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O-acetylation of salicylic acid with acetic anhydride over honeycomb coated with zirconia and its modified forms

M. Shyamsundar[1], S.Z. Mohamed Shamshuddin[2*], S.R. Pratap[3], Venkatesh[4], T.E Mohan Kumar[5],

Research scholar M.Sc. Chemistry .Research Laboratory, HMS Institute of Technology, Tumkur, Karnataka, India[1]
Professor of Chemistry, Chemistry .Research Laboratory, HMS Institute of Technology, Tumkur, Karnataka, India[2]
Research scholar M.Sc. Chemistry .Research Laboratory, HMS Institute of Technology, Tumkur, Karnataka, India[3]
Research scholar M.Sc. Chemistry .Research Laboratory, HMS Institute of Technology, Tumkur, Karnataka, India[4]
Research scholar M.Sc. Chemistry .Research Laboratory, HMS Institute of Technology, Tumkur, Karnataka, India[5]

Abstract: Zirconia and its modified forms such as Mo(VI)/ZrO_2 and Pt-SO_4^{2-}/ZrO_2 were coated on honeycomb monoliths. These materials were characterized for their, total surface acidity by NH_3-TPD, crystallinity by PXRD and morphology by SEM techniques. They were then evaluated for their catalytic activity in o-acetylation of salicylic acid with acetic anhydride to synthesize acetyl salicylic acid. Honeycomb coated with zirconia and their modified forms were found to be eco-friendly, economical & efficient catalysts for o-acetylation. These catalysts were found to be reusable.

Keywords: Honeycomb; ZrO_2; Mo(VI)/ZrO_2; Pt-SO_4^{2-}/ZrO_2; acetyl salicylic acid; o-acetylation.

1. INTRODUCTION

Zirconia and its modified forms as solid acid catalysts are attracting much attention in recent years. For instance, sulfated zirconia proved to be a highly active solid acid catalyst for various organic transformations even at low temperature [1]. But, due to a major disadvantage associated with sulfated zirconia i.e., rapid deactivation at high temperatures, many efforts have been made to synthesize zirconia based solid acids modified with cations. Zirconia based solid acids such as VO_x/ZrO_2, MoO_x/ZrO_2, WOx/ZrO_2, Pt-SO_4^{2-}/ZrO_2, etc have been synthesized and used as solid acid catalysts in a few liquid & vapor phase reactions [2,3].

Further, the physico-chemical, structural and catalytic properties of metal oxides such as zirconia, ceria, etc., can be modified by using proper catalyst carriers, adopting various synthesis and post synthesis routes, etc. Cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb monoliths play a vital role as catalyst carriers in heterogeneous catalysis for fine chemical synthesis [4]. It is also reported that [5] the catalyst coated on HC are economical, since small amount of the active catalyst dispersed on HCs would be more effective than using the same catalyst in its powder form. Effective and easy separation of the HC catalyst from the reaction mixture makes the use of HC as catalyst carrier more economical and environmental friendly.

Acetyl salicylic acid which is also known as aspirin is used for the treatment of a number of conditions including: fever, pain, rheumatic fever, inflammatory diseases and strokes. Commercially, salicylic acid synthesized by Kolbe-Schmidt reaction is acetylated with acetic anhydride in presence of non-ecofriendly, corrosive, liquid acid catalysts such as H_2SO_4, H_3PO_4, etc [6,7].

The present work deals with the synthesis of acetyl salicylic acid by *o*-acetylation of salicylic acid with acetic anhydride over honeycomb coated with solid acids like ZrO_2 and its modified forms such as Mo(VI)/ZrO_2 & Pt-SO_4^{2-}/ZrO_2. Since, these ZrO_2 based solid acid catalysts have shown good catalytic activity in some of the acid catalyzed reactions, with an expectation that honeycomb coated forms of these catalysts would be more eco-friendly, economical & effective *(triple e-concept)* in *o*-acetylation, the present study was taken up. Reactivation and reusability of these honeycomb catalysts was also taken up.

II. EXPERIMENTAL

A. Preparation of honeycomb (HC) catalysts

For coating ZrO_2 (Z) on a honeycomb monolith, dilute solution of zirconyl nitrate with 50 mL of deionised water, was prepared. The resulting solution was coated on a wash coated HC by dipping and drying in a furnace pre-heated at 400 ^oC. The dipping and drying steps were repeated 12 to 15 times till ~0.2 g of ZrO_2 is coated on the honeycomb [5].

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Similarly, Mo(VI)/ZrO_2 (MZ) containing 6%Mo(VI) was coated on a HC by taking a dilute solution containing known amounts of zirconyl nitrate and ammonium molybdate.

Pt-SO_4^{2-}/ZrO_2 (Pt-SZ) was prepared in its powder form by impregnation method. This powder form of Pt-SZ was made into a slurry which was then coated on a wash coated HC by slurry coating method.

HCs coated with Z or MZ or Pt-SZ was calcined at 550 ^oC for 5 h in a muffle furnace before their use as catalysts.

B.Characterization of HC catalysts

The total surface acidity was measured by NH_3-TPD method, powder X-ray diffraction (PXRD) patterns were recorded by X-ray powder diffractometer (Philips X'pert) using CuKα radiation (λ = 1.5418 A^o) using graphite crystal monochromator and SEM pictures were obtained from JEOL JED-2300.

C.Catalytic activity studies of HC catalysts in *o*-acetylation of salicylic acid

O-acetylation was carried out by taking known amounts of salicylic acid, acetic anhydride and HC catalyst in a cylindrical shaped flask equipped with water cooled condenser. The reaction mixture was heated for 1 h at refluxing temperature with constant stirring. After 1 h, the hot reaction mixture was filtered to separate the HC catalyst. The reaction mixture was then cooled to obtain a white solid of acetyl salicylic acid. Thus obtained crude acetyl salicylic acid was filtered, washed with water, dried and characterized by melting point experiment and LC-MS (Varian).

To study the re-usability of used HC catalysts, after removing it from the reaction mixture, washed with acetone, dried at 120 ^oC for 5 h and calcined at 550 ^oC for 1 h. Thus reactivated HC catalyst was subjected to acetylation reaction under same reaction condition. The reactivation and reusability of the used HC catalyst was repeated for 5 times by following the procedure described above.

III. RESULTS AND DISCUSSION

A. Characterization of HC catalysts

HCs coated with Z, MZ and Pt-SZ was characterized for their physico-chemical properties such as total surface acidity (TSA), crystallinity and morphology.

Table 1: Surface properties of HC catalysts used in the present study

HC catalyst	Amount of active catalyst loaded	TSA (mmols/g)
Z	0.193	0.32
MZ	0.201	1.34
Pt-SZ	0.208	1.49

TSA values of HC catalysts followed the order:

ZrO_2 < MZ < Pt-SZ

The surface acidity of pure zirconia was found to be least acidic when compared to either MZ or Pt-SZ (Table 1). Incorporation of Mo(VI) or Pt/SO_4^{2-} ions on ZrO_2 increased the TSA drastically, which can be attributed to the formation of electron deficient states formed upon modification.

PXRD patterns of HC catalysts are shown in Figure 1. HC coated with ZrO_2 consisted of both monoclinic (*M*) and tetragonal (*T*) reflections. However, incorporation of Mo(VI) or Pt/SO_4^{2-} ions in ZrO_2 resulted in transition of monoclinic phase of ZrO_2 to tetragonal phase of ZrO_2. Both MZ and Pt/SZ consisted of only tetragonal phase of ZrO_2 with either very low or nil monoclinic phase.

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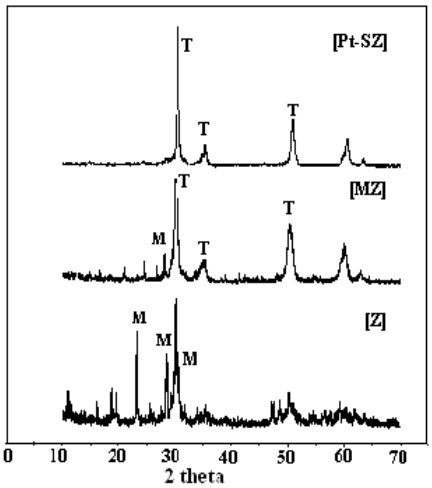


Fig 1. PXRD patterns of ZrO_2, MZ and Pt-SZ *[M- monoclinic ZrO_2, T- tetragonal ZrO_2]*.

SEM images of HC catalysts are shown in Figure 2, showing flake like appearances indicating the strong adherence of the active catalyst on the surface of the HC. This also indicates the suitability of the preparation route used for coating the active catalyst on the surface of the HC. Further, lusty tinge in the SEM images of MZ or Pt-SZ shows the dispersion of Mo or Pt ions in ZrO_2.

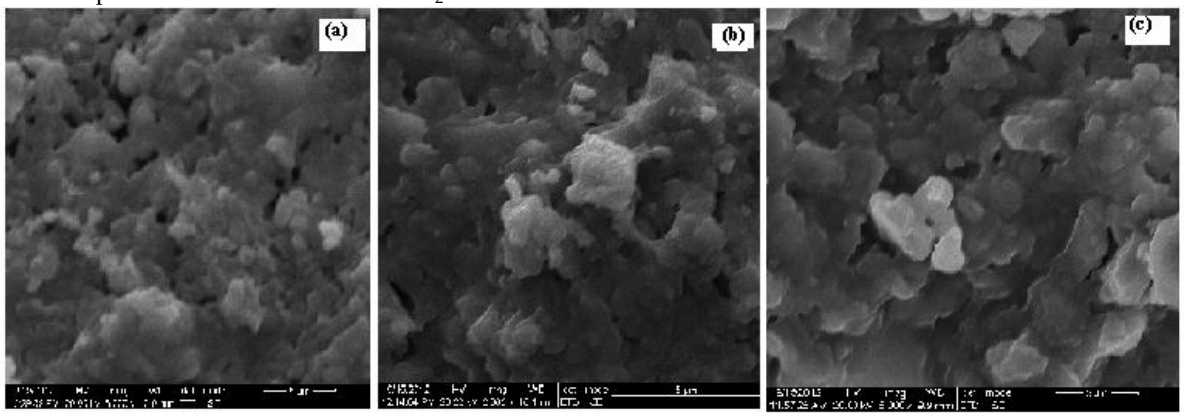
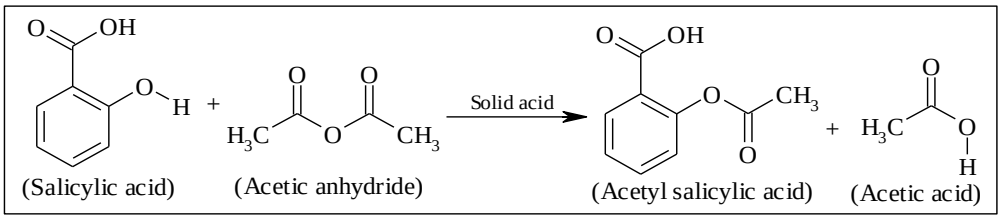


Figure 2. SEM pictures of (a) HC coated with ZrO_2; (b) HC coated with MZ and (c) HC coated with Pt-SZ.

B.Catalytic activity studies of HC catalysts in *o*-acetylation of salicylic acid

O-acetylation of salicylic acid (SA) with acetic anhydride (AA) over HC catalysts was carried out in liquid phase (Scheme 1).

Scheme 1. *O*-acetylation of salicylic acid with acetic anhydride over a solid acid.



Reactions were carried out at refluxing temperature (~80 ^oC) at a molar ratio of SA: AA = 1:3 for 1 h. Since AC_2O acts both as a reactant and a solvent in *o*-acetylation reaction, it plays a positive role as a solvent where SA and catalyst will be well dispersed in AA medium driving the reaction to go to completion.

In general all the HC catalysts used in the present study were active in *o*-acetylation reaction. But the order of catalytic activity was similar to that of the surface acidity i.e.,

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ZrO_2 < MZ < Pt-SZ

ZrO_2 being amphoteric showed least yield of acetyl salicylic acid when compared to either MZ or Pt-SZ (Table 2; Column2). Among MZ & Pt/SZ, Pt/SZ showed highest acidity when compared to MZ which indicates strong interaction of Pt on ZrO_2.

Table 2: Yield of acetyl salicylic acid over HC catalysts for 6 cycles.

HC catalyst	Yield (%) of acetyl salicylic acid					
	Fresh	I cycle	II cycle	III cycle	IV cycle	V cycle
ZrO_2	42	42	41	40	38	38
MZ	91	91	90	90	90	89
Pt-SZ	98	96	97	95	94	94

Further, a good co-relation between TSA, PXRD phases and catalyst activity of HC catalysts was observed. HC coated with pure ZrO_2 which is least acidic with both monoclinic and tetragonal phases was found to be least active in acetylation when compared to MZ or Pt-SZ HC-catalysts. Since, Pt-SZ was highly active among other HC catalysts used in the present study, also consisted of only tetragonal phase which is more catalytically active compared to monoclinic phase showed highest activity in *o*-acetylation.

The used and reactivated HC catalysts were used in *o*-acetylation for 5 more reaction cycles and the results are given in Table-2 (column 3-7). It is clear that the HC catalysts used in the present study can be effectively reactivated and reused at least for 6 reaction cycles with good catalytic activity.

IV. CONCLUSION

O-acetylation of salicylic acid with acetic anhydride over honeycomb monolith coated with zirconia & its modified forms such as Mo(VI)/ZrO_2 or Pt-SO_4^{2-}/ZrO_2 was found to be efficient and ecofriendly process. Use of honeycomb as a catalyst carrier makes the process economical with easy separation, reactivation and reusability.

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BIOGRAPHY

M.Shyamsundar is a research scholar working in the department of chemistry, HMS Institute of Technology,Tumkur,Karnataka,India.He has completed his Master of Science in Chemistry in 2008.He has been working in the field of catalytic chemistry.

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Dr. S.Z. Mohamed Shamshuddin is working as a Professor and Head in the department of Chemistry, HMS Institute of Technology, Tumkur, Karnataka, India. He has completed his Master of Science in Chemistry in 1997 from Bangalore University, PhD from Bangalore University in 2006 and PDF from Indian Institute of Science in 2009. He has been working in the field of Catalytic Chemistry since 13 years.

S.R Prathap is a research scholar working in the department of chemistry HMS institute of Technology, Tumkur, Karnataka, India .He has completed his Master of Science in Biochemistry in 2008.He has been working in the field of catalytic chemistry.

Venkatesh is a research scholar working in the department of chemistry, HMS Institute of Technology,Tumkur,Karnataka,India.He has completed his Master of Science in Chemistry in 1997.He has been working in the field of catalytic chemistry.

Mohan Kumar T.E is a research scholar working in the department of chemistry HMS Institute of Technology kyathsandra, Tumkur, Karnataka, India .He has completed his Master of Science in Biochemistry in 2008.He has been working in the field of catalytic chemistry.