Synthesis, characterization and catalytic activity of new solid acid catalysts, $H_3PW_{12}O_{40}$ supported on to hydrous zirconia

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Abstract

New solid acid catalysts have been synthesized by comprising heteropolyacid (HPA) on to hydrous oxide. A series of catalysts containing 20–70% of 12-tungstophosphoric acid (PW) on to hydrous zirconia (Z) are synthesized. All resulting amorphous materials have been characterized by chemical analysis, chemical stability, ion exchange capacity, FTIR, TGA, surface area measurement and XRD. Catalytic activity of the materials have been evaluated for esterification of cyclohexanol to cyclohexyl acetate. The selected material was calcinated at 300 and 500 °C. The FTIR and DRS spectra of the materials were recorded to study the nature of the species present on the support. These studies indicate that the 12-tungstophosphoric acid keeps its Keggin-type structure unaltered up to 500 °C when supported on to hydrous zirconia. Based on the above experimental findings, catalytic performance was optimal with a loading of 30% of 12-tungstophosphoric acid on to hydrous zirconia.
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1. Introduction

The catalytic function of heteropolyacids (HPAs) and related polyoxometallate compounds has attracted much attention particularly in the last two decades. It is a field of increasing importance [1–7] in which new and promising developments are being carried out both at research and technological level [8]. HPAs are widely used as model systems for fundamental research. They provide good basic for the molecular design of mixed oxide catalysts and they have high capability in particular uses.

HPAs are very good acid catalysts in homogeneous medium. They catalyze a wide variety of reactions in homogeneous phase offering strong option for effi-cient and cleaner processing compared to conventional mineral acids [1,5,6,9–11]. Though, there are many advantages, the main disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area (1–10 m^2/g) and separation from reaction mixture.

Thus, the development of new solid catalyst with advanced characteristics of strength, surface area, porosity, etc. has been a challenge for a long time. The supporting of HPAs on the suitable support is expected to overcome the mentioned problems of HPAs. Various supports like silica [2,12–14], alumina [13], active carbon [15–18], MCM-41 [19] have been used for supporting HPAs.

The literature survey shows that hydrous oxides have multiphase applications. The surface hydroxyl groups of the hydrous oxides are responsible for the ion exchange behavior. Much of the work has been done on the ion exchange and sorption properties of

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hydrous oxides [20–22] of group (IV) since they are interesting from the view point of their acid–base property. Not much work has been done on the catalytic property of the same. The ion exchange process can also be useful in catalyst development. It was therefore thought of interest to make use of the hydrous oxide as the catalyst carrier.

The present contribution consists of synthesis of amorphous new solid acid catalysts comprising 12-tungstophosphoric acid (PW) on to a hydrous oxide, hydrous zirconia (Z). A series of catalysts containing 20–70% PW were synthesized. The new amorphous materials and support have been characterized by chemical analysis, chemical stability, ion exchange capacity, FTIR, TGA, surface area measurement and XRD. The catalytic activity has been investigated by carrying out esterification of cyclohexanol to cyclohexyl acetate. The FTIR and DRS spectra of the selected calcinated materials were recorded to study the nature of the species present on the support.

2. Experimental

2.1. Materials

All chemicals used were of A. R. grade. $H_3PW_{12}O_{40} \cdot nH_2O$ (Lobachemie, Mumbai), $ZrOCl_2 \cdot 8H_2O$ (SD Fine Chemicals, Mumbai) were used as received. Cyclohexanol and glacial acetic acid were obtained from Sisco Chem. Pvt. Ltd., Mumbai, and used as received.

2.2. Preparation of the support, hydrous zirconia (Z)

Hydrous zirconia was prepared by adding an aqueous ammonia solution to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (0.31 M) up to pH 8.5. The precipitates were aged at $100\,^{\circ}C$ over a water bath for 1 h, filtered, washed with conductivity water until chloride free water was obtained and dried at $100\,^{\circ}C$ for 10 h. The obtained material is designated as Z.

2.3. Preparation of the catalysts

A series of catalysts containing 20–70% PW were synthesized by impregnating 1 g of Z with an aqueous solution of $H_3PW_{12}O_{40}$ (PW) (0.2–0.7 g/20–70 ml of conductivity water) at $100\,^{\circ}C$ with stirring for 10 h. The materials thus obtained were designed as H_2, H_3, H_4, H_5, and H_7. Further calcinations of H_3 has been carried out at 300 and $500\,^{\circ}C$ in air for 10 h. The resulting samples were named as H_{33} and H_{35}, respectively.

2.4. Catalytic reaction

The catalytic reactions were carried out in a round bottom flask provided with a double-walled condenser. In a typical reaction, the corresponding glacial acetic acid (18 g) and cyclohexanol (10 g) were taken and the catalyst was then added in the required amount. The amount of ester formed was analyzed on a Shimadzu gas chromatogram using Carbowax 20 column. The esterification reaction has been carried out, for whole series, with varying amount of catalyst.

2.5. Characterization

Zirconium was determined gravimetrically as zirconium oxide by cupferron method. Chemical stability of the materials has been checked in different mineral acids and bases. The ion exchange capacity was determined by column method using the following formula:

$$IEC\,(meq./g) = \frac{\text{normality of NaOH} \times \text{volume of NaOH}}{\text{amount of material}}$$

The thermogravimetric analysis of the samples were performed on Shimadzu thermal analyzer model DT 30 at a heating rate of $10\,^{\circ}C/min$. Adsorption–desorption isotherms of samples were recorded on a Carl Erba Sorptomatic Series 1800 at $-196\,^{\circ}C$. From the adsorption–desorption isotherms, specific surface area was calculated using Brunner–Emmett–Teller (BET) method. The FTIR spectra of the samples were obtained using KBr wafer on BOMEM model MB-104, Canada. The XRD patterns were obtained by using Mini Slex, Ri Kagu XRD. The conditions used were: Cu Kα radiation (1.5417 Å), scanning angle (2θ) from 5–60°. The DRS spectra of PW and H_3, H_{33}, and H_{35} were recorded on a Shimadhu PR 1 instrument using barium sulfate as a reference.

Table 1
Ion exchange capacity of all materials

Materials	Ion exchange capacity (meq./g)
Z	0.16
H_2	0.22
H_3	0.62
H_4	0.58
H_5	0.56
H_7	0.58

Table 2
Surface area measurements (BET method)

Materials	Surface area (m^2/g)
Z	170
H_2	182
H_3	146
H_4	123
H_5	122
H_7	123

3. Results and discussion

The number of water molecules n was determined from TGA curves using Alberti–Torracca formula [23]. From the chemical analysis and thermogravimetric analysis, the formula for the Z is proposed as $ZrO_2 \cdot H_2O$. The present materials show no change in color or form on heating with water. The materials are stable in different mineral acids like HCl, H_2SO_4, HNO_3 and bases like NaOH, Na_2CO_3 up to 4 M concentration.

Table 1 shows the values of ion exchange capacity. The values of ion exchange capacity gives an idea for the acidity of material. It is an indirect way to determine the acidity of the materials. It is seen from Table 1 that the acidity of all supported samples is more than that of Z. But among H_2, H_3, H_4, H_5, and H_7, the ion exchange capacity of H_3 is found to be highest indicating H_3 is more acidic.

The TGA of Z (Fig. 1) indicates about 13% weight loss within a temperature range of 100–180 °C corresponding the loss of adsorbed/hydrogen bonded water molecules, after which there is no significant change in weight obtained till 600 °C. The TGA of H_2, H_3, H_4 (Fig. 1), H_5, and H_7 show only 8, 7, 6, 5, and 3% weight loss, respectively, within the same temperature range and there is no appreciable change in weight till 600 °C indicating increase in the stability. This may be due to the formation of strong intermolecular hydrogen bond between the outer oxygen present in the structure of HPA and H^+ of the support. These intermolecular hydrogen bonded water molecules are strongly held and hence cannot be removed at lower temperatures. This results in the decrease in percentage weight loss indicating the presence of chemical interaction.

The values of surface area for all materials are listed in Table 2. It is known [24] that there may be decrease in surface area in case of the supported catalyst in which oxides are used as supports. This is because of strong interaction of HPA with the oxide support. With increase in the percent loading of HPA, the surface area decreases (expect for H_2). This may be due to strong interaction of HPA with hydrous zirconia, that is suggested by TGA analysis as well. Almost the same value of surface area for H_4, H_5, and H_7 indicates the stabilization/blocking of the sites.

The XRD pattern of H_3 shows no crystalline structure. This may be due to a high dispersion of solute on the support surface.

The FTIR spectra of Z (Fig. 2) shows broad band in the region of $3400 \, cm^{-1}$. This is attributed to asymmetric hydroxo (–OH) and aquo (–OH) stretches. Two types of bending vibrations at 1600 and $1370 \, cm^{-1}$ are observed indicating the presence of –(H–O–H)– bending and –(O–H–O)– bending, respectively. It also shows a weak bending band at $600 \, cm^{-1}$ attributed to a presence of Zr–O–H bond. In addition to these bands, the FTIR spectra of H_2, H_3, H_4, H_5, and H_7 show bands at 812, 964, and $1070 \, cm^{-1}$. FTIR spectra of H_3 is shown (Fig. 2) as an example. These can be assigned to the symmetric stretching of (W–O–W), W=O, P–O, respectively, and the positions are in good agreement with those reported earlier [6] confirming the presence of these groups in the prepared materials. There is a slight shift in the FTIR bands of H_{33} and H_{35} as compared to that of H_3. It shows a weak shoulder at $825 \, cm^{-1}$, bands at 972 and $1078 \, cm^{-1}$ indicating that the 12-tungstophosphoric acid keeps its Keggin-type structure up to 500 °C.

Electronic absorption spectra gives information about the non-reduced heteropolyanion [25] due to ligand (oxygen) to metal charge transfer [26]. The electronic spectra of H_3, H_{33}, and H_{35} are shown in Fig. 3. The spectra shows λ_{max} at 260 nm which is in
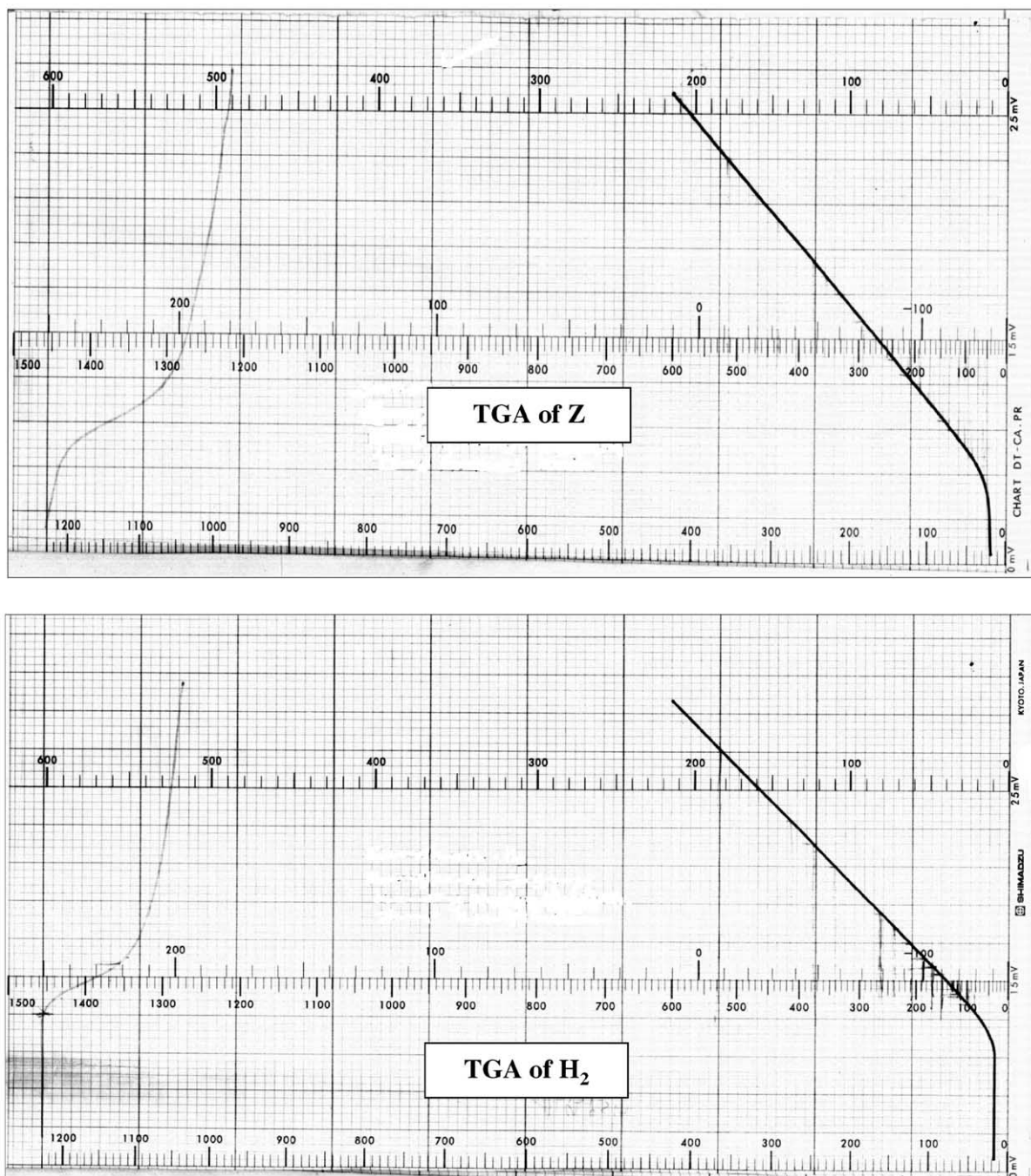
Fig. 1. TGA of: (a) hydrous zirconia (Z); (b) 20% $H_3PW_{12}O_{40}$ supported on to hydrous zirconia (H_2); (c) 30% $H_3PW_{12}O_{40}$ supported on to hydrous zirconia (H_3); (d) 40% $H_3PW_{12}O_{40}$ supported on to hydrous zirconia (H_4).
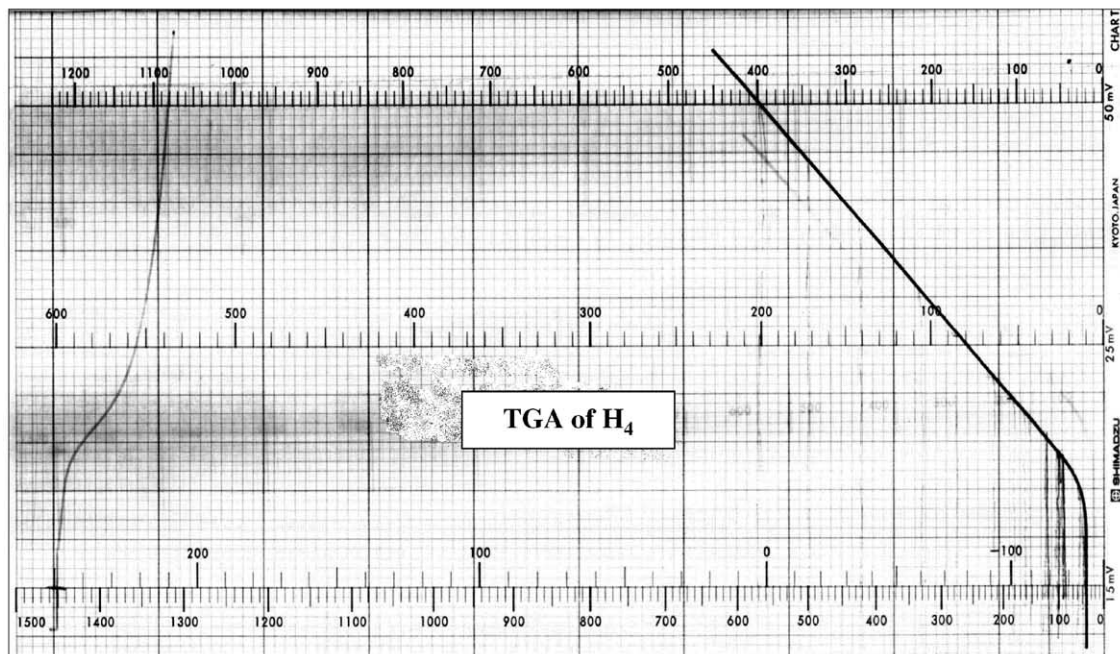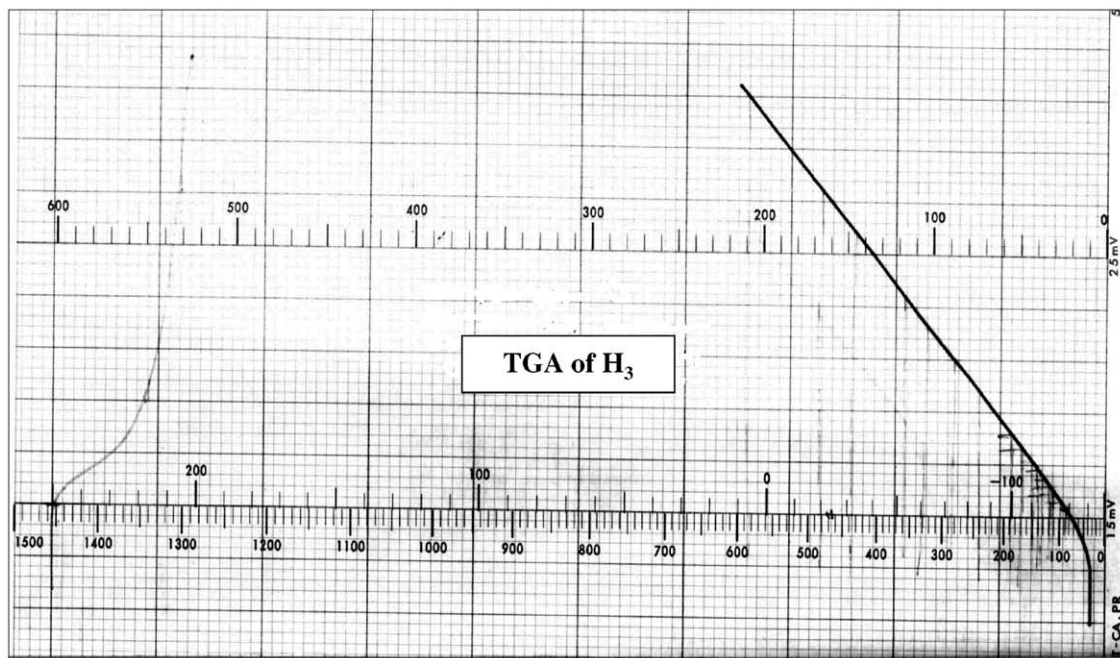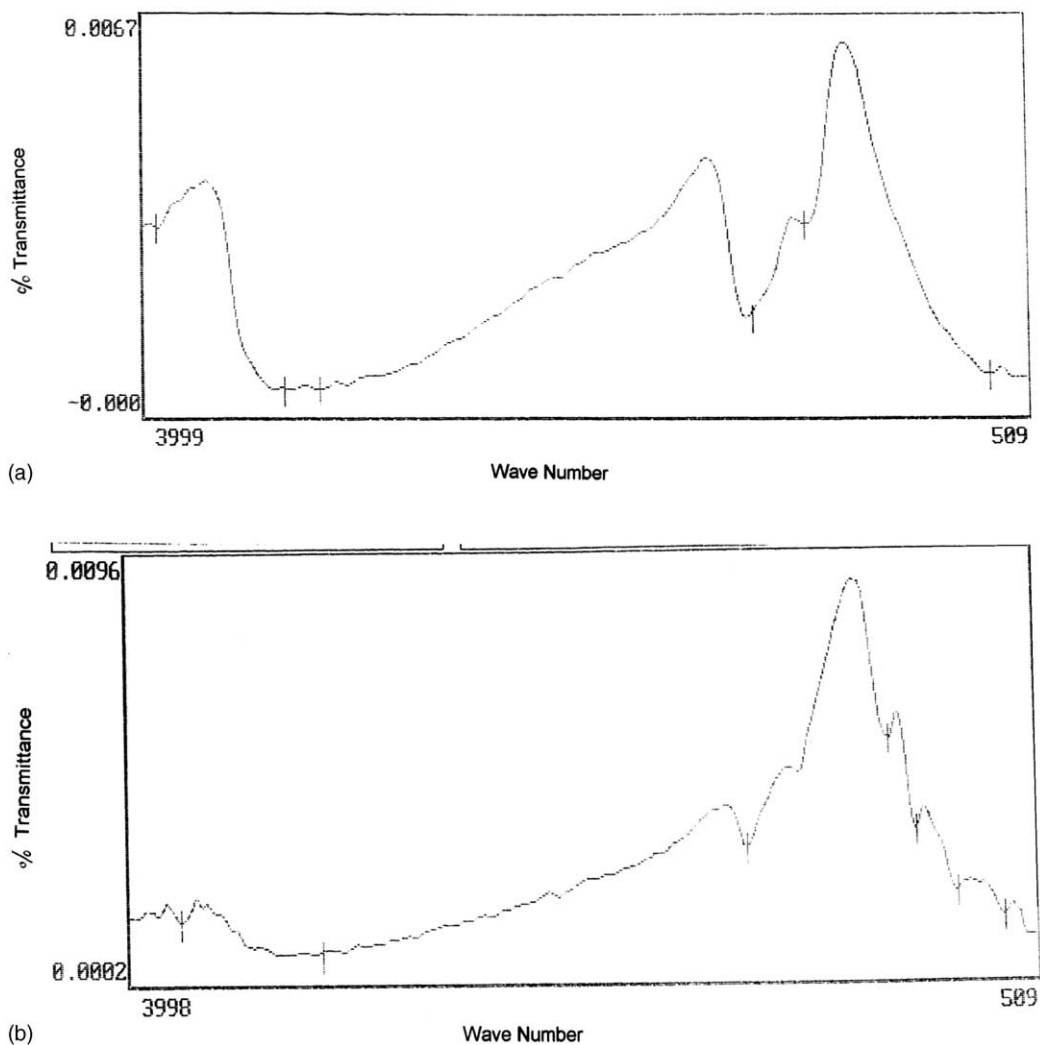
Fig. 1. (*Continued*).

Fig. 2. FTIR spectra of: (a) Z and (b) H_3.

good agreement as reported earlier [6] suggesting the presence of the undegraded $H_3PW_{12}O_{40}$ species. In other words, the Keggin phase remains unaltered up to 500 °C.

3.1. Catalytic reactions

The esterification of carboxylic acid is a straight forward reaction subject to general Bronsted acid catalysis. The reaction of cyclohexanol with acetic acid is carried out as a test reaction to examine the catalytic activity.

The yields can be increased by increasing the concentration of either alcohol or acid [27]. In a practical situation, when one wants to prepare an ester, it is desirable to obtain the maximum yield. For economic reason, the reactant that is usually the less expensive of the two is taken in excess. In the present study, acetic acid has been used in excess.

The percentage yield of cyclohexyl acetate has been listed in Table 3. It is seen from Table 3, that H_3 (yield is 68%) is the best catalyst among all. The optimum conditions for the present reaction are as follows:
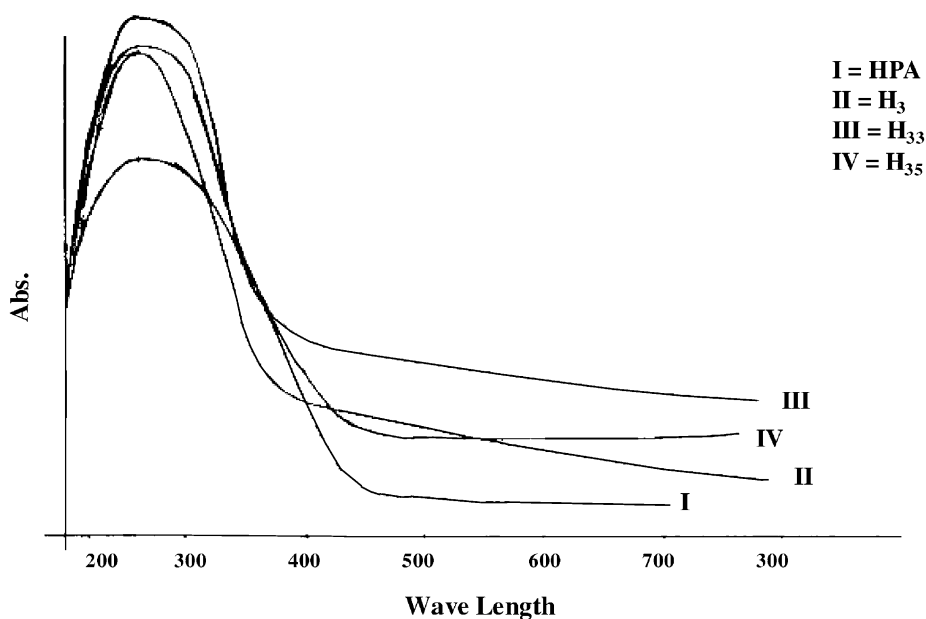
Fig. 3. DRS of: (i) parent $H_3PW_{12}O_{40}$ (PW); (ii) 30% PW supported on to hydrous zirconia (H_3); (iii) H_3 calcinated at $300\,^\circ$C for 10 h (H_{33}); (iv) H_3 calcinated at $500\,^\circ$C for 10 h (H_{35}).

- amount of the catalyst (H_3) = 0.5 g;
- temperature = refluxing temperature
- time = 4 h.

The catalyst (H_3) was regenerated by washing with conductivity water several times and dried at $100\,^\circ$C.

Table 3
Percentage of cyclohexyl acetate by varying the amount of catalyst

Name of the catalyst	Amount of the catalyst (g)	Cyclohexyl acetate (% yield)
Z	0.5	38
	1.0	50
H_2	0.5	40
	1.0	58
H_3	0.5	68
	1.0	72
H_4	0.5	60
	1.0	70
H_5	0.5	63
	1.0	69
H_7	0.5	62
	1.0	70

In the regenerated sample, the yield decreased by 5%. The yield becomes constant on further regeneration.

The method has clear advantages over the conventional method [28] where dry HCl is used as a catalyst for preparing the ester and where the yield is 54%. Further, the use of H_3 as a solid acid catalyst has advantages of better activity, short reaction time, simple distillation of ester produces, low reaction temperature, without post-treatment requirement, non-corrosive and no contamination. Besides the catalyst can be regenerated and reused.

The catalytic activity can be correlated with the values of surface area measurement. Table 3 shows that the percentage yield of H_4, H_5, and H_7 is almost the same which is supported by the value of surface area measurement (Table 2). This is in good agreement with the surface-type catalyst in which catalytic activity is proportional to the surface area of the catalyst [6].

4. Conclusion

FTIR and DRS spectra shows that the 12-tungstophosphoric acid keeps its Keggin-type structure when

supported on to hydrous zirconia and the supported structure does not get destured up to $500\,°C$. The solid acid catalyst H_3 gives 68% of cyclohexyl acetate which is better than the conventional method which gives 54%. There is a wide range of condition in which supported 12-tungstophosporic acid can be used as a catalyst.

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