

## Honeycomb Monolith Coated with Mo(VI)/ZrO<sub>2</sub> as a Versatile Catalyst System for Liquid Phase Transesterification

N. Thimmaraju, S. R. Pratap, M. Senthilkumar<sup>†</sup>, and S. Z. Mohamed Shamshuddin\*

Chemistry Research Laboratory, HMS Institute of Technology, NH4, Kyathsandra, Tumkur - 572 104, Karnataka, India.

\*E-mail: [em\\_es@rediffmail.com](mailto:em_es@rediffmail.com)

<sup>†</sup>Department of Chemistry, SKP Engineering College, Tiruvannamalai, Tamil Nadu, India

(Received March 21, 2012; Accepted August 20, 2012)

**ABSTRACT.** Solid acid Mo(VI)/ZrO<sub>2</sub> with 2-10% Mo(VI) was coated on honeycomb monoliths by impregnation method. These catalytic materials were characterized by BET, NH<sub>3</sub>-TPD/*n*-butylamine back titration, PXRD and SEM techniques. Phenyl salicylate (Salol) was synthesized *via* transesterification of methyl salicylate and phenol over these catalytic materials. An excellent yield (91.0%) of salol was obtained under specific reaction conditions. The effect of poisoning of acid sites of the catalytic material by adsorbing different bases and its effect on total surface acidity, powder XRD phases and catalytic activity was studied. A triangular correlation between the surface acidity, powder XRD phases and catalytic activity of Mo(VI)/ZrO<sub>2</sub> was observed. The thermally regenerated catalytic material was reused repeatedly with a consistent high yield of salol.

**Key words:** Honeycomb monolith, Mo(VI)/ZrO<sub>2</sub>, Transesterification, Salol, Solid acids

### INTRODUCTION

Solid acids as heterogeneous catalysts are extremely useful in many large-volume applications, especially in the production of fine and specialty chemicals as well as in the petrochemical industry.<sup>1,2</sup>

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 metal oxides, zirconia (ZrO<sub>2</sub>) is a versatile oxide used as a catalyst as well as a catalyst support and promisingly has been employed in many industrially important organic transformations. Much work has been done on sulfated zirconia as a solid acid in the field of fine chemical synthesis.<sup>3</sup> Due to a major disadvantage associated with sulfated zirconia i.e., rapid deactivation at high temperatures, many efforts have been made to synthesize sulfate free-zirconia based solid acids. Sulfate free-zirconia based solid acids such as VO<sub>x</sub>/ZrO<sub>2</sub>, MoO<sub>x</sub>/ZrO<sub>2</sub> & WO<sub>x</sub>/ZrO<sub>2</sub> have been synthesized and used as solid acid catalysts in a few liquid & vapor phase reactions.<sup>4-8</sup> Though these sulfate free-zirconias are superior solid acid catalysts and free from deactivation, unlike sulfated zirconia, they are less explored for organic synthesis.<sup>9</sup> It has been reported that the incorporation of VO<sub>x</sub> or MoO<sub>x</sub> or WO<sub>x</sub> on ZrO<sub>2</sub> not only increases the acid site concentration of zirconia but also favors the formation of catalytically more active tetragonal phase of zirconia. Monoclinic phase of

zirconia is less catalytically active when compared to its monoclinic phase.<sup>9</sup>

Further, the physico-chemical, structural and catalytic properties of metal oxides can be modified by using proper catalyst carriers, adopting various synthesis and post synthesis routes, etc. Cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) honeycomb monoliths play a vital role as catalyst carriers in heterogeneous catalysis.<sup>10</sup>

Catalyst coated honeycomb monoliths are widely used in automotive applications which involve gas phase reactions such as combustion of VOCs, automotive applications, ozone abatement in aircrafts, and selective reduction of NO<sub>x</sub>.<sup>11</sup>

However, more interestingly monoliths coated with solid acid catalysts have not been explored so far in the field of organic fine chemical synthesis. Catalyst coated monoliths 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, easy separation and complete recovery of the catalyst from the reaction mixture.

Among various organic reactions catalyzed by solid acids, transesterification is one of the industrially important acid catalyzed reactions to synthesize esters. This reaction is very useful in the synthesis of flavors & fragrances, in pharmaceutical industries and in biodiesel synthesis. Especially, salicylate esters are an important group of esters used in the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, polyesters, solvents,

perfumes and cosmetics.<sup>12</sup>

Phenyl salicylate (SALOL) is an ester, which has got a pleasant taste and odor, is more useful in sun-tan lotions, as an antiseptic, anodyne and pain-relieving agent. It can be prepared by simple esterification of salicylic acid with phenol in presence of a solid acid catalyst. But anhydrous condition prevalent in transesterification of methyl salicylate with phenol is advantageous in increasing the yield and life time of the catalytic system.

Keeping in view the information obtained from the literature and the advantages of honeycomb monolith as a catalyst carrier, importance of Mo(VI)/ZrO<sub>2</sub> as a solid acid catalyst and industrial applications of salol, in this article we report the work done on the coating of Mo(VI)/ZrO<sub>2</sub> on honeycomb monolith, its physico-chemical characterization and catalytic activity study in liquid phase salol synthesis *via* transesterification of methyl salicylate with phenol. To the best of our knowledge it is for the first time that an attempt has been made to coat a solid acid on a monolith and apply it in a liquid phase organic reaction. This is a very cost effective and ecofriendly process and it would be very interesting initiative step in the field of heterogeneous catalysis. Further, effect of poisoning of acid sites by bases such as ammonia or pyridine on the total surface acidity, XPD phases of the Mo(VI)/ZrO<sub>2</sub> and its catalytic activity is correlated. Thermal regeneration and reusability of this catalytic material was also taken up.

## EXPERIMENTAL

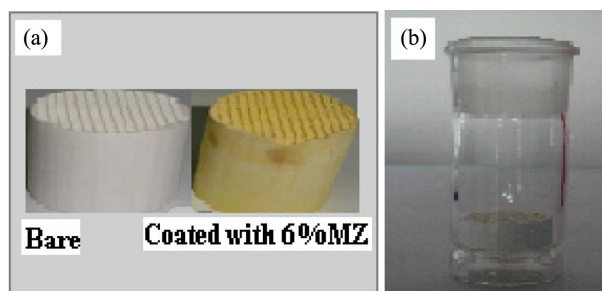
### Materials

Cordierite honeycomb monolith (height=1.20 cm, diameter=2.50 cm and hole size=0.2 cm) was specially prepared and supplied for the present work by Shrey Ceramics, Baroda, India.

Zirconyl nitrate and ammonium molybdate were supplied by M/S LOBA Chemie India Ltd., India.

### Preparation of the Catalytic Material

Mo(VI)/ZrO<sub>2</sub> (MZ) with different Mo(VI) content (2-10%) was coated on different monoliths by impregnation method. Monolith was wash coated with zirconia before coating the active catalyst i.e., Mo(VI)/ZrO<sub>2</sub>. Wash coating is done to increase the surface area and to have a support material that has a better interaction with the active catalyst.<sup>13</sup> For wash coating, a dilute solution of zirconyl nitrate was prepared which was then coated on a bare cordierite monolith by dipping and drying in a furnace maintained at 400 °C.



**Fig. 1.** Photograph of (a) Cordierite honeycomb monolith. (b) Reactor with monolithic catalyst.

Typically, for coating 2% Mo(VI)/ZrO<sub>2</sub> on a monolith, dilute solution containing 7.2 g of zirconyl nitrate [ZrO(NO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O] and 0.12 g of ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] with 50 mL of deionised water, was prepared. The resulting solution was coated on a wash coated monolith by dipping and drying in a furnace preheated at 400 °C. The dipping and drying steps were repeated 12 to 15 times till ~0.2 g of MZ is coated on the monolith. The monolith coated with MZ was calcined at 550 °C for 5 h in a muffle furnace before its use as a catalyst. A photograph of honeycomb monolith (both bare and coated with 6% MZ) is shown in Fig. 1a. In this article, a monolith coated with the active catalyst is referred to as *monolithic catalyst*.

Mo(VI)/ZrO<sub>2</sub> was prepared in powder form by impregnation method. Known amounts of zirconyl nitrate and ammonium molybdate were taken in a china dish and made a paste with small amount of water. The paste was then dried in an air oven at 120 °C and calcined at 550 °C for 5hr in a muffle furnace.

### Catalyst Characterization

The monolithic catalysts were characterized by BET, NH<sub>3</sub>-TPD/*n*-butylamine back titration, powder XRD and SEM techniques for their specific surface area, surface acidity, crystallinity and morphology respectively.

The specific surface area of the catalytic material was evaluated by NOVA 1000 Quanta chrome high-speed gas sorption analyzer instrument. In this analysis, the catalytic material was degassed at 523 K for 5 h before measurements. Specific surface area was calculated using the BET equation. The total surface acidity was measured by NH<sub>3</sub>-TPD method by using Puls Chemisorb 2705 from Micromeritics. Here, the catalytic material was degassed under a helium stream for 1 h, ammonia (99.99%) gas was injected into the stream until saturation was reached, cooled to 323 K. The system was maintained at 323 K for 30 min.

After purging, the system with flowing helium for 2 h at 323 K, the sample was heated at the rate of 5 K min<sup>-1</sup> in helium to 973 K. The change in concentration of the desorbed NH<sub>3</sub> was monitored using an online thermal conductivity detector. The total surface acidity was also measured by *n*-butyl amine back titration method using dry benzene as the solvent and bromothymol blue indicator.<sup>14</sup> The X-ray powder diffraction (PXRD) patterns of the catalytic material were collected on X-pert Pro Philips diffractometer equipped with Ni filtered Cu-K $\alpha$  radiation  $\lambda$ =1.5418 Å using a graphite crystal mono-chromator. The Scanning Electron Micrographs (SEM) were obtained using a JEOL JED-2300 analysis station microscope.

Monoliths coated with pure zirconia or MZ were exposed to different bases such as NH<sub>3</sub> or pyridine vapors for ~15 min and heated them at 120 °C for 2 h in an air oven. It was assumed that, by this time all the acid sites on the surface of the catalytic material get neutralized by NH<sub>3</sub> or pyridine. The total surface acidity of poisoned MZ was measured and its powder XRD patterns were also recorded. In the present article, this type of catalytic material is referred to as *poisoned monolithic catalyst*.

### Catalytic Activity Studies (Transesterification)

The catalytic activity of all the catalytic materials used in the present study was determined in liquid phase transesterification of methyl salicylate (MS) with phenol (P) to synthesize salol. The transesterification was carried out in a specially designed glass reactor (Fig. 1b). In this reactor a ring is fabricated ~3/4" above the bottom to support the monolith. MS, P, and the monolithic catalyst were placed in the reactor and refluxed for a definite period of time (4 h). The total volume of the reaction mixture was always kept constant at 20 mL. After a definite period of time, the reaction mixture was cooled to room temperature, monolithic catalyst was separated from the reaction mixture, and the

products obtained by the transesterification reaction were analyzed quantitatively by gas chromatograph fitted with a (10% SE-30 chromosorb w-AW, 3 m $\times$ 1/8") column coupled with FID detector and qualitatively by GC-MS (Varian).

### Catalyst Regeneration

To study the regeneration and re-use of the catalytic material, the monolithic catalyst was recovered from the reaction mixture, washed with acetone and dried at 120 °C for 2 h followed by thermal activation at 550 °C for 2 h. Thus regenerated monolithic catalyst was subjected to salol synthesis under similar reaction conditions. After every reaction cycle the catalyst was recovered, washed and activated as above.

## RESULTS AND DISCUSSION

Among various methods reported,<sup>13</sup> impregnation method was chosen for coating Mo(VI)/ZrO<sub>2</sub> on a honeycomb monolith because it is easy, fast and does not require a fuel.

### BET Surface Area Measurement

BET surface areas of catalytic materials used in the present study are given in Table 1. The surface area of the catalytic material is strongly influenced by the loading of Mo(VI) ions. The specific surface area increases gradually with increasing Mo(VI) concentration up to 6% and then decreases. This may be due to the stabilizing effect of Mo(VI) on zirconia. It is also possible that the interaction between Mo(VI) ions and zirconia inhibits sintering [16] and delays crystal growth, favoring the stabilization of the tetragonal zirconia as indicated from PXRD pattern (Fig. 2a). It is also reported<sup>16</sup> that the crystallite size of tetragonal zirconia is smaller than the monoclinic form. The decrease in the surface area with increase of Mo(VI) ion

**Table 1.** Physico-chemical characteristics of catalytic materials

Sl. No.	Catalytic material	Amount of active catalyst loaded on the monolith (g)	Surface area by BET (m <sup>2</sup> /g)	Total surface acidity by NH <sub>3</sub> -TPD (mmols/g)
1	ZrO <sub>2</sub>	0.208	42	0.42 (0.44)
2	2% Mo(VI)/ZrO <sub>2</sub>	0.210	76	0.98 (1.00)
3	4% Mo(VI)/ZrO <sub>2</sub>	0.198	92	1.11 (1.16)
4	6% Mo(VI)/ZrO <sub>2</sub>	0.203	109	1.46 (1.39)
5	8% Mo(VI)/ZrO <sub>2</sub>	0.204	96	1.54 (1.46)
6	10% Mo(VI)/ZrO <sub>2</sub>	0.201	82	1.59 (1.51)
7	6% Mo(VI)/ZrO <sub>2</sub> (Powder)	0.200	122	1.35 (1.26)
8	6% Mo(VI)/ZrO <sub>2</sub> (poisoned by ammonia)	0.206	104	0.32 (0.36)
9	6% Mo(VI)/ZrO <sub>2</sub> (poisoned by pyridine)	0.208	105	0.21 (0.31)

Note: Numbers in the parenthesis (column-6) are the total surface acidity values obtained by *n*-butylamine back titration method.

concentration beyond 6% may be related to the blockage of pore structure.

However, in case of poisoned monolithic catalyst not much change in the BET surface area compared to unpoisoned ones was observed. This indicates that poisoning of acid sites does not affect surface area, but only neutralizes the acid sites without affecting the surface area of catalytic material.

#### Surface Acidity Measurements by $\text{NH}_3$ -TPD/*n*-butylamine Back Titration Methods

The concentration and strength of the surface acid sites on monolithic catalyst was determined by  $\text{NH}_3$ -TPD method. The total acidity in terms of mg of  $\text{NH}_3$  per g of the catalyst is presented in Table 1. All the samples were found to possess weak to moderate strength acid sites. In the case of monolith coated with pure  $\text{ZrO}_2$ , complete desorption of ammonia occurred below 130 °C indicating the presence of acid sites with medium strength.<sup>16,17</sup> However, desorption of ammonia from monolith coated with  $\text{Mo(VI)/ZrO}_2$  occurred in the temperature range 180–300 °C. This showed the presence of stronger acid sites on  $\text{Mo(VI)/ZrO}_2$  compared to pure  $\text{ZrO}_2$ . Total surface acidity values obtained from *n*-butyl amine back titration method were almost nearer to the values obtained by  $\text{NH}_3$ -TPD method. Among the catalytic materials used in the present work, total surface acidity of pure  $\text{ZrO}_2$  was found to be the lowest and incorporation of  $\text{Mo(VI)}$  on  $\text{ZrO}_2$  increased the total surface acidity of pure  $\text{ZrO}_2$ . It was also observed that, an increase in the concentration of  $\text{Mo(VI)}$  from 2–10% increased the total surface acidity values of  $\text{ZrO}_2$  drastically upto 6% and increases gradually thereafter.

6%  $\text{Mo(VI)/ZrO}_2$  (6% MZ) monolithic catalyst was selected for the study of effect of poisoning of acid sites by adsorbing bases such as ammonia or pyridine. It was observed that the total surface acidity of poisoned (6% MZ) monolithic catalyst was decreased to an extent that it was slightly lesser than the total surface acidity of pure  $\text{ZrO}_2$ . This suggests that the acidic sites arising due to only  $\text{ZrO}_2$  were also neutralized by these bases to a certain extent in addition to the acidic sites formed due to incorporation of  $\text{Mo(VI)}$  on  $\text{ZrO}_2$ .

Further, the total surface acidity values of 6% MZ monolithic catalyst which was poisoned by pyridine was lesser than the acidity value of 6% MZ monolithic catalyst poisoned by  $\text{NH}_3$ . This is because, in gaseous medium pyridine is more basic than  $\text{NH}_3$  and therefore pyridine interacts more with the acidic sites neutralizing more number of acid sites of the catalytic material.<sup>18</sup>

#### Powder XRD Studies

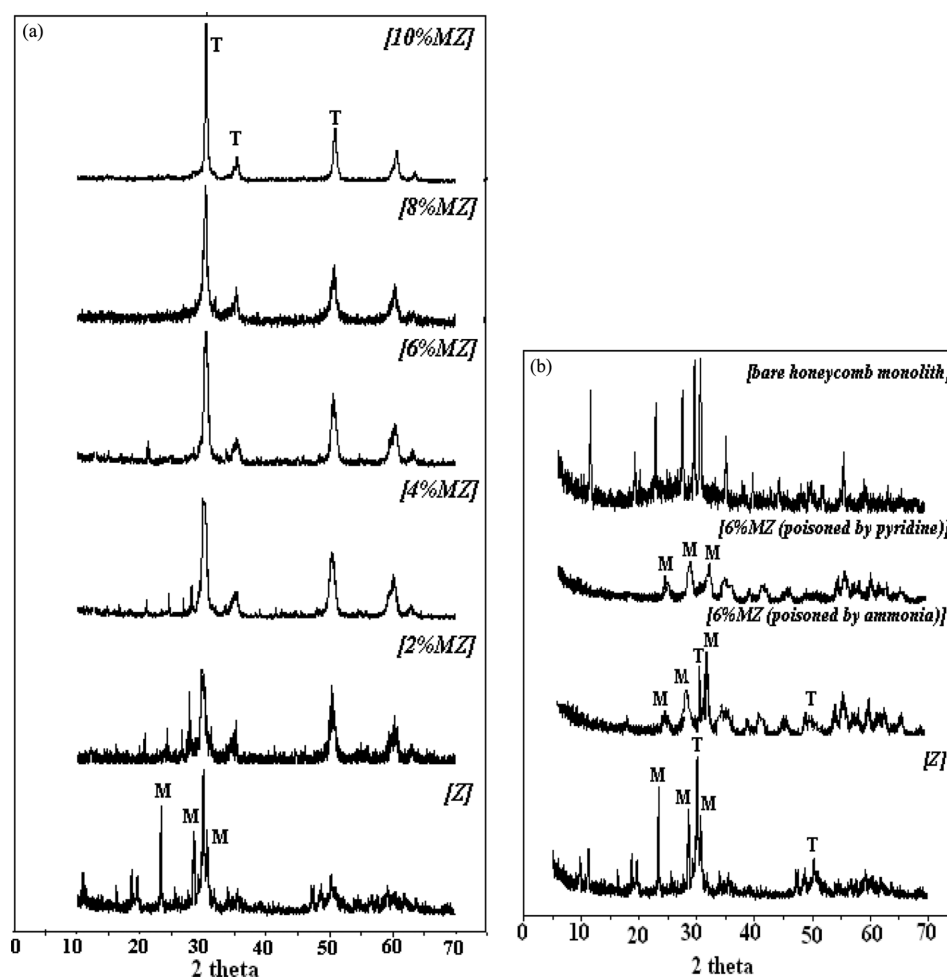
Powder XRD (PXRD) patterns of the monolithic catalysts used in the present study are shown in Fig. 2a. It is seen in the figure that, pure  $\text{ZrO}_2$  consists of peaks from both monoclinic (M) and tetragonal (T) phases. When pure  $\text{ZrO}_2$  was incorporated with  $\text{Mo(VI)}$  and  $\text{Mo(VI)}$  ion concentration was increased in the order 2%, 4%, 6%, 8% and 10%; a gradual decrease in the intensity of peaks corresponding to monoclinic phase with an increase in the intensity of the peaks related to tetragonal phase of  $\text{ZrO}_2$  was observed. This shows that the formation of a predominant tetragonal phase is dependent on the  $\text{Mo(VI)}$  ion concentration. For 6% MZ, it is interesting to note that PXRD peaks corresponding to monoclinic phase have been totally eliminated, and only peaks from tetragonal phase are found. Simultaneously, neither diffraction peaks corresponding to crystalline  $\text{MoO}_3$  nor peaks corresponding to any new crystalline phases are observed. This observation indicates the structure stabilizing effect of highly dispersed surface  $\text{Mo(VI)}$  ions.

PXRD patterns of monoliths coated with pure  $\text{ZrO}_2$ , 6% MZ (*poisoned by ammonia or pyridine*) and bare honeycomb monolith are shown in Fig. 2b. It is interesting to note that the PXRD pattern of poisoned 6% MZ resembled to those of pure  $\text{ZrO}_2$  i.e., former samples possessed more of monoclinic phase than tetragonal phase (Fig. 2b) unlike in the case of PXRD patterns of unpoisoned 6% MZ monolithic catalyst which consists of only tetragonal phase (Fig. 2a). This indicates that poisoning not only decreases the total surface acidity of the catalyst but also results in the formation of monoclinic phase. Further, when PXRD patterns of 6% MZ (*poisoned by ammonia*) and 6% MZ (*poisoned by pyridine*) are compared, the PXRD pattern of the latter showed low intense peaks due to monoclinic phase with no peak arising due to tetragonal phase of  $\text{ZrO}_2$ . This shows that the interaction between pyridine base and the catalytic material is stronger than with ammonia.

It is clearly understood from poisoning study that, total surface acidity and phases of monolithic catalyst are correlated. i.e., more is the tetragonal phase of  $\text{ZrO}_2$  higher will be its surface acidity and more is the monoclinic phase lesser will be its surface acidity. Presence of tetragonal phase in  $\text{ZrO}_2$  based catalysts could be responsible for high surface acidity.

Thus, BET,  $\text{NH}_3$ -TPD and PXRD studies indicated that the textural properties of pure  $\text{ZrO}_2$  were modified by incorporation of  $\text{Mo(VI)}$  ions.

Further, when PXRD patterns of bare monolith and



**Fig. 2.** (a) Powder X-ray Diffraction (PXRD) patterns of Mo(VI)/ZrO<sub>2</sub> with different wt% of Mo(VI) content; (b) PXRD patterns of poisoned Mo(VI)/ZrO<sub>2</sub> along with PXRD pattern of bare honeycomb monolith.

monolith which was wash coated with ZrO<sub>2</sub> or coated with active catalyst Mo(VI)/ZrO<sub>2</sub> are observed, no diffraction lines corresponding to bare monolith could be detected in either wash coated monolith or monolith coated with the active catalyst. This shows that the surface of bare monolith was fully and effectively covered with wash coating or the catalytic material.

### SEM Studies

SEM images of bare monolith, monolith wash coated with ZrO<sub>2</sub> and wash coated monolith coated with 6% MZ (with different magnifications) are given in Figs. 3(a-d) respectively. SEM image of the monolith wash coated with ZrO<sub>2</sub> (Fig. 3b) shows flakes which appear more strongly sticking to the surface of the monolith. When the surfaces of bare monolith and monolith wash coated with ZrO<sub>2</sub> are compared, one cannot see any part of the surface of bare monolith after wash coating with ZrO<sub>2</sub>. In Fig. 3c-

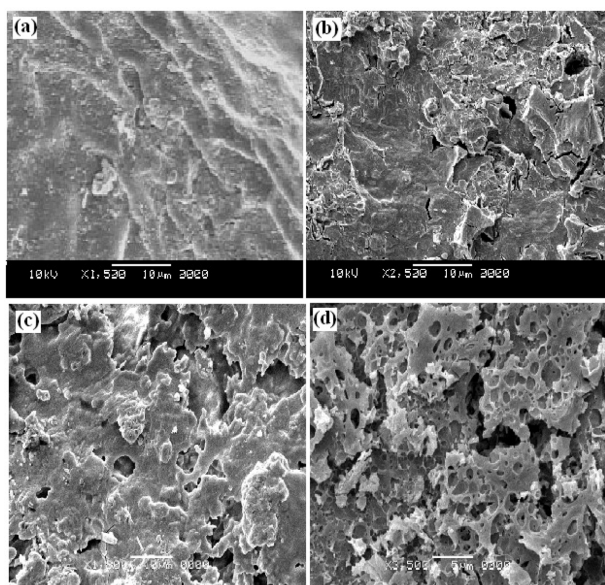
d, the SEM image of the monolith coated with 6% MZ shows that the coating of the catalyst is uniform. This information obtained from SEM also indicates that the method used for coating the catalytic material was suitable enough to obtain adherent and homogenous coating of the catalytic material.

### Transesterification

Transesterification of methyl salicylate (MS) with phenol (P) was carried out by taking MS: P ratio of 2: 1. Concentration of methyl salicylate was taken more because of the fact that, since transesterification is a reversible reaction, excess of MS may favor forward reaction leading to the formation of the desired product.

### Effect of Concentration of Mo(VI) in Catalytic Material on the Yield of Salol

Mo(VI)/ZrO<sub>2</sub> with 2, 4, 6, 8 and 10% Mo(VI) content

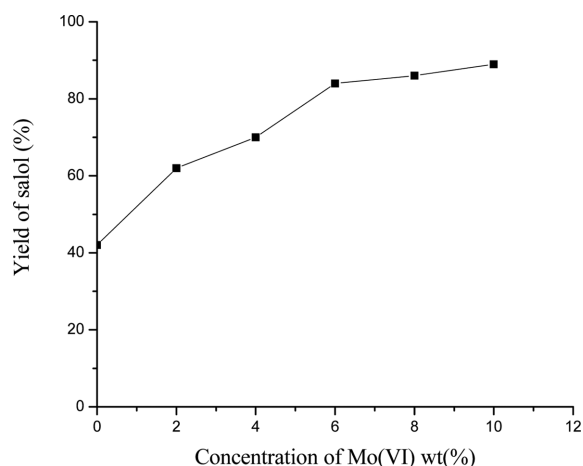


**Fig. 3.** Scanning Electron Micrograph images of (a) bare cordierite monolith; (b) monolith wash coated with zirconia; (c) wash-coated monolith coated with 6% MZ; (d) washcoated monolith coated with 6% MZ (at higher magnification).

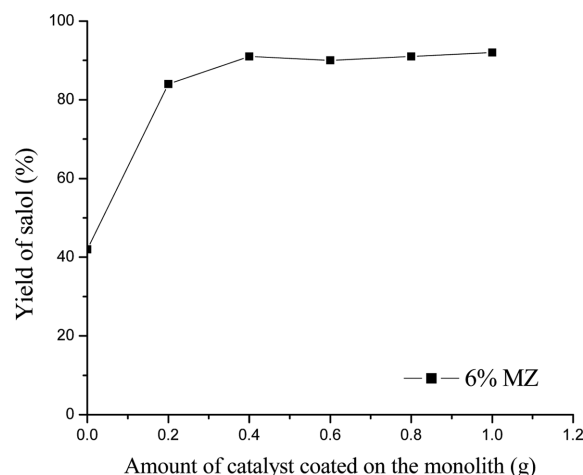
was coated on different monoliths and their catalytic activity was evaluated from the synthesis of salol. The catalytic activity is significantly influenced by dispersion properties of Mo(VI) on  $\text{ZrO}_2$  surface. As shown in Fig. 4, a low catalytic activity was observed over pure zirconia (0% Mo(VI)/ $\text{ZrO}_2$ ). With increase in Mo(VI) concentration, the yield of salol got increased, indicating that a large amount of acid sites are generated. However, higher Mo(VI) concentration beyond 6% in the MZ monolithic material resulted in a not much increase in its catalytic activity probably because of the formation of larger clusters hindering the approach of the reacting molecules to the active sites. In Fig. 4 the results show that the catalytic activity of 6% MZ is higher, so the yield of salol reaches a maximum number of ~85%. Therefore, 6% MZ monolithic catalyst was selected for further studies on optimization of reaction conditions.

#### Effect of Catalyst Amount on the Yield of Salol

The effect of the catalyst amount on yield of salol was investigated over 6% MZ monolithic catalyst. Different amount of 6% MZ (0.2 g to 1.0 g) coated on different monoliths was used to study the effect of amount of catalyst on the yield of salol. As seen from Fig. 5, a maximum yield of 85% has been attained over the monolith loaded with 0.2 g of 6% MZ, which clearly demonstrated the excellent catalytic activity of MZ solid acid catalyst



**Fig. 4.** Effect of concentration of Mo(VI) in MZ coated over monolith on the yield of salol. Molar ratio of MS:P=2:1; reaction temperature=refluxing temperature; catalyst weight=0.2 g of MZ coated on the monolith; reaction time=4 h.

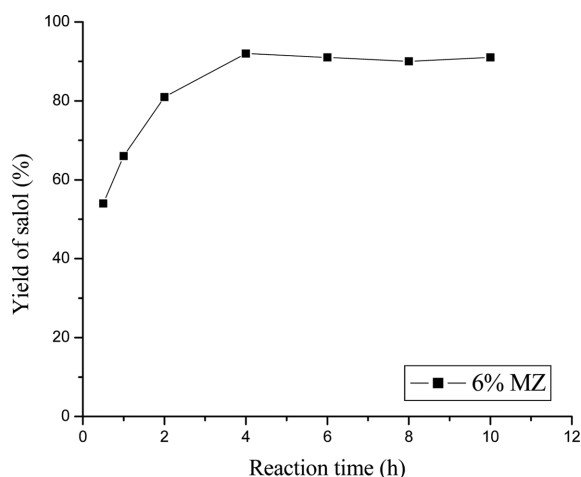


**Fig. 5.** Effect of catalyst amount (6% MZ) coated over the monolith on the yield of salol. Molar ratio of MS:P=2:1; reaction temperature=refluxing temperature; reaction time=4 h.

towards the synthesis of salol. However, the yield of salol stabilizes even after increasing the amount of loading of 6% MZ catalyst on the monolith beyond 0.2 g. This can be attributed to the formation of multilayer of the catalytic material masking the inner layer. Based on the above information, we can infer that, the threshold loading of a catalytic material on a honeycomb monolith used for the present study (dimension: height=1.20 cm, diameter=2.50 cm and hole size=0.2 cm) is upto 0.2 g. This results in better dispersion and best active catalytic surface over the monolith.

#### Effect of Reaction Time on the Yield of Salol

The yield of salol was investigated versus reaction time



**Fig. 6.** Effect of reaction time on the yield of salol. Molar ratio of MS:P=2:1; reaction temperature=refluxing temperature; catalyst weight=0.2 g of 6% MZ coated on the monolith.

ranging from 0.5 to 10 h over 6% MZ monolithic catalyst; the results are shown in Fig. 6. Yield of salol gradually increases with reaction time, and a maximum yield is reached at 4 h. With further increase of reaction time, however, the yield of salol stabilizes. Reaction time beyond 4 h seems to be too long and would result in by-products and in lower yield of salol. Therefore, 4 h was chosen as appropriate reaction time for optimization studies.

#### Effect of Poisoning of Acid Sites on the Yield of Salol

As discussed in the earlier section 3.3. of this article, the acid sites of 6% MZ monolithic catalyst was poisoned by NH<sub>3</sub> or pyridine vapours. It was observed that total surface acidity and powder XRD phases of the catalytic material are related to each other. In order to support this aspect, further, the poisoned catalytic material was used in the title reaction and the results are included in Table 2. The decrease in the yield (%) of salol can be attributed to the loss of acidic sites of catalytic material upon poisoning. Hence, we can infer that the total surface acidity, powder XRD phases and the catalytic activity of catalytic material used in the present study are related with each other.

**Table 2.** Comparative yield of salol over fresh and poisoned 6% MZ monolithic material

Catalyst	Yield of salol (%)
6% MZ (fresh)	84
6% MZ (poisoned by ammonia)	37
6% MZ (poisoned by pyridine)	33

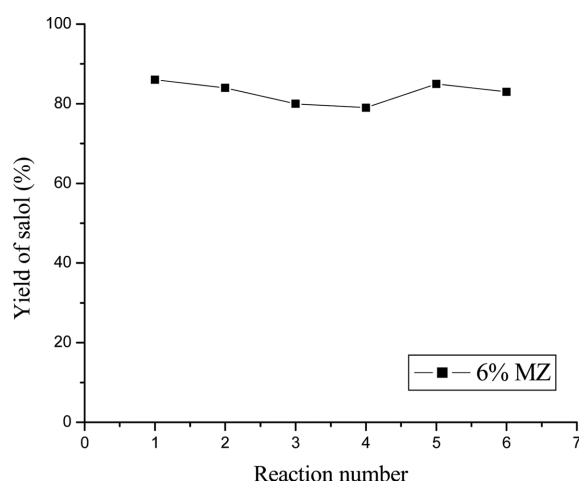
Molar ratio of MS:P = 2:1; reaction temperature = refluxing temperature; catalyst weight = 0.2 g of 6% MZ coated on the monolith; reaction time = 4 h.

#### Effect of Re-use of Catalyst on the Yield of Salol

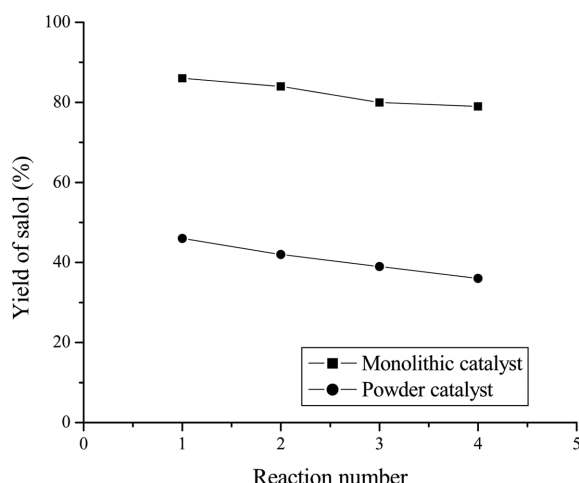
Not only does an ideal catalyst display high catalytic activity and good selectivity, but also offer inherent advantages, such as high stability, low deactivation rate, long life, and easy regeneration. The used monolithic catalyst (6% MZ coated on monolith) recovered from the reaction mixture was washed with acetone, dried at 120 °C for 2 h, and re-used for the salol synthesis under the optimized reaction conditions to study the performance of re-used catalyst. The results are shown in Fig. 7. As seen from the figure, the yield (%) of salol only slightly decreases when used up to 4 reaction cycles. The catalyst re-used for 4 reaction cycles was washed, dried, and calcined at 550 °C for 2 h. The thermally regenerated catalyst was used for the next reaction cycle (5<sup>th</sup> and 6<sup>th</sup> cycles in Fig. 7) and gave similar yield of salol as the fresh catalyst. This clearly indicates that the deactivation on catalyst is attributed to the absorption of the organic substance on the active sites. The absorbed organic species can be burned out at high temperature to regenerate catalytic activity.

#### Comparative Catalytic Activity of MZ in its Powder and Monolithic Forms

Catalytic activity of 0.2 g 6% MZ (powder) and 6% MZ (monolithic catalyst) were compared in transesterification of methyl salicylate with phenol. Even though same amount of the catalyst (0.2 g) was used in powder as well as monolithic form, a ~2 fold increase in the yield of salol was observed over monolithic form of the catalyst (Fig. 8; Reaction no. 1). The number of channels, their diameter and wall thickness determine the cell density, expressed as



**Fig. 7.** Effect of reusability of the catalyst on the yield of salol. Molar ratio of MS:P=2:1; reaction temperature=refluxing temperature; catalyst weight=0.2 g of 6% MZ coated on the monolith; reaction time=4 h.



**Fig. 8.** Effect of reusability of the catalyst in powder and monolithic forms on the yield of salol. Molar ratio of MS:P=2:1; reaction temperature=refluxing temperature; catalyst weight=0.2 g of 6% MZ; reaction time=4 h.

cells per square inch (cpsi), which in turn allows the calculation of the geometric surface area; the sum of the areas of all the channel walls upon which the catalyst is deposited. This leads to one of the most important advantages of the monolith in that it has a large open frontal area. The lower catalyst loading in case of monolithic catalyst is compensated by the higher efficiency due to the good mass-transfer characteristics.<sup>10</sup> This may be attributed to the availability of more number of active sites on the surface of the monolithic catalyst due to homogenous dispersion of the catalyst which is not possible when the catalyst is used in powder form. Further, when reusability of 6% MZ in these two forms was checked, it was observed that the rate of decrease in the catalytic activity in powder form of the catalyst was more compared to the monolithic form (Fig. 8).

## CONCLUSIONS

The catalytic materials coated on cordierite honeycomb monoliths are very efficient catalysts for organic synthesis. These monolithic catalysts are easy to prepare, easy to use, easily recoverable, easily regenerable, re-usable and therefore monolithic catalysts are more advantageous than their powder form. In addition they are eco-friendly. SEM images support the effectiveness of the method used for coating the catalytic material on the honeycomb monolith. The experimental results reveal that the yield (%) of salol over  $\text{ZrO}_2$  was significantly influenced by the incorporation of Mo(VI) ions. Yield of salol up to 91% was

achieved over Mo(VI)/ $\text{ZrO}_2$  coated on honeycomb monolith under optimized reaction conditions. Poisoning studies on Mo(VI)/ $\text{ZrO}_2$  monolithic material indicates that a triangular correlation between total surface acidity, PXRD phases and the catalytic activity.

**Acknowledgments.** Authors are thankful to DST, New Delhi for providing financial assistance for a major research project. Authors are also thankful to the Material Research Group, St Joseph's College Research Centre, Bangalore for powder XRD analysis and authorities of Indian Institute of Chemical Technology, Hyderabad for providing the BET surface area, SEM and  $\text{NH}_3$ -TPD analysis.

## REFERENCES

- Otera, J. *Chem. Rev.* **1993**, 93, 1449.
- Corma, A.; Iborra, S.; Miquel, S.; Primo, J. *J. Catal.* **1998**, 173, 315.
- Reddy, B. M.; Patil, M. K. *Chem. Rev.* **2009**, 109(6), 2185.
- Song, X.; Sayari, A. *Catal. Rev. Sci. Eng.* **1996**, 38, 329.
- Yadav, G. D.; Nair, J. J. *Microporous Mesoporous Mater.* **1999**, 33, 1.
- Hino, M.; Arata, K. *Chem. Commun.* **1980** 851.
- Reddy, B. M.; Reddy, V. R. *Synth. Commun.* **1999**, 29(16), 2789.
- Reddy, B. M.; Reddy, V. R.; Manohar, B. *Synth. Commun.* **1999**, 29, 1235.
- (a) Reddy, B. M.; Sreekanth, P. M. *Synth. Commun.* **2002**, 32, 2815 (b) Reddy, B. M.; Patil, M. K.; Reddy, B. T. *Catal. Lett.* **2008**, 125(1-2), 97.
- Nijhuis, T. A.; Kreutzer, M. T.; Romijn, A. C. J.; Kapteijn, F.; Moulijn, J. A. *Chem. Eng. Sci.* **2001**, 56, 823.
- Heck, R. M.; Gulati, S.; Rarranto, R. J. *Chem. Eng. J.* **2001**, 82, 149.
- Vane, J. R.; Botting, R. M., Eds.; *Aspirin and Other Salicylates*, 1st ed.; Chapman & Hall: London, 1992.
- Patil, K. C.; Hegde, M. S.; Tanu, R.; Aruna, H. T. *Chemistry of Nano Crystalline Oxide Materials, Combustion Synthesis, Properties and Applications*; World Scientific Publishing Pvt. Ltd: Singapore, 2008.
- Benesi, H. A. *J. Phys. Chem.* **1957**, 6, 970.
- Kumbhar, P. S.; Yadav, V. M.; Yadav, G. D. in: Leyden, D. E.; Collins, W. T., Eds.; *Chemically Modified Oxide Surfaces*; Gordon & Breach: 1989; p 81.
- Reddy, B. M.; Reddy, V. R. *Synth. Commun.* **1999**, 29(16), 2789.
- Chary, K. V. R.; Reddy, K. R.; Kishan, G.; Niemantsverdriet, J. W.; Mestl, G. *J. Catal.* **2004**, 226, 283.
- Aline Aroux *Molecular Sieves-Acidity and Basicity*; Springer-Verlag: Berlin, Heidelberg, 2008; p 69.