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Catalytic activity of niobium phosphate in the Friedel–Crafts reaction of anisole with alcohols

Marcus Henrique C. de la Cruz, João F.C. da Silva, Elizabeth R. Lachter *

Instituto de Química da Universidade Federal do Rio de Janeiro (UFRJ), Rio de Janeiro,
Brasil, lha do Fundão, CT, Bloco-A sala 617, Brazil

Abstract

The catalytic activity of niobium phosphate was evaluated in the benzylation reaction of the anisole with benzyl alcohol, 2-phenyl-ethanol and 1-phenyl-ethanol, in liquid phase. The influence of concentration of the catalysts was evaluated. The niobium phosphate was characterized by DRX, thermogravimetry analysis, BET surface area and IV-pyridine. We found high activities (100%) and selectivity (>90%) in the benzylation with benzyl alcohol and 1-phenyl-ethanol. No result was obtained with 2-phenyl-ethanol. In the reaction with benzyl alcohol a side reaction occurs to form dibenzylether. It has been concluded that Lewis acid sites are responsible for the ether formation and Brønsted acid sites (POH and NbOH) are responsible for the benzylation of anisole with alcohols. The isomer composition in benzylation products from anisole alkylation gave predominantly *ortho–para* substitution in accordance with a typical eletrophilic aromatic substitution pathway.

Keywords: Niobium phosphate; Benzylation; Friedel–Crafts reaction; Benzylic alcohol; Solid acid catalyst

1. Introduction

Alkylation of aromatic hydrocarbons is one of the most important reactions used in an industrial scale. The production of long chain alkylbenzenes, as intermediates for detergents, the benzylation of benzene and toluene by benzyl chloride and benzyl alcohol for producing dielectric fluids are excellent examples. In all of these processes, acid catalysts (e.g. $AlCl_3$, H_2SO_4, HF or H_3PO_4) have been used, in spite of their low selectivity and high corrosiveness [1]. There is considerable interest in replacing strongly acidic, homogeneous, corrosive and polluting catalysts in the manufacture of various industrial products, such as petrochemicals, pharmaceuticals, agrochemicals, perfumery, with environmentally clean heterogeneous solid acid catalysts and processes. The uses of solid catalysts such as zeolites and clays in the alkylation of aromatic compounds have been studied [1]. Liquid phase benzylation of *o*-xylene and naphthalene using various zeolite catalysts was carried out by Singh et al. [2]. The benzylation of toluene with benzyl alcohol over iron promoted sulfated zirconia systems was evaluated and along with the benzylated product, benzyl ether, formed by the self condensation of benzyl alcohol, was also obtained as a major product [3]. A nafion–silica composite was evaluated as catalyst in the toluene reaction with benzyl alcohol. The final products were found to be dibenzyl ether, the isomers of benzyltoluenes and dibenzyl toluenes and small amounts of unidentified byproducts [4]. Benzylation of anisole with benzyl alcohol was carried out with H_3PO_4–WO_3–Nb_2O_5-derived catalysts. The authors found that catalytic performance depended significantly on calcination temperature [5].

Efforts have also been made to develop new applications of niobium compounds in chemical industries [6]. Our group has been interested in the alkylation reaction catalyzed by niobium compounds [7–10]. In a previous paper, the present authors have verified that niobic acid treated with phosphoric acid [7] and the amorphous niobium phosphate [9] promoted the benzylation of aromatic compound giving high yield and selectivity. In the present paper we describe a comparison between benzyl alcohol, 2-phenyl-ethanol and 1-phenyl-ethanol in the Friedel–Crafts alkylation of anisole catalyzed by niobium phosphate.

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* Corresponding author. Tel.: +55 25 624140; fax: +55 21 25 627944.
E-mail address: lachter@iq.ufrj.br (E.R. Lachter).

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2. Experimental part

2.1. Materials

Niobium phosphate supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração, Araxá, Brazil) were dried and calcined at 500 °C for 4 h. Anisole and benzylic alcohol were dried before use [11]. 2-Phenyl-ethanol and 1-phenyl-ethanol (Spectrograde, Merck) were used without further purification.

2.2. Surface area

The BET surface areas and pore volume of niobium catalysts were determined from nitrogen adsorption isotherms at the normal boiling temperature of liquid nitrogen. The adsorption isotherms were obtained in a Micromeritics ASAP (Accelerated Surface Area and Porosimetry), model 2010. The samples were pre-treated in situ under vacuum, at 100 and 500 °C.

2.3. XRD

The catalysts were characterized by X-ray Powder Diffraction collected on a Miniflex Rigaku using Cu Kα radiation. The samples were scanned over the angular range 8–38° (2θ), with a step size of 0.04° and a scan rate of 1 s per step.

2.4. TGA

Thermogravimetry analysis (Shimadzu TGA-51) was measured with a heating rate of 10 °C min^{-1} since 25 °C up to 800 °C under N_2 flow.

2.5. Infrared spectroscopy (FT-IR)

Infrared spectra were recorded by a FT-IR spectrometer (Nicolet Protegé) in the spectral range 4000–400 cm^{-1} using KBr pressed disks. Samples were calcined at 500 °C in air before analysis.

2.6. Infrared spectroscopy (FT-IR) of adsorbed pyridine

Infrared (IR) spectra of pyridine adsorption were recorded with a Nicolet spectrometer with 4 cm^{-1} resolution. A self-supported wafer, containing ca. 30 mg/cm^2 of sample, was placed in a glass cell and was evacuated at 300 °C for 16 h, under vacuum of 10^{-5} Torr. After cooling the cell to ambient temperature, still under vacuum, the IR spectrum was recorded. Pyridine vapor was then introduced into the cell at 150 °C. After pyridine adsorption the excess of base was removed and the spectra of adsorbed pyridine were recorded at room-temperature.

2.7. General alkylation procedures

The reaction was carried out in a round-bottom 50 ml three-necked flask provided with a condenser, a nitrogen gas inlet and a septum for sample removal. In a typical run, anisole and benzyl alcohol (15:1 molar ratio) were added to the activated catalyst. The reaction mixture was magnetically stirred at atmospheric pressure, and heated to reflux by means of a constant temperature bath (160 °C). The degree of alcohol conversion was analyzed periodically by gas-chromatography (VARIAN, 3800). The products were also identified by GC/MS (HP5890 series II/HP5972 series, respectively).

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

2.8. 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 i.d., 1 μm d.f. The temperature was programmed from 80 to 280 °C at 20 °C/min with H_2, 2 ml/min, 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 (30 m) fused silica column in the same temperature conditions with He as carrier gas.

3. Results and discussion

3.1. Characterization

The properties of the niobium phosphate are presented in Table 1.

Niobium phosphate has texture properties similar to niobic acid, but it has the advantage that it conserves these properties at higher temperature [10] and the loss of surface area at 500 °C was low. Our results are in agreement with previous reports by Florentino et al. [12] and Martins et al. [13].

The data obtained by XRD analysis showed that the niobium phosphate (after calcinations at 500 °C) used in this work were amorphous.

Fig. 1 shows the TGA curve of niobium phosphate. The mass loss (11% for niobium phosphate) up to 300–350 °C corresponds to water molecules coordinated to niobium atoms and the mass loss (1.8%) in the range 600–800 °C for the niobium phosphate, corresponds to water molecules that interact with the oxygen of the phosphate groups (PO_4) [14].

The IR spectra of niobium phosphate (without calcinations and after calcinations at 500 °C) are presented in Fig. 2 and

Table 1
Textural properties of niobium phosphate

Catalyst	Temperature (°C)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore diameter (Å)
Niobium	100	246	0.33	53.6
Phosphate	500	187	0.29	62.7

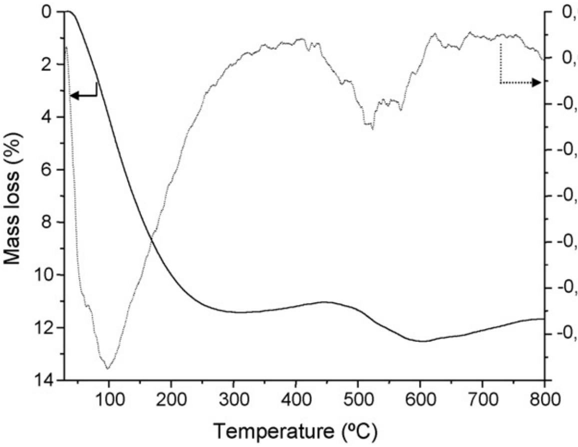

Fig. 1. Thermogravimetry analysis: of niobium phosphate.

show a strong band due to the asymmetric vibration stretching mode of phosphate ion with a maximum at 1010 cm^{-1}. An additional strong band is found at 620 cm^{-1}, which, in agreement with the spectrum of niobic acid, could be mainly due to Nb–O stretching modes. These results are similar to those reported in the literature [10,15].

Fig. 3 shows the infrared spectra of adsorbed pyridine in the wave number range of 1400–1700 cm^{-1}, where bands due to skeletal vibrations of the pyridine ring can be observed [7]. The band most characteristically associated with pyridine adsorbed on Brønsted acid sites (pyridinium ions, PyH$^+$) [7] occurs ca. 1540 cm^{-1}. The bands at ca. 1450 cm^{-1} can be associated with pyridine coordinatively bonded to Lewis acid sites [7]. The infrared spectrum (Fig. 4) shows that niobium phosphate has both Lewis and Brønsted acid sites. Acid site densities were calculated using the integrated molar extinction coefficients published by Emeis [16] (0.34 and 0.55 μmol^{-1} for Brønsted and Lewis acid sites, respectively).

3.2. Alkylation reaction

The benzylation of aromatic hydrocarbons with benzyl alcohol catalyzed by niobium phosphate gave dibenzyl ether and benzylation products in different proportions depending on the substrates. The reaction scheme of the benzylation reaction is presented in Fig. 4.

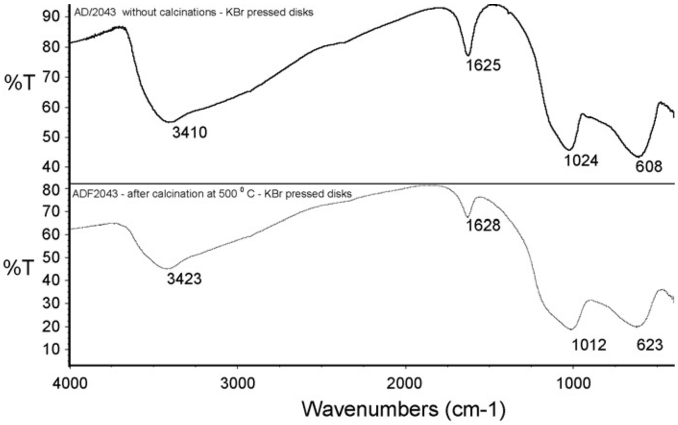

Fig. 2. FT-IR spectra (KBr pressed disks): niobium phosphate without calcinations (continues line), after calcination at 500 °C (dashed line).

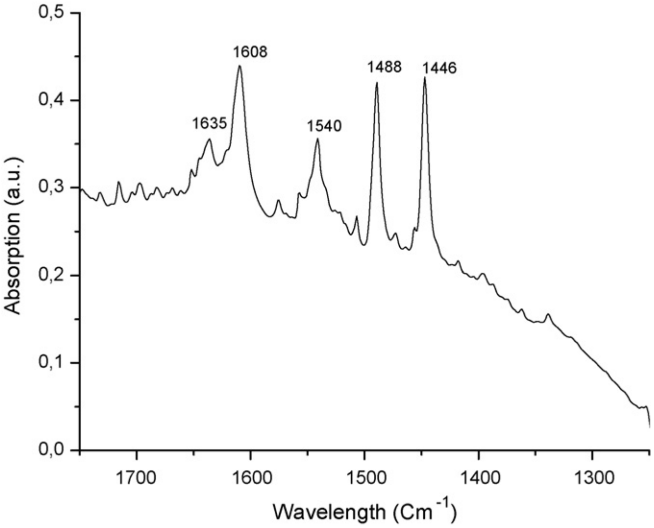

Fig. 3. Spectra of pyridine absorbed on niobium phosphate.

The effect of catalyst loading was studied with commercial niobium phosphate in the benzylation of anisole with benzyl alcohol and 1-phenylethanol. The catalyst weight was varied from 0.5 to 0.050 g for benzylalcohol (Table 2) and 0.125–0.010 g for 1-phenyl-ethanol (Table 3). The conversion of benzyl alcohol was total in the range employed in this work. Dibenzylether was formed and increased with decreased of catalyst loading. The benzylation product occurs through benzylic alcohol and the dibenzylether is the side reaction because of the relatively low rate of the benzylation. Deshpande et al. [17] has already reported that, in the benzylation of benzene with benzyl alcohol the etherification is faster than the alkylation reaction.

In the alkylation with 1-phenyl-ethanol the *para* product was predominantly (Table 3).

The results of the reaction of anisole with different alcohols were presented in Table 4. In the reaction with benzylic alcohol

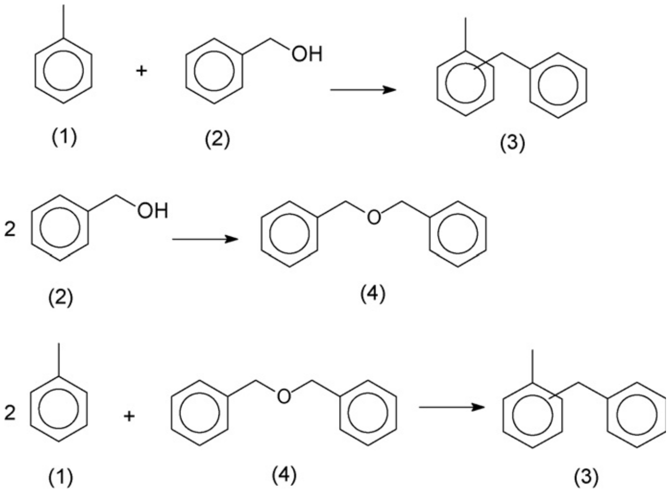

Fig. 4. Scheme of benzylation of aromatic compounds ((1) aromatic compound, (2) benzylic alcohol, (3) alkylated compound, and (4) dibenzylether).

Table 2
Alkylation of anisole with benzylic alcohol

Alkylating	Catalyst weight (mg)	Time (min)	Conversion (%)	Product distributions (%)			
				Alkylated		Dibenzyl ether	Dialkylated
				ortho	*para*		
BzOH	500	<20	100	43.1	49.0	1.5	6.4
BzOH	375	<60	100	36.6	53.7	4.2	5.5
BzOH	250	<80	100	37.7	52.6	3.4	6.3
BzOH	125	<360	100	34.3	53.1	5.2	7.4
BzOH	50	>420	99.4	36.1	46.6	9.8	7.5

Conditions: anisol/substrate = 15/01; reflux; catalyst pre-treated at 773 K.

Table 3
Alkylation of anisole with 1-phenyl-ethanol

Alkylating	Catalyst weight (mg)	Time (min)	Conversion (%)	Product distributions (%)			
				Alkylated		Ether	Dialkylated
				ortho	*para*		
1-PhEtOH	125	<10	100	21.5	74.4	3.1	1.0[a]
1-PhEtOH	50	<10	100	19.7	73.8	6.0	0.5[a]
1-PhEtOH	10	240	97	24.4	61.8	2.7	1.2[a]

Conditions: anisol/substrate = 15/01; reflux; catalyst pre-treated at 773 K.

[a] Others = styrene.

Table 4
Alkylation of anisole with alcohols catalyzed by niobium phosphate

Alkylanting	Catalyst weight (mg)	Time (min)	Conversion (%)	Products distributions (%)			
				Alkylated		Ether	Dialkylated
				ortho	*para*		
1-PhEtOH	125	<10	100	21.5	74.4	3.1	1.0[a]
2-PhEtOH	125	>240	~0	Traces		–	–
BzOH	125	<360	100	34.3	53.1	5.2	7.4

Conditions: anisol/substrate = 15/01; reflux; catalyst pre-treated at 773 K.

[a] Others = styrene.

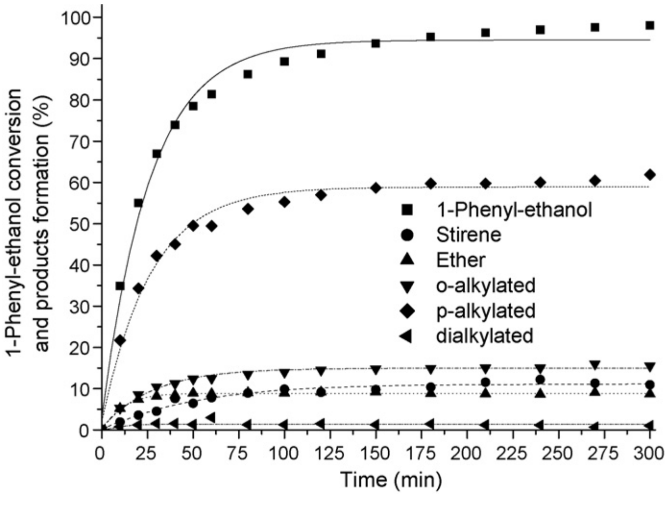

Fig. 5. Reaction of anisole with 1-phenyl-ethanol catalysed by niobium phosphate.

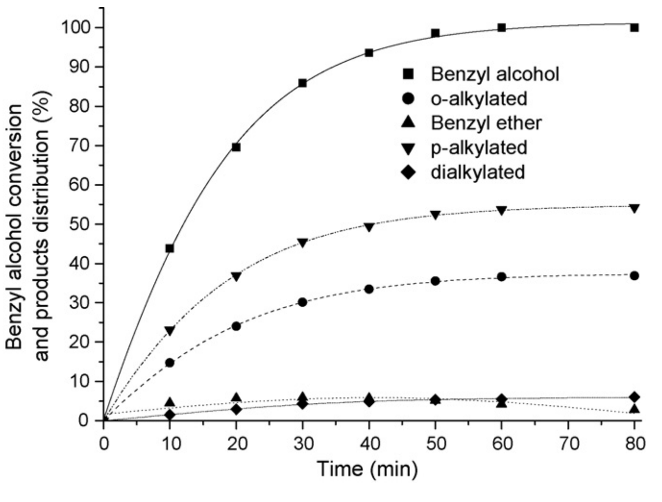

Fig. 6. Reaction of anisole with benzyl alcohol catalyzed by niobium phosphate.

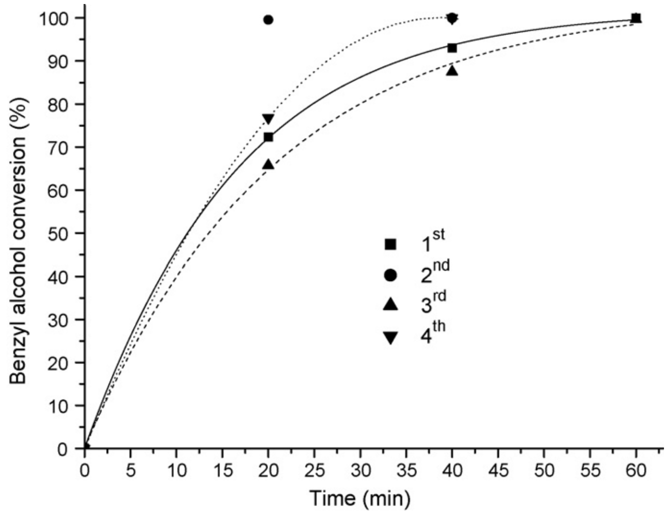

Fig. 7. Reaction of anisole with benzyl alcohol catalyzed by niobium phosphate. Re-utilization of catalyst after four times.

and 1-phenyl-ethanol the yield and selectivity to monoalkylation is high (>90%) dialkylated products and ethers was formed in minor proportions and no other products were observed.

No product was observed in the reaction with 2-phenyl-1-ethanol after 4 h.

Figs. 5 and 6 shows a kinetic study for alkylation of anisole 1-phenyl-ethanol and benzyl alcohol respectively. It can be seen that maximum conversion is achieved with 20 min for 1-phenyl-ethanol and 60 min for benzyl alcohol.

In Fig. 7, the results of alkylation with benzyl alcohol and a previously used, regenerated, niobium phosphate catalyst. It can be see that the conversion is little affected by regeneration of the niobium catalysts, indicating its potential industrial application in environmentally friendly process.

The mechanism for alkylation reaction was demonstrated in Figs. 8–10. Brønsted (NbOH, POH) and Lewis acid sites are probably responsible for alkylation reaction. We believe that the Brønsted sites are the responsible for the alkylation reaction because no product was observed with primary alcohol (2-phenyl-ethanol).

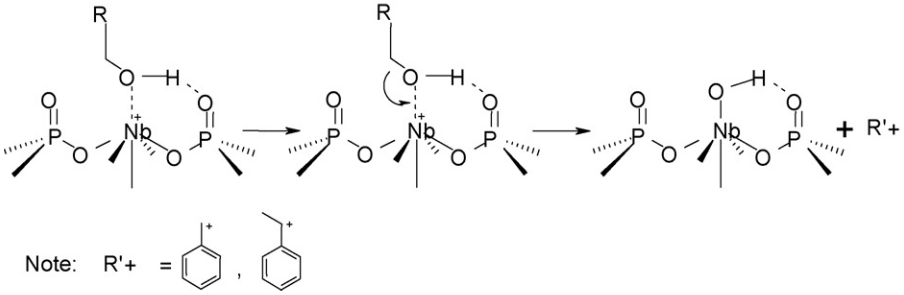

Fig. 8. Lewis sites for alkylation reaction.

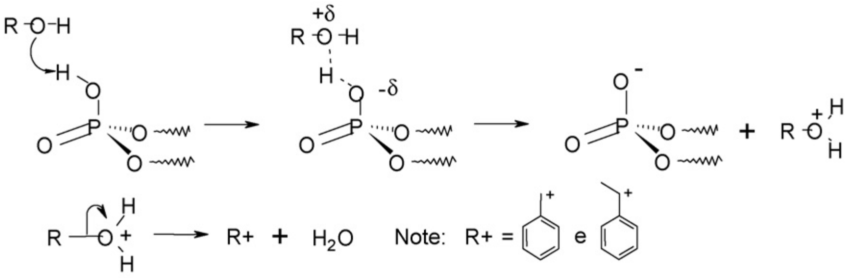

Fig. 9. Brønsted site (P-OH) for alkylation reaction.

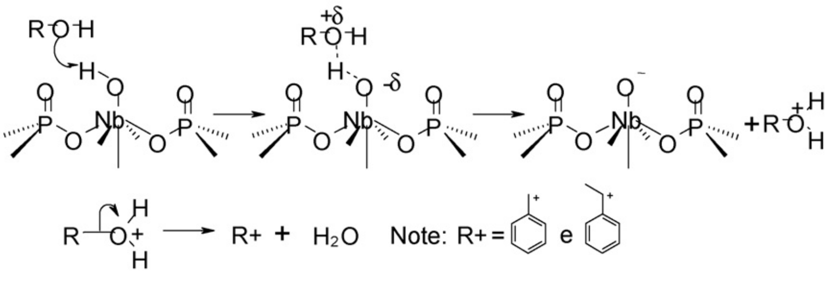

Fig. 10. Brønsted site (Nb-OH) for alkylation reaction.

The formation of ether, observed for these reactions (Tables 2–4), is also reported and can be associated to both Brønsted and Lewis acid sites. The dibenzyl ether generated can act as alkylating agent [9].

The isomer composition in alkylatyion products from anisole alkylation gave predominantly *ortho–para* substitution in accordance with a typical electrophilic aromatic substitution pathway.

4. Conclusions

The niobium phosphate can catalyze the benzylation of anisole with alcohols with high conversion and high selectivity. Initial indications are that catalyst durability is good. Niobium phosphate might be a feasible alternative for the traditional $AlCl_3$ catalyst.

Acknowledgments

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