Synthesis of salicylate esters over cordierite honeycomb monoliths coated with zirconia based solid acids in vapour phase

T E Mohan Kumar[1,2], S Reena Saritha[1,2], S Z Mohamed Shamshuddin*[1,2], V T Vasantha[1] & S R Pratap[1,2]

Chemistry Research Laboratory, HMS Institute of Technology, NH4, Kyathasandra, Tumakuru, Karnataka, India

Research and Development Center, Bharathiar University, Coimbatore, India

Email: em_es@rediffmail.com

Solid acid catalysts such as ZrO_2, Mo(VI)/ ZrO_2, Pt-SO_4^{2-}/ZrO_2 has been coated on honeycomb monoliths and characterized for their physico-chemical properties such as total surface acidity by NH_3-TPD, crystalinity by powder XRD, functionality by FT-IR and morphology by SEM techniques. These solid acid catalytic materials are employed in the vapor phase transesterification of methyl salicylate with different alcohols. The catalytic property of these solid acids has been correlated with their physico-chemical properties. These catalytic materials are found to be very efficient in the transesterification reaction with up to ~98% yield of the desired transester. Reaction conditions are optimized to get highest possible yield of the desired transester.

Keywords: Transesterification, Vapour phase, ZrO_2, Mo(VI)/ ZrO_2, Pt-SO_4^{2-}/ZrO_2, Salicylate esters.

Heterogenous catalysis, especially solid acid catalysis is extremely useful in many large-volume applications, especially in the production of fine and specialty chemicals[1,2]. One class of solid acid catalysts that have received a lot of interest is metal oxides and their modified forms, which exhibit exceptional acidic properties.

Among various metal oxides, zirconia (ZrO_2) and its modified forms are promising and have been utilized as catalytic materials in many industrially important organic transformations. Zirconia based solid acids such as MoO_x/ZrO_2, Pt-SO_4^{2-}/ZrO_2, WO_x/ZrO_2, etc., have been synthesized and used as solid acid catalysts in a few liquid and vapor phase reactions[3,4]. Though these modified zirconias are superior solid acid catalysts and free form deactivation, unlike sulfated zirconia, they are less explored for organic synthesis and transformations[5].

Cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb monoliths play a vital role as catalyst carriers in heterogenous catalysis[6]. These honeycomb (HC) monoliths have been widely used in gas phase reactions such as combustion of VOCs, automotive applications, etc[7]. But, HCs coated with solid acid catalysts have not been explored much in the field of organic fine chemical synthesis. Though, a limited literature could be found on the application of HCs coated with solid acids in liquid phase reactions[8,9], no literature could be found on the application of such HCs for the synthesis of fine chemicals *via* vapour phase.

Catalyst coated on HCs have advantages over powder catalysts, such as formation of thin layer of catalyst with high active surface area, less amount of catalyst loaded on the monolith is highly effective, separation and complete recovery of the catalyst coated with honeycomb from the reaction mixture will be much easier.

Organic fine chemicals are mostly synthesized either by following liquid phase or vapour phase conditions. In certain cases, vapour phase conditions of the experiments are better suited in many equilibrium driven organic reactions than in liquid phase. In vapour phase reactions, the product molecules of the reaction are not in contact with the catalyst during the entire reaction period, thereby preventing backward reaction and hence yield of the desired reaction product will also be high[10].

Transesterification reactions are used to synthesize esters. Among various esters, salicylates are an important class of esters which are found to have various applications including perfumery, cosmetics, fragrances, ointments, sun-tan lotions, antiseptic creams, etc[11]. Salicylates are generally synthesized by the esterification of salicylic acid with alcohols which involve the liberation of water as the addition product. Another method of synthesizing salicylate esters is transesterification of methyl salicylate with alcohols wherein an alcohol is formed as the addition product[10]. Since, in the present work, solid acids are being used as catalytic materials which contain moisture sensitive active centers, anhydrous condition prevalent in transesterification is an advantage.

Based on the above information, in the present article, efforts have been made to synthesize and coat

solid acids such as zirconia (Z) and its modified forms such as 5%Mo(VI)/ZrO$_2$ (MZ) and Pt-SO$_4^{2-}$/ZrO$_2$ (Pt-SZ) on honeycomb monoliths (HCs) with an idea of obtaining catalytic materials with improved activity and stability desirable for the selected acid catalyzed vapour phase transesterification leading to the formation of industrially important salicylate esters. The catalytic material were analysed for their physico-chemical properties such as surface acidity, crystalinity, functionality and morphology before using them as catalysts. Various salicylate esters such as ethyl salicylate, *i*-butyl salicylate, *i*-pentyl salicylate, benzyl salicylate and phenyl salicylate were synthesized under vapour phase conditions. Optimization of reaction conditions was studied by varying the parameters such as nature of the catalyst, catalyst bed temperature, flow-rate of the reactants and time-on-stream.

Experimental Section

Materials

Cordierite honeycomb monoliths used for the present study having dimensions (height = 1.20 cm, diameter = 2.50 cm and hole = 0.2 cm) were supplied by Shreya ceramics, Vadodara, India. Zirconyl nitrate, ammonium molybdate, chloro platinic acid, methyl salicylate and alcohols were supplied by Sd. Fine Chem India (P) Ltd., India.

Preparation of catalytic material

ZrO$_2$, 5%Mo(VI)/ZrO$_2$ and Pt-SO$_4^{2-}$/ZrO$_2$ were coated on honeycomb monoliths (HCs) by following 'dip and dry' method[9].

a) Coating of ZrO$_2$ on honeycomb

A dilute solution of zirconyl nitrate with 50 mL of deionized water was prepared. The resulting solution was coated on a HC by 'dip & dry' method in a furnace preheated to 400°C for 8-10 times till ~0.2 g of ZrO$_2$ is coated on the HC.

b) Coating of Mo(VI)/ZrO$_2$ on honeycomb

A dilute solution consisting of known amounts of zirconyl nitrate and ammonium molybdate was made. This solution was coated on a HC by 'dip & dry' method in a furnace preheated at 400°C. The 'dip & dry' steps were repeated 8-10 times till ~0.2 g of MZ was coated on the HC.

c) Coating of Pt-SO$_4^{2-}$/ZrO$_2$ on honeycomb

A known amount of zirconyl hydroxide and 6 *M* sulphuric acid solution were taken in a china dish and made slurry. The slurry was dried in an air oven for 12 hr at 120°C. The dried material was powdered well,

to which a known volume of 1% H$_2$PtCl$_6$ solution was added and made into a dilute slurry by adding limited amount of water. The resulting slurry was coated on a HC by 'dip & dry' method in a furnace preheated at 400°C. The 'dip & dry' steps were repeated 8-10 times till ~0.2 g of PSZ was coated on the HC.
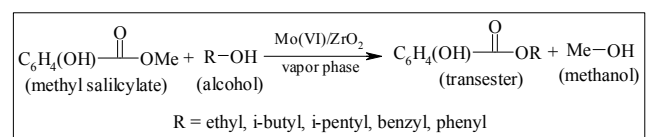
The HCs coated with Z or MZ or Pt-SZ were calcined at 550°C for 2 h before using them as catalytic materials.

Characterization of catalytic material

The solid acid catalytic material were characterized for their physico-chemical properties such as surface acidity by NH$_3$-TPD (Mayura TPD unit), crystalinity by Powder X-ray diffraction (Philips X'Pert X-ray diffractometer using CuKα), functionality by FT-IR (Nicolet) and morphology by SEM (JEOL-2010) techniques.

Catalytic activity studies of catalytic material

Vapour phase transesterification of methyl salicylate with an alcohol (ethyl alcohol, *i*-butyl alcohol, *i*-pentyl alcohol, benzyl alcohol and phenol) was carried out over HC coated with a solid acid (Z or MZ or SZ) in a specially designed fixed bed downstream vapour phase glass reactor maintained at 200°C. The reaction mixture consisting of methyl salicylate and an alcohol was fed into the pre-heater at a flow rate of 10 mL/h maintained at 250°C by means of an infusion pump before passing over the catalytic material. The reaction products obtained after the transesterification reaction were analyzed by gas chromatograph (Mayura) fitted with a column (10% SE-30 chromosorb w-AW, 3 m × 1/800) coupled with a FID detector and also by GC–MS (Varian).

$$\underset{\text{(methyl salilcylate)}}{C_6H_4(OH)\overset{O}{\overset{\|}{-}}OMe} + \underset{\text{(alcohol)}}{R\!-\!OH} \xrightarrow[\text{vapor phase}]{Mo(VI)/ZrO_2} \underset{\text{(transester)}}{C_6H_4(OH)\overset{O}{\overset{\|}{-}}OR} + \underset{\text{(methanol)}}{Me\!-\!OH}$$

R = ethyl, i-butyl, i-pentyl, benzyl, phenyl

Results and Discussion

Characterization of catalytic materials

The values of total surface acidity (TSA) and acid site distribution measured by NH$_3$-TPD method of the catalytic materials are given in Table 1.

The TSA values of the catalytic materials were found to be in the order: Z < MZ < Pt-SZ.

Pure zirconia (Z) was found to be least acidic and Pt-SZ was highly acidic. This order also indicates that the incorporation of Mo(VI) or Pt-SO$_4^{2-}$ ions have a

Table 1 — Surface acidity of catalytic materials used for the present study

Catalytic material	Acid site distribution (mmol/g)				
	Weak	Moderate	Strong	Very strong	TSA
Z	0.04	0.38	-	-	0.42
MZ	-	0.17	0.84	-	1.01
Pt-SZ	-	-	0.87	0.34	1.21

strong influence on the physico-chemical properties of zirconia. When the acid site distribution of Z, MZ and Pt-SZ were compared, Z consisted of only *'weak & moderate'* acid sites whereas, MZ consisted of *'medium & strong'* acid sites and Pt-SZ was found to have *'strong and very strong (super)'* acid sites[5]. The increase in the acidity of zirconia upon incorporation of Mo(VI) or Pt-SO_4^{2-} ions can be attributed to the generation of electron deficient states in the zirconia lattice[5].

The PXRD patterns of Z, MZ and Pt-SZ are shown in Fig. 1. The figure shows the presence of a mixture of monoclinic and tetragonal phases in Z. However, the PXRD patterns of MZ and Pt-SZ show prominent reflections due to tetragonal phase indicating a strong influence of Mo(VI) or Pt-SO_4^{2-} ions on the phase modification of Z from monoclinic phase to the more catalytically active metastable tetragonal phase[5].

Further, it is interesting to note that a triangular co-relationship may exist between TSA, PXRD phases and the catalytic activity of zirconia and its modified forms. The catalytic material which consisted of more tetragonal phase was found to be more acidic and further such material was found to possess more catalytic activity in an acid catalyzed reaction (transesterification).

The FT-IR spectra of Z, MZ and Pt-SZ are given in Fig. 2. The bands at 1391 and 1118 cm^{-1} can be due to Zr-OH bending and Zr-O-Zr stretching modes respectively, which confirm the formation of ZrO_2 phases. The broad band at ~1646 cm^{-1} is attributed to the vibrations of acidic –OH and the band at ~3400 cm^{-1} stretching mode with hydrogen bonding are present in all the catalyst samples.

In case of MZ catalytic material, the peak at ~848 cm^{-1} is due to Mo-O-Mo stretching mode of vibration for Mo(VI) ions. This indicates a strong interaction of Mo(VI) ions on the surface of ZrO_2 wherein peak at ~ 1118 cm^{-1} gets almost disappeared[12].

SEM images of HCs coated with Z or MZ or Pt-SZ are represented in Fig. 3. The SEM images show appearances more strongly adhering on the surface of the HC monolith. This indicates that the method used to
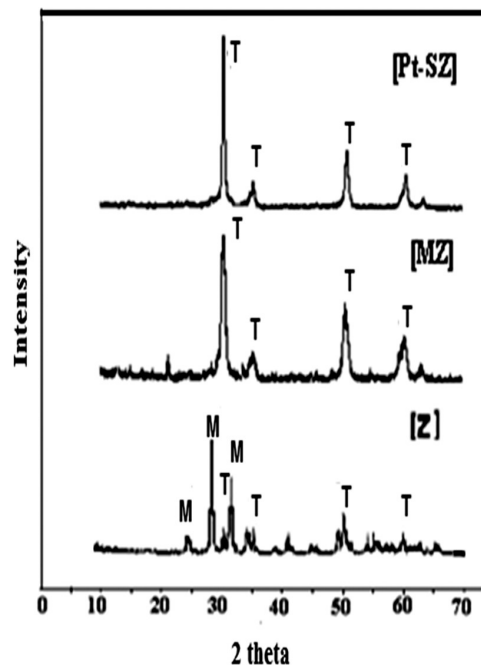

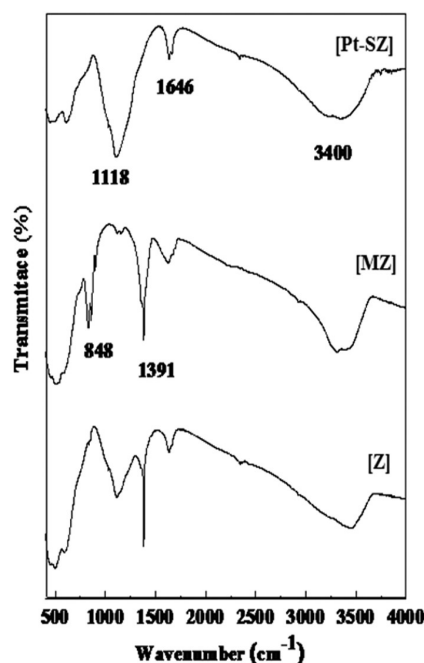Fig. 1 — PXRD patterns of HCs coated with Z, MZ and Pt-SZ. [*M – monoclinic; T - tetragonal phase*].

Fig. 2 —The FT-IR spectra of HCs coated with (a) Z (b) MZ (c) Pt-SZ.

coat the active catalyst (Z or MZ or Pt-SZ) was efficient to get homogenous and adherent coating on the HC.

Catalytic activity studies of catalytic material
Effect of nature of the catalyst

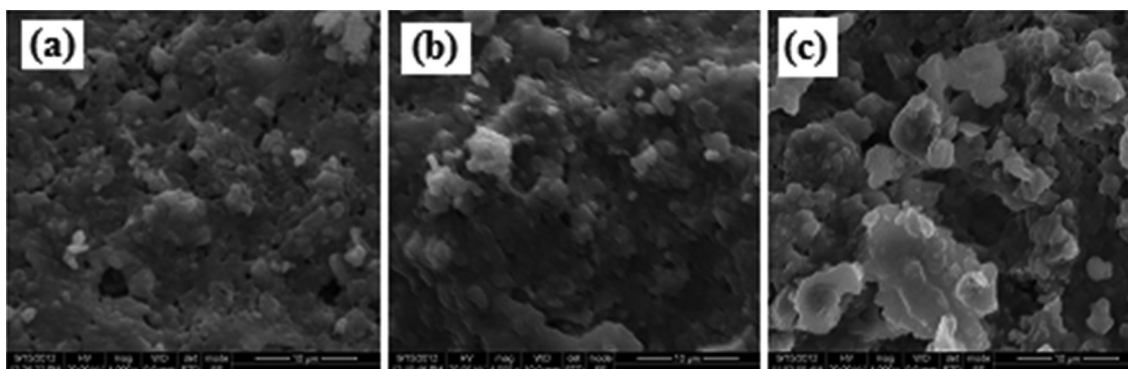In order to find out a facile catalytic material, test reactions were conducted over HCs coated with Z,

Fig. 3 — SEM images of HCs coated with (a) Z, (b) MZ and (c) Pt-SZ.

MZ and Pt-SZ in the vapour phase transesterification of methyl salicylate (MS) with benzyl alcohol (BA) at a flow rate of 10 mL/h by keeping catalyst bed temperature at 200°C and pre-heater temperature at 225°C. The reactions were conducted in a specially designed glass reactor which can accommodate a HC catalytic material. All the catalytic materials (Z, MZ, Pt-SZ) used for the present study were found to be active in the transesterification of MS with BA. A correlation between the total surface acidity (TSA) and the catalytic activity of the catalyst was observed. Z being lowest acidic was found to be least active followed by MZ and Pt-SZ (Table 2).

However, the selectivity of the products was found to depend on the acid site distribution of the catalytic material. Z and MZ being consisted of 'weak or moderate or strong' acid sites, were found to produce only benzyl salicylate (BS) as the product and therefore they were 100% selective. But, Pt-SZ, which consisted of 'very strong (super)' acid sites was found to produce dibenzyl ether (DBE) as the by-product in addition to benzyl salicylate and hence Pt-SZ is less selective than Z or MZ. For further studies, MZ coated on HC was selected as the catalytic material which produced upto 86% of the desired transester (BS) with 100% selectivity.

Effect of catalyst bed temperature

In order to determine the optimized catalyst bed temperature, transesterification of MS with BA was conducted in presence of MZ catalytic material at different catalyst bed temperatures ranging from 180 to 240°C and the results are shown in Fig. 4(a).

The results indicate that the catalyst bed temperature could affect both the conversion of MS as well as selectivity of the products (either transester or ether). When the catalyst bed temperature was increased, the conversion of MS was also found to increase greatly till

Table 2 — Comparative catalytic activity of catalytic materials

Catalytic material	Conversion of MS (%)	Selectivity of BS (%)	Selectivity of DBE (%)
Z	46	100	00
MZ	86	100	00
Pt-SZ	98	78	22

Reaction conditions: Molar ratio of MS: BA = 2: 1, flow-rate of reactants = 10 mL/h, pre-heater temperature = 225°C, catalyst bed temperature = 200°C].

200°C and not much increase was observed beyond 200°C. However, MZ was found to be 100% selective till catalyst bed temperature of 200°C, beyond which the formation of DBE was observed. This indicates that higher catalyst bed temperature can also result in the formation of DBE. Therefore, catalyst bed temperature of 200°C was found to be optimum to obtain reasonably good yield of the transester (benzyl salicylate) with 100% selectivity.

Effect of flow-rate of the reactants

The transesterification of MS with BA was carried out at different flow rates (5.0 mL/h to 12.5 mL/h) and the results are presented in the form of a graph (Fig. 4b). From Fig. 5, it is clear that, the conversion of MS decreases with increasing the flow rate. However, at lower flow rates, (5.0 mL/h and 7.5 mL/h) the selectivity of the transester (BS) was found to be less with an increase in the formation of dibenzyl ether (DBE). Formation of DBE can be due to higher contact time between the reactant molecules and the catalytic material which could lead to the side reactions resulting in the formation of DBE as the by-product. But 100% selectivity was achieved when the flow-rate was 10 mL/h.

Effect of time-on-stream

The effect of time-on-stream in the transesterification of MS with BA was studied between 0 min to
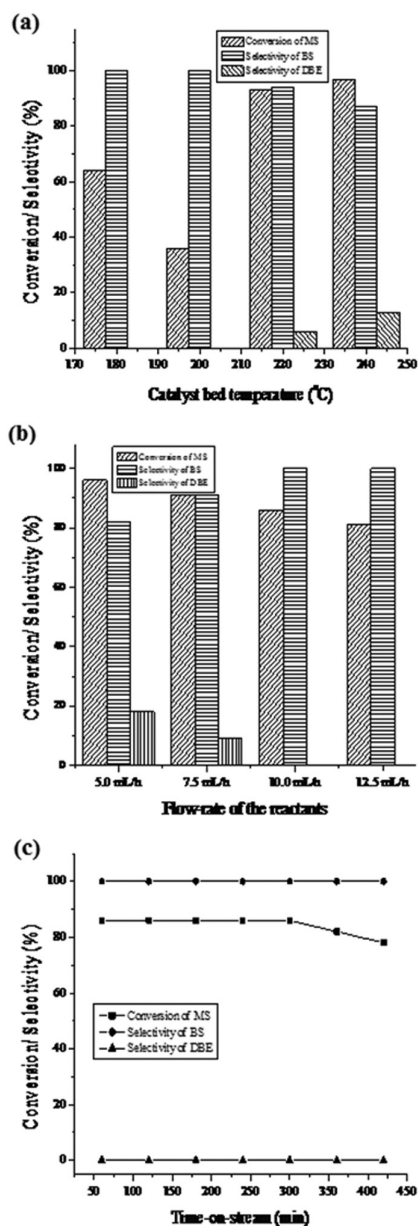
Table 3 — Transesterification of methyl salicylate with different alcohols over MZ catalytic material

Alcohol (R)	Conversion of MS (%)	Selectivity of transester (%)	Selectivity of ether (%)
Ethyl alcohol	64	100	00
i-butyl alcohol	86	100	00
i-pentyl alcohol	93	100	00
phenol	97	100	00

i-butyl salicylate, *i*-pentyl salicylate and phenol over HC coated with MZ catalytic material and the results are shown in Table 3.

The results indicate that the HC coated with MZ catalytic material could be a facile and efficient catalyst for the synthesis of salicylate esters via transesterification. HC coated with MZ catalyst was found to be 100% selective towards the formation of the respective transesters such as ethyl salicylate, *i*-butyl salicylate, *i*-pentyl salicylate and phenyl salicylate (salol).

Conclusion

Salicylate esters can be efficiently synthesized over honeycomb monoliths coated with zirconia and its modified forms *via* transesterification in vapour phase conditions. Especially, Mo(VI)/ZrO$_2$ is found to be highly efficient as it produced the desired transester in good yields with 100% selectivity. However, Pt-SO$_4^{2-}$/ZrO$_2$ is found to be less selective towards the formation of the desired transester as it also produced ether as the by-product. A correlation between the acidity and the yield of the transester has been observed.

Acknowledgements

Fig. 4 — (a) Effect of catalyst bed temperature; (b) flow-rate of the reactants and (c) time-on-stream on the conversion of MS and selectivity of the products. [Reaction conditions: Molar ratio of MS: BA = 2:1, flow-rate of reactants = 10 mL/hr, pre-heater temperature = 225°C, catalyst bed temperature = 200°C, catalyst = HC coated with MZ].

400 min and the results are given in Fig. 4c. The conversion of MS was found to be stable till 300 min and tend to decrease gradually thereafter. However, time-on-stream had no affect on the selectivity of the products (either BS or DBE).

Synthesis of different salicylate esters

Transesterification of methyl salicylate was carried out with different alcohols such as ethyl alcohol,

References

1   Busca G, *Chem Rev*, 107 (2007) 5366.
2   Arata K, *Adv Catal*, 37 (1990) 165.
3   Yadav G D & Nair J J, *Micropor Mesopor Mater*, 33 (1999) 1.
4   Arata K & Hino M, *Chem Commun*, 18 (1980) 851.
5   Reddy B M & Patil M K, *Chem Rev*, 109 (6) (2009) 2185.
6   Nijhuis T A, Beers A E W, Vergunst T, Hoek I, Kapteijin F & Moulijin J A, *Chem Engg Sci*, 56 (3) (2001) 823.

7   Heck R M, Gulati S & Rarranto R J, *Chem Eng J*, 82 (2001) 149-156.

8   Shyamsundar M & Mohamed Shamshuddin S Z, *J Amer Oil Chemists Soc*, 92(3) (2015) 335-344.

9   Mohamed Shamshuddin S Z & Shyamsundar M, *J Porour Mater,* 24 (4) (2017) 1003.

10 Joyce D'Souza & Nagaraju N, *Indian J Chem Technol,* 11 (2004) 401.

11 Van J R & Botting R M, *Aspirin and other salicylates*, (Chapman and Hall: London, 1st Edn.), 1992.

12 Davydov A, *Molecular Spectroscopy of oxide catalyst surfaces*, (2003) DOI: 10.1002/0470867981.Ch.4.