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Factors affecting the efficiency of Nafion-based catalytic membranes in the selective oxidation of light paraffins mediated by the Fenton system

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Abstract

The partial oxidation of propane to oxygenates (isopropanol, *n*-propanol, propionic aldehyde and acetone) is attained in a multifunctional three phase catalytic membrane reactor (3PCMR) operating under mild conditions (T_R, 80–120 °C; P_R, 140 kPa). A comparative testing of different Nafion-based catalytic membranes mediated by Fe^{2+}/H_2O_2 Fenton system has been carried out. The influences of textural and compositional properties and acid functionality on the catalytic performance of the Nafion membranes are outlined. The enhancing effect of the partial heterogenisation of the Fenton system on reaction rate and H_2O_2 yield is discussed.

Keywords: Nafion membrane; *n*-Propanol; Fenton system

1. Introduction

Since the large natural gas reserves, methane and light paraffins appear the cheapest and most available alternative feedstocks for the modern petrochemical industry. However, the development of novel, clean, selective and direct catalytic routes for the conversion of lower alkanes into higher added value products still remains a challenging research area which could imply a significant impact on the framework of the gas and oil industries. In this context, the selective oxidation of methane and light alkanes (C_2–C_4) to oxygenates, fuels and higher hydrocarbons, is currently attracting a great scientific and technological interest. Although the selective oxidation of light alkanes can be achieved in principle by thermal effect in homogeneous gas-phase systems, it is generally pursued by superacid, noble metal catalysts or free radical agents in multiphase reaction media. The low-temperature activation of hydrocarbons would be more attractive from an economical standpoint since the low reaction temperature, besides to ensure rather high selectivity to the desired products, may enhance further possibilities for working out the efficient energy-saving and environmental-friendly technologies. Many authors have attempted to activate the C–H bond using catalysts which mimic enzymes, like methane monoxygenase or cytochrome P450, in hydroxylating light alkanes [1] Namely, Lyons and Ellis [2] have reported the oxidation of propane to isopropanol and acetone at 398 K and 40 bar with air over homogeneous metalloporphyrin catalysts. Recently, Raja and Ratnasamy [3] studied the direct aerobic oxidation of propane over substituted phtalocyanines of Cu, Co and Fe encapsulated in zeolites X and Y at ambient conditions obtaining high yields to isopropanol and acetone. Strong solid acids and heteropoly compounds are largely studied as active species in the catalytic conversion of light alkanes in presence of H_2O_2 [3]. Seki et al. [4,5] reported that Keggin-type vanadium containing $H_4PV_1Mo_{11}O_{40}$ heteropolyacid is an active catalyst precursor for selective oxidation of methane with hydrogen peroxide. In this context, we have disclosed that Nafion-based membrane catalysts in presence of Fe(II)–H_2O_2 Fenton system catalyse the selective oxidation of methane to methanol [6] and ethane to ethanol and acetaldehyde [7]. However, it is not definitively assessed if the oxygenated Fenton chemistry for the selective conversion of hydrocarbons involves a classical reaction mechanism or a single free radical mediated reaction network [8,9]. Recently, it has been reported that an heterogeneous Fenton system constituted by highly dispersed Fe ions

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on Nafion membranes, specifically designed for the photoassisted degradation of azo-dye, decomposes H_2O_2 with a kinetics analogous to that observed in the homogeneous Fenton system [10]. In order to highlight the features and potential of membrane based systems as alternative reaction tools for attaining the partial oxidation of light alkanes at mild conditions, this work outlines the factors controlling the efficiency of Nafion-based catalytic membranes in the selective oxidation of propane, taken as reaction model.

2. Experimental

2.1. Catalytic membranes

Bare membranes ($S = 12\,\mathrm{cm}^2$; $Ø = 4\,\mathrm{cm}$) were obtained by deposition of a carbon (Carbon Vulcan XC-72, Cabot Product, BET S.A., $250\,\mathrm{m}^2/\mathrm{g}$)–Teflon paste on a sheet of Carbon Paper (Toray product, TGP-H-090) or Carbon Cloth (E-TEK product), and subsequent activation at 300 °C in N_2 atmosphere. 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) according to the procedure elsewhere described [7]. Several membranes with different Nafion loading (20, 30 and 40 wt.%), referred to the weight of the carbon ($5\,\mathrm{mg/cm}^2$) deposited on the physical support of the membrane, were prepared. Two 20% Nafion/C_v “Fe(II)-doped” (samples NCF-1 and NCF-2) catalytic membranes were prepared by incipient wetness impregnation of the bare membrane with an isopropanol solution of Nafion-H and Fe^{2+} ($[Fe^{2+}]$, 1×10^{-2} mol/l).

Moreover, a “Nafion film Fe(III)-doped” membrane (NFF) was prepared using a commercial Nafion membrane (Dupont 117, Aldrich product 7.467-4) according to a procedure elsewhere reported [9]. The chemical composition and the sample code of the catalytic membranes are reported in Table 1.

2.2. Apparatus and procedure

Catalytic membranes have been tested in the 3PCMR elsewhere described [6]. 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–helium mixture ($P_{C_3H_8}/P_{He} = 3.7$) 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} mol/l) containing Fe^{2+} ions ($[Fe^{2+}]$, 4×10^{-5} mol/l). Oxygenated products formed during reaction were trapped at 2 °C down-stream of the reactor and analysed by a GC equipped with FID detector using a CP Porabond Q column (l, 25 m; i.d. 0.53 mm) operating at 90 °C. H_2O_2 concentration change was followed by periodical titration with permanganate solution ($[MnO_4^-]$, 1×10^{-1} mol/l).

3. Characterisation of catalytic membranes

3.1. Microcalorimetric measurements with NH_3 chemisorption

Acidic properties of the membranes were comparatively evaluated by ammonia chemisorption tests. Microcalorimetric measurements were run on a Tian-Calvet heat flow calorimetric equipment (Setaram C80d). Each sample was pre-treated in vacuo (1.3×10^{-3} Pa) at 353 K, and then contacted with successive small doses of NH_3. Adsorption runs were carried out at 353 K. The first adsorption run (*primary isotherms*) was stopped at a final equilibrium pressure of 0.13 kPa. The primary adsorption isotherm was followed by a prolonged outgassing at the adsorption temperature, and then by a second adsorption run up to the same final ammonia pressure (*secondary isotherms*). The difference in NH_3 uptake between primary and secondary isotherms, which monitors the irreversible NH_3 adsorption process, has been considered for calculating the total concentration of acid sites.

4. Results and discussion

4.1. Influence of textural and chemical properties on catalytic performance

We have previously documented [5,6] that the catalytic pattern of Nafion-based catalytic membranes in the selective

Table 1
Activity data of Nafion-based catalytic membranes in the partial oxidation of C_3H_8 at 80 °C

Sample code	Chemical composition	Nafion loading ($\mathrm{mg/cm}^2$)	Fe^{n+} loading ($\mathrm{mg/cm}^2$)	C_3H_8[a] conversion (%)	Reaction rate (r_1) ($\mathrm{nmol\,s^{-1}\,g_{memb}^{-1}}$)	Reaction rate (r_2) ($\mathrm{nmol\,s^{-1}\,g_{Naf}^{-1}}$)	H_2O_2 yield (%)
NC-1	20% Nafion/C_v	1.02	–	0.55	12.4	281.0	14
NC-2	30% Nafion/C_v	1.53	–	0.62	23.8	350.0	14
NC-3	40% Nafion/C_v	2.04	–	0.88	28.7	316.0	12
NCT	20%Nafion/C_{cloth}	1.02	–	1.89	36.9	441.1	25
NCF-1	20% Nafion/C_v + Fe^{2+}	1.02	0.0067	0.56	12.8	288.1	31
NCF-2	20% Nafion/C_v + Fe^{2+}	1.02	0.067	1.09	28.8	630.0	28
NFF	Nafion film + Fe^{3+}	–	0.0069	0.63	9.10	–	9

[a] C_3H_8 conversion at reaction time of 180 min.

oxidation of light alkanes to oxygenates under mild conditions mediated by the Fenton system outlining the role of the various reaction parameters (T_R, [H_2O_2], [Fe^{2+}], etc.) and catalyst characteristics (nature and concentration of active species, nature of active carbon, S.A., porosity, hydrophobicity, etc.) on the performance of the various systems. However, the full description of the reaction pathway in the three-phase reaction tool 3PCMR [6] cannot be drawn on the basis of the rules generally invoked for rationalising the catalytic features of solid catalysts. Then, in order to disclose the key factors controlling the efficiency of such Nafion-based catalytic membranes in the selective oxidation of light alkanes, the influence of the textural properties and the role of immobilised Fe^{2+} ions on the membrane surface (partial heterogenisation of the Fenton system) have been evaluated. Namely, the activity of a series of differently loaded Nafion/C_v/C Paper membranes (NC-1, NC-2 and NC-3 samples), a 20% Nafion/C_v/Carbon Cloth membrane (NCT sample), a commercial Nafion film doped with Fe^{3+} ions (NFF sample) and two 20% Nafion/C_v/C Paper "Fe(II)-doped" membranes (NCF-1 and NCF-2 samples) in the partial oxidation of propane at 80 °C, taken as reaction model, has been comparatively determined. In spite of the different chemical composition, all the catalytic membranes ensure a full selectivity to oxygenates with a similar product distribution (isopropanol, ≈20%; *n*-propanol, ≈25%; propionic aldehyde, ≈13% and acetone, ≈42%). No CO_x species have been detected. The activity data are presented in Table 1 in terms of reaction rate, referred to the unity weight of membrane (r_1) and unity weight of Nafion (r_2), propane conversion and molar H_2O_2 yield (calculated on the basis of the amount of "O" of the H_2O_2 source incorporated in the oxygenated products). It is evident that the activity of the 20% Nafion/C_v/C Cloth, compared with that of the same loaded 20% Nafion/C_v/C Paper, results three times higher if referred to the r_1 value and about two times higher in terms of specific activity (r_2). The use of C Cloth instead of C Paper as physical support implies a significant improvement in the H_2O_2 yield (from 14 to 31%). Since the difference between NC-1 and NCT membrane samples lies on the nature of the physical support, being analogous the Nafion loading and the preparation method, their different catalytic activity can be ascribed to any specific interaction, established during the preparation procedure, between the support and the active carbon (C_v)–Teflon paste that could affect the subsequent distribution of the Nafion on the active layer and the accessibility of the sulfonic groups of the Nafion moieties. Evidently, the texture of the C Cloth enables a higher Nafion dispersion which results in a higher catalytic activity. The higher H_2O_2 yield associated with the NCT sample can be attributed to the absence of transition metals impurities on the C Cloth, due to the intrinsic high purity of the precursor or to a severe "pacification" pretreatment (H_2, high T), that inhibits any additional H_2O_2 decomposition which is detrimental for the overall H_2O_2 yield. The doping with Fe^{2+} ions of the 20% Nafion/C_v/C Paper membrane (NC-1 sample) implies a general positive effect on catalytic performance. Indeed, the activity data of NCF-1 and NCF-2 samples indicate that the immobilisation of a small fraction (10%) of the Fe^{2+} ions dissolved in the liquid phase in standard conditions (NCF-1 sample) ensures the same extent of catalytic activity obtained in standard (Fe^{2+} ions dispersed in liquid phase) conditions (see r_1 and r_2 values for NC-1 and NCF-1 samples in Table 1), while when the same amount of Fe^{2+} ions used in liquid phase in standard conditions is anchored on the membrane surface (NCF-2) the activity of the "standard" 20% Nafion/Cv/C Paper system (NC-1 sample) is enhanced more than two times in terms of both r_1 and r_2 values. Even more relevant in terms of practical exploitation of the system is the enhancing effect of the Fe^{2+} immobilisation on the H_2O_2 yield which rises from 14% for NC-1 to 31% and 28% for NCF-1 and NCF-2, respectively (see Table 1). Although XRF and AAS data (here not reported for sake of brevity) probe a partial leaching of Fe^{2+} ions from the surface of the NCF-1 and NCF-2 membranes during the reaction, a regular evolution of the C_3H_8 conversion with reaction time for NCF-1 and NCF-2 samples is observed (Fig. 1). This regular reaction pattern could indicate that even the leached Fe^{2+} ions contribute to the Fenton reaction pathway. On the whole such data constitute a remarkable step forward the heterogenisation of the Fenton-like reaction systems which is generally recognised as a key issue for improving their efficiency as well as for exploiting their practical feasibility. The catalytic performance of the NFF sample does not denote any specific feature being indeed slight lower in terms of catalytic activity (r_1) and H_2O_2 yield with respect to that of NC-1 and NCF-1 samples. However, such Nafion membrane, could be of interest for further studies since the lower thickness and permeability rate should be significant for the optimisation and scaling up of the system.

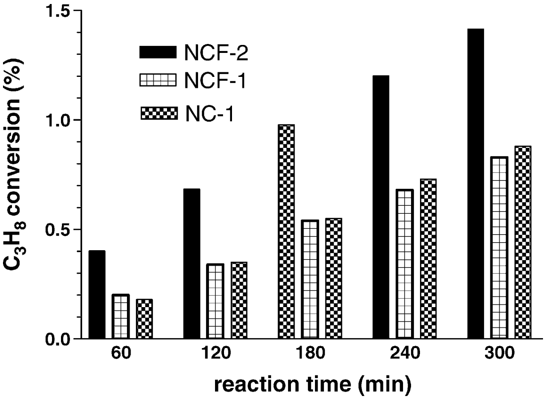

Fig. 1. Propane conversion vs. reaction time on (Fe-doped) Nafion-based catalytic membranes (NC-1, NCF-1 and NCF-2) in the partial oxidation of C_3H_8 at 80 °C.

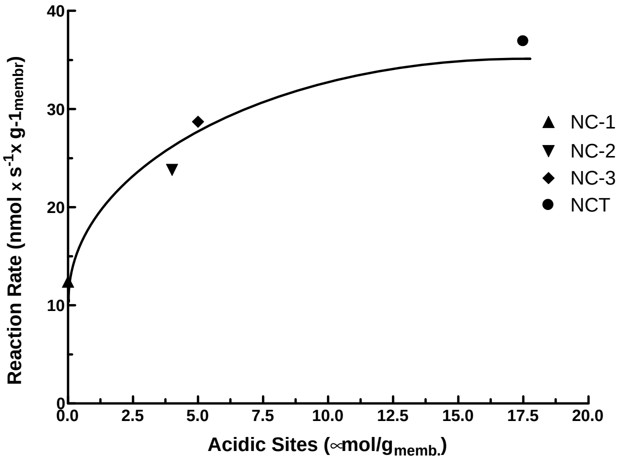

Fig. 2. Reaction rate (r_1) vs. concentration of acidic sites of the Nafion-based catalytic membranes in the partial oxidation of C_3H_8 at 80 °C.

4.2. Catalytic activity and acid functionality of the Nafion-based membranes

Although we have acquired a series of evidences and clues about the nature of the reaction pathway of the selective oxidation of light paraffins on Nafion-based catalytic membranes in presence of Fe^{2+}/H_2O_2 Fenton system which probe the involvement of radical species according to the classical Fenton-like reaction scheme, a direct role of the Nafion species in the reaction mechanism has been also observed [5,6]. Then, in order to gain further insights on the influence of the acid features of the Nafion-based membranes on the catalytic performance in the selective oxidation of propane, the acidic properties of the superacid catalytic membranes, evaluated by means of adsorption microcalorimetry using NH_3 as probe molecule, have been related with the activity data (Fig. 2). For the NC membrane samples the increase in the amount of acidic sites, expressed as NH_3 uptake ($\mu mol\, NH_3/g_{memb}$), is paralleled by an analogous enhancement in the catalytic activity (r_1). However, comparing the acid properties of NC-1 and NCT samples, characterised by the same Nafion loading, it comes out that the latter sample bears a higher extent of acidic sites along with a substantial higher catalytic activity. Such evidences confirm the role of the texture of the composite membrane on the dispersion of the Nafion species and the direct involvement of the acidic functionality of the sulfonic groups in the selective oxidation of light alkanes on the Nafion-based catalytic membranes mediated by the Fenton system.

5. Conclusions

- The nature of the physical support controls the overall catalytic performance of the Nafion-based membranes in the selective oxidation of propane mediated by the Fenton system; the use of C Cloth instead of C Paper enables a higher extent of catalytic activity and H_2O_2 yield.
- The immobilisation of Fe^{2+} ions on the Nafion membranes induces a remarkable enhancing effect on reaction rate and H_2O_2 yield.
- Besides to the experimental evidences which probe the occurrence of a classical Fenton-like radical pathway, a direct relationship between activity and acid properties of Nafion-based catalytic membranes in the selective oxidation of propane under mild conditions has been observed.

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