Catalysis Today 141 (2009) 306–310

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Enhancing effect of S and F moieties on the performance of Fenton system in the selective oxidation of propane

C. Espro [a], S. Marini [a], F. Mendolia [a], F. Frusteri [b], A. Parmaliana [a,*]

[a] Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università degli Studi di Messina, Salita Sperone 31, I-98166 Messina, Italy
[b] Istituto CNR-TAE, Via Salita S. Lucia sopra Contesse 5, I-98126 Messina, Italy

ARTICLE INFO

Article history:
Available online 6 September 2008

Keywords:
Selective oxidation
Propane
Fenton system
Oxygenated products
Solid promoters containing S and F

ABSTRACT

The selective oxidation of propane to oxygenated products (isopropanol, *n*-propanol, propionic aldehyde and acetone) mediated by the Fe(II)/H_2O_2 Fenton system at 80 °C in the presence of solid acid and superacid promoters containing S and F moieties has been studied. The occurrence of a radical reaction pathway accounting for the activation of the C–H bonds of the propane molecule by $OH^{\bullet}$ radicals has been proved by assessing the inhibiting effect of both Cl^- and NO_3^- radical scavengers and organic (CH_3COOH, CH_3CN, DMSO) reaction media on the reaction pattern. S and F functionalities of several solid agents promote the electron transfer processes controlling the H_2O_2 activation. Any effect of the Brönsted acid features of the solid promoters on the reaction kinetics and pathway has been disregarded.

1. Introduction

Alkanes from natural gas are the most abundant and low cost feedstocks for gas and oil industries. Current petrochemical technologies to convert these feedstocks into fuels and chemicals operate at rather high temperature (>400 °C) and utilize expensive multistep processes. The development of novel catalysts along with effective reaction systems and innovative operating strategies for low temperature (<100 °C), selective and direct (one-step) alkane oxidation chemistry could allow remote natural gas to be valuated as alternative or primary feedstock for the chemical and petrochemical industries [1]. In this context, the selective oxidation of alkanes to the corresponding alcohols, aldehydes, ketones and carboxylic acids is a topic of great research interest since it offers an attractive route to synthesize higher added value oxygenated products from relatively cheap raw substrates. Various catalysts in the presence of molecular oxygen [2–8] and H_2O_2 (or alkylhydroperoxide) [9–14] in both homogeneous and heterogeneous systems are able to attain the activation of the C–H bonds of the alkanes. However, hydrogen peroxide is considered the most suitable agent for the industrial exploitation of selective oxidation under mild conditions due to its high oxygen reactivity. Aqueous solutions of Fe(II)/H_2O_2, otherwise known as Fenton's reagent or system, generally used for the treatment of a variety of industrial wastewater [15–20], are also effective in light alkanes oxyfunctionalization [21].

Sawyer et al. [22–24] have studied the selective oxidation of several alkane substrates by the Fenton reagent in organic media under various reaction conditions. It was inferred that, with high H_2O_2/Fe^{II}–bis-picolinato ratios in Py/AcOH, the main reaction path involves a concerted selective process, mediated by an activated iron complex, which is responsible for the direct ketonization of the alkane.

The pathway of oxygenated Fenton chemistry in the functionalization of hydrocarbons in liquid phase systems promoted by different metal/hydroperoxide reaction media is quite complex. The efficiency of the system is affected by a number of factors including pH, solvent, iron oxidation state, iron chelation and nature of the ligands. The addition of an anion (e.g., F^-, SO_3^-) to the ferrous ion ($Fe^{2+} + F^- \rightarrow FeF^+$) leads to a more effective oxidising system [25]. Fernandez et al. [26,27] claimed that the immobilization of Fe^{III} ions on a Nafion membrane improves the performance of the Fenton system in the photoassisted degradation of organic compounds, suggesting that Fe^{III} ions electrostatically interact with the sulphonic groups of the Nafion giving to the ensemble a net charge of 2+ for the $(Fe^{3+}\text{-}SO_3^-)^{2+}$ ion pair.

Our research group has contributed to this topic assessing that carbon and PEEK-WC-supported Nafion catalytic membranes, in the presence of the Fe^{II}/H_2O_2 Fenton system, promote the selective oxidation of light alkanes under mild ($T < 120$ °C; $P < 2$ atm) reaction conditions [28–31]. However, in spite of several studies so far accomplished, the elucidation of the mechanism of the selective

---

* Corresponding author.
E-mail address: adolfo.parmaliana@unime.it (A. Parmaliana).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.07.003

oxidation of light alkanes mediated by the Fenton system still remains an open and hard issue. Namely, it is not decided if the reaction occurs by a concerted mechanism where the $Fe(II)/H_2O_2$ Fenton system and superacid catalyst act in a synergetic way or according to the classical radical mechanism. Several experimental clues allow us to infer that the rate-determining step of the selective oxidation of light hydrocarbons is the generation of OH radicals by hydrogen peroxide decomposition [17,18].

Therefore, this study is aimed to ascertain the effect of certain acid and superacid solid promoters containing S and F moieties, reaction media and radical scavengers on the pathway and efficiency of the selective oxidation of propane to oxygenates mediated by the Fenton system.

2. Experimental

2.1. Solid promoters

Commercial precipitated silica “CS 2133” (PQ Corporation product, B.E.T. S.A. = 365 m^2/g), Carbon Ketjenblack “C_K” (EC 600 grade Akzo product, B.E.T. S.A. = 950 m^2/g) and SiC (Carlo Erba product, B.E.T. S.A. = 0.01 m^2/g) were used as solid agents.

The 20 wt% Nafion/C_K (NC) and the 20 wt% Nafion/SiO_2 (NS) systems were prepared by incipient wetness impregnation of “C_K” and “CS 2133” supports, respectively, with a diluted ethanolic solution containing the designed amount of Nafion-H solution (5% of Nafion-H (1100 EW grade) in isopropanol solution, cod. 527084, Aldrich product) and subsequent drying at 100 °C for 16 h.

The 20 wt% HPF_6/C_K (HF) and the 20 wt% sulphonated polystyrene/C_K (PSC) systems were prepared by incipient wetness impregnation of the C_K support with an isopropanol solution containing the desired amount of HPF_6 (60 wt% grade, cod. 454931, Aldrich product) and Sulphonated Polystyrene (Polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene, sulfonated (cod. 659444, Aldrich product), respectively, and subsequent drying at 150 °C for 12 h.

The 1.5 wt% SO_4^{2-}/ZrO_2 (ZS) system was prepared by contacting a ZrO_2 powder, obtained by a conventional precipitation method, with a H_2SO_4 solution (0.5 M) for 30 min and subsequent drying at 100 °C for 24 h.

The sulphonated PEEK-WC (P) system was obtained by a sulphonation procedure of a PEEK-WC powder (supplied by Chanchung Institute of Applied Chemistry, Academia Sinica, China) elsewhere reported [32].

Nafion (N) (cod. 49,578-6, Aldrich product), Amberlyst 36 (A) (cod. 43,671-2, Aldrich product), Tungstophosphoric Acid ($H_3PW_3O_{40}$) (HP) (Aldrich product, cod. 45,597-0), Potassium Trifluoromethanesulphonate (CF_3SO_3K) (CF) (cod. 42,284-3, Aldrich product) and Amberlite IRA 900 F^- form (F) (cod. 387789, Aldrich product) powders were tested as received.

2.2. Acid capacity measurements

The Brönsted acidity extent of the above acid and superacid agents was electrochemically determined by the zero point charge (ZPC) technique, according to the procedure elsewhere described [33].

The chemical composition along with the code and the acid capacity (meq_{H+}/g_{cat}) values of the various systems are listed in Table 1.

2.3. Apparatus and procedure

The effect of the various acid and superacid catalytic agents in the selective partial oxidation of propane in the presence of the Fenton system has been evaluated in a batch reactor Teflon-covered (Parr Instruments), in the temperature (T_R) range 80–110 °C with a propane absolute pressure of 202.6 kPa. The liquid phase (300 ml) was an aqueous solution of H_2O_2 (1%, v/v) containing Fe^{2+} ions (350 μmol/l). The pH of the solution was 3.8. Reactants and products were analysed by a TRACE GC equipped with a 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^- [10^{-1} mol/l]).

Table 1
List of solid promoters

Code	Composition	H^+-exchange capacity (meq_{H+}/g_{cat})
Solid acid		
HP	$H_3[PW_3O_{40})_4 \cdot xH_2O$	0.89
Solid acid containing S moieties		
ZS	1.5 wt% ZrO_2/SO_4	0.17
PSC	20 wt% sulphonated polystyrene/C_K	1.24
P	Sulphonated PEEK-WC	1.23
Solid acid containing F moieties		
HF	20 wt% HPF_6/C_K	2.89
F	Amberlite IRA 900 F^- form	0.08
Solid acid containing S and F moieties		
N	Nafion powder	0.45
CF	CF_3SO_3K	0.57
A	Amberlyst 36	3.94
F-PSC	20 wt% F/sulphonated polystyrene/C_K	1.22
NC	20 wt% Nafion/C_K	0.45
NS	20 wt%Nafion/SiO_2	0.45

3. Results and discussion

3.1. Bare Fenton system

The efficiency of the Fe^{II}/H_2O_2 Fenton system in the presence of Nafion supported catalytic membranes in promoting the selective oxidation of light alkanes under rather mild ($T < 120$ °C; $P < 2$ atm) conditions has been already assessed [28–30]. However, no proofs have been yet gained about the involvement of S and F moieties of the Nafion backbone on the reaction pathway. In order to shed light on this issue, several blank tests with bare “$Fe(II)/H_2O_2$” Fenton system have been carried out. The experimental results, summarized in Table 2 in terms of reaction rates and product selectivity values after 120 min of reaction time, indicate that the efficiency of the Fenton system in driving the selective oxidation of propane is not greatly affected by the presence of any solid in terms of neither reaction rate nor product distribution. Only when C_K powder is dispersed in the reaction medium a slight decline in the reaction rate from 132.2 to 107.0 μmol s^{-1} is observed. It could be due to the metal impurities of the C_K which promote a higher and not effective H_2O_2 decomposition. The H_2O_2 consumption rate of 5.2 μmol s^{-1} with bare Fenton system signals a H_2O_2 yield (R), calculated on the basis of the amount of “O” of the H_2O_2 incorporated in the oxygenated products, equal to 4.7%. The product distribution entails CH_3COCH_3 (61.9%) as the main reaction product, along with i-C_3H_7OH (9.6%), n-C_3H_7OH (4.4%) and C_2H_5CHO (24.2%) (Table 2). Such findings point to a “free-radical” reaction path proceeding through an unselective attack of the hydroxyl radicals generated by the Fenton system on both the primary and secondary carbons of the propane molecule. However, the selectivity of the radical reactions involving hydrocarbon substrates can be accounted for in terms of relative stability of alkyl radicals. According to such rule the oxy-functionalization of

Table 2
Selective oxidation of propane mediated by the Fenton system at 80 °C (Influence of solid agents)

Solid agent	[a]Reaction rate ($\mu mol\ s^{-1}$)	[a]H_2O_2 conversion rate ($\mu mol\ s^{-1}$)[a]	[a]R (%)	[a]C_3H_8 conversion (mol%)	[a]Product selectivity (%)			
					CH_3CH_2CHO	CH_3COCH_3	i-$CH_3CH_2CH_2OH$	n-$CH_2CH_2CH_2OH$
–	132.2	5.2	4.7	1.9	24.2	61.9	9.6	4.4
C_K	107.0	7.8	2.5	1.6	24.5	55.6	13.1	6.7
SiO_2	132.1	3.5	7.1	1.9	25.0	60.9	10.1	4.0
SiC	136.5	4.3	6.3	2.1	23.6	64.4	8.7	3.4

[a] Reaction rate, H_2O_2 conversion rate, R and C_3H_8 conversion values at reaction time of 120 min.

the alkanes preferentially implies the activation of the secondary carbon as proved in this study by the highest selectivity to acetone (61.9%).

3.2. *Effect of radical scavengers*

In order to acquire further insights on the radical nature of the reaction pathway, a series of experiments by adding different amounts of Cl^- and NO_3^- ions to the liquid phase has been performed. As shown in Fig. 1, the addition of these ions implies a marked decline in the reaction rate the extent of which depends upon the amount of Cl^- and NO_3^- added being more significant at lower anion extents (<10 mmol). The negative effects of chloride ions on the efficiency of the Fe(II)/H_2O_2 and Fe(III)/H_2O_2 systems can be attributed to both formation of iron(III)/chlorocomplexes ($FeCl^+$, $FeCl^{2+}$, $FeCl_2^+$, etc.) and scavenging effect of chloride ions for hydroxyl radicals [17]. The reaction of $HO^\bullet$ with Cl^- leads to the formation of chlorine ($Cl^\bullet$) and dichloride anion ($Cl_2^{\bullet-}$) radicals which act as strong oxidants ($E^\circ(Cl^\bullet/Cl^-) = 2.41$ V and $E^\circ(Cl_2^{\bullet-}/2Cl^-) = 2.09$ V). Indeed, these chlorine radicals can oxidize H_2O_2 and Fe(II) being, however, less reactive than $HO^\bullet$ radicals towards the alkane substrate [17]. At pH ≤ 3 and $[Cl^-] \geq 10^{-4}$ M, the concentration of $Cl_2^\bullet$ - represents always more than 99% of the total concentration of radicals [17]. Such a finding clearly indicates that Cl^- acts as scavenger of any radical species present in the reaction medium resulting in a lower overall reaction rate. The presence of NO_3^- ions in the reaction medium implies an inhibiting effect on the generation rate of OH radicals similar to that observed with Cl^- ions (Fig. 1), however, the involvement of NO_3^- in the Fenton reaction pathway has been not yet highlighted.

3.3. *Effect of reaction medium*

The chemical features of the reaction medium can affect in principle the evolution of any catalytic or radical reaction in liquid phase systems. Therefore, taking into account the above proved radical nature of the studied reaction and the promoting action of Nafion-based superacid species, the influence of several organic media, such as acetonitrile (CH_3CN), acetic acid (CH_3COOH) and dimethyl sulfoxyde (DMSO) on the pattern of the selective oxidation of propane has been evaluated. It is well known that the acid strength of a superacid agent can be remarkably influenced by the nature of the solvent [31]. Namely, the basicity of the solvent reduces the acid strength, while the polarity and the consequent capability to form a hydrogen bond (effect of stabilization of the anion) promote the superacid character. Nafion-H, in fact, shows its remarkable superacidity when it is mediated by a solvent (A^-) that stabilizes the sulfonic groups as follows [34]:

$$nSOH + A^- \leftrightarrow (SOH)_nA^-$$

Thus, the aqueous medium significantly limits the superacid functionality of Nafion. If selective oxidation of light alkanes occurs by a superacid driven mechanism, the use of an organic solvent, instead of H_2O, would enhance the catalytic action of Nafion species. In order to verify this assumption, a specific designed experiment by using CH_3CN as reaction medium of the Fenton system has been performed. The results reported in Fig. 2, in terms of C_3H_8 conversion vs. reaction time, show a significant decrease of propane conversion with respect the standard conditions, where H_2O is used as reaction medium, which accounts for the hindering effect of such organic solvent on the efficiency of the Fenton system

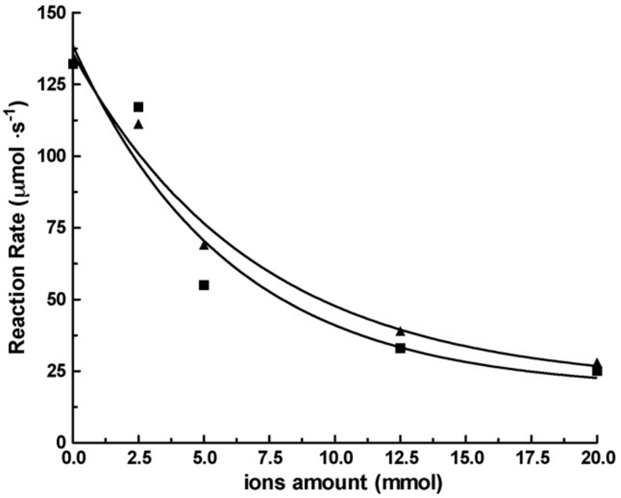

Fig. 1. Selective oxidation of propane mediated by the Fenton system at 80 °C. Influence of (■) Cl^- and (▲) NO_3^- ions amount on the reaction rate.

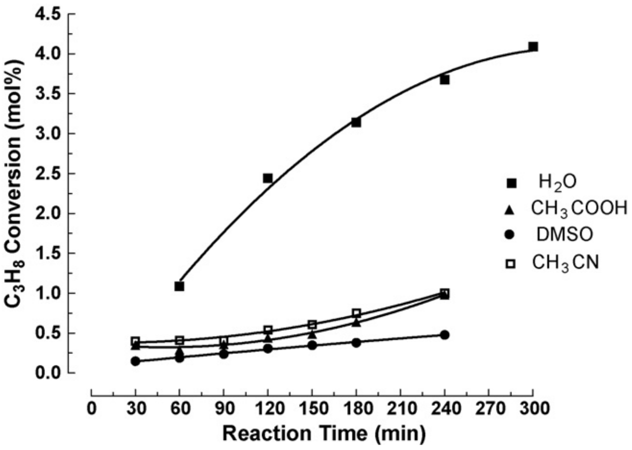

Fig. 2. Selective oxidation of propane mediated by the Fenton system at 80 °C. Influence of the reaction medium (H_2O, CH_3COOH, CH_3CN and DMSO) on C_3H_8 conversion.

Table 3
Selective oxidation of propane mediated by the Fenton system at 80 °C (Influence of acid and superacid solid promoters containing S and F moieties)

Solid promoter	[a]Reaction rate (μmol s^{-1})	[a]H_2O_2 conversion rate (μmol s^{-1})	[a]R (%)	[a]C_3H_8 conv. (%)
Solid acid				
HP	30	7.5	3.2	1.2
Solid acid containing S moieties				
ZS	10	n.d.	n.d.	0.8
PSC	56.3	6.1	1.7	0.8
P	79.0	4.3	3.2	1.2
Solid acid containing F moieties				
HF	132.8	7.8	3.0	1.9
F	90.2	5.2	3.2	1.3
Solid acid containing S and F moieties				
N	163.4	3.5	8.7	2.4
CF	215.7	4.3	9.3	3.2
A	174.8	3.5	9.4	2.6
F-PSC	132.8	7.8	3.0	1.9
NS	267.1	6.9	7.2	3.9
NC	228.7	8.6	4.9	3.4

[a] Reaction rate, H_2O_2 conversion rate, R and C_3H_8 conv. values at reaction time of 120 min.

[25]. On the other hand, such finding could be considered as a proof of the fact that the superacid agent does not play any role in the reaction mechanism. When CH_3COOH or DMSO is used as reaction medium, an inhibiting effect on the reaction rate (Fig. 2), similar to that experienced with CH_3CN, has been observed. On the whole, these results confirm that H_2O is the most effective medium for the Fenton system, since any organic solvent acting as OH scavenger [25] limits the rate of OH radical generation. These results further confirm that the selective oxidation of light alkanes mediated by the Fenton system does not occur by the electrophilic activation of the C–H bond catalyzed by any superacid species.

3.4. Effect of solids containing S and F moieties on the performance of the Fenton system

In order to investigate how solid promoters containing S and F moieties can affect the Fenton system efficiency, a series of experiments in the presence of various S and F functionalised solids has been carried out. The addition of any solid to the reaction system could affect both reaction rate and H_2O_2 yield. The results outlined in Table 2 do not evidence any significant effect exerted by any solid on neither reaction rate nor H_2O_2 yield. However, the presence of S- and F-based functional species in the solid agent could induce any electronic effect on the Fe(II)/H_2O_2 system controlling both kinetics and pathway of the title reaction.

The results of a comparative test in the selective oxidation of propane at 80 °C, dispersing 0.1 g of the various S and F solid promoters in the reaction medium, expressed as C_3H_8 conversion, reaction rate, H_2O_2 consumption rate, molar H_2O_2 yield after 120 min of time on stream are collected in Table 3. Considering that the reaction rate and the H_2O_2 yield for the bare Fenton system (Table 2) are 132 μmol s^{-1} and 4.7%, respectively, the data shown in Table 3 indicate that the addition of CF (r = 215.7 μmol s^{-1}), A (r = 174.8 μmol s^{-1}) and N (r = 163.4 μmol s^{-1}) systems results in a substantial promoting effect on both reaction kinetics and H_2O_2 yield (R attains the values of 8.7, 9.3 and 9.4 % for the samples N, A and CF, respectively). Whereas, the addition of HP (r = 30.0 μmol s^{-1}), P (r = 79 μmol s^{-1}), HF (r = 132 μmol s^{-1}), ZS (r = 10.1 μmol s^{-1}), F (r = 90 μmol s^{-1}) and PSC (r = 56.3 μmol s^{-1}) solids gives rise to a lowering in both reaction kinetics and H_2O_2 yield with respect the bare Fenton system. The reason for such negative effect of HP, HF, PSC, ZS and F solid agents in the efficiency of the Fenton system could lye in their different stability in H_2O_2 media. On this account, it has been observed that Nafion is very stable in the presence of H_2O_2, while other acid and heteropolyacid systems could react with H_2O_2 to form peroxophosphates ($PW_xO_y^{2-}$ and $PMo_xO_y^{2-}$). The low reaction rate obtained with P (r = 79 μmol s^{-1}) and F (r = 90 μmol s^{-1}) systems can be attributed to the chemical instability of the sulphonated PEEK-WC in presence of H_2O_2 and the absence of any S moieties in the Amberlite IRA 900, respectively.

Furthermore, the different effect of the various solid agents cannot be rationalised in terms of acidic properties probed by the "H–proton exchange capacity". In fact, the results depicted in Fig. 3 clearly evidence that among the investigated solid promoters CF and N samples are characterised by rather low H^+ exchange capacity values while they reveal the highest enhancing effect on

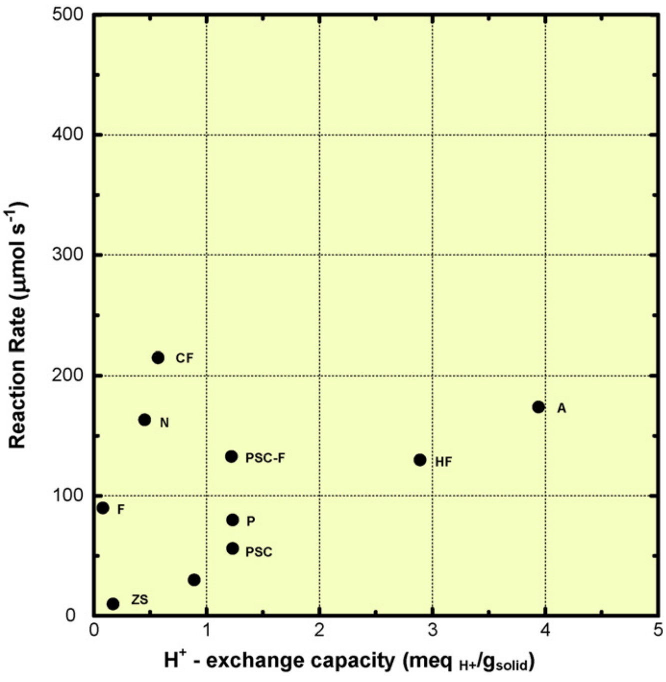

Fig. 3. Selective oxidation of propane mediated by the Fenton system at 80 °C. Reaction rate vs. H^+-exchange capacity of several acid and superacid solid promoters containing S and F moieties.

the reaction rate. It can thus be inferred that the concentration of acidic sites, which can be related with the H^+–proton exchange capacity, does not control the performance of the acid and superacid agents in the selective oxidation of propane. On the whole, these finding suggest that the solid agents act as promoters improving the efficiency of the Fenton system towards the H_2O_2 activation resulting in higher propane conversion rates. Taking into account that it has been already reported [25] that the Fenton system efficiency can be enhanced by complexing the Fe^{II} ions with appropriate anions (such as F^-) that promote its oxidation according to the scheme: $Fe^{2+} + F^- \rightarrow FeF^+$, it can be argued that the "CF_x" units present in the CF, N and A solids favour the electron transfer process which controls the H_2O_2 activation and consequently the kinetics of the selective oxidation of propane. Moreover, according to Fernandez et al. [26,27] it can be inferred that the sulphonic sites of CF, N, and A systems enhance the rate of radical generation via an electrostatic interaction with Fe^{2+} ions, giving the ensemble a net 2+ charge for the $(Fe^{3+}\text{-}SO_3^{-})^{2+}$ ion pair speeding up the rate of electron transfer process to H_2O_2 molecules.

Finally, it is noteworthy that the doping of PSC system ($r = 56.3\ \mu mol\ s^{-1}$) with F^- ions results in a positive effect on the reaction rate (F-PSC sample, $r = 132.8\ \mu mol\ s^{-1}$) definitively confirming the synergic action of S and F functional groups in promoting the Fenton system.

The higher reaction rate of NC ($r = 228.7\ \mu mol\ s^{-1}$) and NS ($r = 267.1\ \mu mol\ s^{-1}$) systems with respect the N one ($r = 163.4\ \mu mol\ s^{-1}$) is a direct evidence of the positive effect of the dispersion of Nafion species on the surface of the C_K and CS-2133 SiO_2 supports likely enhancing the surface availability of S and F functional groups and consequently the promoting effect on the Fenton reaction.

The stability of the supported Nafion agents (NC and NS samples) has been checked by both performing consecutive reaction test on the same batch of powder and determining S and F content on fresh and used samples. Since neither activity decline nor leaching have been noticed, it can be stated that Nafion supported on carbon and silica carriers are suitable solid promoters of the selective oxidation of propane under mild conditions mediated by the Fenton system.

4. Concluding remarks

The results obtained in this study allow to draw the following statements:

(i) the selective oxidation of propane by Fenton system in presence of solid acid and superacid agents containing S and F moieties proceeds via a radical mechanism;

(ii) the addition of Cl^- and NO_3^- anions, acting as radical scavengers, greatly depresses the efficiency of the Fenton system in driving the functionalization of the C_3H_8 molecule;

(iii) the aqueous medium ensures the highest efficiency of the Fenton system, while organic solvents, such as acetonitrile, dimethyl sulfoxide and acetic acid, hinder the generation rate of OH radicals;

(iv) superacid functionalities are not involved in the selective oxidation of propane mediated by the Fenton system;

(v) S and F functional groups act as promoters of the Fenton system towards the H_2O_2 activation resulting in higher propane conversion rates.

References

[1] R.A. Periana, G. Bhalla, W.J. Tenn III, K.J.H. Young, X.Y. Liu, O. Mironov, C.J. Jones, V.R. Ziatdinov, J. Mol. Catal. A: Chem. 220 (2004) 7.
[2] J.M. Thomas, R. Raja, Catal. Today 117 (2006) 22.
[3] J.M. Thomas, R. Raja, G. Sankar, R.G. Bell, Nature 398 (1999) 227.
[4] J.S. Min, N. Mizuno, Catal. Today 71 (2001) 89.
[5] M. Zerella, A. Kahoros, A.T. Bell, J. Catal. 237 (2006) 111.
[6] M. Hartmann, S. Ernst, Angew. Chem., Int. Ed. 39 (2000) 888.
[7] A.M. Valentine, S.S. Stahl, S.J. Lippard, J. Am. Chem. Soc. 121 (1999) 3876.
[8] R. Raja, C.R. Jacob, P. Ratnasamy, Catal. Today 49 (1999) 171.
[9] H.H. Monfared, Z. Amouei, J. Mol. Catal. A: Chem. 217 (2004) 161.
[10] A.P. Pokutsa, R.B. Sheparovich, A.B. Zaborovskii, V.I. Kopylets, Kinet. Catal. 43 (2002) 740.
[11] E.D. Park, Y.S. Hwang, J.S. Lee, Catal. Commun. 2 (2001) 187.
[12] G. Süss-Fink, L. Gonzalez, G.B. Shul'pin, Appl. Catal. A: Gen. 217 (2001) 111.
[13] Y. Seki, N. Mizuno, M. Misono, Appl. Catal. A: Gen. 194–195 (2000) 13.
[14] Y. Seki, J.S. Min, M. Misono, N. Mizuno, J. Phys. Chem. B 104 (2000) 5940.
[15] M.P. Ormad, R. Mosteo, C. Ibarz, J.L. Ovelleiro, Appl. Catal. B: Environ. 66 (2006) 59.
[16] C.K. Duesterberg, W.J. Cooper, T. David Waite, Environ. Sci. Technol. 39 (2005) 5052.
[17] J. De Laat, T.G. Le, Appl. Catal. B: Environ. 66 (2006) 173.
[18] J. De Laat, T.G. Le, B. Legube, Chemosphere 55 (2004) 715.
[19] G.P. Anipsitakis, D.D. Dionysiou, Appl. Catal. B: Environ. 54 (2004) 155.
[20] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Appl. Catal. B: Environ. 47 (2004) 219.
[21] F. Gozzo, J. Mol. Catal. A: Chem. 171 (2001) 1.
[22] A.M. Khenkin, et al. Catal. Lett. 5 (1990) 211.
[23] D.T. Sawyer, A. Sobkowiak, T. Matsushita, Acc. Chem. Res. 29 (1996) 409.
[24] D.T. Sawyer, Coord. Chem. 165 (1997) 297.
[25] G. Strukul, Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic Publishers, The Netherlands, 1992.
[26] J. Fernandez, J. Bandara, A. Lopez, P. Buffat, J. Kiwi, Langmuir 15 (1998) 185.
[27] J. Fernandez, J. Bandara, A. Lopez, P. Albers, J. Kiwi, Chem. Commun. (1999) 1493.
[28] F. Frusteri, L. Spadaro, D. Scerra, C. Espro, A. Parmaliana, F. Arena, J. Nat. Gas Chem. 11 (2002) 180.
[29] C. Espro, F. Frusteri, F. Arena, A. Parmaliana, Topic Catal. 22 (2003) 65.
[30] C. Espro, G. Bonura, F. Frusteri, F. Arena, A. Parmaliana, F. Sini, V. Solinas, Catal. Today 91 (2004) 215.
[31] C. Espro, F. Arena, F. Tasselli, A. Regina, E. Drioli, A. Parmaliana, Catal. Today 118 (2006) 253.
[32] M.G. Buonomenna, A. Figoli, J.C. Jansen, E. Drioli, J. Appl. Polym. Sci. 92 (2004) 576.
[33] A.S. Aricò, V. Antonucci, M. Minutoli, N. Giordano, Carbon 27 (1989) 337.
[34] D. Fărcaşiu, Catal. Lett. 71 (2001) 95.