

## Heterogeneous Fenton like Catalysts for the Selective Oxidation of light alkanes in aqueous medium

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### Abstract

The peculiar features of heterogeneous Fenton chemistry in the selective partial oxidation of light alkanes to oxygenated has been investigated. The activity of a series of Nafion/SiO<sub>2</sub>, Fe(II)/SiO<sub>2</sub>, Fe(II)/Al<sub>2</sub>O<sub>3</sub> samples and a Nafion/Fe(II)/SiO<sub>2</sub> catalyst, in the partial oxidation of methane and propane in batch reactor at 80°C, has been compared. The immobilization of Fe(II) ions on the Nafion/SiO<sub>2</sub> promoter, resulting in a partial heterogenization of the Fenton system, induces a remarkable enhancing effect on reaction rate and light alkanes conversion. Indeed, H<sub>2</sub>O<sub>2</sub>/Fe(II) molar ratio, pH effect have been evaluated. H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio is a critical parameter for improving the efficiency of the Fenton process. Keeping the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratio constant within a specified range, it is possible to decrease FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> concentrations remarkably, still achieving to the highest efficiency. The initial pH value has to be in the acidic range (2-4) to generate the maximum amount of OH radicals to oxidize the organic substrate.

**Keywords:** Fenton System, alkane partial oxidation, liquid phase, heterogeneous catalysts

### 1. INTRODUCTION

Environmental concerns and the limited availability of the world's crude oil reserves are the main driving forces for a future shift towards more sustainable feedstocks for the chemical industry [1-2]. In this scenario, natural gas is becoming progressively important as society's source for chemicals and transportation fuels [3-5]. Therefore, the development of catalytic systems for the direct low temperature selective oxidation

of methane to methanol has attracted the research interest of many academic and industrial research groups [6-10]. In this context, the selective oxidation of methane and light 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 [11-16]. Various catalysts in the presence of molecular oxygen [17-23] and H<sub>2</sub>O<sub>2</sub> (or alkylhydroperoxide) in both homogeneous and heterogeneous systems are studied for the activation of the C-H bonds of the alkanes [24-29]. Aqueous solutions of Fe(II)/H<sub>2</sub>O<sub>2</sub>, otherwise known as Fenton's reagent or system, generally used for the treatment of a variety of industrial wastewater [30-35], are also effective in light alkanes oxyfunctionalization [36]. 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<sup>-</sup>, SO<sub>3</sub><sup>-</sup>) to the ferrous ion ( $\text{Fe}^{2+} + \text{F}^- \rightarrow \text{FeF}^+$ ) leads to a more effective oxidising system [37]. The homogeneous Fenton reaction is performed under acidic condition (pH < 4) to keep the iron soluble and to enhance the oxidative character of the hydroxyl radicals. The process includes a neutralization step to allow the elimination of the ferric ions by precipitation as hydroxide; the deriving, so-called, Fenton sludge creates subsequent disposal problems and constitutes the main limitation of the process. Fe sludge disposal and/or regeneration after the Fenton reaction is a serious problem during pollutant degradation in homogeneous media. The removal of iron ions is a relatively simple operation, commonly carried out by precipitation and re-dissolution of the Fe ions after the treatment of large volumes, but it implies the use of large amount of chemicals and manpower. This costly regeneration step therefore has to be avoided. Then, the development of supported Fenton catalysts has recently become important in the emerging field of advanced oxidation technologies. Fernandez et al. [38-39] claimed that the immobilization of Fe<sup>3+</sup> 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<sup>+</sup> for the (Fe<sup>3+</sup>-SO<sub>3</sub><sup>-</sup>)<sup>2+</sup> ion pair. Kiwi et al. [40] have immobilized Fe<sup>3+</sup> ions into very thin Nafion films cast onto a glass-fiber mat immersed in an alcoholic solution of Nafion oligomers. This immobilized Fenton catalyst was used to abate/mineralize the azo-dye Orange II, taken as a model organic compound. Yue et al. [41] have considered the Fenton degradation of salicylic acid by using SAIER exchanged with Fe ions as catalyst in presence of UV light (254 nm) and H<sub>2</sub>O<sub>2</sub>. The X-ray photoelectron spectroscopy (XPS) results have revealed that the Fe ions are anchored by the sulfonate groups on the surface of the SAIER and are identified as Fe<sup>3+</sup>. The Fe/SAIER catalyst can significantly enhance the degradation rate of salicylic acid, without remarkable Fe leaching to the solution. In this context, we have found that the homogeneous Fe<sup>II</sup>-H<sub>2</sub>O<sub>2</sub> Fenton system in the presence of acid solid promoters, allow to efficiently perform the selective oxidation of light alkanes to higher added value oxygenated products [42-44]. In this work it has been developed a new heterogeneous catalyst consisted of solid acid promoter and

metal ions on inert support, in order to overcome the problems related to homogeneous Fenton system and to exploit innovative systems for enhancing the performance of the Fenton catalyst in the selective oxidation of methane and light alkanes.

Furthermore, role of the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  molar ratio, effect of pH in liquid phase in light alkanes oxidation it has been investigated.

## 2. EXPERIMENTAL

### 2.1. Catalysts Preparation

**0.37wt%Fe/SiO<sub>2</sub>.** Silica (Si CS-2050 - The PQ Corporation product) supported iron catalyst was prepared by the adsorption-precipitation method according to the following experimental procedure: 10 g of a powdered silica carrier were put into 0.3l of distilled water with a resulting pH of 4.5. The suspension was stirred and kept under a nitrogen flow for 1h at room temperature to remove any dissolved oxygen, thus avoiding any further air admission. Then, an amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  corresponding to the designed Fe loading was added to the stirred suspension at room temperature, raising progressively the pH at 7.0-7.5 by addition of a 10%  $\text{NH}_4\text{OH}$  solution. The suspension was kept at the final pH value under stirring and  $\text{N}_2$  bubbling for 1h to attain a complete adsorption of precursor. Thereafter the catalyst was filtered, repeatedly washed with distilled water, dried at 100°C and then calcined at 600°C in air for 16 h.

**0.5wt% Fe/Al<sub>2</sub>O<sub>3</sub>.** Alumina ( $\text{Al}_2\text{O}_3$  - Akzo Nobel product, cod. 000-1.5E) supported iron catalyst was prepared by the adsorption-precipitation method according to the following experimental procedure: to avoid the formation of clusters, iron atoms were deposited on the support surface through the adsorption of  $\text{Fe}^{2+}$  ions by flushing an inert gas into the solution so to prevent their oxidation to  $\text{Fe}^{3+}$ . In fact, the  $\text{Fe}(\text{OH})_2$  Kps is sensibly lower ( $1.8 \cdot 10^{-12}$ ) and at acidic pH (<7) the iron is water soluble. Considering that the pH of ZPC (pH of Zero Point Change) of  $\text{Al}_2\text{O}_3$  ranges between 6 and 8, we can uptake it as  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  onto the negatively polarized support surface suspended in a water solution, adequately adjusting the pH and allowing, thus, for a better active phase dispersion. In our case, 5g of alumina, were put into 0.6 l of distilled water which was vigorously stirred ( $\approx 1000\text{rpm}$ ) and flushed with nitrogen ( $\approx 100\text{ stp cm}^3/\text{min}$ ). Then, after 1.5 hours  $\text{N}_2$  bubbling, the designed amount of  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  was added to the suspension at room temperature with a resulting pH of  $\approx 4.5$ , which was progressively raised till a value of 7.5 by adding dropwise a 5% water solution of  $\text{NH}_4\text{OH}$ . The suspension was kept at this pH for 1h, under  $\text{N}_2$  flux and stirring, to attain the complete adsorption of the precursor and then it was filtered and repeatedly washed with distilled water. At the end of the impregnation catalyst was dried at 100°C overnight and calcined at 500°C for 6 hours.

**20 wt% Nafion/SiO<sub>2</sub>.** Commercial precipitated silica “CS 2133” (PQ Corporation product) was used as solid agents. The systems were prepared by incipient wetness impregnation of “CS 2133” supports with a diluted ethanolic solution containing the designed amount of Nafion-H solution (5% of Nafion-H - 1100 EW grade) in isopropanol solution and subsequent drying at 100 °C for 16 h.

**0.5wt%Nafion/0.37wt%Fe<sup>2+</sup>/SiO<sub>2</sub>.** The synthesis of 0.5wt%Nafion/0.37wt% Fe<sup>2+</sup>/SiO<sub>2</sub> system can be divided into two step: preparation of iron on silica supported solid carrier and Nafion deposition on Fe/SiO<sub>2</sub> system. The Fe<sup>2+</sup>/SiO<sub>2</sub> catalyst was prepared according the adsorption-precipitation method previously described.

The Nafion was deposited by the “incipient wetness” impregnation method of Fe<sup>2+</sup>/SiO<sub>2</sub> support with a diluted ethanolic solution containing the designed amount of Nafion solution (5% of Nafion 1100 EW grade) in isopropanol solution and subsequent drying at 100°C for 16h. Nafion solution (cod. 49,578-6) was received from Sigma Aldrich purum, ~5% in a mixture of lower aliphatic alcohols and water, and was freeze dried before using. Isopropanol (cod. 527084) were purchased by Aldrich.

## 2.2 Catalyst Characterization

**X-Ray Fluorescence (XRF).** X-Ray Fluorescence analytical technique has been utilized in order to determine the promoter loading on the “fresh” and “used” sample. The catalyst composition was analysed by a BRUKER AXS - S4 Explorer X-ray Fluorescence spectrometer, equipped with a Rhodium X-ray generator (AG Rh 22, with a rhodium anode and 75 µm Be-window). The analytical composition of catalysts expressed in weight percentage of iron and sulphur is reported in Table .1.

**Atomic Absorption Spectrophotometry (AAS).** Atomic Absorption Spectrophotometric method has been used to verify the amount of iron effectively deposited on silica or alumina supports and to determine the possible iron leaching during catalytic tests. Chemical analysis was carried out dissolving a small amount of each sample in a 1M hydrofluoric solution which was then analyzed with a Perkin Elmer Analyst 200 instrument equipped with an iron lamp ( $\lambda_{Fe} = 248.3\text{nm}$ ). Atomic absorption results are reported in Table 2.

**Table 1-** X-Ray Fluorescence of solid promoters

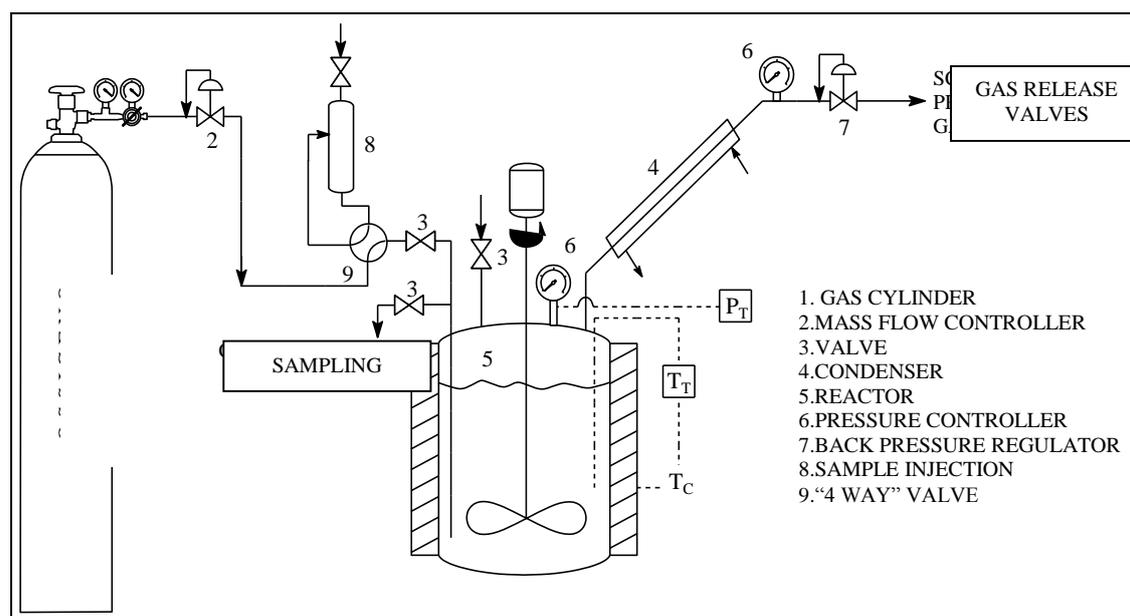
Sample	S (wt%)	Fe (wt%)	C (wt%)	SiO <sub>2</sub> (wt%)
0,5 wt% Nafion - 0,37 Fe/SiO <sub>2</sub> (fresh)	0,17	0,12	-	98,74
0,5 wt % Nafion - 0,37 Fe/SiO <sub>2</sub> (used)	0,21	0,16	-	98,48
0.37wt% Fe/SiO <sub>2</sub> (fresh)	0.01	0.33	-	99.40
0.37wt% Fe/SiO <sub>2</sub> (fresh)	0.04	0.31	-	99.40
0.37wt% Fe/SiO <sub>2</sub> (used)	0.03	0.30	-	99.40
SiO <sub>2</sub> (CS2050)	-	-		99.80

**Table 2-** Atomic Absorption Spectrophotometry of solid promoters

Sample	Fe (wt%) FRESH	Fe (wt%) USED (1st time)	Fe (wt%) USED (2nd time)
Fe/SiO <sub>2</sub> - CS2050	0.37	0.34	0.30
Fe/Al <sub>2</sub> O <sub>3</sub>	0.50	0.46	-

### 2.3 Apparatus and procedure

The effect of the various solid promoters in the selective partial oxidation of propane in the presence of the Fenton system has been evaluated in a batch reactor (“slurry”) PARR INSTRUMENTS totally covered in PTFE (T<sub>max</sub>, 110°C; P<sub>max</sub>, 50 atm; V<sub>max</sub>, 0.500 L). Experiments were carried out in “batch” mode. The schematic diagram of the batch reactor is shown in Fig. 1



**Figure 1-** Batch reactor scheme

Catalyst testing in the selective oxidation of propane were performed in the temperature (TR) range 80-110 °C with a propane absolute pressure of 202.6 kPa. The liquid phase (300 ml) was an aqueous solution of H<sub>2</sub>O<sub>2</sub> (1%, v/v) containing Fe<sup>2+</sup> 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 (1, 25 m; i.d., 0.53 mm) operating at 90 °C. H<sub>2</sub>O<sub>2</sub> concentration change was followed by periodical titration with permanganate solution (MnO<sub>4</sub><sup>-</sup> [10<sup>-1</sup> mol/l]).

### 3. RESULTS AND DISCUSSION

#### 3.1 Activity of Heterogeneous Fenton systems in partial oxidation of light alkanes

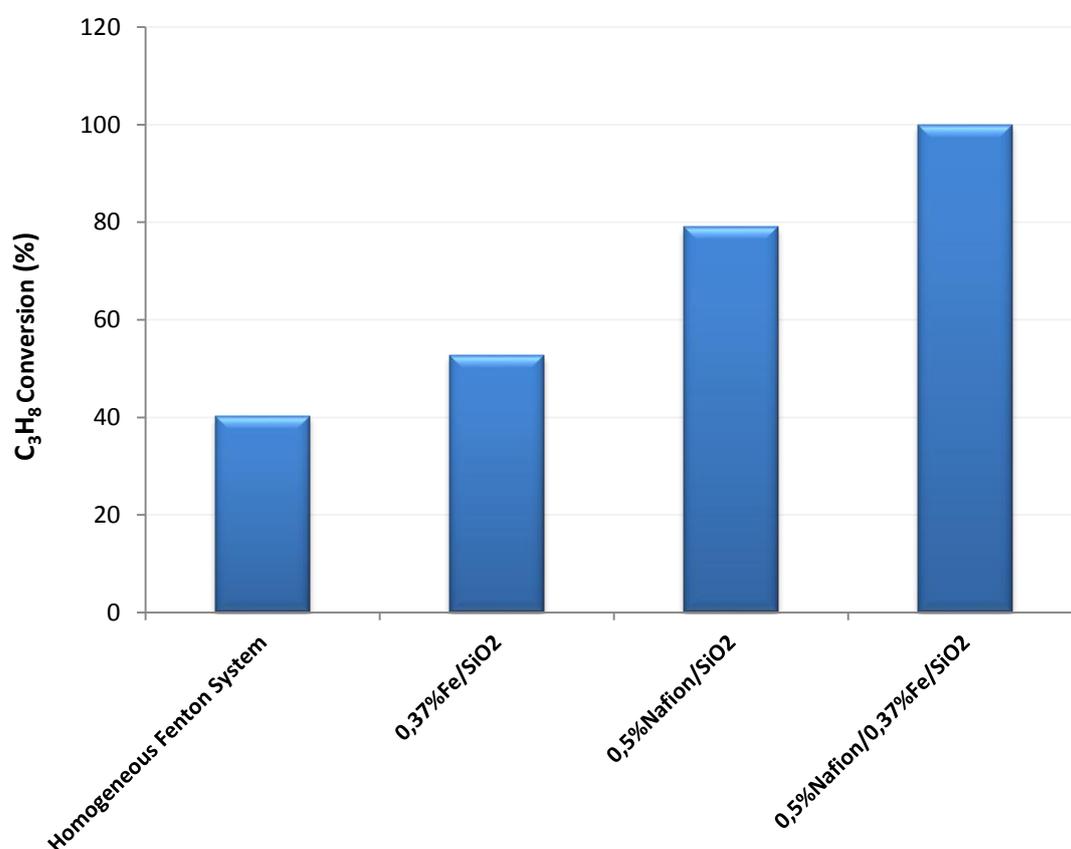
The selective oxidation of light alkanes mediated by the Fenton system implies several drawbacks such as the recovery of iron ions from the reaction mixture and the need to operate at specific pH values (pH, 3-4). Then, it is necessary to adjust the pH before and after the process and to properly dispose of the sludge and, consequently, additional operative cost are required. Therefore, the immobilization of iron species on the surface of an inert carrier could represent a real breakthrough for the further development of such reaction tool. As reported in our previous study [42-43], loading Nafion moieties on “inert” carriers exert an appreciable promoting effect on reaction kinetics, to an extent depending on the support. Therefore considering such interesting clues, Nafion on Silica sample was used as solid matrix for immobilizing iron and the corresponding catalysts were tested in the heterogeneous Fenton process. In order to disclose the key factors controlling the efficiency of such Nafion based heterogeneous Fenton system in the selective oxidation of light alkanes, the influence of the textural properties and the role of immobilised  $\text{Fe}^{2+}$  ions and Nafion moieties on carrier surface (partial heterogenization of the Fenton system) have been evaluated. Namely, the activity of a series of Nafion/ $\text{SiO}_2$ ,  $\text{Fe}^{2+}/\text{SiO}_2$ ,  $\text{Fe}^{2+}/\text{Al}_2\text{O}_3$  sample and a 0.5 wt% Nafion/ $\text{SiO}_2$ -0.37wt%  $\text{Fe}^{2+}$  “doped systems” in the partial oxidation of propane at 80°C, has been compared. The activity data are presented in Table 3 in terms of reaction rate and products selectivity. Results do not evidence any significant effect exerted by the doping of iron on the solid support surface both on reaction rate and products selectivity, while, as expected, the doping of  $\text{SiO}_2$  carrier with Nafion moieties in homogeneous Fenton system causes a remarkable enhancement of reaction rate. The simultaneous doping with  $\text{Fe}^{2+}$  ions and 0.5% Nafion on  $\text{SiO}_2$  sample exert a significant positive effect on catalytic performance. Indeed, the activity data of 0.5wt%Nafion/0.37wt%  $\text{Fe}/\text{SiO}_2$  sample indicate that when the same amount of  $\text{Fe}^{2+}$  ions used in liquid phase in standard conditions, is anchored on the carrier surface doped with Nafion, the activity of the “standard” Fenton system (0.5 wt% Nafion/ $\text{SiO}_2$  with homogeneous Fenton system) is enhanced more than two times in terms of reaction rate values. The enhancing effect of the  $\text{Fe}^{2+}$  immobilisation on the  $\text{H}_2\text{O}_2$  yield which rises from 2.5% for homogeneous Fenton system to 16.5% for 0.5 wt % Nafion/0.37wt%  $\text{Fe}/\text{SiO}_2$  results even more relevant in terms of practical exploitation of the system.

**Table 3.** Partial oxidation of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> at 80°C. Activity data of Nafion /Fe/SiO<sub>2</sub> heterogeneous Fenton system

METHANE PARTIAL OXIDATION					
Sample Code	Reaction Rate <sup>a</sup> ( $\mu\text{mol}\cdot\text{h}^{-1}$ )	Product selectivity <sup>a</sup> (%) CH <sub>3</sub> OH			
Homogeneous Fenton system	23	100			
0.5wt% Nafion/SiO <sub>2</sub>	56	100			
PROPANE PARTIAL OXIDATION					
Sample Code	Reaction Rate <sup>a</sup> ( $\mu\text{mol}\cdot\text{s}^{-1}$ )	Product selectivity <sup>a</sup> (%) CH <sub>3</sub> CH <sub>2</sub> CHO    CH <sub>3</sub> COCH <sub>3</sub> i- CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH    n -CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH			
Homogeneous Fenton system	280	24.2	61.9	9.6	4.4
0.37wt% Fe/SiO <sub>2</sub>	310	24.5	55.6	13.1	6.7
0.5% Fe/Al <sub>2</sub> O <sub>3</sub>	290	25.0	60.9	10.1	4.0
0.5wt% Nafion/SiO <sub>2</sub>	485	23.6	64.4	8.7	3.4
0.5 wt % Nafion/0.37wt% Fe/SiO <sub>2</sub>	705	25.0	60.9	10.2	3.9

<sup>a</sup>reaction rate and product selectivity after 30 min. of time on stream

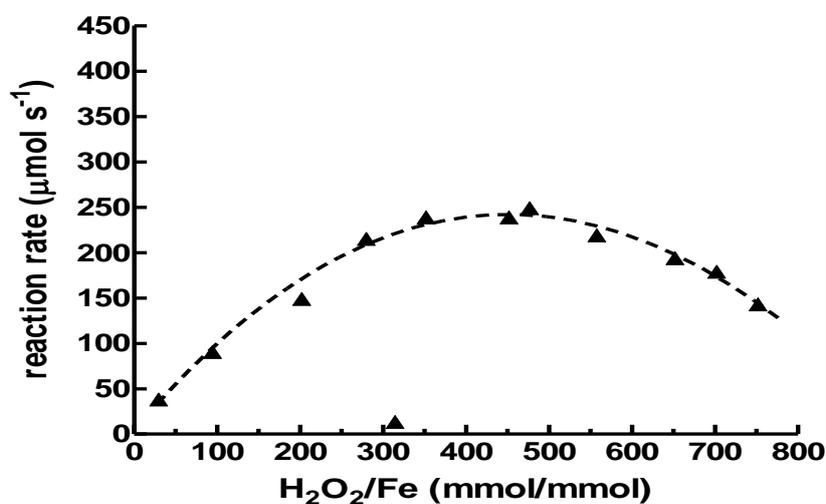
Such data confirm the results obtained in the XRF and A.A.S. analysis (reported in Table 1 and Table 2) and probe that there are not leaching of Fe<sup>2+</sup> ions and Nafion moieties phenomena from the surface of the Fe/SiO<sub>2</sub> and Fe-Nafion-SiO<sub>2</sub> catalysts during the reaction, in fact, as evidenced in Fig. 2, a regular increase of the C<sub>3</sub>H<sub>8</sub> conversion with reaction time for 0.37wt% Fe/SiO<sub>2</sub>, 0.5wt%Nafion/SiO<sub>2</sub> and 0.5wt%Nafion/0.37wt% Fe/SiO<sub>2</sub> samples is observed. On the whole such data constitute a remarkable step for 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.



**Figure 2-** Partial oxidation of the C<sub>3</sub>H<sub>8</sub> at 80 °C. Conversion of propane solubilised in water phase after 25 min.

### 3.2 Role of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> Molar Ratio in homogeneous Fenton System

It has been stated that the use of large quantities of Fe in Fenton system has a negative effect from the industrial application point of view, since it implies the need of an additional treatment step for Fe removal [45]. Hence, one of the major drawback of Fenton's reaction appears as the large concentrations of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> required. On the other hand, both H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> can also react with OH radicals inhibit in so the oxidation reactions, than an optimal H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> has to be maintained to achieve the maximal efficiency since both components can scavenge the radicals generated and reduce the amount of radicals available to substrates. In order to find the optimum H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratio (mol/mol) to obtain high activity and selectivity, a series of experiments at different H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio have been performed at TR=80°C. Results obtained are shown in Fig. 3 in terms of reaction rates vs. the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratio.



**Figure 3** - Selective oxidation of propane mediated by the Fenton system at 80°C. Effect of the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio on the reaction rate.

A volcano trend characterized by a maximum of reaction rate (250 μmol s<sup>-1</sup>) at H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratio close to 400 was obtained. Several groups working with different systems in the area of wastewater treatment have also reported a great variation of optimal H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratios [45] depending on type of organic substrates as well as their concentration. It was seen that the ratio found in this study is remarkably higher than those reported in the literature. This would be attributed to the relatively higher organic load and/or different nature of organic substrate (propane) used in our study with respect to that used in the wastewater treatment.

A series of experiments were further conducted in order to find out the level up which the concentrations of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> added can be decreased or tuned up on the condition that the ratio is kept at optimal value. In Table 4 were depicted results of experiments performed at different H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio obtained with different doses of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>. It is evident that maintaining constant the doses of FeSO<sub>4</sub> (0.27 mmol) and increasing the H<sub>2</sub>O<sub>2</sub> concentration (from 25 up to 150 mmol) the reaction rate increases until the maximum value of 220 μmol s<sup>-1</sup>, corresponding to the value obtained at the molar ratio of 556. While increasing the doses of FeSO<sub>4</sub> (from 0.10 up to 2.7 mmol) and maintaining constant the H<sub>2</sub>O<sub>2</sub> concentration (75mmol) the reaction rate decreases from 216.3 to 39.3 μmol s<sup>-1</sup>. It is also evident that the enhancement of the Fe<sup>2+</sup> concentration implies a remarkably enhancement of the H<sub>2</sub>O<sub>2</sub> consumption (83% after 60 min of reaction). It is likely that high Fe<sup>2+</sup> concentrations have a negative effect on the reactivity of the system because of the fact that the occurrence of secondary reaction between radical oxo-species and iron ions would compete with the activation of the organic substrate molecules dissolved in the liquid medium. Results summarized in Table 4 clearly evidence that the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio is a critical parameter for improving the efficiency of the Fenton's process. In particular it emerges

that the optimal molar ratio for the title reaction is 478 ( $\text{H}_2\text{O}_2$ , 129 mmol and  $\text{FeSO}_4$ , 0.27 mmol). In any case, considering the relative high cost of the  $\text{H}_2\text{O}_2$  reagent is useful to consider as optimal  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio the value of 278 ( $\text{H}_2\text{O}_2$ , 75 mmol and  $\text{FeSO}_4$ , 0.27) which ensures the same efficiency of the Fenton system in terms of reaction rate and  $\text{H}_2\text{O}_2$  consumption rate.

**Table 4** - Selective oxidation of propane mediated by the Fenton system at  $80^\circ\text{C}$ . Influence of  $\text{H}_2\text{O}_2/\text{Fe}^{\text{II}}$  molar ratio in the selective oxidation of propane by the Fenton system at  $80^\circ\text{C}$

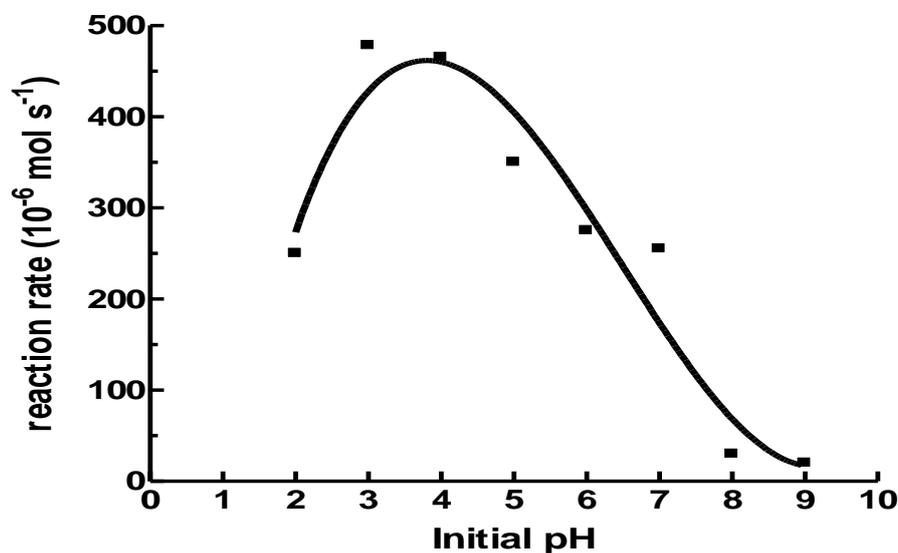
$\text{H}_2\text{O}_2/\text{Fe}^{\text{II}}$ (mmol/mmol)	$\text{H}_2\text{O}_2$ (mmol)	$\text{Fe}^{\text{II}}$ (mmol)	Reaction Rate <sup>a</sup> ( $\mu\text{mol s}^{-1}$ )	$\text{H}_2\text{O}_2$ consumed <sup>a</sup> (%)
28	75	2.7	39.3	83.3
93	25	0.27	91.8	50.3
200	55	0.27	148	48.0
278	75	0.27	216.3	50.0
312	5	0.016	14.6	62.0
350	95	0.27	228.3	71.3
450	122	0.27	225.0	69.1
478	129	0.27	229.6	56.2
556	150	0.27	220.2	45.8
650	175	0.27	178.2	56.2
718	194	0.27	162.1	46.9
750	75	0.10	174.2	33.3

*a) Reaction rate and  $\text{H}_2\text{O}_2$  consumed values have been determined at reaction time of 60 min*

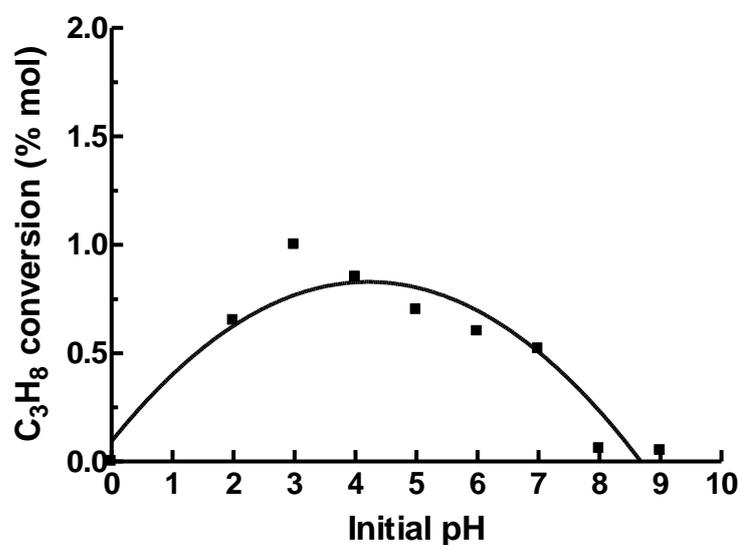
### 3.3 Effect of pH

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of OH radicals production in the Fenton's reaction. Fig. 4 depicts the effect of initial pH in terms of a) reaction rate vs pH and b) propane conversion vs pH. According to the above mentioned literature findings, performing the experiments at pH 3 results in the highest reaction rate value and the highest propane conversion value.

a)



b)



**Figure 4** - Selective oxidation of propane mediated by the Fenton system at 80°C. Effect of initial pH on a) reaction rate and b) propane conversion.

At high pH ( $\text{pH} > 4$ ), the generation of OH radicals gets slower because of the formation of the ferric hydroxo complexes; the complexes would further form  $[\text{Fe}(\text{OH})_4]$  when the pH value is higher than 9.0. On the other hand at very low pH values ( $< 2$ ) the reaction is slowed down due to the formation of complexes species  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , which

reacts more slowly with peroxide compared to that of  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ . In addition, the peroxide gets solvated in the presence of high concentration of  $\text{H}^+$  ion to form stable oxonium  $[\text{H}_3\text{O}_2]^+$ . An oxonium ion makes peroxide electrophilic to enhance its stability and presumably reduces substantially the reactivity with  $\text{Fe}^{2+}$  ion. Therefore, the initial pH value has to be in the acidic range (2-4) to generate the maximum amount of OH radicals to oxidize the organic substrate.

## CONCLUSION

The oxidation of propane could be considered as “reaction model” for the selective oxidation of light alkanes, and therefore results here reported could open potentially new perspectives for the development of innovative processes for the conversion of natural gas and light alkanes to high added oxygenated products. Results presented in this work confirm that Nafion (S and F moieties) play a role of promoting agent towards  $\text{Fe}^{n+}$ - $\text{H}_2\text{O}_2$  Fenton system in the partial oxidation of light alkanes to oxygenates under mild conditions ( $T_R$ , 70-100°C;  $P_R$ , 140kPa). The contact with Nafion and Fe in the Nafion/Fe/Silica system improve the efficiency of reaction. The immobilization of  $\text{Fe}^{2+}$  ions on the Nafion/ $\text{SiO}_2$  promoter, resulting in a partial heterogenization of the Fenton system, induces a remarkable enhancing effect on both reaction rate and  $\text{H}_2\text{O}_2$  yield.  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio is a critical parameter for improving the efficiency of the Fenton process. Keeping the  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio constant within a specified range, it is possible to decrease  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  concentrations remarkably, still achieving to the highest efficiency. The initial pH value has to be in the acidic range (2-4) to generate the maximum amount of OH radicals to oxidize the organic substrate.

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