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Investigation of the catalytic activity of niobium phosphates for liquid phase alkylation of anisole with benzyl chloride

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1. Introduction

ABSTRACT

In this work crystalline niobium phosphate with different degrees of crystallinity was synthesized by two different methods as catalysts for benzylation of anisole with benzyl chloride. The catalysts were characterized by XRD, N₂ physisorption, solid state ³¹P and ⁹³Nb NMR, structural FTIR and FTIR after adsorption of pyridine. The catalytic activities were measured in the benzylation of anisole with benzyl chloride. The NMR technique seems to be more sensitive in evaluating the presence of amorphous phase, compared with DRX data. The crystalline niobium phosphate prepared by recrystallization of a commercial sample presented activity comparable to its parent compound, in contrast with the crystalline catalyst prepared from niobic acid. The activity was attributed to the Lewis sites present mostly on the amorphous phase of the catalysts.

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The benzylation of benzene and toluene by benzyl chloride and benzyl alcohol is important for producing dielectric fluids, pharmaceutical intermediates and fine chemicals. Such reactions are carried out industrially, using conventional strong homogeneous acid catalysts, such as AlCl₃, FeCl₃, BF₃, ZnCl₂ and H₂SO₄ [1,2]. In parallel, the use of solid heterogeneous catalysts has become important in liquid phase applications, since these catalysts can be easily separated from the reactant mixture. They are also reusable and also have high activity for Friedel–Crafts reactions [1,2]. Solid catalysts like zeolites [3,4], sulphated zirconia [5], Fe-containing mesoporous materials [6], ion-exchanged clays [7], zirconium-pillared clays [8], ion-exchange resins [9,10], ironcontaining aluminophosphate [11], Zr-SBA-15 [12] and Ga-, Al-, AlGa-SBA-15 [13] have been reported for this reaction. The liq-

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uid phase benzylation of benzene and various aromatic substrates including benzyl chloride and benzyl alcohol is a key process to the synthesis of diphenylmethane and substituted diphenylmethanes that are building blocks in organic synthesis for the preparation of intermediates in the pharmaceutical and fine chemical industries [13]. The alkylation of toluene with benzyl chloride has been reported to be catalyzed by Lewis acid sites [14].

Efforts have also been made in developing new applications of niobium phosphate for chemical processes. In previous papers [15–17], the present authors have demonstrated that niobium phosphate can be used as a catalyst in the benzylation of anisole with benzyl alcohol, giving high yield and selectivity. The available literature indicates that niobium phosphate shows potential application in alkylation reaction of aromatic compounds with benzyl alcohol [16–18]. The use of niobium catalysts in the benzylation of aromatic compounds with benzyl chloride has not been reported so far. Therefore, the objective of this work is to evaluate the benzylation of anisole with benzyl chloride catalyzed by different niobium phosphates. We have also investigated the characteristics of the niobium phosphates by N₂ physisorption, XRD, FTIR in the structural region and in the region of adsorbed pyridine and by ³¹P and ⁹³Nb solid state NMR.

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2. Experimental

Anisole (Merck) and benzyl chloride (Merck) were dried before use. Three niobium phosphate samples were studied: a commercial calcined material (NbP-C, NbOPO4·3H2O supplied by CBMM, Araxá, Brazil); the same recrystallized (NbP-R); and a crystalline sample prepared from a HF route (NbP-S). Commercial niobium phosphate was dried and calcined at 773 K for 4 h. Recrystallized niobium phosphate (NbP-R) was obtained by adding 35 mL of HF 40% (v/v) to 9.67 g of NbP-C at 353 K with agitation. After homogenization, the obtained solution was maintained under heating and without stirring for 7 days, to allow slow precipitation. The final solid was separated by centrifugation, washed with distilled water until the washing water reached a constant pH, and dried at 333 K for 24 h [18]. Crystalline niobium phosphate (NbP-S) was synthesized by a procedure described in the literature [18,19]. A solution was obtained by reacting 6 g of niobic acid (supplied by CBMM) with 35 mL of HF 40% (v/v) under agitation, and 20.5 mL of H₃PO₄ (85%) were added to this solution. After homogenization, the solution obtained was maintained without stirring or heating, until a precipitate was formed, after 21 days. When the first crystals appeared, the final volume was adjusted to 100 mL with distilled water. After the precipitation, the solid obtained was washed with 140 mL of a 5 M HNO₃ solution, separated by centrifugation, washed with distilled water until pH 5 (in the washing water) and dried in a vacuum oven at 333 K for 24 h. Specific surface area and porous volume of NbP samples were determined through a BET conventional method using an ASAP 2010 apparatus. The catalysts were characterized by X-ray powder diffraction collected in a Miniflex Rigaku instrument using Cu Kα radiation. The samples were scanned over the angular range 8–38° (2 θ), with a step size of 0.04° and a scan rate of 1 s per step. Solid state ³¹P MAS NMR spectra were obtained on a Bruker DRX300 spectrometer by using Bloch decay pulse sequence (90° pulse length $10 \,\mu s$), with a recycle delay of 60 s. H₃PO₄ 85% was used for chemical shifts reference $(\delta = 0.0 \text{ ppm})$. Isotropic chemical shift and half-height width data were obtained through spectral line simulation performed by using the MestReNova[®] program. Solid state ⁹³Nb NMR spectra were obtained on a Bruker DRX300 (7.05T) and Bruker Avance III-400 spectrometers, operating at 73.46 and 97.98 MHz, respectively. The 4 mm CPMAS Bruker probes were used in both instruments, with ZrO₂ rotors and Kel-F caps. The spectra were acquired by using spinecho pulse sequence $(90-\tau-180-\tau-aq)$ with recycle delay of 1 s. A solution of 0.1 M NbCl₅·CH₃CN was used for both chemical shifts reference (δ = 0.0 ppm) and 90° pulse width calibration (1 µs). The spectral simulation was performed using WSOLIDS1 program [20]. FTIR measurements were carried out in a Perkin Elmer Spectrum One spectrophotometer, between 4000 and 400 cm^{-1} .

The benzylation reactions of anisole with benzyl chloride were carried out in a round-bottomed 50 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 the reflux temperature of the mixture by means of a constant-temperature bath. Samples of the reaction mixture were periodically with-



Fig. 1. X-ray diffraction patterns obtained for samples NbP-C, NbP-R and NbP-S.

drawn and analyzed through high-resolution gas chromatography. Reaction products were identified by gas chromatography–mass spectrometry analysis (GC–MS) in a HP 6890 instrument, using a DB-5 (30m) fused silica column, and helium as carrier gas with the same programming used in the VARIAN GC.

3. Results and discussion

The X-ray diffraction patterns of the three niobium phosphate samples are presented in Fig. 1. No diffraction peak was observed for NbP-C (commercial niobium phosphate) indicating that this material is amorphous. Samples NbP-R and NbP-S present quite similar XRD patterns [18].

The textural and acidic properties of niobium phosphate samples are presented in Table 1.

The recrystallized phosphate NbP-R and the prepared by the HF route, NbP-S present very low surface areas and pore volumes $(23 \text{ m}^2 \text{ g}^{-1}, 0.06 \text{ cm}^3 \text{ g}^{-1} \text{ and } 21 \text{ m}^2 \text{ g}^{-1}, 0.02 \text{ cm}^3 \text{ g}^{-1} \text{ respectively})$, while the commercial phosphate NbP-C presents higher surface area $(187 \text{ m}^2 \text{ g}^{-1}, 0.29 \text{ cm}^3 \text{ g}^{-1})$.

The surface area of niobium phosphate can change with pretreatment temperatures. Martins et al. [21] found a surface area of $182m^2 g^{-1}$ after calcinations at 773 K of commercial niobium phosphate. The preparation method can also change the surface area of niobium phosphate. Values from 8 to $167 m^2 g^{-1}$ were found when the niobium phosphate was prepared from orthophosphoric acid and potassium niobate [22]. Armarolli et al. [23] found for amorphous niobium phosphate specific areas in the range $150-180 m^2 g^{-1}$. Our results are thus comparable to the literature.

The niobium phosphates acidities were previously studied by FTIR of adsorbed pyridine after evacuation at different temperatures [18]. The amount of Lewis acid sites (LAS) and Brönsted acid sites (BAS) are presented in Table 1. The commercial phosphate presented the highest LAS concentration per gram of material. Martins et al. [21] evaluated the relative acid strength of commercial niobium phosphate pre-treated at different temperatures (373–773 K), by infrared spectra of adsorbed pyridine and showed both Brönsted and Lewis acid sites are present. Both crystalline phosphates present lower capacity to chemisorb pyridine compared with NbP-C, and the recrystallized material presented more LAS than BAS. The

Table 1

Properties of the niobium phosphate samples studied

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Niobium phosphate	Textural propertie	Textural properties		Acidity				
	$\frac{1}{m^2 g^{-1}}$	PV ^b cm ³ g ⁻¹	Brönsted μmol g ⁻¹	Lewis µmol g ⁻¹	Total μmol g ⁻¹			
NbP-C	187	0.29	163.3	160	323.3			
NbP-R	23	0.06	32.3	46.3	78.6			
NbP-S	21	0.02	24.4	17.4	41.8			

^a Surface area determined by BET method.

^b Pore volume determined around saturation pressure.



Fig. 2. ^{31}P MAS NMR spectra (121 MHz) obtained for samples NbP-C, NbP-R and NbP-S.

amount of LAS on NbP-R is higher than in NbP-S and much lower than NbP-C.

Solid state ³¹P NMR spectra obtained for the three samples studied are depicted in Fig. 2. For sample NbP-C a broad signal centered at –13 ppm could be seen. In contrast, for the samples NbP-R and NbP-S a sharper signal centered at –23 ppm was obtained (Table 2), with similar signal width. These results could be correlated with the crystallinity of the samples obtained by XRD, although the difference between samples NbP-R and NbP-S detected in the ³¹P spectra was not observed in DRX patterns. Amorphous NbP-C presented the largest width, similar to those obtained previously for commercial NbP samples [24], followed by sample NbP-R and NbP-S. On the other hand, the difference in chemical shifts reflects the presence of residual water in coordination to phosphorous sites [25]. In this sense sample NbP-C present more water molecules coordinated, compared with NbP-R and NbP-S ones.

The ⁹³Nb NMR spectra obtained for NbP-S samples are shown in Fig. 3. The ⁹³Nb spin-echo signal of the three materials reflects the degree of crystallinity of the samples. The spectrum of NbP-S (Fig. 3b) has a lineshape resembling the ones of previously analyzed crystalline phosphates [24]. However, a deviation from the perfect crystalline lineshape is indicative, even for this sample, of a certain degree of disorder. Thus, the spectra could be simulated by using the data published recently [25], with the addition of secondary sites in order to mimick to first order the charge disorder (Table 2). Spectrum of NbP-C is a broad Gaussian, which corresponds to an amorphous material, in accordance with DRX pattern. Reis et al. [26] obtained the same result for mesostructured NbP. NbP-R, on the other hand, has a spectrum (Fig. 3c) that can be decomposed in the sum of a crystalline (39%) and an amorphous (61%) line. This result is in accordance with the ³¹P results, in contrast with DRX and evidences that solid state NMR is a more powerful tool in detecting the presence of different phases in NbP samples.

The structural IR spectra (Fig. 4) of the samples are typical of phosphates, as described in the literature [17,22,27]. The samples were manipulated under air, so bands around 3406 and 1629 cm



Fig. 3. ⁹³Nb static spin-echo NMR spectra of samples NbP-C (a); NbP-S experimental (b) and simulation (b1); NbP-R experimental (c) and decomposition in amorphous (c1) and crystalline (c2) contributions, with WSOLIDS program.

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Solid state ³¹P and ⁹³Nb data obtained for niobium phosphate samples studied.

Niobium phosphate	³¹ P MAS ^a		⁹³ Nb Hahn-echo ^b					
	Chemical Shift (δ, ppm)	Width $(\Delta v_{1/2}, \text{Hz})$	Isot. chem. shift (δ_{iso} , ppm)	%	CSA (δ, ppm)	η	Quad. (<i>C</i> _Q , kHz)	η_Q
NbP-C	-13.5	2517	-1302 ^c	-	_	-	-	_
NbP-R	-22.6	2093 ^d	-1290 ^{c,d}	-	-	-	-	-
NbP-S	-23.3	1806	-1330	85	-880	0.2	25	0
			-1330	5	-780	0.2	18	0
			-1330	5	-900	0.2	16	0
			-1330	5	-900	0.2	14	0

^a From optimization with MestReNova[®] processing program.

^b From WSOLIDS program [17].

^c Maximum intensity of amorphous signal, not the δ_{iso}

^d Superposition of the signals of the type NbP-C and NbP-S.



Fig. 4. Structural FTIR obtained for samples NbP-C, NbP-R and NbP-S.



Fig. 5. Benzylation reaction of anisole with benzyl chloride.

⁻¹ typical of water and hydroxyls are observed. Bands around 1220 and 1020 cm ⁻¹ may be related to stretching vibrations of P=O groups, ν_{ass} (P=O) and ν_s (P=O), respectively. Modes related to vibrations of Nb-O and Nb=O groups appear around 640–585 and 910 cm⁻¹, respectively. The two crystalline phosphates present well defined bands, as expected for highly organized structures, as the vibration bands of the commercial niobium phosphate NbP-C appear broadened, similar to those results obtained in a previous work for microporous niobium phosphate [18].

The reaction of anisole with benzyl chloride in the presence of NbP as catalysts to yield alkylated products is presented in Fig. 5. The main products of the alkylation of anisole are isomers of the benzyl anisole and, in some cases, dialkylated products can be found.

The reaction of anisole with benzyl chloride catalyzed by NbP-C occur at temperatures >343 K (Fig. 6). The temperature chosen for the reaction was under anisole reflux, e.g. 427 K. FeCl₃/Al₂O₃ was evaluated in the benzylation of benzene with benzyl chloride in temperature range of 323-393 K [28]. It was found that conversion was very poor at lower temperature (323 K) and a temperature of at least 353 K is required for appreciable conversion, similar to our findings.

Table 3 presents the results of the catalytic activities observed in the alkylation of anisole with benzyl chloride by varying the reaction time. The conversion of benzyl chloride was 100% in all cases, but the reaction occurred slowly in the presence of NbP-S due probably to lower number of Lewis acid sites in this catalyst.



Fig. 6. Effect of temperature on the conversion (%) of benzyl chloride in the presence of NbP-C (*m* = 125 mg) in function of time of reaction (min).

 Table 3

 Benzylation of anisole with benzyl chloride catalyzed by different niobium phosphates.

Time (min)	Conversion (%) Catalyst		
	NbP-C	NbP-R	NbP-S
5	74	-	8
10	100	97	24
20	100	100	65
30	100	100	98
40	100	100	100

Conditions: anisole/substrate = 15/1; 427 K; 60 mg of catalyst pre-treated at 773 K.

The selectivity in monobenzylation product was superior to 90% (Table 4). The isomer composition in benzylation products from aromatic reaction gave predominantly *ortho-para* substitution in accordance with a typical electrophilic aromatic substitution pathway.

Although the specific area and number of acid sites of crystalline NbP-S are lower when compared to NbP-C, the benzyl chloride conversion in the presence of both catalysts was complete. In a previous paper, by using benzyl alcohol as alkylating agent conversions lower than 30% were achieved [18]. The higher performance of NbP-R compared to NbP-S could be correlated with the presence of amorphous phase in this material as confirmed by ⁹³Nb solid state NMR. Oliveira et al. [29] also attributed to amorphous phase the activity of VPO-NbP catalysts for mild oxidation of n-butane to maleic anhydride. Costa et al. [30] reported the activities of amorphous and crystalline zirconium phosphates in Friedel–Crafts alkylation of anisole. They suggested that the higher activity of the amorphous catalyst compared to the crystalline catalyst could be interpreted on the basis of lower accessibility of acid sites present in the crystalline material.

Table 4

Results of benzylation of anisole with benzyl chloride in the presence of heterogeneous catalysts.

Catalyst	Time (min)	Conversion (%)	Products distribut	Products distribution (%)		Ref.
			Monoalkyl.	Dialkyl.		
NbP-C	10	100	92.9	7.1	0.88	This work
NbP-R	20	100	99.6	0.4	0.94	This work
NbP-S	40	100	95.7	4.3	0.92	This work
HZSM-5	1440	0	_	-	-	[31]
Ga/SiO ₂	90	3.7	100	-	-	[32]
Fe/SBA-15	75	89.1	88.5	-	0.82	[33]



Fig. 7. Lewis sites for alkylation reaction.

Our results obtained for the anisole benzylation were compared to other catalysts reported in the literature (Table 4). Niobium phosphate gave the best value for benzyl chloride conversion. It can be noticed that crystalline Nb-P is also active for reactions promoted by Lewis acid sites, whose scheme is showed in Fig. 7.

In conclusion benzyl chloride can be used as reagent for alkylation of anisole, and reacts with aromatic compounds via a mechanism involving Lewis sites. In this pathway, a carbenium ion formed on acid sites attacks the aromatic compound forming the monoalkylated product. *o*- and *p*-alkylated products are predominantly formed, in agreement with a typical eletrophilic aromatic substitution pathway. ³¹P and ⁹³Nb Solid state NMR proved to be more sensitive in evaluating the presence of different Nb-P phases compared with DRX. Both crystalline and amorphous niobium phosphate can catalyze the benzylation of anisole with benzyl chloride with high conversion.

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