Catalysis Today 173 (2011) 32–37

Contents lists available at ScienceDirect

Catalysis Today

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

2-Methoxynaphthalene acylation using aluminum or copper salts of tungstophosphoric and tungstosilicic acids as catalysts

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ARTICLE INFO

Article history:
Received 20 December 2010
Received in revised form 28 February 2011
Accepted 3 March 2011
Available online 30 April 2011

Keywords:
Tungstophosphates
Tungstosilicates
Aluminum
Copper
2-Methoxynaphthalene
Acylation

ABSTRACT

Aluminum or copper salts of the tungstophosphoric (TPA) and tungstosilicic (TSA) acids were synthesized. They present interesting characteristics as catalysts because they can have Lewis and/or Brønsted acidity. The salts were characterized by Fourier transform infrared (FT-IR) spectroscopy, measurement of the specific surface area BET, X-ray diffraction, differential scanning calorimetry (DSC) and estimation of the acidity by potentiometric titration with n-butylamine. The salts keep the Keggin structure of the $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$ heteropolyanions intact during the synthesis. The salts of TPA are thermally more stable than those of TSA. All the salts showed very strong acid sites by potentiometric titration, the acid strength and the number of acid sites being higher for the Al^{3+} salts. The salts also showed an excellent catalytic behavior in the reaction of 2-methoxynaphthalene acylation with acetic anhydride. The aluminum salts led to better yields, which are correlated with their higher acidity. Also, it was observed that the solvent nature has an effect on the attained conversion.

1. Introduction

Many heteropolycompounds with Keggin structure have strong acidity, which leads to their use to catalyze reactions of great interest in the synthesis of organic compounds. They can be employed as replacement of conventional acids, such as e.g., sulphuric acid, with advantages such as lower corrosivity and low waste generation that make them suitable for eco-efficient processes.

The bulk heteropolyacids, such as the tungstophosphoric and tungstosilicic acids, lead to low catalytic yield in some acid reactions, mainly due to their low specific surface area. This disadvantage can be overcome by supporting the heteropolyacid on adequate porous solids [1] or using their salts with different cations.

The properties of the salts of Keggin heteropolyacids are sensitive to the cation type [2]. The salts of small cations (named A type) are soluble in water, have a low specific surface area and they generally behave similarly to the parent acid. In turn, the salts of large cations (named B type) are insoluble in water, have high specific surface area and relatively high thermal stability [3].

The salts of large cations gave excellent catalytic activity in diverse acid reactions [4–6]. However, the salts of the A type have been less utilized. Baba et al. [7] studied the generation of acidic sites in the Al^{3+} and Cu^{2+} neutral salts of tungstophosphoric acid. Shimizu et al. [8,9] showed that polyvalent transition metal salts of tungstophosphoric acid act as effective catalysts for Friedel–Crafts acylation of aromatics with carboxylic acids and alcohols.

The salts of the Al^{3+} or Cu^{2+} cations of the tungstophosphoric and tungstosilicic acids have interesting characteristics for their use as catalysts because they can present Lewis and/or Brønsted acidity. Firouzabadi et al. [10] have studied the effect of the nonhygroscopic $AlPW_{12}O_{40}$ salt in the acylation of aromatic compounds with carboxylic acids, in the presence of trifluoroacetic anhydride.

The acylation is a very important method to obtain aromatic ketones, intermediates in the preparation of numerous chemical and pharmaceutical products [11]. The reaction is normally carried out with greater than stoichiometric amounts of Lewis acid catalysts, such as anhydrous metal halides $AlCl_3$ or $ZnCl_2$, which have the disadvantage of generating a high volume of acid waste and metal salts when they are separated, and acid halides as acylating agent, which are expensive and pollutant reagents. Inorganic acids such as HF have also been used as catalysts [12], with the drawback of being toxic and corrosive. These are some of the reasons to find environmentally friendly solid catalysts, which can be used in catalytic amounts and be easily separated from the reaction medium.

There are some studies on the acylation of 2-methoxynaphthalene, employing different solids as catalyst, such as metal triflates [13], Nafion–silica composites [14], Al-MCM-41 mesoporous molecular sieves [15] and zeolites. Harvey et al. [16,17] studied this reaction over zeolite USY, H-beta and ZSM-12 and showed that in all the cases 1-acyl-2-methoxynaphthalene was obtained as the major product. In comparison to other zeolites,

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doi:10.1016/j.cattod.2011.03.028

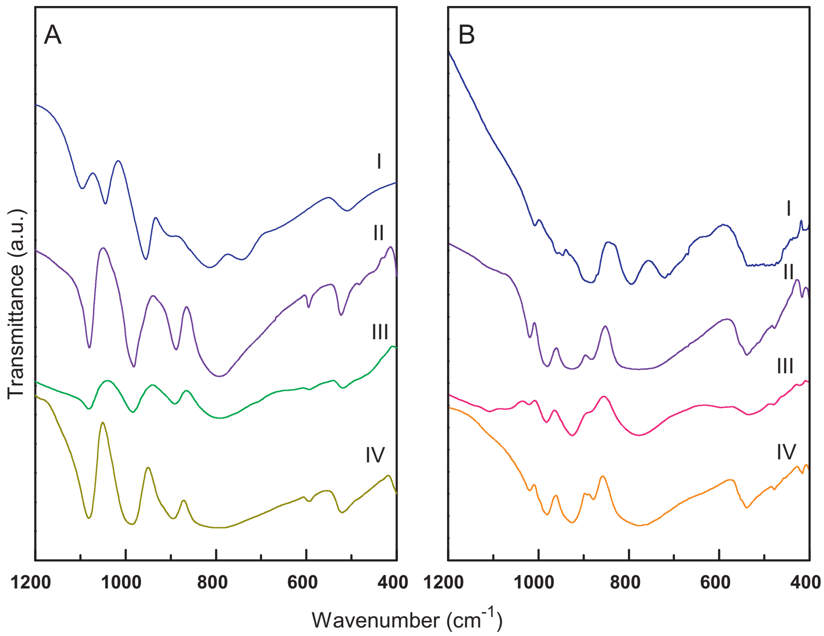

Fig. 1. (A) FT-IR spectra of $Na_7PW_{11}O_{39}$ (I), $H_3PW_{12}O_{40}$ (II), AlTPA salt (III) and CuTPA (IV) salt. (B) FT-IR spectra of $Na_8SiW_{11}O_{39}$ (I), $H_4SiW_{12}O_{40}$ (II), AlTSA salt (III) and CuTSA (IV) salt.

H-beta with narrower 12-ring channels and no super cages showed slightly increased selectivity for 6-acyl-2-methoxynaphthalene. During the acylation of 2-methoxynaphthalene with acetic anhydride the linear 6-acetyl-2-methoxynaphthalene (6-A-2MN) and the bulky 1-acetyl-2-methoxynaphthalene (1-A-2MN) can be formed. It was proposed that the more confined internal environment of H-beta restricts access to the 1-position of 2-methoxynaphthalene [17].

Fromentin et al. [18] studied the acylation of 2-methoxynaphthalene with acetic anhydride in liquid phase, using HBEA zeolite as catalyst, and observed the influence of the solvent on the velocity and the selectivity of the reaction. The importance of this reaction lies in the fact that 6-acetyl-2-methoxynaphthalene is an intermediary of the synthesis of the anti-inflammatory product naproxen [19]; nevertheless, 1-acetyl-2-methoxynaphthalene can be an interesting intermediary in phenylation reactions [20].

Based on previous work and continuing with our studies about the use of salts of heteropolyacids with Keggin structure, the results obtained in the acylation in liquid phase of 2-methoxynaphthalene with acetic anhydride, using Al^{3+} or Cu^{2+} salts of the tungstophosphoric and tungstosilicic acids as catalysts are presented, correlating the behavior with the properties of the salts, such as their acid characteristics, and also observing the effect of the nature of the solvent employed in the reaction.

2. Experimental

2.1. Catalyst preparation

The Al^{3+} or Cu^{2+} salts of the tungstophosphoric acid (TPA), which will be named AlTPA and CuTPA, respectively, were synthesized by slowly adding, under vigorous stirring, aqueous solutions of $Al_2[SO_4]_3$ or $Cu[NO_3]_2$ to an aqueous solution of $H_3PW_{12}O_{40}$ in stoichiometric amount [21,22]. The solutions thus obtained were maintained under stirring at room temperature for 1 h. The salts were obtained by evaporating the solvent in air at 70 °C, and then were washed with ethanol and dried again at 100 °C. The same procedure was employed to obtain the salts of the tungstosilicic acid (TSA), using $H_4SiW_{12}O_{40}$; the Al^{3+} and Cu^{2+} salts will be named AlTSA and CuTSA, respectively. The analysis by atomic absorption spectrometry of the salts gave a W:Al(Cu) molar ratio near to 12:1, 12:1.5, 12:1.33 and 12:2 for AlTPA, CuTPA, AlTSA and CuTSA, respectively.

2.2. Solid characterization

The specific surface area of the salts was estimated by the BET method from the nitrogen adsorption–desorption isotherms at −196 °C, using Micromeritics equipment, model ASAP 2020. Each sample was previously degassed at 100 °C for 1 h.

The X-ray diffraction (XRD) patterns of the bulk salts were recorded with Philips PW-1417 equipment, using Cu Kα radiation, Ni filter, 20 mA and 40 kV in the high voltage source, scanning angle between 5 and 60° of 2θ, and scanning rate of 1° per min.

The Fourier transform infrared (FT-IR) spectra were obtained utilizing Bruker IFS 66 equipment, and pellets of the samples in KBr, measuring in the range 400–4000 cm^{-1}.

The differential scanning calorimetry (DSC) measurements were carried out using Shimadzu DT 50 equipment in argon atmosphere, with a sample weight of 25–50 mg, and a heating rate of 10 °C per min.

The obtained materials were potentiometrically titrated with the purpose of estimating their acidity. To this end, 0.05 g of solid was suspended in 90 cm^3 of acetonitrile, and stirred for 3 h. The suspension was titrated with a 0.05 N solution of n-butylamine in acetonitrile. The potential variation was measured with a Hanna 211 pHmeter, and a double junction electrode.

2.3. Acylation of 2-methoxynaphthalene with acetic anhydride

The activity of the AlTPA, CuTPA, AlTSA, and CuTSA salts in the acylation of 2-methoxynaphthalene (2MN) with acetic anhydride (AA) was measured. The reaction was carried out in a 50 cm^3 glass reactor equipped with a condenser, and magnetically stirred, at 100 °C. The reaction was performed without solvent, employing AA in excess, and using a 2MN:catalyst molar ratio of 1:0.01. The progress of the reaction was followed, and the product analysis