Novel dilacunary phosphotungstate supported onto zirconia: Synthesis, characterization and versatile catalytic activity

Anjali Patel*, Sukriti Singh

Polyoxometalates and Catalysis Laboratory, Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390002, Gujarat, India

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ABSTRACT

Efficient strategy to synthesize dilacunary phosphotungstate has been introduced and a successful attempt was made to stabilize it onto hydrous zirconia. Characterization of the catalyst was carried out by various physicochemical techniques, further confirming its high stability after supporting. Catalytic activity was evaluated for esterification of alcohols as well as oxidation of alkenes with high turn-over numbers. The catalyst was recyclable up to three cycles without any significant loss in the catalytic activity.

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1. Introduction

Lacunary polyoxometalates (LPOMs) are a subclass of POMs and can be formed by removal of one or two M-O units from the fully occupied POMs, $[XM^{VI}_{12}O_{40}]^{n-}$, gives rise to mono and di lacunary POMs, $[XM^{VI}_{11}O_{39}]^{(n+4)-}$ and $[XM^{VI}_{10}O_{36}]^{(n+5)-}$ respectively [1,2]. The replacement of one or more addenda atoms is expected to tune the acidic as well as redox properties which can lead to the development of active and selective catalysts.

Among the LPOMs the mono lacunary derivatives of Keggin type silicotungstate [3–6] and phosphotungstates [7–15] have been well explored by number of groups especially as heterogeneous catalysts. Considerable work has been carried out by Mizuno and group on the synthesis, stability and crystal structure of dilacunary silicotungstates [16–19]. They have also been explored as active catalysts for the oxidation of several hydrocarbons, olefins with H_2O_2 [20–22]. Recently, Ren et al. introduced heterogeneous catalyst based on γ-decatungstosilicate supported on amine functionalized MCM-41 [23]. The catalyst was tested for reusability through repeated catalytic conversions of methyl phenyl sulfide to methylphenyl sulfone with hydrogen peroxide.

A literature survey shows that the di-lacunary analogue of polyoxotungstate (dilacunary decatungstogermanate $[\gamma\text{-GeW}_{10}O_{36}]^{8-}$) has proven to be highly reactive with various electrophiles and the synthesis as well as characterization is well known [24]. The catalytic activity of TBA salt of γ-Keggin germanodecatungstate, $[\gamma\text{-H}_2\text{GeW}_{10}O_{36}]^{6-}$ as homogeneous catalyst for Knoevenagel condensation of active methylene compounds with carbonyl compounds was independently investigated [25]. Thus, most of the work has been reported on dilacunary silico/germanitungstates.

However, the only report on dilacunary phosphotungstate in literature was by Knoth and Harlow in 1981 [26]. in which they reported the direct synthesis of cesium salt of dilacunary phosphotungstates from sodium tungstate, sodium dihydrogen phosphate and cesium chloride at pH 7. The area of dilacunary phosphotungstate has not been explored due to following difficulties: 1) presence of different species, 2) dependence on W:P ratio, 3) counter cation as well as pH. These dilacunary polyanions have been generated insitu in the reaction medium for formation of various transition metal substituted POMs [27]. Moreover, no literature is available on the catalytic aspects of supported di-lacunary phosphotungstate.

In the present work, an attempt has been made for synthesis, isolation as well as stabilization of $[PW_{10}O_{36}]^{7-}$ (PW_{10}) onto a suitable support. It is well known that the support provides an opportunity for active species to be stabilized by dispersion over a large surface area. Hydrous zirconia (ZrO_2) [28] was selected as a support due to following reasons: availability of surface hydroxyl groups of hydrous zirconia; provides chemical or strong interaction with active species and our expertize in using hydrous zirconia as support. Thus the prospect of supporting these species on metal oxide supports emerges as an attractive pathway to exploit the catalytic activity and opened the opportunity to create more active and selective catalytic system.

The synthesized PW_{10} was characterized primarily by ^{31}P solution NMR, cyclic voltammetry, EDS and FT-IR to identify the

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* Corresponding author. Tel.: +91 265 279552.
  E-mail address: aupatelchem@gmail.com, aupatel_chem@yahoo.com (A. Patel).

formation of dilacunary species. A series of catalysts comprising of 10–40% loading of PW_{10} onto ZrO_2 were synthesized. The catalyst was characterized by TG-DTA, FT-IR, FT-Raman, surface area, acidity determination [29] and Leaching test [30], XRD and SEM analysis. The catalytic activity was investigated for acid catalyzed esterification reactions of primary/secondary alcohols with different chain lengths of acids. Solvent free liquid phase oxidation of styrene with H_2O_2 was carried out and the scope of oxidation reaction was also extended to variety of alkene substrates. The recycling capability of the catalyst as well as heterogeneous stability were investigated.

2. Experimental section

2.1. Materials

All chemicals used obtained from Merck (A. R. grade) and used as received. Zirconium oxychloride ($ZrOCl_2$) (Loba Chemie, Mumbai), sodium tungstate, anhydrous disodium hydrogen phosphate, *n*-butanol, *iso*-butanol, 2-butanol, iso-amyl alcohol, cyclohexanol, benzyl alcohol, formic acid, acetic acid, propionic acid, styrene, nitric acid, 30% H_2O_2 and acetone.

2.2. Synthesis of dilacunary phosphotungstate and the support

In a typical synthesis stoichiometric ratio ratios of Sodium tungstate dihydrate (0.2 mol, 6.8 g) and anhydrous disodium hydrogen phosphate (0.02 mol, 0.2 g) were dissolved in 150–200 mL of distilled water. The resultant solution was heated to 80–90 °C and 6.5 pH was adjusted with concentrated nitric acid. By evaporation, the volume was reduced to half and by liquid-liquid extraction with 80–100 mL of acetone the heteropolyanion was separated. The extraction was repeated until the extract shows absence of nitrate ions. The solid was air dried and the acquired sodium salt of dilacunary phosphotungstate was designated as PW_{10}. The support zirconia was prepared by precipitation method reported by us earlier [28].

2.3. Supporting of PW_{10} onto hydrous zirconia (ZrO_2)

Different loading of catalyst was carried out by impregnating 1 g of ZrO_2 with an aqueous solution PW_{10} (0.1–0.4 g/10–40 mL of distilled water) and dried at 100 °C for 10 h. The series catalysts containing 10–40% PW_{10} were designated as $(PW_{10})_1/ZrO_2$, $(PW_{10})_2/ZrO_2$, $(PW_{10})_3/ZrO_2$ and $(PW_{10})_4/ZrO_2$. The selected best catalyst $(PW_{10})_2/ZrO_2$ was calcined at 200, 300 and 400 °C in air for 5 h and designated as $(PW_{10})_{22}/ZrO_2$, $(PW_{10})_{23}/ZrO_2$ and $(PW_{10})_{24}/ZrO_2$.

2.4. N-Butyl amine acidity determination

The acidity determination was carried out by taking 0.025 M solution of n-butylamine in toluene [29]. The 0.5 g catalyst was suspended in 50 mL solution of 0.025 M n-butyl amine solution for 24 h. The excess base was titrated against trichloroacetic acid using neutral red as an indicator. This provides the total acidity of the material.

2.5. Characterization of materials

Cyclic Voltammetry for PW_{10} was performed on the CH 620A system at room temperature. A glassy carbon working electrode and an Ag/AgCl reference electrode was used. ^{31}P solution and NMR (161.97 MHz, external 85% H_3PO_4) was recorded on the BRUKER instrument. Elemental analysis was carried out using the JSM 5610 LV EDX-SEM analyzer. TGA was carried out on

the Mettler Toledo Star SW 7.01 up to 600 °C. FT-IR spectra of the samples were obtained by using the KBr wafer on the Perkin Elmer instrument. The Raman spectra were recorded on a FT-Raman Spectrophotometer (Model Bruker FRA 106). Adsorption-desorption isotherms of samples were recorded on a Micromeritics ASAP 2010 Surface area analyzer at °196 °C. From the adsorption desorption isotherms, specific surface area was calculated using BET method. The XRD pattern was obtained by using PHILIPS PW-1830. The conditions were: Cu Kα radiation (1.5417 Å), scanning angle from 0° to 60°. The support and supported catalyst was characterized for the scanning electron microscopy using a Jeol SEM instrument (model- JSM-5610LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range and images taken at a magnification of 100 X for ZrO_2 and single particle image at 1000 X for $(PW_{10})_2/ZrO_2$.

2.6. Catalytic reactions

The esterification reaction of *n*-butanol with acetic acid (mole ratio 1:4.4) was carried out in a 50 mL round bottom flask (attached with Dean-Stark apparatus) containing catalyst at 80 °C with continuous stirring for 4 h in a magnetic stirrer. Similarly reactions were carried out by changing the corresponding concentration of acid and different amount of catalyst. The mole ratio of alcohol to acid for esterification of *iso*-butanol, 2-butanol and *iso*-amyl alcohol was kept at 1:4.4 while for cyclohexanol it was 1:3. The obtained products were analyzed by a gas chromatograph (Shimadzu-2014) equipped with capillary column.

Oxidation of alkenes were carried out in two necked flask provided with double walled condenser, alkene (10 mmol) and 30% aq. H_2O_2 (30 mmol) with constant stirring. The catalyst was removed and product was extracted with dichloromethane after completion of reaction. The product mixture was dried with magnesium sulfate and analyzed on a GC using a capillary column. GC analyses were carried out according to the following temperature program: initially, the oven temperature was set at 80 °C, then the temperature increased from 80 °C to 220 °C, with a rate of 10 °C/min. Detector temperature was set at 240 °C. Product identification was carried out by comparison with authentic samples and finally by combined GC–MS.

2.7. Leaching test

For any catalyst leaching is a negative property and leaching of the active species from the support will make the catalyst unattractive. When polyoxometalates react with ascorbic acid (a mild reducing agent), it develops blue coloration that is used for the quantitative characterization for the leaching [30]. In the present case there is no development of blue color indicating absence of leaching. On repeating the same procedure with alcohols and acids as well as with the filtrate of the reaction mixture after the reaction there no leaching found.

3. Results and discussion

3.1. Catalyst characterization

^{31}P NMR is the most important method to study the chemical environment around phosphorus in heteropoly compounds. Massart et al. [31] reported, in 1977 that removal of one WO unit from PW_{12} (12-tungstophosphoric acid) has a larger effect on the chemical shift value rather than the successive removal of other W from the parent. As a results δ shift of 4.5 ppm (from PW_{12}) is expected for mono lacunary PW_{11} *i.e.* −10.5 ppm [31] and almost same δ shift value is expected for dilacunary species PW_{10}. In particular, when the successive removals of W atoms affect the same O_a,