

Electro-oxidation of phenol on zeolite/graphite composite electrodes Part 1. Electrochemical behaviour over NaY zeolite

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Abstract

In this work, the electrochemical oxidation of phenol was studied on a zeolite/graphite composite electrode. This electrode is prepared by a simple mixture of the two components (NaY zeolite and graphite in a 2:1 proportion) and pressing, to produce a pellet. The zeolite/graphite composite electrode pellet is mounted on a support that uses a platinum disc to ensure electrical contact.

The oxidation of phenol was studied by cyclic voltammetry and a well-developed wave, due to the oxidation of phenol, is observed. When the concentration of phenol is sufficiently low, the electrode is not fouled by the electrochemical process and the change in the concentration of phenol induces a reversible change in the intensity of the oxidation wave. For higher concentrations of phenol it is likely that some deposition of oxidation products occur at the electrode surface and inactivation is observed.

The overall process seems to be due to the oxidation of the species that is inside the porous volume of the electrode system and not to diffusion-controlled processes involving the solution bulk.

Electro-oxidation of phenol over zeolites may have a significant bearing for applications either in the removal of these pollutants or, for example, the production of fine-chemicals.

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1. Introduction

The oxidation of phenolic compounds has been the subject of many studies due to its industrial importance; not only for the production of catechol and hydroquinone (with applications in pharmaceuticals, perfumes and fine chemistry), but it is also for its importance in the treatment of wastewater contaminations.

Oxidation of phenol using chemical oxidants has been described in the literature making use of various catalysts. Different zeolites (H-ZSM-5, H-MOR, H-USY and H-BEA) [1] have been used in their protonic form for the production of catechol and hydroquinone using chemical oxidants. H-BEA has also been tested when modified by alkaline earth metal ion exchange treatment (Mg, Ca, Sr and Ba) [2]. Different metals (Pt, Ru, Cu, Co, Mo and Mn) supported on a variety of sup-

ports, including TiO₂, ZrO₂, Al₂O₃, MCM-41, activated carbon or graphite [3,4] have also been reported. Another alternative, which could produce cleaner products is the direct electrochemical oxidation, albeit eventually more suitable for low-volume applications.

Although phenolic species can be readily oxidized at Pt electrodes, these electrodes are rapidly fouled [5–13] and, thus, are not suited for this electrochemical process. Modified electrodes, with a suitable catalyst, represent a more suitable choice for many applications. Many of the alternative electrode materials involve supported enzymes and these have been extensively studied in the context of biosensor construction [14–17].

Zeolites constitute suitable materials for electrodes, although their conductivity has to be increased, and many works have been carried out in recent years in the field of electrochemical applications of zeolites; a comprehensive review was recently published by Walcarius [15].

The use of mixtures of zeolite and graphite has been proposed since the 1980s [18]. These mixtures are used in various forms, either as modified carbon paste electrodes, where the carbon

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powder and the zeolite are mixed with a pasting wax [19] or liquid [20], or by pressing the mixture onto a metal grid [21] or disc [23], providing working electrodes with good properties. Most of the works described have been applied to the study of electroactive species entrapped inside the zeolite porous system.

Zeolite/carbon paste mixtures have already been reported for the electro-oxidation of phenol and other species, but only in the context of enzyme-modified electrodes [22], where a positive effect was observed, by the addition of zeolite, but which has been attributed to the interaction of this zeolite with the micro-environment of the enzyme, tyrosinase.

The present work focuses on the electrochemical oxidation of phenol using a zeolite/graphite composite working electrode.

2. Experimental

2.1. Materials

All reagents were of analytical grade.

Sodium phosphate and phenol were purchased from Merck. A 100 mM sodium phosphate buffer solution was prepared so as to ensure a pH of 7.0.

For the construction of the pellets, graphite with a high degree of purity, NaY, in powder form (LZ Y52 from Union Carbide with Si/Al=2.5, BET surface area $\approx 550 \text{ m}^2/\text{g}$) were used. For the control experiments a porous silica (EP10X from Crossfield, BET surface area $\approx 290\text{--}370 \text{ m}^2/\text{g}$), hereafter referenced as $(\text{SiO}_2)_p$, and a non-porous silica (from Carlo Erba Analyticals), referenced as $(\text{SiO}_2)_{np}$, were used. The zeolite and both silica samples were calcined, under air at 793 K, prior to use, to ensure a clean surface. After calcination they were stored under a constant and high humidity atmosphere.

2.2. Instrumentation and equipment

Electrochemical measurements were performed on a DEA101 digital electrochemical analyser coupled to an IMT102 electrochemical interface from Radiometer/Copenhagen. Thermogravimetric measurements were performed on a SDT 2960 simultaneous DSC-TGA from TA Instruments.

To produce the pellets, a Graseby/Specac press was used.

2.3. Electrodes construction

The zeolite/graphite composite electrode was prepared by a simple mechanical mixture with a 2:1 (w/w) proportion between

Table 1

Order and concentration of the phenol solutions used to analyse the response of the electrode—see text for details

Voltammogram number	[Phenol] (mM)
1	0.125
2	1.25
3	0.250
4	12.5
5	2.50
6	0.250
Consecutive cycling until disappearance of the oxidation wave	
9	0.250
10	100

NaY and graphite powder. The pellets had a total mass of around 5 mg of the previously homogenised mixture and were subjected to a 0.5 tonnes pressure for 5 min [23].

The pellet, which was 3 mm in diameter, was placed in a special support where it contacted with the electric circuit by means of a platinum disc that was pressed against the pellet, as shown in Fig. 1.

The silica/graphite composite was prepared in a similar fashion and was used for comparison purposes only.

2.4. Electrochemical behaviour

Cyclic voltammetry was carried out in a three-electrode cell, at a platinum disc or at a zeolite/graphite composite working electrode, probed by a Luggin capillary connected to a silver/silver chloride reference electrode (Ag/AgCl). A platinum auxiliary electrode was employed [23].

All electrochemical measurements were performed at room temperature and with a scanning rate of 10 mV/s. For each case a base line was recorded using the buffer solution.

In order to clarify the importance of the porous volume of the electrode in the electro-oxidation process some experiments were carried out using a clear buffer solution inside the cell during the measurement. In these cases the electrode was plunged in a phenol solution of known concentration for about 15 min, and it was then placed in the cell, containing the buffer solution, and the cyclic voltammetry measurement took place. The procedure was repeated, in succession, for various phenol concentrations; the order in which the various concentrations were used is shown in Table 1.

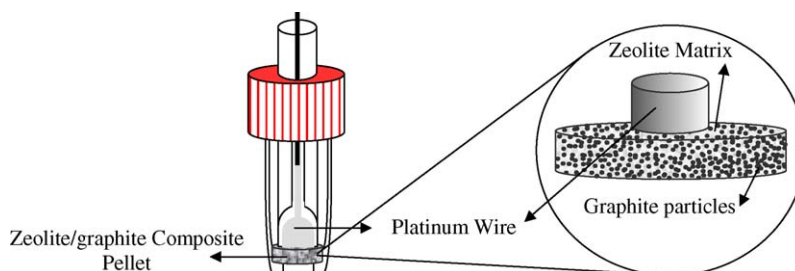


Fig. 1. Scheme of the zeolite/graphite composite electrode.

In order to ascertain the reversibility of the process, another experiment where the electrode was alternately placed, in solutions with two different concentrations was performed.

3. Results and discussion

Typical noble metal electrodes have been shown to be able to participate in the electro-oxidation of phenolic compounds; however, they are very expensive and, most importantly, they present a significant passivation problem.

When a 1 mm platinum disk electrode was used, a 125 mM solution of phenol only produced a very small oxidation wave and; furthermore, after the oxidation of phenol, the electrode's surface was passivated and it had to be mechanically cleaned in order to regain response.

Using the composite electrode containing the zeolite, however, a strong wave can be observed at a potential range from around 500 to 1000 mV, depending on the phenol concentration, as depicted in Fig. 2. As it can be seen the oxidation wave is very well defined and it has a current intensity approximately 245 times higher than the one observed on a platinum electrode with the same cross section, when measured for a phenol concentration of 125 mM.

A blank experiment was carried out using a composite electrode where the zeolite component was replaced by silica (with and without the porous structure), so as to obtain a similar electrode structure and composition without using the zeolite matrix.

The results obtained with these electrodes, again compared with the ones obtained with the zeolite/graphite one, are depicted in Fig. 3. It can be seen that the non-porous silica/graphite composite electrode presents a higher current than the one obtained with the platinum electrode and exhibits two distinct oxidation waves. This electrode is likely to have some porosity due to the pellet construction itself, but only due to the graphite matrix that is used. Replacing the non-porous silica with a porous one we can see that the current increases significantly, while still retain-

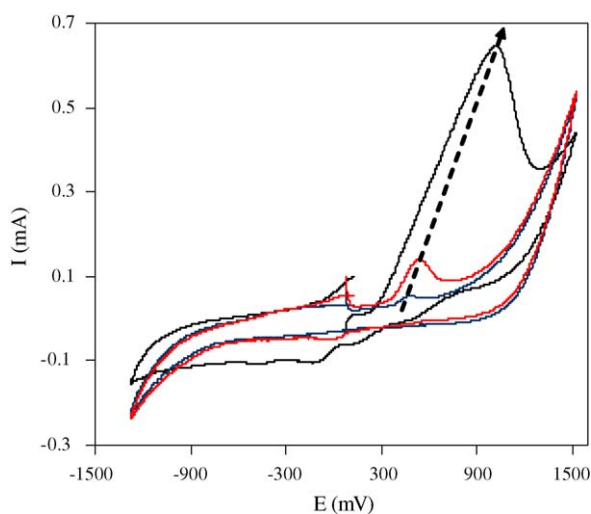


Fig. 2. Cyclic voltammograms obtained using a composite zeolite/graphite electrode, in the conditions described in the text, for 0.50, 7.25 and 125 mM concentrations of phenol (arrow indicates increasing concentration).

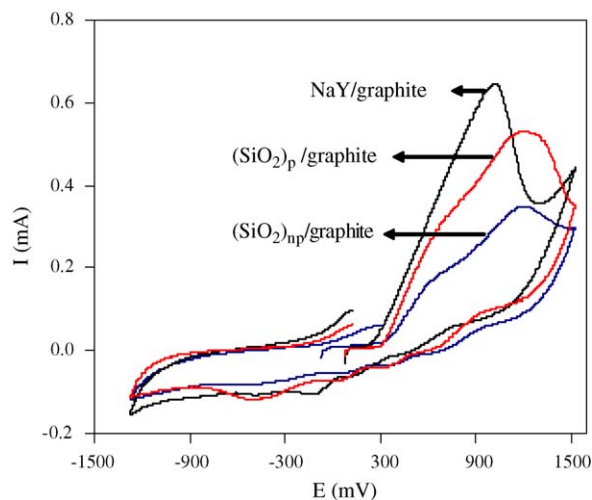


Fig. 3. Voltammograms with 125 mM of phenol at the referred working electrode in buffer solution starting with oxidation (porous silica $(\text{SiO}_2)_p$ and non-porous silica $(\text{SiO}_2)_{np}$).

ing the two successive oxidation waves. When comparing the zeolite/graphite electrode with the silica/graphite ones, for the same conditions, the current is much larger and the potential for the second oxidation wave seems to be reduced, leading to a single oxidation wave.

The enhanced electrochemical activity of zeolite modified electrodes has already been observed for the redox reactions of hydroquinone and resorcinol (among other species), by Schell and co-workers [19].

The wave that is observed does not have the usual appearance of a diffusion-controlled process, which would present the usual $1/\sqrt{t}$ decay; in this case the wave seems to be mostly due to the species that are trapped within the porous structure of the electrode. Zeolites are known to have a large internal porous volume, thus allowing the solution to enter its microporous volume and increasing the available effective area, a fact which can be advantageous to increase the rate of oxidation, and, according to the results in Fig. 3, to decrease the potential needed for it to be carried out. The increased available surface area, however, is not likely to explain, by itself, the behaviour observed, since the use of a silica with a high surface area does not produce the same effects.

Another effect that may play a role is the ability of zeolites to concentrate species within their porous structure. This would also increase the amount of species available for reaction. Phenol is a polar ($\mu = 1.224 \pm 0.008$ D [24]) and polarisable specie and should interact, to some extent, with an hydrophilic zeolite framework, such as the NaY zeolite that is used in this work. Phenol has been reported as adsorbing moderately on NaY [25] and even interacting with the more hydrophilic NaX [26], although more hydrophobic zeolites present a higher adsorption capacity [27].

A complementary explanation has also been proposed by Schell and co-workers [19], for the oxidation of hydroquinone, whereby the zeolite's ability to orient molecules that approach that surface, due to their electrical fields, would also influence the increase in the rate of the redox reaction.

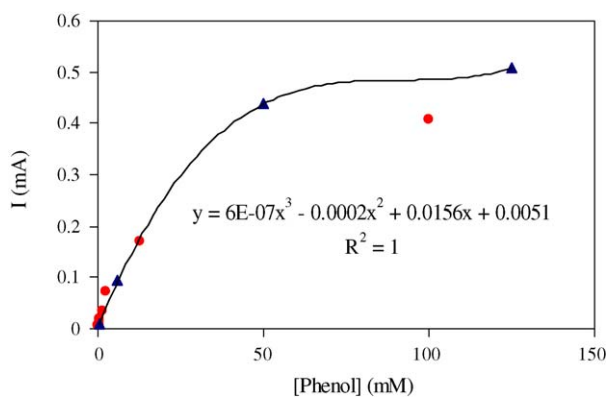


Fig. 4. Current intensity of the oxidation wave as a function of phenol concentration using a fresh electrode for each measurement (\blacktriangle) and the same electrode for the sequence described in the text (\bullet) (see Table 1) where all measurements were carried out in a clear buffer solution.

In order to investigate the assumption that the oxidation wave did not have a significant contribution from diffusion from the bulk of the solution, a series of experiments was carried out in which the measurements were always done on a clear buffer solution, immediately after the electrode itself had been contacted with a solution of known concentration of phenol for a specific amount of time, as described in the experimental section. Fig. 4 compares the current intensities obtained with this sequence with the ones that were observed for measurements in which the electrode was immersed in the respective phenol solution, during the CV experiment. It must be noted that in the latter a fresh electrode pellet was used for each measurement, so as to eliminate interferences from the previous reaction and from the eventual passivation of the electrode.

From the data depicted in Fig. 4, it can be seen that the current intensity is virtually the same, for the same concentration of phenol, regardless of the fact that the measurement was carried out in the clear buffer solution or in the phenol containing solution, except for very high concentrations of phenol, in which case the current intensity is somewhat lower when the measurement took place in the clear buffer solution. This effect occurs, probably, due to the fact that, for higher concentrations, the driving force for phenol to diffuse out of the electrode pellet is very large and, thus, a fast decrease occurs on the concentration inside the pellet as soon as the composite electrode is contacted with the buffer solution for measurement.

From our experimental results we can see that, for sufficiently small phenol concentrations the electro-oxidation of phenol over these composite electrodes seems to occur without passivation or deactivation.

To check the absence of deactivation, a series of measurements where the electrode was contacted alternately with two different phenol concentrations was performed. Ten successive measurements were made by alternately contacting the electrode with a 0.125 and a 0.250 mM solution. This experiment shows that, despite the fact that the electrode was used for various measurements, the wave intensity observed remains practically the same. The observed intensity of the phenol oxidation wave pro-

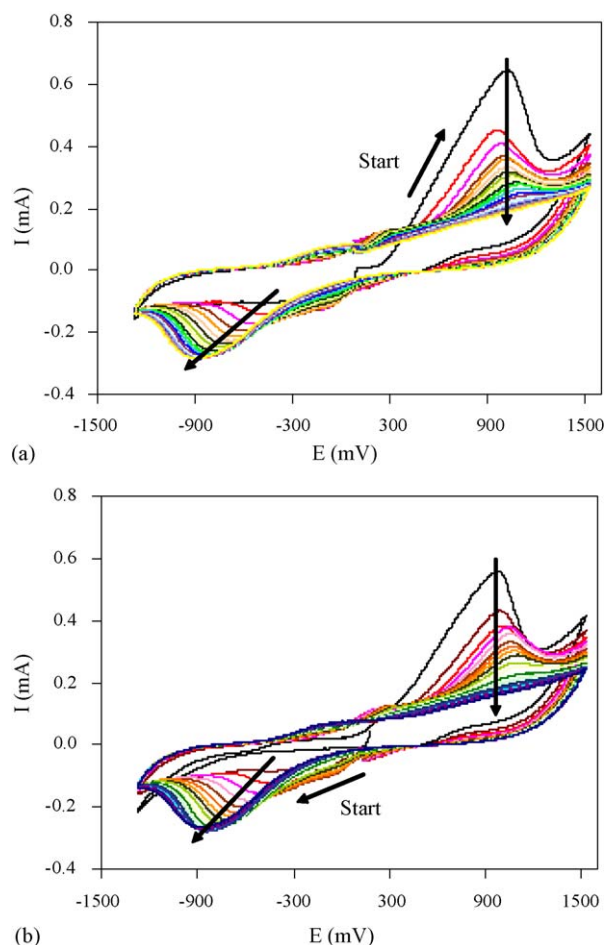


Fig. 5. Successive cyclic voltammograms of zeolite/graphite working electrode in the presence of 125 mM of phenol starting towards the anodic (a) or cathodic (b) directions. Arrows indicate the increase in cycle number or initial scan direction.

duced a value of 0.0038 ± 0.0003 mA for the 0.125 mM solution and 0.0064 ± 0.0005 mA for the 0.250 mM one.

Some deactivation does occur, however, for concentrations of phenol higher than 8 mM. This can be seen in the voltammograms depicted in Fig. 5, representing successive cyclic voltammograms using a 125 mM solution of phenol; these successive cycles were performed with no stirring of the solution between the various voltammograms.

In both cases the oxidation wave is well defined. Fig. 5(b) shows that there is no reduction wave assignable to phenol in the first voltammogram. After the first oxidation wave of phenol, a reduction wave can be observed around -50 mV, which can be attributed to one of the products of phenol oxidation possibly hydroquinone; however, further studies will be made to prove this hypothesis.

The successive scans induce a significant decrease of the anodic wave. As it was seen above, after the first oxidation of phenol a reduction wave appears; this wave, after a short increase in intensity, however, also disappears, as a second reduction wave, at a more negative potential, increases. This second cathodic wave seems to be originated by a product of the oxidation of phenol which remains adsorbed onto the electrode

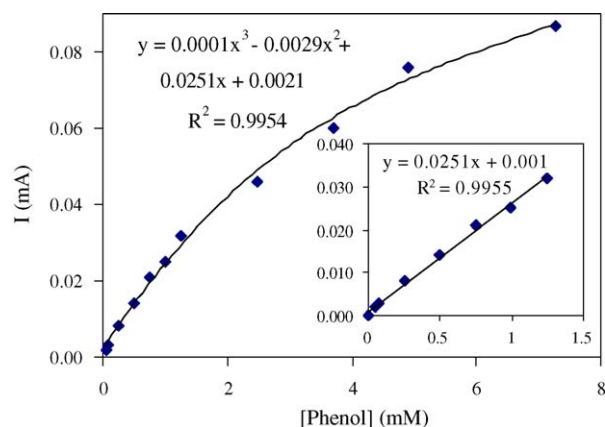


Fig. 6. Oxidation wave intensity as a function of concentration, for low phenol concentrations. In the inserted graph the range of concentrations where a linear relationship is observed has been detailed.

even after phenol oxidation has ceased to occur. It is likely that these species remain strongly adsorbed on, or are even trapped inside, the zeolite.

This fact may represent a limitation for catalytic applications when high concentrations of phenol are to be used.

Looking at Fig. 4 we can see that for the data points collected using a fresh pellet of composite electrode for each measurement (\blacktriangle) the current increases almost linearly at the beginning, but levels off for higher phenol concentrations, probably due to the saturation of the porous volume of the electrode material. Fig. 6 shows a detail of these measurements, for a lower range of phenol concentrations, where we can see that the wave intensity shows a linear relationship with concentration for low concentrations (up to 1.5 mM—see inset in Fig. 6) and starts to deviate from linearity for higher concentrations.

4. Conclusions

Zeolite/graphite composite electrodes seem very promising as electrodes for the phenol electrochemical oxidation, namely in relation to the industrial oxidation of phenol into more valuable products or for wastewater treatment.

The zeolite component seems to confer to these electrodes very important characteristics, increasing the overall current and lowering the potential required for the oxidation to occur, when compared with a graphite electrode.

This work corresponds to a preliminary work on this material, which may still be perfected and optimised, namely by the choice of different types of zeolite and changes in its composition and construction method.

Elucidation of the *modus operandi* of the zeolite in this composite is also important for the objective of improving the

system, although it has already been made clear that the micro-porous volume of the zeolite is of paramount importance in the processes that occur. Additional work will also be done in this elucidation.

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References

- [1] T. Atoguchi, T. Kanougi, T. Yamamoto, S. Yao, *J. Mol. Catal. A: Chem.* 220 (2004) 183–187.
- [2] T. Atoguchi, T. Kanougi, *J. Mol. Catal. A: Chem.* 222 (2004) 253–257.
- [3] C.B. Maugans, A. Akgerman, *Water Res.* 37 (2003) 319–328.
- [4] S. Cao, G. Chen, X. Hu, P.L. Yue, *Catal. Today* 88 (2003) 37–47.
- [5] R.C. Koile, D.C. Johnson, *Anal. Chem.* 51 (1979) 741–744.
- [6] M. Gattrell, D.W. Kirk, *J. Electrochem. Soc.* 140 (1993) 903–911.
- [7] M. Gattrell, D.W. Kirk, *J. Electrochem. Soc.* 140 (1993) 1534–1540.
- [8] J.-L. Boudenne, O. Cerclier, P. Bianco, *J. Electrochem. Soc.* 145 (1998) 2763–2768.
- [9] P.I. Iotov, S.V. Kalcheva, *J. Electroanal. Chem.* 442 (1998) 19–26.
- [10] Y.J. Feng, X.Y. Li, *Water Res.* 37 (2003) 2399–2407.
- [11] R.A. Torres, W. Torres, P. Peringer, C. Pulgarin, *Chemosphere* 50 (2003) 97–104.
- [12] R.M. Carvalho, L.T. Kubota, S. Rath, *J. Electroanal. Chem.* 548 (2003) 19–26.
- [13] S. Andreescu, D. Andreescu, O.A. Sadik, *Electrochem. Commun.* 5 (2003) 681–688.
- [14] A. Walcarius, *Anal. Chim. Acta* 384 (1999) 1–16.
- [15] A. Walcarius, in: S. Auerbach, et al. (Eds.), *Handbook of Zeolite Science and Technology*, Marcel Dekker, New York, 2003, pp. 721–783.
- [16] H. Kotte, B. Gründig, K.-D. Vorlop, B. Strehlitz, U. Stottmeister, *Anal. Chem.* 67 (1995) 65–70.
- [17] T. Ruzgas, J. Emnéus, L. Gorton, G. Marko-Varga, *Anal. Chim. Acta* 311 (1995) 245–253.
- [18] J.-P. Pereira-Ramos, R. Messina, J. Perichon, *J. Electroanal. Chem.* 146 (1983) 157–169.
- [19] M. Xu, W. Horsthemke, M. Schell, *Electrochim. Acta* 38 (1993) 919–925.
- [20] A. Walcarius, P. Mariaulle, L. Lamberts, *J. Electroanal. Chem.* 463 (1999) 100–108.
- [21] E. Briot, F. Bedioui, K.J. Balkus, *J. Electroanal. Chem.* 454 (1998) 83–89.
- [22] G. Marko-Varga, E. Burestedt, C.J. Svensson, J. Emnéus, L. Gorton, T. Ruzgas, M. Lutz, K.K. Unger, *Electroanalysis* 8 (1996) 1121–1126.
- [23] M.A.N.D.A. Lemos, P. Sousa, F. Lemos, A.J.L. Pombeiro, F. Ramôa Ribeiro, *Stud. Surf. Sci. Catal.* 122 (1999) 443–446.
- [24] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 85th ed., CRC Press, Boca Raton, 2004–2005, pp. 9–50.
- [25] B. Okolo, C. Park, M.A. Keane, *J. Colloid Interf. Sci.* 226 (2000) 308–317.
- [26] T. Beutel, M.-J. Peltre, B.L. Su, *Colloids Surf. A* 187/188 (2001) 319–325.
- [27] M. Khalid, G. Joly, A. Renaud, P. Magnoux, *Ind. Eng. Chem. Res.* 43 (2004) 5275–5280.