Journal of Catalysis 348 (2017) 177–188

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Direct synthesis of bulk AlPON basic catalysts in ionic liquids

Ana I. Saugar, Carlos Márquez-Alvarez, Joaquín Pérez-Pariente *

Instituto de Catálisis y Petroleoquímica, ICP-CSIC, C/Marie Curie 2, 28049-Madrid, Spain

ARTICLE INFO

Article history:
Received 15 December 2016
Revised 7 February 2017
Accepted 18 February 2017

Keywords:
AlPON
Basicity
Michael reaction
Pyrrole
Ionic liquid

ABSTRACT

In this work, the direct synthesis of materials formed by a network of Al, P, N and O atoms (AlPON) from the ammonolysis of P and N molecular precursors in an ionic liquid is reported. The as-made samples can be treated under ammonia at high temperature to remove the ionic liquid retained after synthesis. The resulting amorphous materials have high porosity and surface area. The P atoms of the skeleton are involved in single and double bonds with N atoms, whereas bridged —NH— and terminal P-NH_2 groups are also present. However, no evidence for Al—N bonds has been found. It has been shown by pyrrole adsorption that these materials exhibit basic properties, showing a basic strength higher than that of Si—N materials, but weaker than hydrotalcites. Nevertheless, they are active and very selective catalysts for the Michael addition reaction between malononitrile and chalcone.

1. Introduction

The replacement of oxygen atoms by nitrogen atoms in the framework of high surface area aluminophosphate materials has been a subject of continuous interest aiming at the preparation of solids that could behave as selective catalysts in base-catalyzed reactions. The preferred method to accomplish that goal has been traditionally the post-synthesis treatment of aluminophosphate materials with ammonia at high temperature, a procedure that was initially applied for the nitridation of phosphate glasses [1,2]. In this way, the nitridation of amorphous $AlPO_4$ with high surface area led to materials that show basic properties and are able to catalyze the Knoevenagel condensation reaction between benzaldehyde and malononitrile [3–5], a behavior that has also been reported for nitrided ordered mesoporous aluminophosphate [6]. The early works on the nitridation of phosphate glasses also inspired a similar high-temperature treatment with ammonia of the crystalline microporous aluminophosphate AlPO-5 [7]. The nitridation of amorphous aluminophosphate is usually carried out under ammonia flow at high temperature, normally 800 °C, and long period of time in order to replace a significant amount of oxygen by nitrogen. Nevertheless, large amounts of oxygen atoms are still present in the samples in spite of this treatment [4,5,8]. Moreover, it could be expected that the nature of the chemical environment of the nitrogen atoms incorporated in the material would be affected by the severity of the nitridation conditions, as well as the relative proportion of these environments.

It has been reported recently a new solvothermal route for the preparation of silicon-nitrogen materials by the ammonolysis of silicon tetrachloride in ionic liquids under mild conditions [9]. Moreover, this procedure has been further extended to the preparation of (Si,Al)N materials, which exhibit basic properties and are able to catalyze in a very efficient and selective manner the Michael addition reaction between the donor malononitrile and the acceptor chalcone [10]. In this work, this solvothermal route has been followed to prepare high-surface area AlPON materials, which have been characterized by a variety of techniques in order to shed light on the chemical environment of the several atoms present in the materials. Moreover, the basic character of these materials has been tested by pyrrole adsorption and their activity in the Michael reaction has been also explored. Although the Knoevenagel condensation has been the reaction of choice for testing the activity in base catalysis of most if not all the AlPON materials referred to above, it has to be considered that water is also produced along with the desired condensation product. However, the nitride materials are sensitive to water [11], and it might well be possible therefore that its presence in the reaction media affects the reaction outcome. For this reason, the Michael addition reaction has been preferred for catalyst testing, added to the fact that this base-catalyzed reaction, leading to the formation of carbon-carbon bonds, is very useful for the synthesis of a variety of chemical compounds [12,13].

2. Experimental

The phosphorus-aluminum oxyimide gels were prepared under anaerobic conditions through the use of an air-free system by a

---

* Corresponding author.
E-mail address: jperez@icp.csic.es (J. Pérez-Pariente).

http://dx.doi.org/10.1016/j.jcat.2017.02.023

modification of our previously reported method [9]. First, 4.29 g (7.0 mmol) of phosphoryl chloride (Sigma-Aldrich, ≥99 wt%) and 3.73 g (7.0 mmol) of anhydrous aluminum chloride (Panreac, 98 wt%) were dissolved in 31.7 g of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2C_1im][Tf_2N]) (Sigma-Aldrich, 98 wt%) and reacted with gaseous anhydrous ammonia (Air Liquide, H_2O <400 ppm) in a vessel kept in an ice bath to prevent a very vigorous course of the reaction.

The resulting phosphorus-aluminum oxyimide gel was homogenized inside a nitrogen-filled glove bag and introduced into 60-ml Teflon-lined stainless steel autoclaves which were heated statically at 180 °C under autogenous pressure for 14 days or 28 days. In some experiments, pyrrolidine (Sigma-Aldrich, ≥99.5 wt%, purified by distillation) was added to the mixture and ammonia gas was dissolved in the ionic liquid before the heating process. To dissolve the ammonia, static phase equilibrium cells constructed with Swagelok fittings, one Swagelok ball valve, and glass-lined stainless steel tubing were used. The cells were filled inside the glove bag with the mixture resulting from homogenizing the white gel obtained in the ammonolysis reaction, adding pyrrolidine in some cases. Then, ammonia was dissolved in the ionic liquid by the procedure described in our previous report [9] and the cells were heated as described above.

The obtained products were washed with methanol (Scharlau, 0.028% water as received; it was distilled prior to use in the presence of activated molecular sieve 3 Å pellets to remove the traces of water) to remove the ammonium chloride, the ionic liquid and the unreacted pyrrolidine if present, and filtered under a nitrogen flow using a stainless steel pressure filter holder with a nylon membrane disk filter (0.45 μm pore-size). The transfer of the products to the filter holder was performed always in the glove bag, as well as all subsequent manipulations of the washed product. White solids were obtained in all cases. After washing, the samples were heated under flowing ammonia (100 ml/min) at 600 °C for 2 h to remove compounds trapped in the pores of the materials.

In this way, different gels with the starting molar composition *1 $OPCl_3$: 1 $AlCl_3$: x Py: 2.8 [C_2C_1im][Tf_2N]: y NH_3* were prepared, where *x* and *y* were varied as stated in Table 1. Hereafter the samples will be named making reference to the quantity of pyrrolidine (Py), *xPy*, where *x* stands for the Py/P molar ratio, followed by a number indicating the heating time. If ammonia is dissolved in the ionic liquid, the heating time is followed by NH. As an example, AlP-2Py-14d-NH refers to the sample prepared from a phosphorus-aluminum oxyimide gel with a Py/P molar ratio of 2 heated at 180 °C for 14 days with ammonia dissolved in the ionic liquid. The experiments performed are summarized in Table 1.

Table 1
Phosphorus-aluminum oxyimide samples prepared from gels with the following molar composition: *1 $OPCl_3$: 1 $AlCl_3$: x Py: 2.8 [C_2C_1im][Tf_2N]: y NH_3*, where *Py* stands for Pyrrolidine and *y* stands for the quantity of ammonia dissolved in the gel before the heating process. All the gels were heated statically at 180 °C.

Sample	*x*	*y*	*t*[a] (days)
AlP-0Py-14d	0	0	14
AlP-0Py-28d	0	0	28
AlP-0Py-14d-NH	0	5.5	14
AlP-0Py-28d-NH	0	5.5	28
AlP-1Py-14d	1	0	14
AlP-1Py-28d	1	0	28
AlP-1Py-14d-NH	1	5.5	14
AlP-1Py-28d-NH	1	5.5	28
AlP-2Py-14d	2	0	14
AlP-2Py-28d	2	0	28
AlP-2Py-14d-NH	2	5.5	14
AlP-2Py-28d-NH	2	5.5	28

[a] Heating time.

Thermogravimetric analyses of the as-prepared samples were performed in a Perkin-Elmer TGA7 instrument, in an air flow of 40 mL/min, with a heating ramp from 25 to 900 °C at 20 °C/min.

CHNS elemental analyses were obtained in a LECO CHNS-932 analyser provided with an AD-4 Perkin-Elmer scale. The phosphorus and aluminum content of the samples were measured by ICP-OES using a Perkin-Elmer Optima 3300 DV spectrometer. Samples for ICP-OES analysis were dissolved by alkaline fusion.

MAS NMR spectra were recorded with a Bruker AV 400 WB spectrometer operating at 104.26 and 161.97 MHz for registering ^{27}Al and ^{31}P spectra, respectively. A 4 mm probe with a ZrO_2 rotor and a Kel-F tap operating at a spinning rate of 10 kHz were used for all spectra. ^{27}Al MAS NMR spectra were acquired by applying pulse length of 0.4 μs corresponding to a flip angle of π/30 and using a pulse delay of 2 s. The applied pulse length in the ^{31}P MAS NMR spectra was 3 μs corresponding to a flip angle of π/4 and the pulse delay was 100 s. The ^{27}Al chemical shifts were referenced to a 0.1 M $Al(NO_3)_3$ aqueous solution ($\delta = 0$ ppm) using $Al(SO_4)_2(NH_4)\cdot 12H_2O$ ($\delta = -0.4$ ppm) as a secondary reference. The ^{31}P chemical shifts were referenced to a 85 wt% H_3PO_4 aqueous solution ($\delta = 0$ ppm) using $(NH_4)H_2PO_4$ ($\delta = 0.81$ ppm) as a secondary reference. For all the NMR measurements the samples were prepared in a nitrogen-filled glove bag.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) measurements were conducted using a Nicolet Nexus 670 spectrometer provided with a MCT detector and a GladiATR single-bounce monolithic diamond ATR accessory. The spectra were recorded in the 4000–400 cm^{-1} range, at 4 cm^{-1} resolution, by averaging 128 scans.

Nitrogen adsorption-desorption isotherms were measured in a Micromeritics ASAP 2420 apparatus at the temperature of liquid nitrogen (−196 °C). The samples (~100 mg) were loaded in the sample tubes in a nitrogen-filled glove bag and degassed in situ at 350 °C in vacuum for 16 h prior to analysis. Surface areas were determined using the BET method and the external and micropore surface areas were calculated using the t-plot method. The pore volume and the average pore diameter were calculated by applying the BJH protocol to the adsorption branch of the isotherm.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a SPECS GmbH spectrometer equipped with a PHOIBOS 150 9MCD energy analyzer. A non-monochromatic magnesium X-ray source (1253.6 eV) was used with a power of 200 W and voltage of 12 kV. The powder sample was pressed inside a nitrogen-filled glove bag using a hand press and stuck on the sample holder with a double-sided adhesive conductive carbon tape. The sample was introduced into the spectrometer without prior thermal treatment. The instrument operated at pressures near 6×10^{-9} mbar in the analysis chamber. Pass energies of 75 and 25 eV were used for acquiring both survey and high-resolution spectra, respectively. The high resolution scans were taken around the emission lines of interest with 0.1 eV steps and 100 ms dwell time per point. SpecsLab Version 2.78 software was used for spectrometer control. The C 1s emission line of adventitious carbon (binding energy of 284.8 eV) was used to calibrate the energy scale of the spectra. The N1s peak was decomposed using the Casa XPS program (Casa Software Ltd) with a Gaussian/Lorentzian (70/30) product function and after subtraction of a Shirley background.

FTIR measurements of adsorbed pyrrole were carried out using a Thermo Nicolet Nexus 670 spectrometer equipped with a MCT detector. Spectra were acquired in the transmission mode, at a resolution of 4 cm^{-1} by averaging 250 scans. Samples were pressed into self-supporting wafers of ca. 3–7 mg/cm^2 thickness and placed inside a glass cell provided with KBr windows and greaseless stopcocks. All sample manipulations were done inside a dry nitrogen-filled glove bag to prevent contact with oxygen and moisture. Samples were outgassed at 150 °C for 1 h (pressure less than 10^{-3}