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Effective synthesis of n–butyl salicylate over wash coated cordierite honeycomb by zirconia and its mixed oxides: a kinetic study

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Abstract

Cordierite honeycombs were coated with solid acid catalysts such as ZrO_2 (Z), Mo(VI)/ZrO_2 (MZ) and Pt-SO_4^{2-}/ZrO_2 (PSZ) were prepared and characterized for their physico-chemical properties. These catalytic materials were characterized for their total surface acidity, crystallinity, functionality, elemental analysis and morphology by using techniques such as NH_3-TPD, PXRD, FTIR, ICP-OES, SEM and TEM respectively. These honeycomb catalysts were used for the liquid phase transesterification reaction of methyl salicylate (MS) with n-butanol (n-BA). Optimization of reaction conditions such as reaction temperature, reaction time, amount of catalysts and molar ratio of the reactants were carried out to obtain maximum yield of transester (n-butyl salicylate). n-butyl salicylate is obtained as major product and di-butyl ether is obtained as minor product. Highest total transester 70 % obtained by MZ and 80 % n-butyl salicylate and 10 % selectivity of di-butyl ether obtained in the presence of 0.4 g of honeycomb coated catalysts at a molar ratio of MS: n-BA 2:1, reaction temperature 403 K and reaction time 4 h. The energy of activation (16.81 and 14.92 kJ mol^{-1}) and temperature coefficient (1.36 and 1.12) values of the MZ and PSZ were obtained from the kinetic studies. Pre-adsorption studies showed that the transesterification reaction methyl salicylate with n-butyl alcohol over honeycomb catalysts follows Langmuir-Hinshelwood mechanism. A reaction mechanism for transesterification is proposed based on the kinetic data. Reactivation and reusability studies of the honeycomb coated as well as powder form of catalysts up to 6 reaction cycles were also studied.

Keywords: Honeycomb; Solid acid catalyst; Transesterification; N-butyl salicylate; Kinetic studies; Monoliths

Introduction

Cordierite honeycomb (HC) monoliths are the structures which consist of magnesia, silica and alumina in a ratio of 2:5:2 and single blocks of small parallel, non intersecting channels (Theovenin *et al.*, 2003). Honeycomb monoliths as a catalyst support presents excellent operational properties, such as high mechanical strength, high temperature resistance, a low thermal expansion coefficient, low pressure drop and availability in various sizes or shapes. Catalyst coated on HCs have numerous advantages over powder form of catalysts, such as formation of thin layer of catalysts with high active surface area, less amounts of catalysts loaded on the monolith is highly effective, ease of separation and recovery of the catalysts from a liquid reaction mass (Mohamed *et al.*, 2012; Sharma *et al.*, 2009).

Honeycomb coated catalysts are widely used in industrial applications which involve gas phase reactions like combustion of VOCs, automotive applications, ozone abatement in aircrafts and selective reduction of NOx (Heck *et al.*, 2001; Liu Bo *et al.*, 2015). However, HCs coated with solid acid catalysts have not been much examined so far in the field of organic synthesis involving liquid or vapour phase reactions (Thimmaraju *et al.*, 2012; Lachman *et al.*, 1986; Okada *et al.*, Klinghoffer *et al.*, 1998; Lachmann *et al.*, 1992; Trimm, 1995; Knickerbockers *et al.*, 1993;

Subramanian *et al.*, 1993). Similar procedures have been perform coating the monolith walls with support materials called wash coat-like γ-Al2O$_3$, TiO_2, ZrO_2 etc, to obtain a high surface area and abundant pores since cordierite itself exhibits negligible porosity and offers little contribution to catalytic action (Arai *et al.*, 2009). About the deposition method for active phases, different strategies, such as hydrothermal synthesis sol–gel process, chemical vapor deposition and dip-coating, have been employed for initially coating the monolith channels with an additional support material, which is then followed by the accretion of active phases to the coating of ready-made catalyst (Thimmaraju *et al.*, 2012; Nijhuis *et al.*, 2001).

It is worthwhile to find out suitable environmentally benign solid catalysts for the transesterification reaction considering the fact that the existing procedures require expensive or corrosive acids, bases and solvents which cannot be reuse and recycle because of tedious procedures (Otera *et al.*, 1993; Corma *et al.*, 1998; Illankumaran *et al.*, 1999; Otera *et al.*, 1991; Staton *et al.*, 1998; D' Souza *et al.*, 2004; Banzquart *et al.*, 2001; Kim and Lee, 1999). Transesterification is an industrially important acid catalyzed reaction with wide range of applications.

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Consequently, a number of protocols for transesterification are time consuming and the catalysts used are toxic and corrosive in nature have been extensively studied and reported which are catalyzed by conventional organic acids, bases and enzymes. Though, it has known that the reaction seems accelerated by either homogeneous or heterogeneous conditions. Keeping in view of environmental concern still noteworthy to propose a catalyst which is ease of separation from the reaction mixture and more reactivable and reusability (Furlan et al., 1998; Martin Alonso et al, 2009; Qureshi et al., 2009; Ghesti et al., 2009; Monica et al., 2009; Yong and Eun, 2009; Yip et al., 2007; Saravanamurugan et al., 2008; Srinivas et al., 2004).

The salicylates are important group of esters used for the synthesis of drugs, preservatives, plasticizers pharmaceuticals, sun tan preparations, perfumes, sweeteners and solvents (Vane et al., 1992). Predominantly, n-butyl salicylates is a colourless transparent liquid used in many fragrance compounds, and find applications as decorative cosmetics, fine fragrance ingredients and other toiletries like non-cosmetic products such as detergents and household cleaners (Lapczynski et al., 2007).

In continuation of our research work (Shyamsundar et al., 2013; Shyamsundar et al., 2015) on the application of cordierite honeycomb monoliths coated with zirconia and its modified forms, in the present article synthesis, characterization and catalytic activity of cordierite honeycomb coated with solid acids catalysts such as ZrO_2, Mo (VI)/ZrO_2 and Pt-SO_4^{2-}/ZrO_2 is described.

The main goal of this article were to synthesize n-butyl salicylate over honeycomb coated solid acid catalysts such as zirconia and its customized forms (MZ, PSZ) in acid catalyzed transesterification of methyl salicylate (MS) and n-butyl alcohol (n-BA). The catalytic materials used for the present study were characterized total surface acidity, crystallinity, functionality, elemental analysis and morphology by using suitable techniques. The total transester yield and percentage selectivity towards the required product were optimized by varying parameters such as reaction temperature, reaction time, amount of catalysts and molar ratio of reactants. The obtained reaction products were characterized by gas chromatography with the flame ionization detector. In order to find out the right catalysts for the transesterification of MS and n-BA based on the kinetics reaction was carried out to obtain the data such as temperature coefficient and energy of activation (Ea). A reactant pre-adsorption experiment was also conducted and a trial was made to fit the data in Langmuir-Hinshelwood mechanism. Regeneration and reutilization of HC coated catalysts up to 6 reaction cycles were studied.

Materials and methods

Methyl salicylate, n-butanol and n-butyl salicylate were purchased from the Loba Chemie Pvt Ltd. While honeycomb monoliths (silica: alumina: magnesia) from Shreya ceramics

Baroda. The purchasd chemicals were confirmed by gas chromatography. Catalytic materials such as Zirconyl nitrate, ammonium molybdate, chloroplatinic acid, LR grade were purchased from Lab supplies India Pvt Ltd.

Preparation of catalytic materials on the cordierite honeycomb monolith

In the current work the active catalyst such as ZrO_2, Mo (VI)/ZrO_2 and Pt-SO_4^{2-}/ZrO_2 were coated on the HC which was already wash coated with zirconia. Sometimes direct coating of an active catalyst on a non-wash coated bare honeycomb may lead to the loss of active catalyst during its application in an organic reaction due to poor adherence of the active catalyst. Wash coated monoliths lies on the inner surface of the channels and increases the internal surface area

Coating of a catalytic layer on the surface of the HC by ZrO_2 (Z)

In this method calculated amount of zirconyl nitrate (5 g) and required amount of de-ionized water stirred for some time to obtain a clear solution. The resulting solution was coated on a HC by dipping and drying in a furnace at 673 K with desired amount of coating.

Coating of a catalytic layer on the surface of HC by Mo (VI)/ZrO_2 (MZ)

A known amount of zirconyl nitrate (3 g) and ammonium molybdate (0.4 g) with required amount of de-ionized water in a china dish was made into slurry. The resulting slurry was coated on a wash coated HC following by dipping and drying steps in a furnace preheated at 673 K. Process was repeated until we get ~ 0.4 g of MZ was coated on the HC.

Coating of a catalytic layer on the surface of HC by Pt-SO_4^{2-}/ZrO_2 (PSZ)

A known amount of zirconyl hydroxide (4g), 6 M sulphuric acid (2 ml) solution and little amount of de-ionized water was made into a paste. The paste was made into dried at 393 K for 12 h. The dried materials was dried and powdered well this was taken in a china dish, 1 % of H_2PtCl_6 (2 ml) was added with required amount of de-ionized water added to make a slurry. Finally the resulting slurry was coated on a HC by dipping and drying in a furnace at 673 K. Process is repeated until we get ~ 0.4 g of PSZ was coated on HC (Patil et al., 2008).

Finally, all the HC coated catalytic materials were calcined at 873 K for 4 h.

Weights of the honeycomb before and after coating the catalysts were measured. The difference between the two weights gives the amount of catalysts got coated onto the honeycomb.

i.e., if　　X1　= weight of honeycomb before coating the catalysts.

　　　　　　X2　= weight of the honeycomb after coating the catalysts.

Then, (X2-X1) is the amount of the catalyst coated on to the honeycomb.

Preparation of catalytic materials in their powder catalysts

Pure zirconia is prepared by a required amount of zirconyl nitrate and de-ionized water to make a paste and dry at hot air oven at 673 K for 12 h. Mo/ZrO_2 is prepared by calculated amount of ammonium molybdate and zirconyl nitrate with 10 ml of de-ionized water to make paste and dry at 673 K for 12 h.

A known amount of zirconyl hydroxide (2 g), 6 M sulphuric acid (1 ml) and de-ionized water (5 ml) to make paste in a ceramic dish and dry at hot air oven at 393 K for 12 h. Then the powder form with the solution of Hexachloro platinic acid (1 ml) were taken in a china dish make a paste by using small amount of de-ionized water. The resulting paste was then dried in a hot air oven at 393 K for 12 h. Therefore, all the catalytic materials calcined at 823 K for 4 h in a muffle furnace. These powder forms of catalytic materials used for the comparative studies over honeycomb coated catalytic materials.

Catalytic activity studies

The catalytic activity of the honeycomb coated with Z, MZ and PSZ was examined in transesterification of methyl salicylate (MS) with n-butyl alcohol (n-BA).

In general, a liquid phase transesterification reaction was carried out by taking methyl salicylate (2 mmol) and n-butyl alcohol (1 mmol) along with catalytic material (either HC coated or powder forms of Z, MZ and PSZ) were placed in a specially made

reactor and refluxed for a stipulated period of time (39). After a specific period of time the reaction mass was cooled to room temperature, the honeycomb coated catalyst was separated from the reaction mass and the products obtained by the transesterification shown in Scheme 1. The filtrate was examined quantitatively by GC (Mayura) fixed with 10% carbowax column which is connected to a flame ionization detector (FID) as well as qualitatively by GCMS (Varian). Typical GC operating conditions (Thimmaraju *et al.*,) were, FID Temperature = 250 ºC, Split flow = 100 mL/min, Carrier gas = Nitrogen at 1 mL/min, Temperature programming: 150 to 250 °C (at 10 °C/min).

To optimize the reaction condition parameters such as temperature, time, molar ratio of the reactants and amount of the catalysts were varied. Kinetics studies were conducted in the reaction time from the 0 to 10 h, temperature varies from 383 to 423 K, amount of catalysts in the range of 0.1 to 0.4 g and reactants was varied in the range of 1:1 to 4:1. Finally, the effect of nature of catalysts and kinetic studies to find out a facile catalyst for the transesterification reaction.

Regeneration of HC coated catalytic materials

To study the reutilization and regeneration of the HC coated catalytic materials was recovered easily from the liquid reaction mixture, washed with acetone and dried at 393 K for 2 h and followed by 873 k for 1 h to remove organic

Scheme1
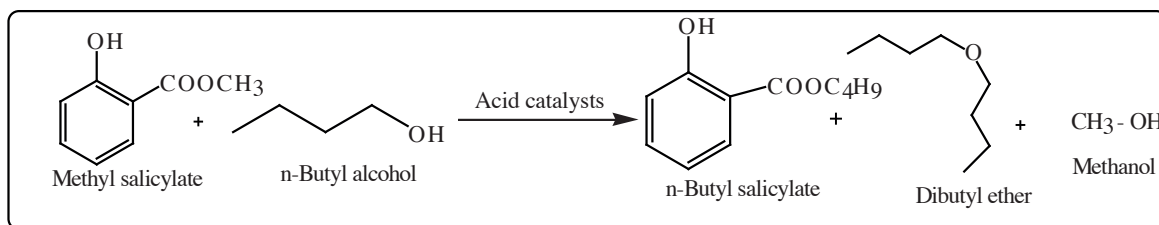
Scheme 2. Possible reaction mechanism of n-butyl salicylate formation over honeycomb coated solid acid catalysts
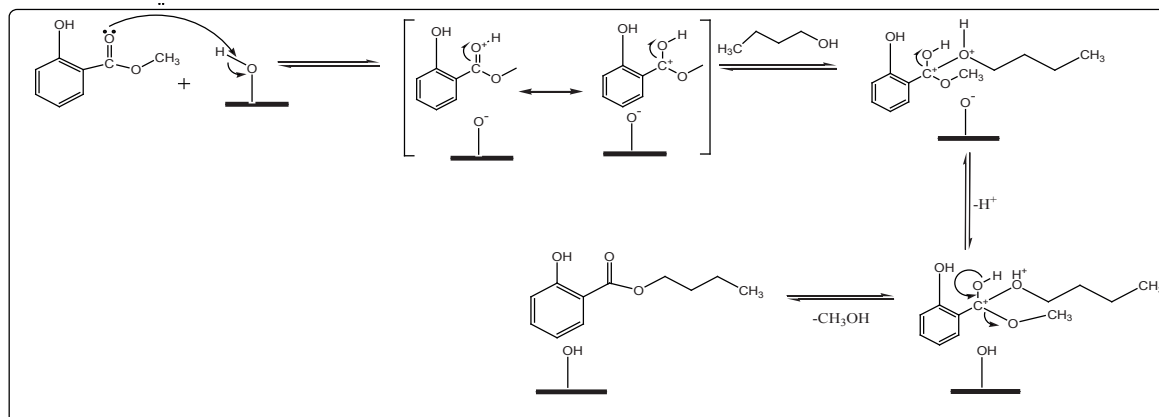
impurities. Consequently, regenerated HC monolithic catalysts used for the n-butyl salicylate synthesis under similar conditions with fresh reaction mixture for 5 successive reaction cycles.

Results and discussion

Physico-chemical techniques of honeycomb coated catalytic materials

The characterization of the materials (both powder and HC coated form). The total surface acidity (TSA) value was analyzed by temperature program desorption of ammonia (NH_3-TPD) experiments were studied on a pulse chemisorb instrument (Micromeritrics) and also by n- butyl amine back titration method with anhydrous benzene solvent. The amount of Mo, S and Pt were estimated by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) analysis techniques using Thermo-icap 5500 series instrument. NOVA 1000 Quanta chrome high- speed gas sorption analyzer instrument was used to measure the specific surface area of all the prepared catalytic materials. Powder X-Ray Diffraction (PXRD) patterns were recorded an X-ray Philips diffractometer equipped with a nickel filtered Cu K α (λ = 1.5418 A0) using a graphite monochromatic with a scanning range of 2theta = 0-70 0. The FTIR spectrum was recorded with 4 cm-1 resolution using a Nicolet IR-200 FT-IR spectrometer in the range of 400-4000 cm-1 using KBR crystal as a standard reference. SEM images were obtained, using a JEOL microscope model JEM 6300 (Japan). Transmission electron microscopy (TEM) images were recorded on a JEOL 2010 with an acceleration voltage of 200 kV IISC Bangalore.

Total surface acidity (TSA) studies and ICP-OES studies

The acid site distribution of HC coated zirconia and its customized forms by NH_3 -TPD and also values obtained by n-butyl amine back titration methods are given in Table I. TSA values of the solid acids were used for the present work followed the order: Z < MZ < PSZ.

The catalytic materials used for the present study are Z, MZ and PSZ and these materials are prepared by slurry coating

Table I. Characterization of catalytic materials used for the present study

Solid acid catalysts	Solid acid distribution		Metal ions by ICP -OES method
	BET surface area	TSA	
ZrO$_2$	43 (49)	0.43 (0.44)	
MZ	96 (114)	1.25 (1.28)	5.65 % (Mo)
PSZ	121(143)	1.49 (1.52)	2.6 % (S) and 1.5 % (Pt)

method. In the present case pure zirconia seems to be lowest acidic and it shows only 'weak' and 'moderate' acidic sites. But, MZ shows the existence of 'moderate' and 'strong' acidic sites attributed sue to the formation of electron deficient states. PSZ shows the existence of 'strong' and 'very strong' acidic sites. On the other hand, the TSA values of honeycomb coated material as well as powder form were found to be independent. There was no difference between the TSA values of honeycomb coated form as well as powder forms (Shyamsundar *et al*., 2015; Shyamsundar *et al*., 2013). The actual percentage of the metal ions obtained for the present study estimated by ICP-OES techniques are given in the Table I, Column 4.

BET Surface area

The surface area of the HC coated catalysts such as Z, MZ and PSZ catalysts were given in the Table 1. The surface area of the catalysts depends on the concentration of Mo and Pt-SO$_4^{2-}$ ions over zirconia. While the percentage of solid acid catalyst loading on the surface of the bare honeycomb. Zirconia is found to be least among the catalytic materials compared to MZ has been increased two fold surface area compared to zirconia and PSZ catalysts. This shows stabilization effect of zirconia.

PXRD studies

XRD patterns of zirconia and its modified forms such as MZ and PSZ were recorded in the range of 2θ = 0-700. The sharp diffraction lines at 2θ = 28.3, 24.46 and 31.58 degrees
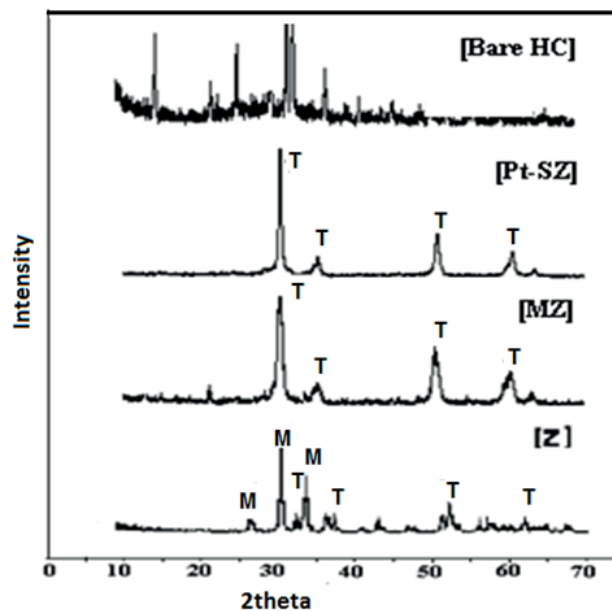

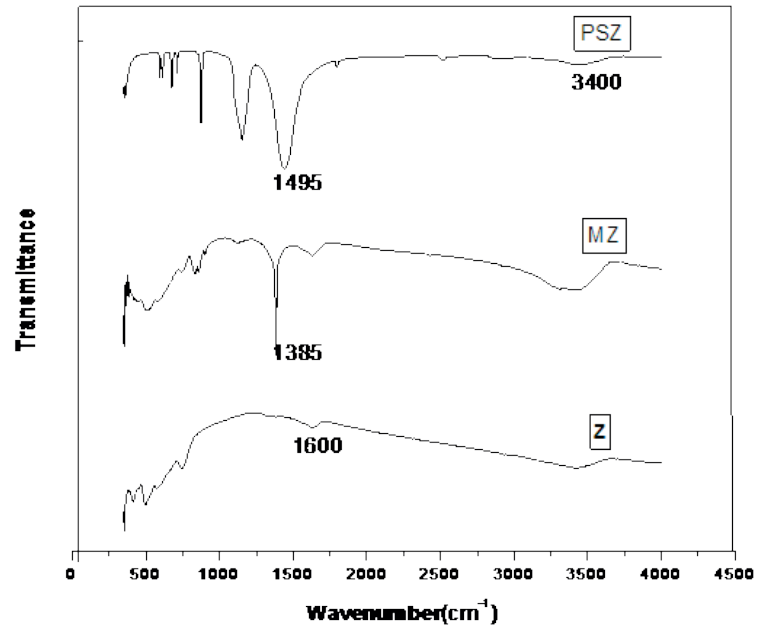**Fig. 1. PXRD patterns of HC coated Z, MZ, Pt-SZ and Bare HC [M- monoclinic ZrO$_2$, Tetragonal**

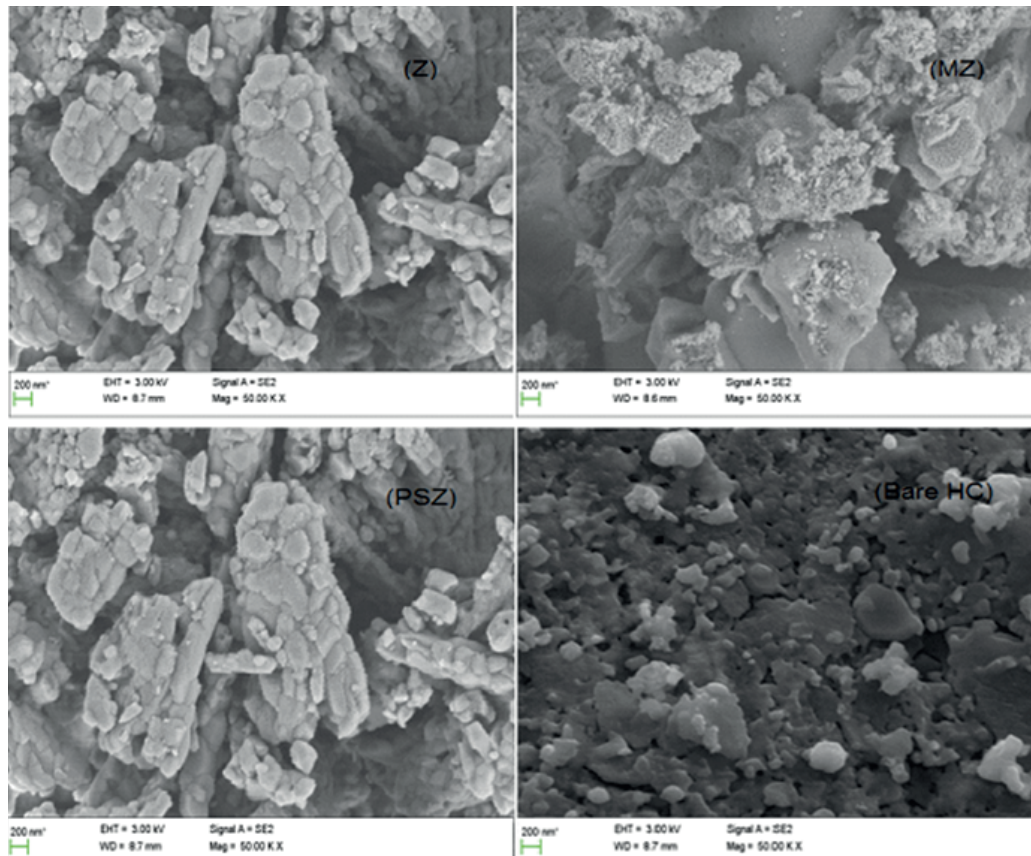**Fig. 2. FTIR spectra of HC coated Z, MZ and PSZ**

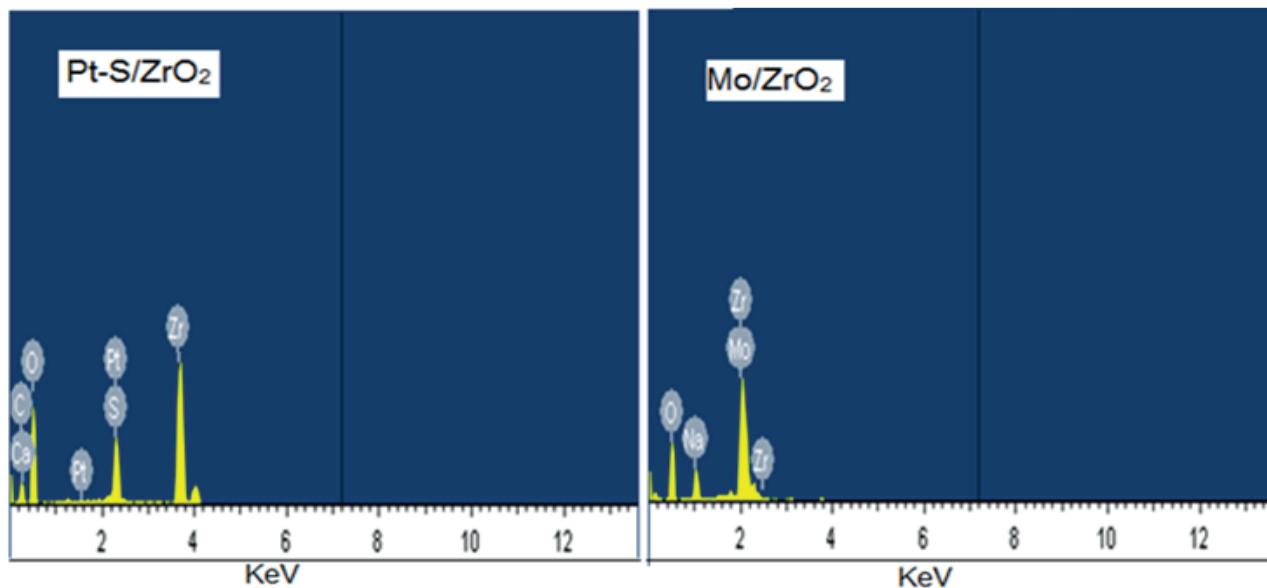**Fig. 3. SEM images of HCs coated with Z, MZ, PSZ and Bare HC**
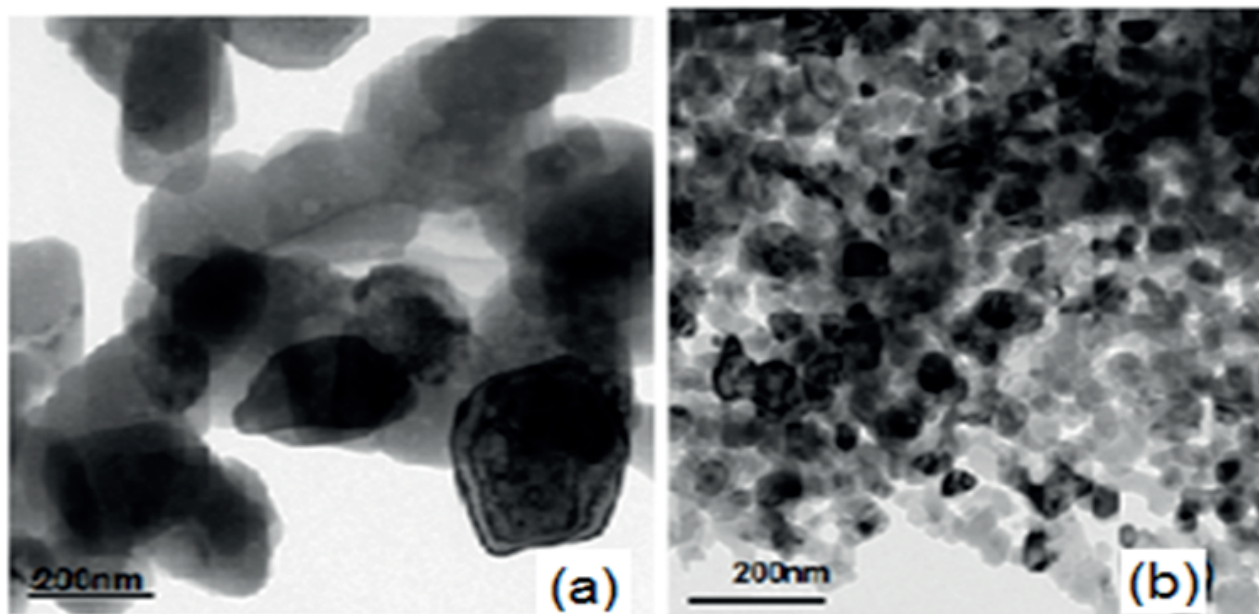
Fig. 4. EDX Spectrum of MZ and PSZ

Fig. 5. TEM images of HC coated (a) MZ (b) PSZ catalysts

correspond to the monoclinic form and the lines at 2θ = 30.27, 35.3 and 49.82 degrees are due to tetragonal form of ZrO_2. The tetragonal phase was found to dominate over the monoclinic phase when dopants such as (Mo (VI) or Pt-SO_4^{2-}) were incorporated into the hydrous zirconia structure. The suppression of monoclinic phase was hardly

observed in the MZ and PSZ has been reported in the literature (Reddy *et. al.*, 2009; Reddy *et al.*, 2008). In case of PXRD pattern of bare honeycomb was effectively covered with active materials and there was no peaks related to bare honeycomb (Thimmaraju *et al.*, 2012). The average crystalline size of the catalytic materials was used for the

preset study is found to be 100-150 nm from Scherer equation.

D= K λ/β Cos θ

FTIR Studies

The FTIR spectra of ZrO_2 and its modified forms are shown in Fig. 2 respectively. A comparison of the spectra of pure zirconia and its customized forms confirms the existence of molybdate and Pt-sulphate species, broad bands in the region of 3350–3450 cm^{-1} indicated by the existence of surface hydroxyl groups (Vijaykumar *et al.*, 2013). The PSZ showed a peak at 1495 and 1150 cm^{-1} indicating the existence of both Bronsted and Lewis acidity respectively.

In case of Mo (VI)/ZrO_2 dominant band at 975 cm^{-1} and the weak signal that appears at 1089 cm^{-1} are feature of the stretching vibration mode (frequency) of Mo=O terminal bonds and the band at 836cm^{-1} is linked with the vibration of Mo-O-Mo bridging bonds (Davydov *et al.*, 2003).

SEM and TEM Images

The SEM images clearly show a very wide distribution in texture and particle size. Both the morphologies show the active components equally spread on the surface of the honeycombs and are almost uniformly distributed with the particle size. Modified ZrO_2 shows flake like appearances with existence of certain cracks on the surface which may be due to the loss of water molecules during calcinations (Reddy *et al.*, 2007). The EDX spectrum of the catalytic materials such as MZ and PSZ shows the composition of the zirconia, molybdenum, platinum and sulphur. These materials show the presence of atomic weights similar to the catalytic composition.

TEM images clearly show zirconia has spherical shape of crystalline sizes were also in good compliance with crystalline sizes acquired from the PXRD. The average particle size of MZ and PSZ was found to be 180-200 nm. These morphological changes observed higher surface area due to incorporation of Mo (VI) and Pt-SO_4^{2-} species.

Catalytic activity studies (Transesterification)

In order to influence the liquid phase transesterification reaction, the reaction was carried between the methyl salicylate (MS) and n-butyl alcohol (n-BA) in presence of HC coated solid acids Z, MZ and PSZ catalysts (Scheme 1). When the reaction was carried out with the bare honeycomb it shows very less conversion of products. Therefore transesterification is a HC coated catalyzed reaction. Hence all the HC coated catalysts as well as powder form of catalysts showed very active in this reaction (Thimmaraju *et al.*, 2015).

Effect of nature of catalysts (HC coated as well as powder forms)

The catalytic activity of honeycomb coated with Z or MZ or PSZ was compared with their powder form. The results

indicate that ~ 1.8 fold increases in the catalysts activity of HC catalysts was observed (Table II). For instance PSZ (powder form) showed 38 % yield of trans-ester whereas PSZ (HC coated form) showed 80 % yield of transester. Higher activity of HCs catalysts could be attributed to the dispersion of the catalysts in the form of thin layer on the surface of channels present in the HC which is not possible when the catalysts is used in the powder form. The minimal catalyst loading in case of HC catalysts is compensated by the higher competence due to the high quality transfer characteristics. This may be indicated to the availability of more number of shifting centres on the surface of the HC catalysts due to homogeneous dispersion of the catalysts (Thimmaraju *et al.*, 2012; Nijhuis *et al.*, 2001). Unfortunately, no change in the selectivity of either n-butyl salicylate (n-BS) or di-butyl ether (DBE) was observed over both HC coated form as well as powder form of a catalyst.

Effect of reaction temperature

The influence of reaction temperature on the transesterification of MS and n-BA is investigated by varying the temperature range of 383 to 423 K over HC coated Z, MZ and PSZ. The n- BA conversion has been increased with the increase the temperature of the reaction accompanied by an

Table II. Catalytic materials used for the transesterification of MS with n-BA over solid acids in both powder and honeycomb coated forms

Catalyst	Total transester Yield	Selectivity of n - BS	Selectivity of DBE
Z (HC)	32	100	-
Z (powder)	18	100	-
MZ (HC)	70	100	-
MZ (powder)	32	100	-
PSZ (HC)	80	90	10
PSZ (powder)	38	88	12

[Reaction conditions for Column 3: Reaction time 4 h; reaction temperature 403 K; weight of HC coated catalyst 0.4 g; molar ratio of MS: n-BA 2:1]

increase in the selectivity of n-butyl salicylate over the HC coated Z and MZ catalysts. However, the tendency of self condensation of n-butyl alcohol increases with the increase in temperature resulting in the formation of di-butyl ether (DBE). Hence, 403 K could be set as an optimized temperature for the present transesterification reaction to get highest possible yield (%). The obtained results are shown in the Fig. 6.

Effect of amount of catalysts

The HCs with different amounts of MZ or PSZ catalysts in the range of 0.1 to 0.4 g were coated. The effects of quantity of the active catalyst coated on HC were studied in transesterification reaction of MS with n-BA, and the results are obtainable in Fig. 7. It can be seen that as the amount of catalyst coated on HC increased from 0.1 to 0.3 g, the

reasonable increase in the conversion of n-BA to n-BS. This shows that the coating of a catalyst up to 0.3 g is suitable to get good conversion of n-BA.

Effect of reaction time

The effect of reaction time on the conversion of n-BA and selectivity towards the n-BS over HC coated with MZ and PSZ was also taken up by changing the reaction time from 0 to 10 h and the results are presented in the form of a graph as shown in Fig. 8. The conversion of n-BA increased rapidly in the beginning (up to 2 h) and gradually levelled off after 6 h. On the other hand, the conversion of n- BA increased from 10 to 40 % in the first 4 h and only 42 % in the next 4 h over MZ.
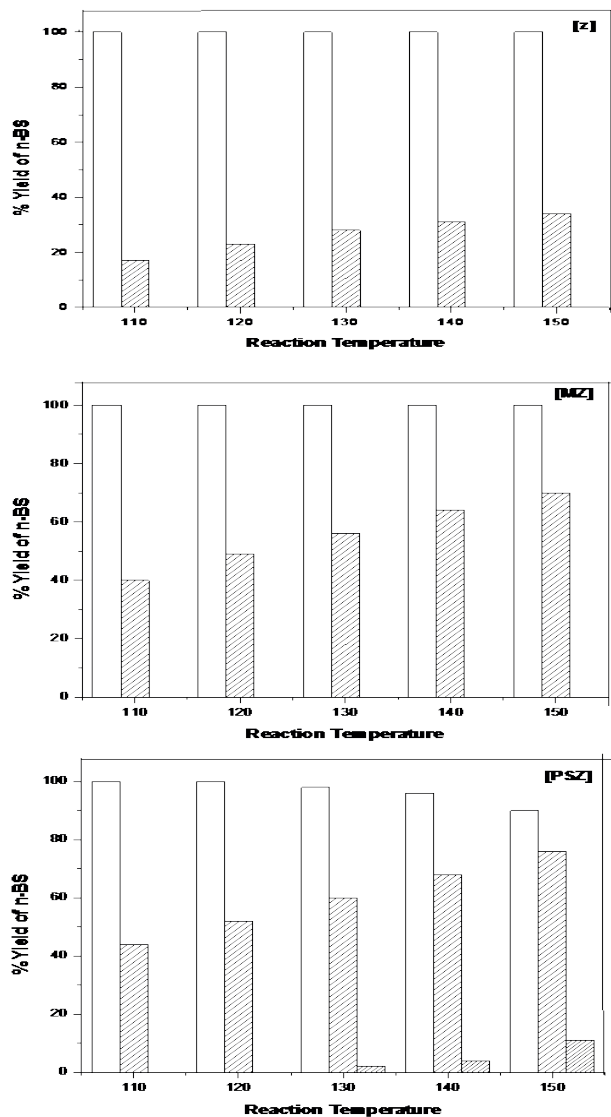

Fig. 6. Influence of reaction temperature [Reaction conditions: reaction temperature = 403 K, weight of the catalysts HC coated 0.4 g, Molar ratio 2:1, reaction time = 4 h, Selectivity of n-BS, Conversion of n-BA and Selectivity of n-DBE]
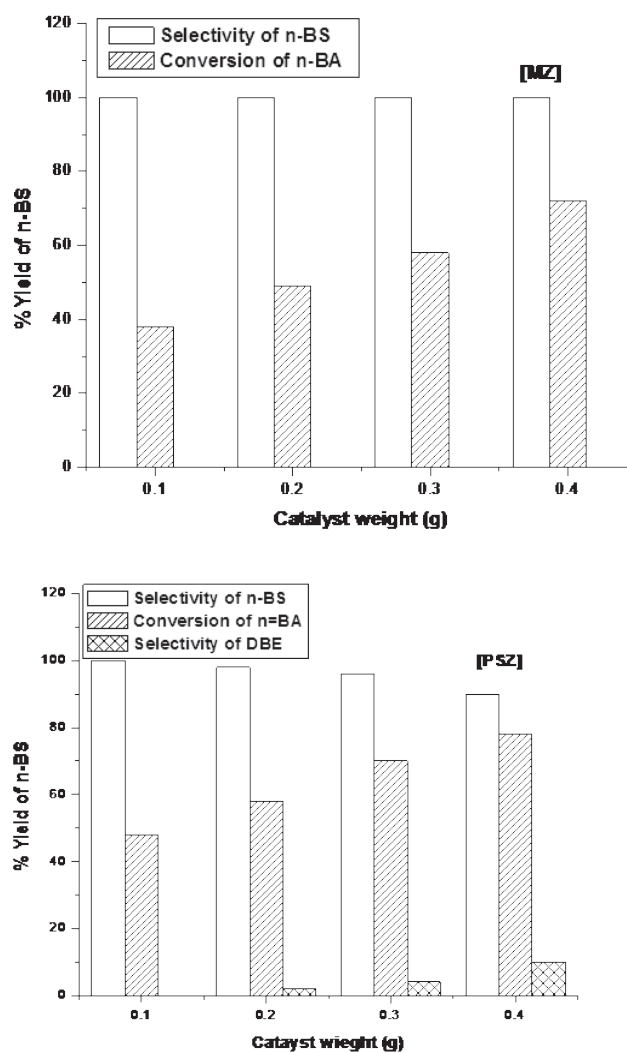

Fig. 7. Influence of amount of catalysts [Reaction conditions: reaction temperature = 403 K, weight of catalyst=0.4 g HC coated, Molar ratios= MS: n-BA (2:1), reaction time 4 h]

conversion of n-BA also increased. But an increase in the amount of catalysts beyond 0.3 g did not result in a

Although, in case of PSZ (honeycomb coated), the conversion of n-BA has increased from 25 % in the first 2 h and in next 4 h 65% has been improved. The amount of n-BA to n-BS increased up to 88 % in the next 10 h.

Selectivity of n- butyl salicylate remained 100 % up to 6 h over HC coated with MZ, but after 6 h a thick oily compound started forming on the surface of the HC which couldn't be separated or detected by GC or GC-MS. Therefore a reaction period of 4 h seems to be needed for reasonable conversion of n-butyl alcohol to n-butyl salicylate.

Effect of molar ratio of the reactants (MS: n-BA)

In order to study the effect of mole ratio of methyl salicylate and n-butyl alcohol reaction were carried out to different molar ratios such as 1:1, 1:2, 1:3, 1:4, 2:1, 3:1, 4:1 over MZ and PSZ HC coated catalysts. The yield of n-BS increases when molar ratio of MS: n-BA was increased from 1:3 to 2:1 over HC coated with MZ and PSZ catalysts. The selectivity of n-BS was found to be 100% over MZ. In case of PSZ (HC
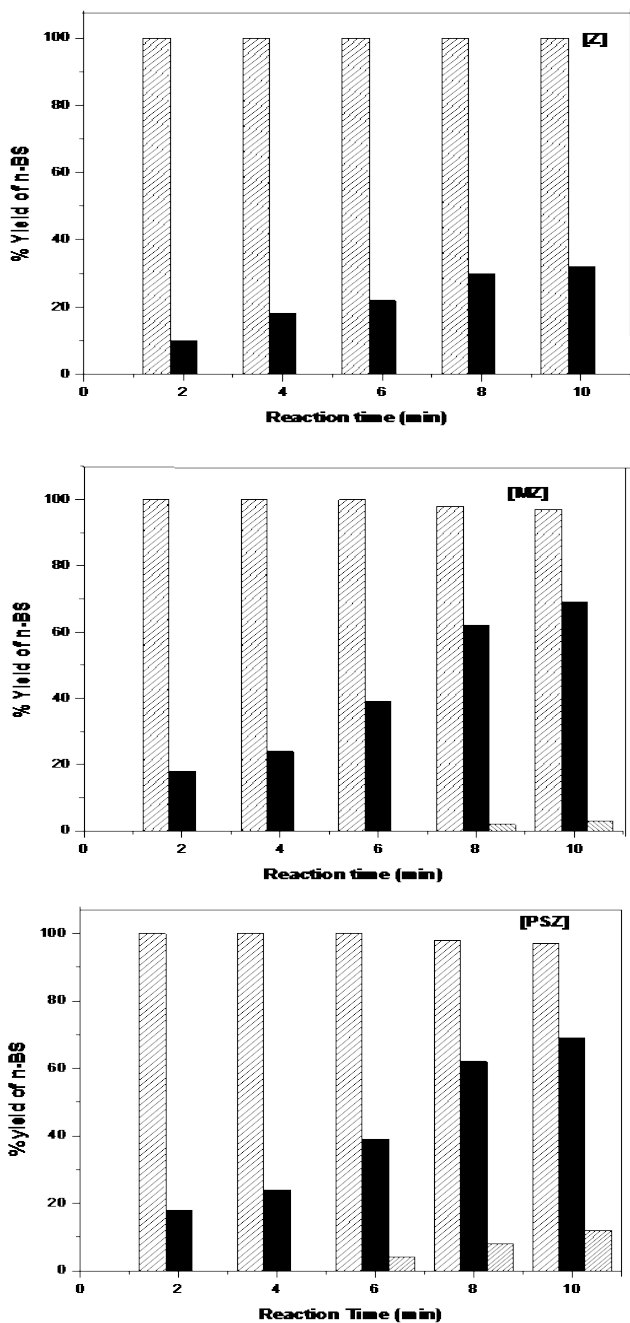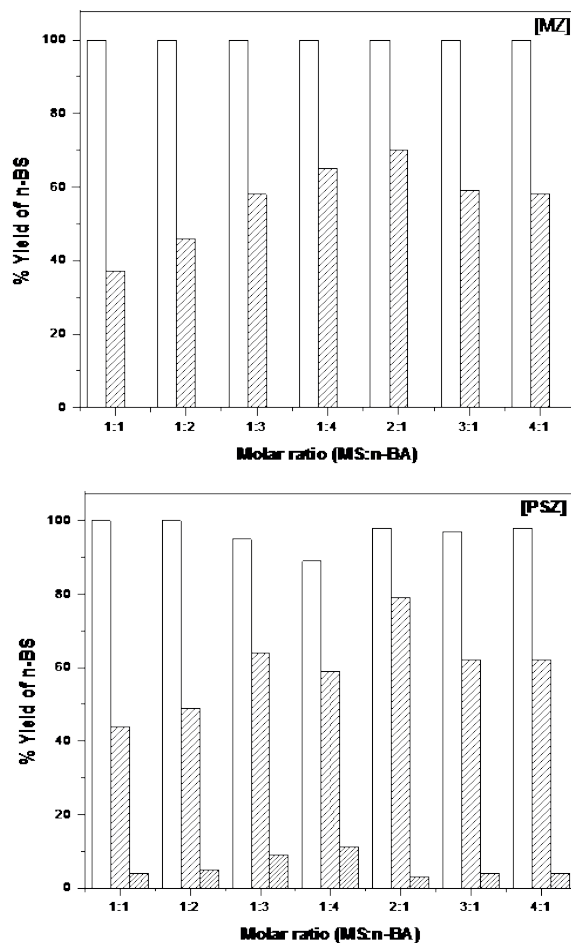

Fig. 8. Influence of reaction time [Reaction conditions: reaction temperature = 403 K, weight of HC coated catalyst 0.4 g, molar ratios 2:1, reaction time = 4 h, Selectivity of n-BS, Conversion of n-BA and Selectivity of DBE]

Fig. 9. Influence of molar ratio [Reaction conditions reaction temperature = 403 K, weight of the catalysts HC coated = 0.4 g, Molar ratio =2:1, reaction time 4 h. Selectivity of n-BS, Conversion of n-BA, Selectivity of DBE]
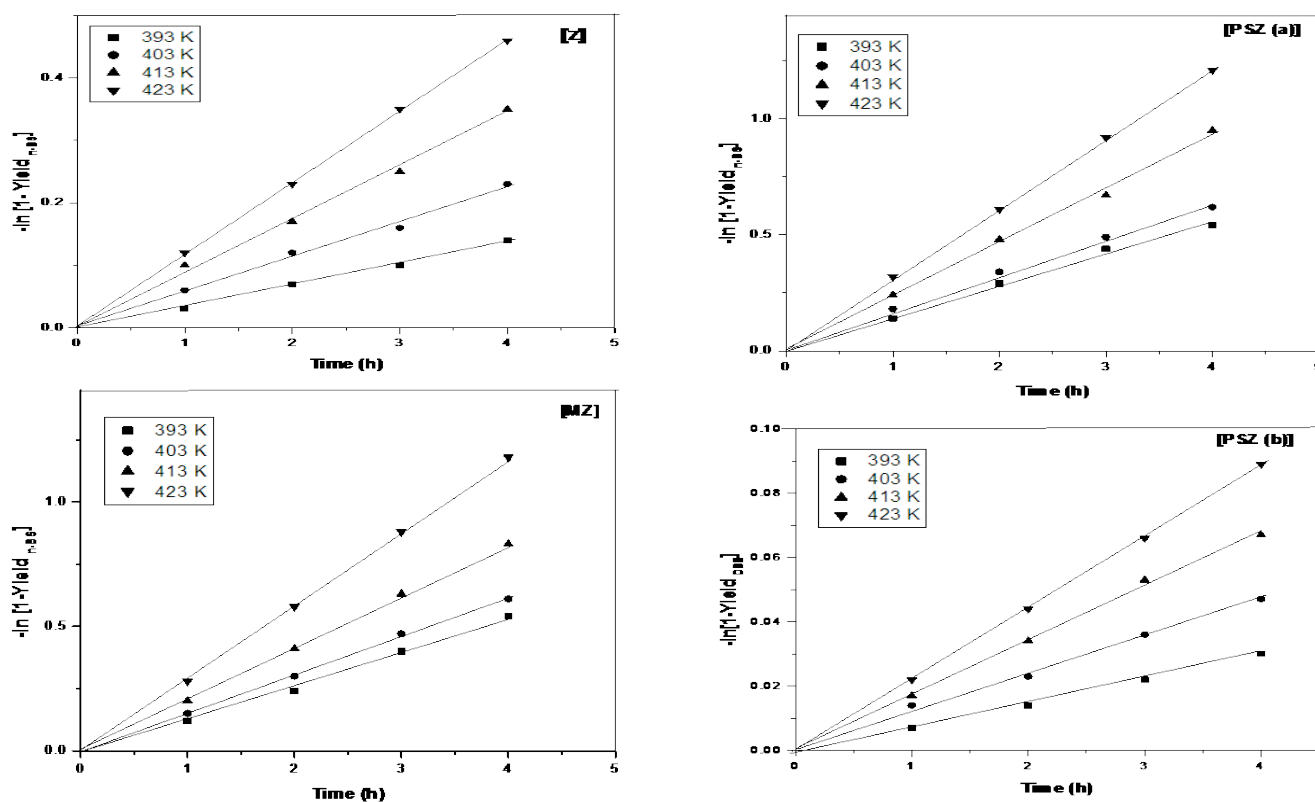
Fig. 10. Plot of first order equation for the formation of n-butyl salicylate and di-butyl ether over Z, MZ and PSZ at 383 K, 393 K, 403 K and 413 K

coated), when the concentration of n-BA increased, the selectivity of n-butyl salicylate was found to decrease due to the formation of di-butyl ether. But the effect was only to an extent of 5 to 12 % as shown in Fig. 9. In the present case, the molar ratio of methyl salicylate to n- butyl alcohol 2:1 was found to be the best adequate performance.

Kinetic studies

In order to influence of kinetics studies, The effect of activation energy, temperature coefficient and mass transfer limitations were calculated from the molar ratio of 1:1 to 4:1 (n-BA: MS) were synthesis of n- butyl salicylate reaction were carried out over HC coated Z, MZ and PSZ catalysts.

The effect of mass transfer limitations by varying the amount of catalysts with increase the conversion of n-BA over amount of the catalysts has been observed. The plots are nearly linear in all the cases, indicating the transesterification (and etherification in case of HC coated PSZ only) to be a first-order reaction. In case of detail study, the lack of mass transport limitation, rate of the reaction would be relative to the weight of the HC coated catalytic materials (Madon *et al.*, 1982; Mallik *et al.*, 2006; Thimmaraju *et al.*, 2015). In figure

9, plots of –ln (1-yield n-BS) vs reaction time at different temperature ranging from 393- 423 K carried out over HC coated catalytic materials (Z, MZ and PSZ). Since di-butyl ether was also formed over HC coated PSZ, the transesterification and etherification were treated separately to get the kinetic data (Fig. 10). The energy of activation (Ea) and temperature coefficients are calculated from the Arrhenius equation and the eqn 1 and 2 are given in Table III. The values of energy of activation for transesterification reaction was follow the order;

Z > MZ > PSZ.

HC coated with zirconia has the highest energy of activation among the catalysts used in the study. As for as HC coated with PSZ (14.92 KJ/mol) and MZ (16.81 KJ/mol) catalysts are concerned, the Ea is almost similar, which means that the reaction proceeds under the same kinetic mechanism. This indicates that the transesterification is equally facile over HC coated PSZ and MZ. The energy of activation for the formation of di-butyl ether over HC coated with PSZ catalyst was found to be 60.5 KJ/mol. Consequently, HC coated with MZ could be a preferred catalyst for n-butyl salicylate

Table III. Reaction rate constant, energy of activation and temperature coefficients of HC coated Z, MZ, and PSZ catalysts for transesterification of MS with n-BA

Catalyst	Rate constant (n-BS)		Rate constant (ether)		Energy of activation [Ea] -BS and DBE		Temperature Coefficient (K$_2$/K$_1$)	
	393 K(K$_1$)	403 K(K$_2$)	393 K(K$_1$)	403 K(K$_2$)	n-BS	DBE	n-BS	DBE
Z(HC)	0.7	1.1	-	-	59.52	-	1.57	-
MZ(HC)	2.2	2.5	-	-	16.81	-	1.36	-
PSZ(HC)	2.5	2.8	1.2	1.9	14.92	60.51	1.12	1.58

[Reaction conditions for Column 3: Reaction time 4 h; reaction temperature 130 0C; amount of HC coated catalyst 0.4 g; molar ratio of MS: n-BA 2:1]

synthesis due to 'moderate and strong' acid sites which are present in MZ catalyst used for the present work (Mohamed and Nagaraju, 2007).

Ea = 2.303 R log K2 / K1 (T1 x T2 / T2 –T1) ----------- (1)

Temperature coefficient = (K2/K1) ----------- (2)

Effect of reactant pre-adsorption

Consequently, the influence of reactant pre-adsorption has been studied under with the MS: n-BA (2:1), HC coated MZ (0.4 g). It has been premixed with the methyl salicylate, n-butyl alcohol and both methyl salicylate and n-butyl alcohol for 24 h at room temperature and then reaction
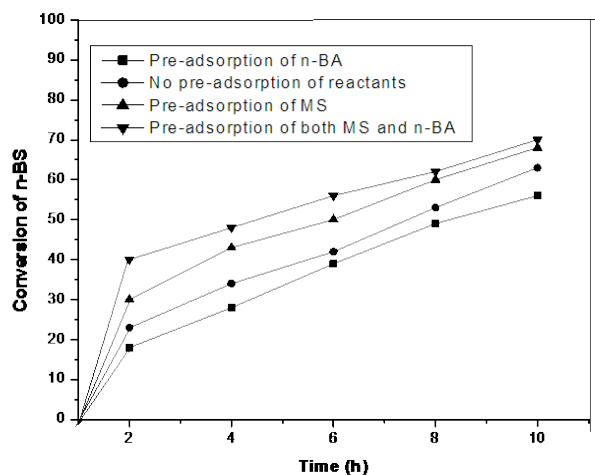

Fig. 11. Influence of Pre-adsorption studies of reactants on HC coated catalysts on transesterification of MS with n-BA [Reaction conditions: reaction temperature =130 0C, weight of the catalysts HC coated = 0.4 g, Molar ratio =2:1, reaction time 4 h

temperature has been raised up to 130°C after adding remaining reactants. (Mitran G et. al., 2015). The plots are shown yield (%) of n-butyl salicylates vs reaction time as shown in the figure 10. It shows that the highest yield of n-butyl salicylate obtained when premixing with the HC coated MZ catalysts. Fig. 10 indicates that the premixing of both the reactants (MS and n-BA) shows maximum and minimum yield was obtained by premixing with n-butyl alcohol. As the reaction rate was higher when premixing the catalyst with both methyl salicylate and n-butyl alcohol compared with the reaction with no premixing, this suggests that the reaction needs the chemisorption of both methyl salicylate and n-butyl alcohol involving a Langmuir – Hinshelwood type mechanism (Teo et al., 2004).

The results in Fig. 10, also suggested a strong adsorption of n-butyl alcohol and a weak adsorption of methyl salicylate competing for the same adsorption sites. This shows that the linear line in the Fig. 11 results proposing a stronger chemisorption of the alcohol than the ester. The resultant plot without premixing of MS and n-BA is also obtainable for similarity. n-butyl alcohol with moderate yield was obtained under non-premixing condition of reactant with the HC coated MZ catalyst. The obtained (Fig. 11) conversion of n-butyl salicylate vs reaction time has been concerning to Langmuir Hinshelwood method.

Transesterification of n-butyl salicylate follows L-H mechanism, It is possible by aliphatic alcohol and an aromatic ester (Scheme 2) of methyl group are adsorbed on the acidic sites of the modified zirconia, protonation of the carbonyl group by acidic catalysts to the formation of carbocation. Then after that a nucleophilic attack of the alcohol produces a tetrahedral carbocation intermediate. Finally it eliminates

methanol and the formation of new ester (n-butyl salicylate) and to regenerate of the acidic catalysts H+.

Effect of reusability of honeycomb form of catalysts as well as powder form of catalysts

The used catalysts (Z, MZ and PSZ) recovered from the liquid sample was washed with acetone, dried at 393 K for 2 h and calcined to remove organic impurities at 823 K for 1 h. The test reaction carrying out the repeated runs of the fresh reaction mixture with the same honeycomb coated catalyst for the synthesis of n-butyl salicylate (Shyamsundar *et al.,* 2015). After every reaction cycle the used catalysts were reactivated by using the procedure as described above. The recycled catalysts show good conversion towards the formation of trans-ester. It could be seen that the HC coated catalysts have more reusability compared to their powder forms. It was observed that small amount of coated catalysts has been decreased. The result related to the reusability studies are given in Table IV.

Conclusion

From a series of examination, Honeycomb coated zirconia and its modified forms such as Z, MZ and PSZ are effective acid catalysts in the transesterification of n-butyl salicylate. Mo(VI)/ZrO$_2$ can be used as excellent among the catalytic materials for the transesterification of MS with n-BA. A good correlation between the yield of the transester and the acidity of the catalytic material was observed. Mo(VI)/ZrO$_2$ were found to be 100 % selective and ~70 % of the formation of

Table IV. Reusability of solid acid catalysts (both HC coated and powder forms)

Sl No	Acid catalysts	No of reaction cycles					
		1	2	3	4	5	6
1	Z	38(20)	38(19)	36(19)	35(17)	33(15)	32 (14)
2	PSZ	80 (38)	79 (36)	69 (34)	64 (32)	63 (30)	63 (29)
3	MZ	70 (32)	68 (32)	67 (30)	65 (28)	60(26)	60 (25)

[Reaction conditions for Column 3: Reaction time 4 h; reaction temperature 403 K; weight of HC coated catalyst 0.4 g; molar ratio of MS: n-BA 2:1]

n-butyl salicylate under suitable reaction conditions. But in case of PSZ was found to be 80% product and 10% as by-product (di-butyl ether) was found to be related to the strength of the catalysts. A good correlation between the total surface acidity, PXRD and catalytic activity was observed over zirconia and its modified forms. Kinetic study also reveals Molybdenum (Mo(VI)/ZrO$_2$) could be a facile

catalyst as it exhibits the lowest Ea (16.81 kJmol–1), is easily reactivable, and is reusable without formation of byproduct (DBE). The reactant pre-adsorption experiments of n-butyl salicylate follow Langmuir-Hinshelwood mechanism. HC coated catalysts are inexpensive and more reusable catalysts up to 6 reaction cycles without deactivation and no loss in catalytic activity and can be replace traditionally by homogeneous acid catalysts. As a result HC coated catalysts are more valuable than their powder forms.

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