Liquid Phase Alkylation of Anisole and Phenol Catalyzed by Niobium Phosphate

Cynthia C. M. Pereira,[a] Marcus H. C. de la Cruz[b] and Elizabeth R. Lachter*,[a]

[a]Instituto de Química, Universidade Federal do Rio de Janeiro, 21949-900 Rio de Janeiro-RJ, Brazil

[b]Instituto Nacional de Controle de Qualidade em Saúde, Fundação Oswaldo Cruz, 21040-900 Rio de Janeiro-RJ, Brazil

A atividade catalítica do fosfato de nióbio foi avaliada na reação de alquilação em fase líquida do anisol com 1-dodeceno, 1-octeno, 2-octanol e 1-octen-3-ol e na reação do fenol com 1-octen-3-ol. Melhores resultados foram alcançados na alquilação do anisol e do fenol com 1-octen-3-ol que produziu principalmente produtos monoalquilados. Na reação com o fenol e 1-octen-3-ol os principais produtos formados foram os octenil-fenóis (C-alquilação) e o fenil-octenil éter (O-alquilação). A reação favorece a formação de C-alquilados em relação aos O-alquilados.

The catalytic activity of niobium phosphate was evaluated in the liquid phase 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

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.[1-5] Both homogeneous and heterogeneous catalysts have been applied to the phenol alkylation. Homogenous acid catalysts such as HF, H_2SO_4, $AlCl_3$, or BF_3 are commonly used in Friedel-Crafts reaction,[6] but the toxic aqueous waste resulting from catalyst remains problematic. On the other hand, utilization of the eco-friendly heterogenous catalysts such as macroporous cation-exchanged resins (Amberlyst-15),[7] zeolites,[8,9] SAPO-11,[10] mesoporous materials[11] 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 disvantage 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[8,9] and others solid acids like zirconia,[1] 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).[11-13] Information about the use of niobium compounds for the alkylation of phenol with allylic alcohol is almost unexistent in the available literature.

Continuing our interest in the catalytic activity of niobium compounds in the Friedel-Crafts reaction,[14-16] 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 over niobium phosphate.

Experimental

General alkylation procedures

The reaction was carried out in a round-bottom 50 mL 2-necked flask provided with a condenser, and a septum for sample removal. The reaction mixture was magnetically stirred at atmospheric pressure, and the bath

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, alikylating 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 H$_2$, 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 resonable value for the surface area, 138 m^2 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 Brϕnsted (BAS) and Lewis acid sites (LAS) NbP-Com has almost the same amount of total Brϕnsted and Lewis sites, 163.3 and 160 μmol g^{-1} respectively as shown in previous works.[17] The catalytic activity of niobium phosphate was evaluated in the 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. The results are presented in table 1.

The alkylation of anisole with 2-octanol did not proceed to any appreciable extent at the end of 7 h (entry 3). The conversion of 1-dodecene was higher than the 1-octene one after 4h, 65 and 22%, respectively (entry 1,2). This results is due to, probably, the reaction temperature that is higher for dodecene (150 °C) than for 1- octene (110 °C). Best results were achieved with 1-octen-3-ol and the conversions were total for the anisole[15] and phenol (entry 4,5). Ours results was superior to those present in the literature.[18]

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

Entry	Alkylation Agent	Aromatic Compounds	time / h	Conversion / (%)	Reference
1	1-Dodecene[a]		4	65	This work
2	1-Octene[b]	Anisole	4	22	This work
3	2-octanol[b]		7	0	This work
4	1-octen-3-ol[c]		4	100	15
5	1-octen-3-ol[d]	Phenol	2	100	This work

[a]molar ratio anisole/1-dodecene was 15/1, 250 mg catalysts, reflux temperature; [b]molar ratio anisole/1-octene was 10/1, 250 mg catalysts, 110 °C; [c]reference 15; [d]molar ratio phenol/1-octen-3-ol was 10/1, 250 mg catalyst, 110 °C.

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 2. Products distribution in alkylation reaction

| Entry	Aromatic Compound	Alkylating Agent	time / h	Monoalkylation / (%)
1		1-octene	4	100[a]
2	Anisole	1-dodecene	7	65[b]
3		1-octen-3-ol	4	86[c]

[a]76% of the 2-octyl-anisole; [b]40% of the 2-dodecyl-anisole; [c]reference 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 isomerization[19] and anisole alkylation in presence of catalyst. The different isomers of dodecene and octene react with anisole to form isomeric mixture of dodecyl and octylanisole. 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 aimaing to produce alkylating products (Scheme1).

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.
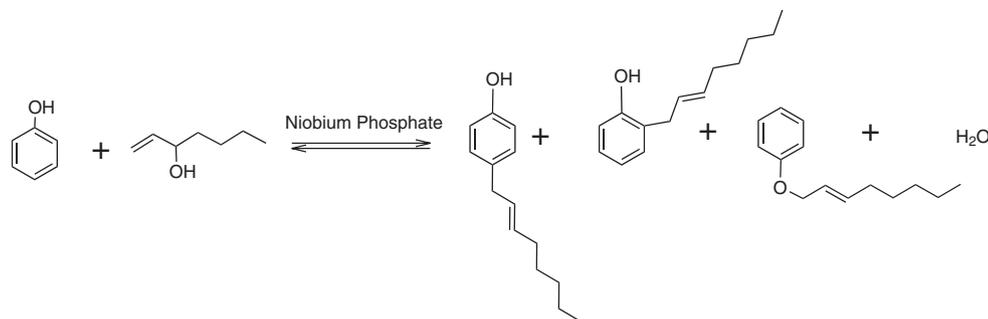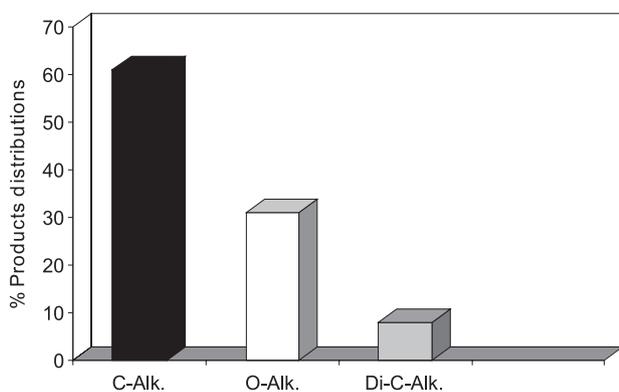
Scheme 1. Alkylation of phenol with 1-octen-3-ol in presence of niobium phosphate.
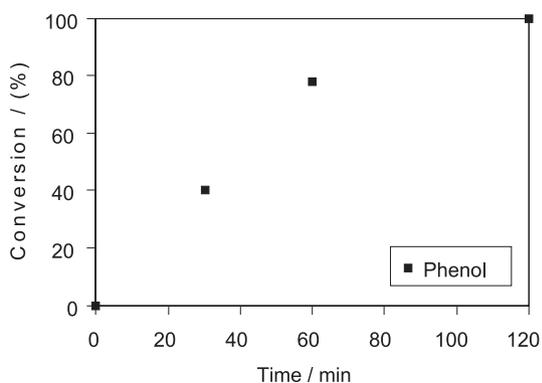
Figure 1. Conversion of 1-octen-3-ol in the alkylation reaction of phenol catalyzed by niobium phosphate.

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.

Figure 2. Products distribution formed on the reaction of phenol with 1-octen-3-ol at 110 ºC and 2 h catalyzed by niobium phosphate. Mono and Di-stands for the (1- and 2-) octenyl-phenols, (C-alkylation) and octenyl-phenyl ethers (O-alkylation).

In the alkylation of phenol the O-alkylation requires weak acid sites and low temperatures (range of 50-80 ºC) while C-alkylation ocurs on stronger acid sites and higher temperatures.[2] In this work the reaction temperature was superior to 110 ºC and the mainly product in the phenol alkylation reaction were the C-alkylated product (65%) in accordance with the literature.[2] 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 Nb^{+5} 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 producs. The Py-FTIR experiments show that the commercial phosphates[15] present a high density of Brønsted acid sites with predominantly weak or moderate strenght. 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.[13] A systematical theoretical study using *ab initio* calculation[21] and *ab initio* density functional theory (DFT)[12] 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.[12,21] 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 di-alkyl-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 alkylating reagent and the linear product is predominantly formed.

Acknowledgments

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