

New Perspectives in Removal of Organic Pollutants from Industrial Wastewater mediated by the Fenton Process

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Abstract

The role of the paraffin solubilisation in the liquid phase in the heterogeneous Fenton chemistry occurring in the selective partial oxidation of light alkanes to oxygenated selected as model molecules has been investigated. The activity of a series of Nafion/SiO₂, Fe(II)/SiO₂, Fe(II)/Al₂O₃ samples and a Nafion/Fe(II)/SiO₂ catalyst, in the partial oxidation of methane and propane in batch reactor at 80°C, has been evaluated. Indeed, The effect of the cyclodextrins on the solubility of propane has been investigated, evidencing that the addition of cyclodextrin implies a substantial rising of the propane solubility going from 1.9 %, when no cyclodextrin is added, to 11.6, 12.5, 33 and 14.0 % with the α, β, methyl-β and γ-cyclodextrines, respectively. It reveals that the addition of any cyclodextrin to the reaction system could affect both the propane solubility and consequently the Fenton system efficiency.

Keywords: Fenton System, alkane partial oxidation, paraffin solubilisation, cyclodextrin

INTRODUCTION

The development of heterogeneous catalysts is a topic of great interest, since their huge application fields [1-16]. In this context, design, development and optimization of catalytic systems for the direct low temperature selective oxidation of organic substrates has attracted the research interest of many academic and industrial research groups during last years [17-28]. Various catalysts in the presence of molecular oxygen [29-32] and H₂O₂ (or alkylhydroperoxide) in both homogeneous and heterogeneous systems are studied for the activation of the C-H bonds of the alkanes [33-36]. Aqueous solutions of Fe(II)/H₂O₂, otherwise known as Fenton's reagent or system, generally used for the treatment of a variety of industrial wastewater, 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 [37-39]. 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⁻, SO₃⁻) to the ferrous ion (Fe²⁺ + F⁻ → FeF⁺) leads to a more effective oxidising system. In this context, we have found that the homogeneous Fe^{II}-H₂O₂ 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 [40-41]. An issue of great importance for the optimization of the selective oxidation of light hydrocarbons under mild conditions is the paraffin solubilisation in the liquid phase. Cyclodextrin is a cyclic oligosaccharide that increases the aqueous solubilities of several low-polarity organic compounds and enhances transport and removal of those compounds. There are three common cyclodextrins with 6, 7 or 8 D-glucopyranosyl residues (α-, β-, and γ-cyclodextrin respectively) linked by α-1,4 glycosidic bonds, with the glucose residues C1 (chair) conformation. All three cyclodextrins have similar structures (that is, bond lengths and orientations) apart from the structural necessities of accommodating a different number of glucose residues. The otherwise hydrophilic cyclodextrin molecules may bind non-polar suitably-sized aliphatic and aromatic compounds such as aroma compounds and lipophilic drugs. The binding is driven by the enthalpic and entropic gain on the reduction in the hydrophobe-aqueous surface and the release of water molecules from the cavity to the bulk phase. Such binding also allows cyclodextrins to be used to increase the water solubility of normally hydrophobic compounds. In the present study, we are interested in studying the possibility of application of Fenton oxidation process, as an advanced chemical technology technique, for removal of organic compounds from industrial wastewater. On these premises, this work has been focused on the study of the effect of a cyclodextrin addition on propane (selected as model molecule) solubilisation in the reaction medium and the subsequent role in the heterogeneous Fenton system performance.

EXPERIMENTAL

Catalys Preparation

0.37wt%Fe/SiO₂. 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 FeSO₄·7H₂O 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% NH₄OH solution. The suspension was kept at the final pH value under stirring and N₂ 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/Al₂O₃. Alumina (Al₂O₃ - 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 Fe²⁺ ions by flushing an inert gas into the solution so to prevent their oxidation to Fe³⁺. In fact, the Fe(OH)₂ K_{ps} is sensibly lower (1.8·10⁻¹²) and at acidic pH (<7) the iron is water soluble. Considering that the pH of ZPC (pH of Zero Point Change) of Al₂O₃ ranges between 6 and 8, we can uptake it as [Fe(H₂O)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 (≈1000rpm) and flushed with nitrogen (≈100 stp cm³/min). Then, after 1.5 hours N₂ bubbling, the designed amount of FeSO₄·4H₂O was added to the suspension at room temperature with a resulting pH of ≈ 4.5, which was progressively raised till a value of 7.5 by adding dropwise a 5% water solution of NH₄OH. The suspension was kept at this pH for 1h, under N₂ 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/SiO₂. 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%Fe²⁺/SiO₂. The synthesis of 0.5wt%Nafion/0.37wt% Fe²⁺/SiO₂ system can be divided into two step: preparation of iron on silica supported solid carrier and Nafion deposition on Fe/SiO₂ system. The Fe²⁺/SiO₂ catalyst was prepared according the adsorption-precipitation method previously described.

The Nafion was deposited by the “incipient wetness” impregnation method of Fe²⁺/SiO₂ 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. 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_{max}, 110°C; P_{max}, 50 atm; V_{max}, 0.500 L). Experiments were carried out in “batch” mode. 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 H₂O₂ (1%, v/v) containing Fe²⁺ 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. H₂O₂ concentration change was followed by periodical titration with permanganate solution (MnO₄⁻ [10⁻¹ mol/l]).

RESULTS AND DISCUSSION

Activity of Heterogeneous Fenton systems in partial oxidation of light alkanes

The activity of a series of Nafion/SiO₂, Fe²⁺/SiO₂, Fe²⁺/Al₂O₃ sample and a 0.5 wt% Nafion/SiO₂-0.37wt% Fe²⁺ “doped systems” in the partial oxidation of propane at 80°C, has been compared. The results are summarised in Table 1 in terms of reaction rate and products selectivity. The doping of SiO₂ carrier with Nafion moieties in homogeneous Fenton system causes a remarkable enhancement of reaction rate. The simultaneous doping with Fe²⁺ ions and 0.5% Nafion on SiO₂ sample exert a significative positive effect on catalytic performance. Results obtained with the 0.5wt%Nafion/0.37wt% Fe/SiO₂ sample indicate that when the same amount of Fe²⁺ 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/SiO₂ with homogeneous Fenton system) is enhanced more than two times in terms of reaction rate values.

Table 1. Partial oxidation of C₃H₈ at 80°C. Activity data of Nafion /Fe/SiO₂ heterogeneous Fenton system

PROPANE PARTIAL OXIDATION					
Sample Code	Reaction Rate ^a (μmol·s ⁻¹)	Product selectivity ^a (%)			
		CH ₃ CH ₂ CHO	CH ₃ COCH ₃	i-CH ₃ CH ₂ CH ₂ OH	n-CH ₂ CH ₂ CH ₂ OH
Homogeneous Fenton system	280	24.2	61.9	9.6	4.4
0.37wt% Fe/SiO ₂	310	24.5	55.6	13.1	6.7
0.5% Fe/Al ₂ O ₃	290	25.0	60.9	10.1	4.0
0.5wt% Nafion/SiO ₂	485	23.6	64.4	8.7	3.4
0.5 wt % Nafion/0.37wt% Fe/SiO ₂	705	25.0	60.9	10.2	3.9

^areaction rate and product selectivity after 30 min. of time on stream

Role of Paraffin Solubilisation in Liquid Phase

An issue of great importance for the optimization of the selective oxidation of light hydrocarbons under mild conditions is the paraffin solubilisation in the liquid phase. Therefore, in order to strengthen the primary role of the paraffin solubilisation on the title reaction, it has been determined the real propane concentration in liquid phase. In the reaction conditions adopted, only 0.3% of propane was dissolved into the liquid phase. Indeed, in order to point out the optimal reaction conditions allowing the maximum propane solubilization in liquid phase, the effect of the total pressure of propane in the range 2-5 bar at 80°C and the effect of the partial pressure of propane in the range 0.5- 1.5 bar of P_{C₃H₈} (P_{tot}: 2 Bar ; with helium at 80°C in aqueous solution) were studied.

Table 2: Propane solubility in aqueous solution at different total pressure

P C ₃ H ₈ (bar)	C ₃ H ₈ dissolved in liquid phase (mmol)
2	0.89
3	0.89
4	0.93
5	1.10

Table 3: Propane solubility in aqueous solution at different partial pressure

P _{tot} (bar)	P _{He} (bar)	P _{C₃H₈} (bar)	C ₃ H ₈ dissolved in liquid phase (mmol)
2	1.5	0.5	0.26
2	1.0	1.0	0.43
2	0.5	1.5	0.75
2	0	2.0	0.89

Data reported in Table 2 and Table 3 evidence that the propane solubility agree with the Henry's law. In fact the amount of propane dissolved in liquid phase rises with C₃H₈ partial pressure up to a value of 2 bar, keeping constant for higher pressure values. Therefore, in order to evaluate a possible relationship between the reaction rate and the propane solubility a series of catalytic tests at different propane partial pressure has been accomplished. Fig. 1 outlines the effect of the propane partial pressure on the reaction rate of the title reaction. As expected, high values of propane pressure (until 2 bar), enhance propane solubility in liquid phase, giving high values of reaction rate (300 mmol s⁻¹ after 30 min of reaction), while lower propane partial pressure results in lower reaction rate (100 mmol s⁻¹ after 30 min of reaction).

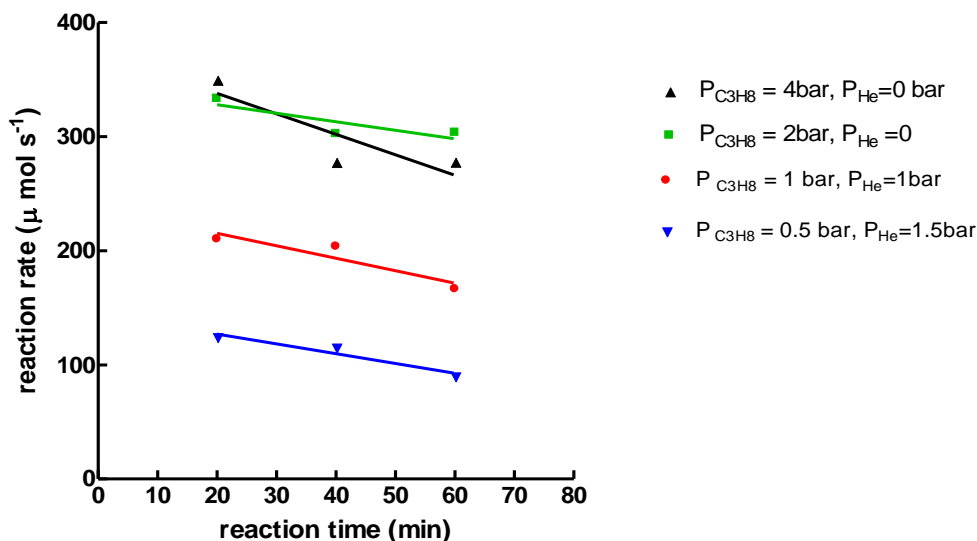


Figure 1: Selective oxidation of propane at 80°C- Reaction rate vs reaction time at different P_{C₃H₈}

It has been demonstrated that the use of solubility-enhancing agents can overcome limitations due to the low propane solubility. Cyclodextrin is a cyclic oligosaccharide that increases the aqueous solubilities of several low-polarity organic compounds and enhances transport and removal of those compounds. The effect of the cyclodextrins on the

solubility of propane has been investigated by performing a series of blank tests in presence of different cyclodextrins dissolved in the reaction medium. Table 4. shows relationship between the type of cyclodextrin present in the aqueous solution and the propane solubility expressed as percentage of propane dissolved with respect to that present in the gas phase.

Table 4: Evaluation of C₃H₈ water solubility with cyclodextrins

Cyclodextrins (100 mg)	C ₃ H ₈ in liquid phase (%)
Without cyclodextrins	1.9
α - cyclodextrins	11.6
β - cyclodextrins	12.5
γ - cyclodextrins	14.0
Methyl- β - cyclodextrins	33.0 (create foam)

It emerges that the addition of cyclodextrin implies a substantial rising of the propane solubility going from 1.9 %, when no cyclodextrin is added, to 11.6, 12.5, 33 and 14.0 % with the α, β, methyl-β and γ- cyclodextrins, respectively. It is evident that the addition of any cyclodextrin to the reaction system could affect both the propane solubility and consequently the Fenton system efficiency. The result of a comparative test in the selective oxidation of propane at 80°C, by dispersing 0.1 g of various cyclodextrins, expressed as reaction rate, C₃H₈ conversion, H₂O₂ consumption rate, molar

H₂O₂ yield are collected in Fig.2 and Fig.3. Considering that the reaction rate and H₂O₂ yield (after 15 min of time on stream) for the bare Fenton system are 200 μmol s⁻¹ and 1%, respectively, indicate that the addition of α-CD (r=1100 μmol s⁻¹, H₂O₂ yield= 5 %), methyl-β-CD (r = 1100 μmol s⁻¹, H₂O₂ yield= 4 %), β-CD (r= 800 μmol s⁻¹, H₂O₂ yield= 3 %), and γ-CD (r= 500 μmol s⁻¹, H₂O₂ yield= 2 %) systems results in a substantial promoting effect on both reaction kinetics and H₂O₂ yield.

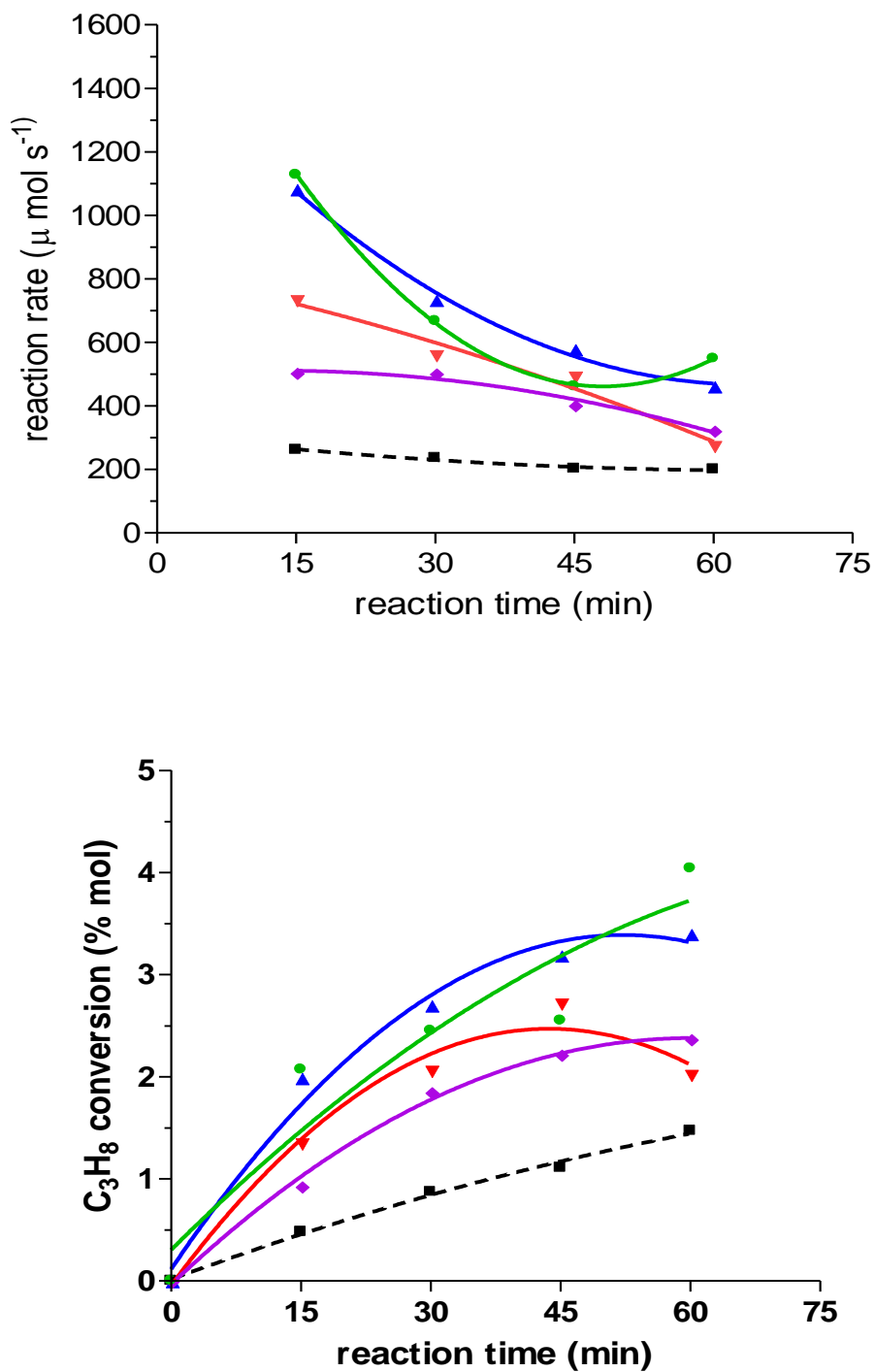


Figure 2. Selective oxidation of propane at 80°C - Effect of cyclodextrins on reaction rate and propane conversion (▲) α -cyclodextrin, (●) methyl- β -cyclodextrin, (▼) β -cyclodextrin, (◆) γ -cyclodextrin, (■) Fenton system without cyclodextrin

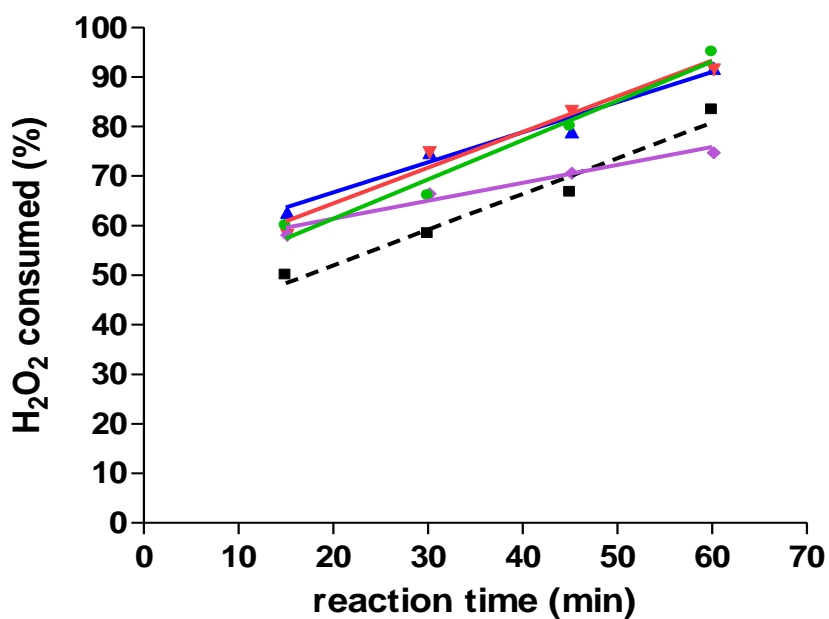
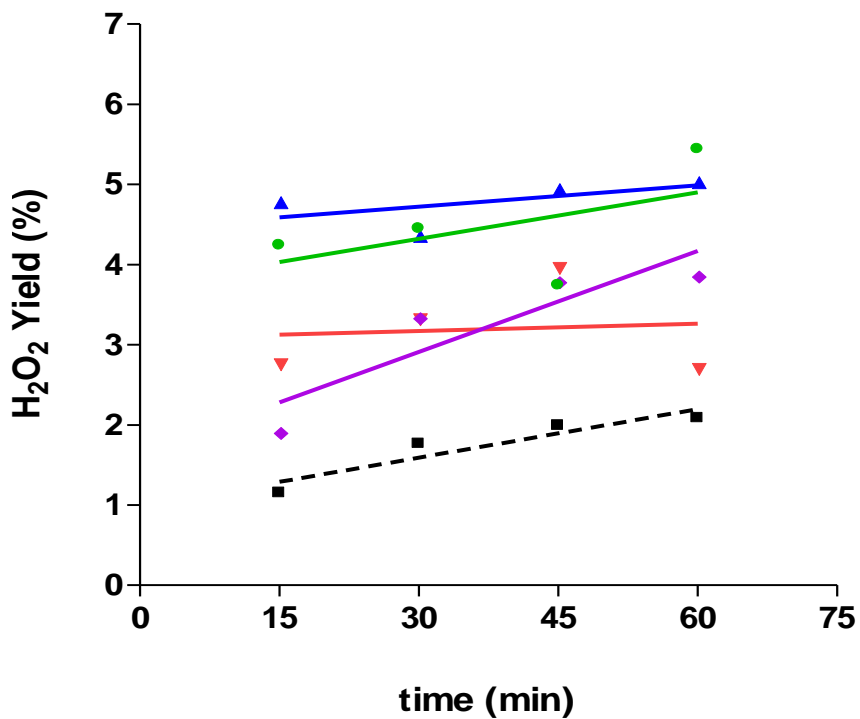


Figure 3. Selective oxidation of propane at 80°C ; Effect of cyclodextrins on H₂O₂ yield ; ▲) α- cyclodextrin, ●) methyl-β - cyclodextrin, ▼) -β cyclodextrin, ◆) γ- cyclodextrin ■) Fenton system without cyclodextrin

The stability of cyclodextrins in the reaction medium has been evaluated by performing a series of reproducibility tests employing the same α -cyclodextrin sample recovered after

each run. The results depicted in Fig. 4 in terms of reaction rate versus reaction time, are diagnostic of the good stability of the studied cyclodextrin.

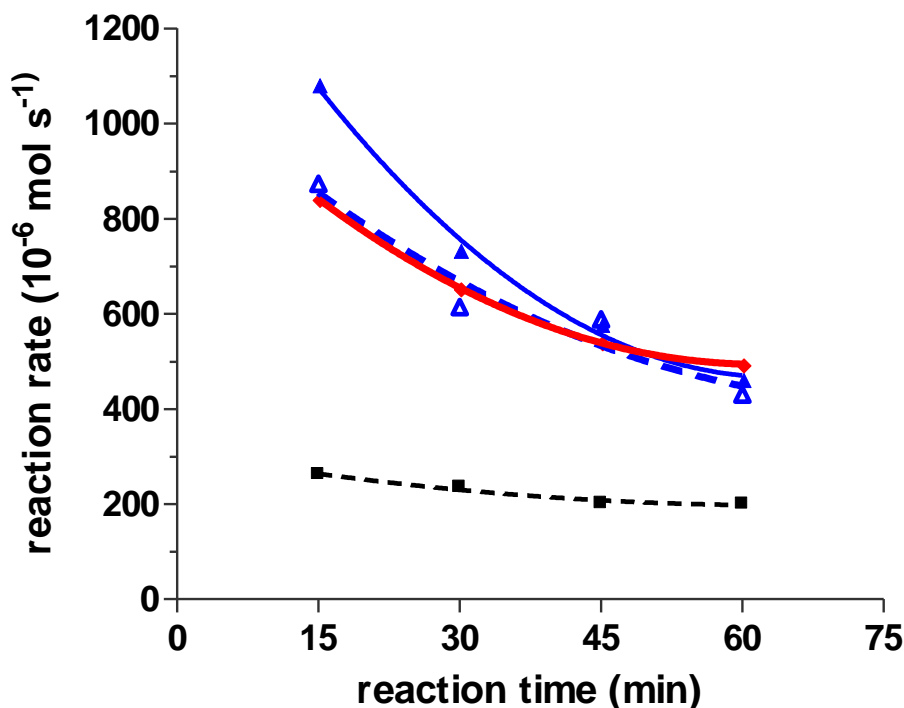


Figure 4. Selective oxidation of propane at 80°C ; Stability tests

▲) α - cyclodextrin, Δ) α -cyclodextrin (run 1), ◆) α -cyclodextrin (used), ■) Fenton system without cyclodextrin

CONCLUSIONS

The oxidation of propane could be considered as “reaction model” for the selective oxidation of light alkanes, and results here reported open new perspectives for the development such a process for the conversion of 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 Fe^{n+} - H_2O_2 Fenton system in the partial oxidation of light alkanes to oxygenates under mild conditions. Indeed, the addition of cyclodextrin implies a substantial rising of the propane solubility evidencing that the addition of any cyclodextrin to the reaction system could affect both the propane solubility and consequently the Fenton system efficiency.

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