

Silicotungstic acid supported zirconia: An effective catalyst for esterification reaction

K.M. Parida*, Sujata Mallick

Colloids and Material Chemistry Department, Regional Research Laboratory (CSIR), Bhubaneswar 751013, Orissa, India

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Abstract

A series of solid acid catalysts were synthesized by incipient wetness impregnation method by varying the wt% of silicotungstic acid on hydrous zirconia (ZSTA). The prepared catalysts were characterized by PXRD, FTIR, UV–vis DRS, EPMA, BET surface area, acid sites, etc. FTIR and UV–vis DRS studies indicate that the material retain the Keggin-type structure of silicotungstic acid up to 500 °C. The suitability of the materials was studied for acid catalysed esterification reactions using formic, acetic, propionic, *n*-butyric acid and *n*-butyl alcohol (NBA), isobutyl alcohol (IBA) and *sec*-butyl alcohol (SBA). Material with 15 wt% STA on hydrous zirconia having high surface area and acid sites acts as better catalyst for esterification reactions. The esterification of acids with NBA was found to be higher than IBA and SBA. In all the cases, the selectivity for the corresponding esters is nearly 100%. The straight-line plot of $-\ln(1 - \text{conversion})$ versus reaction time for the reactions carried out at 98 °C supports that the esterification reaction obeys first order kinetics with respect to acid concentration. The reusability study justifies that the catalyst is stable and active.

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1. Introduction

Heteropoly acids (HPA) have attracted attention as catalysts for various industrial processes such as oxidation, hydration, esterification and etheration [1,2]. These HPA are stronger acids and they have higher catalytic activity compared to homogeneous and acid catalysts such as sulphuric acid, silica-alumina or ion exchange resins [3–5]. The use of HPA as catalysts is important in the development of clean technologies, since it avoids the drawbacks of environmental pollution and corrosion of the conventional technologies. Other advantage is the ability of recovering and reusing them in liquid phase reactions compared to the homogeneous catalysts and the possibility of their use in continuous processes. The disadvantage of bulk HPA as catalysts is their relatively low stability and also of their low surface area ($1\text{--}10\text{ m}^2\text{ g}^{-1}$) and separation problem from reaction mixtures [6,7]. To minimize these disadvantages the HPA are usually supported on a carrier. Heteropoly acids supported

on solids with high surface area are also a useful method for improving catalytic performance.

Esterification of carboxylic acids is one of the fundamental reactions in organic chemistry [8]. Liquid phase esterification is an important method for producing various esters. Esterification of acetic acid with *n*-butyl alcohol is commercially important as the product *n*-butyl acetate is widely used in the manufacture of lacquer, artificial perfumes, leather, flavoring extract, photographic films, plastics, pharmaceuticals and safety glasses [9–11]. It is also used as dehydrating agent. Conventional method of esterification reaction involves the use of mineral acids such as H_2SO_4 , HCl , HF , H_3PO_4 and ClSO_2OH , etc. These acids are corrosive and the excess acid has to be neutralized after the reaction leaving considerable amount of salts to be disposed off into the environment. So the replacement of these conventional hazardous and polluting corrosive liquid catalysts by solid acid catalysts is the demand of the day to create a cleaner technology. Reduction of environmentally unacceptable waste to minimize environmental pollution is the crucial factor for developing environmentally friendly catalyst.

The study of hydrous zirconia is of interest due to its special properties, which allow their use as catalyst or support. One of

* Corresponding author. Tel.: +91 674 2581636x425; fax: +91 674 2581637.
E-mail address: kmparida@yahoo.com (K.M. Parida).

the main reasons that have drawn great attention to the use of hydrated zirconia as a precursor of a catalyst carrier is due to its large number of surface hydroxyl groups, which can undergo chemical reaction or strong interaction with incorporated components. The present study aims at synthesis, characterization and evaluation of the catalytic activity of silicotungstic acid supported on hydrous zirconia (ZSTA) towards esterification of formic acid, acetic acid, propionic acid and butyric acid using various alkylating agents such as *n*-butyl alcohol (NBA), isobutyl alcohol (IBA) and *sec*-butyl alcohol (SBA). Further effect of various reaction parameters such as time, temperature, molar ratio of the reactants and the amount of the catalyst on *n*-butyl acetate formation was evaluated to optimize the reaction conditions.

2. Experimental

2.1. Preparation of support, hydrous zirconia

Zirconium hydroxide gel was prepared from aqueous solution of zirconium oxychloride (Fine Chemical) by drop wise addition of ammonium hydroxide solution (25% ammonia) (Merck, India) till it attains pH 9.5. The hydrogel was refluxed at 100 °C for 24 h, filtered, washed with deionized water and dried in an oven at 120 °C for 24 h (named Z herein after).

2.2. Preparation of silicotungstic acid; $H_4SiW_{12}O_{40} \cdot nH_2O$ (STA)

Ist step: Preparation of silicic acid: A small amount of sodium silicate (meta) was dissolved in minimum amount of water. Then 6N HCl was added drop wise with constant stirring till the solution is neutral to litmus paper. Then it was stirred for 15 min and then a small amount of 6N HCl was added to precipitate silicic acid. It was then filtered, washed with double distilled water.

2nd step: About 6 g of sodium tungstate was dissolved in water. Then 6N HCl was added drop wise with constant stirring to dissolve the white precipitate formed. The addition of HCl continues till it is neutral to the litmus paper. Then to this solution the freshly prepared silicic acid was added. The whole solution is boiled for 2 h. The solution is kept acidic by adding little HCl to the solution during the above process. Then it was filtered and the filtrate is evaporated to minimize the volume.

The above solution is shaken with ether and HCl vigorously. A adduct was formed with ether which settled down at the bottom. This is separated from the aqueous solution. The adduct is white in colour. It was exposed to air to remove ether and then dried at around 45 °C. The content of Si and W in STA was analyzed by ICP and found to be 1.05 and 76.5 wt%, respectively.

2.3. Preparation of catalyst

The catalysts were prepared by wet impregnation method. A series of catalysts having different loading ranging from 3 to 20 wt% were synthesized by impregnating 2 g of neat Z with an aqueous solution of silicotungstic acid (STA) (0.06–0.30 g/10–50 ml of conductivity water) under constant

stirring followed by heating till complete evaporation of water. Then it was dried in an oven at 120 °C for 24 h. The catalysts will be termed: *x*ZSTA (*x* varies from 3 to 20 wt%).

2.4. Physico-chemical characterization

The X-ray powdered diffraction pattern was recorded on a Philips PW 1710 diffractometer with automatic control. The patterns were run with a monochromatic Cu K α radiation with a scan rate of 2° min⁻¹.

The UV–vis DRS spectra of the samples were recorded in a Varian UV–vis spectrophotometer loaded with Carry 100 software. The spectra were recorded against the boric acid background.

DTA analysis of samples dried at 120 °C was carried out under air atmosphere using a Thermal Analyzer (Perkin-Elmer TG-DTA, Model: Diamond). The differential thermal analysis (DTA) experiments were performed in N₂-using 4–5 mg samples at a heating of 10 °C/min.

The FTIR spectra were taken using Jasco FTIR 5300 in KBr matrix in the range of 400–4000 cm⁻¹.

Micrographs showing X-ray image mapping of different elements of zirconia impregnated STA was taken using a Japanese Model (JXA-8100) EPMA.

The ammonia-TPD of all the samples was carried out in a CHEMBET-3000 (Quantachrome) instrument. About 0.1 g sample was taken inside quartz ‘U’ tube and degassed at 350 °C for 1 h with He gas flow. The sample was then cooled to 30 °C and at this temperature the gas flow was changed to ammonia. It was then heated at a heating rate of 10 °C/min up to 800 °C and the spectra were recorded.

The surface area measurement was carried out by BET method using Quantasorb instrument (Quantachrome, USA) by nitrogen adsorption-desorption measurements. The samples were degassed at 120 °C at 10⁻³ Torr vacuum.

Surface acidity was determined spectrophotometrically on the basis of irreversible adsorption of organic bases such as pyridine (PY, pK_b = 3.5) and 2,6-dimethyl pyridine (DYPY, pK_b = 8.7) [12]. In this method, adsorption experiment was carried out in a 50 ml stoppered conical flask taking 10 ml of each freshly prepared adsorbate (Fluka, Switzerland) solution, along with 0.05 g of sample preheated at 393 K with constant shaking. The concentration range for each adsorbate was varied from 0.005 to 0.01 M in cyclohexane (Merck). After 2 h the contents were filtered and absorbance of the filtrate was measured at preset wavelengths. For all cases, the sorption experiments were carried out in the adsorbate concentration range where Beer–Lambert’s law was valid. The time required to reach equilibrium at room temperature was checked for all of the samples and was never more than 1 h. In other words, the time required for all the solute to adsorb on the active sites of the catalyst is optimum in 1 h. All the absorbance measurements were recorded in a spectrophotometer (Varian, Cary 1E) using 10 mm matched quartz cells.

The chemical interaction between the adsorbate and the catalyst may be described by the linear transferred Langmuir adsorption isotherm.

$$\frac{C}{X} = \frac{1}{bX_m} + \frac{C}{X_m}$$

where C is the concentration of organic substrate in solution in equilibrium with the adsorbate substrate, b the constant and X is the monolayer coverage, which corresponds to the theoretical amount of solute required to cover all the active sites for base adsorption.

2.5. Catalytic reaction

The esterification reaction was carried out taking 0.025 g of the calcined sample (dried at 120 °C for 6 h in an oven), 2 mmol of acetic acid (Merck, 99.8%), 32 mmol of alcohol (Merck, 98%) and 0.20 mmole of *n*-heptane (Merck, 99%) as an internal standard in a 100 ml round-bottomed flask equipped with a reflux condenser. The contents were then refluxed gently at 98 °C. Then the reaction mixture was filtered and the products were analysed by means of gas chromatograph (GC-17A Shimadzu).

3. Result and discussion

The XRD patterns of different weight percentage of silico-tungstic acid impregnated on hydrous zirconia show similar pattern to that of the support. This may be probably because, the STA impregnated on the support is highly dispersed and exhibits a non-crystalline to amorphous form and hence do not show any additional X-ray reflection peak.

Fig. 1 shows the background subtracted UV–vis DRS spectra of (a) hydrous zirconia, (b) 15 wt% ZSTA and (c) 15 wt% ZSTA calcined at 500 °C. The hydrous zirconia (Fig. 1a) exhibits a strong absorption band at 230 nm, which may be attributed to the charge transfer from oxide species to zirconium cation ($O^- \rightarrow Zr^{4+}$). In contrast the spectra of both 15 wt% ZSTA dried at 120 °C and 15 wt% ZSTA calcined at 500 °C sample, show broad band at 260 nm, which match well with the literature value [13], suggesting thereby the presence of undegraded $H_3SiW_{12}O_{40}$ species. This also indicates that the Keggin phase remains unaltered up to 500 °C.

The catalysts with different STA loadings dried at 120 °C were characterized by differential thermal analysis (Fig. 2). The DTA of hydrous zirconia showed exothermic peaks at 450 °C

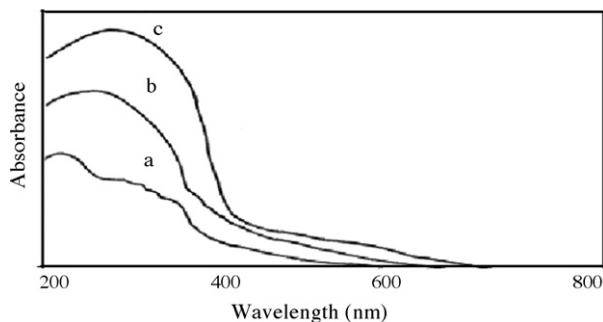


Fig. 1. DRS spectra of (a) Z (b) 15 wt% ZSTA and (c) 15 wt% ZSTA calcined at 500 °C.

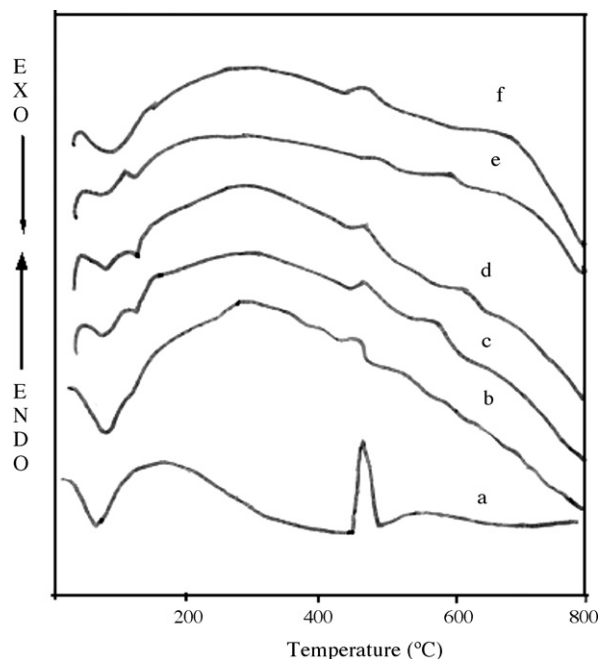


Fig. 2. DTA spectra of (a) Z (b) 6 wt% ZSTA, (c) 9 wt% ZSTA (d) 12 wt% ZSTA, (e) 15 wt% ZSTA and (f) 20 wt% ZSTA.

due to the crystallization to zirconia. The DTA of all samples show an endothermic peak at around 80–135 °C associated with the loss of water molecule. The 6 wt% ZSTA showed an exothermic peak at 460 °C, whereas other catalysts such as 9, 12, 15 wt% ZSTA showed an additional exothermic peak at around 570–596 °C. The 20 wt% ZSTA exhibited a broad exothermic effect at around 690–735 °C, which could be due to the crystallization of WO_3 .

The FTIR spectra of hydrous zirconia and silicotungstic acid impregnated on hydrous zirconia dried at 120 °C (15 wt% ZSTA) are presented in Fig. 3a and b. The FTIR spectrum of Z (Fig. 3a) shows broadband in the region of 3410 cm^{-1} due to asymmetric

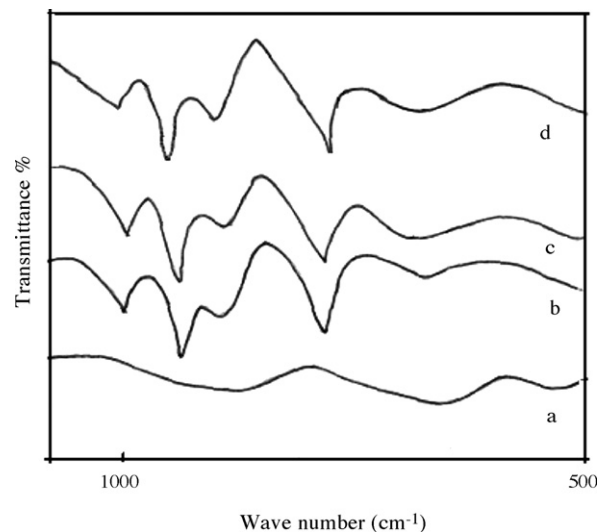


Fig. 3. FTIR spectra of (a) Z (b) STA, (c) 15 wt% ZSTA and (d) 15 wt% ZSTA calcined at 500 °C.

stretching of OH group and two bands at 1621 and 1386 cm^{-1} are due to bending vibration of $-(\text{H}-\text{O}-\text{H})-$ and $-(\text{O}-\text{H}-\text{O})-$ bond. The band at 600 cm^{-1} can be attributed to the presence of $\text{Zr}-\text{O}-\text{H}$ bond. The fingerprint bands of the STA Keggin anion (Fig. 3b) appeared at 978, 915, 885 and 798 cm^{-1} , which could be assigned to the typical antisymmetric stretching vibrations of $\text{W}=\text{O}$, $\text{Si}-\text{O}$, $\text{W}-\text{O}_c-\text{W}$ and $\text{W}-\text{O}_e-\text{W}$, respectively, where c for the corner sharing oxygen atom connecting W_3O_{13} units and e for the edge sharing oxygen connecting W's. [14]. This was also observed in case of 15 wt% ZSTA (Fig. 3c).

The FTIR spectra of 15 wt% ZSTA sample calcined at 500 °C is shown in Fig. 3d. There is slight shifting of bands, indicating that the Keggin phase remains unaltered up to 500 °C.

Fig. 4 illustrates the X-ray image maps of W, P, Zr elements in a selected area (SA) showing their level of concentration through clustering of pixels. It can be seen from the maps that W is adsorbed in Zr grain more than Si. This is obvious since in original STA, tungsten content is 12 times more than silicon.

Table 1 shows the BET surface area and acid sites of zirconia and different weight percentage of ZSTA samples. The pure hydrous zirconia dried at 120 °C showed a surface area of 412 $\text{m}^2 \text{g}^{-1}$. With the increase in STA content from 0 to 15 wt%,

Table 1

Surface area and acid sites of various STA impregnated hydrous zirconia

Catalysts	Surface area ($\text{m}^2 \text{g}^{-1}$)	Acid sites ($\mu\text{mol g}^{-1}$)	
		PY	2,6 DMPY
Z	412.3	156.5	58.20
ZSTA-3	413.8	165.2	95.58
ZSTA-6	434.6	192.7	106.1
ZSTA-9	467.4	211.6	154.7
ZSTA-12	475.9	238.1	198.3
ZSTA-15	505.9	285.3	202.7
ZSTA-20	456.1	247.5	179.9

the surface area increases from 412 to 505 $\text{m}^2 \text{g}^{-1}$. However, from 15 wt% onwards, the surface area decreases gradually. This implies that the presence of STA play a role in making the material more porous up to the amount required to form monolayer. However, when the STA content increases beyond 15 wt%, pore blocking takes place due to the presence of an excess amount of silicotungstic acid.

In case of the surface acid sites, adsorption of pyridine (PY) measures the total acidity where as 2,6-dimethyl pyridine (DMPY) can be adsorbed on the Brønsted acid sites. It

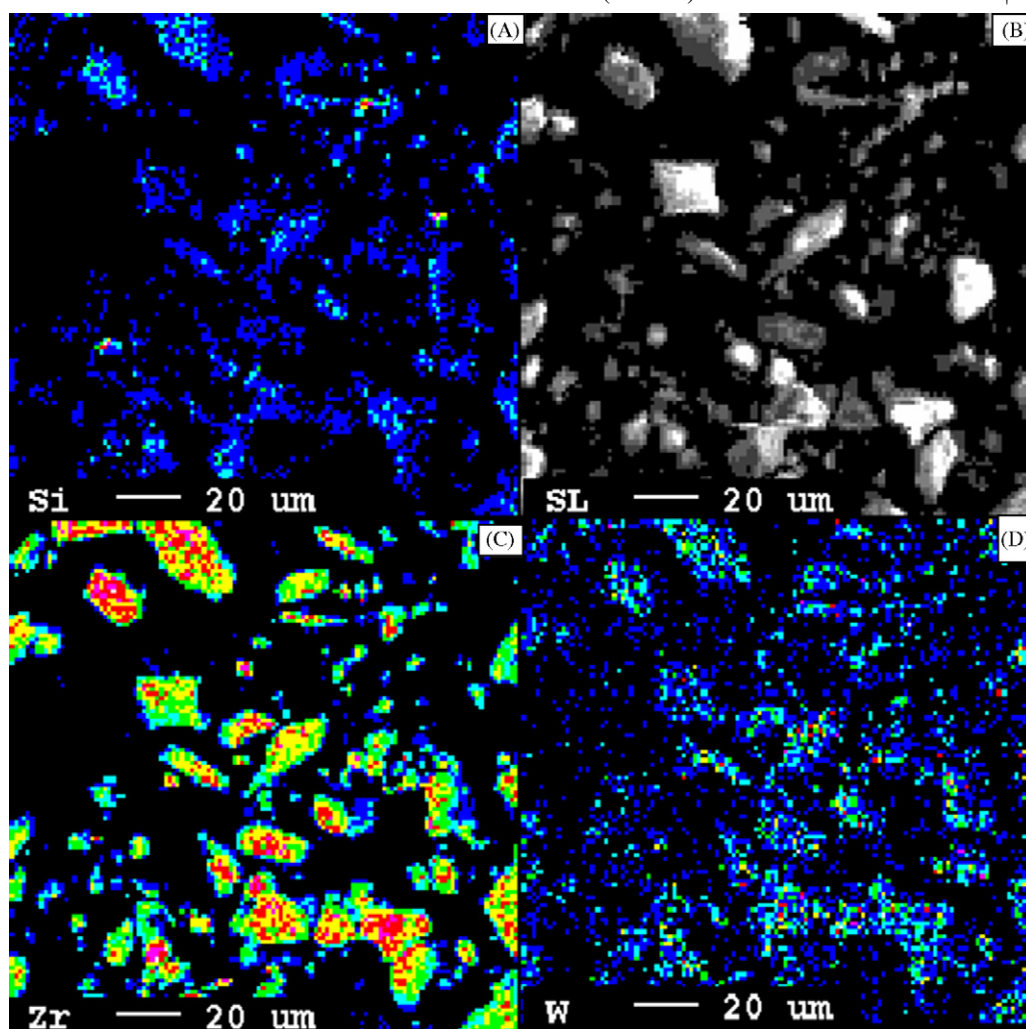


Fig. 4. Scanning electron micrograph of 15 wt% ZSTA sample. (A) X-ray image map of Si, (B) secondary electron image of morphological view of 15 wt% ZSTA, (C) X-ray image map of Zr and (D) X-ray image map of W.

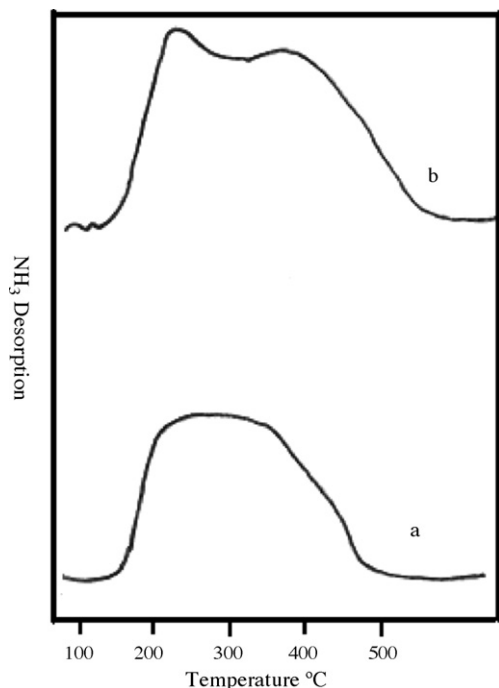


Fig. 5. Temperature programmed desorption of ammonia (a) Z (b) 15 wt% ZSTA.

is observed that by increasing the STA loading up to 15 wt% the acidity gradually increases (from 165 to 285 $\mu\text{mol g}^{-1}$), thereafter it decreases to 247 $\mu\text{mol g}^{-1}$ for 20 wt% ZSTA. The same trend is also found for Brønsted acid sites. The increase in surface acidity, with an increase in STA loading may be due to the formation of patchy monolayer of STA on zirconia. The decrease in the surface acidity at high STA concentration is probably due to the formation of polylayer coverage of STA on zirconia, which decreases the number of Brønsted acid sites and consequently that of total acid sites.

Temperature programmed reduction desorption (TPD) of ammonia is a common method for investigating both the strength and number of acid sites present on the surface of an acidic solid. The TPD profile of zirconia and 15 wt% ZSTA are shown in Fig. 5. The zirconia sample showed only one maxima in the low temperature region, whereas for the 15 wt% ZSTA samples, ammonia could still be desorbed at 500 °C. This corroborates the observation that 15 wt% ZSTA contains highest Brønsted acids as well as total acid sites (Table 1) determined by spectroscopic method.

3.1. Catalytic activity

The esterification of acetic acid with various alcohols is an electrophilic substitution reaction. The reaction is relatively slow and need activation either by higher temperature or by catalyst to achieve higher conversion to a reasonable amount. Samantray and Parida [15] and Namba et al. [16] reported that the reaction of acetic acid and *n*-butanol in liquid phase catalysed by solid acids proceeds according to a rate equation, which are first order with respect to acetic acids and zero order with respect to *n*-butyl alcohol.

Table 2

Catalytic activity of various catalysts for esterification of acetic acid with various alcohols

Catalysts	Conversion (%) with NBA	Conversion (%) with IBA	Conversion (%) with SBA
Z	50.28	48.5	38.25
3 ZSTA	65.12	63.89	50.54
6 ZSTA	72.53	70.42	64.56
9 ZSTA	79.25	77.36	69.87
12 ZSTA	86.21	83.64	70.63
15 ZSTA	91.45	89.1	75.26
20 ZSTA	88.68	85.91	71.24

Time = 4 h, reaction temperature = 98 °C, catalyst amount = 0.025 g, acid:alcohol = 1:16.

Such an esterification reaction can be catalysed by strong Brønsted acid sites. The reaction following the Eley–Rideal mechanism takes place between alcohol chemisorbed on the active Brønsted acid sites of the catalyst surface, forming a carbocation. Then nucleophilic attack by acetic acid on the stable carbocation takes place resulting the formation of the *n*-butyl acetate or isobutyl acetate. The role of an acid catalyst here is to facilitate the formation of the carbocation, and to help remove OH^- from the alcohol [17].

The mechanism involved in the reaction is as follows.

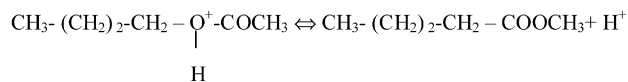
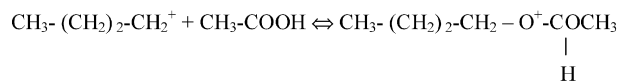
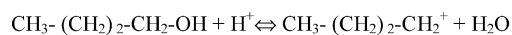


Table 2 exhibits the data on the conversion of acetic acid with various alcohol over neat and STA promoted zirconia. The product analysis by GC showed that the selectivity *n*-butyl acetate, iso-butyl acetate and *sec*-butyl acetate is 100%. When the esterification reaction was carried on hydrous zirconia, 50% of conversion of acetic acid to *n*-butyl acetate takes place. The conversion of acetic acid increases with silicotungstic acid loading on zirconia, reaching a maximum at 15 wt% ZSTA and decreasing thereafter. This may be due to increase of Brønsted acid sites and surface area with STA loading over zirconia.

The conversion of acetic acid with various alcohols decrease in the order NBA > IBA > SBA. The difference in conversion may be due to the degree of positive charge of the carbonium ion. Since each alcohol after chemisorption on the Brønsted acid sites give a carbonium ion for nucleophilic reaction with acetic acid. NBA can give a carbonium ion of high degree of positive charge compared to that of IBA and SBA, so the conversion for esterification of acetic acid with NBA is higher than IBA and SBA. The variation of different reaction parameters was studied on 15 wt% of ZSTA catalyst using *n*-butyl alcohol.

3.1.1. Influence of reaction time

The influence of reaction time on the acetic acid conversion was given in Fig. 6 using 15 wt% ZSTA as catalyst (0.025 g) under other identical reaction conditions. A gradual rise in the

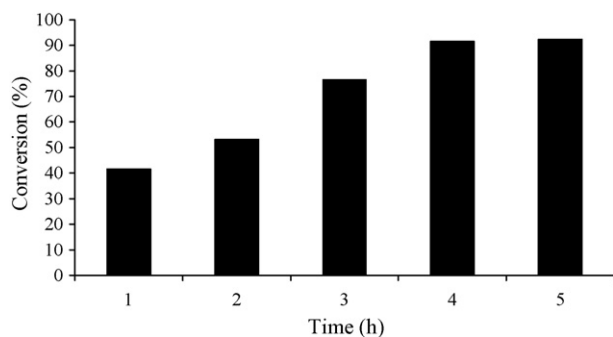


Fig. 6. Effect of reaction time on esterification of acetic acid using 15 wt% ZSTA as catalyst, catalyst amount = 0.025 g, reaction temperature = 98 °C, acetic acid:*n*-butyl alcohol = 1:16.

conversion was seen with increase in duration of the reaction period. As seen from Fig. 6, in 4 h of reaction time, 91.5% of conversion is obtained, where as at the end of 5 h only 92% of the reaction is complete. The selectivity towards *n*-butyl acetate on the other hand remains same, i.e. 100% in 5 h. This suggests that 4 h is sufficient to optimize the reaction parameters.

3.1.2. Influence of catalyst amount

The amount of catalyst was varied from 0.01 to 0.03 g using 15 wt% ZSTA while keeping the molar ratio of acid:alcohol at 1:16 and reaction temperature at 98 °C. The reaction was carried out for 4 h and the products were analyzed. The results are represented in Fig. 7. With the increase in catalyst amount from 0.01 to 0.03 g, the conversion of acetic acid increases from 62.5 to 93.7%. This is due to the availability of large surface area and acid sites, which favors the dispersion of more active species. Therefore, the accessibility of the large number of molecules of the reactants to the catalyst surface is favored. The selectivity towards butyl acetate is nearly 100% in all cases.

3.1.3. Influence of reaction temperature

Fig. 8 illustrates the effect of reaction temperature on the esterification of acetic acid with *n*-butanol. The reaction was carried out in the temperature region 80–110 °C taking 15 wt% ZSTA as catalyst without altering other reaction parameters. The conversion of acetic acid increases (57–93%) with increase in reaction temperature having nearly 100% selectivity. This suggests that increase in reaction temperature favors the formation

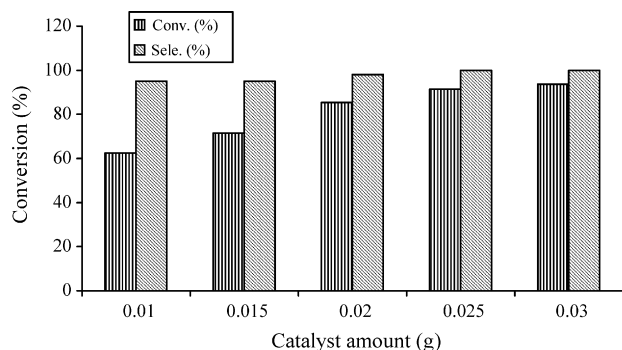


Fig. 7. Effect of catalyst amount on esterification of acetic acid carried out at reaction temperature = 98 °C, acetic acid:*n*-butyl alcohol = 1:16, time = 4 h.

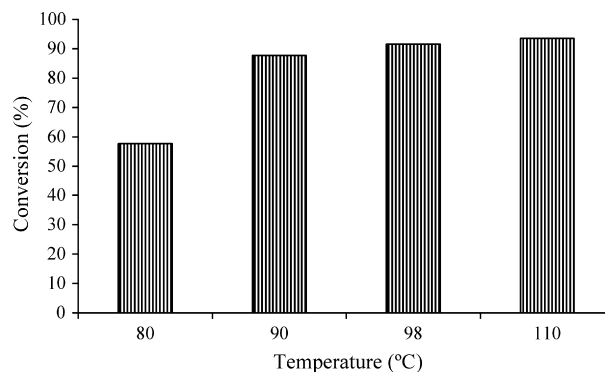


Fig. 8. Effect of reaction temperature on esterification of acetic acid using 15 wt% of ZSTA as catalyst; catalyst amount = 0.025 g, acetic acid:*n*-butyl alcohol = 1:16, time = 4 h.

of carbonium ion which react with acetic acid to produce *n*-butyl acetate.

3.1.4. Influence of molar ratio of reactants

Mole ratios of acetic acid to *n*-butanol were varied from 1:10 to 1:18 and the result was shown in Fig. 9. In all cases and in all mole ratios of the reactants, *n*-butyl acetate was observed as the main product. The conversion increased from 68.7 to 91.5% with a change in mole ratio of acetic acid to *n*-butanol from 1:10 to 1:16. With further increase in mole ratio of acetic acid to *n*-butanol, a slightly decrease in conversion was observed. The reaction rate at different alcohol concentration increases linearly with low alcohol concentration, but it is nearly independent of alcohol concentration at high level. Decrease in conversion in higher molar ratio of acid to alcohol (1:18) may be due to the saturation of the catalytic surface with the alcohol or prevention of nucleophilic attack by shielding the protonated alcohol by its own excess. This analysis confirms that the reaction mechanism can be represented by Eley–Rideal mechanism, that is, the reaction takes place with chemisorption of alcohol on the Brønsted acid sites of the catalyst. This result is very similar to Kirumakki and co-workers [18] who used zeolite as catalyst over esterification of benzyl alcohol with acetic acid and Jermy and Pandurangan [9], who used Al-MCM-41 catalyst over esterification of acetic acid with *n*-butyl alcohol,

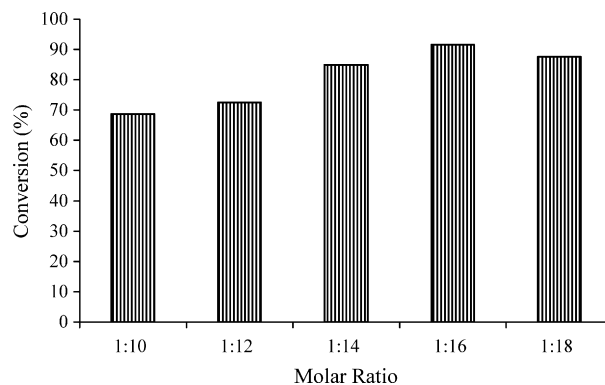


Fig. 9. Effect of molar ratio of acid/alcohol on esterification of acetic acid using 15 wt% ZSTA as catalyst, catalyst amount 0.025 g, reaction temperature = 98 °C, time = 4 h.

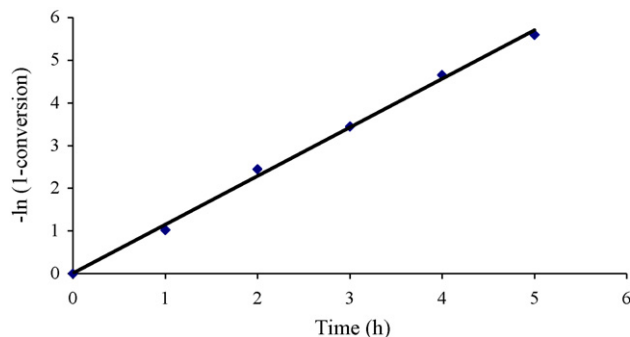


Fig. 10. Plot of $-\ln(1 - \text{conversion})$ vs. reaction time for the reactions carried out at 98°C .

although in both the cases the experiments were performed in a lower molar ratio of acid and alcohol compared to this present work.

3.1.5. Kinetics of esterification of acetic acid with *n*-butanol

Fig. 10 shows the first order nature of the esterification reaction, which gives a straight-line plot of $-\ln(1 - \text{conversion})$ versus reaction time for the reactions carried out at 98°C . Namba et al. [16] showed the reaction between acetic acid and *n*-butanol proceeds according to a rate equation, which is first order with respect to acetic acid and zeroth order with respect to *n*-butanol.

3.1.6. Reaction with other acids and alcohol

Formic acid, propanoic acid and *n*-butyric acid were subjected to esterification reaction with *n*-butanol, iso-butanol, *sec*-butanol under identical condition using 15 wt% ZSTA as catalyst to test the generality of this method and the results are summarized in Table 3. The percentage of conversion of these acids follows the following order: formic > acetic > propanoic > *n*-butyric which can be explained on the basis of the strength and size of the reacting acids. The strength of these aliphatic acids follows the same order as that of conversion, i.e. formic > acetic > propanoic > *n*-butyric. This may be due to the +I effect of the alkyl group of the acids. As the bulkiness of the acids increases the steric hindrance also decreases which results increase in acid conversion.

3.2. Reusability of the catalyst

The catalyst with 15 wt% loading was used for recycling experiments. In order to regenerate the catalyst after 4 h reaction, it was separated by filtration, washed with conductivity

Table 3
Esterification of different acids with various alcohols over 15 wt% ZSTA

Acids	Conversion (%) with NBA	Conversion (%) with IBA	Conversion (%) with IBA
Formic	95.1	87.3	73.9
Acetic	91.5	89.1	75.2
Propanoic	86.0	84.6	69.4
<i>n</i> -butyric	78.5	75.6	62.8

Time = 4 h, reaction temperature = 98°C , catalyst amount = 0.025 g, acid:alcohol = 1:16.

water several times, dried and calcined at 120°C and used in the esterification reaction with a fresh reaction mixture. In the regenerated sample after five cycles, the yield decreases by 5%.

4. Conclusion

Silicotungstic acid (15 wt%) supported on hydrous zirconia acts as an efficient and stable solid acid catalyst for esterification of acids using alcohols. Probably the high surface area and Brønsted acid sites will play a key role in the high activity of the catalyst. FTIR spectra and UV–vis spectra confirm that the silicotungstic acid keeps its Keggin type structure even at 500°C calcination when supported on hydrous zirconia. EPMA studies support that the STA is well dispersed on the surface of hydrous zirconia. The highly dispersed STA on hydrous zirconia possibly provide active sites for the esterification of acids using alcohols. The percentage of conversion of formic, acetic, propionic, *n*-butyric acid with various alcohols follows the order: *n*-butyl alcohol > iso-butyl alcohol > *sec*-butyl alcohol. The esterification of different acids with the above mentioned alcohols over 15 wt% ZSTA follows the order: formic > acetic > propionic > *n*-butyric. In all the cases the selectivity towards the formation of ester is 100%. The catalyst can be regenerated easily and reused at least five times.

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