Use of zirconium tungstate in acid catalysis:
Some esterification reactions

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Amorphous zirconium tungstate, an inorganic cation exchanger has been prepared. The protons of the hydroxyl groups are the active sites. Such a material indicates good potential for application in Brönsted catalysis. Esterification has been studied as a model reaction wherein ethyl acetate has been synthesized. The variation of several parameters has established the use of zirconium tungstate as a Brönsted acid catalyst.

Acid salts of tetravalent metals are usually obtained as amorphous materials¹, but of late they have been obtained as crystalline compounds². An extensive literature on their synthesis, structure and properties has accumulated³-⁶. These compounds have general formula M(IV)(HXO₄)₂nH₂O where M(IV) = Ti, Zr, Ce, Th etc. and X = P, As, W, Mo. They can be prepared in the form of granules in a range of mesh sizes, by simply combining tetravalent metals and polybasic acids to obtain insoluble gelatinous precipitates at room temperature, with or without refluxing. The compounds show a great promise in preparative reproducibility, and stability, both thermal and chemical.

The hydroxyl protons of the acid salts can be easily replaced by other cations. Owing to their peculiar properties, such as selectivity for certain ions, high stability in strongly acidic and/or oxidising solutions, high thermal stability and resistance to radiation, acid salts are attractive inorganic ion exchangers, for particular uses, especially when organic resins cannot be employed because of their degradability³-⁷. The presence of acid sites on such materials indicates good potential for application in Brönsted catalysis. It has also been observed that amorphous materials possess greater number of acid sites as compared to crystalline materials⁸. Thus amorphous materials are catalytically more active as compared to their analogous crystalline varieties.

The ion exchange property of α-zirconium phosphate, Zr(HPO₄)₂H₂O has been examined in detail⁵-⁷ and in the hydrogen form shown to be an acidic catalyst⁸,⁹. It has been shown by us earlier, the potential use of zirconium molybdate as a Brönsted acid catalyst¹⁰. The synthesis and ion exchange properties of zirconium tungstate has been studied earlier¹¹-¹³. So far no work has been done to examine the catalytic properties of these compounds. The present work consists of synthesis, characterisation and study of catalytic behaviour (Brönsted acid catalyst) of amorphous zirconium tungstate (ZW) using esterification as a model reaction.

Experimental

Preparation of the catalyst

Zirconium tungstate was prepared by adding sodium tungstate to an aqueous solution of zirconium oxychloride till complete precipitation. The gel was digested at room temperature for several hrs, washed with conductivity water till the removal of any excess chloride, filtered and dried at 100°C. The dried material was broken down to the desired particle size (30-60 mesh) and sized by sieving. It was converted to the hydrogen form by immersion in 1 M HCl, the acid being intermittently replaced. It was then washed several times with conductivity water, filtered and dried at 100°C. ZW prepared is in the form of white hard granules.

Acid catalysis (Esterification reactions)

The esterification reactions were carried out varying particle size, amount of the catalyst and mole ratio of alcohol and acid.

For the preparation of the ester, acetic acid and ethyl alcohol were combined in a refluxing assembly. The catalyst was then added in the required amount. The mixture was heated at 60°C for 2 hrs and ester formed was distilled over slowly. The amount of ester formed was monitored on gas chromatograph.

Catalyst characterisation

The sample ZW was analysed for zirconium and tungsten. Zirconium was determined gravimetrically as zirconium oxide. Tungsten was deter-
If.

\[
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\]

As observed from the data in Table 1, the yields of ethyl acetate can be increased, with increase in the amount of catalyst. The yields can also be increased by increasing [acid]. However, maximum yields are obtained when amount of catalyst taken is 2 g and alcohol to acid proportion is 1:2. With change in mesh size there is no change observed in the yields.

The catalyst was regenerated by washing several times with water and finally treating it with 1 M HCl (as per method suggested in experimental section). In the regenerated samples the yields decrease by 4% in the case where excess acetic acid is taken while 10% in the case where the alcohol to acid proportion is 1:1 (Table 2).

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Thermogravimetric analysis of the sample was performed on Shimadzu Thermal Analyzer model, DT 30 at a heating rate of 10°C/min. TGA of ZW indicated the presence of about 20% hydrated water which was lost very slowly within the temperature range of 80-180°C. There was no evidence of the decomposition of the solid within the temperature range of 30°C-1000°C.

Differential scanning calorimetric analysis of ZW was obtained at a heating rate of 20°C/min. on Perkin Elmer (range up to 500°C). DSC showed only one exothermic peak at 120°C indicating the presence of water. There was no endothermic peak up to 500°C, indicating that there was no phase change.

IR spectra of the samples were obtained on Shimadzu IR-408 spectrometer using KBr discs. The spectrum of ZW showed broad bands in the region ~3400 cm\(^{-1}\) which were attributed to asymmetric and symmetric hydroxo-OH and aquo-OH stretches. A sharp medium band at ~1620 cm\(^{-1}\) was attributed to \(-(\text{H-O-H})\) bending.

Results and discussion

Esterification of carboxylic acid is a reaction subject to general Brönsted acid catalysis and the reaction of ethyl alcohol with acetic acid was selected as a model reaction.

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During the course of reaction there is a change in the colour of the catalyst from white to grey. The IR spectra of this sample gives additional bands in the region ~1400 cm\(^{-1}\) which may be attributed to aliphatic \(-\text{CH}\) bending vibrations. This gives an indication that during the course of the reaction the reacting molecules come on to the surface of the catalyst. Some of them enter into reaction to give the ester but a few of them get adsorbed on the surface which is marked by change in colour of the catalyst. The fact that the adsorption is weak is observed from the fact that the ca-
The catalyst regains its original colour when treated with acid for regeneration. The possibility of molecules entering interstices cannot be ruled out. This is observed from the fact that the yields go down by 5% after every regeneration leading to deactivation of the catalyst.

The above results establish the use of zirconium tungstate as a Bronsted acid catalyst. Conventional methods use H$_2$SO$_4$ as a catalyst while preparing esters. The yields are high but traces of H$_2$SO$_4$ are difficult to remove. The use of solid acid catalyst such as zirconium tungstate is definitely advantageous, since the ester formed can be simply distilled over and there is no catalyst contamination; besides the catalyst can be regenerated and reused.

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References