



Methoxymethylation of Substituted Alcohols using Dimethoxymethane over Mo(VI)/ZrO₂

M. SHYAMSUNDAR^{1,2,3}, S.Z. MOHAMED SHAMSHUDDIN^{1,3*}, A. ANANDA⁴ and S.R. PRATAP^{1,3}

¹Chemistry Research Laboratory, HMS Institute of Technology, NH-4, Kyathsandra, Tumakuru-572 104, India

²The Oxford College of Engineering, Bommanahalli, Hosur Road, Bangalore-560 068, India

³Research and Development Centre, Bharathiar University, Coimbatore-641 046, India

⁴Dayananda Sagar Academy of Technology and Management, Kanakapura Main Road, Bangalore-560 082, India

*Corresponding author: E-mail: mohamed.shamshuddin@gmail.com

Received: 12 October 2017;

Accepted: 6 January 2018;

Published online: 31 January 2018;

AJC-18761

The methoxymethylation reaction of alcohols was studied on Mo/ZrO₂ (MZ) catalysts. The catalyst containing 5, 10 and 15 % Mo(VI) ions was prepared by solution combustion method. These solid acid catalytic materials were characterized by NH₃-TPD, powder XRD, BET, FTIR spectroscopy, scanning electron microscopy, transmission electron spectroscopy and ICP-OES techniques. These catalysts were evaluated for their catalytic activity in the synthesis of methoxymethylation reactions of various substituted alcohols with dimethoxymethane in shorter reaction times (20 min) at moderate temperature (40 °C) with excellent yields (around 99 %). The main features of the Mo/ZrO₂ catalyzed reaction are high yields, ease of scale up to gram scale, recyclable catalysts, inexpensive reagents, eco-friendly catalysts and a solvent free approach for the synthesis of methoxymethylated products.

Keywords: Solution combustion method, Methoxymethylation, Dimethoxymethane, Mo(VI)/ZrO₂, Solid acid catalysts.

INTRODUCTION

Solid acids as heterogeneous catalysts are extremely useful in large quantity of applications, especially in the production of fine and specialty chemicals [1,2]. Among various solid acid catalysts metal oxides exhibit exceptional acidic properties are more interesting with a variety of applications as catalysts as well as a catalyst supports [3,4]. One class of solid acid catalysts that have received lots of interest in metal oxides *i.e.* zirconia and their modified forms. Zirconia is the only metal oxide that possesses all four chemical properties specifically acidic, basic, reducing and oxidizing ability [5-9]. Zirconia and its modified form catalysts have received more interest in which exhibit exceptional acidic properties. These catalysts are finding frequent applications in many catalytic processes involving liquid vapour and gas phase reactions [10,11].

A promoted zirconia solid acid in particular has been the target catalysts among various solid acids described in earlier reports due to their established advantages. Sulphate free-zirconia based solid acids such as MoO_x/ZrO₂, VO_x/ZrO₂ and WO_x/ZrO₂ have been synthesized and used as solid acid catalysts in a little liquid and vapour phase reactions. Although this sulphate free-zirconia is superior solid acid catalysts and free form de-activation, unlike sulphated zirconia. The best alternative catalyst for sulfated zirconia might be molybdate

promoted catalysts which are considered to be green catalysts [12-16]. Molybdenum and tungstate based zirconia catalysts are used for several organic reactions such as acetylation, alkylation, esterification, transesterification, 1,3-dioxalanes, biphenyl urea, *etc.* It is suitable for both liquid as well as vapour phase reactions. Nevertheless, the use of modified zirconia catalysts for fine chemical synthesis has not been studied extensively so far there have been only a few research results on the application of modified zirconia as catalysts in acid catalyzed *o*-methoxymethylation reactions. Finally, zirconia and its modified forms exploit green solid acid catalysts for organic synthesis and transformation reactions in the liquid phase under solvent-free or with environmentally benign solvents represent an ultimate green chemical technology procedure from both environmental as well as economical point of view.

In recent studies the protection of alcohols and phenols is one of the most frequently employed reactions in organic synthesis and is normally achieved by protecting groups. Especially, methoxymethyl (MOM) ethers are commonly used in protecting alcohols in the synthesis of natural products. The methoxymethyl moiety is a commonly used protecting group for alcoholic hydroxyl groups in the organic synthesis [17]. There are several methods to synthesize methoxymethyl ether with various substituted alcohols in the presence of a variety of catalysts [18,19]. A number of catalytic methods have been

developed for the synthesis of methoxymethyl ethers are Na-Y zeolite [20], molybdenyl(VI) acetylacetonate [21], anhydrous FeCl_3 [22], envirocat EPZGR [23], sulfated metal oxides [24], $\text{Bi}(\text{OTf})_3$ [25], $\text{Sc}(\text{OTf})_3$ [26], melamine trisulfonic acid [27], $\text{TiO}_2/\text{SO}_4^{2-}$ [28], *etc.*

For this reason, the attention of the researchers is directed towards the development of green as well as cleaner catalytic technologies for the synthesis of methoxymethyl ethers. In view of these impacts, alumina zirconia has been selected as an inexpensive, green, eco-friendly, efficient and reusable catalytic system for the present study. Conversely, only a few literatures have scrutinized simple preparation of methoxy-methylation reactions. Although various reagents have been used to synthesize methoxymethyl ethers, they suffer from one or more disadvantages such as stringent reaction conditions, moisture sensitive metallic reagents, tedious work up procedures, long reaction times, use of expensive reagents, poor yields, high reaction temperature, *etc.* Consequently, the research for new catalysts and preparation methods that develop eco-friendly protocol is still in demand.

The main goal of the current study has been made to prepare Mo/ZrO_2 (MZ) by solution combustion method [29]. All the catalytic materials were characterized by their own physico-chemical techniques such as crystallinity, surface acidity, functionality, percentage of metal ions and morphology. This catalytic material has been used in methoxymethylation reactions of various substituted alcohols by using dimethoxymethane at moderate temperature (40 °C) within a shorter reaction time (20 min). Mo/ZrO_2 is simple versatile low cost, ecofriendly and reusable catalysts. The reactivation and reusability of Mo/ZrO_2 solid acids were also taken up.

EXPERIMENTAL

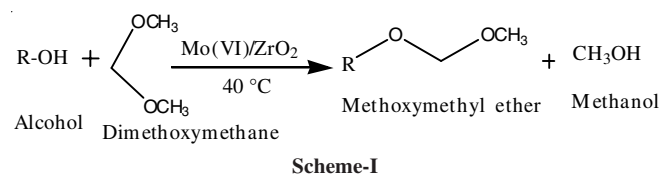
All the chemicals used were L.R. grade as well as analytical grade zirconyl nitrate, ammonium molybdate, dimethoxy methane and various substituted alcohols were supplied by LOBA chemie India Pvt. Ltd.

Preparation of catalyst: Typically, 10 % of Mo/ZrO_2 was prepared with specified amount of zirconyl nitrate (9.0 g), ammonium molybdate (0.45 g) with required amount of a urea (7.5 g as a fuel) taken in a Pyrex glass container as reported by Patil *et al.* [30]. Combustion was carried out in a preheated muffle furnace (400 °C). Where in foamy solid was formed. Thus obtained foamy solid was powdered and calcined in a muffle furnace at 873 K for 5 h. Similarly, 5 and 15 % Mo/ZrO_2 were prepared by the above method. The catalytic material such as ZrO_2 , $\text{Mo(VI)}/\text{ZrO}_2$ prepared by solution combustion method and it is abbreviated as Z and 5 Mo/ZrO_2 , 10 Mo/ZrO_2 and 15 Mo/ZrO_2 .

The crystallinity was analyzed by obtaining powder X-ray diffraction (PXRD) patterns recorded by X-ray powder diffract

meter (Philips X'pert) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) using graphite crystal monochromator with a scanning range of 20-70°. The TSA of the catalytic materials were obtained from NH_3 -TPD method using Mayura analytical temperature program desorption unit. NOVA 1000 Quanta chrome high-speed gas sorption analyzer instrument was used to measure the specific surface area of all the prepared catalytic materials. The FT-IR spectrums were recorded over a range of 4000-400 cm^{-1} using a Nicolet IR200 instrument by the KBr pellet technique. The amount of zirconia present in all the solid acid catalysts was estimated by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) analysis techniques using Thermo-iCAP 6000 Series instrument. SEM images and EDAX of all the prepared catalytic materials were obtained using a JEOL JXA-8530 microscope. TEM images of all prepared catalytic materials were performed on PHILIPS CM200 electron microscope at an acceleration voltage of 20-200 kV.

Catalytic activity studies of ZrO_2 and 5, 10 and 15 % $\text{Mo(VI)}/\text{ZrO}_2$: A calculated amount of alcoholic compounds (1 mmol), dimethoxymethane (10 mmol) and solid acid catalysts (ZrO_2 , 5, 10 and 15 % $\text{Mo(VI)}/\text{ZrO}_2$) were transferred to a dried round bottom flask fitted with a water cooled condenser and the reaction mixture stirred at moderate temperature of 40 °C with nitrogen (**Scheme-I**). The progress of the reaction was monitored by thin layer chromatography. Once completion of the reaction the catalysts were recovered from the reaction mass by adding acetone solvent. The crude product was purified by column chromatography by using suitable mobile phase pet ether: ethyl acetate (80:20). Hence obtained products were characterized by ^1H , ^{13}C NMR and GC-MS for the selected compounds.



RESULTS AND DISCUSSION

Total surface acidity studies and ICP-OES studies: The total surface acidity (TSA) values of solid acid catalytic materials used in the present study are given in the Table-1.

The acidity values increase by incorporation of Mo ions to zirconia catalysts shows a strong impact on acidic properties. Acid sites compared with the zirconia and different % of Mo incorporation to zirconia. On the other hand, it was observed that zirconia consists of weak and medium acid sites. Whereas, 5 and 10 % Mo/ZrO_2 consists of 'moderate' to 'strong' acid sites the value has been increased drastically up to 10 %. Thereafter,

TABLE-1
CHARACTERIZATION OF SOLID ACIDS USED FOR THE PRESENT STUDY

Solid acid	Acid site distribution				BET surface area	Mo(VI) (%)
	Weak	Medium	Strong	Total surface acidity (mmol/g)		
ZrO_2	0.02	0.41	–	0.45	42	–
5 % Mo/ZrO_2	–	0.05	0.69	0.97	78	4.6
10 % Mo/ZrO_2	–	0.25	0.75	1.26	105	9.56
15 % Mo/ZrO_2	–	0.28	0.82	1.15	89	14.65

in case of 15 % Mo/ZrO₂ acidity value was found to be slightly decreased due to presence of excess molybdenum oxide [29,31]. The total surface acidity values were shown in the order of

$$\text{ZrO}_2 < 5\% \text{ Mo/ZrO}_2 < 15\% \text{ Mo/ZrO}_2 < 10\% \text{ Mo/ZrO}_2$$

Percentage of Mo present in the catalyst samples is also given in Table-1. There is no significant loss during calcination of the Mo/ZrO₂ catalysts at 873 K. It is to be noted that the definite amount of metal ions such as 4.6, 9.65 and 14.65 % Mo ions is less than the amount expected from the amount to be used.

BET surface area: The surface area of the catalytic materials used for the present study is given in the Table-1. The results attributed that zirconia shows the least surface area among the catalytic materials which was used for the present work. The catalytic materials were used 10 Mo/ZrO₂ shows a highest surface area than 5-15 Mo/ZrO₂. It is also observed that when the percentage of Mo(VI) is increased above 10 % Mo/ZrO₂, it is found that surface area to be decreased, which is due to excess of molybdenum content on zirconia. The decrease in the surface area with an increase in the concentration of molybdenum cation beyond 10 % is due to blockage of pore structures as reported by Zapien *et al.* [32].

Powder XRD studies: Powder XRD patterns of the solid acid catalysts are shown in Fig. 1. ZrO₂ consisted of both monoclinic (M) and tetragonal (T) phases. Sharp diffraction lines at $2\theta = 28.3, 24.46$ and 31.58° correspond to the monoclinic phase and the lines at $2\theta = 30.27$ and 49.21° are because of tetragonal phase of ZrO₂. As the findings in the earlier literature [32], incorporation of Mo(VI) ions into ZrO₂ results in transition of monoclinic phase of ZrO₂ to tetragonal phase of ZrO₂. It is interesting to note that when an increase in the percentage of Mo(VI) cation promotes a stronger influence on the tetragonal phase. In case of 10 % and 15 % Mo/ZrO₂ peaks corresponding to monoclinic phase have been totally eliminated and only metastable tetragonal phase could be seen.

FT-IR studies: The Fourier Transform Infrared spectra of ZrO₂ and 5, 10, 15 % of Mo(VI)/ZrO₂ are shown in Fig. 2.

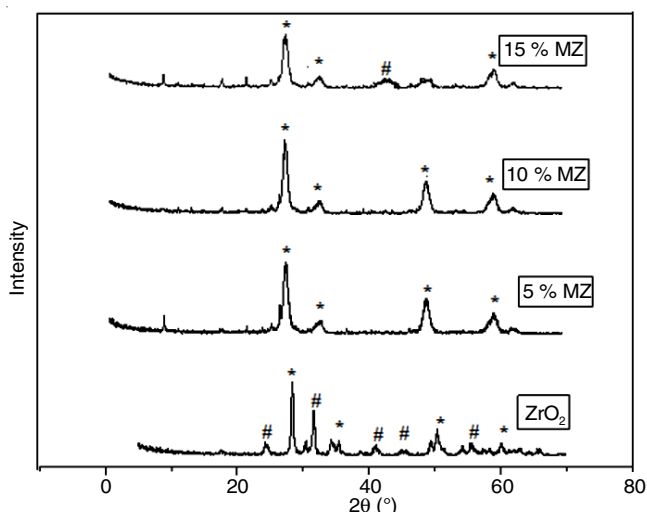


Fig. 1. Powder-XRD patterns of solid acid catalysts [Z, 5 % Mo/ZrO₂, 10 % Mo/ZrO₂, 15 % Mo/ZrO₂ calcined at 550 °C for 4 h. * tetragonal, # monoclinic phase of zirconia]

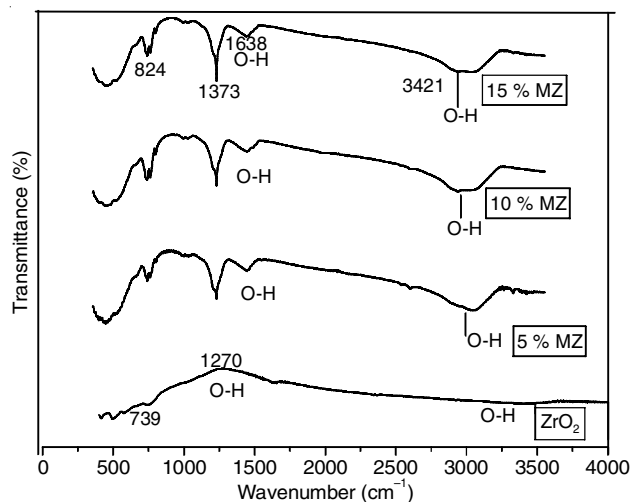


Fig. 2. FTIR spectra of ZrO₂, 5, 10 and 15 % Mo(VI)/ZrO₂

The bands at about 739 and 1373 cm⁻¹ are due to stretching mode of Zr-O-Zr zirconium oxide confirmed the structure of zirconia phases respectively. The broad band at 824 cm⁻¹ were shown that the Mo-O-Mo stretching mode of vibration for MoO₃. The band at about 1638 cm⁻¹ attributed acidic hydroxyl proton and about 3421 cm⁻¹ stretching mode of hydrogen bonding exists in all the catalysts [33,34].

SEM/TEM studies: SEM images of zirconia and its modified forms such as 10 Mo/ZrO₂ are shown in Fig. 3. Zirconia and its modified form Mo/ZrO₂ shows the presence of irregular shaped coarse grains with inter-granular porosity. Mo/ZrO₂ catalysts non-uniform particles are micrometer in size and show porous in nature. TEM analysis clearly shows big crystalline particles of zirconia and molybdenum ions are dispersed with negligible agglomeration on the surface of the zirconia with the particle size 45-58 nm (Fig. 4). The change in morphology shows higher surface area of Mo/ZrO₂ when compared to ZrO₂ [35,36].

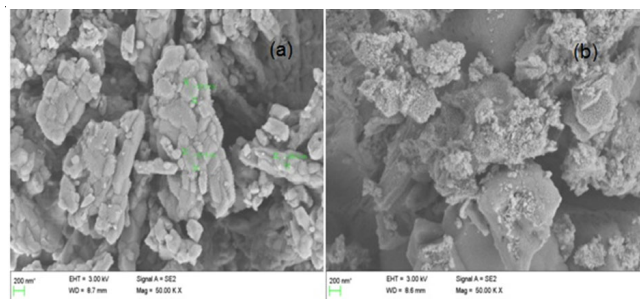


Fig. 3. SEM images of ZrO₂ and 10 % Mo/ZrO₂

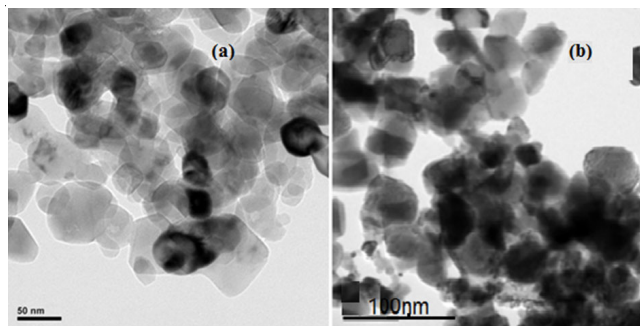


Fig. 4. TEM images (a) ZrO₂ (b) 10 % Mo(VI)/ZrO₂

Effect of nature of catalysts (ZrO₂, 5, 10 and 15 % Mo/ZrO₂): In order to investigate, the catalytic activity of all the materials such as ZrO₂, 5 Mo/ZrO₂, 10 Mo/ZrO₂ and 15 Mo/ZrO₂ were compared in *O*-methoxymethylation reaction of substituted alcohols with dimethoxymethane. Dimethoxymethane serves both as a solvent as well as methoxymethylating reagent (**Scheme-I**). To optimize the reaction conditions for the improved yield of *O*-methoxymethyl ether derivatives, 2-[(methoxymethoxy)methyl]furan and dimethoxymethane used as model substrates in presence of 0.05 g of catalysts. The mixture was refluxed under nitrogen at moderate temperature 40 °C for 20 min.

It was interesting to note that the highest yield 99.2 % of 2-[(methoxymethoxy)methyl]furan was observed with 10 % Mo/ZrO₂ by solution combustion method (Table-2). However, when *O*-methoxymethylation reaction were carried out without any catalysts, it shows very less yield of 2-[(methoxymethoxy)methyl]furan (19 %). This indicates *O*-methoxymethylation is a catalyzed reaction. It is worth to mention that Mo/ZrO₂ catalysts allylic and tertiary alcohols also smoothly converted to *O*-methoxymethyl ethers without any trace amount of elimination products.

TABLE-2
O-METHOXYMETHYLATION OF 2-(METHOXYMETHOXY)
METHYL FURAN OVER 10 % Mo/ZrO₂ CATALYSTS

Solid acid catalysts	Total surface acidity (mmol/g)	% Yield of 2-(methoxymethoxy)methylfuran (%)
ZrO ₂	0.45	58.5
5 % Mo/ZrO ₂	0.97	75.6
10 % Mo/ZrO ₂	1.26	99.2
15 % Mo/ZrO ₂	1.19	91.3

Reaction conditions: Reaction temperature = 40 °C, reaction time = 20 min, molar ratio of alcohols and dimethoxy methane (1:10 mmol)

Synthesis of *O*-methoxymethylated compounds over 10 % Mo/ZrO₂: In general a mixture of various alcohols, dimethoxymethane (1:10 mole ratio) and 0.05 g of 10 Mo/ZrO₂ was added and the mixture was refluxed at 40 °C for an appropriate time under nitrogen. The progress of the reaction was monitored by TLC. After completion of the reaction the mixture was cooled to room temperature filtered and the solid catalyst was washed with diethyl ether (5 mL). The filtrate was washed with brine solution and dried over anhydrous sodium sulphate. The solvent was evaporated in rota-vapour to get the residue. Thus obtained crude product was purified in silica gel (60-120) column chromatography by using suitable mobile phase pet ether-ethyl acetate (80:20) mixture. The isolated products are characterized by ¹H and ¹³CNMR, GC-MS spectroscopic.

Spectral data

2-Iodo-3-(methoxymethoxy)pyridine: Physical state: liquid; yield (%): 90; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.42 (s, 3H), 6.02 (s, 2H), 7.289 (t, 1H, 4.4 Hz), 7.372 (d, 1H, 8 Hz), 8.271 (d, 1H, 3.6 Hz). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 94.1, 164.1, 121.6, 123.0, 142.3, 108.7, GC-MS (*m/z*) Calculated for C₇H₇NO₂I [M+H⁺]: 264.94, found 265.

1-(4-Chloro-2-(methoxymethoxy)phenyl)ethanone: Physical state: liquid; yield (%): 89; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.41 (s, 3H), 6.02 (s, 2H), 2.538 (s, 3H), 6.94 (d, 1H, 1.6 Hz), 6.89 (dd, 1H, *J*₁ = 8.8 Hz, *J*₂ = 1.6 Hz), 7.69 (d, 1H, 8.4 Hz). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 95.00, 161.56, 115.4, 139.7, 121.2, 131.25, 118.8, 29.06, 199.274. GC-MS (*m/z*) Calculated for C₁₀H₉O₃Cl [M+H⁺]: 213.02, found 214.0.

2-Bromo-4-(methoxymethoxy)-1-methylbenzene: Physical state: liquid; yield (%): 90; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 2.35 (s, 3H), 3.42 (s, 3H), 6.02 (s, 2H), 6.59 (dd, 1H, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz), 6.84 (d, 1H, 8 Hz), 6.82 (d, 1H, 1.6Hz). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.65, 22.248, 95.06, 159.9, 117.5, 125.0, 16.52, 130.4, 132.3 and 113.2. GC-MS (*m/z*) Calculated for C₉H₉O₂Br [M+H⁺]: 231.98, found 229.9.

1-Cyclopropyl-2-(methoxymethoxy)benzene: Physical state: liquid; yield (%): 89; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.63 (m, 2H), 0.63 (m, 2H), 1.50 (m, 1H), 3.3 (s, 3H), 6.02 (s, 2H, 7.6 Hz), 7.02 (m, 2H), 6.74 (d, 2H), 6.69 (d, 2H), 6.97 (d, 2H) ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 5.7, 8.8, 8.8, 55.6, 95.3, 154.7, 113.7, 126.2, 120.5, 126.1 and 131.3. GC-MS (*m/z*) Calculated for C₁₁H₁₂O₂ [M+H⁺]: 178.1, found 178.9.

2-(Methoxymethoxy)-1,2-diphenylethanone: Physical state: liquid; yield (%): 99.1; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.45 (s, 3H), 5.45 (s, 2H), 5.63 (s, 1H), 7.19 (m, 3H), 7.39-7.48 (d, 2H, 6 Hz), 7.86 (m, 2H) ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 94.6, 87.4, 194.3, 136.6, 129.7, 129.4, 127.7, 129.3, 127.7, 136.8, 128.8, 128.7, 128.8, 133.3 and 128.7. GC-MS (*m/z*) Calculated for C₁₆H₁₆O₃ [M+H⁺]: 256.07, found 257.1.

2-Fluoro-6-(methoxymethoxy)benzonitrile: Physical state: liquid; yield (%): 88; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.41 (s, 3H), 6.02 (s, 2H), 6.71-6.72 (m, 2H, 8 Hz), 7.41 (dd, 1H, *J*₁ = 14.4 Hz, *J*₂ = 6 Hz). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 94.5, 164.9, 110.6, 135.7, 108.5, 161.5, 81.5, 115.8. GC-MS (*m/z*) Calculated for C₉H₈NO₂F [M+H⁺]: 181.04, found 181.16

2-Chloro-3-(methoxymethoxy)methyl pyridine: Physical state: liquid; yield (%): 99.2; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.41 (s, 3H), 5.45 (s, 2H), 4.63 (d, 2H), 8.19 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 4.8 Hz), 7.71 (d, 1H, 7.6 Hz), 8.75 (d, 1H, 5.2 Hz). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 97.3, 62.2, 133.38, 138.014, 138.05, 121.9, 150.05, 148.34. GC-MS (*m/z*) Calculated for C₈H₁₀NO₂Cl [M+H⁺]: 187.02, found 188.04

1,3-Di-tert-butyl-2-(methoxymethoxy)-5-methylbenzene: Physical state: liquid; yield (%): 89; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 1.34 (s, 18H), 3.48 (s, 3H), 6.02 (s, 2H), 2.33 (s, 3H), ¹³C (CDCl₃, 400 MHz): δ (ppm) 55.6, 95.6, 24.9, 31.4, 31.74, 35.25, 135.91, 124.80, 129.0, 146.8. GC-MS (*m/z*) Calculated for C₁₇H₂₈O₂ [M+H⁺]: 264.14, found 265.21.

1-(4-(2-(Methoxymethoxy)ethyl)benzyloxy)benzene: Physical states: liquid; yield (%): 98; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.42 (s, 3H), 5.45 (s, 2H), 3.70 (d, 2H), 2.72 (d, 2H), 7.05 (d, 1H), 7.14 (d, 1H), 7.05 (d, 1H), 7.14 (d, 1H), 5.20 (s, 2H), 6.77 (d, 1H), 6.77 (d, 1H), 7.15 (d,

1H), 7.15 (d, 1H), 6.82 (m, 1H); ¹³C (CDCl₃, 400 MHz): δ (ppm) 55.6, 97.6, 72.2, 36.1, 138.4, 128.0, 127.1, 70.9, 160.7, 114.3, 129.8, 121.2. GC-MS (*m/z*) Calculated for C₇H₂₀O₃ [M+H-⁺] 272.14, found 273.21.

1-((E)-3-(Methoxymethoxy)prop-1-enyl)benzene:

Physical states: liquid; yield (%): 97.8; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.42 (s, 3H), 5.45 (s, 2H), 4.04 (d, 2H), 6.25 (d, 1H), 6.62 (d, 1H), 7.30 (d, 1H), 7.21 (d, 1H), 7.14 (m, 1H). ¹³C (CDCl₃, 400 MHz): δ (ppm) 55.6, 97.8, 70.2, 123.9, 129.7, 135.2, 126.1, 128.0, 128.9, 128.7, 126.3. GC-MS (*m/z*) Calculated for C₁₁H₁₄O₂ [M+H-⁺] 178.14, found 178.10.

1-Bromo-4-[(methoxymethoxy)methyl]benzene:

Physical states: liquid; yield (%): 98.6; time (min): 20; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.43 (s, 3H), 5.45 (s, 2H), 4.63 (d, 1H), 7.08 (d, 1H), 7.36 (d, 1H, *J* = 7.2 Hz), 7.08 (d, 1H), 7.36 (d, 1H). ¹³C (CDCl₃, 400 MHz): δ (ppm) 55.6, 97.3, 71.3, 129.7, 131.6, 122.2, 131.6, 129.7, 136.5. GC-MS (*m/z*) Calculated for C₉H₁₁BrO₂ [M+H-⁺]: 229.99, found 229.10.

2-[(Methoxymethoxy)methyl]furan: Physical states: liquid; yield (%): 99.2; ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 3.3 (s, 3H), 4.48 (s, 2H), 6.19 (d, 1H), 6.25 (d, 1H), 7.30 (d, 1H, *J* = 8.8 Hz), ¹³C (CDCl₃, 300 MHz): δ (ppm) 55.6, 94.8, 67.2, 152.8, 109.2, 108.2, 110.7, 144.1. GC-MS (*m/z*) Calculated for C₇H₁₀O₃ [M+H-⁺]: 142.14, found 142.04.

4-Bromo-2-methoxy-1-[(methoxymethoxy)methyl]benzene: Physical state: liquid; yield (%): 97.8; time (min): 20; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 3.38 (s, 3H), 5.45 (s, 2H), 3.73 (s, 3H), 6.97 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 1.2 Hz), 6.87 (d, 1H, *J* = 8 Hz), 4.63 (d, 2H). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 97.3, 61.061, 56.2, 122.7, 123.9, 130.71, 123.22, 117.51, 159.93. GC-MS (*m/z*) Calculated for C₁₀H₁₃BrO₃ [M+H-⁺]: 261.1, found 262.0.

Methoxymethoxy(methyl)cyclobutane: Physical state: liquid; yield (%): 98.2; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 3.32 (s, 3H), 5.45 (s, 2H), 3.33 (d, 2H), 2.28 (m, 1H), 1.79-2.04 (m, 2H), 1.91-2.01 (m, 2H), 1.79-2.04 (m, 2H). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) 55.6, 98.0, 76.7, 33.0, 24.7, 19.4, 24.7. GC-MS (*m/z*) Calculated for C₇H₁₄O₂ [M+H-⁺]: 131.1, found 130.0.

Comparison of 10 Mo/ZrO₂ catalysts with reported catalysts: In order to obtain the good yield with the advantages of 10 Mo/ZrO₂ catalysts compare with the earlier protocols (Table-3). Interestingly, good yields obtained from the 10 Mo/ZrO₂ catalysts with some of the sterically hindered alcohols such as tertiary and allylic alcohols.

Reusability and Reactivation of 10 Mo/ZrO₂ solid acid catalysts: The solid acid catalysts recovered from the liquid reaction mass washed with acetone, dried at 120 °C for 2 h calcined at 550 °C for 1 h and used in methoxymethylation reaction with fresh reaction mixture to study the performance

at reactivated catalysts. After reactivations of used catalyst were compared with weight of the catalysts there is no change in weight after 6 reaction cycles. The reused catalysts were 100 % selective towards the product formation. The yield of 2-[(methoxymethoxy)methyl] furan over 10 % Mo/ZrO₂ was found to minimal extent shows a stable and suitable for reuse after 6 reaction cycles of PXRD pattern shows intense peak of tetragonal phase has shown after 6th reaction cycle are shown in Fig. 5.

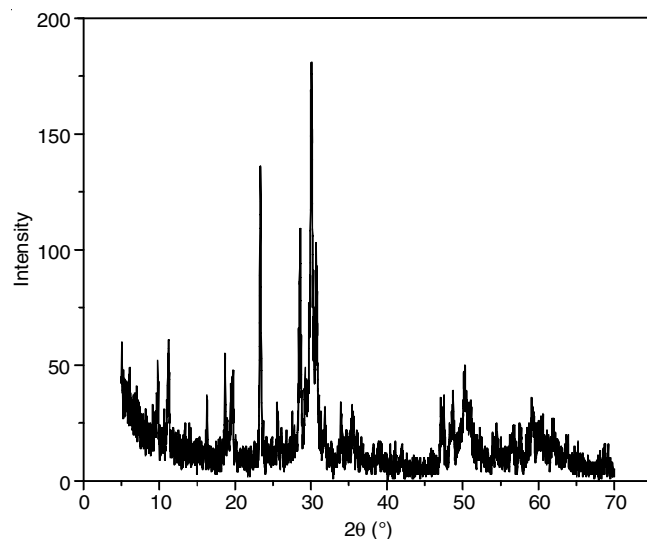


Fig. 5. 10 % Mo/ZrO₂ used after 6 reactions cycles

Conclusion

In summary, Mo/ZrO₂ is a simple ecofriendly and green catalyst was prepared by the solution combustion method. 10 % Mo/ZrO₂ shows a high surface acidity than 5 % and 15 % Mo/ZrO₂. Hence these catalytic materials have been used for the methoxymethylation reaction between the various substituted alcohols and dimethoxymethane were methoxymethylated with excellent yields of desired products. A good correlation between the surface acidity, surface area and tetragonal phase of the PXRD. These catalytic materials were recovered and reused up to six reaction cycles without loss of its catalytic activity. Mo/ZrO₂ is an environment benign catalyst, because of their mild reaction conditions, experimentally simple procedure and high yield of products with shorter reaction times.

ACKNOWLEDGEMENTS

The authors are grateful to Department of Chemistry HMS Institute of Technology and VGST Project, Government of Karnataka, Poornaprajna Institute of Analytical Research Bangalore, India for PXRD analysis, BIT College for BET &

TABLE-3
COMPARISON OF 10 Mo/ZrO₂ CATALYSTS WITH REPORTED CATALYSTS

S. No.	Catalyst used	Reaction condition	Yield (%)	Time (h)	Ref.
1	10 % Mo(VI)/ZrO ₂	Solvent free, 40 °C	99.2	0.20	Present work
2	Sulphonic acid sodium montmorillonite	Chloroform	92.0	2.00	[27]
3	Molybdenyl acetylacetonate	Chloroform	85.0	4.00	[21]
4	Sulphated Titania	Solvent free, 40 °C	90.0	3.00	[27]
5	Na-Y zeolite	Solvent free, 40 °C	80.0	8.00	[20]

NH₃-TPD analysis. Thanks are also due to Indian Institute of Science, Bangalore, India for providing LC-MS and NMR data by analysis. Special thanks to Department of Chemistry, The Oxford College of Engineering for supporting.

REFERENCES

1. J. Otera, *Chem. Rev.*, **93**, 1449 (1993); <https://doi.org/10.1021/cr00020a004>.
2. A. Corma, S. Iborra, S. Miquel and J. Primo, *Catal.*, **173**, 315 (1998); <https://doi.org/10.1006/jcat.1997.1930>.
3. X. Song and A. Sayari, *Catal. Rev., Sci. Eng.*, **38**, 329 (1996); <https://doi.org/10.1080/01614949608006462>.
4. T. Yamaguchi, *Catal. Today*, **20**, 199 (1994); [https://doi.org/10.1016/0920-5861\(94\)80003-0](https://doi.org/10.1016/0920-5861(94)80003-0).
5. P.D.L. Mercera, Ph.D. Thesis, Twente Institute of Technology, Netherland (1991).
6. J. Nawrocki, M. Rigney, A. McCormick and P.W. Carr, *J. Chromatogr. A*, **657**, 229 (1993); [https://doi.org/10.1016/0021-9673\(93\)80284-F](https://doi.org/10.1016/0021-9673(93)80284-F).
7. B.M. Reddy and A. Khan, *Catal. Rev., Sci. Eng.*, **47**, 257 (2005); <https://doi.org/10.1081/CR-200057488>.
8. M. Vrinat, D. Hamon, M. Breyse, B. Durand and T. des Courieres, *Catal. Today*, **20**, 273 (1994); [https://doi.org/10.1016/0920-5861\(94\)80006-5](https://doi.org/10.1016/0920-5861(94)80006-5).
9. E. Iglesia, D.G. Barton, S.L. Soled, S. Miseo, J.E. Baumgartner, W.E. Gates, G.A. Fuentes and G.D. Meitzner, *Stud. Surf. Sci. Catal.*, **101**, 533 (1996); [https://doi.org/10.1016/S0167-2991\(96\)80264-3](https://doi.org/10.1016/S0167-2991(96)80264-3).
10. A. Khodakov, J. Yang, S. Su, E. Iglesia and A.T. Bell, *J. Catal.*, **177**, 343 (1998); <https://doi.org/10.1006/jcat.1998.2143>.
11. B.M. Reddy and P.M. Sreekanth, *Synth. Commun.*, **32**, 2815 (2002); <https://doi.org/10.1081/SCC-120006465>.
12. B.M. Reddy, M.K. Patil and B.T. Reddy, *Catal. Lett.*, **125**, 97 (2008); <https://doi.org/10.1007/s10562-008-9518-1>.
13. C. Martin, I. Martin and V.J. Rives, *Chem. Soc. Faraday. Trans.*, **89**, 4131 (1993); <https://doi.org/10.1039/ft9938904131>.
14. M. Niwa, H. Yamada and Y. Murakami, *J. Catal.*, **134**, 331 (1992); [https://doi.org/10.1016/0021-9517\(92\)90232-7](https://doi.org/10.1016/0021-9517(92)90232-7).
15. Y. Matsuoka, M. Niwa and Y. Murakami, *J. Phys. Chem.*, **86**, 1477 (1990); <https://doi.org/10.1021/j100367a051>.
16. H. Miyata, S. Tokuda, T. Ono, T. Ohno and F. Hatayama, *J. Chem. Soc., Faraday Trans.*, **86**, 2291 (1990); <https://doi.org/10.1039/ft9908602291>.
17. T.W. Greene and P.G.M. Wuts, *Protective Groups in Organic Synthesis*, Wiley: New York, edn 2 (1991).
18. T.S. Jin, T.S. Li and Y.T. Gao, *Synth. Commun.*, **28**, 837 (1998); <https://doi.org/10.1080/00032719808006481>.
19. B.C. Ranu, A. Majee and A.R. Das, *Synth. Commun.*, **25**, 363 (1995); <https://doi.org/10.1080/00397919508011367>.
20. P. Kumar, S.V.N. Raju, R.S. Reddy and B. Pandey, *Tetrahedron Lett.*, **35**, 1289 (1994); [https://doi.org/10.1016/0040-4039\(94\)88046-8](https://doi.org/10.1016/0040-4039(94)88046-8).
21. M.I. Kantam and P.L. Santhi, *Synlett*, 429 (1993); <https://doi.org/10.1055/s-1993-22483>.
22. H.K. Patney, *Synlett*, 567 (1992); <https://doi.org/10.1055/s-1992-21417>.
23. B.P. Bandgar, C.T. Hajare and P.P. Wadgaonkar, *J. Chem. Res. (S)*, 90 (1990).
24. C.H. Lin, M.Y. Wan and Y.M. Huang, *Catal. Lett.*, **87**, 253 (2003); <https://doi.org/10.1023/A:1023472029190>.
25. B. Sreedhar, V. Swapna and Ch. Sridhar, *Catal. Commun.*, **6**, 293 (2005); <https://doi.org/10.1016/j.catcom.2005.02.003>.
26. B. Karimi and L. Ma'mani, *Tetrahedron Lett.*, **44**, 6051 (2003); [https://doi.org/10.1016/S0040-4039\(03\)01481-3](https://doi.org/10.1016/S0040-4039(03)01481-3).
27. F. Shirini, M.A. Zolfigol and J. Albadi, *Synth. Commun.*, **40**, 910 (2010); <https://doi.org/10.1080/00397910903026707>.
28. T.-S. Jin, J.-J. Guo, Y.-H. Yin, S.-L. Zhang and T.-S. Li, *J. Chem. Res.*, 188 (2002); <https://doi.org/10.3184/030823402103171627>.
29. J.R. Sohn, E.W. Chun and Y. I. Pae, *Bull. Korean Chem. Soc.*, **24**, 1785 (2003); <https://doi.org/10.5012/bkcs.2003.24.12.1785>.
30. K.C. Patil, M.S. Hegde, T. Rattan and S.T. Aruna, *Chemistry of Nano-crystalline Oxide Materials: Combustion Synthesis, Properties and Applications*, World Science Publishing Pvt. Ltd.: Singapore (2008).
31. K. Tanabe, M. Misson, Y. Ono and J. Hattori, *New Solid Acids and Bases*, Elsevier Science, Amsterdam (1989).
32. A.H. Zapien, J.M.H. Enriquez, R.G. Alamilla, G.S. Robles, U.P. Garcia and L.A.G. Serrano, *Adv. Mater. Sci. Eng.*, **Article ID 43203** (2014); <https://doi.org/10.1155/2014/432031>.
33. S.Z.M. Shamshuddin, M. Shyamsundar, N. Thimmaraju, Venkatesh, G. Vatsalya and M.Senthilkumar, *Comptes Rend. Chem.*, **15**, 799 (2012); <https://doi.org/10.1016/j.crci.2012.05.020>.
34. J.R. Sohn, E.W. Chun and Y. I. Pae, *Bull. Korean Chem. Soc.*, **24**, 1785 (2003); <https://doi.org/10.5012/bkcs.2003.24.12.1785>.
35. K.V.R. Chary, K.R. Reddy, G. Kishan, J.W. Niemantsverdriet and G. Mestl, *J. Catal.*, **226**, 283 (2004); <https://doi.org/10.1016/j.jcat.2004.04.028>.
36. J.M.H. Enriquez, L.A.G. Serrano, R.G. Alamilla, L.A.C. Lajas and A.C. Hernandez, *Superficies y Vacío*, **22**, 1 (2009).