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Mo (VI)/ZrO_2 coated on honeycomb monolith as solid acid green catalyst for the acetylation of substituted alcohols and amines under solvent free conditions

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Honeycomb (HC) monolith coated with solid acids such as Mo (VI)/ZrO_2 (MZ) with different Mo loadings (2, 6 and 10%) have been prepared by wet impregnation method and characterized by NH_3 –TPD, BET surface area, PXRD, ICP-OES, SEM, TEM and EDAX techniques. These catalysts have been used as for the synthesis of *O* and *N*-acetylation reactions by the condensation of various alcohols with acetic anhydride under solvent free conditions in shorter times (20 min) at moderate temperature (70°C). Especially, 6% Mo (VI)/ZrO_2 catalysts are found to be highly acidic and also resulted in high yields of *O* and *N* acetylated products up to ~99%. This methodology offers several advantages such as excellent yields, easy procedure, mild and environmentally benign conditions. MZ catalysts are found to be economical, efficient and highly active, recyclable and reusable up to 6 reaction cycles without much loss of their activity.

Keywords: Honeycomb, Zirconia, Mo (VI)/ZrO_2, Solid acid, Wet impregnation method, Acetic anhydride.

Functional group protection strategies are central part of the target molecule synthesis, protection of alcohols, phenols and amines are fundamental and useful transformations in organic synthesis both for research and industrial development. For the protection of alcohols or amines group into the corresponding acetate or acetamide is preferably used. Even though, there are several reagents such as acetic acid or acetic anhydride or acetyl chloride methods are easy to prepare acetates [1-3].

Acetylation of amines, alcohols acetamide or acetate is necessary due to its importance in therapeutic value, example: paracetamol confirms the presence of amino or hydroxyl group in a compound. Even though, addition, protection of hydroxyl functionality as acetate or amides is preferred due to its simplicity of introduction, stability under mild acidic conditions and ease of removal by mild alkaline hydrolysis. The acetylation of alcohols, phenols, thiols and amines is usually performed with acetic anhydride or acetyl chloride in the presence of strong bases such as pyridine, triethylamine, 4-pyrrolidinopyridine, 4-dimethyl amino pyridine (DMAP), 4-pyrrolidinopyridine and tri-butyl phosphine etc., it shows corrosive in nature [4-8].

Recently a series of heterogeneous catalysts such as $AlPO_4$[8], ZrO_2-AlO_2[9], Ni/SiO_2[10], Al $(OTf)_3$[11], Ti-Cl3 (OTf)[12], methylene diphosphonic acid[13], ultra-zirconia[14], modified mesoporous $AlPO_4$[15] silica-bonded N-propyl sulphamic acid and S-propyl sulphamic acid[16, 17] etc. have been reported. Although these catalysts have their own drawbacks such as low yields, tedious separation processes, complex work-up and purification procedures, expensive reagents, harsh conditions for catalyst preparation etc.

The best alternative method for sulfated or phosphate or borated zirconia could be the incorporation of cation such as molybdate (Mo), vanadium (V) tungstate (W) etc., which are suspicious to be green catalysts[18-20]. It has been reported that the modified forms of honeycomb coated as well as powder forms of zirconia (Mo/ZrO_2 or W/ZrO_2) have super acid sites. The MZ is very important promising modified zirconia solid acid catalyst. Recently a lot of research work is going on over this catalyst other than the sulfated zirconia catalysts. Generally it is used in vapor phase reactions. Especially, few researches have been studied by using this catalyst in the field of liquid phase reactions. Although the Mo/ZrO_2 also considered as solid super acids and free from deactivation disadvantages like sulfated or phosphated or borated zirconia they are least explore for organic synthesis and transformation reactions [21].

Currently, cordierite honeycomb (HC) monolith catalysts are playing an important role in the catalyst carrier. These are widely used in automotive applications, ozone abatement in aircrafts, and selective reduction of NO_x etc. However, more interestingly monoliths coated with solid acid catalysts have not been much explored so far in the field of organic synthesis. Honeycomb coated catalysts have more advantages than in their powder form of catalysts ease of separation and recovery of the catalysts from the reaction mixture and lesser amount of the catalysts loaded on the monolith is highly effective[22-26].

In continuation of our research work the honeycomb coated zirconia and its modified forms for the liquid phase reactions[27, 28]. The present article to prepare HC coated ZrO_2, Mo (VI)/ZrO_2 (2, 6, 10% molybdenum loadings to the zirconia) was prepared by the wet impregnation method and characterized by their total surface acidity by NH_3-TPD method, surface area by BET, crystallinity by powder X-ray diffraction (PXRD) technique, % of metal ions by ICP-OES method and morphology studies by SEM, EDAX and TEM techniques. The main goal of the present study to find out the honeycomb coated catalytic ability for the synthesis of liquid phase acetylated products. The prepared catalytic materials used for the various alcohols, amines with the acetic anhydride (acts as a solvent and reagent) at moderate temperature (70 °C) in a shorter reaction time (20 min) with excellent yields ~ 95 – 97%. The honeycomb coated catalysts are more reactivated and reusable catalysts for the ease of separation in the liquid phase reaction medium up to 6 reaction cycles.

Experimental Section

Honeycomb coated catalytic materials

In the present work the active catalyst such as ZrO_2, 2, 6 and 10% Mo (VI)/ZrO_2 was coated on the honeycomb which was already a wash coated with zirconia. Sometimes direct coating of an active catalyst on a non-wash coated bare honeycomb may lead to the loss of active catalyst during its application in an organic reaction due to poor adherence of the active catalyst[27].

Preparation of wash coated Zirconia [Z]

The wash coated zirconia were mixing zirconyl nitrate (3 g) and 40 mL of de-ionized water in a beaker stir for clear solution in a magnetic stirrer. The honeycomb was dip-dry method in a beaker for 6-8 times in a muffle furnace till 0.03 g of zirconia gets coated on the HC.

Preparation of impregnation slurry on cordierite honeycomb monoliths (2, 6 and 10% Mo (VI) loaded on ZrO_2) [MZ]

In this study Mo (VI)/ZrO_2 with Mo loadings (2, 6, 10 mol%) was prepared by wet impregnation method[48]. In general 10% of MZ was prepared with known amount of zirconyl nitrate (9 g) and ammonium molybdate (0.45 g) along with binder (cellulose) with required volume of de-ionized water. The resulting slurry solution was coated on a muffle furnace at 673 K by dipping and drying 8-10 times till ~ 0.03 g of Mo (VI)/ZrO_2.

Finally all the HCs were calcined in a muffle furnace at 873 K for 5 h.

The catalytic material such as ZrO_2, Mo/ZrO_2 prepared by slurry coating method and it was abbreviated as Z and 2MZ, 6MZ and 10MZ.

Characterization of the catalytic materials

The catalytic material such as ZrO2 and Mo (VI)/ZrO_2 were characterized by total surface acidity by temperature program desorption of ammonia (NH_3-TPD) experiments were performed on a pulse chemisorb instrument (Micromeritrics). Surface area by NOVA 1000 Quanta chrome high-speed gas sorption analyser instrument was used. Crystallinity by Powder XRD (PXRD) were recorded on X-ray diffractometer (Philips X’ pert) using Cu Kα (λ = 1.5418 Å). The percentage of Mo ion present on the zirconia was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) technique using Thermo-iCAP 6000 series instrument. Morphological studies by SEM analysis by using JEOL - JXA 8530 microscope. TEM images of the catalytic materials were performed for the sample by using PHILIPS CM200 electron microscope at an acceleration voltage of 20- 200 kV. ^1H and ^{13}C NMR were analyzed by Brucker instrument. GC-MS determined by Agilent instrument.

Catalytic activity studies

Z, 2, 6 and 10MZ were prepared by HC coated solid acid catalysts by slurry coating method. The condensation reaction between the hydroxyl or amines group containing organic compounds, acetic anhydride and HC coated catalysts were placed in a 25 mL of specially designed reactor heated in an oil bath up to 70°C for a stipulated reaction time[30]. The expected acetylated products in maximum yield with a shorter reaction time and ease of the separation of the HC coated catalysts. The reaction mass was cooled, filtered and washed with ethyl acetate to recover the HC coated catalyst. The solvent was evaporated in rota-vapor to get the crude product. Thus obtained crude product was purified in silica gel (60-120 mesh size) column chromatography using suitable mobile phase i.e. pet-ether-ethyl acetate (90:10) mixture. The obtained products were characterized by/ ^{1}HNMR, ^{13}C (Varian) and GCMS (Agilent).

Results and Discussion

Characterization of honeycomb coated solid acids

HC monolith coated solid acids were characterized for their physico-chemical properties such as P-XRD, BET surface area, NH_3 -TPD, SEM and TEM analysis, ICP–OES techniques respectively.

Total surface acidity (TSA)

Solid acids such as ZrO_2 and different % of Mo (VI) loadings on the ZrO_2 are coated on the honeycomb monolith were determined by NH_3-TPD (temperature program desorption) values are given in the Table 1. It is observed that all the samples show from 'weak' to 'strong' strength of acid sites. In case of HC coated zirconia shows 'weak' to 'medium' acidic sites. The mixture of ZrO_2 and Mo/ZrO_2 (2, 6 and 10% Mo) consists of 'moderate' to 'strong' acidic sites distributions were observed[26].

ZrO_2 and 6% Mo/ZrO_2 NH_3-TPD has shown in the Fig. 1. An increase in concentration of Mo (VI) ions (2, 6%) to the zirconia the TSA value will be increased although slightly decreased the TSA value of 10% Mo (VI)/ZrO_2 due to increase in the concentration of molybdenum content[29].

Percentage (%) of metal ions by ICP-OES

The percentage of metal ions obtained for the current study estimated by ICP-OES techniques. Mo/ZrO_2 containing 1.78, 5.76 and 9.85% Mo ions, is less than the amount of expected from the amount to use in starting material catalyst as support (Table 1). It shows that there is no much loss during calcinations of the HC coated catalysts at 873 K.

BET surface area

The BET surface area of the honeycomb coated solid acid used for this study is HC coated zirconia and different percentage of Mo ions incorporated to the ZrO_2. The results pertained that the zirconia show least surface area among the catalytic materials used for the present study shown in Table 1. Although, the concentration of Mo ions is increase to the zirconia, the specific surface area of the HC coated catalysts should also be increased due to variation in physical properties. The BET surface area of the HC coated catalytic materials for the present study: Z < 2% MZ < 10% MZ < 6% MZ. The specific surface area increase above 6% MZ beyond that the surface area will be to decrease. This can be due to crystalline effect of molybdenum oxide as reported by earlier literatures[30,31].

PXRD studies

PXRD patterns of HC catalysts are shown in Fig. 2. HC coated with ZrO2 consisted of both monoclinic (M) and tetragonal (T) reflection. A sharp diffraction lines at $2\theta = 28.3$, 24.46 and 31.58 degrees correspond to the

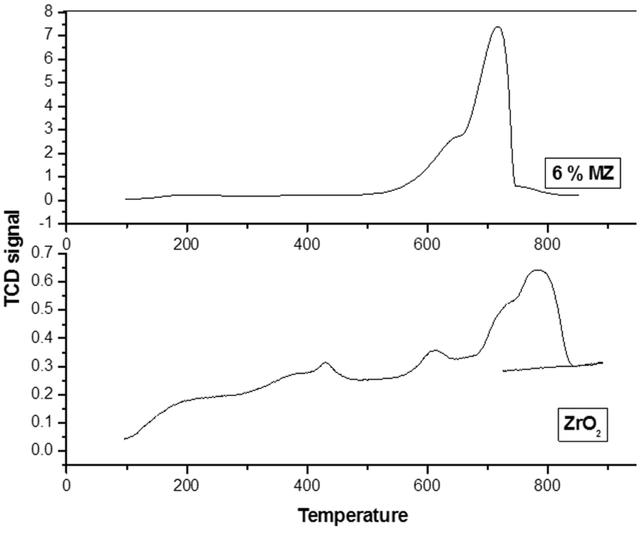


Fig. 1 — NH_3-TPD profiles of ZrO_2 and 6% Mo(VI)/ZrO_2

Table 1 — Physico - chemical properties of solid acids used for the present study.

Solid acid	Acid site distribution				BET surface area	Metal ions
	Weak	Medium	Strong	TSA		
ZrO_2	0.02	0.41	_	0.43	42	-
2% MZ	-	0.03	0.69	0.74	66	1.69
6% MZ	-	0.25	0.75	1.12	92	5.56
10% MZ	-	0.22	0.74	1.26	71	9.65

monoclinic form and the lines at 2θ = 30.27 and 49.21 degrees are due to tetragonal form of zirconia[51]. As cited in the earlier literature (44) incorporation of Mo ions in ZrO_2 resulted in transition of monoclinic to tetragonal phase of ZrO_2. It is interesting to note that when an increase the concentration of Mo cation promotes a stronger influence on the tetragonal phase. 6% and 10% MZ peaks corresponding to monoclinic phase have been totally eliminated and only meta-stable tetragonal phase has been obtained. Bare HC wash coated with zirconia catalyst show no diffraction lines detected. It shows that bare honeycomb was fully and effectively wash coated with the solid acid catalysts[26,29].

SEM and TEM morphologies of the HC coated catalysts

In the present study, Fig. 3 show the morphology of the surface dispersion of the active components over the honeycomb coated catalysts. Honeycomb coated synthesized zirconia spherical particles and it shows the presence of coarse grains and inter-granular porosity. The modified forms of 6% MZ incorporation of molybdenum shows flake like particles distributed on the surface of zirconia[32].

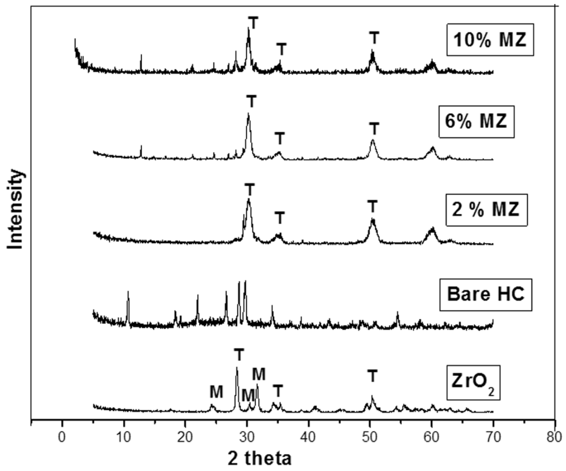


Fig. 2 — PXRD patterns of HC coated Z, Bare HC, 2 % MZ, 6% MZ and 10% MZ

TEM analysis clearly shows big crystalline particles of zirconia on the surface of honeycomb as shown in the Fig. 4. The percentage of molybdenum deposition is dispersed on the surface of the honeycomb shows the higher surface area of 6% Mo (VI) / ZrO_2 compared to ZrO_2.

EDAX analysis of catalysts

EDAX spectrum of the 6% MZ catalyst report shows the presence of molybdenum and zirconia metal ions as shown in the Fig. 5.

Effect of reaction temperature on the yield (%) of 2-acetyl-5-chlorophenyl acetate (2-ACPA) over HC coated with 6% MZ catalyst

The acetylation reaction between 2-hydroxy-5-chlorophenyl acetate and acetic anhydride was carried out over HC coated with MZ catalyst under solvent free conditions with the reaction temperature ranging from 30°C to 80°C. While the formation of 2-acetyl-5-chlorophenyl acetate product started at room temperature, the conversion (%) of the product was found to increase with reaction temperature. A maximum conversion of the acetic anhydride was observed when the temperature was increased from 60°C to 70°C, however, there was not much increase in the conversion when the temperature was increased from either 80°C to 90°C.

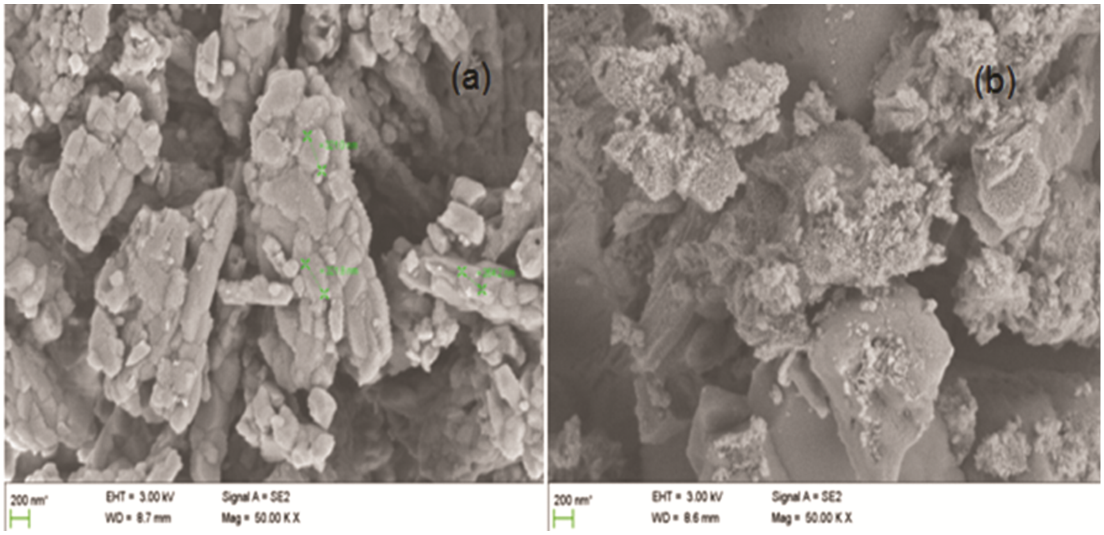


Fig. 3 — SEM images of honeycomb coated ZrO_2 and 6 % Mo (VI)/ ZrO_2

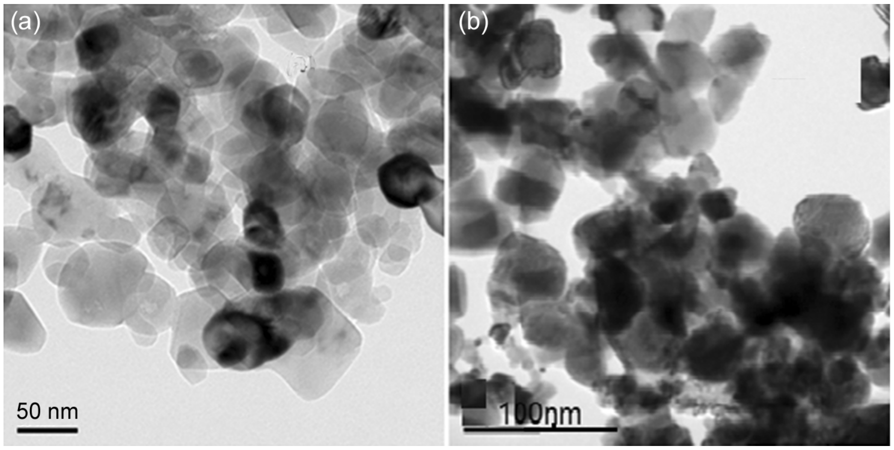


Fig. 4 — TEM images of honeycomb coated (a) ZrO_2 (b) 6% Mo (VI)/ZrO_2

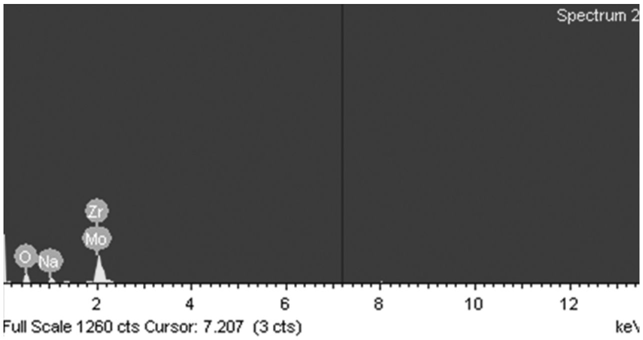


Fig. 5 — EDAX Spectrum of 6% Mo (VI)/ZrO_2

Effect of nature of catalyst (whether HC coated or powder form of catalysts)

Acetylation reactions were carried out over 2-acetyl-5-chlorophenol with acetic anhydride (1:2) over honey coated catalysts as well as powder form of catalysts. The results are given in the Table 2. It depends on the TSA value of pure ZrO_2 and Mo loading ZrO_2. 6% MZ shows the highest yield of the product when compared to other Z, 2 and 10% MZ. There is no formation of other products and color of the catalysts has not been changed after completion of the reaction mass. Among the catalysts, ZrO_2 shows ‘weak’ and ‘moderate’, MZ shows that ‘moderate’ and ‘strong’ acid site, it is suitable for the acetylation reaction over alcohols, amines and the acetic anhydride. This can be attributed that HC coated MZ (2, 6 and 10%) catalysts shows that good catalytic activity for the acetylation reaction. Therefore, 6% HC coated MZ was found to be good catalyst for the acetylation reaction[26,29].

Table 2 — Yield of 2-acetyl-5-chlorophenyl acetate (%) over different catalysts used in the present study.

Sl. No.	Catalytic material	% Yield of 2-acetyl-5-chlorophenyl acetate
1	Z (HC)	50 (20)
2	2% MZ (HC)	65 (36)
3	6% MZ (HC)	95 (48)
4	10% MZ (HC)	92 (46)

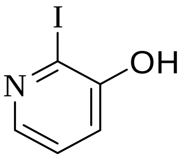
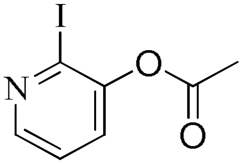
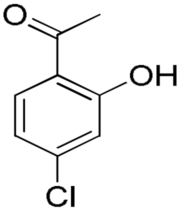
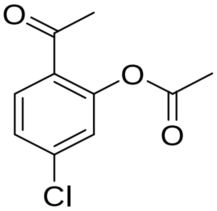
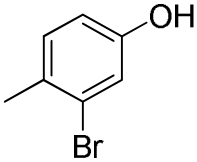
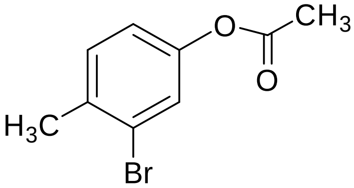
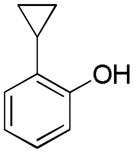
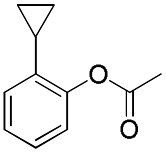
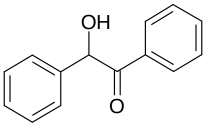
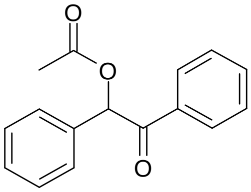
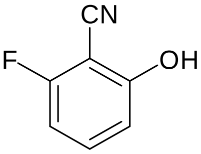
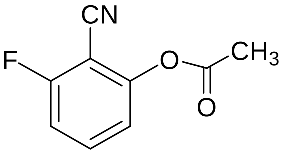
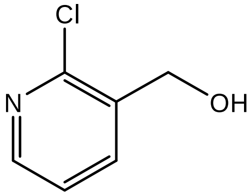
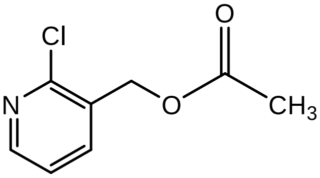
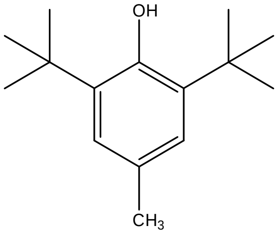
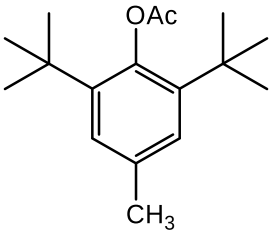
- ➢ Note: Numbers in the parenthesis correspond to the values obtained for powder form of the catalysts.
- ➢ [Reaction conditions: Reaction temperature = 70 °C, Mole ratio of the reactants= 1:2 and 0.03 g HC coated 6 % MZ catalysts and reaction time 20 min].

Honeycomb coated catalysts are more inexpensive and efficient catalysts than their powder forms. Although, same amount of catalysts (0.03 g) have been used in both honeycomb coated as well as powder form of catalysts for the acetylation reaction. The yield was observed in the Table 2 column 2, because more number of active channels on the monolithic catalyst and the homogeneous dispersion on the surface of the honeycomb. But it is not possible in the form of powder catalyst[23-25].

Synthesis of various acetylation compounds over 6% Mo (VI)/ZrO_2

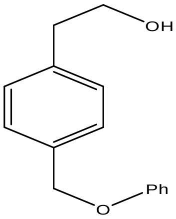
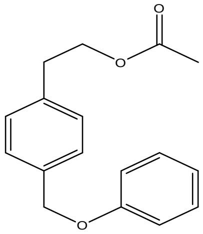
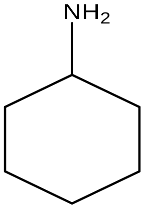
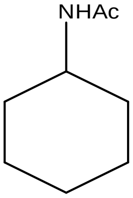
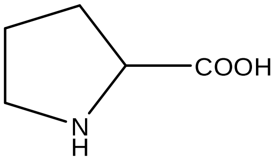
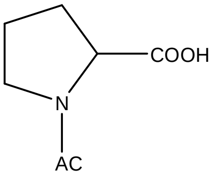
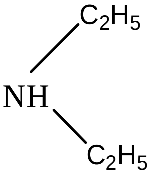
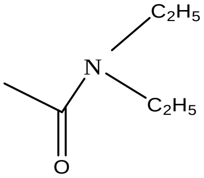
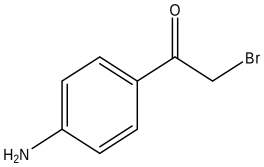
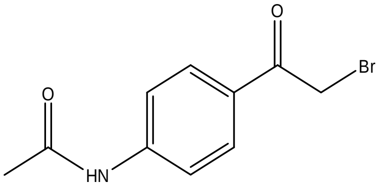
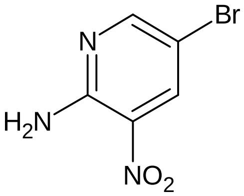
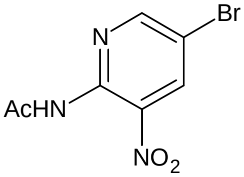
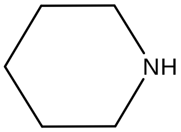
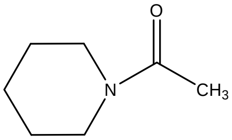
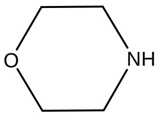
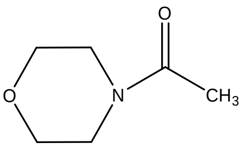
The acetylation reaction between alcohols and amines over acetic anhydride (1:2), 6% MZ catalysts, the reaction mixture was stirred at 70°C and the progress of the reaction was monitored by thin layer chromatography[9]. Once completion of the reaction the honeycomb coated catalysts easily recovered from the reaction mixture and wash with acetone[17]. Thus obtained crude product was purified in silica gel (60-120 mesh size) column chromatography using suitable mobile phase *i.e.* pet-ether-ethyl acetate (90:10) mixture. The reaction time and yield (%) of the products were recorded in the Table 3 and the spectral data of the obtained products were mentioned in the supplementary information (Table S1).

Table 3 — Acetylation of various liquid alcohols, amines over HC coated MZ catalysts.

Sl. No.	Reactant	Product	Time (min)	Yield
1			20	99%
2			20	96%
3			20	97%
4			20	99%
5			20	98%
6			20	99%
7			20	95%
8			20	96%

(*contd.*)

Table 3 — Acetylation of various liquid alcohols, amines over HC coated MZ catalysts. (*contd.*)

Sl. No.	Reactant	Product	Time (min)	Yield
9			20	98%
10			20	96%
11			20	95%
12			20	96%
13			20	98%
14			20	97%
15			20	98%
16			20	96%

Reaction conditions: Reaction temperature = 70°C, Mole ratio of the reactants = 1: 2 and 0.03 g HC coated 6% MZ catalysts and reaction time =20 min.

Table 4 — Reusability of the HC catalysts.

Catalysts	Fresh	1	2	3	4	5
Z	50%	48%	45.4%	45.2%	44.8%	43.2%
2% MZ	65%	64.5%	64.1%	63.8%	63%	62.5%
6% MZ	96%	96%	95.4%	95.2%	94.8%	94.2%
10% MZ	94%	94%	93.5%	93.2%	93%	95.5%

Reusability of the HC coated MZ catalysts

The used honeycomb coated catalysts recovered from the liquid reaction mass washed with acetone, dried at 120°C for 2 h and calcined at 550°C for 1 h. Moreover used in acetylation reaction (Table 4) with fresh reaction mixture to study the performance of recycled catalysts. After reactivation of used honeycomb catalyst compared and there was no change in weight[28]. The reused catalyst shows that good conversion and selective towards the formation of product remains almost same after each cycle (Table 4). ICP-OES of the 6% MZ honeycomb coated catalysts has been 5.65 to 5.25% of Mo content has been decreased after 6th reaction cycle. XRD showed the intense peak of tetragonal phase and minimal decrease the amount of catalysts. These results attributed the integrity of the HC coated catalysts. The yield of 2-acetyl-5-chlorophenyl acetate over 6 % MZ was found to maximum extent shows a stable and suitable for reuse after 6 reaction cycles.

Conclusion

In conclusion, Honeycomb coated Mo (VI)/ZrO_2 shows highly valuable green catalysts for the liquid phase acetylation reactions. Incorporation of Mo ions to the zirconia the acidity value will be increased, 6% MZ (0.03 g) shows best among the studied catalyst under mild liquid phase afford to the ester and amides products with maximum conversion and selectivity. This catalyst showed maximum conversion in the remarkable reusability for 6 reaction cycles with stability being retained. The recycled catalysts proved that the active *O* and *N* - acetylation reactions under solvent free conditions. The honeycomb coated catalyst showed as a catalyst carrier simple operation mild reaction conditions reactivation and recyclability. These honeycomb coated catalysts further used for the various industrially important organic reactions.

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