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Vapor Phase Transesterification of Dimethyl Malonate with Phenol over Cordierite Honeycomb Coated with Zirconia and Its Modified Forms

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***Abstract*—**The transesterification of dimethyl malonate (DMM) with phenol has been studied in vapour phase over cordierite honeycomb coated with solid acid catalysts such as ZrO_2, Mo(VI)/ZrO_2 and $SO4^{2-}$/ZrO_2. The catalytic materials were prepared honeycomb coated, powder forms, and characterized for their total surface acidity by NH_3-TPD and crystalinity by powder XRD methods. Phenyl methyl malonate (PMM) and diphenyl malonate (DPM) were obtained as the reaction products. A good conversion of DMM (up to 82%) of MPM with 95% selectivity was observed when the reactions were carried out at a catalyst bed temperature of 200 °C and flow-rate of 10 mL/h in presence of Mo(VI)/ZrO_2 as catalyst. However, over SO_4^{2-}/ZrO_2 catalyst, the yield of DPM was found to be higher. The results have been interpreted based on the variation of acidic properties and powder XRD phases of zirconia on incorporation of Mo(VI) or $SO4^{2-}$ ions. Transesterification reactions were also carried out over powder forms of the catalytic materials and the yield of the desired phenyl ester products were compared with that of the HC coated catalytic materials. The solid acids were found to be reusable when used for at least 5 reaction cycles.

***Keywords*—**Cordierite honeycomb, methyl phenyl malonate, vapour phase transesterification, zirconia.

I. Introduction

THE cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb monoliths play a vital role as catalyst carriers in heterogeneous catalysis [1]. Catalyst coated honeycomb monoliths are widely used in automotive catalytic convertors (TWCs), combustion of VOCs, selective reduction of NO_x, etc., which involve mainly gas phase reactions [2]. The catalyst coated honeycomb monoliths have advantages over powder catalysts, such as formation of a 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. Though cordierite honeycomb monoliths have been used mostly for automotive applications, their use in liquid phase/vapor phase organic synthesis is less explored.

Solid acids are safe alternatives for conventional liquid acid catalysts used in synthetic organic chemistry in petroleum refineries, synthesis of fine chemicals, pharmaceuticals, etc. [3]. Due to the environmental hazards and technical difficulties associated with the use of liquid acids, extensive research is in progress to phase out these catalysts from chemical industry. Solid acids like zeolites, cation exchange resins, metal oxides, and their modified forms have been used successfully as catalysts for several acid-catalyzed reactions [4].

Among various solid acid catalytic materials, zirconia and its modified forms are an interesting group of solid acidic catalytic material that have been employed in many industrially important acid/base or redox reactions such as isomerization, esterification, alkylation, condensation, etc. [5].

Transesterification is an industrially important acid-catalyzed reaction with wide range of applications [6]-[8]. It is worthwhile to explore the possibility of finding a suitable environmentally benign solid catalyst for this reaction considering the fact that the existing procedures require expensive or corrosive liquid acids and solvents which cannot be reused due to tedious methods of isolation. Malonate esters, especially phenyl malonates and their derivatives are an important group of esters used in perfumery, flavoring as well as either starting materials or intermediates in organic fine chemical synthesis [9].

Generally, phenyl malonates are synthesized by esterification of malonic acid with phenol in presence of an acid catalyst. As the solubility of an organic acid in phenol is very low, this method requires the use of the latter in higher molar ratios. Hence, the method of transesterification of dimethyl malonate or diethyl malonate with phenol is employed wherein the reactants, being mutually soluble in one another, can be mixed in different molar ratios. Also, the solid acid catalysts that have been chosen for this work are known to possess moisture-sensitive active centers, which get poisoned by water molecules produced during the direct esterification reaction [10] between phenol and the malonic acid. Thus, the anhydrous condition prevalent in transesterification of methyl malonate with phenol is an added advantage. Transesterification is an equilibrium-driven reaction. Hence, vapor-phase conditions of the experiment are better suited than liquid phase reaction conditions. Another advantage of a vapor-phase reaction is, the products of the reaction will not be in contact with the catalyst during the entire reaction period, thereby preventing backward reaction.

In the present article, an effort has been made to explore the use of cordierite honeycomb coated with zirconia based solid acids such as (pure zirconia, Mo(VI)/ZrO_2, SO_4^{2-}/ZO_2) in the vapor phase transesterification of dimethyl malonate with phenol to synthesize industrially important phenyl ester

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derivatives under a set of reaction conditions. Moreover, the advantage of vapor phase transesterification as well as the advantage of honeycomb monoliths as carriers for solid acids was investigated. Reactivation and reusability studies of these solid acids were also taken up.

II. Experimental

A. Materials

Cordierite honeycomb monoliths (height = 1.20 cm, diameter = 2.50 cm and hole size = 0.2 cm) were used for the present work and they were supplied by Shreya Ceramics, Baroda, India. Zirconyl nitrate, ammonium molybdate and sulphuric acid were supplied by M/S LOBA Chemie India Ltd., India.

B. Synthesis of Catalytic Materials

Solid acids such as ZrO_2, Mo/ZrO_2 (%Mo = 10) and SO_4^{2-}/ZrO_2 were coated on different monoliths by impregnation method. The honeycomb was wash coated with zirconia before coating the active catalysts. Wash coating is done to increase the surface area and to have a support material which has a better interaction with the active catalyst [11]. For wash coating, a dilute solution of zirconyl nitrate in presence of a binder (cellulose) was prepared which was then coated on a bare honeycomb monolith by dipping and drying in a furnace maintained at 400°C.

Typically, for coating $10\%Mo/ZrO_2$ on a honeycomb (HC), dilute solution containing 0.96 g of zirconyl nitrate $[ZrO(NO_3)_3.\ 8H_2O]$ and 0.50 g of ammonium molybdate $[(NH4)_6Mo_7O_{24}.\ 4H_2O]$ 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 for 12 to 15 times until ~0.2 g of the solid acid catalyst is coated on the monolith. Similarly, $SO_4^{2-}/ZrO_2$was coated on a wash coated honeycomb by taking a mixture consisting of 2 g of zirconium hydroxide and 1.2 ml of 3 *M* sulphuric acid. The honeycomb coated with $10\%Mo/ZrO_2$ or SO_4^{2-}/ZrO_2were calcined at 550°C for 5 h in a muffle furnace before their use as a catalyst. Thus, prepared catalytic materials such as ZrO_2, $10\%Mo/ZrO_2$ and SO_4^{2-}/ZrO_2 coated on HCs were abbreviated as Z, MZ and SZ respectively.

The catalytic materials (Z, MZ, SZ) were also prepared in their powder forms by impregnation method.

C. Characterization of Catalytic Materials

The catalytic materials were characterized by NH_3-TPD, powder XRD, FTIR and SEM techniques for their surface acidity, crystalline, functionality and morphology respectively.

The total surface acidity was measured by NH_3-TPD method by using Puls Chemisorbs 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 for30 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^{-1} in helium to 973 K. The change in concentration of the desorbed NH_3 was monitored using an online thermal conductivity detector. The X-ray powder diffraction (PXRD) patterns of the catalytic material were collected on anX-pert Pro Philips diffractometer equipped with Ni filtered-Ka radiation l = 1.5418 A˚ using a graphite crystal monochromator. FTIR spectra of the catalytic materials were obtained by KBr pellet technique over Nicolet spectrometer. The Scanning Electron Micrographs (SEM) was obtained using a JEOL JED-2300 analysis station microscope.

D. Catalytic Activity Catalytic Materials

Transesterification of dimethyl malonate with phenol was carried out in vapor phase and is schematically represented in Fig. 1. Typically, HC coated with a solid acid (Z or MZ or SZ) was placed on the specially designed fixed bed downstream vapor phase glass reactor maintained at 200°C. The reaction mixture consisting of dimethyl malonate and phenol 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.

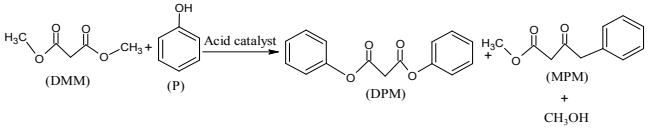


Fig. 1 Transesterification of dimethyl malonate with phenol over an acid catalyst

The reaction products obtained by the transesterification reaction were analyzed quantitatively by gas chromatograph (Mayura) fitted with a column (10% SE-30 chromosorb w-AW, 3 m x 1/800) coupled with a FID detector and qualitatively by GC–MS (Varian). Similarly, transesterification reactions were carried out over powder form of the catalysts (0.2 g of Z, MZ, SZ) and the yield of the desired phenyl esters were compared with that of the HC catalytic materials.

III. Results and Discussion

A. Characterization of Catalytic Materials

The total surface acidity (TSA) as well as acid site distribution of zirconia and its modified forms measured by NH_3-TPD method are given in Table I.

TABLE I
Surface Acidity of Catalytic Materials Used for the Present Work

Catalyst	Acid Site Distribution (mmol/g)				
	Weak	Medium	Strong	Very strong	TSA
ZrO_2	0.03	0.40	-	-	0.43
MZ	-	0.16	0.86	-	1.02
SZ	-	-	0.87	0.44	1.31

The TSA of the catalysts are in the order: $ZrO_2 < MZ < SZ$. Pure zirconia was found to be least acidic and SZ was highly acidic. This order also indicates that the impregnated MoO_x and SO_4^{2-} ions have a strong influence on the acidic properties of zirconia. When the values of acid site distribution of

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different zirconia catalysts were compared, pure zirconia consisted of only 'weak & medium' acid sites. Whereas, modified form of zirconia i.e., MZ consisted of 'medium and strong' acid sites. However, SZ was found to have 'strong and very strong' acid sites (super acid sites).

The PXRD patterns of zirconia and its modified forms are shown in Fig. 2. As seen from the Fig. 2, pure zirconia has a mixture of monoclinic and tetragonal phases. However, upon modification with Mo(VI) or SO_4^{2-} ions, zirconia samples exhibited prominent lines due to tetragonal phase indicating the strong influence of impregnated ions on the phase modification of zirconia from monoclinic phase to the metastable tetragonal phase. It is reported that the tetragonal phase of zirconia is more catalytically active than its monoclinic form [5].

In modified form of zirconia increase in the concentration of tetragonal phase can be attributed to the strong interaction of Mo(VI) or SO_4^{2-} ions with zirconia which inhibits the monoclinic phase of zirconia. No diffraction peaks corresponding to MoO_x and SO_4^{2-} are observed in the PXRD patterns of MZ or SZ samples. This indicates that in modified form of zirconia, MoO_x and SO_4^{2-} ions are satisfactorily incorporated with ZrO_2 ions. Further, it is interesting to note that triangular co-relationship exists between TSA, catalytic activity and crystalinity of the catalysts, i.e., the catalytic material which consisted of more tetragonal phase was found to be more acidic and further such materials are found to be more catalytically active. This observation indicates that the tetragonal phase of zirconia is responsible for higher surface acidity of zirconia catalysts [5].

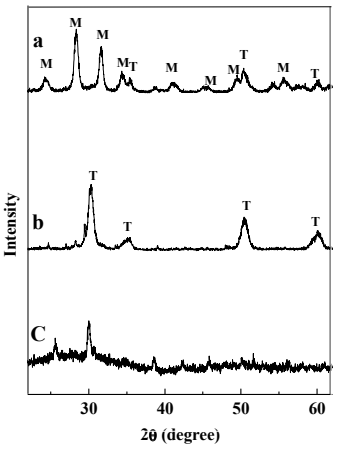


Fig. 2 Powder XRD patterns (a) ZrO_2 (b) MZ (c) SZ. [where, M indicates monoclinic and T indicates tetragonal phase]

The FT-IR spectra of zirconia and its modified forms are represented in Fig. 3. In all the spectra, the bands at 1391 cm^{-1} 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 catalysts.

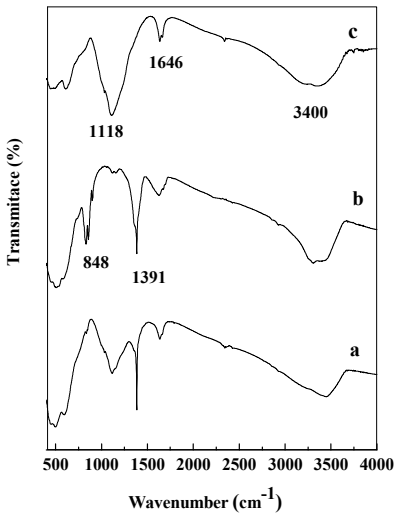


Fig. 3 The FT-IR spectrum (a) ZrO_2 (b) MZ (c) SZ

In case of MZ samples the peak at ~848 cm^{-1} is due to Mo-O-Mo stretching mode of vibration for MoO_3. This indicates that MoO_3 is strongly dispersed on the surface of ZrO_2 wherein peak at ~ 1118 cm^{-1} gets disappeared.

SEM images of honeycomb catalysts are shown in Fig. 4. The SEM image of the monolith coated with Z or MZ or SZ shows flake like structures which appear more strongly sticking to the surface of the monolith. 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.

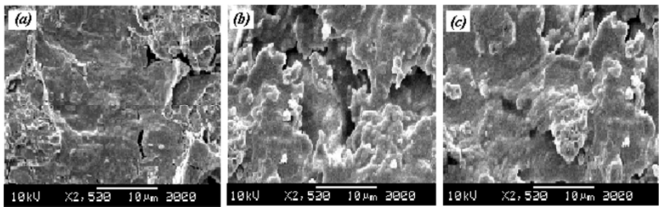


Fig. 4 SEM images of (a) ZrO_2 (b) MZ (c) SZ

B. Catalytic Activity of Catalytic Materials

In general, it was found that all the catalytic materials (Z, MZ, SZ) used for the study exhibited good catalytic activity in transesterification of dimethyl malonate (DMM) with phenol (P). The conversion of DMM, selectivity of methyl phenyl malonate (PEM) and selectivity of diphenyl malonate (DPM) over different solid acid catalytic materials is given in Table II.

A correlation between the total surface acidity (TSA) and the catalytic activity of the catalytic materials was observed. Zirconia being least acidic showed lowest activity in the reaction followed by MZ and SZ catalytic materials. The increased activity of modified zirconias (MZ and SZ) could be attributed not only to the higher TSA but also can be due to the presence of more catalytically active tetragonal phase of zirconia. However, the selectivity of the reaction products i.e., either methyl phenyl malonate or dipheny malonate was found to depend on the acid site distribution. Since Z and MZ

consisted of 'weak' or 'moderate' acid sites, the major product formed was methyl phenyl malonate. However, over SZ catalyst diphenyl malonate was found to be the major product. This indicates that the formation of methyl phenyl malonate (MPM) require 'weak' or 'moderate' acid sites but the formation of diphenyl malonate (DPM) was influenced by 'strong' acid sites. Further, since SZ consisted of 'very strong' acid sites (super acid sites), a small amount of diphenyl ether (DPE) was also formed as the addition product. It is reported that the dehydration of phenol to produce DPE require 'very strong' acid sites [12].

When the catalytic activity of catalytic materials in their HC coated forms was compared with that of their powder forms, ~1.7 fold increase in the conversion (%) of DMM was observed over HC form of the catalytic materials. This increase in the activity of HC coated catalytic materials can be attributed to the availability of more number of active sites on the surface of HC catalysts due to homogenous dispersion of solid acids on HCs which is not possible when used in their powder forms [13]. However, not much change in the selectivities of the products was observed over a catalyst irrespective of their forms.

TABLE II
CATALYTIC ACTIVITY OF SOLID ACID CATALYTIC MATERIALS *(HONEY COMB COATED OR POWDER FORMS)* USED FOR THE PRESENT WORK

Catalytic material	Conversion of DMM (%)	Selectivity of MPM (%)	Selectivity of DPM (%)	Selectivity of DPE (%)
Z (HC)	42	100	00	00
MZ (HC)	82	95	05	00
SZ (HC)	92	62	29	09
Z (powder)	28	100	00	00
MZ (powder)	59	94	06	00
SZ (powder)	65	60	32	08

Reaction Conditions: Molar Ratio of DMM:P = 1:2, Amount of Catalyst = 0.2 g, Flow-Rate of Reactants = 10 mL/g, Pre-heater Temperature = 250 °C, Catalyst Bed Temperature = 200 °C.

C. Reactivation and Reusability of Catalytic Materials

The used catalytic material (HC coated and powder forms of MZ) were recovered from the glass reactor, washed with acetone, dried at 120°C for 2 h, calcined at 550°C for 1 h and used again in the next transesterification reaction cycle to study the performance of the reactivated catalytic material. After reactivation of used HC catalyst, when weighed, no change in the weight of the catalyst between the fresh HC catalytic material and the reactivated ones was observed. However, in case of powder form of the catalytic materials, 100% recovery of the catalyst from the reaction vessel was not possible.

When the catalytic activity of the reactivated HC catalytic material was compared with that of its powder form, not much change in the catalytic activity of HC catalytic material was observed (Table III). However, over powder form of the catalysts a gradual decrease in the catalytic activity was observed which may be due to loss of catalyst during separation of the powder catalyst from the vapor phase glass reactor. Not much change in the selectivity of the products was observed in both the forms of the catalytic materials.

TABLE III
EFFECT OF REACTIVATION ON THE REUSABILITY OF MZ CATALYST IN TRANSESTERIFICATION OF DMM WITH P

Catalytic material	Conversion of DMM (%) (fresh, 1st, 2nd, 3rd, 4th cycles)	Selectivity of MPM (%) (fresh, 1st, 2nd, 3rd, 4th cycles)	Selectivity of DPM (%) (fresh, 1st, 2nd, 3rd, 4th cycles)
MZ (HC)	82, 82, 81, 81, 80	95, 95, 95, 95, 96	05, 05, 05, 05, 04
MZ (powder)	59, 57, 56, 54, 50	94, 94, 95, 95, 96	06, 06, 05, 05, 04

Reaction Conditions: Molar Ratio of DMM:P = 1:2, Amount of Catalyst = 0.2 g, Flow-Rate of Reactants = 10 mL/g, Pre-heater Temperature = 250 °C, Catalyst Bed Temperature = 200 °C.

IV. CONCLUSION

The honeycomb catalytic materials were found to be more efficient, reactivable and reusable materials when compared to their powder forms. Phenyl malonates can be effectively synthesized via vapour phase transesterification of dimethyl malonate with phenol over zirconia catalysts coated on honeycomb monoliths. HC coated with $Mo(VI)/ZrO_2$ was effective in the synthesis of methyl phenyl malonate and SO_4^{2-}/ZrO_4 produced both methyl phenyl malonate and diphenyl malonate as reaction products. A correlation between the total surface acidity, tetragonal PXRD phase of zirconia and conversion of dimethyl malonate was observed. However, selectivity of a particular product was co-relatable with the strength of the acid sites on the catalytic material.

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