# Catalytic activity of anion-modified zirconia, alumina and silica in the esterification of benzyl alcohol with acetic acid

Joyce D'Souza & N Nagaraju*

Department of Chemistry, St. Joseph's College Post-Graduate Centre, 46, Langford Road, Bangalore 560 027, India

Email: nagarajun@yahoo.com

The catalytic activity of zirconia, alumina and silica and their sulphate, phosphate and borate modified forms has been studied in the liquid phase esterification of benzyl alcohol with acetic acid for the synthesis of benzyl acetate. All these catalysts have been found to be active for the formation of benzyl acetate with 100% selectivity. A small amount of dibenzyl ether was formed only in the case of sulphated zirconia when refluxed for more than 12 h. The active sites with 'weak to intermediate' acid strengths may be responsible for the catalytic activity towards the esterification. Sulphated zirconia is the most suitable catalyst providing 53 to 90% yield of benzyl acetate when refluxed for 30 min to 24 h with 0.1 to 3 g of the catalyst. This catalyst has been found to be effective in catalyzing the esterification of *n*-propanol, *iso*-propanol, *n*-butanol and *iso*-butanol with acetic acid to form the respective esters in good yields.

Esterification of alcohols with carboxylic acids is a reaction of industrial importance[1–3]. Though most of the esterification reactions are auto-catalyzed, condensing agents have been used to optimize the yield of ester in the reaction especially when equimolar amounts of reactants are taken. Typical catalysts for the reaction are Brönsted acids[4] like sulphuric, *p*-toluene sulphonic, methane sulphonic acids, etc. that are corrosive or Lewis acids[5] like anhydrous $ZnCl_2$, $AlCl_3$, Sn-octoate, etc., which lead to the formation of large amounts of waste during separation. Therefore, in esterification, the use of heterogeneous catalysts[6] is preferred and this line of research is heavily pursued since the solid catalysts can be easily separated from reaction mixture by filtration or decantation, and allow the use of continuously operated fixed bed reactor. Many heterogeneous catalysts such as ion exchange resins[7,8], zeolites[9-15], amorphous silica-alumina, MCM-41[16], niobic acid[17,18] and sulphated oxides[19] of Zr, Al and Si have been reported to be active in esterification. Polymer-protected anhydrous $AlCl_3$[20], graphite bisulphate[21] and superacidic perfluorinated resin sulphonic acid (Nafion-H) have been successfully employed for esterification[8]. Microwave-induced esterification has also been studied over ion-exchange resin and compared with that of sulphuric acid[22].

Metal salts, metal oxides and modified metal oxides such as zirconium tungstate[23], zirconium oxide[24], sulphated zirconia[25-30], etc. have been reported to catalyze esterification of various alcohols. Esterification of organic acids and alcohols is a type of reaction which is not highly demanding from point of view of acid strength, and can be catalyzed even by relatively weak acid sites present on zirconia[24]. Sulphation of zirconia has been reported to strongly decrease the activity for the esterification of acetic acid and methanol. With the possibility of esterification, dehydration and Friedel-Craft's acylation[31], the reaction between benzyl alcohol and acetic acid has been chosen in this study to know the product of the reaction over a superacid such as sulphated zirconia. A study of this reaction over oxides and their modified forms is important, both from industrial point of view as well as academic interest[32-35]. Benzyl acetate is the product of the reaction between benzyl alcohol and acetic acid in the presence of conc. sulphuric acid[36] and is an industrially important ester. Commercially, benzyl acetate is synthesized by treating benzyl chloride with acetic anhydride in the presence of bismuth oxide or by treating benzyl alcohol with acetic acid using conc. sulphuric acid as catalyst[37]. In this work, the synthesis of benzyl acetate via esterification of benzyl alcohol

using acetic acid over solid acids such as zirconia, alumina and silica and their sulphate, phosphate and borate modified forms under refluxing conditions has been investigated for their catalytic activity and chemoselectivity.

## Experimental Procedure

Zirconium hydroxide was obtained from Aldrich, aluminium hydroxide and precipitated silicic acid from Loba chemie, and conc. sulphuric acid, phosphoric acid and boric acid from sd. fine chemicals.

### Catalyst preparation

The catalysts, zirconia, alumina and silica and their sulphate, phosphate and borate modified forms, were prepared by following the procedure given below.

#### Hydrated zirconia, alumina and silica

Hydrated zirconia [$Zr(OH)_4.xH_2O$], alumina [$Al(OH)_3.xH_2O$] and silica [$SiO_2.xH_2O$] were obtained by calcining separately zirconium hydroxide, aluminium hydroxide and silicic acid at 550°C and are represented as $ZrO_2$, $Al_2O_3$ and $SiO_2$, respectively.

#### Modified oxides

A calculated amount of zirconium hydroxide, aluminium hydroxide and silicic acid, was taken before calcination and subjected to impregnation separately with sulphate, phosphate and borate ions.

For instance, 1.0 g of each sample was treated with 2.0 mL of 1 M $H_2SO_4$/$H_3PO_4$/$H_3BO_3$ solution and mixed with 3.0 mL of deionized water to form slurry and stirred for 1 h at room temperature, filtered without washing and dried at 120°C for 12 h.

Thus prepared samples were calcined at 550°C for 4 h. The sulphated oxides were labeled as S-$ZrO_2$, S-$Al_2O_3$ and S-$SiO_2$ (SZ, SAl and SSi in figures). Similarly, the phosphated and borated samples were denoted with a prefix P- and B-, respectively.

### Catalyst characterization

The BET surface area of the calcined samples was analyzed by nitrogen adsorption at liquid nitrogen temperature using NOVA-1000 high speed gas sorption analyzer version-3.70. Total surface acidity of the samples was measured by $n$-butylamine back titration method using bromothymol blue indicator. Powder XRD patterns were recorded with Seimens-D5005 X-ray diffractometer with a Ni filtrated Cu-Kα radiation (1.5418 Å). The FTIR spectra of all the catalyst samples were obtained from Nicolet instrument by KBr pellet technique.

### Catalytic activity studies

A mixture of alcohol and acid (1:1 molar ratio, total volume = 16 mL) was taken along with known amount of the catalyst and refluxed under solvent-free conditions over a mantle in a 100 mL RB flask fitted with an ice-water cooled condenser. The reaction mixture was cooled to room temperature after a specified time and analyzed for the products using GC (Netel Gas Chromatograph with 2 m stainless steel column packed with `10% AT−1200 + 1% $H_3PO_4$ on Chromosorb W-HP'). The retention times of the peaks in the chromatograms were compared with that of the authentic samples. The catalytic activity measurements were made by varying the reaction conditions such as molar ratio of the reactants, amount of catalyst and time of reflux. The reaction conditions were optimized using sulphated zirconia as the catalyst since it provided a better yield of benzyl acetate. The reaction was also carried out with other alcohols such as $n$-propanol, $iso$-proponol, $n$-butanol and $iso$-butanol with acetic acid to obtain the respective esters.

## Results and Discussion

The physico-chemical characteristics of the catalysts were found to match with those reported in literature. The total surface acidity and surface area of the catalysts are presented in Table 1. It was observed that the acidity of $ZrO_2$, $Al_2O_3$ and $SiO_2$ increases on treatment with various anions. There was a remarkable increase in acidity of all the metal oxides on treatment with $SO_4^{2-}$ while $PO_4^{3-}$ and $BO_3^{3-}$ did not lead to any significant increase in the acidity. The powder XRD patterns of all the calcined oxides and sulphated oxides were recorded. The hydrated alumina and silica as well as their sulphated forms were found to be amorphous both in their calcined and uncalcined forms. The peaks in the X-ray diffraction of catalyst samples are found to match well with that reported in the literature[25]. In case of zirconia it was found that during calcination at 550°C, zirconia transforms from tetragonal phase ($2\theta = 30.3$, 35.3, 50.7) into monoclinic phase ($2\theta = 24.7$, 28.4, 31.6)[39]. This transformation was not observed in the case of S-$ZrO_2$, which indicates that sulphate ions delay the phase transformation resulting in the tetragonal phase. The phosphate and borate ions were

Table 1 — Total surface acidity (*n*-butylamine back titration, indicator:bromothymol blue) and surface area of simple oxides and the anion-modified samples by BET method

| Catalyst | Total surface acidity (mmolg$^{-1}$) | Surface area (m$^2$g$^{-1}$) | Catalyst | Total surface acidity (mmolg$^{-1}$) | Surface area (m$^2$g$^{-1}$) | Catalyst | Total surface acidity (mmolg$^{-1}$) | Surface area (m$^2$g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $ZrO_2$ | 0.20 | 64 | $Al_2O_3$ | 0.44 | 190 | $SiO_2$ | 0.40 | 132 |
| S-$ZrO_2$ | 1.20 | 91 | S-$Al_2O_3$ | 1.00 | 198 | S-$SiO_2$ | 1.44 | 111 |
| P-$ZrO_2$ | 0.4 | 151 | P-$Al_2O_3$ | 0.70 | 209 | P-$SiO_2$ | 0.67 | 121 |
| B-$ZrO_2$ | 0.6 | 103 | B-$Al_2O_3$ | 0.75 | 192 | B-$SiO_2$ | 0.85 | 136 |

found to be less effective in introducing this type of effect on zirconia. In the IR spectra of all the catalysts, the appearance of absorption bands in the range of 500-1500 cm$^{-1}$ corresponding to $SO_4^{2-}$, $PO_4^{3-}$ and $BO_3^{3-}$ confirm the presence of these ions on the surface of the catalysts[25]. The FTIR spectra of S-$ZrO_2$, P-$ZrO_2$ and B-$ZrO_2$ exhibit peaks in the regions of 1200 cm$^{-1}$, whereas pure $ZrO_2$ does not show any bands. The spectrum of S-$ZrO_2$ shows a broad peak having shoulder peaks at 1218, 1152, 1066 and 1058 cm$^{-1}$ confirming the presence of sulphate ions on the surface. The IR spectra of P-$ZrO_2$ and B-$ZrO_2$ show a broad band with peak maximum at 1056.8 and 1072 cm$^{-1}$ characteristic of phosphate and borate ions on the surface of the catalyst.

The gas chromatogram of the products of all the reactions using different catalysts indicated the presence of only three components in the reaction mixture i.e., acetic acid, benzyl alcohol and benzyl acetate. Thus, zirconia, alumina and silica and their sulphate, phosphate and borate modified forms have been found to catalyze esterification between benzyl alcohol and acetic acid to yield benzyl acetate and exhibit 100% selectivity towards ester formation. The only product formed is benzyl acetate, exception being the case of sulphated zirconia wherein excess catalyst and long hours of reflux resulted in a small amount of dibenzyl ether as the side-product. The percentage yields of benzyl acetate over zirconia-based catalysts reported in this work are different from those reported earlier under similar reaction conditions[32]. This is due to the difference in the procedures followed for the preparation of the catalysts. The catalysts prepared from the commercial hydroxides appear to have a better catalytic activity towards formation of benzyl acetate though the general trend of the activities upon modification with various anions remained the same.

On deposition of sulphate, phosphate and borate ions on the surface of these oxides, the catalytic activity did not increase in a significant manner (38 to 60%) under the same conditions which is an important observation. In some cases, it was observed that the blank reaction provided better yield than those in the presence of the catalyst. This can be explained by considering the nature and concentration of acetic acid in the reaction mixture. Acetic acid is a protonic acid which functions as the homogeneous catalyst with all the H$^+$ ions active for the reaction. At the same time acetic acid can get adsorbed on the surface catalyst causing, firstly, a block of those active sites and secondly, rendering those acetic acid molecules unavailable for reaction. For this reason, a correlation between acetic acid concentration and catalytic activity cannot be directly ascertained. The catalytic activity of sulphate, phosphate and borate modified oxides are almost the same as that of the untreated oxides, the only exception being sulphated zirconia where there is a definite and significant increase (10 to 20% increase) in the yield of ester as compared to phosphated, borated and the unmodified forms. With 0.1 g of sulphated zirconia, there is a 10% increase in the yield of benzyl acetate when refluxed for 30 min, and with 0.5 g of the same catalyst for the same time of reflux, the increase in the yield is almost 20%.

**Effect of catalyst**

The percentage yield of benzyl acetate obtained by refluxing benzyl alcohol with acetic acid for 30 min (molar ratio=1:2, total volume=16 mL, amount of catalyst=0.1 g) over various catalysts taken in this study was compared with the total surface acidity determined by *n*-butylamine back titration measurements (Table 1) and the results indicate that the reaction yield does not depend on the total number of acid sites on the catalysts. Sulphated silica with the highest total surface acidity and zirconia with the least total surface acidity have similar yields of benzyl acetate (40 to 46%) with 0.1 g catalyst when refluxed

for 30 min, and is almost the same as that obtained in the blank reaction. Also, the various catalysts have total surface acidity over a wide range (0.2-1.44 mmolg$^{-1}$), but the yield of benzyl acetate is almost the same under similar conditions.

It may be observed that for smaller reaction times, the percentage yield of the blank reaction is almost the same as that in the presence of a catalyst. In the absence of a catalyst, the reactant acetic acid being a weak protonic acid catalyzes the esterification resulting in 38% benzyl acetate on refluxing for 30 min. It may be noticed that addition of catalyst does not further increase the yield of the ester. This may be due to the fact that the esterification reaction being a reversible reaction attains a state of equilibrium when a certain percentage of ester is formed in the reaction mixture. The effect of addition of catalyst becomes more pronounced only when the reaction mixture is heated for longer period of time.

When refluxed for 12 h, the blank reaction yielded 58% benzyl acetate whereas in the presence of catalysts the yield was in the range of 60 to 84%. This is because, in the blank reaction the number of active sites, the protons from acetic acid, available for catalytic activity decreases with time as more and more acetic acid molecules get converted to the ester. Hence for longer reaction times, the blank reaction provides lesser yield of benzyl acetate when compared to that in the presence of the catalysts. It may be noted that in the presence of catalyst, however, the number of active sites continues to remain the same irrespective of the reaction time. However, a better strategy would be to reflux the reaction mixture for 30 min which yields about 60% product in the presence of sulphated zirconia catalyst, and then separate the product for recycling the unreacted alcohol and acid.

Comparative study of this reaction in the absence and presence of catalysts, especially for longer reaction periods, suggests that all the acidic sites on the surface of the catalyst are not responsible for ester formation, partly attributed to the equilibrium nature of the reaction. To identify the exact range of acidic strength that may be required by these solid acids to catalyze this reaction, the zirconia-based catalysts were considered, particularly because of the exception, sulphated zirconia, which provided a 20% higher yield than untreated, phosphated and borated forms under the reaction conditions considered here. The distribution of acid sites with varied acid-strengths in zirconia-based catalysts is categorized into weak, intermediate, strong and very strong acid regions as shown in Table 2. It is a well-known fact that esterification does not require highly acidic active sites and those with weak to moderate acid strengths are sufficient to catalyze this reaction[6]. It may be observed in Table 2 that sulphated zirconia does not possess weak acid sites but has good catalytic activity. Thus, one may infer that weak acid sites alone are not responsible for this reaction. For the same reason, one may rule out the possibility of acid sites of 'intermediate', 'strong' and 'very strong' strengths individually catalyzing this reaction because all the zirconia-based catalysts influence the rate of this reaction. Also, the acidity of any one individual range of the four regions considered here cannot be correlated with the percentage yield of the ester over the corresponding catalysts, keeping in mind the fact that one of the reactant, acetic acid, itself is catalytic in nature. A similar comparison of the total acidity of 'weak to intermediate'[6], weak to strong' and such combinations were compared with the percentage yield of benzyl acetate and it was observed that the only region which fitted closely with the activity was acid sites with 'weak to intermediate' strength. Here again, there was a small deviation in the acidity-activity correlation, which could be explained by taking into consideration the surface areas of the catalysts (Table 1). The surface areas of the zirconia-based catalysts have been considered and the number of sites in the range of 'weak to intermediate' acidity available per unit surface area of the catalysts were

Table 2 — Acidity distribution of various modified forms of zirconia determined by NH$_3$ TPD[25]

| Catalyst | Acidity (mmolg$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Weak (<100°C) | Intermediate (100-200°C) | Strong (200-400°C) | Very strong (<400°C) | Total |
| ZrO$_2$ | 0.0735 | — | 0.0608 | — | 0.1343 |
| S-ZrO$_2$ | — | 0.2858 | 0.2529 | 0.0653 | 0.6040 |
| P-ZrO$_2$ | 0.1290 | 0.1493 | — | — | 0.2783 |
| B-ZrO$_2$ | 0.1482 | 0.0822 | 0.0784 | — | 0.3030 |

compared and found to correlate well with the activity of the catalysts. The 'weak to intermediate' sites per unit surface area of the catalysts, zirconia, phosphated zirconia and borated zirconia are almost equal and that of sulphated zirconia is about 10-15% higher. A correlation of acidity per unit surface area with the percentage yields of benzyl acetate as zirconia, phosphated zirconia and borated zirconia providing similar yields (~41%) and that of sulphated zirconia about 10% higher (53%) has been observed. Thus, it can be concluded that the type of sites required for the esterification of benzyl alcohol with acetic acid is in the range of 'weak to intermediate' acid strength which is in agreement with the literature[6,39,40]. The strength and the number of corresponding sites are not sufficient to explain the activity of the various catalysts. It also depends on the number of the appropriate acid-sites present per unit surface area of the catalyst. Several factors may be expected to play a role when surface area is found to effect significantly the activity of the catalysts, such as possibility of either/both the reactant molecules being adsorbed on the adjacent active sites and steric-hindrance of the huge benzyl alcohol molecule adsorbed on the surface of the catalyst blocking the active sites of the suitable acid strength. When the total number of acid sites per unit area is high, the probability of these sites being blocked by adsorption of comparatively bulky benzyl alcohol molecules is low. Hence, the active sites required for catalyzing this reaction are more available to be adsorbed by the smaller acetic acid molecules, thus favouring the formation of benzyl acetate. When the number of active sites per unit area is low, the probability of each of the sites being adsorbed by benzyl alcohol molecules is high. There will be no scope for steric hindrance by the adsorbed benzyl alcohol molecule as it is situated far away from the next nearest active site and will be available for another benzyl alcohol molecule for adsorption, thereby preventing the adsorption of acetic acid molecules and hindering the reaction. In general, it may be seen that for this reaction, the total number of acid sites of 'weak to intermediate' strength per unit surface area of catalyst decides the yield of benzyl acetate.

### Effect of amount of catalyst and reaction time and reusability

The effect of the amount of catalyst has been studied for the synthesis of benzyl acetate by esterification over all the catalysts considered in this work by taking 0.1 and 0.5 g of each of the catalysts

and refluxing up to 12 h. It has been observed that there is only a marginal increase in the yield of benzyl acetate by increasing the amount of the catalyst five-fold. This can be explained on the basis of the reversibility of this reaction. Even if the amount of catalyst added is increased, the catalytic effect operates in both forward as well as backward direction, resulting in only slight increase in the yield of benzyl acetate. With varied amounts of sulphated zirconia, from 0.1 to 3 g, it was observed that there was an increase in the yield of benzyl acetate by about 10% when refluxed for 30 min. A comparatively significant increase in the yield of benzyl acetate was observed when the amount of catalyst as well as the reaction time was increased. When the reaction mixture was refluxed with 0.1 g of sulphated zirconia for 30 min, the yield was 53% and that with 3 g for 24 h was almost 90% (Fig. 1). However, it was noticed that with refluxing for longer duration of more than 12 h and larger amount of catalyst of 2 g, dibenzyl ether was formed as the side-product (5%). With all other catalysts, 100% selectivity was observed with no side product formation. The percentage yield of benzyl acetate for the reactions over zirconia, alumina and silica based catalysts for the two conditions (i) 0.1 g catalyst for 0.5 h and (ii) 0.5 g catalyst for 24 h is depicted in Fig. 2(a-c). It may be observed that the conversion of benzyl alcohol was almost double for larger amount of the catalyst and reaction time. When refluxed beyond 12 h, selectivity towards benzyl acetate decreased and a small amount of dibenzyl ether was formed depending on the amount of the catalysts used (5 to 15% dibenzyl ether for
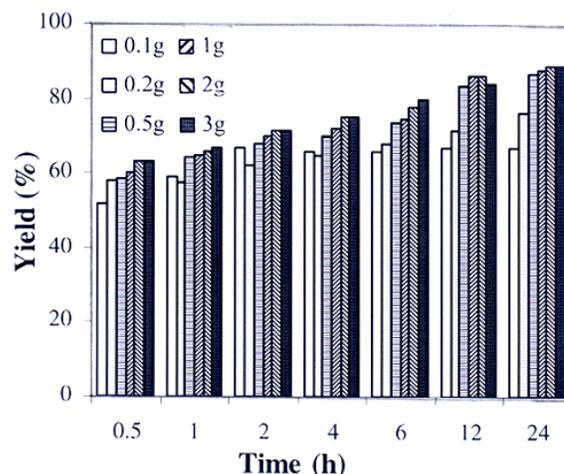


Fig. 1 — Effect of amount of catalyst and duration of reflux on the percentage yield of benzyl acetate over sulphated zirconia (benzyl alcohol:acetic acid = 1:2, total volume = 16 mL).
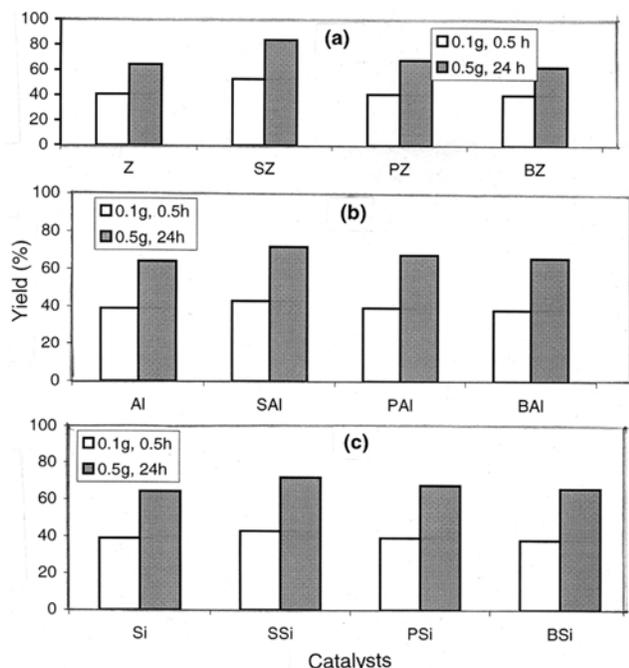
Fig. 2(a-c) — Effect of amount of catalysts and time of reaction in the synthesis of benzyl acetate over $ZrO_2$, $Al_2O_3$ and $SiO_2$ based catalysts.



Fig. 3(a-c) — Effect of molar ratio of benzyl alcohol:acetic acid in the synthesis of benzyl acetate over $ZrO_2$, $Al_2O_3$ and $SiO_2$ based catalysts.

2-3 g of S-$ZrO_2$). The reusability of sulphated zirconia has been verified by using the catalyst after a simple washing and recalcination step (550°C). There was only a marginal decrease in the catalytic activity (2%) even after repeated use up to five times.

**Effect of molar ratio**

The effect of relative concentration of acid and alcohol was studied to probe the mechanism of the reaction and it was observed that the rate of the reaction increased with acid concentration. The molar ratio of the reactants of benzyl alcohol and acetic acid was varied as 1:2, 1:1 and 2:1 and the results are shown in Fig. 3. A decrease in the rate was observed when the alcohol concentration was increased which could be explained by the saturation of the catalyst surface with the alcohol, thereby blocking acid adsorption. Thus, one can say that the acid adsorption is a must for the esterification to proceed and that there is a competitive adsorption of benzyl alcohol[34]. The esterification takes place between acetic acid adsorbed on the surface forming an electrophile and benzyl alcohol in the liquid phase. The efficiency of the catalyst in this reaction depends, therefore, on its acid character as well as its ability to adsorb the alcohol which would hinder the reaction.
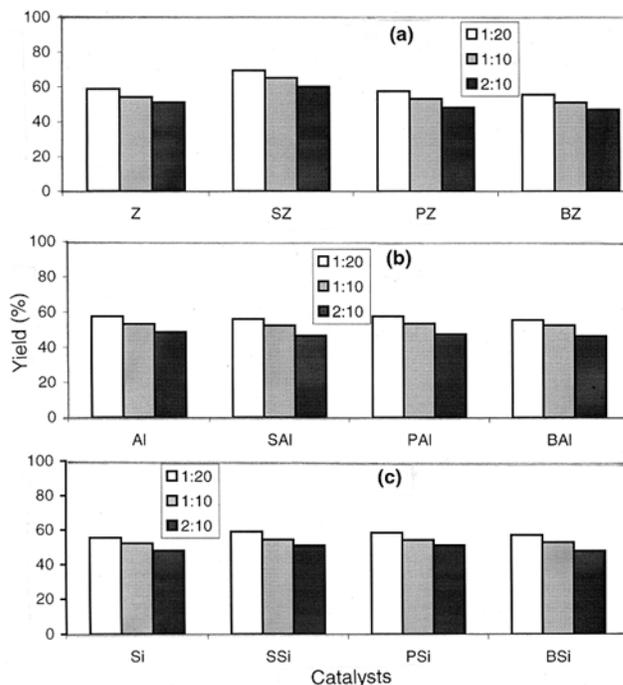
**Effect of reaction temperature**

The effect of reaction temperature was studied in this reaction to check the variation in selectivity due to the possibilities of side reactions. The esterification was carried out in the temperature range of 383 to 403 K keeping the molar ratio of alcohol to acid as 1:2, with 0.1 g of catalyst and 4 h of refluxing. The results are shown in Fig. 4. The conversion of the alcohol increased by about 10%, when the reaction temperature was increased from 383 to 403 K. No side product formation was observed up to reaction temperature of 403 K, which indicates the absence of dehydration or Friedel-Craft's acylation. However, on increasing the temperature beyond 403 K, the formation of small amount of dibenzyl ether was noticed which is the result of dehydration reaction. Thus, 100% selectivity towards the formation of benzyl acetate can be achieved up to a temperature of 403 K.

**Kinetics and mechanism of the reaction**

An attempt is made to study the kinetics and obtain the reaction rate constants and the energy of activation for this reaction over sulphated zirconia. A plot of rate as a function of the weight of catalyst shown in Fig. 5 is linear and the rate increased proportionally with the weight of S-$ZrO_2$ indicating
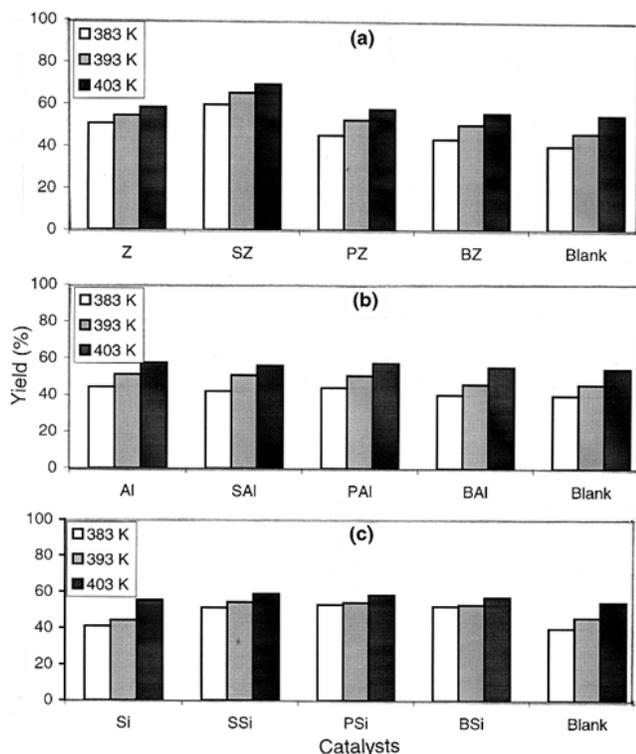
Fig. 4(a-c) — Effect of catalysts and temperature of reaction in the synthesis of benzyl acetate over $ZrO_2$, $Al_2O_3$ and $SiO_2$ based catalysts.
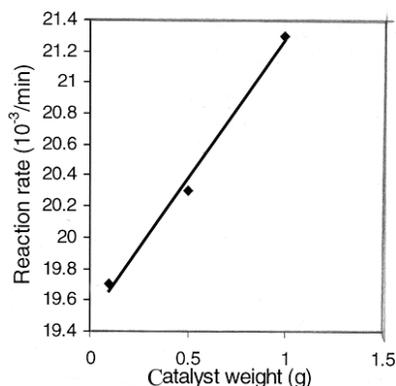


Fig. 5 — Effect of catalyst weight on rate of conversion of benzyl alcohol at 403 K (molar ratio of alcohol:acid = 1:1).

the absence of any mass transfer limitation during the reaction[34]. A plot of the first order equation for the esterification of benzyl alcohol with acetic acid over $ZrO_2$ and S-$ZrO_2$ at 403, 393 and 383 K is given in Fig. 6. Plots of –ln(1-yield) versus duration of reaction are nearly linear in all cases indicating the esterification reaction to be a first order reaction. The rate constants obtained from the slopes of these plots and the energy of activation calculated from Arrhenius equation for S-$ZrO_2$ was lower than that of
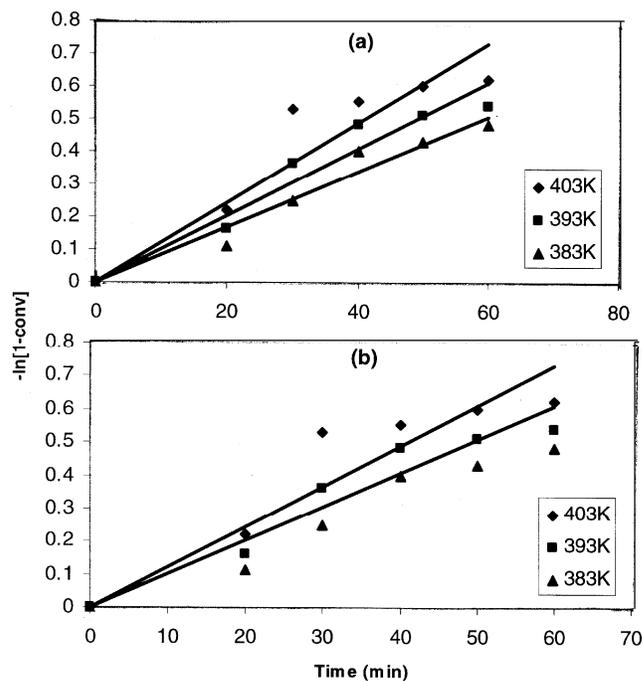


Fig. 6 — Plot of the first order rate equation for the esterification of benzyl alcohol with acetic acid over (a) $ZrO_2$ and (b) S-$ZrO_2$ at 383K, 393K and 403 K.

Table 3 — Reaction rate constants and energy of activation for the formation of benzyl acetate

| Catalyst | Rate constant ($10^{-3}$ min$^{-1}$) | | | Energy of activation (kcal/mol) |
|---|---|---|---|---|
| | 383K | 393K | 403K | |
| $ZrO_2$ | 8.4 | 10.1 | 12.2 | 5.95 |
| S-$ZrO_2$ | 12.5 | 17.2 | 19.7 | 4.28 |

$ZrO_2$ as shown in Table 3. The results obtained thus far have been compared with the earlier work done over zeolites[34] and found to be similar, based on which the Scheme 1 may be suggested for the possible reaction mechanism for the esterification of benzyl alcohol with acetic acid over sulphated zirocina.

**Esterification of other alcohols with acetic acid**

The esterification of n-propanol, iso-propanol, n-butanol and iso-butanol with acetic acid over zirconia-based catalysts led to the formation of the respective acetates and the results are given in Fig. 7(a-d). The only product formed is the corresponding acetate with 100% selectivity. The percentage of ester formed depends on the type of catalysts as well as the alcohol used. Blank reactions were conducted in the absence of catalyst and it was
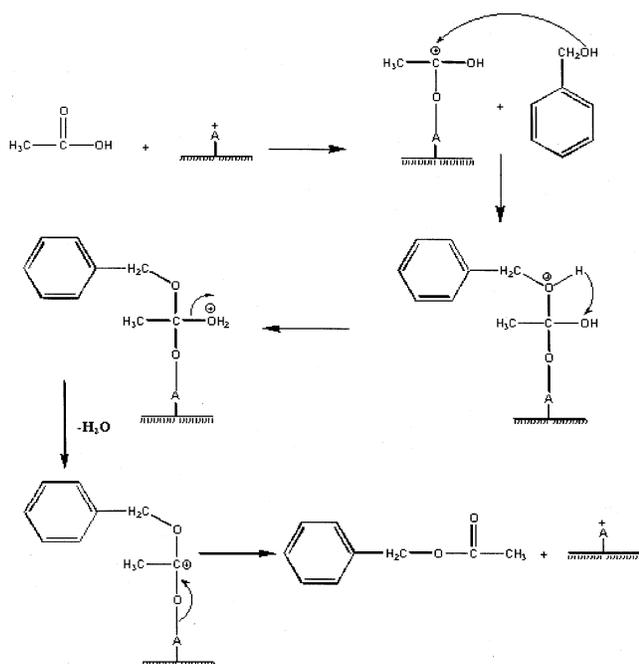
Scheme 1 — Possible mechanism for the esterification of benzyl alcohol with acetic acid over sulphated zirconia.
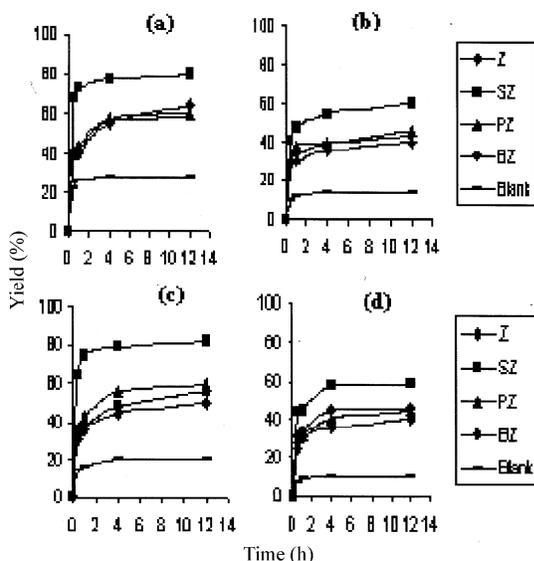


Fig. 7 — Effect of reaction time on the percentage yield of the respective esters over zirconia-based catalysts. (a) *n*-propanol (b) *iso*-propanol (c) *n*-butanol (d) *iso*-butanol.

found that small amount of ester was formed. The conversion of alcohol was almost equal on $ZrO_2$, $P$-$ZrO_2$ and $B$-$ZrO_2$ and was much higher on $S$-$ZrO_2$. The conversion was found to decrease in the order of *n*-propyl > *n*-butyl > *iso*-propyl > *iso*-butyl. The conversion of straight chain alcohols was more than their branched isomers in the esterification reaction,

which may be due to steric hindrance. Thus, it may be observed that zirconia based catalysts are active for the esterification of various alcohols and sulphated zirconia can be conveniently used for the synthesis of several esters with 100% selectivity.

## Conclusion

The catalytic systems, zirconia, alumina and silica and their sulphate, phosphate and borate modified systems, have been found to be catalytically active for this reaction with 100% selectivity. A small amount of dibenzyl ether was formed only in the case of sulphated zirconia when refluxed for more than 12 h. The acid sites with 'weak to intermediate' strengths are responsible for the catalytic activity towards the esterification. Sulphated zirconia is the most suitable catalyst providing 53 to 90% yield of benzyl acetate for the reaction time of 30 min to 24 h with 0.1 to 3 g of the catalyst. This catalyst has been found to be effective in catalyzing the esterification of *n*-propanol, *iso*-propanol, *n*-butanol and *iso*-butanol with acetic acid to form the respective esters in good yields. Metal oxides and their modified forms may be used to replace the conventional homogeneous catalysts, which cannot be recovered and reused, thus presenting a cost-effective and eco-friendly process for the synthesis of benzyl acetate.

## Acknowledgements

## References
1  Giovanni Sartori & Raimondo Maggi, *Chem Rev,* 106 (2006) 1077.
2  Larock R C, *Comprehensive Organic Transformations,* Chap. 9 (VCH Publishers, New York), 1989.
3  Zaidi A, Gainer J L & Carta G, *Biotechnol Bio-Eng,* 48 (1995) 601.
4  Liu W T & Tan C S, *Ind Eng Chem Res*, 40 (2001) 3281.
5  Nagaraju N & Mehboob P, *Indian J Chem Technol*, 3 (1996) 253.
6  Corma A, *Chem Rev*, 95 (1995) 559.
7  Gimenez J, Costa J & Cervera S*, Ind Eng Chem Res*, 26 (1987) 198.
8  Olah G A, Keumi T & Meidar D, *Synthesis*, 1978, 929.
9  Santacesaria E, Gelosa D, Danise P & Carra S, *J Catal*, 80 (1983) 427.
10  Zhang H B, Zhang B Z & Li H X, *J Nat Gas Chem*, 1992, 49.
11  Corma A, Garcia H, Iborra S & Primo J, *J Catal*, 120 (1989) 78.

12 Corma A & Garcia H, *Catal Today*, 38 (1997) 257.

13 Ma Y, Wang Q L, Yan H, Ji X & Qiu Q, *Appl Catal*, 139 (A) (1996) 51.

14 Lasperas M, Graffin P & Geneste, *J Catal*, 139 (1993) 362.

15 Nagaraju N, Mehboob P & Deva Prasad, *React Kinet Catal Lett*, 61(1) (1997) 155.

16 Koster R, Linden B, Poels E & Bliek A, *J Catal*, 204 (2001) 333.

17 Izuka T & Tanabe K, *Chem Lett*, 1984, 1085.

18 Okazaki S & Wada N, *Catal Today*, 16 (1993) 349.

19 Tanabe K, Misono M, Ono Y & Hattori H, *Stud Surf Sci Catal*, 51 (1989) 285.

20 Blossey E C, Turner L M & Neckers D C, *Tetrahedron Lett*, 21 (1973) 1823.

21 Bertin J, Kagan H B & Luche J J, *J Am Chem Soc*, 96 (1974) 8113.

22 Kabza K G, Chapados B R, Gestwicki J E & McGrath J L, *J Org Chem*, 65 (2000) 1210.

23 Patel P, Shivanekar A & Chudasama U, *Indian J Chem*, 31(A) (1992) 803.

24 Takahashi K, Shibagaki M & Matsushita H, *Bull Chem Soc Japan*, 62 (1989) 2353.

25 Yadav G D & Nair J J, *Microporous and Mesoporous Materials*, 33 (1999) 1.

26 Hino M & Arata K, *Chem Lett*, 1981, 1671.

27 Yadav G D & Mehta P H, *Ind Eng Chem Res*, 33(9) (1994) 2198.

28 Arata K, *Adv Catal*, 37 (1990) 165.

29 Nagaraju N & Mohamed Shamshuddin S Z, *Indian J Chem*, 44A (2005) 1165.

30 Arata K & Hino M, *Appl Catal*, 59 (1990) 197.

31 Panich R C & Stock L M, *Tetrahedron Lett*, 1964, 1285.

32 D'Souza J & Nagaraju N*, Indian J Chem*, 40B (2001) 266.

33 Sharath K R, Vijayashree S & Nagaraju N, *Indian J Chem Technol*, 8 (2001) 362.

34 Kirumakki S R, Nagaraju N, Chary K V R & Narayanan S, *Appl Catal*, 248(A) (2003) 161.

35 Kirumakki S R, Nagaraju N & Narayanan S, *Appl Catal*, 273(A) (2004) 1.

36 Vogel A I, *Text book of Practical Organic Chemistry*, 3rd edn (Longmans), 1956, 783.

37 *Aromatic Chemicals, Perfumes and Flavor Technology*, Series no-4 (SBP publications, Delhi).

38 Benesi H A, *J Phy Chem*, 61 (1957) 970.

39 Nagaraju N & Mohamed Shamshuddin S Z, *Indian J Chem*, 43A (2004) 2060.

40 Kazama Y, Shimamura Y & Hiyama O, *Chem Abstr*, 81 (1974) 1357535.