Vapor-phase selective o-alkylation of catechol with methanol over lanthanum phosphate and its modified catalysts with Ti and Cs

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A B S T R A C T

Vapor-phase o-alkylation of catechol with methanol over lanthanum phosphate catalyst is studied. Also, the effects of the reaction temperature and the weight hourly space velocity (WHSV) on the catalyst performance were evaluated. Expectedly, the catechol conversion and the guaiacol selectivity were inversely correlated as the secondary reactions proceed further at higher guaiacol concentrations. Catalyst characterization indicated that the medium acidic sites played the major role in the conversion of catechol. Addition of titanium into lanthanum phosphate (La, Ti, PO₄, x varies from 0.0 to 0.5) increased the surface area and acidity of the catalyst whereas a dramatic decline in the number of acidic sites, BET surface area was observed when catalyst was impregnated with up to 10% cesium. The catechol conversion first increased by addition of small quantities of titanium after which it substantially decreased. However, the catalyst selectivity to guaiacol monotonically decreased by increasing the titanium loading on the catalyst. The highest guaiacol yield was obtained using La₀.₄Ti₀.₆PO₄ where a maximum in catalyst acidity per specific surface area was also observed (i.e. 0.336 µmol g⁻¹). Moreover, a linear relation between the numbers of catalyst acid sites per surface area and the catechol conversion was observed.

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1. Introduction

Recently, there has been a high demand to reduce the negative environmental impacts of chemical processes. High selectivity for the production of a desired product, and minimizing the side-products, has become increasingly significant, both for economical (less separation steps) and product quality purposes.

Heterogeneous catalysis can be utilized to meet those requirements because it allows the replacement of stoichiometric reactants and may improve the reaction pathway leading to the formation of the desired product. The alkylation of phenol and polyhydroxybenzenes such as catechol on the oxygen atom (o-alkylation) for the synthesis of alkylarylethers is an example of an industrially important reaction that needs a proper alternative in order to produce higher-quality products [1].

The desired product in catechol alkylation is guaiacol. This product is produced when the reaction goes to o-alkylation pathway rather than c-alkylation. If o-alkylation continues further, another product which is veratrole may be produced. Since the separation of guaiacol and veratrole is an expensive process, o-alkylation should be controlled accurately. c-Alkylation products are 3- and 4-methyl catechol.

Guaiacol is an essential synthetic intermediate in fine chemical production. It is widely used for production of flavoring additives, fragrances, agricultural chemicals, and pharmaceuticals [2]. Traditionally, guaiacol is synthesized by alkylation of catechol with corrosive reagents like dimethyl sulfate and dimethyl iodide in the presence of stoichiometric quantities of sodium hydroxide as a homogeneous catalyst. Recently, vapor-phase alkylation of catechol for the synthesis of guaiacol in the presence of heterogeneous catalysts has received more attention [3].

The general alkylation agents include dimethyl carbonate (DMC) and methanol. A few catalysts such as Al₂O₃ [4], alkaline Al₂O₃-based [5–7], and Mg–Al hydrotalcite [8] have been employed for the reaction using DMC as the alkylation agent. In comparison with DMC, methanol is considered as the most suitable agent for practical applications due to its lower cost. Several heterogeneous catalysts have been tested in the vapor-phase alkylation of catechol with methanol, including BPO [1], AlPO₄ [9], Al₄TiPO₄ and Al₄TiSiPO₄ [10], alkaline loaded silica [11], ZnCl₂ on Al₂O₃ [12], ammonium metatungstate impregnated SiO₂, TiO₂ and Al₂O₃ [13], and sulphate-modified zirconia [14].

Govic et al. [15] found that rare-earth phosphates including lanthanum phosphate could be used for selective o-alkylation of phenols including catechol.

Some authors proposed mechanisms based on the contribution of acid-base sites for some catalysts such as BPO, AlPO₄, Al₄TiPO₄, Al₄TiSiPO₄, and ammonium metatungstate impregnated SiO₂, TiO₂, and Al₂O₃.

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Some others proposed acidic mechanism for ZnCl₂ on Al₂O₃, sulphate-modified zirconia, alkaline loaded silica and rare earth phosphates specially 3SmPO₄.

Thus, there is no generally accepted mechanism. However, most of researches show that catechol alkylation needs mild acidity as reported by several authors [1,9,10,13,14].

In this research, we show that acidic sites are responsible for o-alkylation of catechol over LaPO₄. Addition of cesium and titanium can considerably affect the acidic property of the catalysts and their performance consequently.

2. Experimental

2.1. Catalyst preparation

Lanthanum phosphate was synthesized by the reaction of lanthanum nitrate and phosphoric acid. Lanthanum nitrate dissolved in distilled water and phosphoric acid was added to the mixture drop wise (La/P = 1 mol). Lanthanum phosphate precipitated suddenly. The mixture was stirred using a magnetic stirrer for 6 h at 96 °C. The precipitated gel was filtered and washed with distilled water several times to assure that no excess acid or nitrate remained. The filtrate was dried overnight at 96 °C and calcined at 400 °C for 2 h.

Lanthanum phosphates with various amounts of cesium were prepared by impregnation method. The proper amount of cesium nitrate was dissolved in distilled water and cesium-lanthanum phosphate was prepared by impregnation method. Catalysts were dried overnight at 130 °C and calcined at 400 °C for 2 h.

The titanium containing lanthanum phosphate catalysts were prepared by ammonia gelation method. The proper amount of lanthanum nitrate was dissolved in distilled water. Lanthanum hydroxide was precipitated by addition of ammonia solution. The addition of ammonia was continued until the pH of the solution became 10. Afterwards, the tetraisopropyl orthotitanate was added into the slurry while stirring vigorously. Phosphoric acid was then added to the mixture gradually. The final mixture was stirred at 96 °C for about 6 h. The white powder was filtered and washed with distilled water several times until the pH of the aqueous phase in filtration step became 7. The powder was dried overnight at 130 °C and calcined at 600 °C for 2 h. By this method, we prepared the catalyst with a general formula of La₁₋ₓTiₓP (x = 0.0, 0.10, 0.23, and 0.50).

2.2. Catalyst characterization

X-ray diffraction powder (XRD) was performed with a Philips diffractometer operated at 50 kV and 150 mA using nickel-filtered Cu Kα radiation.

BET surface area measurements and temperature-programmed desorption (TPD) experiments were accomplished using a CHEMBET 3000 (Quantachrome). Before the experiment, the samples were pretreated under flow of pure nitrogen at 400 °C for about 1.5 h.

For the TPD experiments pyridine was used as the probe molecule. In a standard procedure, 100 mg of fresh sample was used. The sample was saturated with the probe molecule by several consecutive injections. Following the saturation, the system was purged with He for one hour. The sample was heated at the rate of 10 °C/min in a He flow of 17 spm/min. Concentration of the desorbed pyridine was monitored.

Lanthanum and titanium content of the catalysts were measured by an inductivity coupled plasma apparatus, a Varian 150Ax Laboratory Turbo.

![Fig. 1. XRD pattern of lanthanum phosphates. (a) LaPO₄, (b) 1% Cs-LaPO₄, and (c) 3% Cs-LaPO₄.](image)

2.3. Catalytic tests

The vapor phase o-alkylation of catechol with methanol was carried out in a fixed bed continuous down-flow reactor at atmospheric pressure. Temperature of the reaction was controlled by a PID temperature controller. Prior to the reaction, the catalyst (0.8 g, 40–60 mesh) was activated in the glass-tube reactor (i.d. = 10 mm and length = 25 cm) at 500 °C for 1 h in a nitrogen flow. A pre-mixed catechol–methanol mixture was then fed from the top of the reactor by means of a Sage-Instrument syringe pump along with Ar (15 ml/min). The products were cooled in an ice-water bath condenser, collected in a receiver and analyzed in a gas chromatograph (Varian 3800; capillary column DB-5, 50 m × 0.2 mm; FID detector).

The reaction conditions were as follows: catechol/methanol = 1/5 (mole ratio), reaction temperature = 255–300 °C, weight hourly space velocity (WHSV) = 2.2 h⁻¹.

3. Results and discussion

3.1. Lanthanum phosphate performance

The XRD patterns of LaPO₄ and Cs-LaPO₄ catalysts are presented in Fig. 1. The sample has three peaks covering the 2θ range of 28–32 and 40–45. This figure indicates that the crystalline lanthanum phosphate forms clearly with monoclinic phase.

In order to measure the molar ratio of La to P in LaPO₄, ICP measurements were performed. The ICP results revealed that this ratio was 0.98. The measured concentrations were generally comparable with the nominal amounts.

The BET surface area measurement of LaPO₄ indicated that the surface area of the lanthanum phosphate catalyst was fairly high (94 m²/g).

Alkylation of catechol with methanol over lanthanum phosphate in the gas phase shows promising results. The reaction over this catalyst, as seen in Table 1, proceeds via the o-alkylation pathway. Catechol conversion reaches to 67.1% and 90.9% of catechol converts to guaiacol. Small amounts of veratrole and c-alkylation products (3 and 4 methyl catechol) were detected.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Catechol conversion</th>
<th>Selectivity</th>
<th>Guaiacol</th>
<th>Veratrole</th>
<th>c-Alkylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>255</td>
<td>67.1</td>
<td>90.9</td>
<td>6.5</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>75.2</td>
<td>79.9</td>
<td>14.7</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>84.3</td>
<td>63.6</td>
<td>25.6</td>
<td>10.8</td>
<td></td>
</tr>
</tbody>
</table>

Reaction condition: catechol/methanol = 1/5 mol; WHSV = 2.2 h⁻¹.
As is evident the lanthanum phosphate performance is affected by temperature. The catechol conversion improves as the temperature increases. In particular, it increases from 61.7% at 255 °C to 84.3% at 300 °C. However, selectivity in o-alkylation products decreases with an increase in the temperature. As o-alkylation decrease, c-alkylation increases gradually. In o-alkylation products, guaiacol replaces by veratrole as the temperature rises. The veratrole selectivity also improves at higher temperatures, e.g. it reaches to 25.6% at 300 °C. These observations are consistent with those reported by Gilbert [15] for the lanthanum phosphate catalyst. The performance of lanthanum phosphate is also affected by WHSV as is shown in Table 2. The best result was achieved when WHSV was 2.2 h⁻¹. At this velocity, catechol conversion is 67.1% which corresponds to the maximum guaiacol production of 90.7%. A small amount of c-alkylation product, i.e. 2.6%, was detected.

Raising the feed velocity results in an increase in WHSV (catalyst weight is constant) which is followed by the gradual reduction in the catechol conversion. Particularly, as the WHSV changes from 2.2 to 5.2 h⁻¹, catechol conversion drops from 67.1 to 32.5%, respectively. Selectivity to c- and o-alkylation does not change by variation in WHSV. These results show that the value of WHSV at 2.2 h⁻¹ is the best velocity for the catechol conversion.

The temperature desorption profiles of pyridine on the LaPO₄ and 3% Cs-LaPO₄ samples are presented in Fig. 2. The lanthanum phosphate exhibited one sharp pyridine desorption peak centered at about 200 °C and one very broad peak around 400 °C. This result indicates that the sample possess mainly acid sites.

Deactivation of LaPO₄ during the course of catechol conversion was investigated. As shown in Fig. 3, the catechol conversion decreases as the reaction proceeds with the time on stream. After 10 h from the start of the reaction, catechol conversion decreases from 69.1 to 48.9%.

Despite the conversion, guaiacol selectivity was not affected. Moreover, selectivity to c- and o-alkylation product did not change significantly even after 10 h. The color of the two catalyst samples after 1 and 10 h exposure to the reaction showed that the sample exposed longer to the reaction was visibly darker. This observation

<table>
<thead>
<tr>
<th>WHSV (h⁻¹)</th>
<th>Catechol conversion</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Guaiacol</td>
<td>Veratrole</td>
</tr>
<tr>
<td>2.2</td>
<td>67.1</td>
<td>90.7</td>
</tr>
<tr>
<td>3.6</td>
<td>59.9</td>
<td>89.4</td>
</tr>
<tr>
<td>4.4</td>
<td>45.3</td>
<td>91.1</td>
</tr>
<tr>
<td>5.2</td>
<td>32.5</td>
<td>90.2</td>
</tr>
</tbody>
</table>

Reaction condition: LaPO₄ catalyst, catechol/methanol = 1/5 mol.

Table 2: Catechol conversion versus WHSV at 255 °C.

![Pyridine TPD results](a) 3% Cs-LaPO₄ and (b) LaPO₄.

![Catechol deactivation results during first 10 h over LaPO₄: (●) guaiacol selectivity and (■) catechol conversion. Reaction condition: catechol/methanol = 1/5 mol; WHSV = 2.2 h⁻¹; reaction temperature = 255 °C.](image)

3.2 Cs impregnated on lanthanum phosphate catalysts performance

The XRD patterns of various amounts of Cs over LaPO₄ catalysts are presented in Fig. 1. Crystalline lanthanum phosphate in monoclinic phase can be observed clearly in the Cs free sample. When cesium is impregnated, the peak intensities of the lanthanum phosphate decrease dramatically. By increasing the amount of cesium up to 3%, the peak intensities of the catalysts reduce even further. The sample exhibits only three minor peaks indicating the transformation of crystalline form into amorphous one.

BET surface areas of lanthanum phosphate with various amount of Cs are shown in Table 3. As may be seen, the addition of cesium over is responsible for significant reduction in surface area. The cesium free sample has a high surface area of 94.1 m²/g.

Addition of 3% cesium has significantly affected the surface area and lowers it to 25.3 m²/g, which is nearly a quarter of the value of that for the cesium free sample. The sample containing 10% cesium has the lowest surface area than other Cs containing catalysts.

As is observed in Fig. 2, addition of cesium into the lanthanum phosphate catalyst results in a significant decrease both in density and strength of acid sites.

Addition of various amounts of cesium (1, 3 and 10 wt%) to the lanthanum phosphate resulted in reduction of catechol conversion, keeping the selectivity unaffected (see Table 4). Selectivity to c- and o-alkylation does not change by addition of cesium. These results reveal that addition of various amounts of cesium into lanthanum phosphate influence the structure, surface area and acidity of the catalysts. It seems that cesium is mostly precipitated in the acidic sites. Thus, this observation shows to a large extent the correspondence between the decrease in the density and strength

<table>
<thead>
<tr>
<th>Cs% on LaPO₄</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>94.1</td>
</tr>
<tr>
<td>1</td>
<td>85.2</td>
</tr>
<tr>
<td>3</td>
<td>25.3</td>
</tr>
<tr>
<td>10</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table 3: BET surface area of various amount of Cs loaded on LaPO₄.
Table 4
Effect of Cs addition to LaPO₄ on catechol conversion.

<table>
<thead>
<tr>
<th>Cs% on LaPO₄</th>
<th>Catechol conversion</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Guaiacol</td>
<td>Veratrole</td>
</tr>
<tr>
<td>0</td>
<td>67.1</td>
<td>90.7</td>
</tr>
<tr>
<td>1</td>
<td>61.5</td>
<td>89.4</td>
</tr>
<tr>
<td>3</td>
<td>20.8</td>
<td>91.1</td>
</tr>
<tr>
<td>10</td>
<td>14.8</td>
<td>90.2</td>
</tr>
</tbody>
</table>

Reaction condition: catechol/methanol = 1/5 mol; WHSV = 2.2 h⁻¹; reaction temperature = 255 °C.

Fig. 4. XRD patterns of the La₁₋ₓTiₓP catalysts: (a) x = 0.0, (b) 0.1, (c) 0.23, and (d) 0.5.

of acid sites with suppression of the activity of the catalyst for catechol alkylation.

3.3. La–Ti phosphates performance

The XRD patterns of La₁₋ₓTiₓP catalysts are presented in Fig. 4. Crystalline lanthanum phosphate in monoclinic phase may be observed clearly in the titanium-free sample.

When titanium is introduced, the peak intensities of lanthanum phosphate decrease dramatically. By increasing the amount of titanium, the peak intensities of the catalysts reduce even further. The sample with Ti/La ratio of 1 exhibits only three very broad peaks covering the 2θ range of 28–32 and 40–45. These peaks indicate that the sample is transformed from a highly crystalline form into a less s crystalline compound. These results suggest that addition of different amounts of titanium into lanthanum phosphate can considerably affect the structure of the catalyst.

The results of the BET surface area measurement of various La₁₋ₓTiₓP catalysts are reported in Table 5. It can be observed that, the surface area of the titanium-free sample is high. Addition of titanium, while x varies from 0.1 to 0.5, leads to an increase in the BET surface area. For x = 0.5, the highest surface area is achieved. In the last case, BET surface area exceeds more than twice of the Ti-free sample, i.e. about 216 m²/g.

In order to check the amount of titanium in the La₁₋ₓTiₓP samples and comparing it with the nominal amounts, ICP measurements were performed. The ICP results revealed that the measured amount of titanium within the samples was comparable with nominal amounts within about 97% accuracy.

Table 5
BET surface area of La₁₋ₓTiₓP catalysts.

<table>
<thead>
<tr>
<th>x</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>94.4</td>
</tr>
<tr>
<td>0.10</td>
<td>143.7</td>
</tr>
<tr>
<td>0.23</td>
<td>153.0</td>
</tr>
<tr>
<td>0.50</td>
<td>216.2</td>
</tr>
</tbody>
</table>

Table 6
Effect of different amount of Ti in La₁₋ₓTiₓP performance.

<table>
<thead>
<tr>
<th>x</th>
<th>Catechol conversion</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Guaiacol</td>
<td>Veratrole</td>
</tr>
<tr>
<td>0.00</td>
<td>67.5</td>
<td>90.3</td>
</tr>
<tr>
<td>0.10</td>
<td>81.4</td>
<td>85.4</td>
</tr>
<tr>
<td>0.23</td>
<td>61.3</td>
<td>79.1</td>
</tr>
<tr>
<td>0.50</td>
<td>54.7</td>
<td>70.8</td>
</tr>
</tbody>
</table>

Reaction condition: catechol/methanol = 1/5 mol; WHSV = 2.2 h⁻¹; reaction temperature = 255 °C.

The pyridine TPD profiles of the catalysts are presented in Fig. 5. All the samples exhibit one sharp pyridine desorption peak centered at about 200 °C. The presence of different amounts of titanium in the catalysts does not affect the first desorption peak position. However, by introducing titanium, a broad peak appears in right shoulder of the first peak. It seems that second desorption peak becomes more detectable as titanium content of the samples increases.

The first larger desorption peak at 200 °C represents the weak acidic sites and the second smaller broad peak at higher temperatures reveals intermediate and strong acidic sites; the same as Takita [16] reported elsewhere.

These observations indicate that the presence of titanium does not affect the strength of weak acid sites of the catalysts. However, appearance of the second peak especially for the sample with x = 0.5, indicates that the density of stronger acid sites increases when titanium is introduced into the lanthanum phosphate structure.

A remarkably high o-alkylation selectivity of 90.3% is obtained over titanium free catalysts with relatively high catechol conversion. The activity of the catalysts considerably improves by addition of small amounts of titanium. The catalytic activity enhances with the increase in titanium content, and reaches a maximum of 81.4% catechol conversion at x = 0.1. However, it falls gradually upon further addition of titanium. The guaiacol selectivity decreases when the added titanium is within the range just mentioned. At x = 0.5, catechol conversion drops to 54.7%, but c- and o-alkylation selectivity (veratrole) reaches the highest values. The best results are obtained at x = 0.1. Table 6 shows the performance of La₁₋ₓTiₓP catalysts in catechol alkylation.

As it can be seen in the TPD results presented in Fig. 5, strong acid sites appear in the catalysts when titanium content (x) increases. Thus, it may be concluded that the stronger acid sites in the catalysts are responsible for formation of larger amount of veratrole and c-alkylation products.
Table 7
Various amount of titanium on LaPO₄ versus number of acidity per surface area.

<table>
<thead>
<tr>
<th>x</th>
<th>Catechol conversion</th>
<th>BET (m²/g)</th>
<th>Acidity (µmol)</th>
<th>Acidity/BET (µmol g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>67.5</td>
<td>94.42</td>
<td>28.5</td>
<td>0.302</td>
</tr>
<tr>
<td>0.10</td>
<td>81.4</td>
<td>143.71</td>
<td>48.4</td>
<td>0.336</td>
</tr>
<tr>
<td>0.23</td>
<td>61.3</td>
<td>153.02</td>
<td>42.7</td>
<td>0.279</td>
</tr>
<tr>
<td>0.50</td>
<td>54.7</td>
<td>216.21</td>
<td>57.6</td>
<td>0.266</td>
</tr>
</tbody>
</table>

Table 8
Effect of temperature in La₀.₉Ti₀.₁P performance.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Catechol conversion</th>
<th>Selectivity</th>
<th>Guaiacol</th>
<th>Veratrole</th>
<th>C-alkylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>255</td>
<td>81.4</td>
<td>89.9</td>
<td>6.7</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>87.9</td>
<td>76.2</td>
<td>14.9</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>93.2</td>
<td>65.3</td>
<td>20.0</td>
<td>14.7</td>
<td></td>
</tr>
</tbody>
</table>

Reaction condition: catechol/methanol = 1/5 mol; WHSV = 2.2 h⁻¹

Catechol conversion does not show a specific trend with total acidity as x varies in the La₁₋ₓTiₓP samples. It seems that total acidity of each sample may have been significantly affected by the change in BET surface area. Looking at the results reported in Table 7, which is obtained by combining the results presented in Tables 5 and 6 and in Fig. 5, one could find analogous similar pattern between two sets of data, i.e., catechol conversion versus x and catechol conversion versus total acidity per unit BET surface area (acid site density).

Plotting catechol conversion versus acidity per unit BET surface area suggests an obvious linear relationship between these two parameters. This linear relationship shows that availability of acidic sites is absolutely significant in the reaction. As the surface area increases from 94 to 143 m²/g, the total acidity rises from 28 to 48 suggesting that acid site density is enhanced by introducing titanium into LaPO₄ structure. When more titanium is introduced (e.g., x = 0.23), the acid site density of the catalyst is reduced in spite of the fact that the surface area has been increased. The same pattern is repeated at x = 0.50 since acid sites are not formed adequately, emphasizing that the adsorption of catechol and methanol on the acid sites speeds up the reaction.

When larger numbers of acid sites per unit surface are present, more conversion is achieved. It can be concluded that the adsorbed methanol is reacts more easily with the absorbed catechol when more acid sites are available per unit surface of catalyst. In other words the catalyst with larger acid site density facilitates the reaction and more catechol is converted into the products. The product distribution depends highly on the type and strength of acid sites as discussed previously.

The effect of temperature on La₀.₉Ti₀.₁P catalyst is presented in Table 8. As demonstrated, again as the temperature increases the following results may be observed: growth in catechol conversion, drop in selectivity to guaiacol and o-alkylation, and increase in production of veratrole and c-alkylation products.

It may be concluded that at higher temperatures, more activated molecules are available at the catalyst surface and more catechol conversion is achieved. Further amounts of guaiacol are converted to veratrole at higher temperatures.

4. Conclusion

This study revealed that lanthanum phosphate is an active catalyst for the vapor phase o-alkylation of catechol. This catalyst has weak and medium acid sites, which are responsible for catechol conversion.

Addition of cesium into lanthanum phosphate can considerably degrade the textural and surface acidic properties of the catalysts. More cesium content of the lanthanum phosphate catalyst results in the suppression of the catalytic performance of the catalyst.

Addition of titanium can considerably affect textural, BET surface area and acidic properties of the catalysts. The best result is obtained when titanium content (x) in La₁₋ₓTiₓP becomes 0.1. Pyridine TPD, BET surface area and La₁₋ₓTiₓP catalytic tests showed that there was a linear relationship between the catechol conversion and the density of acid sites. These observations revealed that on the catalysts with larger density of acid sites, the reaction rate increases and more catechol can be converted to the products.

References