

Electro-oxidation of phenol on zeolite/graphite composite electrodes Part 2. Influence of zeolite type and composition

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Abstract

In this work, the electro-oxidation of phenol was investigated by cyclic voltammetry using composite electrodes built with graphite and different types of zeolites; porous and non-porous silica were also used for comparison purposes. In part 1 of this series it was shown that a NaY/graphite composite electrode has a very good response for phenol oxidation. In this work the influence of the nature and structure of the zeolite component by using different zeolites, such as Y, Beta, ZSM5, X and A, both in their sodium and protonic forms was analysed.

Among all the zeolites that were used in this study, NaY with a Si/Al ratio of 2.5 seems to produce the best results for the electrochemical oxidation of phenol, by producing a larger current and a lower oxidation potential. It was also concluded that sodium zeolites consistently show better results than acidic ones and that the increase in hydrophobicity is not advantageous either.

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1. Introduction

Although the electrochemistry of phenolic compounds has been studied extensively, due to its importance in various fields of chemical engineering, it is always important to develop a new and better way to analyse and convert these compounds.

Their elimination as wastewater contaminants is very important, since they can cause bad taste and undesirable odour contamination and are highly toxic and hazardous to human health. Removal is often carried out by oxidation, either using some form of catalysts [1–6] or by direct and indirect electrochemical oxidation [7–10].

The oxidation of phenolic compounds is also relevant in the fields of fine chemistry.

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 [11].

Mixtures of zeolite and graphite, such as the ones that are used in this work, have been proposed since the 1980s [12]. They have been used as modified carbon paste electrodes (mixing the

carbon powder and the zeolite with a liquid [13] or wax [14]), or just by pressing the mixture onto a metal grid [15] or disc [16]. Most of the work described, however, has been related with applications 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 [17].

In a previous work [18] it was reported that composite electrodes prepared from a simple mechanical mixture of the zeolite powder and graphite are able to catalyse the electro-oxidation of phenol, even at low concentrations.

Zeolites are crystalline solids with very regular microporous structures which have a very significant bearing on their applications, namely in what relates to catalysis and adsorption. A particular pore system exerts a steric influence on the reaction, controlling the access of reactants and products, by shape-selectivity. Apart from the geometrical aspects related to the pore structure, zeolites can be fine-tuned by changing the composition both of the structure itself (changing the Si/Al ratio) and of the cations that serve as counter-ions to the structure itself (namely by ion-exchange of these cations). Changing structure and composition allows us to have zeolites with different properties.

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This work evaluates the difference in behaviour, for the electrochemical oxidation of phenol between different types of zeolites, changing both structure and composition (the Si/Al ratio is indicated as a subscript), NaY_{2.5}, NaY₁₅ (with sodium deposition), HNaY_{2.5} and NaHY₁₅ (with different sodium contents), HY₁₅, USHY_{4.5}, HBeta_{12.5}, HBeta_{32.5}, HBeta₇₅, HZSM5₁₅, NaHZSM5₁₅ (with three different sodium concentrations), NaX_{1.23} and NaA₁, and compares their behaviour with the one observed when replacing the zeolite material by a porous silica (EP10X). This comparison allows us to extract information on the way this electrode works and will help in development of this kind of electrodes.

2. Experimental

2.1. Materials

All reagents were of analytical grade.

Sodium phosphate and phenol were purchased from Merck.

For the construction of the pellets, graphite with a high degree of purity and zeolites in powder form were used. The zeolites used in this work are based on a series of starting materials: LZ Y52 (NaY) with Si/Al=2.5 (which will, hereafter, be referenced as NaY_{2.5}) from Union Carbide, USHY with Si/Al=4.5 from UOP, HNaY (which will, hereafter, be referenced as HNaY_{2.5}(1.9)) with Si/Al=2.5 and a 1.9% Na/Al ratio, NaX with Si/Al=1.23 and NaA with Si/Al=1.0 all from Sigma–Aldrich, HY and HZSM5 with Si/Al=15 and HBeta with Si/Al=12.5, Si/Al=32.5 and Si/Al=75 from Zeolyst; the latter will be referenced hereafter as HBeta_{12.5}, HBeta_{32.5}, HBeta₇₅. For the control experiments a porous silica (EP10X from Crosfield), hereafter referenced as (SiO₂)_p, and a non-porous silica (from Carlo Erba Analyticals), referenced as (SiO₂)_{np} were used. The zeolites and the 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. All zeolites will be referenced with the Si/Al ratio indicated as a subscript and the sodium content, as Na/Al ratio molar percentage, in parenthesis. NaY_{2.5}, NaX_{1.23} and NaA₁ have a Na/Al ratio of 1 and, thus, is not indicated.

2.1.1. Ion exchange

In order to have a better understanding of the influence of the sodium content on the behaviour of the catalyst the parent zeolite LZ Y52 (NaY_{2.5}) was subjected to an ion exchange using an aqueous solution of ammonium nitrate (NH₄NO₃) of 0.5 M and 4 ml of solution per gram of zeolite. The exchange was performed at room temperature for a total of 30 min. This produced the zeolite HNaY_{2.5}(61). After characterisation, it was observed that the zeolite maintained the same Si/Al ratio and that the sodium to aluminium molar ratio was 61%.

For the purpose of comparison with the NaY_{2.5}, a high sodium form of Y₁₅, with approximately the same sodium content as NaY_{2.5}, was produced. This catalyst was made by sequential ion exchange and impregnation procedure with sodium nitrate, as described below.

To produce the NaY₁₅(440) zeolite, the original HY₁₅ was subjected to a first ion exchange using an aqueous solution of sodium nitrate (NaNO₃) of 2 M and 4 ml of solution per gram of zeolite. The exchange was performed at 100 °C for a total of 2 h. The zeolite was then calcined and after that subjected to an impregnation with the same solution. After characterisation, it was observed that the zeolite maintained the same Si/Al ratio and that the sodium to aluminium molar ratio was 440%.

Two additional preparations were done based on HY₁₅. This parent zeolite was subjected to two successive ion exchanges with 2M sodium nitrate solutions, given the samples that, after calcinations will be referenced as NaHY₁₅(66) and NaHY₁₅(76).

To complement this information, protons in the original HZSM5 zeolite were also partially replaced by sodium cations, to varying extent, by ion exchange, using an aqueous solution of sodium nitrate (NaNO₃). Each exchange was performed at room temperature for a total of 4 h, varying the concentration of the solution and the number of exchanges that each sample was subjected to. Using 4 ml of solution per gram of zeolite, the sample NaHZSM5₁₅(24) correspond to one exchange with 0.5 M, the NaHZSM5₁₅(30) correspond to one exchange with 1 M and NaHZSM5₁₅(32) correspond to two successive exchanges with 1 M solutions. After characterisation, all zeolites maintain the same Si/Al ratio and the sodium to aluminium molar ratio in the three samples were 24%, 30% and 32%, respectively [19].

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. These measurements were only used to determine the amount of water that is adsorbed in the zeolite under storage conditions and, thus, establish a suitable dry calculation basis for the weight of the zeolites that were used in the experiments.

The pellets were produced using a Graseby/Specac press.

2.3. Electrodes construction

The zeolite/graphite composite electrode was prepared by a simple mechanical mixture of the powders of the zeolite or silica with graphite in a 2:1 (w/w) proportion. 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.

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 it was described in previous works [16,18].

2.4. Electrochemical behaviour

All the electrochemical measurements were performed as described in previous works [16,18] where the conditions were optimised.

Cyclic voltammetry was carried out in a three-electrode cell, at a zeolite/graphite or at a silica/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.

A 100 mM sodium phosphate buffer solution was prepared so as to ensure a pH of 7.0.

For all the experiments a standard solution was used containing 125 mM of phenol in the sodium phosphate buffer.

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

3. Results and discussion

In the following, voltammograms obtained in the standard phenol solution with electrodes built by combining different zeolite materials with graphite are compared.

In order to have a base for comparison, as already presented in part 1 of this study, blank experiments were carried out with electrodes which were built in the same way as the ones containing the zeolite material but where the zeolite was replaced with the equivalent amount of non-porous (SiO_2)_{np} and porous (SiO_2)_p. An electrode was also built only with graphite; this electrode has very poor mechanical properties when compared with the ones with the zeolite or silica, but was stable enough to obtain a few voltammograms. The voltammograms obtained with these electrodes, and compared with the one obtained with $\text{NaY}_{2.5}$, are shown in Fig. 1. It should be noted that all pellets have a total mass of 5 mg, with a proportion of 2 parts of zeolite (or silica) and 1 part of graphite, except for the graphite-only pellet which, thus, has three times more graphite than the other electrodes.

As it can be seen graphite presents two distinct waves, a low intensity one, with a maximum at about 500 mV, and another one, with higher current intensity, around 1200 mV. As the structure and porosity of the pellet change, from pure graphite to the (SiO_2)_{np} and to (SiO_2)_p, the current associated with the wave

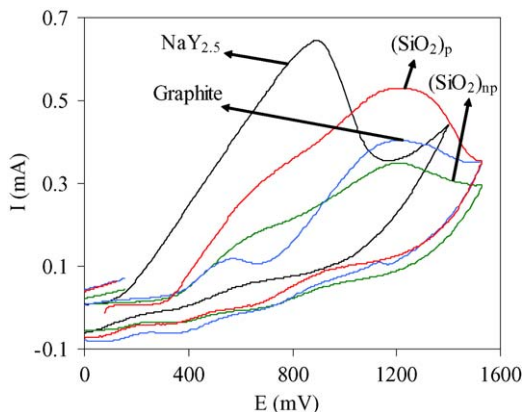


Fig. 1. Voltammograms obtained using the standard phenol solution on various working electrodes, starting with an anodic sweep. Electrodes shown include pellets with graphite only and with a porous (SiO_2)_p and a non-porous silica (SiO_2)_{np}, as well as with $\text{NaY}_{2.5}$.

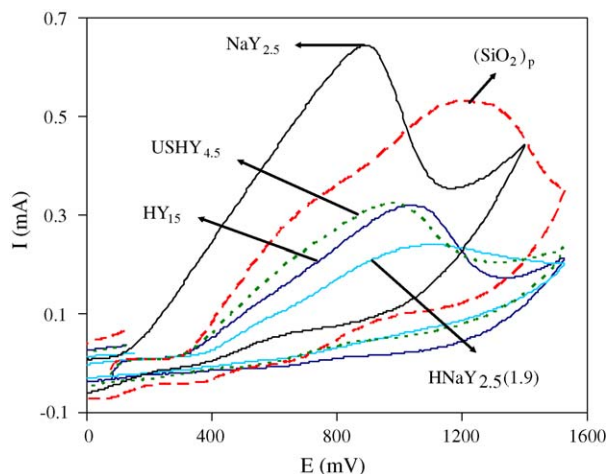


Fig. 2. Voltammograms obtained using the standard phenol solution on various Y zeolite/graphite working electrodes starting with an anodic sweep. Porous silica/graphite electrode is shown for comparison.

at lower potential increases. Within the electrodes that do not contain any zeolite, the higher intensities are obtained with the porous silica composite; since this electrode is the one that more closely resembles, in terms of structure and porosity, the zeolite-containing electrodes, it will be used for comparison purposes hereafter.

Zeolites with totally different characteristics, such as $\text{HNaY}_{2.5}(1.9)$, $\text{USHY}_{4.5}$, and HY_{15} are compared with $\text{NaY}_{2.5}$ and other sodium exchanged zeolites and to a porous silica in order to better understand the contribution of zeolite porosity and composition to the overall behaviour.

Fig. 2 compares a series of Y zeolites, with different characteristics, with the porous silica electrode. Although all the zeolites compared in this figure have the structure of Y zeolite, $\text{NaY}_{2.5}$ and $\text{HNaY}_{2.5}(1.9)$ have a $\text{Si}/\text{Al} = 2.5$, while USHY has a $\text{Si}/\text{Al} = 4.5$ and HY has a $\text{Si}/\text{Al} = 15$. Thus, they differ substantially in terms of hydrophobicity, $\text{NaY}_{2.5}$ being the most hydrophilic. The cation content is also different, both in total number of cations and in composition.

It can be seen that, in this group of catalysts, the porosity is clearly not the main factor. In fact, $\text{NaY}_{2.5}$ has a larger wave intensity and a lower oxidation potential, in relation to the phenol oxidation, than all of the other materials. All the Y zeolite samples possessing some acidity produce very low currents and higher oxidation potentials, even when compared with the porous silica sample.

Thus, it seems that the presence of acid sites induces a lower current and an increase in the potential at which the oxidation occurs.

It is interesting to note that, although zeolite $\text{NaY}_{2.5}$ has the same Si/Al ratio of $\text{HNaY}_{2.5}(1.9)$ the non-acidic zeolite has a better response. This can be rationalized by the fact that the oxidation of phenol involves the release of one proton; thus, high pH values should favour this process [20]. The presence of protons inside the micropores of the zeolite changes the effective pH in the microenvironment where the reaction is occurring and could reduce the rate of oxidation. However, there are also reports

indicating that the cyclic voltammometric wave intensity associated with phenol oxidation increases when the pH is decreased, due to the reduction of passivation effects [21]. It can also be seen that $\text{HNaY}_{2.5}(1.9)$ which has the larger number of acid sites, when compared to $\text{USHY}_{4.5}$ and HY_{15} , is the catalyst with the lower current and the higher over-potential.

When comparing this set of zeolites, which share the same structure, two main factors are likely to affect the final results: on one hand we have the number and strength of the acid sites, and on the other hand the zeolites with a lower Si/Al ratio are more hydrophilic than the ones with a higher Si/Al ratio. Observing the set of catalysts that includes $\text{HNaY}_{2.5}(1.9)$, $\text{USHY}_{4.5}$ and HY_{15} , which share in common the fact that they have a small sodium content, it can be seen that the increase of the Si/Al ratio also induces an increase in the current that is observed from $\text{HNaY}_{2.5}(1.9)$ to $\text{USHY}_{4.5}$ and HY_{15} (which have approximately the same response). However, this effect may come either from the decrease in total acidity or from the hydrophobicity, which should increase the phenol adsorption capability of the zeolite [22].

It is also important to note that the acidic zeolites have a lower current than the electrode produced with the porous silica, which corresponds to a non-acidic and highly hydrophobic material.

It is known that zeolite Beta adsorbs phenol more easily than Y zeolite [22]; several samples, with different Si/Al ratios were also tried in this work, to check on the influence of this parameter, as shown in Fig. 3.

It can be seen that, despite the fact that the Beta zeolite, with very high Si/Al ratios, is much more hydrophobic than $\text{NaY}_{2.5}$, the current levels that are achieved are much lower.

It is noteworthy to say that the cyclic voltammogram for the electrodes with these zeolites shows two successive oxidation waves, similar to the ones obtained with the porous silica, which may be due to oxidation at different topological sites of the electrode. Nevertheless, it is not possible to identify a clear pattern in this series of zeolites.

Fig. 4 shows a comparison between zeolites with an identical Si/Al ratio but with different structures; they are all in the acidic form so, despite the fact that the acid strength of their acid

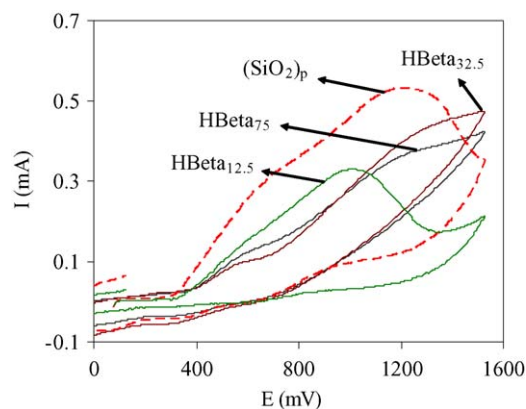


Fig. 3. Voltammograms obtained using the standard phenol solution on various Beta zeolite/graphite working electrodes starting with an anodic sweep. Porous silica/graphite electrode is shown for comparison.

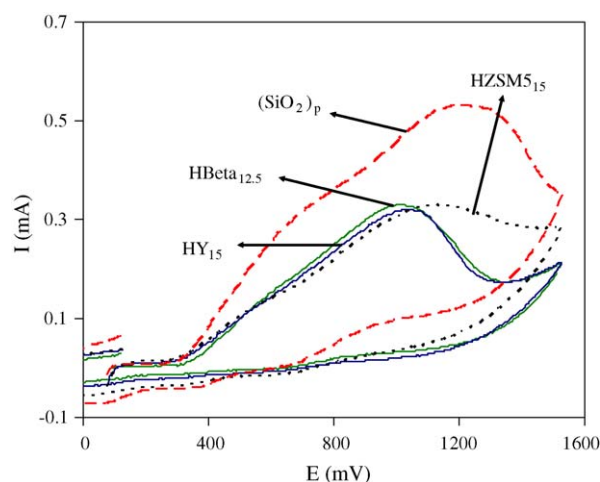


Fig. 4. Voltammograms obtained using the standard phenol solution on various zeolite/graphite working electrodes, with identical Si/Al ratio but with different structures, starting with an anodic sweep. Porous silica/graphite electrode is shown for comparison.

sites may differ from zeolite to zeolite, the total amount of sites should remain more or less the same. The comparison reveals that in respect to the wave intensity all the catalysts have practically the same behaviour. However, HZSM5/graphite composite electrode has a broader oxidation wave than the two other zeolites.

The influence of the Si/Al ratio, when moving from $\text{NaY}_{2.5}$ towards more siliceous zeolites has been inspected above; we will now focus on zeolites with Si/Al ratios lower than $\text{NaY}_{2.5}$. Fig. 5 compares three different structures of zeolites, Y, X and A all in the sodium form. All these zeolites are rather hydrophilic but, despite the difference in their Si/Al ratios, their behaviour is very similar, although $\text{NaY}_{2.5}$ still presents an oxidation wave that has better definition and larger intensity.

Pore volume is clearly not the main factor. In fact, pore volumes for $\text{NaY}_{2.5}$ [23], $\text{NaY}_{15}(440)$ [24], $\text{NaX}_{1.23}$ [25], NaA_1 [26] and porous silica (EP10X) are, respectively, 0.29, 0.27, 0.28 and $1.77 \text{ cm}^3/\text{g}$ and, nevertheless, porous silica has a lower current intensity.

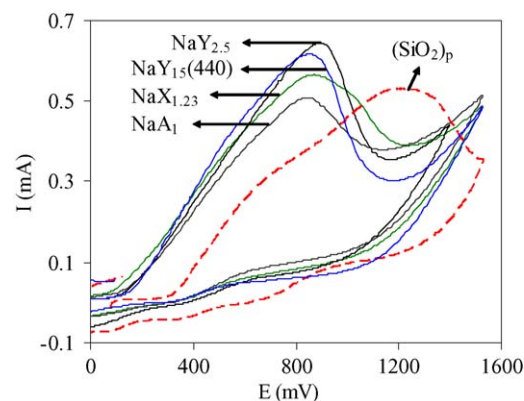


Fig. 5. Voltammograms obtained using the standard phenol solution on various zeolite/graphite working electrodes, in the sodium form but with three different structures and Si/Al ratios, starting with an anodic sweep. Porous silica electrode/graphite is shown for comparison.

It should be noted that it is clear that, although the structure type has some influence, with a significant decrease in wave intensity when moving from $\text{NaY}_{2.5}$ towards less siliceous zeolites. However, all these zeolites, with virtually no acidity, present a significantly higher oxidation intensity than the

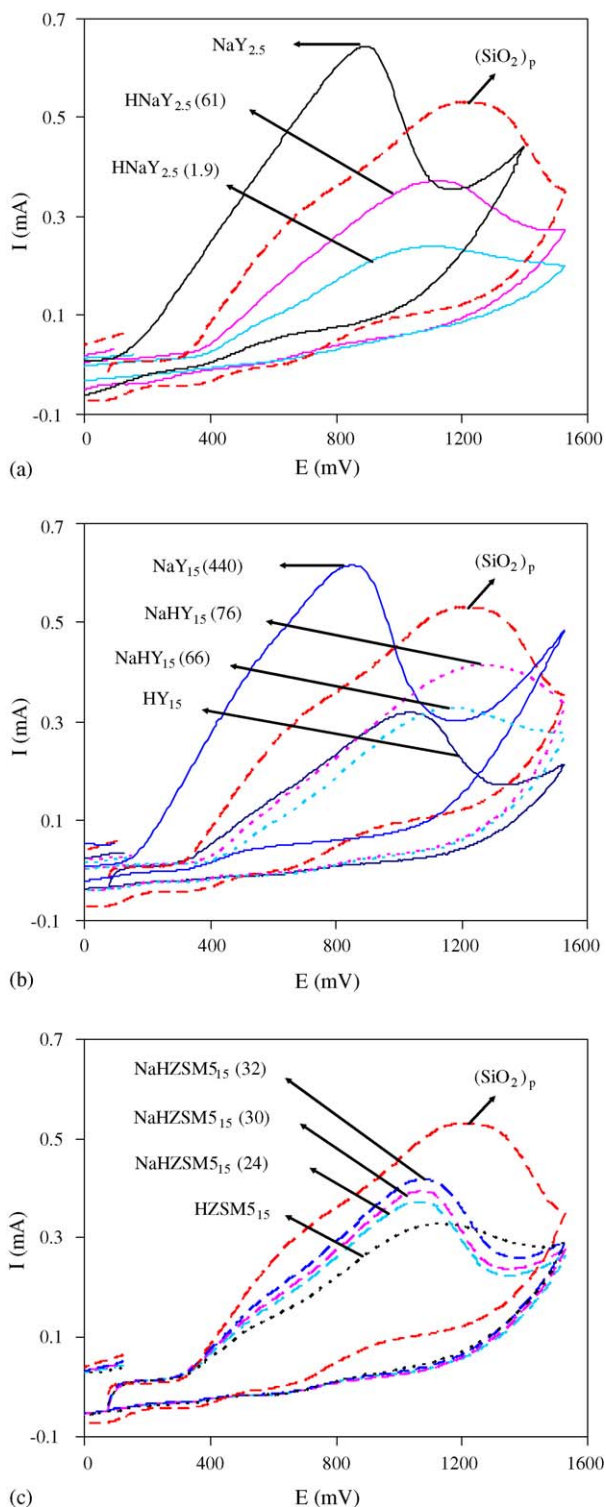


Fig. 6. Voltammograms obtained using the standard phenol solution on various zeolite/graphite working electrodes for the Y zeolite series with $\text{Si}/\text{Al} = 2.5$ (a) and $\text{Si}/\text{Al} = 15$ (b) and for the ZSM5 zeolite series with $\text{Si}/\text{Al} = 15$ (c), starting with an anodic sweep. Porous silica/graphite electrode is shown for comparison.

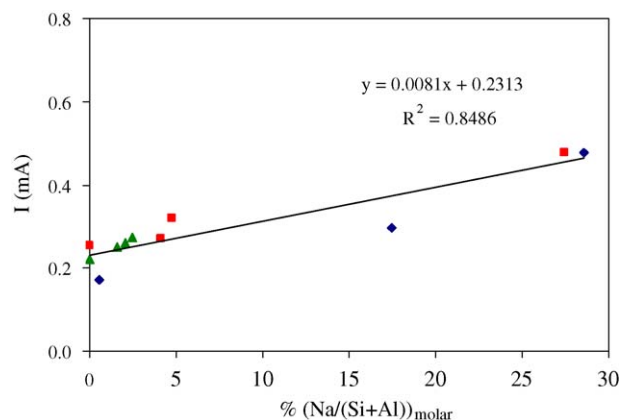


Fig. 7. Comparison between current intensity and the $\text{Na}/(\text{Si} + \text{Al})$ molar ratio for the Y zeolite series with $\text{Si}/\text{Al} = 2.5$ (\blacklozenge) and $\text{Si}/\text{Al} = 15$ (\square) and for the ZSM5 zeolite series with $\text{Si}/\text{Al} = 15$ (\blacktriangle).

ones with acid sites. It should also be noted that the sample $\text{NaY}_{15}(440)$, with a higher Si/Al ratio but with a sodium content similar to $\text{NaY}_{2.5}$, shows a remarkably similar response to the latter.

The results above indicated that the presence of acid sites is detrimental to the oxidation process. This can be clearly seen by the comparison of the three catalysts that have the same Si/Al ratio but have different proton contents in Fig. 6(a)— $\text{NaY}_{2.5}$, $\text{HNaY}_{2.5}(61)$ and $\text{HNaY}_{2.5}(1.9)$.

To complement the information, various electrodes were prepared with the catalysts, some obtained by impregnation, such as $\text{NaY}_{15}(440)$ and others by ion exchange departing from HY_{15} and HZSM5 zeolite. The Y zeolite with higher Si/Al ratio also shows a significant current increase with the increase of sodium content, as it can be seen in Fig. 6(b). However, only when the sodium content is similar to the one in $\text{NaY}_{2.5}$ does the current intensity resemble that of $\text{NaY}_{2.5}$. Fig. 6(c) shows that, although the amount of sodium that was introduced was limited, a significant increase of the intensity wave and a decrease of the potential oxidation occurs when the number of acid sites is reduced. Nevertheless, the wave current results are still quite lower.

To better visualise the sodium influence on the electrode response, Fig. 7 shows the relation between the peak current intensity and the sodium content, as measured by the $\text{Na}/(\text{Si} + \text{Al})$ molar ratio, for Y zeolite with two different Si/Al ratios and for a different zeolite structure such as ZSM5 (series shown in Fig. 6(a–c)). It can be seen that the relation is nearly linear and almost independent of the zeolite in question.

4. Conclusions

The results obtained indicate that the zeolite may play an important role in the electrochemical oxidation of phenol over composite zeolite/graphite electrodes. This influence is not restricted to porosity effects, but is connected with the composition of the zeolitic framework.

The fact that the effect is not restricted to porosity effects is clear when the results obtained with NaY were compared with those obtained with the porous silica. Despite the fact that the

porous silica has a larger pore volume than the zeolite samples, the wave current is higher for the latter and the oxidation potential is lower. It is also noteworthy that the zeolites with acid sites, although they also possess similar porosities, present lower current than the porous silica sample.

In fact, zeolites with a more hydrophobic character seem to produce lower currents and higher over-potentials for the oxidation of phenol than NaY, despite the fact that it is known that hydrophobic zeolites adsorb phenol more easily than hydrophilic ones, like NaY_{2.5} and NaX_{1.23}.

Structure effects seem also to play a minor role, as it can be seen both by the comparison of the low-silica zeolites (Fig. 5) and the high silica zeolites with similar Si/Al ratios but different structures (Fig. 4), as well as by the relation between wave intensity and sodium content depicted in Fig. 7.

Among the zeolites that were tested in this work, the NaY_{2.5}/graphite composite electrode is the one with the best performance, both in terms of peak wave current and in terms of showing the lower oxidation potential for the phenol oxidation.

Sodium content has also revealed itself as a very important parameter as it was shown by the comparison between NaY₁₅(440) and NaY_{2.5}. It seems that sodium which is not in cationic places also has an important contribution for the electro-oxidation process.

It is still unclear the mechanism by which the zeolite affects the oxidation of phenol on these composite electrodes, although it is clear that it is not restricted to the porosity effect, that the presence of acid sites induces a lowering in performance, that cation content is extremely relevant and that it is likely that an hydrophylicity/hydrophobicity balance is involved.

This type of electrodes seems promising for electro-oxidation of phenol, namely in the context of remediation of wastewaters that are contaminated with this chemical.

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