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Autoxidation of p-cresol to p-hydroxy benzaldehyde using CoCl₂, CoAPO-5 and CoAPO-11

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Abstract

CoCl₂, CoAPO-5 and CoAPO-11 are active and selective catalysts for the autoxidation of p-cresol to p-hydroxy benzaldehyde (p-HBA) in methanolic sodium hydroxide solution at 313–353 K. The yield of p-HBA is 70–75% at approximately 95% conversion, by-products being p-hydroxy benzyl alcohol (p-HBAlc; 5%) and p-hydroxy benzyl methylether (p-HBME; 10%) for the reactions catalysed by CoAPO-5 and CoAPO-11. Using CoCl₂ a selectivity for p-HBA of 80% can be obtained with p-HBME (10%) and p-HBAalc (5%) as by-products. Some oligomers/polymer are formed. However, these could not be determined by HPLC analysis. Oxidation of p-HBAalc to p-HBA is observed for all three catalyst systems at these low reaction temperatures. The oxygen selectivity, defined as the moles of p-cresol converted per mole of oxygen consumed, is remarkably low (maximally 60%). This is due to the oxidation of the solvent (methanol) to formic acid. The use of sodium hydroxide is undesirable from an environmental point of view, but cannot be avoided. Below a NaOH/p-cresol ratio of 1 no reaction occurs. A maximum reaction rate is observed at a NaOH over p-cresol ratio of 3–4. A maximum reaction rate is observed at a cobalt/p-cresol ratio of 0.6–0.7 mg/g, independent of the catalyst source. Not only the reaction rate but also the oxygen selectivity and selectivity to p-HBA show the same dependence upon the cobalt/p-cresol ratio. This indicates a comparable reaction mechanism in the homogeneous (CoCl₂) and the supposedly heterogeneous CoAPO systems. Recycling of the catalysts at sufficiently low cobalt over p-cresol ratios indicates that the CoAPO catalysts are not stable under reaction conditions; cobalt is released from the partially dissolved CoAPO molecular sieve. The observed catalytic activity mainly stems from this dissolved cobalt.

Keywords: CoAPO-5; CoAPO-11; Cresol autoxidation; Leaching

1. Introduction

Cobalt salts are frequently used as catalysts in oxidation reactions [1–8]. The reversible change of the oxidation state between Co²⁺ and Co³⁺ seems to be a
condition for these applications. Several papers have appeared dealing with the substitution of cobalt in AlPO molecular sieves [9-24]. It has been reported that framework cobalt in CoAPO-5 and CoAPO-11 is also able to change its oxidation state between $2^+$ and $3^+$ reversibly, making them possible candidates for application as heterogeneous oxidation catalysts.

Recently, the autoxidation of p-cresol to p-hydroxy benzaldehyde in sodium methoxide solution using CoAPO-5 and CoAPO-11 as heterogeneous catalysts has been reported in the patent literature [25]. A selectivity of 90% for p-HBA was claimed at 90% conversion of p-cresol.

The catalytic autoxidation of p-cresol to p-HBA (Fig. 1) using a cobalt chloride catalyst in methanol in the presence of three moles of sodium hydroxide is a potentially interesting route [1,26-30]. The selective catalytic oxidation of p-cresol (Fig. 1) with molecular oxygen is a viable proposition due to the fact that the phenolic hydroxyl group acts as a built-in inhibitor to further oxidation of the aldehyde group under mild reaction conditions.

The process reported by Nishizawa and co-workers [27], however, apart from the use of large amounts of sodium hydroxide suffers from two major drawbacks:

(a) By-product formation (25-30%). Up to 20% p-hydroxy benzylalcohol and 10% p-hydroxy benzyl methylether are formed in the oxidation of p-cresol using CoCl$_2$ as catalyst. The p-hydroxy benzylalcohol is not further oxidised under the reaction conditions employed. Only at 100°C can the oxidation of p-hydroxy benzylalcohol to p-hydroxy benzaldehyde be accomplished but, unfortunately, in a consecutive reaction the p-HBA is oxidised to p-hydroxy benzoic acid [26].

(b) Slow reaction rate due to catalyst deactivation. Catalyst deactivation is believed to be caused by the formation of inactive, hydroxyl-bridged, cobalt complexes under basic conditions in the presence of water. If water is removed from the reaction mixture, to suppress catalyst deactivation, a high reaction rate is observed. However, only p-hydroxy benzyl methylether is formed under these conditions according to Sheldon and de Heij [26]. On the other hand, Sharma and Chandalia [28] reported some contrasting results. Only a slight increase of the reaction rate (8%) without any significant change of the selectivity was observed, upon removal of water.

Mechanistic studies of the system described above [31], using a homogeneous cobalt catalyst, showed that the oxidation state of the cobalt changed, reversibly, between $2^+$ and $3^+$. Since cobalt on a T-position in AlPOs has the same ability, the catalytic activity of cobalt substituted AlPOs was tested in the present study.
The use of CoAPOs might evade the above mentioned disadvantages. Dimerisation (and thus deactivation) of cobalt is suppressed because the cobalt resides on (isolated) framework T-sites. Furthermore, preliminary experiments have shown that the yield of p-hydroxy benzaldehyde is high (75%) due to the fact that p-hydroxy benzylalcohol, a major by-product in the homogeneous system, is further oxidized to p-hydroxy benzaldehyde at this low reaction temperature using the CoAPO molecular sieves. However, the use of large amounts of NaOH is still necessary for the autoxidation of p-cresol. Since the reaction is carried out in strong alkaline solutions (NaOH/methanol), the stability of the catalyst may be questioned.

In this paper the results obtained with CoCl₂, CoAPO-5 and CoAPO-11 in the autoxidation of p-cresol to p-hydroxy benzaldehyde in methanolic sodium hydroxide solution are reported. Although initial experiments pointed in the direction of heterogeneous catalysis by the CoAPO samples, it will be shown that the catalytic activity is in fact due to partial dissolution of the molecular sieves. In consequence, the catalytic activity observed stems from dissolved cobalt species (homogeneous catalysis).

2. Experimental

2.1. Synthesis

CoAPO-5 and CoAPO-11 samples were prepared essentially following the procedures described in the patent literature [32,33]; the agglomerate size was approximately 30 μm. The (Al+P)/Co ratio varied between 400 and 25. Calcination was performed by heating the samples in a flow of dry oxygen at a rate of 5 K min⁻¹ to 823 K and keeping them at the final temperature for 5 hours. The weight percent of cobalt in the samples, as determined with AAS, varied between 0.25 and 3.8 wt.-%. Samples will be denoted as CoAPO-x (wt.-% Co). CoAPO-5 and CoAPO-11 samples with an agglomerate size of approximately 3 μm were synthesized in a stirred autoclave; these samples will be denoted CoAPO-x(wt.-% Co)s.

2.2. Characterization

X-ray powder diffraction data of the CoAPO molecular sieves were collected on a Philips PW 7200 X-ray powder diffractometer using Cu Kα radiation. In order to examine the cobalt environment and oxidation state diffuse reflectance electronic absorption spectroscopy (DREAS) spectra were obtained on a Hitachi 150-20 spectrophotometer equipped with a diffuse reflectance unit. Spectra were recorded after diluting the samples four times with MgSO₄, using quartz cuvets. The measured reflectance was converted to the Kubelka–Munck function to obtain a linear relationship between the concentration of cobalt and the absorption [34]. Elemental
analyses of the catalysts and reaction solutions were determined with atomic adsorption spectroscopy (Perkin-Elmer 3030 atomic absorption spectrophotometer).

2.3. Catalytic oxidation reactions

Typically, oxidation reactions were performed with the following experimental conditions. A reaction mixture (approximately 75 ml) of p-cresol (12 g, 1.46 mol/l), sodium hydroxide (13.2 g, 4.38 mol/l) and methanol (50 ml, 20 mol/l) and CoAPO (0.5–2 g, 6–26 g/l) was heated to 313–353 K under vigorous stirring (3000 rpm) in an oxygen atmosphere (1 atm). Stirring was performed using a hollow glass stirrer to optimize the oxygen transfer from the gas to the liquid phase. Veratrole (1,2 dimethoxy benzene; 0.2 mol/l) was used as an internal standard for the HPLC analysis. The oxygen consumption was followed volumetrically.

Samples of approximately 1 ml were withdrawn from the reaction vessel with a syringe at various reaction times and diluted 1000 times with water prior for HPLC analysis. HPLC analysis was performed on a 25 cm RP-18 column (Chrompack) using a water methanol eluents (70:30). The products were detected using a UV detector operating at 210 nm. Calibration curves for the various components were obtained using the same experimental conditions. Conversion, selectivities and yields were calculated using the internal standard, and are therefore based on the real concentration in the reaction mixture. The amount of polymeric products was maximally 10 percent.

3. Results and discussion

All CoAPO samples had X-ray diffraction patterns identical to those of the corresponding AlPOs. No crystalline or amorphous impurities could be detected. Diffuse reflectance electronic absorption spectroscopy (DREAS) was performed on all samples in the as-synthesized form. An approximately linear increase of the integrated DREAS intensity (converted to the Kubelka–Munk function) as a function of the weight percentage cobalt in the samples was observed. There were no indications for the presence of non-framework (octahedrally coordinated) cobalt. The integrated DREAS intensities of the samples synthesized in the stirred autoclave are significantly lower due to the smaller crystallite sizes, at comparable cobalt concentrations. DREAS spectra showed no difference between the CoAPO-5 and CoAPO-11 samples.

These cobalt-containing molecular sieves were used as catalysts in the autoxidation of p-cresol. A typical progress of the reaction, using CoAPO-11(1.0) as a catalyst is displayed in Fig. 2 and Fig. 3.

The concentration of p-cresol decreases rapidly. A conversion of 85 percent is obtained within 5 hours at 343 K and 1 atmosphere oxygen pressure. A steady increase of the p-HBA concentration is observed, while a maximum in the concen-
Fig. 2. Molar concentrations as a function of time in the autoxidation of p-cresol with CoAPO-11(1.0), 343 K, 6.4 g/l catalyst.

The oxidation of p-HBAalc to p-HBA was confirmed by experiments where 75:25 mixtures of p-cresol and p-HBAalc were oxidized. The yield of p-HBA in these experiments did not depend on the p-cresol-to-p-HBAalc ratio, confirming the consecutive oxidation of p-HBAalc to p-HBA at this low reaction temperature. A maximum in the p-hydroxy benzaldehyde concentration was also observed for reactions catalyzed by CoCl₂. No formation of p-hydroxy benzoic acid is observed. The concentration of p-hydroxy benzyl methylether increases rapidly at the beginning of the reaction, but flattens off after longer reaction times. The maximum yield of p-HBME is 10 percent.

In Fig. 3 it can be seen that the selectivity to p-HBA increases strongly at the beginning of the reaction, but levels off after a period of time. The initial strong increase is due to the oxidation of p-HBAalc to p-HBA. Another striking characteristic is the low oxygen selectivity. The low oxygen selectivity, defined as the number of p-cresol molecules converted to p-HBA, p-HBAalc and p-HBME, divided by the number of oxygen molecules used, is caused by oxidation of the solvent. Methanol...
is oxidized to formic acid, which reacts with sodium hydroxide to form water and sodium formate. Formation of the formic acid was verified with gas chromatography and elemental analysis. Oxidation of methanol is an undesired side reaction due to sodium hydroxide consumption.

The yield of p-HBA is defined as the product of selectivity to p-HBA and the conversion of p-cresol (both based on the molar concentration in the reaction mixture as determined with HPLC using an internal standard).

Sharma and Chandalia [28] fitted their experiments with a first-order reaction rate constant. In the present study experiments are fitted with first-order kinetics as well as with second order kinetics. Neither of the methods leads to satisfactory fits. Therefore, the activity of the catalyst is defined by the conversion after a certain period of time (1, 3, 20 hours).

3.1. Variation of the amount of catalyst

The cobalt-to-p-cresol ratio was varied by using CoAPOs with different weight percentages of cobalt in the crystals, or, by variation of the amount of catalyst at a constant substitution level. The activity as a function of the amount of catalyst is given in Fig. 4 and Fig. 5. The conversion of p-cresol after 3 hours as a function of the cobalt/p-cresol ratio (mg/g) is displayed in Fig. 4. After an initial steep increase in conversion with increasing amounts of CoCl₂ the conversion flattens off at maximum conversion levels of 70–75%. This indicates that in the system catalyzed by CoCl₂ only a small amount of cobalt is active in the oxidation of p-cresol at higher Co-to-p-cresol ratios. This can be reconciled with the low solubility of cobalt in the reaction medium. Higher cobalt concentrations lead to the precipitation of catalytically inactive cobalt hydroxide. AAS measurements of the filtered reaction mixture indicated that approximately 0.5–0.7 mg of cobalt was present per gram
of p-cresol. This corresponds with the bending point of the curve in Fig. 4. Although, the conversion by the CoAPO-5(1.0)s and CoAPO-11(1.0)s samples is lower at low Co/p-cresol ratios, the conversion reaches the same maximum level at higher Co/p-cresol ratios.

Fig. 5 displays the conversion after 3 hours (343 K) as a function of the cobalt-to-p-cresol ratio, using CoAPO-11 samples with different cobalt contents. The same behaviour is observed for all samples. The maximum conversion level is increased to approximately 85% due to the higher reaction temperature.

The selectivity for p-HBA shows the same trend as the p-cresol conversion and the oxygen selectivity upon increasing the cobalt-to-p-cresol ratio (Fig. 6 and Fig. 7). A strong increase of the selectivity up to a cobalt-to-p-cresol ratio of 0.7–0.8 is observed, which does not increase any further. Slight differences in maximum selectivity between the CoAPO-5, CoAPO-11 and CoCl₂ systems are observed, in favour of the CoCl₂ system.

Calcined samples as well as-synthesized samples were used as a catalyst. The differences in activity and selectivities between these two systems are only minor. There are a number of possible explanations for this observation. The template may be extracted from the molecular sieve by the solution, or only cobalt present on the external surface is active in the reaction. The third possibility is that dissolution of the molecular sieve occurs, resulting in homogeneous catalysis. The detection of template in the reaction mixture by GC analysis makes extraction of the template or dissolution of the catalyst more likely, but no discrimination can be made between these two.

The activity, selectivity for p-HBA and oxygen selectivity show the same dependence upon the cobalt-to-p-cresol ratio using CoCl₂ or CoAPO molecular sieves, suggesting a similar mechanism. The results obtained with the CoAPOs can be explained by assuming (partial) dissolution of the molecular sieve, resulting in
homogeneous catalysis. To decide whether heterogeneous catalysis contributes to the activity further experiments were performed.

3.2. Recycling of the catalyst

In order to check the stability of the catalysts a number of reaction cycles were carried out using the same catalyst. A mixture of p-cresol (9 g, 83.4 mmol), sodium hydroxide (9.9 g, 252 mmol), methanol (21.4 g, 670 mmol) and CoAPO-11 (1.0) (1.5 gram, 0.26 mmol Co) was heated at 328 K under 1 atmosphere of oxygen for 20 hours. No internal standard was added. The cobalt-to-p-cresol ratio amounted 1.7 mg/g. The sum of the normalized peak areas measured with HPLC was normalized at 100%. After completion of the reaction, the catalyst was separated from the reaction mixture via sedimentation, filtration and subsequent washing with methanol. The reaction was performed 10 times, corresponding to a TON of about 3200. In Fig. 8 the conversions and product distributions obtained in these experiments are plotted. It seems that the activity and selectivity are maintained at the initially high values, suggesting that a stable, heterogeneous catalyst is used.

In order to check the structure of the catalyst after reaction, X-ray powder diffraction patterns were recorded in various stages of the experiment. XRD measurements indicated that the catalyst retains the AlPO₄-11 structure. Atomic absorption spectroscopy revealed that approximately 10% of the total amount of cobalt was dissolved in the reaction mixture after one reaction cycle. The extra amount of cobalt dissolved decreased with the number of batches. The accuracies of these AAS measurements are limited because of the large amounts of sodium ions present in the solution, leading to a strong yellow colour of the flame of the spectrophotometer.

Since small amounts of cobalt are able to catalyse the reaction, reactions were followed in time using a lower cobalt-to-p-cresol ratio. Both CoAPO-5 and CoAPO-11 containing 1.0 wt.-% of cobalt were tested. Conversion after 5 hours was used to measure the activity, while the reaction continued for 22 hours. The
cobalt-to-p-cresol ratio, the catalyst and the resulting conversions (after 5 hours) are displayed in Fig. 9.

A decrease of the activity and selectivity is observed for the CoAPO-5(1.0) sample with increasing number of catalytic cycles, while it seems that the activity of the CoAPO-11(1.0) sample remains at a high level before it suddenly drops off. The CoAPO-11(1.0)s (the reaction with the lowest cobalt-to-p-cresol ratio) shows an immediate decrease of the activity after the first reaction cycle. The observed decrease of activity cannot be explained by a loss of catalyst during catalyst work up or sampling.

These contradictory results (Fig. 8 versus Fig. 9) can be explained using Table 1 and Figs. 4 and 5. The initially high cobalt-to-p-cresol ratio of 1.7 mg/g will yield the same conversion (after 3 hours) as a ratio of 0.5 mg/g. The same conversion after 20 hours can be obtained with an even smaller amount of cobalt (Table 1), indicating that the conversion after 20 hours is not an accurate measure of the catalyst stability. A conversion of 90% can be obtained with a cobalt-to-p-cresol ratio of 0.15, more than 10 times less than the initial ratio. On the contrary, a decrease of the initial cobalt-to-p-cresol ratio will immediately result in a decreased conversion after 3 hours, if some cobalt is lost during catalyst recycling. It is clear that cobalt originating from dissolved CoAPO molecular sieves, contrib-

Table 1
Conversion of p-cresol (after 3 and 20 h) using CoAPO-11(1.0)s as a function of the cobalt-to-p-cresol ratio; 338 K

<table>
<thead>
<tr>
<th>Cobalt/p-cresol (mg/g)</th>
<th>Conversion (3 h)</th>
<th>Conversion (20 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
<td>16</td>
</tr>
<tr>
<td>0.04</td>
<td>20</td>
<td>61</td>
</tr>
<tr>
<td>0.08</td>
<td>41</td>
<td>85</td>
</tr>
<tr>
<td>0.13</td>
<td>36</td>
<td>91</td>
</tr>
<tr>
<td>0.210</td>
<td>65</td>
<td>97</td>
</tr>
<tr>
<td>0.42</td>
<td>69</td>
<td>96</td>
</tr>
</tbody>
</table>
Table 2
Conversion of p-cresol after 1, 3 and 20 h; cobalt/p-cresol 0.42 mg/g, 333 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion(^a) (1 h)</th>
<th>Conversion(^a) (3 h)</th>
<th>Conversion(^a) (20 h)</th>
<th>Presence of catalyst(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAPO-11(1.0)s</td>
<td>25</td>
<td>41</td>
<td>81</td>
<td>1 h</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>22</td>
<td>38</td>
<td>88</td>
<td>Continuous</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>15</td>
<td>26</td>
<td>-</td>
<td>1 h</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>22</td>
<td>38</td>
<td>-</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

\(^a\) Conversion of p-cresol as measured with HPLC after 1, 3 and 20 h.  
\(^b\) Time during which the catalyst was present in the reaction mixture.

utes to the observed catalytic activity. The XRD data suggest that no specific leaching of the cobalt occurs, but rather dissolution of the AlPO structure.

Whether the observed catalytic activity stems from homogeneous catalysis alone was checked in separate experiments. The CoAPO samples were mixed with the reactant solution under exclusion of oxygen for 1 hour. Using this procedure it was possible to prevent the autoxidation and to filter off the catalyst, without any salts (sodium formate). After filtering off the catalysts, the cobalt content of the solution was estimated with AAS. The autoxidation of the solution without the solid catalyst was performed and compared with a reaction containing the CoAPO samples. The results are summarized in Table 2 and Table 3.

It is clear from Table 2 that the reaction rate of the reaction mixture without the catalyst is comparable to the reaction rate of systems where the CoAPO was present for the entire time. Either cobalt is just acting as an initiator, which is in contradiction with the reaction mechanism, or dispersion of the CoAPO for 1 hour results in a sufficiently high cobalt concentration to yield comparable reaction rates. The latter seems more likely in view of the AAS results (Table 3).

Leaving the first measurement out of consideration, it is clear that the cobalt-to-p-cresol ratio in the solution varies between 0.05 and 0.20 mg/g. Although this ratio is lower than 0.5 mg/g, necessary to obtain a maximal reaction rate (using CoCl\(_2\)), the reaction rate of CoAPO-11(1.0)s reaches the maximum rate. It is, however, unlikely that cobalt of the CoAPO molecular sieve contributes to the

Table 3
Cobalt concentration in reactant solution, measured with AAS

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cobalt/p-cresol (mg/g)</th>
<th>Cobalt/p-cresol (mg/g)</th>
<th>Percentage dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(initial)(^a)</td>
<td>(solution)(^b)</td>
<td></td>
</tr>
<tr>
<td>CoAPO-11(1.0)s</td>
<td>0.42</td>
<td>0.30</td>
<td>72</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>0.83</td>
<td>0.11</td>
<td>13</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>1.67</td>
<td>0.11</td>
<td>6</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>3.33</td>
<td>0.18</td>
<td>5</td>
</tr>
<tr>
<td>CoAPO-5(1.0)</td>
<td>0.83</td>
<td>0.05</td>
<td>6</td>
</tr>
<tr>
<td>CoAPO-11(1.0)</td>
<td>0.42</td>
<td>0.05</td>
<td>11</td>
</tr>
</tbody>
</table>

\(^a\) The initial ratio of cobalt (in the molecular sieve) to p-cresol (reaction mixture).  
\(^b\) The ratio of cobalt-to-p-cresol in the reaction mixture at the end of the reaction.
conversion of p-cresol, since filtering of the catalyst does not influence the reaction rate (Table 2). Probably, some hydroxyl bridged cobalt species are present in the solution starting with CoCl₂, which contribute to the AAS measurement, but not to the catalytic activity. The last two samples of Table 3 show a lower reaction rate, so the differences in catalytic activity appear to correlate with the dissolution speed of the CoAPO molecular sieves.

4. Conclusions

p-Cresol can be oxidized to p-HBA using CoCl₂ or with 'heterogeneous' CoAPO-5 and CoAPO-11 catalysts in methanolic sodium hydroxide solution at 313–353 K. The yield of p-HBA is 70–75% at approximately 95% conversion for the CoAPO systems and 80% in the case of CoCl₂, by-products being p-hydroxy benzylalcohol (p-HBA; 5%) and p-hydroxy benzyl methylether (p-HBME; 10%). Oxidation of p-HBAc to p-HBA is observed for all three catalyst systems at these low reaction temperatures. The oxygen selectivity, defined as the moles of p-cresol converted per mole of oxygen consumed, is remarkably low (maximally 60%). This is due to the oxidation of the solvent (methanol) to formaldehyde and formic acid. This leads to a consumption of sodium hydroxide.

The reaction rate initially increases with increasing cobalt-to-p-cresol ratios. A maximum reaction rate is observed at a cobalt/p-cresol ratio of 0.6–0.7 mg/g, independent of the catalyst source. The oxygen selectivity and selectivity to p-HBA show the same dependence upon the cobalt/p-cresol ratio for all three systems indicating a comparable reaction mechanism.

Below a NaOH/p-cresol ratio of 1 no reaction occurs. A maximum reaction rate is observed at a NaOH over p-cresol ratio of 3–4. Recycling of the catalysts at sufficiently low cobalt over p-cresol ratios indicate that the catalyst is not stable under reaction conditions, but that the observed activity originates from dissolved cobalt. Dissolution of cobalt from the 'heterogeneous' catalysts is demonstrated by AAS and by the catalytic activity of the reaction solution. It is therefore concluded that the major contribution in all autoxidations of p-cresol studied here, originate from catalytically active cobalt ions in solution. The system should henceforth be considered as homogeneous rather than heterogeneous.

References