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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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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, N_2 physisorption, solid state ^{31}P and ^{93}Nb 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.

1. Introduction

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 $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$ and H_2SO_4 [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], iron-containing aluminophosphate [11], Zr-SBA-15 [12] and Ga-, Al-, AlGa-SBA-15 [13] have been reported for this reaction. The liquid 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 N_2 physisorption, XRD, FTIR in the structural region and in the region of adsorbed pyridine and by ^{31}P and ^{93}Nb 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, $NbOPO_4·3H_2O$ 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 H_3PO_4 (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 HNO_3 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° (2θ), with a step size of 0.04° and a scan rate of 1 s per step. Solid state ^{31}P MAS NMR spectra were obtained on a Bruker DRX300 spectrometer by using Bloch decay pulse sequence (90° pulse length 10 μs), with a recycle delay of 60 s. H_3PO_4 85% was used for chemical shifts reference ($\delta = 0.0$ ppm). Isotropic chemical shift and half-height width data were obtained through spectral line simulation performed by using the MestReNova® program. Solid state ^{93}Nb 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 ZrO_2 rotors and Kel-F caps. The spectra were acquired by using spin-echo pulse sequence (90-τ-180-τ-aq) with recycle delay of 1 s. A solution of 0.1 M $NbCl_5·CH_3CN$ was used for both chemical shifts reference ($\delta = 0.0$ 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 withdrawn 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.

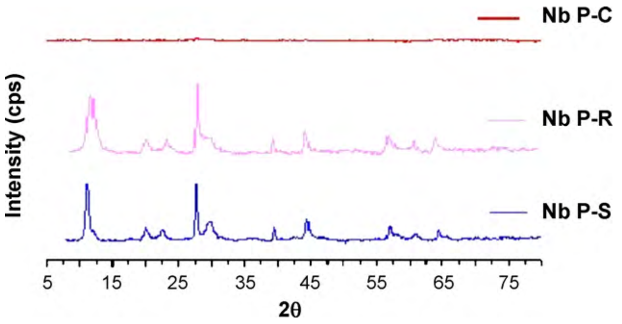

Fig. 1. X-ray diffraction patterns obtained for samples NbP-C, NbP-R and NbP-S.

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 m^2 g^{-1}, 0.06 cm^3 g^{-1}and 21 m^2 g^{-1}, 0.02 cm^3 g^{-1} respectively), while the commercial phosphate NbP-C presents higher surface area (187 m^2 g^{-1}, 0.29 cm^3 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]. Armaroli 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.

Niobium phosphate	Textural properties		Acidity		
	S.A.[a] 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.