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Facile and smart synthesis of benzyl salicylate via vapor-phase transesterification over monoliths coated with zirconia and its modified versions

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Al(III)/ZrO_2 catalysts with Al(III) content ranging from 5–25 wt% have been coated on honeycomb monoliths by dip & dry technique. These catalysts have also been prepared in their powder form. All the prepared catalysts have been characterized by surface acidity, crystallinity, functionality and morphology. The catalytic activity of Al(III)/ZrO_2 has been determined in vapor-phase as well as liquid-phase transesterification of methyl salicylate with benzyl alcohol. The honeycomb form of the catalysts shows almost a 1.4 fold time increase in the catalytic activity when compared to the powder forms. Further, the effect of calcination temperature on the activity has also been discussed. The effect of poisoning of acid sites by adsorbed pyridine (base) and its effect on the surface acidity has been correlated with PXRD phases along with catalytic activity. Catalytic recyclability of Al(III)/ZrO_2 catalysts has also been measured.

Keywords: Zirconia, Benzyl salicylate, Vapor-phase, Transesterification

In view of environmental concern and technical difficulties associated with conventional acid catalysts, solid acids like zeolites, aluminium phosphates, zirconia and its modified forms, cation exchange resins were successfully adopted as catalysts for several acid-catalyzed reactions like dehydration[1], acylation[2], oligomerization[3], esterification[4], catalytic cracking[5], transesterification[6-7] etc. Transesterification is a classic reaction in conventional, modern fine (specialty) chemical process as well as a scientific study[8]. Most of the compounds which are very difficult to prepare by the conventional methods can be easily synthesized by transesterification route[9,10]. For instance, asymmetrical esters, can be easily prepared by these processes. Especially, salicylate esters are prominent classes of esters used in the synthesis of medicines, pharmaceuticals, fine chemicals, food preservatives, agrochemicals, chiral auxiliaries, solvents, plasticizers, cosmetics as well as perfumes[11,12]. The majority of literature related to the synthesis of salicylate esters has reported the use of toxic chemicals such as sulfuric acid or dimethyl formamide, which are environmentally hazardous[13]. In view of the impact of these chemicals on the environment, there is a requirement to establish an environmentally-friendly method as well as a catalytic system for the synthesis of such esters. The utilization of solid acids viz., zirconia and its modified versions are effective as well as convenient for acid-catalyzed organic transformations[13-16].

In general, salicylate esters are prepared by esterification of salicylic acid with an alcohol. But, the solubility of acid in an alcohol is comparatively less, hence this process necessitates the utility of latter in high molar ratios. Therefore, transesterification route is adopted, in which the reactants are mutually soluble with one another. Moreover, solid acidic catalytic materials selected for the present work are branded to own active centers, which are moisture-sensitive and may be poisoned by water molecules produced in transesterification reaction of an alcohol and an acid[16]. Previous literature has reported that benzyl salicylate was synthesized from sodium salicylate and benzyl chloride in a homogeneous system but, in the presence of dimethyl formamide as a solvent[17]. In this study the conversion of benzyl chloride was achieved in 110 min at 110 °C. But one of the products sodium chloride precipitates as the reaction proceeds, which may be due to its poor solubility in dimethyl formamide. Benzyl salicylate was synthesized from sodium salicylate and benzyl chloride by using imidazolium-based ionic liquids at

100 °C for 170 min to get 90% yield[18]. Further, benzyl salicylate was synthesized by the esterification of sodium salicylate and benzyl bromide using third-liquid phase-transfer catalysts and in this case also, the yield was 85% in 120 min[19]. But, the third-liquid phase can be obtained by the addition of large amounts of extra inorganic salts with hydrogen-bonding effects which may affect the overall reaction rates as there is a variation of the interfacial tension as well as the resistance of transportation between organic reactants and the catalytic intermediates. However, in the above studies, the coupling of a phase-transfer catalyst and an ionic liquid might exhibit a high level of the combined effect of enhancing the catalytic activity. In order to overcome all these drawbacks an environmentally benign and efficient method for the synthesis of benzyl salicylate ester by using a simplistic catalytic system like cordierite honeycomb monolith coated with solid acids were developed. Besides, in the field of synthetic organic chemistry, honey comb monolith coated with solid acids have not been much investigated in vapor-phase organic transformations.

The vapor-phase mode is preferred over liquid-phase as transesterification is an equilibrium-driven reaction. The vapor-phase mode is advantageous over liquid-phase mode in terms of reduction of catalyst deactivation, no requirement of high-pressure conditions, environmental impact and additional advantages like safety, efficiency, etc.[20] Furthermore, the inherent advantage of the vapor-phase mode is that the products produced during the reaction period will never be in contact with catalysts, which completely prevents backward reaction.

Zirconia is a remarkable catalytic material as it has both reducing and oxidizing properties as well as is amphoteric in nature. Zirconia and their modified versions were employed as acidic/basic catalytic materials in numerous industrially vital reactions like esterification, isomerization, condensation, and alkylation[21]. The incorporation of MoO_x/VO_x/AlO_x into zirconia enhances the concentration of acid sites as well as favors the formation of the tetragonal phase of ZrO_2 which is catalytically more active than its monoclinic phase[22,23]. Further, catalytic, physicochemical and structural properties of zirconia and their modified forms can be enhanced to a maximal extent by using catalyst carriers like honeycomb monolith[24]. In the field of heterogeneous catalysis, cordierite honeycomb ($Mg_2Al_4Si_5O_{18}$) acts as catalytic carriers. Honeycomb monolith (HM) coated catalysts are extensively utilized in automotive applications as 3-way catalytic converters, for selective reduction of NOx, as well as for ozone abatement in aircraft. Catalysts coated HMs have many advantages over powder form like, thin layer formation with more active surface areas, easy recovery and separation of the catalysts from reaction mass, and lower amounts of the catalyst loaded on HM is extremely effective[24-33].

The aim of the present study is to investigate the utility of honeycomb monolith coated with zirconia modified with Al(III) ions as solid acids in the vapor-phase transesterification reaction of methyl salicylate (MS) with benzyl alcohol (BA). The (%) conversion of MS and (%) selectivity of the products were optimized by varying reaction temperature as well as the molar ratio of the reactants in the reaction. A comparison between the vapor-phase and liquid-phase transesterification was carried out. The effect of calcination temperature on the activity has also been addressed. Moreover, the effect of acid sites on HM catalysts was established by adsorbing base like pyridine and its effect on surface acidity, PXRD phases with catalytic activity were studied. The catalytic activity of honeycomb catalyst was compared with its powder form. Reusability of zirconia catalysts was also evaluated.

Materials and Methods

HMs (diameter = 2.5 cm, height = 1.2 cm and size of hole = 0.1 cm) were procured from Shreya Ceramics, Baroda, India. The chemical composition of HM substrate used in the present study was found to be [SiO_2 = 50.2±1%, Al_2O_3 = 35.1±1%, MgO = 13.2±1%, and others < 1%]. The chemicals such as zirconyl nitrate, aluminum nitrate, LR grade methyl salicylate, benzyl alcohol was supplied by Sigma-Aldrich.

Preparation of catalysts

Preparation of catalytic materials in powder form (PF)

Impregnation method was used to prepare 5% Al(III)/ZrO_2 (5Z-A), 10% Al(III)/ZrO_2 (10Z-A), 15%Al(III)/ZrO_2 (15Z-A), 20% Al(III)/ZrO_2 (20Z-A) and 25% Al(III)/ZrO_2 (25Z-A). In a typical method, 5Z-A (PF) was prepared by taking 11.40 g of zirconyl nitrate and 3.476 g of aluminum nitrate in 40 mL of distilled water and made into a paste. The obtained paste was dried at 120 °C in a hot air oven for 12 h and the obtained solid was finely powdered and calcined for 450 °C for 4 h.

Wash coating of HMs

As bare HMs possess less catalytic activity and have negligible porosity, different methods have been employed for coating walls of monoliths with support materials like alumina, titania, zirconia etc., termed as 'wash-coating'. In this procedure different techniques like dip-coating, sol-gel, chemical vapor deposition, hydrothermal, etc., were extensively used for the initial coating of monolith with a support material, which is then consequently coated with a handy catalyst (Z-A) to augment active phases.

Typically, 2 g of zirconyl nitrate $ZrO(NO_3)_2$ was dissolved in 40 mL deionized water. The obtained solution was coated on bare HM through 'dip & dry' technique in a furnace pre-heated to 400 °C for 8-10 times till ~0.05 g ZrO_2 was coated.

Coating of active catalysts (5-25%) on wash coated HMs

In a typical method, for coating 5Z-A (HM), a dilute solution of 11.40 g of zirconyl nitrate and 3.476 g of aluminum nitrate was made using 40 mL distilled water. The obtained solution was coated on wash-coated HM through 'dip & dry' technique in a furnace pre-heated to 400 °C for 15 times till ~0.2 g Z-A was coated, HMs were calcined at 450 °C for 4 h. Compressed air was blown gently through dip coated HMs to ensure that there were no blockages in the channel. A similar procedure was used to prepare all other solid acid catalysts.

Powder form of 5% Al_2O_3/ZrO_2 is abbreviated as 5Z-A (PF), 10% Al_2O_3/ZrO_2 as 10Z-A (PF), 15% Al_2O_3/ZrO_2 as 15Z-A (PF), 20% Al_2O_3/ZrO_2 as 20Z-A (PF) and 25% Al_2O_3/ZrO_2 as 25Z-A (PF). Honeycomb monolith coated 5% Al_2O_3/ZrO_2 is abbreviated as 5AZ (HM), 10% Al_2O_3/ZrO_2 as 10Z-A (HM), 15% Al_2O_3/ZrO_2 as 15Z-A (HM), 20% Al_2O_3/ZrO_2 as 20Z-A (HM) and 25% Al_2O_3/ZrO_2 as 25Z-A (HM) respectively. Images of typical HM catalysts with different (wt %) coatings [Bare HM, 5Z-A (HM), 10Z-A (HM), 15Z-A (HM), 20Z-A (HM) and 25Z-A (HM)] is presented in Supplementary Data Fig. S1.

Characterization of catalysts

Excluding SEM and EDAX characterizations, the monolithic catalysts were milled to acquire powder form and the obtained powder was used for characterization[34].

By NH_3-TPD method, surface acidity (SA) of all the catalysts was measured by (Plus chemisorb-2705 Micrometrics instrument) as well as by *n*-butylamine back titration method by using dry benzene as a solvent. In this method, 0.3 g of the catalyst was suspended in 20 mL of a dry benzene solution of 0.05 M *n*-butylamine. The mixture was left for 24 h. During this period all the acid sites on the surface of the solid get neutralized. The unreacted *n*-butylamine was estimated by titrating against 0.05 M HCl using bromothymol blue as an indicator. Surface acidity of the solid catalyst was calculated from the decrease in concentration of *n*-butylamine. The surface acidity was calculated by using formula:

Surface acidity of the catalyst = (x-y) 1000 / W = mmol/ g of the catalyst …(1)

where, x = molarity of *n*-butylamine before adding the catalyst; y = molarity of *n*-butylamine after treating with the catalyst and W = Weight of the catalyst (g).

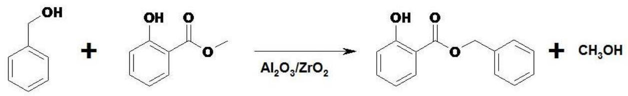
The PXRD patterns of catalytic materials were recorded on Philips X'pert X-ray powder diffractometer by Cu-Kα radiation (λ = 1.5418 Å) using a graphite crystal monochromator.

ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) technique was used to determine the amount of aluminum present in modified zirconia catalysts by employing (Thermo icap-6000) instrument. SEM and EDAX images were recorded by using Japan made JEOL-2010 instrument working with an accelerating voltage of 5.0 kV. TEM images were recorded on an electron microscope (PHILIPS CM-200) with an accelerated voltage (20–200kV).

HMs were exposed to pyridine vapors for 15 min and heated in an oven to 120 °C for 60 min. During this period, it was expected that the total acid sites present in the HM got neutralized completely. Surface acidity of poisoned catalytic materials was measured in addition PXRD patterns were also recorded.

Measurement of catalytic activity

Transesterification of methyl salicylate (MS) with benzyl alcohol (BA) using modified zirconia (both in HM and PF forms) was conducted in vapor phase heating (VPH) and are represented in Scheme 1. Typically, HM coated over solid acids [5Z-A (HM)/ 10Z-A (HM)/ 15Z-A (HM)/ 20Z-A (HM)/ 25Z-A (HM)] was kept above a specially fabricated continuous down-flow vapor phase reactor maintained



Scheme 1

at catalyst bed temperature of 60 °C. The reactant mixture was supplied into the reactor maintained under pre-heated temperature 200 °C as well as a flow-rate of 5 mL/h. The liquid products were collected at the bottom of the vapor phase reactor at time intervals of 10 min for analysis. The liquid products were cooled and filtered. The error distribution in the case of conversion is 4% and selectivity was 2%. The filtrate was analyzed quantitatively by GC (Mayura) fixed with 10% carbowax column (10% SE-30 chrome Sorb w-AW, 3m-1/8) which is connected to a FID and qualitatively by GCMS (Varian). Typical operating conditions for GC: FID temperature = 250 °C; split flow = 100 mL/min; carrier gas = nitrogen at 1 mL/min and temperature programming = 150 to 250 °C (at 10 °C/min).

Similarly, the transesterification reaction was also conducted in liquid-phase heating (LPH) by using a specially designed glass reactor or 50 mL round bottom flask fitted with a hot plate, with constant stirring. The total volume of the reaction mixture was always kept at 20 mL. After a fixed reaction time, the reaction mixture was cooled and filtered. The filtrate was analyzed quantitatively by GC and qualitatively by GCMS as mentioned above. The conversion of MS was calculated by the following equations:

$$\text{Conversion (\%)} = \frac{\text{Amount of MS converted (mol)}}{\text{Total amount of MS in the feed (mol)}} \times 100 \quad \ldots(2)$$

$$\text{Selectivity (\%)} = \frac{\text{Amount of one product (mol)}}{\text{Amount of all products (mol)}} \times 100 \quad \ldots(3)$$

Surface acidity (SA) by the NH_3-TPD method/ n-butyl amine back titration method

The surface acidity (SA) and acid site distribution values of all the catalysts measured by the NH_3-TPD technique are given in Table 1. The surface acidity of the catalysts was found to follow the order: 5Z-A (PF) < 5Z-A (HM) < 10Z-A (PF) < 10Z-A (HM) < 20Z-A (PF) < 20Z-A (HM) < 25Z-A (PF) < 25Z-A (HM) < 15Z-A (PF) < 15Z-A (HM). SA values of all the catalysts were also determined by *n*-butyl amine back titration method and their values are in good agreement with the values obtained by the NH_3-TPD technique.

Table 1 — Physicochemical properties of catalysts (PF & HM)

Catalytic material	(SA) Surface acidity (mmol/g)	Catalyst loaded on HM (gm)	(%) of Al (III)
Z (PF)	0.45 (0.47)	-	-
Z (HM)	0.58 (0.59)	0.197	-
5Z-A (PF)	0.68 (0.69)	-	4.9
5Z-A (HM)	0.81 (0.80)	0.209	-
10Z-A (PF)	0.85 (0.84)	-	10.1
10Z-A (HM)	0.95 (0.96)	0.225	-
15Z-A (PF)	1.52 (1.53)	-	14.9
15Z-A (HM)	2.21 (2.24)	0.250	-
20Z-A (PF)	0.99 (0.98)	-	19.8
20Z-A (HM)	1.10 (1.12)	0.230	-
25Z-A (PF)	1.14 (1.13)	-	25.2
25Z-A (HM)	1.49 (1.50)	0.235	-
5Z-A (HM) *[poisoned by pyridine]*	0.49 (0.48)	0.214	-
10Z-A (HM) *[poisoned by pyridine]*	0.55 (0.54)	0.231	-
15Z-A (HM) *[poisoned by pyridine]*	0.74 (0.72)	0.258	-
20 Z-A (HM) *[poisoned by pyridine]*	0.60 (0.61)	0.236	-
25 Z-A (HM) *[poisoned by pyridine]*	0.66 (0.67)	0.241	-

Numbers in parenthesis correspond to the surface acidity (SA) values obtained by *n*-butyl amine back titration method.

The surface acidity values of (PF) and (HM) catalysts are given in Table 1. Pure ZrO_2 was found to be less acidic, the surface acidity of Z-A is generally due to the coordination number of the inserted cation preserved in the host oxide lattice i.e., when Zr^{4+} is inserted into Al^{3+} lattice, imbalance of positive charge takes place which results in the generation of Lewis acid sites. Surface acidity may be because of the formation of charge imbalance over the surface of the metal oxide. To maintain the electrical neutrality Brønsted acidity is likely to come out as the charge imbalance is negative. Lewis acid sites may be produced, when the imbalance of charge is positive[35]. 15Z-A (HM) and 15Z-A (PF) possessed higher surface acidity when compared to all other catalytic materials.

Crystallinity by PXRD

In the XRD patterns of (HM) coated catalysts, no diffraction peaks corresponding to bare HM was detected (Fig. 1). This clearly indicates that the surface of the bare HM was entirely and efficiently covered with the active catalyst. Pure zirconia consists of monoclinic (M) as well as tetragonal (T) phases. When pure zirconia was incorporated with 5 to10% of Al(III), gradual reduction in the intensity of peak pertaining to monoclinic phase with an augment in the intensity of the tetragonal phase of the zirconia was noticed. This implies a predominant dependence of the tetragonal phase on Al(III) ion loadings. Interestingly, for 15% Z-A, peaks pertaining to monoclinic phases were completely eliminated, whereas the peaks pertaining to only tetragonal phase were observed. This may be due to the strong interaction of Al^{3+} ions with zirconia which inhibits the formation of monoclinic phase, which may further stabilize into a metastable tetragonal phase of zirconia[36]. It is reported that the tetragonal phase of the zirconia catalysts is more catalytically active than its monoclinic phase[37]. Concurrently, PXRD peaks pertaining to either Al_2O_3 or any other new crystalline phases were not found.

The effect of calcination temperature on the stability of tetragonal phase of zirconia over the catalytic activity of 15Z-A (HM) catalyst by PXRD studies

Effect of calcinations temperature on the stability of tetragonal phase of zirconia over the catalytic of 15Z-A (HM) catalyst by PXRD studies

The calcination temperature of 15Z-A (HM) catalyst was varied from 250 to 650 °C and represented in the Fig. 2. The PXRD pattern of 15Z-A (HM) calcined at 250 and 350 °C consists of both monoclinic as well as tetragonal phases. But, at 450 °C, monoclinic peaks were completely eliminated and only peaks pertaining to tetragonal phases were observed. From these observations, it could be inferred that the complete phase modification from monoclinic to the catalytically active tetragonal phase occurred. Moreover, the absence of characteristic peaks of Al_2O_3 implies that metal oxide is highly dispersed in ZrO_2. The dispersion of Al_2O_3 particles may also have imparted higher internal surface area of the HMs[38]. But, when the calcination temperature increases beyond 550 °C, the formation of stable monoclinic phase from tetragonal phase was noticed. This clearly indicates that the calcination temperature of 450 °C was found to be suitable for the present work.

The fraction of tetragonal phase (f_t) in the case of 15Z-A (HM), calcined at different temperatures is estimated by the following formula suggested by Valigi *et al.*[39]

$$f_t = \frac{A_t(1\,0\,1)}{A_{total}(ZrO_2)} \quad \ldots(4)$$

where, A_t (101) is the peak area of the (101) of tetragonal phase and A_{total} is the area of all the

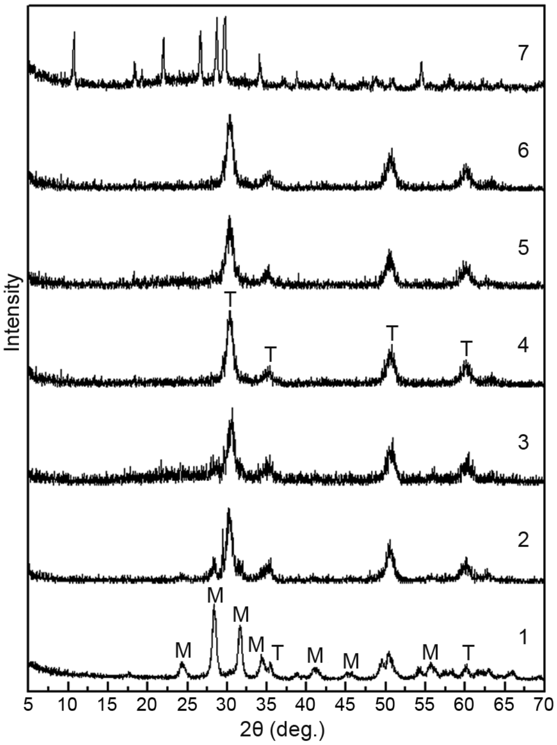


Fig. 1 — PXRD patterns of: ZrO_2 (1), 5Z-A (2), 10Z-A (3), 15Z-A (4), 20Z-A (5), 25Z-A (6), and, Bare HM (7) (where, M indicates monoclinic and T indicates tetragonal phase).

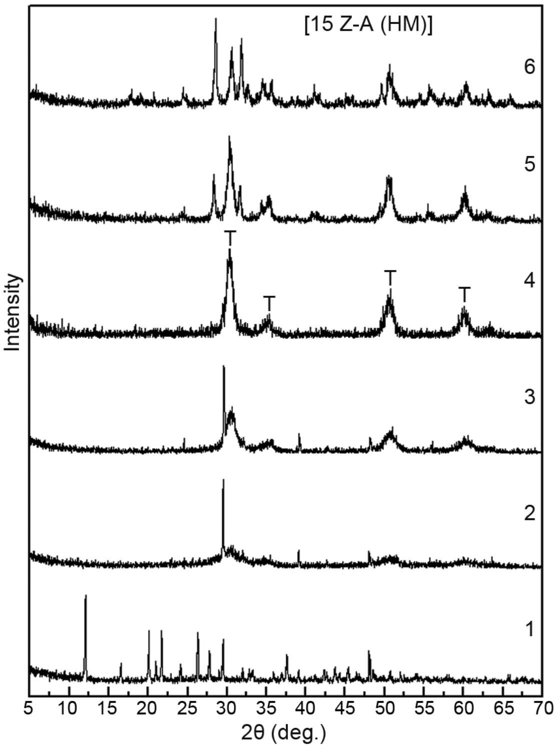


Fig. 2 — The influence of PXRD patterns of 15Z-A (HM) catalyst on the effect of calcination temperature over the stability of the tetragonal phase of zirconia: Un-calcined (1), 250 °C (2), 350 °C (3), 450 °C (4), 550 °C (5), and, 650 °C (6).

tetragonal as well as monoclinic peaks in the pattern. The tetragonal and monoclinic phases were determined by considering them symmetric. It is noticed that as the calcination temperature increases from 250 to 450 °C the value of f_t was also found to increase, which results in the higher conversion of BS (%). Moreover, as the calcination temperature increases from 450 to 650 °C the values of f_t were found to decrease, which results in the comparatively lesser conversion of BS (%). But at the highest calcination temperature i.e., about 650 °C the value of f_t as well as its catalytic activity were found to be negligible because the phase stability of the catalyst was not satisfactory. Hence, a linear correlation exists between the fraction of tetragonal phase and the conversion of MS (%) in the transesterification.

FTIR analysis

FTIR spectra of all the catalysts are given in Supplementary Data Fig. S2. The peaks around 835 cm^{-1} and 1145 cm^{-1} correspond to O-Al vibrations. A peak around 1088 cm^{-1} corresponds to the vibration of Al_2O_3 phase[40]. The peaks around 1545 cm^{-1} and 1455 cm^{-1} are due to Brønsted and Lewis acid sites respectively[41]. The peaks around 1788 cm^{-1}, 2430cm^{-1} and 3675 cm^{-1} correspond to bending vibrations of –OH group, coupling effect of stretching of –OH group, and stretching vibration of –OH bond respectively[42].

Effect of calcination temperature and calcination period over the catalytic activity of 15Z-A (HM) catalyst by FTIR studies.

The activity of the catalyst can be influenced by its calcination temperature due to the activation of active sites. The effect of calcination temperature on the catalytic activity was assessed by varying the calcination temperature ranging from uncalcined, 150 °C to 650 °C over 15Z-A (HM) catalyst (Table 2 and Supplementary Data Fig. S3(a)). As the calcination temperature increases from 150 to 450 °C, the conversion of BS and the selectivity of the desired products were found to increase, which may be attributed to the increase in the active sites of the catalyst. A maximum conversion and selectivity at 450 °C indicated that 450 °C is the optimum calcination temperature in the present study. But, as the calcination temperature increases beyond 450 °C the conversion of BS and the selectivity of the desired products found to decrease which may be due to the decrease in the active sites of the catalyst[43].

Further, the effect of calcination period over the catalytic activity was evaluated by varying the calcination period ranging from 1 to 6 h over 15Z-A (HM) catalyst (Table 3 and Supplementary Data, Fig. S3(b)). As the calcination period increases from 1 h to 4 h, the conversion of BS and the selectivity of the desired products were found to increase, which may be due to increase in the contact time of the catalyst. At 4 h, maximum conversion of BS and selectivity of the desired products were observed, indicating that 4 h was found to be an optimum calcination period in the present work. But, as the calcination period increases beyond 4 h, the conversion of BS and selectivity of the desired products were found to decrease which may be attributed to the depletion of active sites as the catalyst was at a high temperature for a long duration[43].

SEM analysis

SEM images of HM catalysts are given in Fig. 3. In case of 15Z-A (HM), flake-like shapes could be observed, which indicates uniform as well as strong adherence of active catalytic material on the surface of (HM). This also specifies that the technique employed to coat the active catalyst on (HM) is highly efficient. At lower loadings of Al_2O_3 the average

Table 2 — Comparative analysis of catalytic activity of the catalysts (PF & HM)

Catalytic material	Conversion of MS (%)	Selectivity of BS (%)	Selectivity of DBE (%)
Bare (HM)	4	100	0
Z (PF)	5	100	0
Z (HM)	12	100	0
5Z-A (PF)	17	88	12
5Z-A (HM)	27	90	10
10Z-A (PF)	29	85	15
10Z-A (HM)	44	92	8
15Z-A (PF)	70	94	6
15Z-A (HM)	97	95	5
20Z-A (PF)	46	60	40
20Z-A (HM)	53	68	32
25Z-A (PF)	55	65	35
25Z-A (HM)	69	70	30
5Z-A (HM) *[poisoned by pyridine]*	7	69	31
10Z-A (HM) *[poisoned by pyridine]*	11	74	26
15Z-A (HM) *[poisoned by pyridine]*	25	80	20
20 Z-A (HM) *[poisoned by pyridine]*	14	75	25
25 Z-A (HM) *[poisoned by pyridine]*	18	78	22

Reaction conditions: molar ratio (BA:MS) = 2:1, flow-rate (reactants) = 5mL/h, pre-heated temperature = 200 °C, catalyst temperature = 60 °C].

Table 3 — Conversion/Selectivity's with variation of calcination temperature and calcination period over 15Z-A (HM) catalyst on the transesterification of BA with MS

Calcination temperature (°C)	% of tetragonal phases f_t (%)	Conversion MS (%)	Selectivity (%)		Calcination period (h)	Conversion MS (%)	Selectivity (%)	
			BS	DBE			BS	DBE
250	69	77	73	27	2	73	71	29
350	78	88	86	14	3	87	85	15
450	90	97	95	5	4	97	95	5
550	50	60	70	30	5	65	78	22
650	30	40	60	40	6	45	65	35

Reaction conditions: molar ratio (BA:MS) = 2:1, flow-rate (reactants) = 5mL/h, pre-heated temperature = 200 °C, catalyst temperature = 60 °C]. Calcination temperature (for column 5) = 450 °C.

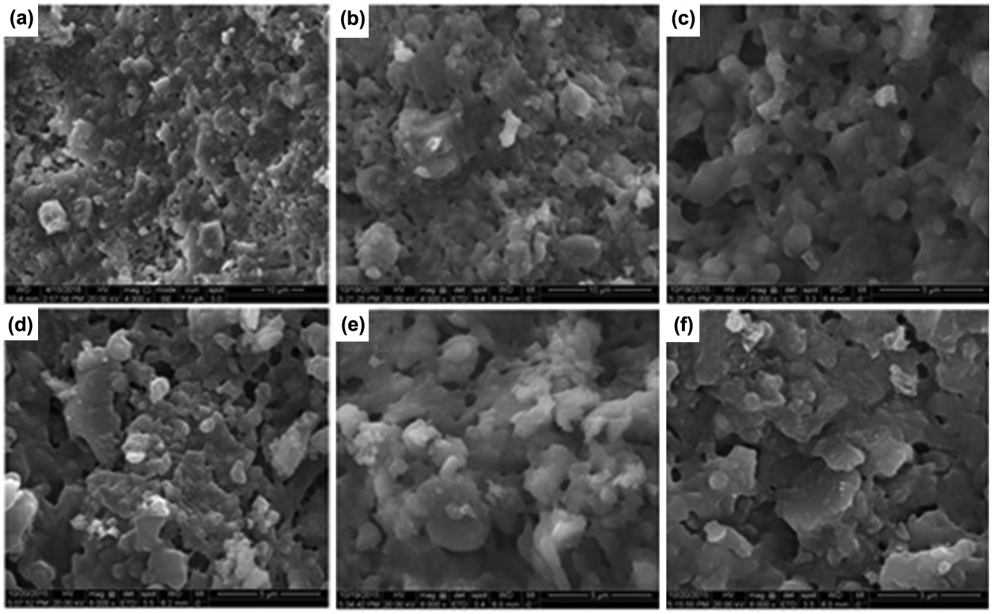


Fig. 3 — SEM images of: Bare HM (1), 5Z-A (HM) (2), 10Z-A (HM) (3), 15Z-A (HM) (4), 20Z-A (HM) (5), and, 25Z-A (HM) (6).

crystalline sizes of Al_2O_3 are very small but at higher loadings, a slight increase in the size of Al_2O_3 particles was noticed on HM support. A similar observation was noticed by Harishekar *et al.*[44]

EDAX analysis

EDAX analysis clearly discloses the homogeneous distribution of wash-coat as well as active catalysts throughout the monolithic channels of HM. The presence of zirconia, oxygen as well as alumina in all the prepared HMs is observed (Supplementary Data, Fig. S4).

TEM analysis

TEM images of 15Z-A (HM) are given in Fig. 4. Compact distribution of particles with spherical geometry with particle size ranging from 60 to 80 nm was observed.

ICP-OES analysis

Amount of metal content in the case of Z-A (PF) samples, was determined by ICP-OES analysis. The amount of aluminum content exchanged over modified zirconia is given in Table 1.

Results and Discussion

Effect of the nature of catalysts

In order to find out a facile catalyst for the transesterfication of methyl salicylate (MS) with benzyl alcohol (BA), the reactions were carried out over all the catalysts and the results are given in Table 1.

The conversion of MS followed the order: 5Z-A (PF) < 5Z-A (HM) < 10Z-A (PF) < 10Z-A (HM) < 20Z-A (PF) < 20Z-A (HM) < 25Z-A (PF) < 25Z-A (HM) < 15Z-A (PF) < 15Z-A (HM).

When the reaction was conducted without any catalyst, there was a negligible formation of products (< 1%). It can be inferred that transesterification (MS with BA) is a catalyzed reaction. However, when the reaction was carried out in the presence of Z-A (HM) catalyst, the percentage conversion of MS increased up to 97% (Table 3). When the reaction mixture obtained after the transesterification reaction was analyzed using GC-MS, the formation of only two products namely benzyl salicylate (BS) and dibenzyl ether (DBE) was observed.

Effect of wash-coating process over HMs

In order to study the effect of wash-coating, the HMs were dipped in zirconyl nitrate solution through 'dip & dry' technique in a furnace pre-heated to 400 °C for 8-10 times till ~0.05 g ZrO_2 was coated and were finally calcined at 450 °C for 4 h to avoid the development of any crack on the coating. The wash-coat was then scraped off from the HMs. Previously, [15 Z-A (HM)] wash coated and the wash-coat scrapped HMs were subjected to transesterification reactions under the same set of reaction conditions. Interestingly, wash-coated ones show the highest conversion when compared to wash-coat scrapped HM (Supplementary Data, Fig. S5). Almost threefold increase in the conversion of MS was noticed in the case of wash-coated HM, because wash-coating process increases the internal surface area of HM by completely coating the inner surface of the monolithic material[45]. Additionally, the lower catalyst loading is compensated by higher catalytic efficiency attributed to mass-transfer characteristics[24-33].

Effect of Al_2O_3 loading

A series of A-Z catalysts (both PF and HM forms) were prepared by varying Al_2O_3 concentrations ranging from 5 to 25 wt%, in the vapor-phase transesterification of MS with BA (Tables 1 and 2). The transesterification activity of the catalysts increased with Al_2O_3 loadings (5 to 15 wt %) showing the presence of high SA. But the addition of Al_2O_3 beyond 15 wt% decreased the transesterification activity indicating the decrease in SA. This may be due to excess coverage of Al_2O_3 species over the catalyst support i.e., HM[39].

A correlation between the surface acidity and the conversion of MS was observed. 15Z-A being highly acidic showed the highest percentage conversion of MS and 5Z-A being the least acidic showed the least percentage conversion of MS. Hence, the 15Z-A catalyst was preferred for further optimization studies.

Effect of vapor-phase heating V/s liquid-phase heating

To study the effect of vapor-phase heating (VPH) on the conversion of MS, the transesterification of MS with BA was conducted over 15Z-A (HM) catalyst with and without VPH heating and the results are given in Tables 4 and 5. The reactions were conducted by varying the reaction temperature and molar ratio of the reactants (BA: MS) from 30 °C to 90 °C in case of VPH, but in case of LPH from 50 °C

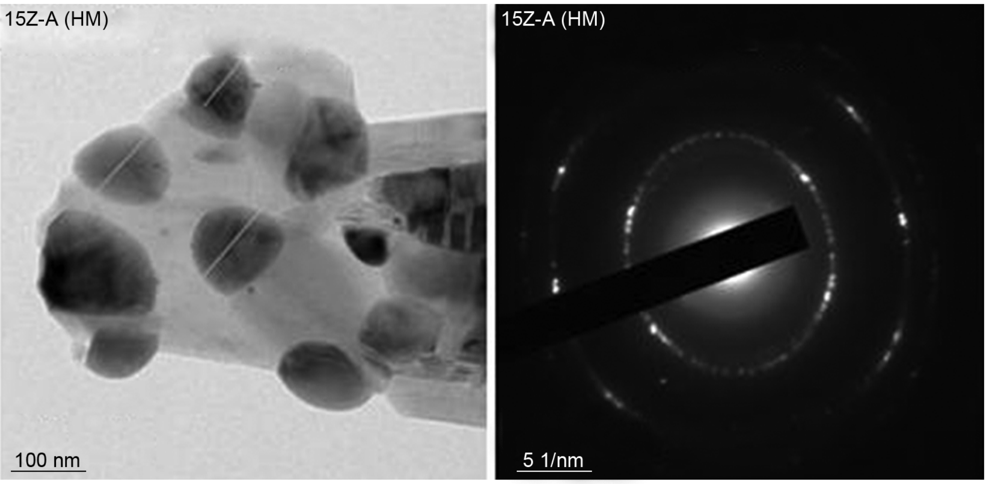


Fig. 4 — TEM images of 15Z-A (HM).

Table 4 — Effect of VPH and reaction temperature on transesterification of BA with MS

	Temperature (°C)				
15Z-A (HM)	30	45	60	75	90
Conversion of MS (%)	70 (10)	83 (21)	97 (32)	85 (28)	77 (25)
Selectivity of BS (%)	65 (55)	80 (70)	95 (85)	78 (75)	70 (60)
Selectivity of DBE (%)	35 (45)	20 (30)	5 (15)	22 (25)	30 (40)

Reaction conditions for VPH: molar ratio (BA: MS) =2:1, flow-rate (reactants) =5mL/h, pre-heated temperature = 200 °C and, Reaction conditions for LPH: molar ratio (BA: MS) =2:1, temperature=60 °C, time=30 min]. Numbers in parenthesis indicates LPH.

Table 5 — Effect of VPH and molar ratio (BA:MS) on transesterification of BA with MS.

	Molar ratio (BA:MS)				
15Z-A (HM)	1:3	1:2	1:1	2:1	3:1
Conversion of MS (%)	65 (9)	70 (18)	75 (25)	97 (32)	85 (28)
Selectivity of BS (%)	60 (50)	65 (55)	70 (60)	95(80)	80 (70)
Selectivity of DBE (%)	40 (50)	35 (45)	30 (40)	5 (20)	20 (30)

Reaction conditions for VPH: flow-rate (reactants) =5mL/h, pre-heater temperature=200 °C.

Reaction conditions for LPH: molar ratio (BA: MS) =2:1, temperature=60 °C, time=30 min]. Numbers in parenthesis indicates LPH.

to 150 °C and from 1:3 to 3:1 respectively. Approximately three fold time increase in the conversion of MS was observed in the case of VPH. It was noticed that the conversion of MS was found to be the highest (97%) in case of VPH (molar ratio (BA: MS) = 2:1, flow-rate (reactants) = 5mL/h, pre-heater temperature = 200 °C, catalyst temperature = 60 °C), but in case of liquid-phase heating (LPH) (molar ratio (BA: MS) = 2:1, temperature = 60 °C, time = 30 min) it was found to be the least (32%). VPH is advantageous over LPH as it decreases the reaction time, reagent consumption as well as minimizes the environmental impacts. In addition, it is observed that the reactivity of the chemical reagent in VPH is higher compared to that of LPH. This study reveals that transesterification of MS with BA under vapor-phase heating is highly effective compared to liquid-phase.

Effect of catalyst bed temperature

Transesterification reactions were conducted with a constant pre-heated temperature of 200 °C over Z-A catalytic materials by changing the catalyst bed temperature from 30 °C to 90 °C with ±2 °C accuracy. Effect of temperature on the conversion of MS as well as selectivity towards the products (benzyl salicylate or dibenzyl ether) is represented in Supplementary Data, Fig. S6. When the temperature was below 60 °C, conversion of MS was found to be less. As the temperature increases beyond 60 °C, the conversion of MS was found to decrease with a decrease in the selectivity of BS but with an increase in the selectivity of DBE. Temperature beyond 60 °C could also result in the deactivation of catalyst, which may be due to the polymerization of the reactant or product molecule on the catalyst surface. Hence the catalyst bed temperature of 60 °C was found to be appropriate for conversion of MS with a reasonable selectivity towards BS and DBE.

Effect of molar ratio (BA: MS)

Effect of molar ratio (BA: MS) on the conversion of MS (%) and selectivity of BS was evaluated over HMs coated with modified zirconia catalysts. The molar ratio was varied in the range of BA:MS ranging from 1:3 to 3:1. The obtained results are presented in Supplementary Data, Fig. S7.

Since transesterification is an equilibrium reaction, an increase in the concentration of any one of the reactant results in the higher conversion of MS because the forward reaction is facilitated.

In this study increase in the concentration of benzyl alcohol was more advantageous because the conversion (%) of MS increases as BA:MS (molar ratio) increases from 1:1 to 2:1. Therefore, 2:1 molar ratio was found to be an optimal molar ratio.

Effect of flow rate of reactants

Transesterification (MS and BA) was conducted by varying flow rates from 2.5 mL/h to 10 mL/h and is represented in Supplementary Data, Fig. S8. The figure shows that the conversion of MS decreases as the flow rate increases beyond 5mL/h. Nevertheless, higher flow rates result in the decrease in selectivity of BS which may be attributed to the higher contact time of both reactants as well as products which may further cause the formation of side-products. Hence, 5mL/h was chosen as the optimum flow rate.

Effect of weight hour space velocity (WHSV)

The reaction is a function of WHSV in the range from 0.1 to 0.6 h^{-1}(Fig. 5). There was no decrease in the conversion of MS as WHSV was increased from 0.1 to 0.3 h^{-1}. However, there was a slight decrease in the conversion of MS as the WHSV was increased beyond 0.3 h^{-1}. This clearly specifies that a WHSV of up to 0.3 h^{-1} provides an optimal residence time for the occurrence of transesterification. It is possible that selectivity of BS decreases as WHSV increases beyond 0.3 h^{-1}. It may be due to higher contact time of reactants or products or both.

Effect of time on stream

The effect of time on stream experiment was conducted by using 15Z-A (HM) catalyst from 30 to

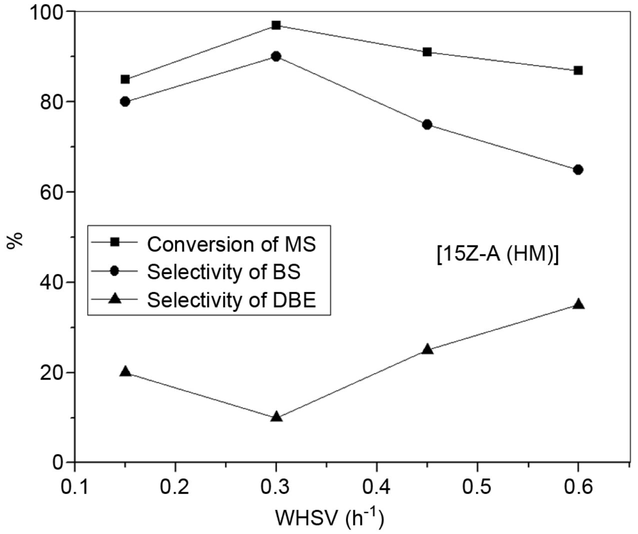


Fig. 5 — Effect of WHSV on the conversion of MS (%) and selectivity of products (%). [Reaction conditions: molar ratio (BA: MS) = 2:1, pre-heated temperature = 200 °C, catalyst temperature = 60 °C].

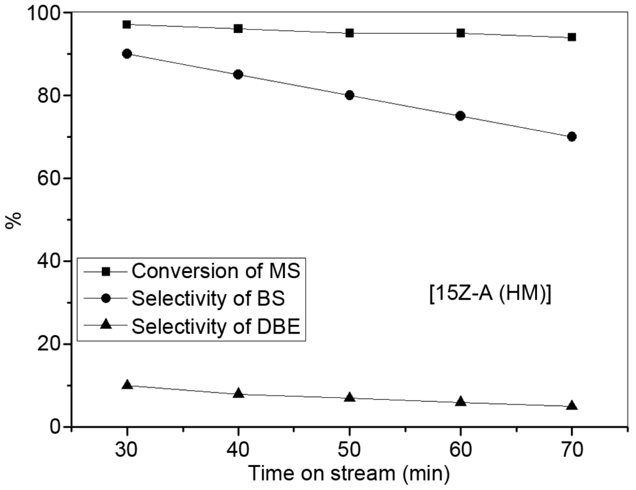


Fig. 6 — Effect of time on stream on the conversion of MS and selectivity (%) of products. [Reaction conditions: molar ratio (BA:MS) = 2:1, pre-heated temperature = 200 °C, catalyst temperature = 60 °C, flow-rate (reactants) = 5mL/h].

70 min and the results are given in Fig. 6. The conversion of MS remains constant up to 30 min but, gradually decreases afterwards. The selectivity of BS or DBE remain quite nearly constant during the experiment.

Effect of turnover frequency

The vapor phase transesterification of MS and BA was expressed in terms of turnover frequency (the number of molecules of MS converted per atom of exposed alumina atoms on the surface per unit time). The relationship between Al_2O_3 loading and TOF in the vapor phase transesterification of MS and BA is represented in Fig. 7. TOF studies were conducted for both PF and HM catalytic samples. The TOF increases up to 15 Z-A and there is further decrease in TOF at higher loadings of Al_2O_3 (beyond 15 Z-A) which may be attributed to the decrease in the number of active sites of Al_2O_3 over zirconia due to agglomeration of Al_2O_3 particles. The TOF in case of HM catalysts is almost threefold as compared to PF forms which is due to the increased accessibility of active sites in the case of HM catalysts. The findings of PXRD, SA are in good agreement with TOF results.

Leaching test

The filtrate (obtained after transesterification reaction) was analyzed for leached metal content by ICP emission spectroscopy and no metal was detected. This confirms that metal leaching also did not take place during the reaction.

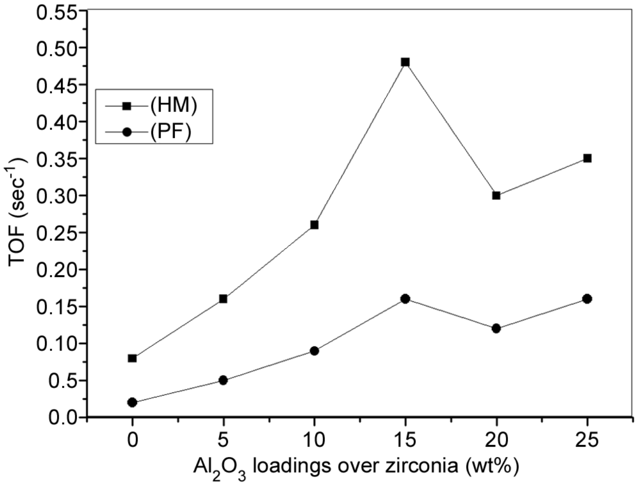


Fig. 7 — Turn over frequency studies on the Al_2O_3 loadings over zirconia catalysts.

Effect of poisoning of acid sites by adsorption of pyridine on A-Z catalysts and its catalytic activity

HM catalysts were poisoned by pyridine since it interacts more with acid sites by means of neutralizing more number of acid sites present in the catalyst[46]. PXRD patterns of HM catalysts (poisoned by pyridine) are given in Fig. 8. It is fascinating to notice that the PXRD pattern of 15A-Z (HM) poisoned by pyridine possesses more of the monolithic phase but in the case of un-poisoned 15A-Z (HM), only tetragonal phases were noticed (Supplementary Data, Fig. S1). It can thus be inferred that poisoning enhances monoclinic phases, resulting in a decrease in tetragonal phase of zirconia. In

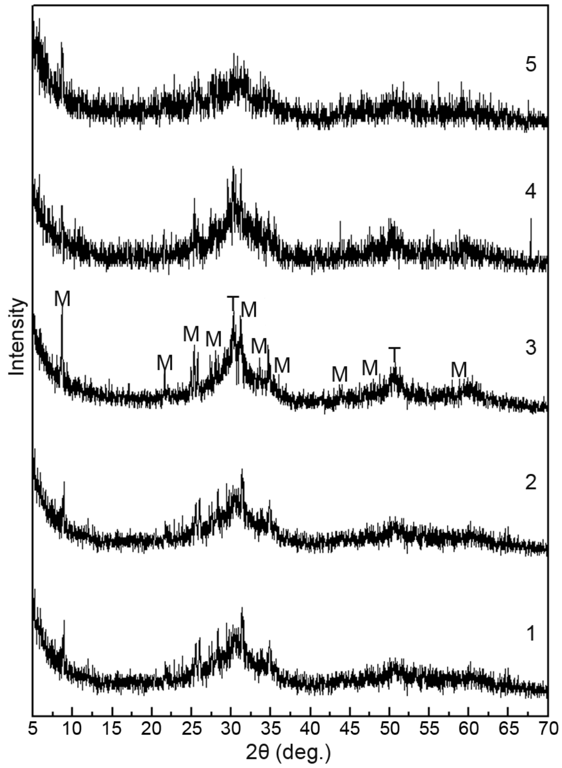


Fig. 8 — PXRD patterns of HMs poisoned by pyridine 5Z-A (1), 10Z-A (2), 15Z-A (3), 20Z-A (4), and, 25Z-A (5).

addition, when the surface acidity (SA) was measured in the case of 15A-Z (HM) catalyst, a decrease in the SA values was noticed (Table 1) which may be due to loss of acidic sites. Thus, an increased tetragonal phase of zirconia was responsible for more SA and conversely, an increased monoclinic phase was accountable for lower SA. In general, the presence of the tetragonal phase of zirconia is predominantly liable for its high SA.

Further, the poisoned HM catalysts were subjected to vapor-phase transesterification under the same set of reaction conditions and the results are incorporated in Tables 1 and 2. In case of pyridine poisoned (HM) catalysts, almost four fold decrease in the conversion of MS was noticed as compared to that of un-poisoned counterparts. The decrease in the conversion of MS (%) could be attributed to the loss of acid sites present in the catalyst upon poisoning. Therefore, in the case of A-Z (HM) catalysts, surface acidity (SA), PXRD phases and their catalytic activity were found to be co-relatable. Consequently, a triangular correlation exists between surface acidity (SA), PXRD phases as well as catalytic activity.

Mechanism

MS reacts with BA in the presence of Z-A catalysts to give benzyl salicylate (BS) ester as represented in Scheme 1. This is a chemical equilibrium reaction. It is reported in literature[47] that an adsorbed alcohol (benzyl alcohol in the present study) blocks the active sites, but does not react with the catalyst. It has been assumed that BA reacts with MS (adsorbed). As the amount of BA is increased, the rate of the reaction was found to decreas. Similarly, when the concentration of MS increases conversion of MS also increases. This clearly indicates that MS adsorbs on the active site of catalytic material but not BA. A probable mechanism for an acid catalyzed transesterification is proposed in Supplementary Data, Fig. S9.

Catalytic reusability

Spent catalysts (HM & PF) were recovered from the reactor, washed with acetone and dried at 120 °C for 60 min, calcinated at 450 °C for 60 min in a muffle furnace and used for further reaction cycles. It was observed that 15 Z-A (HM) used in the present work were found to be more efficient and useful catalysts when used for 10 consecutive reaction cycles (Supplementary Data, Fig. S10). Pertaining to PF catalytic materials, 100% recovery was not viable mainly due to the problems associated with the separation process from the vapor phase reactor. However, after reactivation when HM catalytic materials were weighed, no change in the weight was observed which may enhance its catalytic activity. This evidently specifies the suitability of the method used to coat the active catalyst over HM.

Comparative analysis of catalytic activity of HM v/s PF forms

Transesterification of MS and BA was conducted over catalytic materials (both HM & PF forms). The HM forms of catalysts were more economical and efficient over PF forms (Table 2). An approximately 1.4 fold time increase in percentage conversion of MS was observed. This increase over HM forms may be mainly due to the accessibility of more active sites which may be attributed to their cell density, cell diameter and availability of a number of channels articulated as cpsi (cells/square inch) where the catalytic material is found to be deposited. This leads to the most inherent characteristic of HM i.e., its huge open frontal area. Even the least loading of catalytic material in HMs may be compensated by its better mass-transfer characters[48] and their high efficiency.

Conclusions

In general, HM forms of zirconia were found to be more active in the transesterification of methyl salicylate with benzyl alcohol to synthesize benzyl salicylate ester *via* the vapor-phase route. A correlation between the conversion (%) of methyl salicylate and surface acidity was observed. The product selectivity specifically, benzyl salicylate or dibenzyl ether was observed to be correlatable with the strength of the acid sites of zirconia.

Approximately three fold time decrease in the conversion of MS was observed in the case of liquid-phase heating (LPH) which may be due to rapid deactivation of the catalyst. Almost 1.4 folds time increase in percentage conversion of MS was observed in the case of the honeycomb monolith (HM forms) which may be mainly due to the accessibility of more active sites. Almost three fold increase in the conversion of MS was noticed in the case of wash-coated HM compared to their wash-coated scrapped counter parts since, wash-coating process increases the internal surface area of HM. TOF studies in case of HM catalysts is almost three fold more as compared to their PF forms which may also be due to the increased accessibility of the more active sites. About four fold time decrease in the catalytic activity was noticed in the case of catalysts poisoned by pyridine which may be due to the loss of acidic sites upon poisoning. From all these experimental studies, the present work reveals that 15Z-A (HM) is more stable, efficient and an active catalyst for the transesterification of methyl salicylate (MS) with benzyl alcohol (BA). HM forms of catalytic materials used in the current work were noticed to have significant reusability as well.

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Supplementry Data

Supplementry data associated with this article are available in the electronic form at http://www.niscair.res.in/iinfo/ijca/IJCA_57A(10)1257-1269_SupplData.pdf.

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