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Tin exchanged heteropoly tungstate: An efficient catalyst for benzylation of arenes with benzyl alcohol

Ch. Ramesh Kumar, K.T. Venkateswara Rao, P.S. Sai Prasad, N. Lingaiah*

Catalysis Laboratory, Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad, AP 500 607, India

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ABSTRACT

The partial exchange of tin with the protons of 12-tungstophosphoric acid (TPA) results in a highly active heterogeneous catalyst for benzylation of arenes with benzyl alcohol as benzylating agent. The catalysts were characterized by X-ray diffraction, Laser-Raman and FT-IR of pyridine adsorption. The catalytic activity depends significantly on the extent of tin exchanged with the protons of heteropoly tungstate. The characterization results suggest the presence of Lewis acidic sites by the exchange of tin. The catalyst with partial exchange of Sn showed high benzylation activity, which in turn related to variation in acidity of the catalysts. The catalyst is highly active for benzylation reaction irrespective of the nature of substituted arenes and benzyl alcohols. These catalysts are highly active compared to other acid catalysts used for benzylation of different arenes. The catalyst is easy to separate from reaction mixture and exhibit consistent activity upon reuse. The plausible reaction mechanism based on the role of both Lewis and Bronsted acid sites of the catalyst was discussed.

1. Introduction

Benzylation of arenes is an important reaction in the synthesis of diarylmethane derivatives, which are useful intermediates in organic and polymer synthesis [1]. Diphenylmethane and substituted diphenylmethanes are industrially important compounds used as pharmaceutical intermediates and fine chemicals [2]. These diarylmethane derivatives have interesting biological and physiological properties. Benzylnaphthalenes are useful as intermediates for organic synthesis in the field of additives for lubricants, dyes and anti oxidants [3]. The common synthetic method for diarylmethane derivatives has been the Friedel–Crafts type alkylation of arenes with benzyl halides using Lewis acid or Bronsted acids as catalysts.

In recent times, a switch from alkyl halide to alcohol, ester or olefins as alkylating agent using late d-block and f-block metal catalysts have been reported [4]. Rare earth metal triflates, Ir/Sn bimetallic complexes [4], are reported for the Friedel–Crafts alkylation. These homogeneous catalysts are not desirable as they are required in stoichiometric quantities, generate waste and involve multi step procedure for their preparation.

There exist few studies where heterogeneous catalysts are used for Friedel–Crafts alkylation [5–10]. However, in most of the cases the benzylating agents are benzyl chlorides. Heterogeneous catalysts such as supported metal triflates [5,6], zeolites [7,8], clay materials [9,10] and mesoporous solid acid catalysts [3,11] are reported. Many of these catalysts are not selective and require longer reaction times to obtain reasonable yields.

Heteropoly acids (HPAs) are promising catalysts with strong acidity used as catalysts for various types of reactions, particularly in selective oxidation and acid-catalyzed reactions [12–14]. The major disadvantage of HPAs as catalysts lies in their low thermal stability, low surface area (1–10 m^2/g) and solubility in polar media. The advantage of HPAs is that they can be made as heterogeneous acid catalysts with high thermal stability by supporting them on suitable supports and/or by exchanging the protons present in HPAs with metal ions [15].

In this paper, tin exchanged 12-tungstophosphoric acid (Sn_xTPA) catalysts with varying Sn content were prepared and evaluated for benzylation of arenes with benzyl alcohols. The catalyst activities were correlated to the extent of Sn exchanged, which results in the variation of Lewis and Bronsted acidity. Benzylation of different arenes with benzyl alcohol, substituted benzyl alcohols and secondary benzyl alcohols were carried to reiterate the scope of the catalysts.

2. Experimental

2.1. Catalyst preparation

A series of tin-exchanged 12-tungstophosphoric acid (Sn_xTPA) catalysts were prepared with varying tin content. In a typical

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* Corresponding author. Tel.: +91 40 27193163; fax: +91 40 27160921.
E-mail address: nakkalingaiah@iict.res.in (N. Lingaiah).

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method required amount of TPA was dissolved in distilled water and to this solution calculated amount of $SnCl_2$ was added with continuous stirring. The resultant mixture was stirred for 3 h and the excess water was evaporated on a water bath at 100 °C. The dried catalyst masses were kept for further drying in an air oven and finally calcined at 300 °C for 2 h. The catalysts are denoted as Sn_xTPA, where x indicates number of Sn atoms in $H_3PW_{12}O_{40}$.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns of the catalysts were recorded on Rigaku Miniflex diffractometer using Cu Kα radiation (1.5406 Å) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045° with account time of 0.5 s and in the 2θ range of 10–80°.

The Fourier Transform Infrared (FT-IR) spectra were recorded on a Bio-rad Excalibur series spectrometer using KBr disc method. The nature of the acid sites (Bronsted and Lewis) of the catalyst samples was determined by FT-IR spectroscopy with chemisorbed pyridine. The pyridine adsorption studies were carried out in the diffuse reflectance infrared Fourier transform (DRIFT) mode. The ratio of Bronsted and Lewis acidities was estimated from the IR peak intensity corresponding to these acid sites.

The total acidity of the catalysts was measured by temperature programmed desorption of ammonia (TPD-NH_3). In a typical experiment, 0.1 g of catalyst was loaded and pretreated in He gas at 300 °C for 2 h and cooled to room temperature. The adsorption of NH_3 is carried out by passing a mixture of 5% NH_3 balanced He gas over the catalyst for 1 h at 100 °C. The catalyst surface was flushed in He gas at 100 °C for 2 h to flush off the physisorbed NH_3. The TPD of the catalysts was carried in a He gas flow at a flow rate of 30 ml/min with a temperature ramp of 10 °C/min. The NH_3 desorption was monitored using thermal conductivity detector (TCD) of a gas chromatograph.

Confocal Micro-Raman spectra have been recorded at room temperature in the range of 100–4000 cm^{-1} using a Horiba Jobin-Yvon LabRam HR spectrometer with a 17 mW internal He–Ne (Helium–Neon) laser source of excitation wavelength 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were usually loosely spread onto a glass slide below the confocal microscope for Raman measurements.

2.3. General alkylation reaction procedure

The alkylation reaction was carried-out in a 50 ml two-necked round bottom flask provided with a reflux condenser. In a typical run, 10 g of anisole and 3.37 g of benzyl alcohol (15:5 molar ratios) along with 0.1 g catalyst were taken in flask. The reaction was carried out at a reaction temperature of 120 °C. The reaction mixture was withdrawn at different intervals and analyzed by a gas chromatography (VARIAN GC-3800) equipped with a SE-30 column and flame ionization detector. The identification of products was made from GC–MS (SHIMADZU-2010) analysis.

3. Results and discussion

3.1. Characterization

FT-IR patterns of Sn_xTPA are shown in Fig. 1. The catalysts showed four characteristic bands in the region of 1100–500 cm^{-1}. The main peaks observed at 1081, 981, 888, and 800 cm^{-1}, were related to the asymmetric stretching vibrations of P–O, $W{=}O_t$, $W{-}O_c{-}W$, and $W{-}O_e{-}W$ respectively of characteristic Keggin ion [16]. This indicates that the Keggin structure remained unaltered during the exchange of TPA protons with tin.

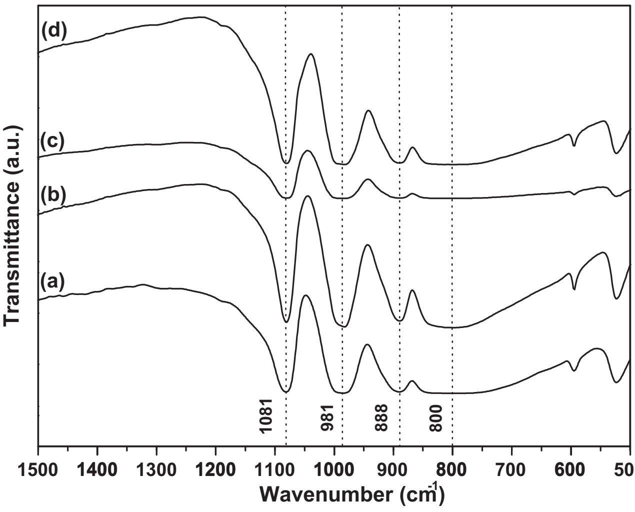

Fig. 1. FT-IR spectra of (a) TPA, (b) $Sn_{0.5}$TPA, (c) Sn_1TPA, and (d) $Sn_{1.5}$TPA catalysts.

Fig. 2 shows the X-ray diffractograms of the catalysts. The XRD pattern suggests the presence cubic structure of highly crystalline heteropoly tungstate. There was no change in the patterns with variation in tin content suggests the existing of Keggin ion structure of tin containing heteropoly tungstate. The XRD results are in support of the observations made from FT-IR.

Raman spectra of Sn_xTPA catalysts are presented in Fig. 3. Heteropoly tungstate shows characteristic Raman bands at 1006, 992 and 905 cm^{-1} related to Keggin ion of TPA [17,18]. The present catalyst showed the symmetric vibration of $W{=}O_t$ band at 1006 cm^{-1} with a shoulder at 992 cm^{-1} [19]. The Raman results endorse the XRD and FT-IR results, which suggest the presence of intact heteropoly tungstate Keggin ion structure even after exchange of tin.

Pyridine adsorption on the surface of solid acid allows one to distinguish different acid sites. FT-IR pyridine adsorption spectra of Sn_xTPA catalysts are shown in Fig. 4. The spectra showed pyridine adsorption bands at 1635, 1607, 1536, 1442, and 1421 cm^{-1}. The band at 1635, and 1536 cm^{-1} were related to Bronsted acid sites [20–22]. Pyridine molecules bonded to Lewis acid sites showed the vibrations at 1607, 1442, and 1421 cm^{-1} [20,21]. The band at 1486 cm^{-1} is a combined band originating from pyridine bonded to both Bronsted and Lewis acid sites [20]. The pyridine adsorption FT-IR spectra suggest the presence of both Lewis and Bronsted acidity.

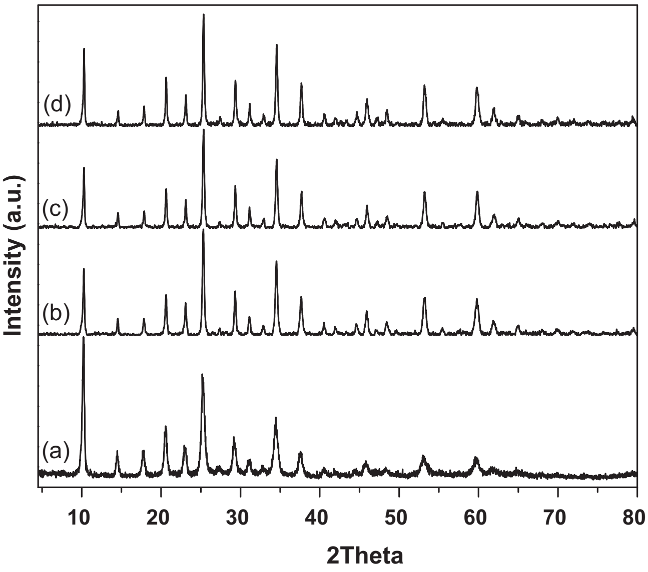

Fig. 2. XRD pattern of (a) TPA, (b) $Sn_{0.5}$TPA, (c) Sn_1TPA, and (d) $Sn_{1.5}$TPA catalysts.