Introduction

The alkylation of phenol with alcohols and olefins is an important process used in industrial scale. Alkylated phenols are widely used as additives in gasoline, lubricants and surfactants. Both homogeneous and heterogeneous catalysts have been applied to the phenol alkylation. Homogenous acid catalysts such as HF, H$_2$SO$_4$, AlCl$_3$, or BF$_3$ are commonly used in Friedel-Crafts reaction, but the toxic aqueous waste resulting from catalyst remains problematic. On the other hand, utilization of the eco-friendly heterogeneous catalysts such as macroporous cation-exchanged resins (Amberlyst-15), zeolites, SAPO-11, mesoporous materials have advanced in recent years.

Conventionally, the alkylation of phenol is carried out by the reaction of phenol with 1-dodecene in presence of cation-exchange resin. Although cation-exchange resin catalysts are environmentally friendly, they have the disadvantage of low stability at high temperatures. Therefore, considerable efforts have been made for the development of suitable heterogeneous catalysts. The catalysts reported for this reaction include zeolites and others solid acids like zirconia, but its poor stability limits its applicability.

Alkylation of phenol has an additional complication because of the possibility of the alkyl attacking to the phenolic oxygen (O-alkylation) that leads to an ether formation beside desirable alkylations at the aromatic ring (C-alkylation). Information about the use of niobium compounds for the alkylation of phenol with allylic alcohol is almost nonexistent in the available literature.

Continuing our interest in the catalytic activity of niobium compounds in the Friedel-Crafts reaction, we have investigated the alkylation reaction of anisole with 1-dodecene, 1-octene, 2-octanol and 1-octen-3-ol and in the reaction of phenol with 1-octen-3-ol. Best results were achieved in the alkylation of anisole and phenol with 1-octen-3-ol that produced mainly monoalkylate products. In the reaction with phenol the major products formed were octenylphenols (C-alkylation) and phenyl-octenyl ether (O-alkylates). The reaction favors the formation of C-alkylates over O-alkylates.

**Keywords:** alkylation, niobium phosphate, acid catalysis, phenol
temperature was kept at 110 °C. The molar ratio anisole/alkylating agent was 15/1 and for phenol/alcohol was 10/1 (150 mmol, 16.2 g anisole/10 mmol, alkylation agent; 200 mmol phenol, 18.8 g / 20 mmol, 2.56 g allylic alcohol) and the catalyst amount was 250 mg. The catalyst, niobium phosphate from CBMM, Companhia Brasileira de Metalurgia e Mineração, was calcined at 400 °C or 500 °C in an oven, under static air for 2 h before use.

Samples of the reaction mixture were periodically withdrawn and analyzed by high-resolution gas chromatography (n-dodecane was used as internal standard).

**Analytical procedure**

The variations of the substrate, alkylating agents and product contents were followed using a VARIAN model 3800 gas-chromatograph equipped with a hydrogen flame ionization detector system and capillary column VA-5, 30 m, 0.32 mm ID, 1µm df. The temperature was programmed from 80 °C to 280 °C at 20 °C min⁻¹ with H₂, 2 mL min⁻¹, as carrier gas.

The identification of the products obtained previously was carried out by gas-chromatography mass spectrometry analysis (CG-MS) on a HP 6890, utilizing a DB-5 (30m) fused silica column in the same temperature conditions with He as carrier gas.

**Results and Discussion**

The commercial niobium phosphate present reasonable value for the surface area, 138 m² g⁻¹. The data obtained by XRD analysis showed that the niobium phosphate used in this work were amorphous. Py-FTIR characterization of these catalyst indicated the presence of Brønsted (BAS) and Lewis acid sites (LAS) NbP-Com has almost the same amount of total Brønsted and Lewis sites, 163.3 and 160 µmol g⁻¹ respectively as shown in previous works. The catalytic activity of niobium phosphate was evaluated in the reaction of anisole with 1-dodecene, 1-octene, and phenol (entry 3). Ours results were superior to those present in the literature. The catalytic properties of niobium oxide were evaluated in the alkylation reaction of dodecene with benzene. At 80 °C and a benzene /dodecene molar ratio 10/1 the conversion was 1.2% after 30 min.¹⁸

The alkylation of anisole with 1-octene and 1-dodecene over niobium phosphate resulted mainly in the formation of monoalkylated products (Table 2, entry 1 and 2).

**Table 1. Alkylation of anisole and phenol catalyzed by niobium phosphate**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkylation Agent</th>
<th>Aromatic Compounds</th>
<th>time / h</th>
<th>Conversion / (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Dodecene⁴</td>
<td></td>
<td>4</td>
<td>65</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>1-Octene</td>
<td>Anisole</td>
<td>4</td>
<td>22</td>
<td>This work</td>
</tr>
<tr>
<td>3</td>
<td>2-octanol⁰</td>
<td></td>
<td>7</td>
<td>0</td>
<td>This work</td>
</tr>
<tr>
<td>4</td>
<td>1-octen-3-ol</td>
<td></td>
<td>4</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>1-octen-3-ol</td>
<td>Phenol</td>
<td>2</td>
<td>100</td>
<td>This work</td>
</tr>
</tbody>
</table>

²molar ratio anisole/1-dodecene was 15/1, 250 mg catalysts, reflux temperature; ³molar ratio anisole/1-octene was 10/1, 250 mg catalysts, 110 °C; ⁴reference 15; ⁵molar ratio phenol/1-octen-3-ol was 10/1, 250 mg catalyst, 110 °C.

The catalytic activity of niobium phosphate is presented in Figure 1.

**Table 2. Products distribution in alkylation reaction**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aromatic Compound</th>
<th>Alkylation Agent</th>
<th>time / h</th>
<th>Monoalkylation / (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>1-octene</td>
<td>4</td>
<td>100°</td>
</tr>
<tr>
<td>2</td>
<td>Anisole</td>
<td>1-dodecene</td>
<td>7</td>
<td>65°</td>
</tr>
<tr>
<td>3</td>
<td>1-octen-3-ol</td>
<td></td>
<td>4</td>
<td>86°</td>
</tr>
</tbody>
</table>

⁰76% of the 2-octyl-anisole; ⁴40% of the 2-dodecyl-anisole; ³reference 13, 80% 1-phenyl-(o,p-methoxy)-2-octene. Conditions: (1) molar ratio anisole/1-octene was 10/1, 250 mg catalysts, 110 °C; (2) molar ratio anisole/1-dodecene was 15/1, 250 mg catalysts, reflux temperature; (3) as reference 15.

1-Dodecene and 1-octene undergoes double bond shift isomerization¹⁹ and anisole alkylation in presence of catalyst. The different isomers of dodecene and octene react with anisole to form isomeric mixture of dodecyl and octyl anisole. The liquid phase alkylation with 1-octen-3-ol producing mainly 1-phenyl-(o,p-methoxy)-2-octene.

Alcohols are preferable alkylating agents rather than alkyl halides and olefins because hydrogen halides are not co-produced and no polymerization takes place. Using allylic alcohols allows formation of 1-aryl-2-alkenes.¹⁵,²⁰

This process was shown to be of interest for producing biodegradable alkyl aromatic compounds.

After choosing allylic alcohol as the best alkylating agent we studied the alkylation of phenol aiming to produce alkylation products (Scheme 1).

The conversion of 1-octen-3-ol as function of time for the alkylation of anisole and phenol over niobium phosphate is presented in Figure 1.
The reaction between phenol and 1-octen-3-ol produced mainly carbon alkylated (C-alkylated) and oxygen alkylated (O-alkylated) products (Figure 2). These appear to be formed in parallel and constitute isomeric (1- and 2-) octenyl-phenols and octenyl-phenyl ethers. The products distributions were presented in Figure 2.

In the alkylation of phenol the O-alkylation requires weak acid sites and low temperatures (range of 50-80 °C) while C-alkylation occurs on stronger acid sites and higher temperatures. In this work the reaction temperature was superior to 110 °C and the mainly product in the phenol alkylation reaction were the C-alkylated product (65%) in accordance with the literature. Dialkylation of the phenol to produce dioctenyl-phenol was limited to < 10%. The selectivity for 1-phenyl-(o,p-hydroxy)-2-octene was 65% and for 3-phenyl-(o,p-hydroxy)-1-octene, 35%. BAS (NbOH and POH) and LAS (coordinatively unsaturated Nb⁵⁺ sites) are probably responsible for alkylation reaction. However, we believe that BAS are the more important sites for the alkylation reactions because are they capable of generating a carbenium intermediate from octene, dodecene and allylic alcohol. The carbenium ion formed on acid sites attacks the aromatic compound forming the monoalkylated products. The Py-FTIR experiments show that the commercial phosphates present a high density of Brønsted acid sites with predominantly weak or moderate strength. This acidity characteristics could be responsible for the high alkylation activity of this catalyst. The alkylation of m-cresol with t-butanol were evaluated and the authors suggested that the strong acidic sites present in the catalysts are responsible for the C-alkylation. A systematical theoretical study using ab initio calculation and ab initio density functional theory (DFT) were reported in the literature. They concluded that O-alkylation to form the phenolic ether is the product most energetically favorable in neutral conditions and an ionic rearrangement mechanism describes intramolecular migrations of the alkyl group from the phenolic ether to form C-alkylphenols. The intermediate from the C-alkylation is more stable and as a result, the O-alkylated products disappear gradually. The liquid phase alkylation of phenol with 1-octen-3-ol over niobium phosphate an ionic rearrangement of the O-alkylated products to C-alkylated products can occur. A mechanistic study are in progress in our laboratory to clarify this point.

In this work, the reaction was carried out in solvent-free liquid phase conditions, with 100% conversion of one of the reactants. Thus the niobium phosphate is also a very good environment-friendly option against the conventional solid and liquid acid catalyst.
Conclusions

The liquid phase alkylation of the anisole with 1-octene and 1-dodecene to produce octyl- and dodecyl-anisole was shown high selectivity in monoalkylation products. No dialkyl-anisole was formed under the reaction conditions. The alkylation of phenol with 1-octen-3-ol can be successfully carried out in the presence of niobium phosphate as a catalyst. This process displays good regioselectivity with respect to the 1 position of the allylic alkylation reagent and the linear product is predominantly formed.

Acknowledgments

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References