Nafion-H (1100EW product, Dupont, Wilmington, DE). Two types of carbon have been used: Ketjenblack (EC 600, Akzo Chemie; surface area (SA), 950 $m^2\ g^{-1}$) and Vulcan (XC-72, Cabot Corp.; SA, 250 $m^2\ g^{-1}$). The catalysts were tested in the three phase catalytic membrane reactor (3PCMR), shown in Fig. 1, suitably designed to prevent the consecutive oxidation of the intermediate products.[8] The experimental equipment is provided with liquid and gas recycle pumps which allow operations in batch, semi-batch and continuous mode. The catalyst (thickness = 0.6 mm, diameter, ϕ = 80 mm) was sandwiched between two stainless steel plates provided with turbulence nets. The

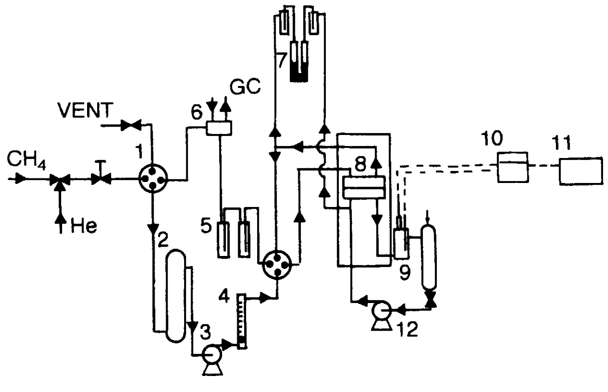

Fig. 1 Schematic diagram of the experimental equipment: (1) 4-port valve; (2) vessel; (3) gas displacement pump; (4) rotameter; (5) condenser; (6) sampling valve; (7) Hg manometer; (8) cell reactor; (9) potentiometric cell; (10) digital multimeter; (11) recorder; (12) liquid displacement pump

Table 1 Oxidation of light alkanes on Nafion-H[a] supported thin-layer catalysts

Cat.[b]	S.A./$m^2 g^{-1}$	Teflon content (wt%)	Alkane	$[H_2O_2]$/ mol dm^{-3}	T_R/°C	Reaction rate of alkane /10^{-8} mol $g_{cat}^{-1} s^{-1}$
V3-1	20	30	CH_4	0.44	100	0.082
V3-1	20	30	CH_4	2.20	100	0.21
K1-1[c]	253	15	CH_4	0.44	120	0.31
V3-1	20	30	C_2H_6	0.44	120	1.70
V1-1	17	15	C_2H_6	0.44	120	2.10
K1-1	253	15	C_2H_6	0.44	120	5.20
K1-2	270	10	C_2H_6	0.44	80	4.20
K1-2	270	10	C_2H_6	0.88	120	8.30
K1-2[c]	270	10	C_2H_6	0.44	120	7.20
K1-2	270	10	C_2H_6	0.15	120	6.80
K1-3	142	30	C_2H_6	0.44	120	1.50
K1-4	125	40	C_2H_6	0.44	120	0.75
V3-2[c]	18	30	C_3H_8	0.44	120	4.30

[a] The Nafion-H loading for all the samples is 8 wt%. [b] K and V codes refer to Ketjenblack and Vulcan carbons respectively. [c] Experiments considered to depict Fig. 3.

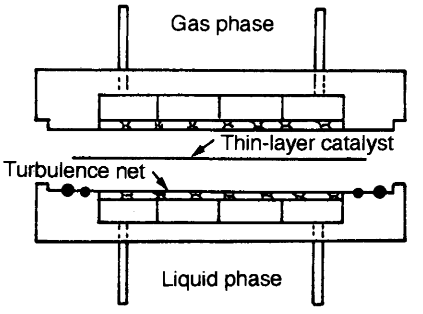

Fig. 2 'Cell reactor' scheme

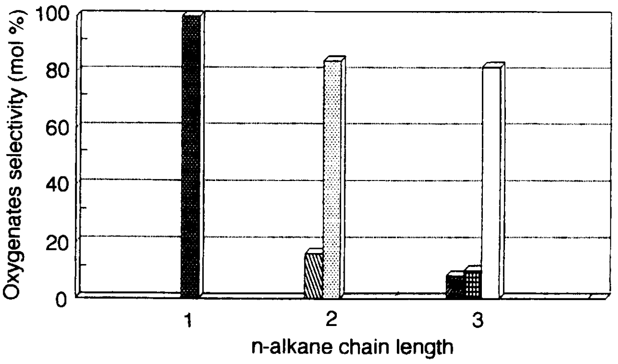

Fig. 3 Partial oxidation of light alkanes on Nafion-H thin-layer catalysts. Selectivity to oxygenated products. T_R = 120 °C; $[H_2O_2]$ = 0.44 mol dm^{-3}: ■ = CH_3OH, ▧ = CH_3CH_2OH, ▨ = CH_3CHO, ▦ = $(CH_3)_2CHOH$, ■ = CH_3CH_2CHO and □ = CH_3COCH_3.

scheme of the 'cell reactor' is presented in Fig. 2. During reaction care was taken to maintain a pressure difference of 3 kPa ($\Delta P = P_g - P_l$) between the gas and the liquid sides in order to control the filling of the pores in the hydrophobic catalytic layer with gas and the occurrence of physical damage to the catalyst. Experimental runs have been performed in batch mode with separate recirculation of both the gas and liquid phases. Oxygenated products were condensed at 2 °C downstream of the reactor.

Typical oxidation experiments were carried out in the range 80–120 °C, for 2–3 h, at 1.4 bar (1 bar = 10^5 Pa) absolute pressure, with 1.6 g of catalyst, 17 mmol of alkane, 0.044–0.22 mol of H_2O_2. The reaction products were analysed by GC, while the H_2O_2 concentration change was followed by periodical titration with permanganate (0.1 mol dm^{-3}).

The main experimental results, obtained at different reaction temperatures and H_2O_2 concentrations, are summarised in Table 1. The reaction rate increases with the catalyst surface area, while it decreases with the catalyst Teflon content. The positive effect of surface area on the reaction rate can be associated with a better Nafion distribution on a high surface area carbon support, while the lower activity of the samples with higher Teflon content can be attributed to the partial blockage of the carbon micropores[9] which prevents a homogeneous Nafion-H dispersion.

It has also been found that the concentration of H_2O_2 slightly enhances the reaction rate without altering the distribution of products. Notably, while the reactivity of the C_1–C_3 light paraffins, compared in terms of reaction rate, depends upon the chain length, the selectivity to oxygenates remains always very high (>98%) for all the paraffins, as clearly shown in Fig. 3. The high selectivity 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. Methane was oxidised selectively to methanol while ethane and propane were oxidised mainly to acetaldehyde and acetone respectively. The catalysts have been found to be very stable. Nafion is well anchored on the carbon surface denoting either a good resistance to the leaching action exerted by the water or a high chemical stability in the presence of H_2O_2.

To elucidate the role of the catalyst and the nature of oxidising species, the following experimental runs have been carried out by using: (*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 neither H_2O_2 nor Nafion-H alone led to any reaction products, we infer that the oxidation reaction mechanism, in the presence of H_2O_2, probably involves the electrophilic hydroxylation of the C–H bond with the hydroperoxonium ion ($H_3O_2^+$) formed from the interaction of Nafion-H with H_2O_2.[4]

Therefore, from the bulk of our results it emerges that thin-layer supported Nafion-H catalysts mediated by aqueous H_2O_2 are able to activate light paraffins at mild conditions. Furthermore, the proposed 3PCMR is a novel tool to achieve selective partial oxidation of C_1–C_3 light alkanes.

This work was supported by 'Progetto Finalizzato-Chimica Fine II' CNR, Rome, Italy.

Received, 5th March 1991; Com. 1/01035B

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