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## ARTICLE

## Carbonates as reactants for the production of fine chemicals: the synthesis of 2-phenoxyethanol

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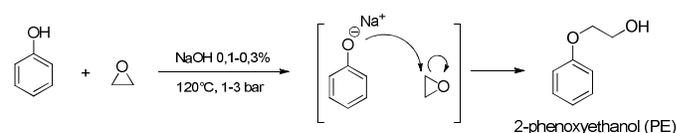
The solventless and heterogeneously catalysed synthesis of 2-phenoxyethanol (ethylene glycol monophenyl ether) via the reaction between phenol and ethylene carbonate was investigated using Na-mordenite catalysts, as an alternative to the industrial process using ethylene oxide and homogeneous basic conditions. Under specific reaction conditions, it was possible to obtain total selectivity to phenoxyethanol up to 75% phenol conversion and 82% selectivity at total phenol conversion in 5-7 hours reaction time and using a moderate excess of ethylene carbonate; the main by-product was the linear carbonate of phenoxyethanol, bis(2-phenoxyethyl)carbonate (selectivity 15%), which could then be converted to phenoxyethanol by reacting with phenol in basic medium, with 100% yield; so in overall, the yield to phenoxyethanol was as high as 97%. With a stoichiometric feed of phenol and ethylene carbonate the maximum conversion of phenol was just 60%, still with 100% selectivity to phenoxyethanol. An autocatalytic phenomenon was also observed, due to the higher basicity of 2-phenoxyethanol compared to phenol, which overlapped the Na-catalyzed activation of phenol. Starting from a commercial Na-mordenite, which showed significant deactivation, and by applying a post-treatment aimed at the reduction of microporosity, it was possible to minimize both the deactivation and the Na leaching, while keeping the selectivity enhancement effect shown by the mordenite structure.

### Introduction

2-Phenoxyethanol (PE) is an organic compound that, at room temperature, is a colourless oily liquid with a mild smell of roses. It is used as solvent for dyes, inks, and resins; it is a synthetic intermediate in the production of plasticizers, pharmaceuticals, and fragrances. It is also used as component for the preparation of textile detergents and the synthesis of paraben-free, formaldehyde-free cosmetic preservatives (in a mixture with ethylhexylglycerine), showing a balanced spectrum of effectiveness against bacteria, yeasts, and mould fungi, as well as being a solvent and fixative-extender for perfumes, as such or after esterification with isobutyric acid.<sup>1</sup>

Nowadays PE is produced by reacting phenol with ethylene oxide (Scheme 1). The hydroxyethylation is carried out in the presence of basic catalysts; in patents, the catalysts reported are mainly homogeneous, and include various basic compounds: e.g. ammonia, urea, amines, phenates of Na and Li; an heterogeneous catalyst based on hydroxide-exchanged resins is also reported.<sup>2-10</sup> However, the most commonly used catalysts in the current processes are the hydroxides of alkali metals, especially sodium hydroxide, typically added in quantities of 0.1-0.3% by weight. The reaction is conducted at a temperature of 110-130°C and 1-3 bar pressure. In order to optimize the selectivity towards the monoethoxylated product, reactants are used in an equimolar amount; furthermore, ethylene oxide is

added slowly to the reactor. At present, the yearly world capacity for PE is around 170,000 tons.<sup>11</sup>



**Scheme 1** The reaction between phenol and ethylene oxide catalyzed by NaOH.

One significant disadvantage of the current industrial production is that the product obtained cannot be used as such by the cosmetic and fragrance industry because of its pungent metal odour, which is likely due to the residues of alkali metal catalysts. This problem is not completely solved even by a subsequent distillation, which is carried out in order to separate the product from unconverted phenol and heavy by-products. Post-treatments have been proposed whereby the ether is put in contact with sodium borohydride;<sup>12</sup> the alkali metal borohydride can be directly added in the reaction medium, together with the alkali metal hydroxide.<sup>13</sup> Another drawback of the current industrial production is the formation of polyethoxylated by-products with 2 to 80 condensed ethylene oxide molecules; polymeric glycol ethers of phenols are formed

from a further reaction of the desired product with ethylene oxide. These compounds cause the product to darken, and post- or in-situ treatments are necessary to prevent this. Patents report maximum conversions of phenol around 99% with variable selectivity towards the 2-phenoxyethanol (from 88 to 96%), depending on the conditions.<sup>2-10</sup>

Alternatively, phenol is reacted with either 2-chloroethanol or ethylene carbonate (EC), again in the presence of alkalis.<sup>14</sup> This last route was claimed in early patents to be a smooth, controllable reaction that makes it possible to obtain phenoxyethyl alcohols at high yields<sup>15-18</sup> and, more recently, it was also used for introducing aryl nuclei into the chemical structure of acrylic esters (phenoxyethyl alcohols can easily condense with acrylic acid).<sup>19,20</sup> The use of carbonates as reactants for the synthesis of fine chemicals and intermediates has now become one of the research areas of major scientific and applied interest. The use of carbonates instead of conventional reactants, such as alkylhalides and dialkylsulphates, aims not only to avoid both the use of toxic compounds and the generation of waste effluents necessitating disposal, but also to develop a chemistry which may offer advantages in terms of selectivity to the desired compound; important examples are the use of dimethylcarbonate for the O-methylation and the carboxymethylation of phenolic compounds.<sup>21-26</sup>

EC as an alkylating agent for phenol has been reported using homogeneous catalysts such as alkali carbonates, alkaline metal iodides, lithium hydride, and tetraethyl ammonium iodide for the synthesis of glycol phenyl ethers.<sup>27-29</sup> However, the main problems with all these systems are the recovery of catalyst, the purification of the product, and – with some catalysts – also the formation of tar compounds. Recently, some authors have reported on solid basic catalysts made of alkali-loaded large-pore zeolites, while an excellent PE yield of 98.5% in the reaction of phenol with ethylene carbonate was reported with the KL zeolite.<sup>30</sup> However, so far, there has been no report on how the tuning of both acid properties and reaction parameters for the hydroxyethylation of phenol with EC and solid basic catalysts affects their performance.

In the present work, we report a more sustainable process, which avoids the use of any solvent, and is based on an heterogeneous basic catalysts made of Na-mordenite, which avoids the problem of Na contamination of the product, and can be easily recovered and reused.<sup>31-34</sup> The detailed study underpinning such achievements, namely the systematic studies on the parameters affecting the yield and selectivity to PE, is also reported.

## Experimental

The catalyst used for reactivity experiments was a “CBV 10A” sodium mordenite molecular sieve from ZEOLYST International with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio 13 (Na<sub>2</sub>O weight% = 6.5; surface area = 425 g/m<sup>2</sup>). The zeolite was used either as such, without any pre-treatment, or after post-treatment using the liquid-phase deposition of tetraethylortosilicate (TEOS). In the former case, experiments carried out for comparison with the thermally pre-treated zeolite (at 400°C for 3 h in air flow) gave the same results as for the untreated zeolite. The liquid-phase post-treatment was carried out using a 20 mL mixture of 5 vol% TEOS in *n*-hexane mixed with 2.5 g zeolite at room temperature for 15 h. The system was filtered, dried at 120°C and calcined at 450°C for 3 h. The procedure was repeated twice.

X-ray diffraction patterns of zeolites were carried out using a Philips PW1710 instrument, Ni-filtered CuK $\alpha$  radiation, ( $\lambda$ = 0.15418 nm), interval 2 $\Theta$  5-80°, step 0.1°.

Ar adsorption/desorption isotherms (77K) were carried out in a Micromeritics ASAP 2020 instrument. Samples were previously outgassed for 120 minutes at 423K and 30  $\mu$ mHg, and then heated for 240 minutes at 623K. Specific surface area values were obtained by multi-point BET equation in the 0.05-0.2 p/p<sup>0</sup> range and total pore volume values were calculated at 0.95 p/p<sup>0</sup>. The micropore size distribution was calculated with the NLDFT-statistic method.

Both in solvents used for the analytical measurement and in solutions after reactions, atomic absorption analyses were carefully performed to determine the Na concentration in reactants, with the aim of determining the amount of Na leached during the catalytic reaction. The different Na concentration between the initial solution and the final one was very low, just a few ppm, thus close to the analytical error. Indeed, traces of this element are always present, thus leading Na to be considered an ubiquitous contaminant. Because of this, we took extreme care to carry out the analysis in such a way as to minimize occasional errors. Due to the insolubility of PE in water, we dissolved our samples in 2-propanol (Sigma-Aldrich): a solvent chosen because of both its chemical-physical characteristics and its very low Na content. The procedure adopted for the analysis was the following: (a) 50  $\mu$ L of sample (either the reactant, or the reaction mixture after reaction) were brought to 5 mL volume with 2-propanol; (b) the sample was then analysed with a SpectraA-100 Varian instrument, equipped with graphite furnace GTA 110, radiation source Na/K. The line at 330.3 nm was used, instead of the main one at 589.6 nm, because the analysis of the organic solution led to an out-of-range absorption; a further dilution of the solution would have led to a major error in the measurement, and therefore the weaker line was used. A 10  $\mu$ L sample was injected. The furnace temperature ranged from 75°C up to 2000°C, with intermediate steps at 85, 95, 120 (solvent removal), and 700°C (pyrolysis and incineration of organics). The analysis was carried out using an Ar flow of 3 mL/min. (c) The final Na concentration was obtained after subtracting the Na content from the solvent. For each sample, the analysis was repeated 6 times. Because of the insolubility of Na salts in organic medium, the calibration curve was made by means of an aqueous solution of NaNO<sub>3</sub> (500 ppb Na), obtained by dilution of a standard solution (1000 ppm Na); the volume of standard solution injected was 10  $\mu$ L.

Reactivity experiments were carried out as follows: in a round bottom pyrex cylinder equipped with an internal cooling circuit, phenol (3 mmol), EC (6 mmol) and Na mordenite (0.5% weight with respect to the phenol fed, if not otherwise specified) were added. The reaction mixture was stirred at 210°C for 7 h under nitrogen atmosphere. 50  $\mu$ L samples were taken without interrupting the reaction; they were then brought to a 10 mL volume with acetone (HPLC grade, Sigma-Aldrich); then an aliquot (approx. 2 mL) was filtered (0.45 $\mu$ m PTFE filter) to separate the catalyst, and then analysed by means of GC.

The analysis of the reaction mixture was performed using an Agilent GC6850 instrument, equipped with HP-1 capillary column (30m x 320  $\mu$ m x 0.25  $\mu$ m), and a FID held at 280°C (H<sub>2</sub> 40 mL/min, air 450 mL/Min); carrier gas was H<sub>2</sub> (108 mL/min). The injector was held at 250°C, in the split mode (50:1). The volume of the sample injected was 1  $\mu$ L. The oven

temperature was the following: 50°C (2 min), ramp 10°C/min, 120°C, ramp 25°C/min, final T 280°C (3 min).

Products were isolated from the reaction mixture by means of flash chromatography (230-400 mesh) by using as eluent a petroleum ether/ethyl acetate mixture (vol ratios from 8/2 to 7/3). Then the products (PE, DPE and BPEC) were identified by means of ESI-MS and NMR. The exception was 2-[2-(2-phenoxyethoxy)ethoxy]ethanol (TPE), because the signals due to C14 and C15 triplets overlapped the signals of other CH<sub>2</sub> moieties in other by-products (DPE). With this compound, identification was achieved by means of ESI-MS and GC-MS. ESI-MS spectra (positive or negative), were recorded using a Waters Micromass ZQ4000, equipped with a capillary probe (3.54 kV), with 20 Volts cone voltage, and direct injection (20 μL/min).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in deuterated chloroform at 25 °C on a Varian Inova 300, at 300 MHz and 75 MHz respectively. Details concerning NMR spectra of products are reported in the Supplementary information.

## Results

### Identification of the best reaction conditions

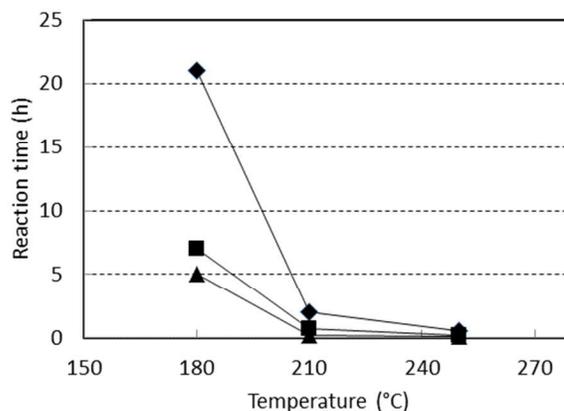
Preliminary experiments were aimed at finding the reaction conditions necessary for obtaining high conversion of the substrate using the Na-mordenite catalyst. Figure 1 compares the time needed to reach given values of PE yield for different reaction temperatures. At 150°C (not shown in the Figure), there was a 10% yield to PE only after 35h reaction time, while increasing the temperature to 180°C and 210°C led to a remarkable decrease in the reaction time needed. By pushing the temperature further (250°C), the reaction time was shorter, but at a higher conversion the extent of consecutive reactions increased also while selectivity declined. For example, at 210°C the selectivity to PE was close to 97-98% even at a very high phenol conversion, but it dropped to less than 95% when the reaction temperature was 250°C. Therefore, we decided to carry out the experiments at the optimal temperature of 210°C, which was the best compromise between an acceptable reaction rate and lower formation of by-products.

In regard to the latter, three side-products were identified (Scheme 2): the di-hydroxyethylated compound 2-(2-phenoxyethoxy)ethanol (DPE), the tri-hydroxyethylated compound 2-(2-(2-phenoxyethoxy)ethoxy)ethanol (TPE), and the linear carbonate of PE, bis(2-phenoxyethyl)carbonate (BPEC). The two by-products DPE and TPE usually formed in low amounts (overall yield less than 2%), with the exception of experiments where a large excess of ethylene carbonate was used. Conversely, the yield to BPEC was as high as 10-15% at complete phenol conversion; this by-product may form by means of two different reaction pathways (Scheme 3):

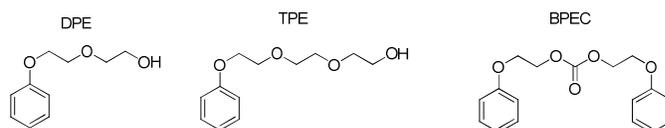
- by successive reactions between PE and the unconverted EC, and then again with another molecule of PE, with the release of ethylene glycol (transesterification mechanism);
- by the formation of the intermediate obtained by reacting phenol with EC (carboxyalkylation reaction); the latter either eliminates CO<sub>2</sub> to form PE, or may be transformed further by esterification with PE.

It is worth noting that we did not notice the formation of diphenylcarbonate, the product of transesterification of phenol

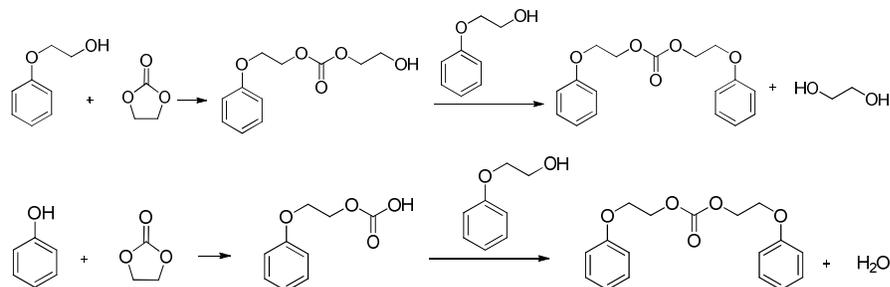
with EC, which might be a parallel reaction competing with PE formation. This has been interpreted as being due to the fact that the softer nucleophile phenol will preferably react with the soft alkyldene C atom in the carbonate to produce glycol ether.<sup>30</sup> In the case of PE, however, the aliphatic alcohol may react with the hard C atom of the carbonyl to yield the transesterification product; therefore, the (a) mechanism still is possible. In regard to the (b) mechanism, the intermediate compound might react preferably with PE, instead of releasing CO<sub>2</sub> and yield PE, under conditions leading to PE accumulation. Therefore, both mechanisms (a) and (b) would be more encouraged at conditions of high phenol conversion, and are in any case promoted at high EC concentration.



**Figure 1** Reaction time needed to obtain the overall yield to PE + BPEC equal to 95% (◆), 50% (■) and 30% (▲), in function of the reaction temperature used. Reaction conditions: Phenol/ethylene carbonate 1/4 (molar ratio), catalyst/phenol 1/2 (wt ratio). Catalyst Na-mordenite SAR 13.



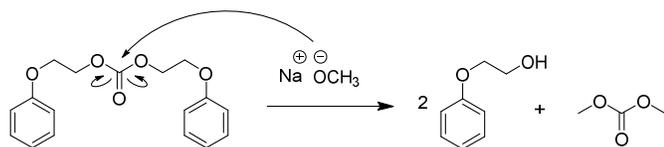
**Scheme 2** By-products in the reaction between phenol and EC.



**Scheme 3** Plausible mechanisms for the formation of BPEC by-product during the reaction between phenol and EC. Top: mechanism (a); bottom: mechanism (b) (see text).

An important point is that BPEC could be completely hydrolyzed to yield PE (Scheme 4). In fact, after separation by flash chromatography, BPEC was completely converted into PE (100% yield) within 5 h reaction time, using 2% NaOCH<sub>3</sub> catalyst, in refluxing methanol. The same reaction also occurred

in acidic conditions, but was much slower compared to the basic medium. Therefore, this product would not be a waste compound of the process, but an intermediate compound for PE synthesis. The same is not true for DPE and TPE, which could be converted neither to phenol nor to PE.



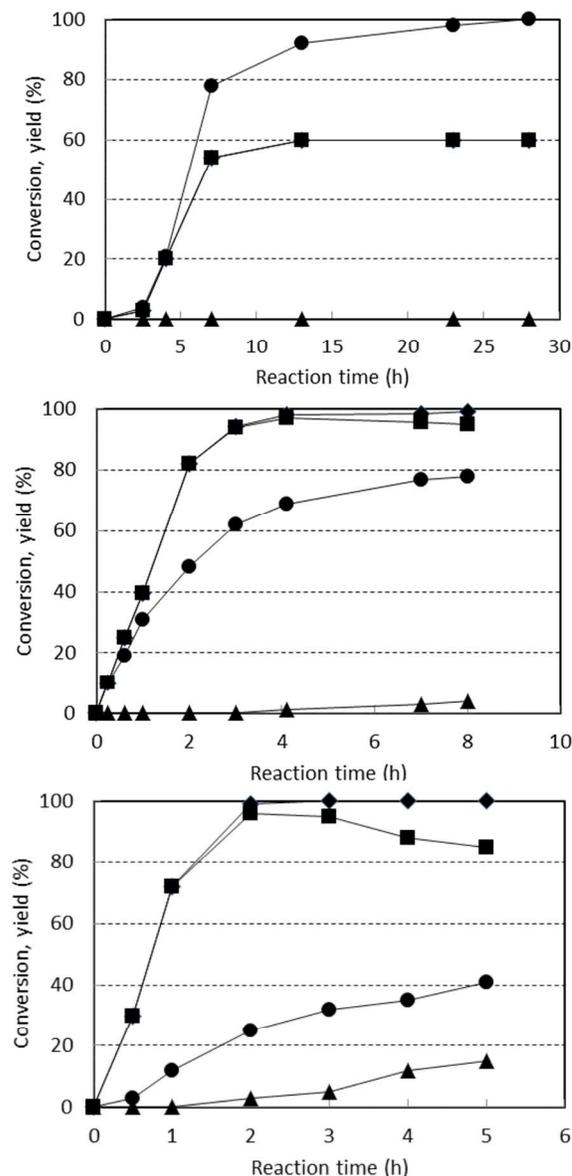
**Scheme 4** The reaction of BPEC transformation into PE.

Figure 2 shows the effect of the reaction time on phenol and EC conversion, and on the yield to PE (the desired product) + BPEC (the by-product which could be converted to PE in a separate vessel), as well as on by-products DPE and TPE, at the temperature of 210°C, for three different phenol/EC molar ratios, equal to 1/1, 1/2, and 1/4. The catalyst used was Na-mordenite SAR13 (50 wt% with respect to phenol, which corresponds to 10% mol Na). The results obtained highlight the following aspects:

- a decrease in the phenol/EC molar ratio led to a progressive increase in the reaction rate; in fact, complete conversion of the limiting reactant (i.e. EC with the 1/1 phenol/EC molar ratio, but phenol with 1/2 and 1/4 phenol/EC molar ratios) was seen in 28 h in the former case, in 6–8 h with the 1/2 ratio, and in less than 3 h with the 1/4 ratio.
- with the 1/1 phenol/EC feed ratio, the maximum conversion of phenol was just 60%. Despite the use of a stoichiometric feed, EC was clearly the limiting reactant; this was due to the fact that EC underwent the parallel decomposition via decarboxylation and successive oligomerisation of ethylene glycol; this was confirmed by carrying out experiments with EC alone, under the same reaction conditions used for the reaction with phenol. Selectivity to PE was very high, close to 100%, because of the negligible formation of DPE, with no TPE and BPEC at all.
- when lower phenol/EC feed ratios were used, EC conversion was less than 100%, even though EC still went on reacting even after total phenol conversion had been reached, because of the formation of DPE, TPE (consecutive reactions upon PE, with further consumption of EC), and ethylene glycol oligomers. The selectivity to PE was total only for phenol conversion lower than 100%, because longer reaction times led to a rapid increase in by-product formation, especially with the phenol/EC feed ratio equal to 1/4. In general, however, when the complete phenol conversion was approached the selectivity declined, mainly because of the formation of BPEC, since the formation of the more undesired by-products, DPE and TPE, remained very low, especially if higher phenol/EC ratios were used.

Figure S1 (Supporting Information) shows the effect of the catalyst amount on catalytic behaviour, at fixed reaction conditions. The conversion of phenol and EC were proportional to the catalyst amount in the catalyst/phenol wt ratio interval ranging between 0 and 0.5%. For higher amounts of catalysts, the conversion of phenol decreased while that of EC increased; as shown in Figure 2 (top), with an equimolar phenol/EC ratio – at which complete conversion of phenol is theoretically possible – the conversion of phenol was indeed less than 100% because of EC transformation into non-useful products; in other words, the decrease in the phenol conversion shown for

increasing catalysts amount (Figure S1) was due to the increased contribution of EC decomposition.

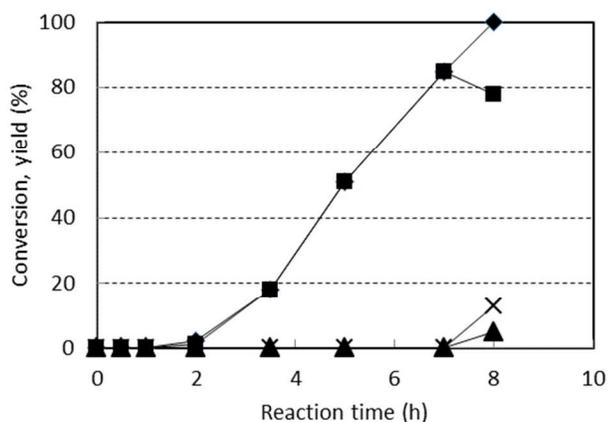


**Figure 2** Effect of reaction time on phenol conversion (◆), EC conversion (●), and yield to PE + BPEC (■), and DPE + TPE (▲). Reaction conditions: T 210°C; catalyst/phenol 1/2 wt ratio; Na-mordenite catalyst; Phenol/EC molar ratios 1/1 (top), 1/2 (middle) and 1/4 (bottom).

Therefore, under these circumstances, the decomposition of EC becomes kinetically more facilitated than its reaction with phenol, which causes a decline in both yield to PE and phenol conversion. On the other hand, there was only a small % increase in phenol conversion when the catalyst amount was increased from 0.5 to 5 wt%, despite the fact that the EC conversion was still similar to that of phenol (i.e. with a very low amount of EC decomposition). Therefore, it cannot be ruled out that for high catalyst loadings, i.e. at over 0.5 wt%, a poorer contact between reactants (because of the absence of solvent) and catalyst may have made the reaction slower compared to experiments carried out with lower catalyst

amount. Lastly, it is also worth noting that at such conditions – with an equimolar ratio between phenol and EC, and a phenol conversion no higher than 70% – the selectivity to PE was always close to 99%, with the formation of less than 1% BPEC, and no formation of DPE and TPE.

The final result of this preliminary investigation is that the best reaction conditions – i.e. those making it possible to obtain fast reaction rates with almost total conversion of phenol within a few hours' reaction time, while maintaining both high selectivity ( $\geq 98\%$ ) to PE+BPEC and minimal EC transformation into by-products – were as follows: T 210°C, feed ratio phenol/EC 1/2, and catalyst/phenol wt ratio 1/200 (0.5 wt% catalyst). Figure 3 summarizes the catalyst performance under optimized reaction conditions; it can be seen that the total conversion of phenols was achieved within 9 h reaction time; selectivity to PE was total up to more than 60% conversion, whereas at total phenol conversion the selectivity to the more undesired DPE (with traces of TPE) was 4%, while the selectivity to BPEC was 17-18%.



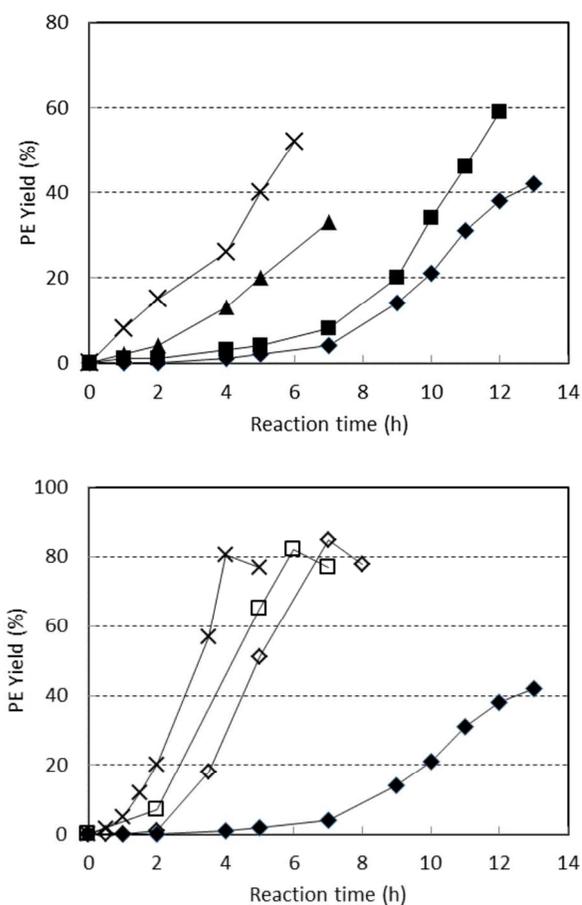
**Figure 3** Effect of reaction time on phenol conversion ( $\blacklozenge$ ), and on yield to PE ( $\blacksquare$ ), BPEC ( $\times$ ), and DPE + TPE ( $\blacktriangle$ ). Reaction conditions: T 210°C, phenol/EC molar ratio 1/2, catalyst amount 0.5 wt% with respect to phenol.

An important effect registered under these conditions was the presence of an induction period, which led to negligible yield to PE in up to 2 h reaction time. It is worthy of note that such an effect was not registered under conditions of high catalyst loading with the same 1/2 phenol/EC feed ratio, while, it was apparently seen when the equimolar feed ratio was used (Figure S2). Therefore, the induction period may be attributable to the use of a low catalyst amount, and may be due to problems related to the scarce access of reactants to the basic active sites located in zeolites, a problem which may be overcome by using large catalyst amounts, probably because of the contribution of external sites.

On the other hand, the initial induction period was followed at first by a slow increase in conversion, but later on by an acceleration with a rapid increase in the conversion within a short reaction time which is clearly not something one might expect under usual catalytic conditions. One possible explanation for the phenomenon observed is the presence of an autocatalytic effect, i.e. an acceleration in the rate due to the PE itself.

### The induction period, and the autocatalytic effect

In order to confirm our hypothesis, we planned a series of experiments without any catalyst. The experiments shown in Figure 4 (top) were carried out by adding increasing amounts of PE in the reaction medium, at 210°C (no reaction was observed in the absence of catalyst at 180°C, even after 24 h), with a phenol/EC ratio equal to 1/2. Worthy of note, we first treated the commercial PE with silica plug in order to remove any traces of alkali metal cations. Figure 4 (bottom) compares the yield to PE shown in function of time, both in the absence of any catalyst (and without preliminary addition of PE), and in the presence of the catalyst (0.5 wt% Na-mordenite, in respect to phenol). The following considerations may be made:



**Figure 4** Effect of reaction time on yield to PE. Top: experiments without any catalyst, with increasing amounts of PE added from the beginning (wt% with respect to phenol): 0% ( $\blacklozenge$ ), 4% ( $\blacksquare$ ), 17% ( $\blacktriangle$ ), and 126% ( $\times$ ). Yields were calculated after subtraction of the PE amount added. Bottom: comparison between PE yields without catalyst ( $\blacklozenge$ ), with 0.5 wt% (with respect to phenol) Na-mordenite catalyst ( $\diamond$ ), or 0.5 wt% treated Na-mordenite ( $\square$ ), and with 3±1 ppm NaOH ( $\times$ ). Reaction conditions: T 210°C, phenol/EC ratio 1/2.

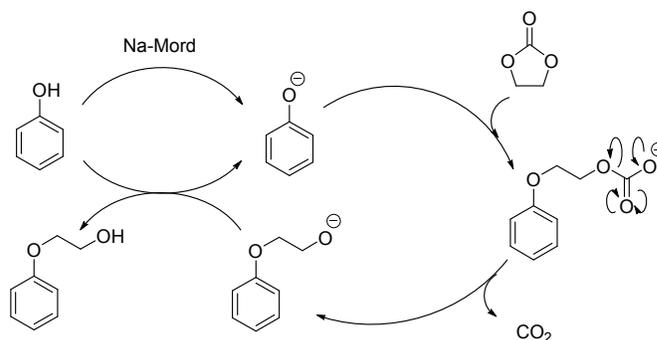
- (a) The reaction proceeded even in the absence of any catalyst, but was clearly slower than in the presence of the catalyst (Figure 4 bottom). After 7 h reaction time yield to PE was about 4% (as also shown in Figure S1, for a phenol/EC ratio equal to 1/1). There was an induction period of a few hours, after which the reaction started. It is important to note that the possible contamination of the reactants used because of

alkali metals was ruled out, based on the negligible Na content analytically found. It is possible that the reaction took some time (i.e. the induction period) to show a non-negligible reaction rate in the absence of added catalysts, because of the slow formation of the phenate anion (although accelerated at 210°C, compared to lower temperatures). Then, however, the reaction was accelerated because of the formation of PE (see below for the explanation of the autocatalytic effect).

- (b) Addition of increasing amounts of PE from the beginning of the reaction, shortened the induction period, until it became negligible when the reaction was carried out in the presence of a rather high amount of PE. Also, addition of PE accelerated the reaction rate: a rapid increase of the yield in function of time was observed in the presence of the greater amounts of added PE.
- (c) In all cases, the selectivity to PE was 100%, because of the relatively low phenol conversion seen. Only in the case of the experiment carried out with the highest amount of PE did we notice the formation of BPEC, with 1.2% selectivity.
- (d) Also shown in Figure 4 (bottom) is the catalytic behaviour seen with the addition of 3±1 ppm NaOH. It can be seen that the homogeneous catalyst was the most efficient, with no induction period but still with the autocatalysis effect shown.

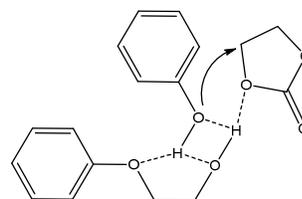
Assuming that the formation of phenate is the rate-determining step (accelerated in the presence of the basic catalyst), and because of the stronger basicity of the deprotonated form of PE compared to the phenate, the generation of the former species within the catalytic cycle (Scheme 5) leads to a rapid deprotonation of phenol, which is activated for a further transformation into PE, thus explaining the autocatalytic effect. In other words, as long as phenol is present in the reaction medium, the deprotonated form of PE will readily react and generate the phenate species, whereas at the end of the reaction, under conditions of phenol scarcity, it will pick up the proton initially released by phenol to the Na-mordenite catalyst. The loss of CO<sub>2</sub> from the adduct formed by the nucleophilic attack of phenate onto EC is also a strong driving factor for the generation of the strong base, the deprotonated form of PE; the latter species, however, is soon converted into PE, because of its basic character.

Some experimental evidences support the hypothesis formulated. The by-product BPEC forms only when the conversion of phenol is very high; even though this compound is formed by a consecutive reaction, one should in any case expect that a small, but non-negligible, amount of it will start to form at intermediate values of phenol conversion. This occurs because under conditions of phenol starvation the deprotonated form of PE may attack the carbonyl bond of EC, and start the reaction sequence leading to the formation of BPEC (Scheme 3). In this regard, the basic catalyst (either the ppm of Na<sup>+</sup> or the Na-mordenite) acts as an initiator, more than as a true catalyst, whereas the main role of increasing the reaction rate is played by the deprotonated form of PE (Scheme 5). This suggests the presence of a heterogeneously-initiated and heterogeneously-terminated reaction (in the presence of the zeolite), but with a fundamental contribution of the proton-exchange between phenol and PE alkoxide playing the role of a homogeneous catalysis action. However, the zeolite may play an important role in improving the reaction selectivity (see below), which confirms that the reaction occurs, at least in part, within the confined environment of the mordenite pores.



**Scheme 5** The autocatalytic effect of PE on the reaction rate.

With regard to the induction period, and to the role shown by the added PE (Figure 4, top), it must be remembered that we operated in the absence of any solvent; therefore the favoured interaction between the nucleophilic O atoms of PE and the proton of phenol might lead to the development of a concerted weakening of the O-H bond in phenol and a facilitated interaction with EC (Scheme 6), thus finally leading to a considerably shortened induction period. Moreover, we experimentally observed that PE makes the solution less viscous, thus playing a solvent effect which may help in facilitating diffusion in the presence of the zeolite catalyst.



**Scheme 6.** A hypothesis of a concerted H-bonding interaction between phenol, PE, and EC under solventless conditions, facilitating the attack of the Ph-O<sup>δ-</sup> species onto EC.

On the other hand, the efficiency of the catalyst determines the length of the induction period; for example, the use of high amounts of catalyst (Figure S2) also permitted a considerable shortening of the induction time, but this is clearly not very sustainable from the Green Chemistry standpoint. Data obtained also highlight that diffusion in zeolite pores can play a role in the reaction. In order to investigate the effect of a modification of porosity on catalytic behavior, we carried out a post-treatment on the Na-mordenite,

#### Post-treatment of the Na-mordenite: a comparison of catalytic performance

The silanization procedure on unidimensional and aluminum-rich zeolites, such as mordenite, showed a pore mouth narrowing effect more significant than with other zeolites, such as ZSM-5.<sup>35</sup> In order to reduce the microporosity through pore mouth blocking, a post-treatment on the industrial mordenite was carried out using a chemical liquid deposition with TEOS as silanization agent.

The characteristics of the two samples, the original Na-mordenite and the treated one, are summarized in Table 1. The treatment did not lead to any change in the XRD pattern of the sample. Indications of textural changes are given from the surface area and porosity, where the surface area of parent mordenite was high (452 m<sup>2</sup>/g), and after post-treatment decreased down to 109 m<sup>2</sup>/g. Also, both the total pore volume

and micropore volume showed a dramatic decrease, thus indicating a clogging in the microporosity, while the mesopore volume and area were left substantially unchanged.

**Table 1** Main features of the Na-mordenites used for reactivity experiments.

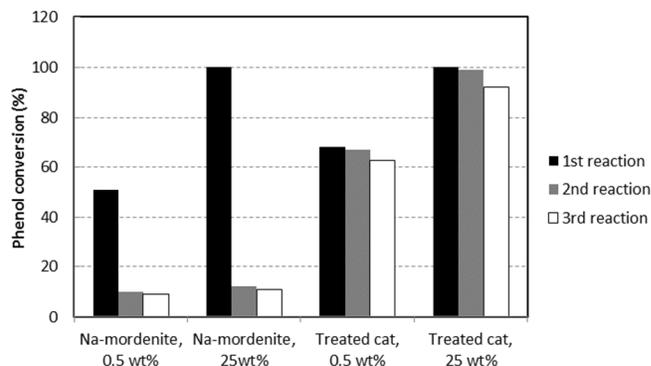
|                                     | Original Na-mordenite | Treated Na-mordenite |
|-------------------------------------|-----------------------|----------------------|
| Total pore volume (cc/g)            | 0.189                 | 0.069                |
| Micropore volume (cc/g)             | 0.151                 | 0.030                |
| Surface area (m <sup>2</sup> /g)    | 452                   | 109                  |
| Micropore area (m <sup>2</sup> /g)  | 418                   | 77                   |
| Mesopore area (m <sup>2</sup> /g)   | 34                    | 32                   |
| Average pore diameter (Å)           | 17                    | 23                   |
| Maximum pore diameter DFT (Å)       | 5.9                   | 5.9                  |
| Na content (wt % Na <sub>2</sub> O) | 6.5                   | 6.0                  |

The catalytic behaviour of the two zeolites is compared in Figure 4 (bottom). It can be seen that the induction time was considerably shorter with the treated zeolite; however, the overall amount of Na accessible was probably decreased in the treated zeolite because of the less pore volume accessible to reactants. The autocatalytic effect cannot be the only one responsible for the different initial behaviour shown by the two zeolites, because the amount of PE formed during the first 1-2 h reaction time was too low to have any effect on the initial behaviour. This result suggests that the delay in starting the reaction is affected by the accessibility of reactants to the Na sites: an event which does not play an important role only when a very high loading of catalyst is used.

Another important implication seen after catalyst treatment was on catalyst reusability, as shown in Figure 5, by comparing the conversion of phenol at 210°C and after 5 h reaction time, with the untreated and post-treated zeolites. Catalysts were separated from the reaction medium by filtration, and then reloaded again for the successive reaction after a washing with acetone during filtration and a subsequent drying in an oven at 100°C overnight; tests were carried out using both low (0.5 wt% in respect to phenol) and high (25 wt%) catalyst loading. The untreated catalyst showed a clear deactivation effect already after the first use, whereas the treated catalyst showed negligible deactivation. The deactivation of the untreated Na-mordenite was mainly due to the accumulation of organic residues inside catalyst pores, as evident from the brownish colour of the zeolite; the same effect was by far less relevant in the treated catalyst, in keeping with a considerably reduced deactivation. In fact, the IR spectrum of the used untreated catalyst showed bands at 1775 and 1800 cm<sup>-1</sup>, which are attributable to C=O moiety-containing organics. A regeneration treatment of the used catalyst at 400°C for 3 h in flowing air did not lead to a complete recovery of the catalytic activity. The accumulation of organic matter with the untreated catalyst may once again be attributed to difficulties in the diffusion of reactants, a phenomenon which might be conducive to consecutive reactions to heavier compounds.

However, another possible reason for deactivation is a small, but non-negligible leaching of Na. More specifically, the analysis of the residual Na content in the untreated zeolite after the first use highlighted a loss of ca 1.6±0.4 % (relative amount) of the overall Na content, which would correspond to ca 3±1 ppm Na concentration in the reaction medium. The

leaching of Na was found to be lower in the case of the treated zeolite, after analysis of Na in the solution; however, we would like to mention that due to the difficulties encountered in the analysis of such a tiny amount of Na, and to the experimental error dealt with during these measurements (see Experimental), we cannot state that the treated catalyst gave no leaching at all.



**Figure 5** Phenol conversion after 5 h reaction time at 210°C, phenol/EC ratio 1/2, with both untreated and treated Na-mordenite catalyst, for the fresh catalyst, and after recovery and reuse in a 2<sup>nd</sup> and 3<sup>rd</sup> reaction. Tests carried out using either 0.5 or 25 wt% catalyst (with respect to phenol).

The data shown highlight the possible role of Na ions leached from the Na-mordenite during reactivity experiments. In order to verify this contribution, we stopped the reaction with the untreated Na-mordenite at about 10% phenol conversion – the reaction being carried out at the usual conditions, i.e. T 210°C, 0.5 wt% catalyst, phenol/EC 1/2 – and filtered off the catalyst, and then went on with the reaction in the absence of catalyst. The PE yield in relation to time showed a trend very similar to that obtained when using NaOH (a few ppm) as the catalyst, shown in Figure 4 (bottom). Even though the interpretation of data is complicated by the autocatalytic effect of the PE (which was present in the filtered solutions, although with a yield of just 10%), this result demonstrates that the Na leached from the catalyst most likely also contributed to the catalytic behaviour seen.

When the same experiment was carried out with the treated catalyst, the reaction rate after catalyst filtration was slower than that shown both by the Na (3 ppm) catalyst and after filtering off the untreated Na-mordenite; after 2 h reaction time, the rank for PE yield was the following: solution after filter-off of the untreated Na-mordenite, 26% > fresh solution with 3 ppm Na, 20% > solution after filter-off of the treated Na-mordenite, 12%. The difference between the three solutions was decreased after 4-5 hours reaction time, because of the autocatalytic effect due to the formed PE. The lower leaching of Na shown with the treated catalyst may again be related to a quicker diffusion of reactants which limits the chemical interaction between acidic molecules and basic sites.

The better performance of the treated catalyst highlighted that using a Na-mordenite with controlled porosity makes it possible to overcome problems related to hindered diffusion, with reduced induction time, less deactivation, and improved catalyst reusability. As shown in Figure S1, the catalytic behaviour was also considerably affected by the amount of catalyst used, whereas, however, the optimal amount of catalyst to use depends on the catalyst features. Therefore, we repeated

some experiments by using increasing amounts of the treated catalyst, in order to see whether it was possible to optimise both the conversion rate and the yield to PE. The conditions used were once again a phenol/EC ratio equal to 1/2, and a reaction temperature of 210°C, because a higher feed ratio or lower temperature would have led to a much slower reaction rate. The results of these experiments are shown in Figure S2, which shows the conversion and yields to products depending on the reaction time with 0.5 and 5 wt% (in respect to phenol) of the treated catalyst. It is seen that with the latter catalyst, and in conditions where phenol is the limiting reactant, 98% conversion of phenol was obtained after 5 h reaction time with 5 wt% catalyst, and after 7 h with 0.5 wt% catalyst. Remarkably, the yield to PE was 86% in the former case (with 12% BPEC and 2% DPE), and 82% in the latter case (14 % BPEC, 2% DPE). The use of 25 wt% catalyst led to 100% phenol conversion in 5 h reaction time, but selectivity to PE was only 75%, with 6% BPEC and a high yield to DPE+TPE (19%). With regard to the conversion of EC, in the two former cases it was close to 50% (which implies a negligible transformation of EC into waste by-products), whereas in the latter case it was 90%, indicating an important contribution of EC decomposition. Overall, the optimized conditions with the best catalyst were T 210°C, 5 wt% catalyst and phenol/EC molar ratio 1/2; at these conditions, the induction period shown was 1 h only.

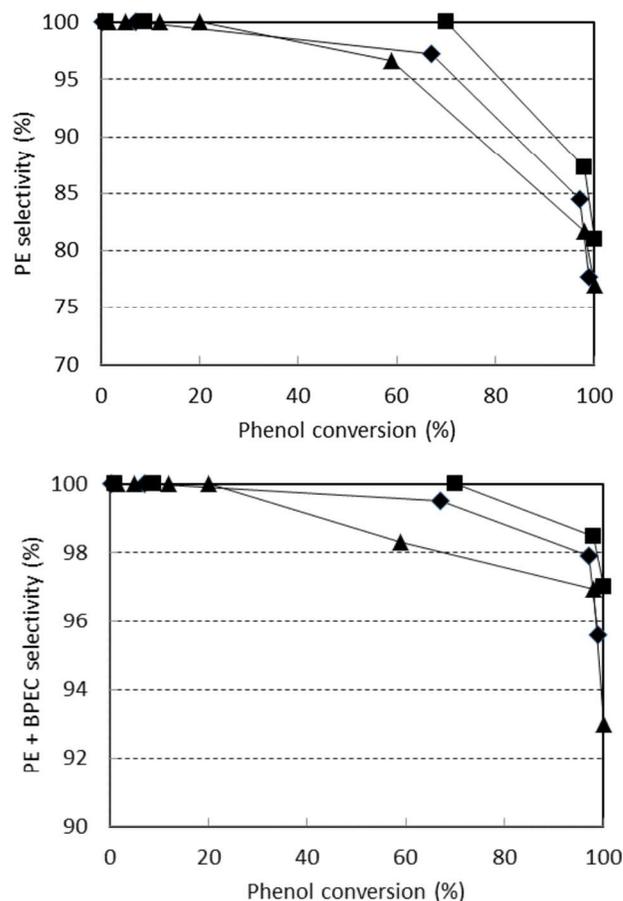
Concerning the role of microporosity in retarding the start-up of the reaction, and considering that the mesopores are also present in the untreated Na-mordenite, we can hypothesize that in the presence of the smaller pores a higher degree of reactants retention, both phenol and EC, leads to a greater extent of EC transformation into heavy compounds. The latter partially block both smaller and larger pores, thus retarding diffusion and counterdiffusion, and finally delaying the initiation of the reaction between phenate and EC. This hypothesis was also confirmed by the experimental evidence that the untreated zeolite soon became brown even in the presence of EC only, because of the formation of polymeric compounds.<sup>36</sup> The same phenomenon was much less relevant in the case of the treated zeolite.

#### Homogeneous vs heterogeneous catalysis

Overall, under our reaction conditions and in the absence of solvent, the use of a heterogeneous catalyst clearly suffers from problems such as a much lower TOF (3 ppm NaOH are enough to catalyse the reaction more efficiently than 5 wt% solid catalyst based on Na-mordenite), and diffusional limitations which, however, can be overcome by a proper catalyst modification. Overcoming these problems leads to better activity, with shorter induction time (not observed with the homogeneous catalyst), catalyst reusability, and negligible Na leaching. On the other hand, Figure 6 shows that the most significant result concerned the selectivity to PE achieved with the optimal heterogeneous catalyst, under conditions which make it possible to minimize the parallel EC decomposition.

The Figure shows the selectivity to both PE and PE + BPEC for the treated catalyst (at both low and high catalyst loading), and for the homogeneous NaOH catalyst; the better selectivity achieved with the zeolite is evident. This difference is lower if the comparison is made with the untreated Na-mordenite catalyst, probably because of the relevant contribution of the homogeneous reaction due to Na leached from the catalyst. This also demonstrates that with the treated catalyst the reaction occurred, at least in part, within the zeolite mesoporosity, which

made it possible to limit the formation of the bulkier by-products and, in the end, provide a better selectivity to PE at high phenol conversion.



**Figure 6** Selectivity to PE (top) and to PE + BPEC (bottom) in relation to phenol conversion at 210°C, phenol/EC molar ratio 1/2, and variation of reaction time. Catalysts: treated Na-mordenite 0.5 wt% in respect to phenol (◆), 5 wt% in respect to phenol (■), and NaOH 3±1 ppm (▲).

#### Conclusions

The synthesis of phenoxyethanol by means of the reaction between phenol and ethylenecarbonate, as an alternative to the current industrial process carried by reaction with ethylene oxide, was investigated in detail under both homogeneous (NaOH) and heterogeneous (Na-mordenite) catalytic conditions, without any solvent. We found that an outstanding selectivity to phenoxyethanol and bis(2-phenoxyethyl)carbonate of over than 98% could be achieved at 98% phenol conversion, but total selectivity was shown under conditions where phenol conversion was only 60%, because ethylene carbonate was the limiting reactant. The bis(2-phenoxyethyl)carbonate could be easily separated and transformed with 100% yield to phenoxyethanol. The Na-mordenite heterogeneous catalyst proved to be reusable and to cause a negligible Na leaching; however, in order to do that it had to undergo a post-synthesis treatment aimed at decreasing the micropore volume.

Indeed, since few ppm of Na are enough to catalyse the reaction, a contribution to reactivity derived from a minimal amount of Na released (below the detection limit of the analytical method used) even with the treated catalyst cannot be completely ruled out. Despite this, the role of the heterogeneous Na-zeolite is evident in finally providing a better selectivity than that achieved with the homogeneous NaOH catalyst. The treated zeolite also showed a much shorter induction period than the untreated one. An autocatalytic effect was seen, which was explained by considering the basicity of the phenoxyethanol itself.

Finally, it is worth noting that even though the proposed process requires an additional step, i.e., the production of ethylene carbonate by reaction between ethylene oxide and carbon dioxide, a similar technology is also used in the new Omega process for the production of ethylene glycol (MEG) developed by Shell. MEG is produced by first reacting ethylene oxide with CO<sub>2</sub> to produce EC, which is then transformed to MEG. The advantage of the Omega process, compared to conventional ethylene oxide hydrolysis, is the final better selectivity to MEG. The same occurs in the process proposed here: the final selectivity to PE achieved using EC is better than that achieved using ethylene oxide as the reactant for phenol.

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### Notes and references

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A new process for the synthesis of 2-phenoxyethanol, which avoids the use of solvents, and is based on an heterogeneous catalyst made of Na-mordenite.

