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Benzylation of toluene and anisole by benzyl alcohol catalysed by niobic acid

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Abstract

The catalytic activities of commercial niobic acid, niobium pentoxide prepared in laboratory and niobic acid treated with phosphoric acid, were evaluated in the benzylation of toluene and anisole with benzyl alcohol, in liquid phase. The best results were achieved with niobic acid treated with phosphoric acid (pretreatment at 423 K), the conversion of benzyl alcohol was 99.2% with anisole and the main product was the benzylation product. The acidity of these solids has been determined by infrared spectrometry using pyridine as a probe molecule. The ratio of Lewis acidity/Brønsted acidity was higher for niobic acid treated with phosphoric acid.

Keywords: Benzylation; Niobic acid; Benzyl alcohol; Friedel–Crafts reaction

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1. Introduction

The alkylation of aromatic compounds is an important process in both the petroleum and chemical industries [1]. The reaction is generally carried out with alkylating reagents such as alkenes and alkyl chlorides by using stoichiometric amount of a Lewis acid, such as $AlCl_3$. However, use of standard Lewis acid catalyst causes corrosion and environmental problems and the necessity of using large amounts with alcohols substrates. For such reasons, a greater ease of working up with solid catalysts has attracted much interest [2].

The alkylation of benzene and toluene by benzyl chloride and benzyl alcohol is important for producing dielectric fluids and solid catalysts, such as zeolite [3], sulphated zirconia [4], ion-exchanged clay [5] and ion exchange resins [6], have been reported for this reaction.

Efforts have also been made to develop a new application of niobic acid in the chemical industry [7]. We have interest in the Friedel–Crafts alkylation of aromatic compounds with alcohol catalysed by niobic acid.

In this work, we evaluated the catalytic activities of commercial niobic acid, niobium pentoxide prepared in laboratory and niobium acid with phosphoric acid adsorbed, in benzylation of toluene and anisole with benzyl alcohol.

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2. Experimental

2.1. Catalysts and materials

Niobic acid was supplied by CBMM. (Araxá, Brasil), HY-340, was dried and calcined at 423 K. Niobium oxide was prepared as described in the literature [8]. For the preparation of H_3PO_4-treated niobic acid, niobic acid, supplied by CBMM, was immersed in a phosphoric acid solution (1 M) for 3 h. The suspension was filtered and the solid was dried at 120°C for 6 h.

Toluene, anisole and benzyl alcohol are commercial products (spectrograde) and were dried as described in the literature [9].

2.2. Surface area

Specific surface area and pore volume of niobic acid were determined by a BET conventional method using ASAP 2000 apparatus.

2.3. Acidity

The total acidity was determined by butylamine titration with the Hammett indicator [10].

Infrared spectra of adsorbed pyridine were obtained by a FT–IR (60X-Nicolet). The concentrations of Brønsted and Lewis acid sites were calculated from the intensities of PyH (ca. 1540 cm^{-1}) and PyL (ca. 1450 cm^{-1}) bands with their corresponding extinction coefficients after subtracting spectra.

2.4. General reaction procedure

The reaction was carried out in a round-bottom 100 ml 3-necked flask provided with a reflux condenser, a nitrogen gas inlet and a septum for sample removal. The reaction mixture was magnetically stirred at atmospheric pressure and the temperature was kept at reflux temperature of mixture by means of a constant-temperature bath. Samples of the reaction mixture were periodically withdrawn and analyzed by high-resolution gas-chromatography.

2.5. Analytical procedure

The variations of the substrates, alkylating agents and product contents were followed by using a CG Model 500 gas-chromatograph equipped with a hydrogen flame ionization detector system and capillary column SE-54, 25 m, the temperature was programmed from 80 to 280°C (10°C/min) with H_2/2 ml/min as carrier gas.

The identification of some products detected as described above was carried out by using computerized gas-chromatography mass spectrometry analysis (C–CG–MS) on a HP-5988 instrument utilizing a PONA fused silica column (25 m, 0.22 mm ID, 0.5 μm) programmed from 100 to 250°C (7°C/min), with He (15 psi) as carrier gas.

3. Results and discussion

The results of surface area and total acidity for commercial catalysts and catalysts prepared in laboratory are shown in Table 1.

3.1. Effect of different catalysts

Preliminary screening reactions were carried out in order to compare the catalytic activity of the commercial niobium oxides and niobium oxides prepared in the laboratory in the benzylation of anisole with benzyl alcohol. The scheme of the reaction is shown in Fig. 1. The data obtained are summarized in Table 2. The best result was achieved with niobic acid (HY-340) which has a larger number of acid sites (Table 1). But the niobium oxide prepared in the laboratory presented activity comparable with the commercial niobic acid.

3.2. Effect of catalyst loading

The effect of catalysts loading was studied with commercial niobic acid (HY-340). The catalyst weight was varied from 0.5 to 2 g. The

Table 1
Properties of the catalyst

Catalyst	Internal surface area (m^2 g^{-1})	Volume (cm^3/g)	Dp (A)	Total acidity (mmol/g)	Site types
$Nb_2O_5 \cdot nH_2O$ [a] (AD-589)	113.8	0.1873	47.04	–	B,L
$Nb_2O_5 \cdot nH_2O_5$ [a] (HY-340)	153.45	0.1879	42.7	0.785	B,L
Nb_2O_5 (AMI-3) [b]	27.0	0.1	111.0	0.36	B,L
Nb_2O_5 (AM23) [b]	29.0	0.08	81.0	0.25	B,L

[a] Commercial catalyst.
[b] Catalyst prepared in laboratory.
B: Brønsted acidity.
L: Lewis acidity.

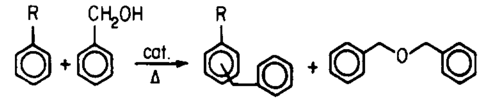

Fig. 1. Reaction scheme of the benzylation of aromatic compounds with benzyl alcohol catalysed by acidic catalyst.

overall reaction rate was found to increase with the increase of the catalyst loading in the range employed in this work. The number of acids sites increased, leading to the formation of more carbenium ions per unit of time which, in turn, increased the reaction rate. The conversion of benzyl alcohol was plotted as a function of time for the benzylation of anisole (Fig. 2) in the presence of different concentrations of catalyst.

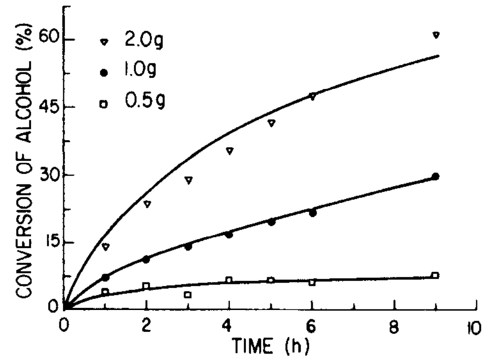

Fig. 2. Effect of calalyst loading in the benzylation of anisole with benzyl alcohol catalysed by niobic acid (HY-340).

3.3. Effect of phosphoric acid adsorbed in niobic acid

We studied the effect of phosphoric acid adsorbed in commercial niobic acid on the benzylation of anisole and toluene to verify the differences that occurred in the conversion and products distributions.

The characteristics of the catalyst after the treatment with phosphoric acid are described in Table 3. The P content was 7%.

The surface acidity of the amorphous phosphate was determined by amine titration. As a result, it was confirmed that the surface acidity

Table 2
Benzylation [a,b] of anisole with benzyl alcohol catalysed by different niobium oxides

Catalyst	D-589	HY-340	AM2-3 [c]	AMI-2 [c]
Conversion of benzyl alcohol(%)	2.1	6.5	5.5	5.6

[a] Reaction time, 4 h.
[b] Anisole/benzylalcohol = 10/1; catalyst = 0.5 (dried at 423 K).
[c] Niobium pentoxide prepared in laboratory as in Ref. [8].

Table 3
Properties of niobic acid after treatment with phosphoric acid

Catalyst	Specific area (cm^3 g^{-1})	Volume (cm^3 g^{-1})	Dp (A)	Total acidity [a]	Ratio (B/L)
$Nb_2O_5 \cdot nH2O/H_3PO_4$	93.15	0.162	57.87	1.11	0.4
HY-340	153.45	0.188	42.7	0.785	0.6

[a] Mmol acid sites/g.

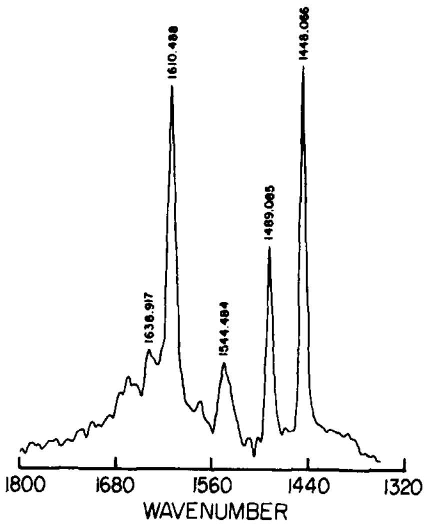

Fig. 3. The infrared spectrum of pyridine adsorbed on niobic acid after treatment with H_3PO_4.

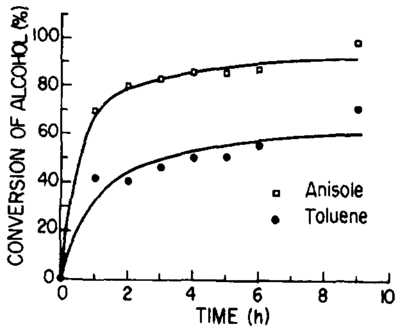

Fig. 4. Benzylation of toluene and anisole with benzyl alcohol catalysed by niobic acid after treatment with H_3PO_4.

is much higher than that of niobic acid. Furthermore, the infrared spectrum (Fig. 3) of adsorbed pyridine indicated a ratio of Brønsted sites to Lewis sites of 0.4 as compared to a 0.6 ratio for the untreated niobic acid catalyst. This observation explains the fact that the treated niobic acid led to a higher conversion in benzylation products as compared to the etherification products (Table 4). A similar observation has recently been made during the alkylation of benzene with methanol and 2-propanol where the catalytic activity was markedly enhanced by treatment of the niobic acid catalyst with a diluted phosphoric acid dilution [11,12]. It is possible that the amorphous niobium phosphate formed on the niobic acid surface is the active species promoting the benzylation [11]. The conversion of benzyl alcohol is plotted as a function of time (Fig. 4).

It is known that the heat treatment of a niobic acid catalyst decrease the ratio of Brønsted sites to Lewis sites, thus favouring the benzylation reaction as compared to the etherification reaction [13]. In the present case it has been observed that the niobic treated with dilute phosphoric acid solution led qualitatively to the same result. However, the benzylation was more enhanced than the case of the heat treatment [13].

3.4. Effect of the substrates

In all cases, the conversion of benzyl alcohol was higher with anisole than with toluene (runs 1,3 and 2,4, Table 4) and the formation of by-products like benzyl ether was higher for

Table 4

Benzylation of toluene and anisole with benzyl alcohol catalysed by niobic acid before and after treatment with phosphoric acid

Run	R in I	Catalyst	Conversion of alcohol (%)	Distribution of products [d] (%)			Ref.
				II [e]	III [e]	other	
1	CH_3	$Nb_2O_5 \cdot nH_2O$	10.8	3.3	65.5	31.2	[13]
2	CH_3	$Nb_2O_5 + H_3PO_4$	71.3	31.8	57.3	10.9	this work
3	OCH_3	$Nb_2O_5 \cdot nH_2O$	61.1	37.6	51.7	10.7	[13]
4	OCH_3	$Nb_2O_5 + H_3PO_4$	99.2	85.2	12.8	2.0	this work

[a] Reaction time, 9 h.

[b] [anisole or toluene]/benzyl alcohol = 10/1; catalyst = 2 g.

[c] Pretreatment temperature = 423 K.

[d] By CG.

[e] II: benzyl product, III: ether.

toluene. Benzyl ether was also observed in the auto-etherification of benzyl alcohol catalysed by Lewatiti-SP-112 [14] and in the benzylation of benzene, toluene and anisole catalysed by ion-exchange resins [8]. It should still be mentioned that the dibenzyl ether formation is a result of the protonation of benzyl alcohol followed by nucleophilic displacement of water by a neighbouring unprotonated benzyl alcohol molecule [15,16].

4. Conclusion

The benzylations of anisole and toluene with benzyl alcohol can be successfully carried out in the presence of niobic acid treated with phosphoric acid. These reactions occurred under mild conditions with high activities and selectivities. The benzylation product can occur on Lewis and Brønsted sites but the auto-etherification of benzyl alcohol occurred on Brønsted sites.

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