An enhancement in the thermal stability and acidity of hydrous zirconia in presence of 12-tungstophosphoric acid

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A new solid acid catalyst, 12-tungstophosphoric acid supported on hydrous zirconium(IV) oxide has been prepared, and designated as PW/Z. The solid catalyst as well as hydrous zirconium(IV) oxide have been characterized by chemical analysis, chemical stability, ion exchange capacity, FTIR, TGA and surface area measurement (BET method). The catalytic activity has been examined by carrying out esterification as a model reaction.

There is a strong demand for new solid acid catalyst, having advanced characteristics to replace conventional liquid catalysts such as sulfuric acid in the title reaction. The renewed interest in this area is primarily because the replacement of homogeneous liquid acids by heterogeneous solid acid as catalysts in the chemical industry is expected to bring many advantages such as ease of separation from reaction mixture, which allows continuous operation, as well as regeneration and reutilization of the catalyst. Hydrous oxide can act as a Brønsted acid since H+ of the hydroxyl group is replaceable. Many studies have been reported on the ion exchange and sorption properties of hydrous oxides of group IV since they are interesting from the viewpoint of their acid-base property. The ion exchange process can also be useful in catalyst development.

On the other hand, heteropolyacids (HPAs) are very good acid catalysts in homogeneous medium. They catalyse a wide variety of reactions in homogeneous phase offering strong option for more efficient and cleaner processing compared to conventional mineral acids. Being stronger acids (HPAs) will have significantly higher catalytic activity than mineral acids. Further, HPA catalysis lacks side reactions such as sulfonation, chlorination, nitration, etc., which occurs with mineral acids. Unfortunately, as they are highly soluble in polar media, it is difficult to separate them from the reaction products.

It is known that there is formation of new active centers as well as high concentration of surface active species in the case of supported catalyst. This results in a significant increase in the activity of the anchored catalyst. Hence it was thought of interest to prepare a new solid acid catalyst by combining two types of acid catalysts. For this purpose the strongest heteropolyacid in the Keggin’s series, 12-tungstophosphoric acid, H₃PW₁₂O₄₀ (PW) was selected. Among the hydrous oxides, zirconium(IV) oxide(Z) was selected because of its interesting acid-base properties for supporting the HPA.

The present note consists of synthesis and characterization of amorphous hydrous zirconium(IV) oxide(Z) and PW supported onto Z(PW/Z). Both the materials have been characterized by chemical analysis, chemical stability, ion exchange capacity, FTIR, TGA, surface area measurement (BET method) and esterification reaction.

Experimental

The tungstophosphoric acid, H₃PW₁₂O₄₀·nH₂O, zirconium oxychloride, ZrOCl₂·8H₂O and Liq. NH₃ were obtained from Loba Chemie, GR grade.

Preparation of hydrous zirconium(IV) oxide and H₃PW₁₂O₄₀ supported onto hydrous zirconium(IV) oxide

Hydrous zirconium(IV) oxide(Z) was prepared by adding an aqueous ammonia solution to an aqueous solution of ZrOCl₂·8H₂O (0.31 M) up to pH 8.5. The precipitates was aged at 100°C over a water bath for 1 hour, filtered, washed with conductivity water until chloride-free water was obtained and dried at 100°C for 10 hrs. The obtained gel was converted to 60 - 100 mesh size by sieving. H₃PW₁₂O₄₀ supported on Z was prepared by impregnation of Z with an aqueous solution of heteropolyacid, PW (0.3 gm in 30 ml of conductivity water). The resulting suspension was dried at 100°C for 10 hrs. The sample obtained was designated as PW/Z.

The catalytic reactions were carried out in a round bottom flask provided with a double walled condenser. In a typical reaction, the corresponding acid and alcohol were taken and the catalyst was added in the required amount. The mixture was heated to gentle reflux for 2 hrs. The amount of ester formed was
analyzed on a Shimadzu gas chromatogram using Carbowax 20 column. The esterification reaction was carried out with varying amounts of the catalyst.

Zirconium was determined gravimetrically as zirconium oxide by cupferron method. Chemical stability of the materials was checked in different mineral acids and bases. The ion exchange capacity was determined for Z as well as for PW/Z by column method.

The thermogravimetric analysis of the samples were performed on a Shimadzu thermal analyser model DT 30 at a heating rate of 10°C/min. The plot of % wt present against temperature was plotted. The activation energy for the degradation of the materials was determined. The number of water molecule, n, was also determined from TGA. The FTIR spectra of the samples were obtained using KBr wafer on BO-MEM (Model MB - 104, Canada). Adsorption-desorption isotherms of samples were recorded on a Carl-Erba Sorptomatic series 1800 at -196°C. From the adsorption-desorption isotherms, specific surface area was calculated using Brunauer-Emmett-Teller (BET) method.

Results and discussion

The number of water molecule ‘n’ was determined from TGA curves using Alberti-Torracca formula. From the chemical analysis and thermogravimetric analysis, the formula for the Z may be proposed as, ZrO$_2$.H$_2$O.

The prepared materials showed no change in colour or form on heating with water. They were found to be stable in different mineral acids like HCl, H$_2$SO$_4$, HNO$_3$ and bases like NaOH, Na$_2$CO$_3$ up to 4 M concentration.

The ion exchange capacity for Z and PW/Z was found to be 0.16 meq/g and 0.58 meq/g respectively indicating an increase in acidity of Z by supporting PW on it.

The TGA of Z indicates about 13% weight loss within a temperature range of 100-180°C corresponding to the loss of adsorbed/hydrogen bonded water molecules, after which the change in weight was highly reduced till 600°C. The TGA of PW/Z showed only 6% weight loss within the same temperature range and there was no appreciable change in weight till 600°C. This decrease in percentage weight loss may be explained by the interaction of PW with Z. The outer oxygen present in the structure of heteropolyacid (PW) may interact with the H$^+$ of the hydrous zirconium oxide and form strong intermolecular hydrogen bond. 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 TGA of a simple mixture containing Z and 12-tungstophosphoric acid showed two weight losses in two different stages, i.e., at 120°C and at 350°C. The weight loss at 120°C corresponds to the loss of adsorbed/hydrogen bonded water and the weight loss at 350°C due to the decomposition of 12-tungstophosphoric acid. The plot of percentage weight present versus temperature (Fig. 1) indicates an increase in the stability of PW/Z as compared to that of Z. The thermal stability of the present systems was quantified in terms of activation energy. The values for the energy of activation were calculated from the Broido equation, $\ln[\ln(1/y)] = -E/RT + C$, where y = fraction of weight at tempera-

![Fig. 1—% Weight present versus temperature (1, hydrous zirconia oxide; 2, PW/Z)](image-url)
ture \( T, E \) = activation energy, \( R \) = gas constant in Joules.

From straight line plots of \( \ln[\ln(1/y)] \) versus \( 1/T \), the activation energies were found to be 24 and 28 KJ for Z and PW/Z respectively. This shows that the energy required for degradation of PW/Z is larger than that for Z, indicating that the stability of PW/Z is more than that of Z. The increased stability of PW/Z may be due to the chemical interaction between PW and Z.

The FTIR spectra of Z shows a 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 the presence of Zr-O bond. In addition to these bands, the FTIR spectra of PW/Z shows bands at 812, 964 and 1070 cm\(^{-1}\). These can be assigned to the asymmetric stretching of (W-O-W), W=O, P-O, respectively and are in good agreement with that reported earlier\(^{13}\) confirming the presence of these groups in the prepared material. The corresponding bands in free HPA were observed at 812, 982 and 1080 cm\(^{-1}\) position. The shifts in these bands indicate chemical interaction between PW and Z.

The surface area for Z and PW/Z were found to be 170 and 123 m\(^2\) g\(^{-1}\) respectively. It is known\(^{22}\) that there may be decrease in surface area in the supported catalyst in which oxides are used as supports. This is because of strong interaction with the oxide support. A decrease in the surface area of PW/Z is observed as compared to that of Z. This may be due to strong interaction of heteropolyacid with hydrous zirconium(IV) oxide. This is suggested by TGA analysis as well.

**Catalytic reactions**

The esterification of carboxylic acid is a straightforward reaction subject to general Brönsted acid catalysis. The reaction of ethyl alcohol with acetic acid was selected as a model reaction.

\[
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{H^+} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}
\]

The yields can be increased by increasing the concentration of either alcohol or acid\(^{23}\). In a practical situation, when one wants to prepare an ester, it is desirable to obtain the maximum yield of pure products. For economic reasons, the reactant that is usually the less expensive of the two is taken in excess. In the present study, acetic acid was used in excess. The optimum conditions for the present reaction was found to be, amount of catalyst (PW/Z) = 0.5 g; temp. = 70°C; time = 2 h; yield=24.

The catalyst was regenerated by washing with conductivity water several times and dried at 100°C. In the regenerated sample the yields decreased by 5%. The yield became constant on further regeneration. A comparison of yield in presence of Z or PW/Z as catalysts shows that PW/Z is a better catalyst than Z. This is in agreement with the greater acidity and ion exchange capacity of PW/Z as discussed earlier.

The method has clear advantages over the conventional method where sulfuric acid is used as a catalyst for preparing the ester; while the yields are high, traces of sulfuric acid are difficult to remove. When PW/Z is used as a solid acid catalyst, the ester can be simply distilled over and there is no catalyst contamination. Besides the catalyst can be regenerated and reused.

**References**


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