

# Catalytic performances of silicotungstic acid/zirconia supported SBA-15 in an esterification of benzyl alcohol with acetic acid

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## Abstract

Liquid phase esterification of benzyl alcohol (BA) to benzyl acetate (Peach fragrance) with an acetic acid (AA) has been investigated with 12-silicotungstic acid supported on zirconia embedded inside SBA-15 (STA/ZrO<sub>2</sub>/SBA-15) as the catalyst. Catalysts were unambiguously characterized by XRD, N<sub>2</sub> adsorption–desorption, FT-IR pyridine adsorption techniques and the total amount of acidity of different STA loaded catalysts was estimated by TPD of NH<sub>3</sub>. The optimization of reaction conditions of an esterification of BA with AA was performed with 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K by varying catalyst concentration (1–10 wt.% of reaction mixture); temperature, 353–383 K and AA:BA molar ratio as 0.5–3. The 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K was found to have the highest acidity and more active in the reaction. Under the optimized reaction conditions, the 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K gave 59% BA conversion with selectivity for benzyl acetate as high as 96% within 2 h of reaction time.

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## 1. Introduction

The esterification of carboxylic acids and the acylation of alcohols are fundamental reactions in organic chemistry [1,2]. Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used in the chemical industry such as drugs, plasticizers, food preservations, pharmaceuticals, solvents, perfumes, cosmetics, and chiral auxiliaries [3,4]. Benzyl acetate finds extensive uses in perfumery, food, and chemical industries [5].

The chemical synthesis of benzyl acetate is carried out by acetoxylation of toluene by using inorganic catalysts [6,7]. This chemical synthesis produces unwanted side products [5,8] and it also has an associated problem of catalyst deactivation [9]. There has been some work on the formation of benzyl esters using enzymes [10,11]. Majumder et al. [12] reported the lipase catalyzed synthesis of benzyl acetate in solvent-free medium using vinyl acetate as acyl donor. For enzyme catalyzed ester-

ification and transesterification reactions in non-aqueous media vinyl acetate is considered as a very good choice for acyl donor [13]. Cobalt(II) chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) efficiently catalyzes the acetylation of alcohols with acetic acid (AA) in high yields [14].

Esterification reactions can be carried out without a catalyst, although the reaction is extremely slow, since the rate is dependent on the autoprotolysis of the AA. Consequently, esterification is enhanced by an acid catalyst, which acts as a proton donor to the acid. Both homogeneous and heterogeneous catalysts are used in esterification reaction. Typical homogeneous catalysts are mineral acids, such as H<sub>2</sub>SO<sub>4</sub>, HCl, HF, ClSO<sub>2</sub>OH, etc. Heteropoly acids (HPAs) are typical strong Brønsted acids which catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing [15]. HPAs are well-defined molecular clusters that are remarkable for their molecular and electronic structural diversity and their significance is quite diverse in many areas, e.g., catalysis, medicine, and materials science [16,17]. The major disadvantages of HPAs, as catalysts are their low thermal stability, low surface area (1–10 m<sup>2</sup> g<sup>-1</sup>), separation problem from reaction mixtures, and the solubility [18,19]. HPAs can be made ecofriendly insoluble

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solid acid with high thermal stability and high surface area by supporting them onto suitable supports having huge surface area, large pore diameter, pore volume, and well-ordered pore structure. The support provides an opportunity to HPAs to get dispersed over a large surface area, which increases catalytic activity. Acidic or neutral solids such as activated carbons, acidic ion-exchange resins,  $\text{SiO}_2$  and  $\text{ZrO}_2$  are used as suitable support [20–33]. Preyssler catalyst,  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  is a green, efficient and reusable catalyst which is used for esterification of salicylic acid with aliphatic and benzylic alcohols [34].

The synthesis of phosphomolybdic acid impregnated over hydrous zirconia catalyst samples and their catalytic activity toward the esterification of AA using *n*-butanol has been reported [32,35]. The esterification of benzoic acid and substituted benzoic acids over zeolite H $\beta$  and H-ZSM-5 using dimethyl carbonate as the methylating agent has also been studied. It has been found that the pore architecture of the zeolites comes into play when the molecular diameter of the reactant molecules is greater than the pore size of the zeolites [36]. Protonated forms of zeolites have been found to be efficient catalysts in esterification reactions [36–39]. The esterification of benzyl alcohol (BA) with AA has been studied over zeolites H $\beta$ , HY, and H-ZSM-5 [33]. Recently, we systematically investigated the catalytic behavior of HPA/ $\text{ZrO}_2$  for many acid-catalyzed reactions and found that the catalysts are more active than zeolites and zeotype catalysts [40–45]. Very recently, we have also studied the catalytic performances of the tungstophosphoric acid (TPA)/ $\text{ZrO}_2$  supported over mesoporous silica (MS) catalysts in acetylation and alkylation of veratrole and phenol, respectively [46,47], while silicotungstic acid (STA)/ $\text{ZrO}_2$ /MS has been studied in an esterification of isoamyl alcohol [48]. In order to perform a new contribution to the field of ecofriendly acid-catalyzed reactions, we report here on the results of esterification of benzyl alcohol (BA) with acetic acid (AA) using STA supported on zirconia embedded over mesoporous silica, SBA-15 (STA/ $\text{ZrO}_2$ /SBA-15). It has been found that the catalyst with 15 wt.% loading of STA is highly active and shows high BA conversion with selectivity for benzyl acetate as high as 96% within 2 h of reaction time.

## 2. Experimental

### 2.1. Materials

Triblock copolymer of ethylene oxide (EO) and propylene oxide (PO),  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  (Pluronic P123) (Aldrich,  $M_{\text{avg}} = 5800$ ) was obtained from Aldrich and used as the structure directing template for the synthesis of MS, SBA-15. Tetraethylorthosilicate was purchased from Aldrich and used as the silica source. Zirconium oxychloride  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (99.5%) and 12-silicotungstic acid (STA) (99.9+%) were obtained from Merck and used without further purification. BA (>99%) and AA (>99%) were procured from Aldrich. All the chemicals were research grade and used as received without further purification in the catalyst preparation and esterification experiments. Zeolites H $\beta$  (30) and HY (13.5) where the number in the parenthesis indicates the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio were obtained from catalysis pilot

plant (CPP-NCL, Pune). All catalysts used in the reactions were in the powder form and were activated prior to their use in the reaction.

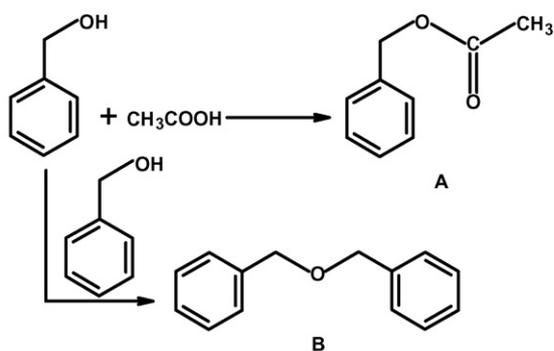
### 2.2. Preparation of STA/ $\text{ZrO}_2$ /SBA-15

Pure siliceous SBA-15 was synthesized according to the procedure reported in the literature [49–52] and STA/ $\text{ZrO}_2$ /SBA-15 composite materials were prepared by following procedure described in our previous report [48]. The supported catalysts were prepared first by impregnating pure siliceous SBA-15 with an aqueous solution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  with a predetermined  $\text{ZrO}_2$ :SBA-15 (22.4%) weight ratio as per literature, which corresponded to monolayer coverage [53]. The resulting mixture was stirred in a rotary evaporator for 2–3 h followed by evaporation to dryness. The resultant solid was recovered, dried at 373 K for 12 h and powdered well for further use. A series of catalysts with different STA loadings were prepared by suspending a known amount of an aqueous solution of STA (10–12 ml distilled water) per 1 g of dried  $\text{ZrO}_2$ /SBA-15 support. This mixture was stirred in a rotary evaporator for 2–3 h followed by evaporation to dryness and the samples were dried, powdered and calcined at 1123 K in air for 4 h. Neat 15 wt.% STA/ $\text{ZrO}_2$  was synthesized by mixing aqueous solutions of STA with  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and stirred in a rotary evaporator for 2–3 h followed by evaporation to dryness. The resulting material was collected, dried at 373 K for 12 h and calcined at 1123 K in air for 4 h.

### 2.3. Characterization techniques

Zr, W and Si contents in the resulting solids were independently determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and X-ray fluorescence spectrophotometer (Rigaku 3070 E Model with Rh target). Crystallographic identification of the samples was performed using X-ray powder diffraction with  $\text{Cu K}\alpha$  radiation (Rigaku model D/MAXIII VC, Japan,  $\lambda = 1.5418 \text{ \AA}$ ). The nitrogen adsorption–desorption isotherms were measured at 77 K on an Omnisorb 100CX (Coulter, USA) analyzer. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms by Barrett–Joyner–Halenda method. The nature of acid sites (Brønsted and Lewis) of the catalyst samples with different loadings was characterized by in situ FT-IR spectroscopy with chemisorbed pyridine in drift mode on a FT-IR-8300 Shimadzu SSU-8000 instrument by averaging 500 scans with a resolution of  $4 \text{ cm}^{-1}$ . Prior to the analysis, the calcined powder samples were heated in situ from room temperature to 673 K with a heating rate of  $5 \text{ K min}^{-1}$  in a flowing stream ( $40 \text{ ml min}^{-1}$ ) of pure  $\text{N}_2$ . The samples were kept at 673 K for 3 h and then cooled down to 373 K. Thereafter, the pyridine vapors ( $20 \mu\text{l}$ ) were introduced under  $\text{N}_2$  flow and the IR spectra were recorded at different temperatures up to 673 K. The acidity of the catalysts was estimated by temperature-programmed desorption (TPD) of  $\text{NH}_3$  on Micromeritics AutoChem 2910 instrument. About 0.1 g of the catalyst sample was dehydrated at 773 K in dry air for 1 h,

### Reaction scheme:



where, A : Benzyl acetate and  
B : Dibenzyl ether

Scheme 1. Reaction pathway for the esterification of benzyl alcohol with acetic acid.

purged with helium for 0.5 h. Then, the sample was cooled down to 398 K under the flow of helium and then 0.5 ml NH<sub>3</sub> pulses was supplied to the samples until no more uptake of NH<sub>3</sub> was observed. NH<sub>3</sub> was desorbed in a He flow by increasing the temperature to 813 K with a heating rate of 10 K min<sup>-1</sup> and the amount of ammonia desorbed was measured by TCD detector.

### 2.4. Esterification of BA by AA

The esterification of BA by AA has been used as a probe reaction for studying the activity of the catalysts. The schematic representation of the reaction is shown in Scheme 1. The reaction was carried out in a 50 ml round-bottomed flask under continuous stirring equipped with condenser, a N<sub>2</sub> inlet for maintaining an inert atmosphere, and an additional port for sample withdrawal. Temperature was maintained by placing the above assembly using a thermostated oil-bath. The reaction was carried out at selected reaction conditions (373 K with a acid to alcohol molar ratio of 2 and the catalyst amount of 5 wt.% of total reaction mixture). Clear liquid samples withdrawn periodically were analyzed by using a gas chromatograph (GC) with a SE-52 capillary column and a FID detector. The conversions were based on the consumed BA in the reaction mixture. The product identifications were achieved by GC–MS and GC–IR.

## 3. Results and discussion

### 3.1. Catalyst characterization

The ratio of Si and W in 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 corresponding per Keggin unit obtained from XRF and ICP-OES analysis was found to be 12.13 and 12.07, respectively. Wide-angle XRD patterns for different STA (%) loadings over 22.4 wt.% ZrO<sub>2</sub>/SBA-15, Different ZrO<sub>2</sub> (%) loading over 15 wt.% STA/ZrO<sub>2</sub>/SBA-15 calcined at 1123 K, and 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at different calcination temperatures were shown in Fig. 1(A), (C) and (B), respectively. The wide-angle XRD patterns displayed three well-defined

peaks at  $2\theta \sim 30^\circ$ ,  $50^\circ$  and  $60^\circ$ , which are indexed to (1 1 1), (2 0 2), and (1 3 1) reflections, characteristics of tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) phases. Fig. 1(A) shows that the monolayer coverage of STA over 22.4 wt.% ZrO<sub>2</sub>/SBA-15 is occurred up to 15 wt.% loading of STA and it started to decompose into WO<sub>3</sub> ( $2\theta \sim 23.12^\circ$ ,  $23.59^\circ$  and  $24.38^\circ$ ) crystalline peaks

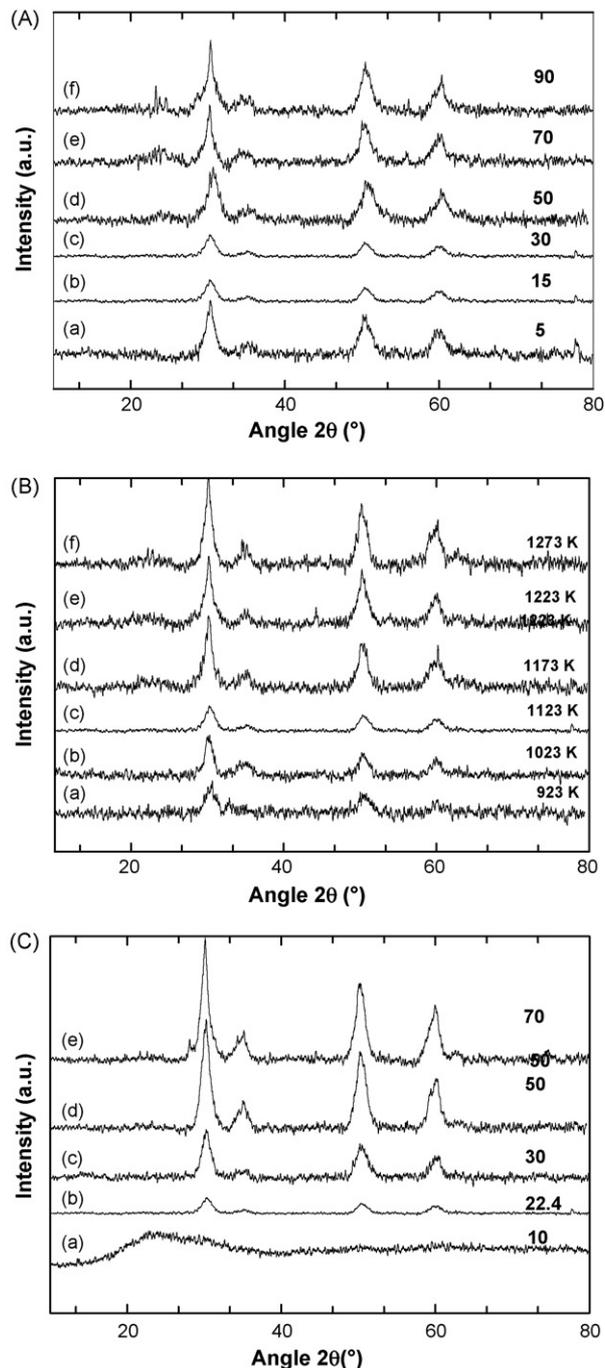


Fig. 1. (A) Wide angle XRD patterns of 22.4 wt.% ZrO<sub>2</sub>/SBA-15 with different loadings of STA calcined at 1123 K: (a) 5 wt.%, (b) 15 wt.%, (c) 30 wt.%, (d) 50 wt.%, (e) 70 wt.%, and (f) 90 wt.%. (B) Wide angle XRD patterns of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at different temperatures: (a) 923 K, (b) 1023 K, (c) 1123 K, (d) 1173 K, (e) 1223 K, and (f) 1273 K. (C) Wide angle XRD patterns of 15 wt.% STA/ZrO<sub>2</sub>/SBA-15 with different loadings of ZrO<sub>2</sub> calcined at 1123 K temperature: (a) 10 wt.%, (b) 22.4 wt.%, (c) 30 wt.%, (d) 50 wt.%, and (e) 70 wt.%.

Table 1  
Physico-chemical properties and catalytic activities 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K

| STA loading (%) | SA <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> ) | TA <sup>b</sup> (mmol g <sup>-1</sup> ) | BA conv. (wt.%) | TOF (s <sup>-1</sup> ) | Rate constant (×10 <sup>-5</sup> s <sup>-1</sup> ) | Selectivity (%) |                |
|-----------------|---|---|-----------------|------------------------|--|-----------------|----------------|
|                 |   |   |                 |                        |  | Benzyl acetate  | Dibenzyl ether |
| 5               | 396   | 0.29                                    | 29.8            | 0.154                  | 3.28   | 100             | –              |
| 15              | 372   | 0.40                                    | 59.0            | 0.102                  | 8.26   | 96.1            | 3.9            |
| 30              | 334   | 0.35                                    | 49.2            | 0.043                  | 6.27   | 98.3            | 1.7            |
| 50              | 333   | 0.30                                    | 32.1            | 0.017                  | 3.58   | 98.9            | 1.1            |
| 70              | 200   | 0.27                                    | 22.3            | 0.008                  | 2.34   | 100             | –              |
| 90              | 200   | 0.22                                    | 16.7            | 0.005                  | 1.69   | 100             | –              |

Reaction condition: BA = 1.42 g, AA = 1.58 g, catalyst = 0.15 g, reaction temp. = 373 K, reaction time = 3 h.

<sup>a</sup> Surface area.

<sup>b</sup> Total acidity.

Table 2  
Effect of calcination temperature on the textural parameter and catalytic activity of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15

| Calcination temperature (K) | SA (m <sup>2</sup> g <sup>-1</sup> ) | TA (mmol g <sup>-1</sup> ) | BA conv. (wt.%) | TOF (s <sup>-1</sup> ) | Rate constant (×10 <sup>-5</sup> s <sup>-1</sup> ) | Selectivity (%) |                |
|-----------------------------|--------------------------------------|----------------------------|-----------------|------------------------|--|-----------------|----------------|
|                             |                                      |                            |                 |                        |  | Benzyl acetate  | Dibenzyl ether |
| 823                         | 484                                  | –                          | –               | –                      | –  | –               | –              |
| 923                         | 472                                  | 0.25                       | 16.8            | 0.029                  | 1.70   | 100             | 0.0            |
| 1023                        | 412                                  | 0.31                       | 32.8            | 0.057                  | 3.68   | 98.3            | 1.7            |
| 1123                        | 372                                  | 0.40                       | 59.0            | 0.102                  | 8.26   | 96.1            | 3.9            |
| 1173                        | 325                                  | 0.34                       | 31.4            | 0.055                  | 3.49   | 98.9            | 1.1            |
| 1223                        | 250                                  | 0.30                       | 13.5            | 0.023                  | 1.34   | 100             | 0.0            |
| 1273                        | 210                                  | 0.12                       | 12.9            | 0.022                  | 1.28   | 100             | 0.0            |

Reaction conditions: BA = 1.42 g, AA = 1.58 g, catalyst = 0.15 g, reaction temp. = 373 K, reaction time = 3 h.

above 15 wt.% of loading. Similarly, 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 also shows the monolayer coverage of STA up to the calcinations temperature of 1123 K. However, the STA is decomposed into WO<sub>3</sub> crystallites (Fig. 1B) at the calcination temperature above 1123 K. The XRD patterns of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 with different ZrO<sub>2</sub> (%) loading over SBA-15 are shown in Fig. 1C. It has been found that the monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>, 2θ ~ 28°) phase is formed on the surface of the support when the weight ratio of ZrO<sub>2</sub>/SBA-15 is more than 0.5 (Fig. 1C).

The textural properties of STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 with different loadings of STA, 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at different temperatures and 15 wt.% STA/wt.% ZrO<sub>2</sub>/SBA-15 with different loadings of ZrO<sub>2</sub> are presented in Tables 1–3, respectively. The comparison of the specific surface area, pore size, and pore volume data of STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 and the parent SBA-15 reveals that STA/ZrO<sub>2</sub> particles are well dispersed inside the mesochannels of SBA-15

support [48]. The surface area of the samples decreased drastically when the loading of STA is above 50 wt.%. This may be due to the fact that a low loading of STA forms strong interaction with the support leading to stabilization of the tetragonal phase of zirconia, resulting in a small reduction in the surface area and pore volume. It is clear from Table 2 that the surface area of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 decreases with increasing the calcination temperature. Interestingly, a remarkable reduction is observed when the calcination temperature is raised above 1123 K. It should be noted that a remarkable decrease in the surface area is observed for 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 catalyst systems calcined at 1123 K (Table 3). This may be due to the multilayer formation above 22.4 wt.% ZrO<sub>2</sub> which reduces the interaction with STA. Consequently, the sintering of zirconia is occurred on the support.

The total acidity of the catalysts with different STA loadings, calcined at different temperatures and with different ZrO<sub>2</sub> loadings is also depicted in Tables 1–3, respectively. Further, the

Table 3  
Effect of (%) ZrO<sub>2</sub> on the textural parameter and catalytic activity of 15 wt.% STA/wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K

| ZrO <sub>2</sub> loading (%) | SA (m <sup>2</sup> g <sup>-1</sup> ) | TA (mmol g <sup>-1</sup> ) | BA conv. (wt.%) | TOF (s <sup>-1</sup> ) | Rate constant (×10 <sup>-5</sup> s <sup>-1</sup> ) | Selectivity (%) |                |
|------------------------------|--------------------------------------|----------------------------|-----------------|------------------------|--|-----------------|----------------|
|                              |                                      |                            |                 |                        |  | Benzyl acetate  | Dibenzyl ether |
| 10                           | 415                                  | 0.32                       | 40.5            | 0.157                  | 4.81   | 98.4            | 1.6            |
| 22.4                         | 372                                  | 0.40                       | 59.0            | 0.102                  | 8.26   | 96.1            | 3.9            |
| 30                           | 296                                  | 0.33                       | 42.9            | 0.056                  | 5.19   | 98.6            | 1.4            |
| 50                           | 188                                  | 0.20                       | 22.4            | 0.017                  | 2.35   | 100             | 0.0            |
| 70                           | 166                                  | 0.10                       | 12.9            | 0.007                  | 1.28   | 100             | 0.0            |

Reaction conditions: BA = 1.42 g, AA = 1.58 g, catalyst = 0.15 g, reaction temp. = 373 K, reaction time = 3 h.

Table 4  
Comparison of the activity of the catalysts in the esterification of BA

| Sample   | SA (m <sup>2</sup> g <sup>-1</sup> ) | TA (mmol g <sup>-1</sup> ) | BA conv. (%) | TOF (× 10 <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup> | Rate constant (× 10 <sup>-5</sup> s <sup>-1</sup> ) | Selectivity (%) |                  |
|--|--------------------------------------|----------------------------|--------------|--|---|-----------------|------------------|
|  |                                      |                            |              |  |   | BA              | DBE <sup>b</sup> |
| 15 wt.% STA/22.4 wt.% ZrO <sub>2</sub> /SBA-15                                   | 372                                  | 0.40                       | 59           | 0.102  | 8.26  | 97.3            | 2.7              |
| Hβ (30)  | 540                                  | 0.94                       | 57.8         | 0.001  | 7.99  | 98.2            | 1.8              |
| HY (13.5)  | 530                                  | 2.25                       | 43           | 0.0004   | 5.20  | 100             | 0.0              |
| 15 wt.% STA/ZrO <sub>2</sub>   | 3                                    | 0.02                       | 11.2         | 0.058  | 1.09  | 96.1            | 3.9              |
| Reusability of 15 wt.% STA/22.4 wt.% ZrO <sub>2</sub> /SBA-15 calcined at 1123 K |                                      |                            |              |  |   |                 |                  |
| First cycle  | –                                    | –                          | 58.2         | –  | –   | 96.7            | 3.3              |
| Second cycle   | –                                    | –                          | 57.5         | –  | –   | 97.8            | 3.2              |

Reaction conditions: BA = 1.42 g, AA = 1.58 g, catalyst = 0.15 g, reaction temp. = 373 K, reaction time = 3 h.

<sup>a</sup> TOF is calculated by considering three protons per Keggin unit (mol mol<sup>-1</sup> H<sup>+</sup> s<sup>-1</sup>).

<sup>b</sup> Dibenzyl ether.

comparison of the total acidity of different catalysts has been made and the results are presented in Table 4. The results reveal that the total acidity of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 system increases with increasing the STA loading up to 15 wt.%, 1123 K calcination temperature, and 22.4 wt.% ZrO<sub>2</sub> loading and then decreases with further increase in factors, respectively. For higher loadings, the density of the acid sites decreases which could be mainly due to the decomposition of STA into its constituent oxides. This has also been further confirmed by the presence of tungsten oxide crystallites peaks in the powder XRD patterns of those samples. Therefore, it can be concluded that the structure of Keggin-like unit of heteropoly acid is retained in the 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 catalyst calcined at 1123 K, which shows maximum acidity among the catalysts studied.

### 3.2. Catalytic activity

The liquid phase esterification of BA with AA was carried out using 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 with different loading of STA calcined at 1123 K, 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at different temperature, 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 with different loading of ZrO<sub>2</sub> and the results are presented in Tables 1–3, respectively. Esterification of BA with 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K catalyst under selected reaction conditions gave 59% BA conversion with 96.1% selectivity for benzyl acetate. Turn over frequency (TOF) which is calculated by considering three protons per Keggin unit (mol mol<sup>-1</sup> H<sup>+</sup> s<sup>-1</sup>), and the rate constant (s<sup>-1</sup>, by considering esterification of BA as a pseudo-first order reaction) of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K in the esterification of BA are found to be 0.10 mol mol<sup>-1</sup> H<sup>+</sup> s<sup>-1</sup> and 8.26 × 10<sup>-5</sup> s<sup>-1</sup>, respectively (Table 1). TOF of the catalyst decreases with increasing the STA loading from 5 to 90 wt.% as shown in Table 1. The conversion of BA increases with increasing the loading of ZrO<sub>2</sub> up to 22.4 wt.% and then decreases with the further increase of ZrO<sub>2</sub> loading (Table 3). The effect of calcination temperature on the conversion of BA and the selectivity to benzyl acetate is displayed in Table 2. It is interesting to note that the calcination temperature of the catalysts has a strong influence on the cat-

alytic activity of the materials. It is found that the conversion of BA increases with increasing the calcination temperature of the catalyst up to 1123 K and then decreases upon raising the calcination temperature of the catalyst above 1123 K. This is mainly due to the fact that 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K has the maximum total acidity, where STA forms a monolayer coverage over the support.

The catalytic activities of different catalysts such as H-beta, H-Y, 15 wt.% STA/ZrO<sub>2</sub> and 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K in the esterification of BA with AA under identical reaction conditions are compared and the results are depicted in Table 4. It is evident that 15 wt.% STA/ZrO<sub>2</sub> calcined at 1123 K gave a little conversion, which is at least 5 times lower as compared to that of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K under the same optimized reaction conditions. The high activity of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K is mainly attributed to the fact that the catalyst possesses a large number of acid sites, high surface area, and large pore diameter of the supports, which help the easy access of the acidic protons for the reactant molecules. Among the zeolite catalysts studied, Hβ is more active as compared to that of HY because the former having much stronger and medium acid sites than those of the latter. The catalytic activity of 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 is almost similar to that of the highly active Hβ catalyst. Therefore, 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K was chosen for further investigations on the esterification of BA with AA.

The results of esterification of different alcohols with AA, propionic acid and acrylic acid using 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K under solvent-free conditions are presented in Table 5. All the reactions except the esterification of BA with AA shows 100% product selectivity with variety of conversions for all the reactants in a period of 3 h. For complete conversion, the reactions have been carried out for a longer time. It is clearly evident from Table 5 that the role of the acid is very critical in combination with the acidity of the catalyst to control the conversion of the alcohols used in the esterification reactions. It is worth to mention that the conversion of the alcohols is much higher when the esterification reaction is carried out with acrylic acid while the catalyst show a low conversion

Table 5  
Results of esterification of different alcohols and acids and their possible applications

| Alcohol                   | Alcohol conv. (%) | Ester                     | Uses   | Fragrance                 |
|---------------------------|-------------------|---------------------------|--|---------------------------|
| BA <sup>a</sup>           | 59                | Benzyl acetate            | In perfume formulation and as a solvent  | Peach                     |
| Isoamyl alcohol (IAA)     | 49                | Isoamyl acetate           | Flavor esters in the food industry   | Banana                    |
| <i>tert</i> -Amyl alcohol | 20                | <i>tert</i> -Amyl acetate | In perfume formulation and as a solvent  | Banana                    |
| Dodecyl alcohol           | 57                | Dodecyl acetate           | Dodecyl acetate is the first repellent allomone  | Characteristic odor       |
| 1-Octanol                 | 37                | Octyl acetate             | Flavorings   | Orange, jasmine           |
| Methanol                  | 6                 | Methyl acetate            | Solvent in lacquers and paint removers and to make pharmaceuticals   | Sweet                     |
| Ethanol                   | 46                | Ethyl acetate             | Solvent in lacquers and paint removers and in pharmaceuticals  | Fruity                    |
| Isobutanol                | 35                | Isobutyl acetate          | Lacquers   | Polish remover            |
| Ethanol                   | 12                | Ethyl propionate          | Solvent, flavoring agent and fragrance   | Pear                      |
| Isobutanol                | 14                | Isobutyl propionate       | Solvent or lacquer thinner, in perfumes and flavors  | Rum                       |
| IAA                       | 34                | Isoamyl propionate        | Flavorings   | Pineapple, apricot        |
| Benzyl alcohol            | 36                | Benzyl propionate         | An additives in tobacco products, alcoholic lotion, anti perspirant, deo-stick, detergent perborate, detergent TAED, fabric softener, shampoo and soap | Sweet, apple, banana, jam |
| Methanol                  | 48                | Methyl acrylate           | Ingredients in paints, coatings, textiles, adhesives and in polymer industry   | Sharp fruity              |
| Ethanol                   | 52                | Ethyl acrylate            | Ingredients in paints, coatings, textiles, adhesives, and used in making acrylic resins  | Sharp, ethereal rum       |
| IAA                       | 60                | Isoamyl acrylate          | Manufacturing polymers and as a feedstock for synthesis  | Sharp fruity              |

Entries from 1 to 8 with HOAc, 9 to 12 with PrOAc and 13 to 15 with ArOAc (reaction conditions:  $n_{\text{Acid}}/n_{\text{Alcohol}} = 2$ , catalyst = 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 (0.15 g), temp. = 373 K, time = 3h).

<sup>a</sup> 96.1% benzyl acetate and 3.9% DBE, all other entries from 2 to 15 shows 100% selectivity for respective products.

of alcohols using acetic acid in the esterification reaction. This could mainly due to the fact that the affinity between the catalysts with a high acidity and the unsaturated carboxylic acid is much higher as compared to that with the saturated carboxylic acid, which promotes the reaction with the alcohol.

The effect of catalyst concentrations on the BA conversion was studied by varying the catalyst concentration from 1 to 10 wt.% of the total weight of the reaction mixture and the results are shown in Fig. 2(A). It can be obviously seen that BA conversion increases from 15.6 to 72.3% with increasing the catalyst concentration up to 10 wt.%, while the selectivity for benzyl acetate decreases from 100 to 94.2% with a concomitant raise of the selectivity for dibenzyl ether. The effect of the molar ratio of AA to BA ( $n_{\text{AA}}/n_{\text{BA}}$ ) on the activity and the selectivity over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 at the reaction temperature of 373 K, catalyst weight of 5 wt.% of total reaction mixture is shown in Fig. 2(B). With increasing the  $n_{\text{AA}}/n_{\text{BA}}$  ratio from 0.5 to 3, the conversion of BA increases from 30.3 to 68.7%. The effect of reaction temperature on the conversion of BA and the product selectivity over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 was studied in the temperature range 353–383 K and the results are shown in Fig. 3. It is seen that the conversion of BA increases up to 72.3% with increasing the reaction temperature to 383 K where as the selectivity for benzyl acetate is decreased from 99.3 to 95.4%. Under the optimized reaction conditions, i.e. at the reaction temperature of 373 K, catalyst weight of 0.150 g (5 wt.% of total reaction mixture),  $n_{\text{AA}}/n_{\text{BA}}$  ratio of 2, and the reaction time of 3 h, the esterification of BA with AA performed and the results are shown in Fig. 4. With increasing the reaction time, the conversion of BA increases from 23.6 to 84.3% with a decrease in the selectivity for benzyl acetate from 100 to 93.1% while the selectivity of dibenzyl ether increases from 0 to 6.9%.

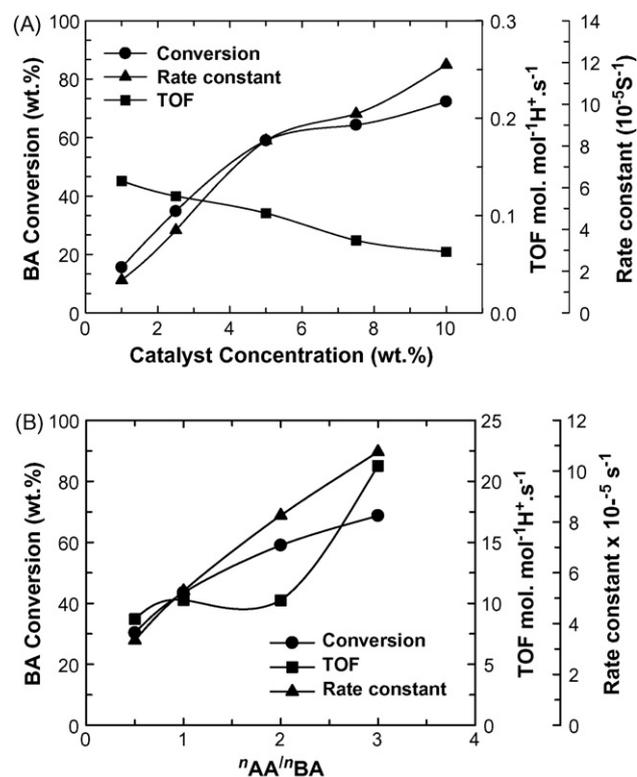


Fig. 2. (A) Effect of catalyst concentration on BA conversion, TOF and rate constant over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K (reaction conditions: temperature = 373 K,  $n_{\text{AA}}/n_{\text{BA}} = 2$ , reaction time = 3h). (B) Effect of the reactant feed ratio ( $n_{\text{AA}}/n_{\text{BA}}$ ) on BA conversion, TOF and rate constant over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K (reaction conditions: temperature = 373 K, catalyst weight = 0.15 g (5 wt.% of total reaction mixture), time = 3h).

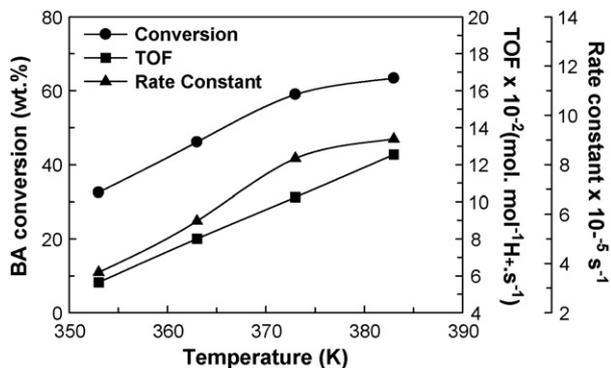


Fig. 3. Effect of the reaction temperature on BA conversion, TOF and rate constant over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K (reaction conditions:  $n_{AA}/n_{BA} = 2$ , catalyst weight = 0.15 g (5 wt.% of total reaction mixture), reaction time = 3h).

For catalyst reusability, the used catalyst in the first cycle of the reaction was separated by filtration, washed three times with 1,2-dichloromethane, dried in an oven at 373 K for 24 h, and activated at 773 K for 4 h in an air. The activated catalyst was used for esterification of BA under the optimized reaction conditions. The procedure was repeated for the second cycle and the data on the conversion of BA are presented in Table 4. From these results, it can be concluded that the catalyst can be reused as there is no appreciable loss in catalytic activity and product selectivity in the two cycles.

To check the leaching of STA into the reaction mixture, the reaction was carried out for 2 h under the optimized reaction conditions using fresh 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K. The reaction was stopped, the catalyst was separated by filtration and then the filtrate was stirred for 1 h under the same reaction conditions. It was found that in the absence of the catalyst, there was no further increase in the conversion of BA, indicating the absence of STA leaching into the reaction mixture. This observation also confirmed that the reaction was catalyzed heterogeneously. In addition, leaching of STA (i.e., dissolution of Si or W) into the hot filtrate was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES), which did not show the presence of Si or W in the filtrate.

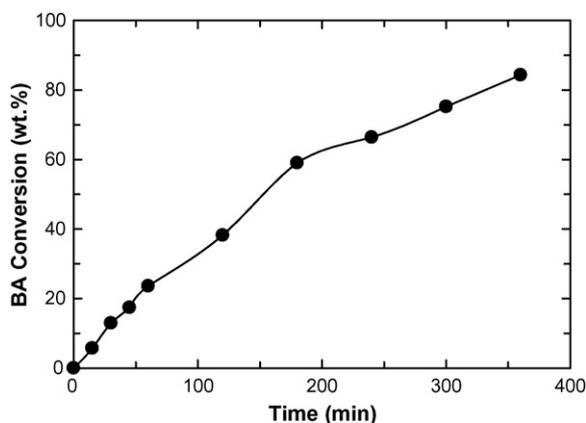


Fig. 4. Time-on-stream study over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 calcined at 1123 K (reaction conditions: temperature = 373 K,  $n_{AA}/n_{BA} = 2$ , catalyst weight = 0.15 g (5 wt.% of total reaction mixture), reaction time = 3h).

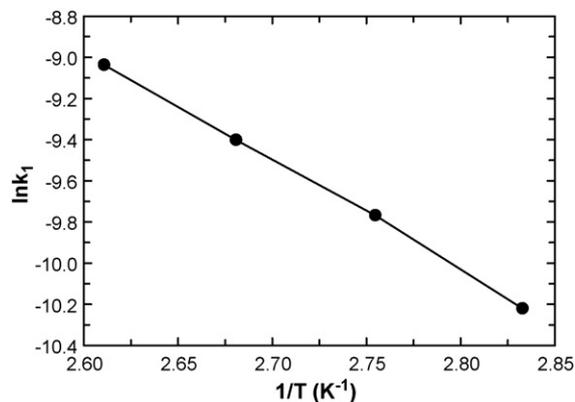


Fig. 5.  $\ln k_1$  vs.  $1/T$ , i.e. Arrhenius plot.

The standard equation for a first order series reaction,  $C_A/C_{A0} = e^{-kt}$ , was used to determine the rate constant, where  $C_{A0}$  and  $C_A$  are the concentration of BA at initial time and the reaction time,  $t$ , respectively. At one particular temperature, first-order rate constants were calculated at different reaction times and then the constant values of ' $k_1$ ' showed that the esterification of BA is a first-order reaction. Energy of activation of the reaction was evaluated graphically (Fig. 5). The activation energy ( $E_a$ ) was obtained from an Arrhenius plot and a linear plot with negative slope equivalent to ( $E_a/R$ ). The activation energy was calculated to be 10.5 kcal mol<sup>-1</sup>.

#### 4. Conclusions

Nano-sized STA/ZrO<sub>2</sub>/SBA-15 with different loading of STA and ZrO<sub>2</sub> have been synthesized and characterized by various sophisticated techniques such as XRD and N<sub>2</sub> adsorption–desorption measurements. The acidic behavior of the catalysts has been studied by TPD of NH<sub>3</sub>. The effect of the loading of STA (wt.%), calcination temperature and the loading of ZrO<sub>2</sub> (wt.%) on the textural characteristics of the catalysts has also been studied and the results have been clearly discussed. Esterification of BA with an AA was carried out over 15 wt.% STA/22.4 wt.% ZrO<sub>2</sub>/SBA-15 catalyst calcined at 1123 K in liquid phase conditions under N<sub>2</sub> atmosphere. Catalytic activities have been correlated with the acidity of the catalysts. Effects of reaction parameters such as mole ratio of reactants, reaction temperature, catalyst concentration, and reusability of the catalyst have been studied so as to get higher substrate conversions and product selectivities. The catalyst with 15 wt.% loading showed good catalytic activity with a maximum conversion of BA (59%) with >96.1% selectivity to benzyl acetate as compared with other isomers at 373 K. The above catalyst was recyclable, cost effective and environmental friendly and could be used in similar reactions.

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