



Synthesis of Some Aromatic and Aliphatic Esters Using WO_3/ZrO_2 Solid Acid Catalyst under Solvent Free Conditions

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A simple method is delineated for the synthesis of substituted ester products in superior yields by esterification reaction under solvent unbound condition using tungsten upgraded ZrO_2 solid acid catalyst at 353 K. The WO_3/ZrO_2 catalyst has been prepared by using impregnation method followed by calcination at 923 K over a period of 6 h in air atmosphere. SEM, XRD, FTIR, and BET surface area techniques were used to categorize this catalyst. Zirconia has both acidic and basic possessions which can be changed by incorporating suitable promoter atom like tungsten which in turn increases the surface area thereby enhancing the surface acidity. Impregnation of W^{6+} ions exhibits a strong influence on phase modification of zirconia from thermodynamically solid monoclinic to metastable tetragonal phase. Amalgamation of promoter W^{6+} will stabilize tetragonal phase which is active in catalyzing reactions. In esterification reaction WO_3/ZrO_2 catalyst was found to be stable, efficient and environmental friendly, effortlessly recovered by filtration, excellent yield of product and can be reusable efficiently.

Keywords: Heterogeneous catalyst, Solvent-free condition, Esters.

INTRODUCTION

Esters impart artificial flavours, essences in perfume industry and are useful as solvents, plasticizers. In synthetic organic chemistry, esters are used in alkylation and acylation [1-5]. Conventionally, esters are synthesized using H_2SO_4 as catalyst [6]. The use of H_2SO_4 often causes problems such as corrosion and environmental pollution. In order to reduce environmental pollution, solid acids are introduced as catalysts which are less toxic, readily separable and reusable. Esterification is performed under batch and flow conditions over cerium ammonium nitrate [7], iodine [8], niobium(V) oxide [9], molecular sieves using higher alcohols [10], ionic liquids [11] and heteropoly acids [12]. The mechanical strength and thermal stability of promoted metal oxide catalysts provides the advantage of using them at different temperatures and in presence of different solvents to catalyze the reactions in liquid phase.

The commercial applications of solid acid catalysts have led to develop new solid acid catalyst which improves activity, selectivity and yield towards the target product. The chemical and physical properties of zirconia based catalysts make them

attractive catalysts which can compete with zeolites, clays and oxides in industry. Molybdenum on zirconia used for esterification and trans esterification [13], bismuth on zirconia in Biginelly condensation [14], ZnO and selenium dioxide on zirconia for Knoevenagel condensation [15,16]. The advantages of the solid acid catalysts in organic synthesis prompted us to carryout esterification reaction between different aliphatic, substituted aromatic acids with alcohol using tungsten supported zirconia catalyst. The catalyst was characterized by XRD, SEM, FTIR, UV-DRS and BET surface area and compared with literature values [17]. Physico-chemical properties of the catalyst were also correlated with the catalytic activity.

EXPERIMENTAL

Commercially purchased materials were used. To monitor progress of the reaction TLC was used. XRD 7000 Shimadzu instrument was used to record X-ray diffraction patterns of catalyst. BRUKER AV-III 400 MHz was used to record proton NMR. Bruker Optik GmbH, Germany Model: TENSOR 27 was used for FTIR spectra. On a VG-Micro mass 7070H spectro-

meter, mass spectra were recorded. Scanning electron microscope (SEM) investigations were done on a Hitachi model SEM-EDS S3700N scanning electron microscopy at a pragmatic voltage of 15.0 KV. Nitrogen physisorption at 77 K was used to determine BET surface area of the catalyst.

Preparation of catalyst: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (50 g) was dissolved in water and to obtain a white precipitate of zirconia, a 1 M NH_4OH solution was added by continuous stirring. The white precipitate was washed with double distilled water till free from all the chloride ions and thereafter dried in an oven at 393 K for a day. Ammonium paratungstate ($(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6$, 0.358 g) was dissolved in water until clear solution was obtained. To this solution, 5 g of hydrated zirconia was added. The additional water was evaporated, dried the sample in an oven finally calcined at 923 K. The pure ZrO_2 sample was also prepared for comparison.

General procedure: An organic acid (1 g), alcohol (excess) and catalyst (0.1 g) mixture was heated in a round bottomed flask. The completion of reaction is indicated by the total disappearance of acid. Then after, the catalyst was separated by filtration and reused. Sodium bicarbonate solution was added to the filtrate and removed with ether. With anhydrous sodium sulphate, the extract was dried and solvent was removed. Using ethyl acetate and petroleum ether, the pure product was isolated by column chromatography.

Benzyl acetate (3a): Liquid, b.p.: 210-212 °C, IR (KBr, ν_{max} , cm^{-1}): 3458, 3066, 3035, 2955, 1739, 1455, 1381, 1362, 1229, 1027, 750, 698. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 2.10 (s, 3H), 5.10 (s, 2H), 7.37-7.32 (m, 5H); Mass (ES) $\text{C}_9\text{H}_{10}\text{O}_2$: m/z 150 $[\text{M}]^+$, 151 $[\text{M}+\text{H}]^+$.

Benzyl benzoate (3b): Liquid, b.p.: 322-324 °C, IR (KBr, ν_{max} , cm^{-1}): 3420, 3090, 3065, 3034, 1716, 1451, 1270, 1109, 1069, 1026, 735, 710. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 5.37 (s, 2H), 7.46-7.32 (m, 7H), 7.56 (t, 1H, $J=8.4$ Hz), 8.08 (d, 2H, $J=8.4$ Hz); Mass (ES) $\text{C}_{14}\text{H}_{12}\text{O}_2$: m/z 212 $[\text{M}]^+$, 213 $[\text{M}+\text{H}]^+$.

Ethyl benzoate (3c): Liquid, b.p.: 213-214 °C, IR (KBr, ν_{max} , cm^{-1}): 3063, 2982, 1719, 1276, 1108, 1070, 1027, 710. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 1.39 (t, 3H, $J=7.2$ Hz), 4.39 (q, 2H, $J=7.2$ Hz), 7.45-7.41 (dd, 2H, $J=12$ Hz, $J=1.6$ Hz), 7.55 (t, 1H, $J=7.6$ Hz), 8.06-8.03 (dd, 2H, $J=7.2$ Hz, $J=1.6$ Hz); Mass (ES) $\text{C}_9\text{H}_{10}\text{O}_2$: m/z 150 $[\text{M}]^+$, 151 $[\text{M}+\text{H}]^+$.

Ethyl 4-aminobenzoate (3d): Solid, m.p.: 88-90 °C, IR (KBr, ν_{max} , cm^{-1}): 3421, 3343, 2984, 1682, 1280, 846, 772. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 1.37 (t, 3H, $J=7.2$ Hz), 4.07 (s, 2H), 4.34 (q, 2H, $J=7.2$ Hz), 6.64 (d, 2H, $J=8.4$ Hz), 7.86 (d, 2H, $J=8.4$ Hz); Mass (ES) $\text{C}_9\text{H}_{11}\text{O}_2$: m/z 165 $[\text{M}]^+$, 166 $[\text{M}+\text{H}]^+$.

Isopropyl 3, 4-dihydroxybenzoate (3e): Liquid, b.p.: 358-360 °C, IR (KBr, ν_{max} , cm^{-1}): 3458, 3316, 2984, 1676, 1609, 1443, 1296, 1238, 1102, 957, 768. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 1.36 (d, 6H, $J=6.4$ Hz), 5.23 (m, 1H), 6.15 (bs, 1H), 6.46 (bs, 1H), 6.92 (d, 1H, $J=8.4$ Hz), 7.55-7.7 (dd, 1H, $J=6.8$, 2 Hz), 7.71 (d, 1H, $J=2$ Hz); Mass (ES) $\text{C}_{10}\text{H}_{12}\text{O}_4$: m/z 196 $[\text{M}]^+$, 197 $[\text{M}+\text{H}]^+$.

Methyl 3,4-dimethoxybenzoate (3f): Solid, m.p.: 60-62 °C, IR (KBr, ν_{max} , cm^{-1}): 3404, 3086, 3021, 2957, 1722, 1595, 1517, 1414, 1106, 1020, 869, 760. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.89 (s, 3H), 3.94 (s, 6H), 6.90 (d, 1H, $J=8.4$ Hz), 7.55 (s,

1H), 7.69-7.67 (dd, 2H, $J=8.4$ Hz, $J=2.4$ Hz); Mass (ES) $\text{C}_{10}\text{H}_{12}\text{O}_4$: m/z 196 $[\text{M}]^+$, 197 $[\text{M}+\text{H}]^+$.

Methyl 3,5-dimethoxybenzoate (3g): Solid, m.p.: 44-46 °C, IR (KBr, ν_{max} , cm^{-1}): 3408, 3017, 2958, 1717, 1597, 1350, 1208, 1159, 1102, 987, 845, 761, 674. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.82 (s, 6H), 3.90 (s, 3H), 6.65 (t, 1H, $J=2.4$ Hz), 7.19 (d, 2H, $J=2.4$ Hz); Mass (ES) $\text{C}_{10}\text{H}_{12}\text{O}_4$: m/z 196 $[\text{M}]^+$, 197 $[\text{M}+\text{H}]^+$.

Methyl 4-bromobenzoate (3h): Solid, m.p.: 77-79 °C, IR (KBr, ν_{max} , cm^{-1}): 3420, 2951, 1714, 1590, 1439, 1288, 1277, 1115, 1010, 847, 758, 686. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.91 (s, 3H), 7.59 (d, 2H, $J=8.8$ Hz), 7.91 (d, 2H, $J=8.8$ Hz); Mass (ES) $\text{C}_8\text{H}_7\text{O}_2\text{Br}$: m/z 215 $[\text{M}]^+$, 216 $[\text{M}+\text{H}]^+$.

Methyl 4-fluorobenzoate (3i): Liquid, b.p.: 196-198 °C, IR (KBr, ν_{max} , cm^{-1}): 3079, 3000, 2954, 1728, 1602, 1508, 1436, 1154, 1112, 1015, 967, 855, 767, 607. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.91 (s, 3H), 7.13 (3, 2H), 8.07 (m, 2H); Mass (ES) $\text{C}_8\text{H}_7\text{O}_2\text{F}$: m/z 154 $[\text{M}]^+$, 155 $[\text{M}+\text{H}]^+$.

Methyl 3-amino-4-methoxybenzoate (3j): Solid, m.p.: 84-86 °C, IR (KBr, ν_{max} , cm^{-1}): 3431, 3354, 2953, 1698, 1688, 1593, 1517, 1445, 1182, 1117, 1025, 881, 763. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.86 (s, 3H), 3.87 (s, 2H), 3.90 (s, 3H), 6.80 (d, 1H, $J=8.4$ Hz), 7.38 (s, 1H), 7.48-7.45 (dd, 1H, $J=8.8$ Hz, $J=2.0$ Hz); Mass (ES) $\text{C}_9\text{H}_{11}\text{O}_3$: m/z 181 $[\text{M}]^+$, 182 $[\text{M}+\text{H}]^+$.

Methyl 3-chloro-4-methoxybenzoate (3k): Solid, m.p.: 95-96 °C, IR (KBr, ν_{max} , cm^{-1}): 3385, 2957, 1703, 1601, 1504, 1430, 1240, 1061, 1018, 762. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.89 (s, 3H), 3.96 (s, 3H), 6.90 (d, 1H, $J=8.8$ Hz), 7.95-7.92 (dd, 1H, $J=8.8$ Hz, $J=2.0$ Hz), 8.05 (s, 1H); Mass (ES) $\text{C}_9\text{H}_9\text{O}_3\text{Cl}$: m/z 200 $[\text{M}]^+$, 201 $[\text{M}+\text{H}]^+$.

Methyl 4-methoxybenzoate (3l): Solid, m.p.: 48-50 °C, IR (KBr, ν_{max} , cm^{-1}): 3397, 2952, 2842, 1925, 1713, 1608, 1511, 1428, 1286, 1168, 1105, 964, 847, 770, 698. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.86 (s, 3H), 3.88 (s, 3H), 6.93 (d, 2H, $J=9.2$ Hz), 8.01 (d, 2H, $J=9.2$ Hz); Mass (ES) $\text{C}_9\text{H}_{10}\text{O}_3$: m/z 166 $[\text{M}]^+$, 167 $[\text{M}+\text{H}]^+$.

Methyl 4-nitrobenzoate (3m): Solid, m.p.: 96-98 °C, IR (KBr, ν_{max} , cm^{-1}): 3423, 3112, 3078, 1718, 1524, 1442, 1275, 1104, 721. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.98 (s, 3H), 8.23 (d, 2H, $J=8.8$ Hz), 8.30 (d, 2H, $J=8.8$ Hz); Mass (ES) $\text{C}_8\text{H}_7\text{O}_4$: m/z 181 $[\text{M}]^+$, 182 $[\text{M}+\text{H}]^+$.

Methyl 4-hydroxybenzoate (3n): Solid, m.p.: 127-128 °C, IR (KBr, ν_{max} , cm^{-1}): 3314, 1680, 1607, 1588, 1162, 955, 850, 772, 698. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.89 (s, 3H), 6.02 (b, 1H), 6.89 (d, 2H, $J=8.8$ Hz), 7.97 (d, 2H, $J=8.8$ Hz); Mass (ES) $\text{C}_8\text{H}_8\text{O}_3$: m/z 152 $[\text{M}]^+$, 153 $[\text{M}+\text{H}]^+$.

Ethyl acrylate (3o): Liquid, b.p.: 98-100 °C, IR (KBr, ν_{max} , cm^{-1}): 2985, 1743, 1409, 1198, 1063, 809. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 1.32 (t, 3H, $J=7.2$ Hz), 4.24 (q, 2H, $J=7.2$ Hz), 5.83 (d, 1H, $J=9.2$ Hz), 6.15 (q, 1H, $J=10.4$ Hz), 6.42 (d, 1H, $J=16$ Hz); Mass (ES) $\text{C}_5\text{H}_8\text{O}_2$: m/z 100 $[\text{M}]^+$, 101 $[\text{M}+\text{H}]^+$.

Butyl acrylate (3p): Liquid, b.p.: 145-146 °C, IR (KBr, ν_{max} , cm^{-1}): 2962, 1727, 1408, 1192, 1067, 810. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 0.96 (t, 3H, $J=7.2$ Hz), 1.45 (m, 2H), 1.69 (m, 2H), 4.18 (t, 2H, $J=6.4$ Hz), 5.82 (d, 1H, $J=8.8$ Hz), 6.13 (t, 1H, $J=6.4$ Hz), 6.42 (d, 1H, $J=16$ Hz); Mass (ES) $\text{C}_7\text{H}_{12}\text{O}_2$: m/z 128 $[\text{M}]^+$, 129 $[\text{M}+\text{H}]^+$.

RESULTS AND DISCUSSION

In present work, from XRD analysis (Fig. 1), it was observed that both samples of ZrO_2 and tungsten promoted ZrO_2 exhibited only in the tetragonal phase [18]. Using Debye-Scherrer equation, average crystallite size calculated was found to be 28 nm for ZrO_2 and tungsten promoted ZrO_2 catalysts.

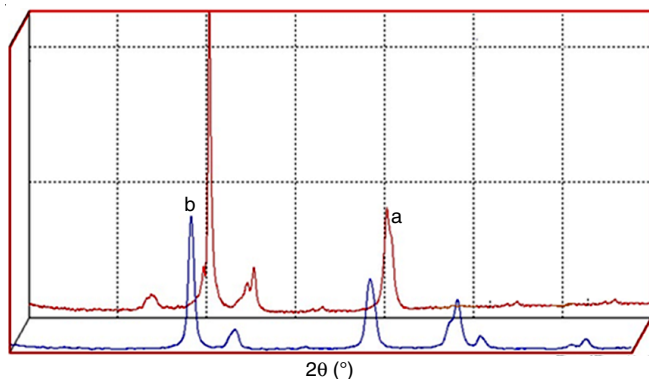


Fig. 1. XRD patterns of (a) 3% WO_3/ZrO_2 (b) Pure ZrO_2

SEM studies: SEM photographs of both catalysts are shown in Fig. 2. There is not much change in SEM photographs of ZrO_2 and tungsten endorsed ZrO_2 catalysts signifying small change in structure of ZrO_2 by incorporating W atoms. It is observed that the particles are homogeneously distributed all over the surface and spherical in shape. Average crystallite size of the particles is detected to be same in both the samples.

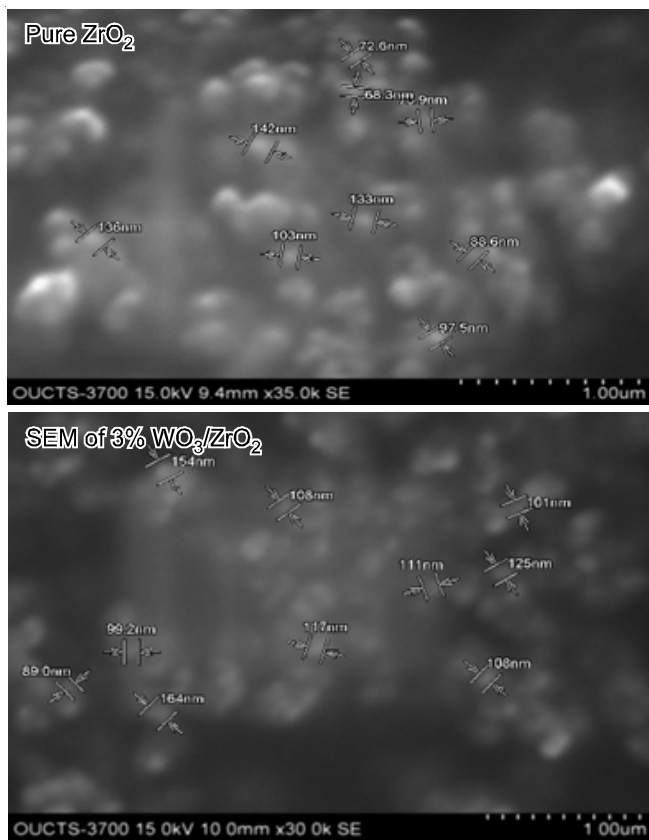


Fig. 2. SEM images of ZrO_2 and 3% WO_3/ZrO_2

UV-DRS studies: A conspicuous shift of the absorption spectrum (Fig. 3) to a lower energy region was observed for WO_3/ZrO_2 . Besides, the surface acidity of WO_3/ZrO_2 catalysts [17] and hence its catalytic activity could have been increased due to the inclusion of WO_3 .

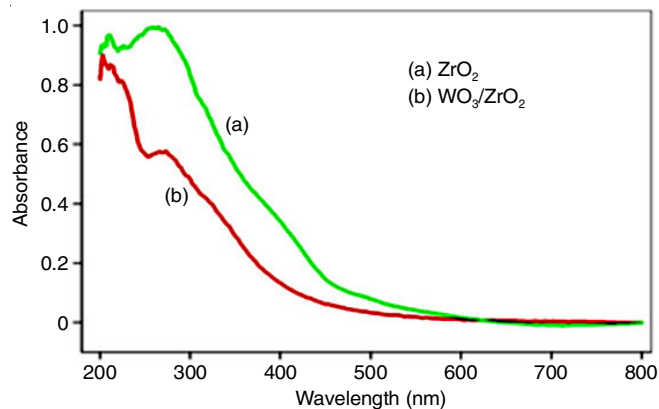


Fig. 3. UV-DRS spectra of ZrO_2 and 3% WO_3/ZrO_2

FTIR studies: After calcination at 650 °C, FTIR spectrum (Fig. 4) displays two shoulders at 1067 and 937 cm^{-1} . At 3400 cm^{-1} , the peak is corresponding to condensed hydroxyl groups and other major bands were observed at 746, 557, 514 and 500 cm^{-1} , which are the characteristics of crystalline zirconia [19,20].

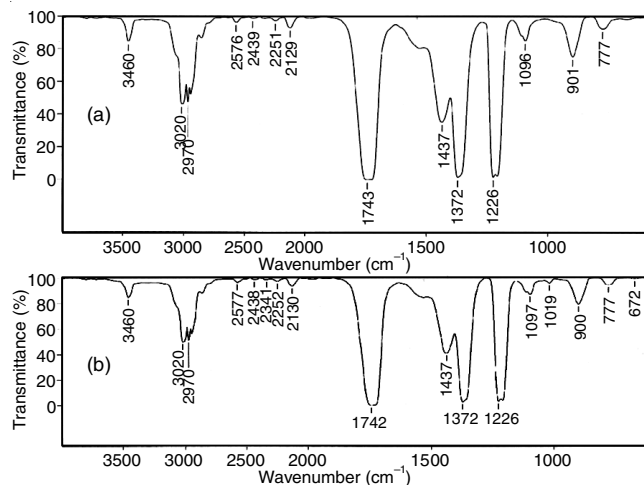
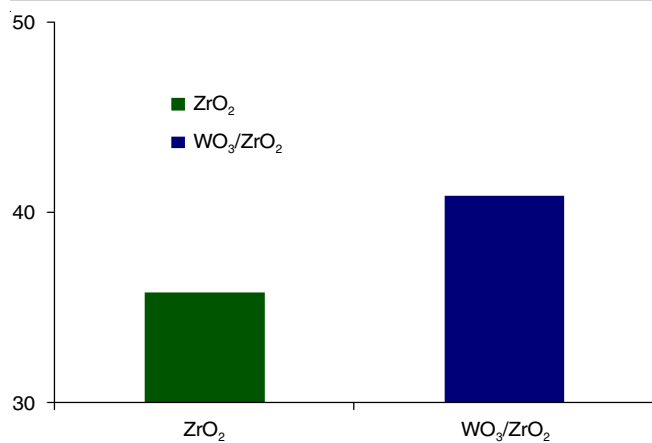


Fig. 4. IR spectra of (a) Zirconia and (b) WO_3

Surface area: In comparison to pure ZrO_2 , the presence of WO_3 in ZrO_2 increases the surface area (Fig. 5), which reflects an increase in the surface acidity of the catalyst.

Catalytic activity of esterification: The esterification reaction was carried out between organic acids and alcohols in presence of tungsten promoted ZrO_2 under solvent free condition. Pure ZrO_2 and tungsten promoted ZrO_2 do not have the same activity in esterification reactions to form esters at 80 °C. Tungsten promoted ZrO_2 forms the product ester in 2.5-4.0 h, whereas pure zirconia is totally inactive. Higher activity of tungsten promoted ZrO_2 catalyst is due to the uniform distribution of spherical particles all over the zirconia lattice

Fig. 5. Surface area of ZrO₂ and WO₃/ZrO₂

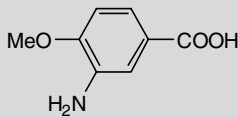
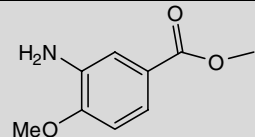
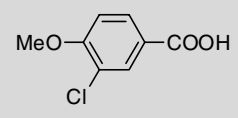
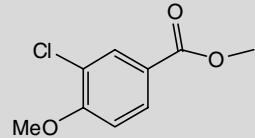
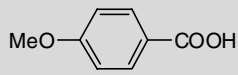
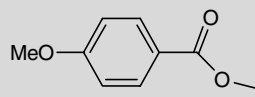
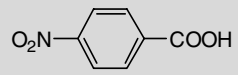
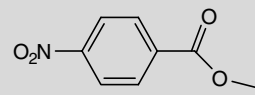
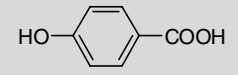
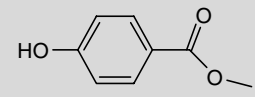
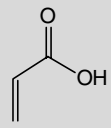

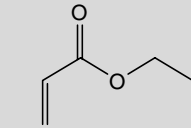
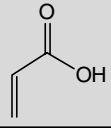
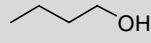
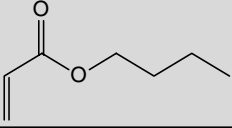
and producing lattice defects by altering surface and bulk properties to the small extent. Isolated yields (Table-1) are compared with reliable samples.

Conclusion

By using impregnation method, WO₃/ZrO₂ catalyst has been prepared and calcined at 923 K for 6 h in atmospheric air. Both ZrO₂ and WO₃/ZrO₂ samples exhibited a tetragonal phase but incorporation of promoter WO₃ into ZrO₂ lattice stabilizes the tetragonal phase. According to SEM images, the higher activity of WO₃/ZrO₂ particles is due to uniform distribution of particles on the surface producing lattice defects by altering surface and bulk properties. Esterification reaction is carried out using WO₃/ZrO₂ catalyst under solvent free condition with high yields.

TABLE-1
CATALYTIC ESTERIFICATION OF CARBOXYLIC ACID USING WO₃/ZrO₂

Entry	Reactant (1)	Reactant (2)	Product (3)	Reaction time (h)	Yield (%)
a	CH ₃ COOH			3.0	88
b				3.5	89
c				3.5	90
d				3.0	92
e				4.0	92
f		CH ₃ -OH		3.0	90
g		CH ₃ -OH		3.5	93
h		CH ₃ -OH		3.5	95
i		CH ₃ -OH		3.0	95

j		CH ₃ -OH		3.0	90
k		CH ₃ -OH		3.5	91
l		CH ₃ -OH		3.0	95
m		CH ₃ -OH		3.0	94
n		CH ₃ -OH		4.0	94
o				2.5	89
p				3.0	90

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- J. Otera, *Chem. Rev.*, **93**, 1449 (1993); <https://doi.org/10.1021/cr00020a004>
- A.S. Franklin, *J. Chem. Soc. Perkin Trans.*, 2451 (1998); <https://doi.org/10.1039/a705687g>
- Y. Nishimoto, S.A. Babu, M. Yasuda and A. Baba, *J. Org. Chem.*, **73**, 9465 (2008); <https://doi.org/10.1021/jo801914x>
- S.P. Chavan, S. Garai, A.K. Dutta and S. Pal, *Eur. J. Org. Chem.*, **2012**, 6841 (2012); <https://doi.org/10.1002/ejoc.201201181>
- M.S. Newman, *J. Am. Chem. Soc.*, **63**, 2431 (1941); <https://doi.org/10.1021/ja01854a033>
- J. Otera, *Angew. Chem. Int., Ed.*, **40**, 2044 (2001); [https://doi.org/10.1002/1521-3773\(20010601\)40:11<2044::AID-ANIE2044>3.0.CO;2-Y](https://doi.org/10.1002/1521-3773(20010601)40:11<2044::AID-ANIE2044>3.0.CO;2-Y)
- W.B. Pan, F.R. Chang, L.M. Wei, M.J. Wu and Y.C. Wu, *Tetrahedron Lett.*, **44**, 331 (2003); [https://doi.org/10.1016/S0040-4039\(02\)02578-9](https://doi.org/10.1016/S0040-4039(02)02578-9)
- K. Ramalinga, P. Vijayalakshmi and T.N.B. Kaimal, *Tetrahedron Lett.*, **43**, 879 (2002); [https://doi.org/10.1016/S0040-4039\(01\)02235-3](https://doi.org/10.1016/S0040-4039(01)02235-3)
- M.I. De Sairre, E.S. Bronze-Uhle and P.M. Donate, *Tetrahedron Lett.*, **46**, 2705 (2005); <https://doi.org/10.1016/j.tetlet.2005.01.158>
- L.I. Koval, V.I. Dzyuba, O.L. Ilnitska and V.I. Pekhnyo, *Tetrahedron Lett.*, **49**, 1645 (2008); <https://doi.org/10.1016/j.tetlet.2008.01.018>
- D. Jiang, Y.Y. Wang, M. Tu and L.Y. Dai, *Chin. Chem. Lett.*, **19**, 889 (2008); <https://doi.org/10.1016/j.cclet.2008.04.035>
- G.B.B. Varadwaj and K.M. Parida, *Catal. Lett.*, **141**, 1476 (2011); <https://doi.org/10.1007/s10562-011-0684-1>
- B.M. Reddy, V.R. Reddy and B. Manohar, *Synth. Commun.*, **29**, 1235 (1999); <https://doi.org/10.1080/00397919908086095>
- V.C. Guguloth, G. Raju, M. Basude and S. Battu, *Int. J. Chem. Anal. Sci.*, **5**, 86 (2014).
- V. Banothu, M. Basude and S. Battu, *J. Chem. Pharm. Res.*, **5**, 97 (2013).
- M. Basude and V.S. Sunkara, *J. Chem. Pharm. Res.*, **5**, 46 (2013).
- H.R. Chen, J.L. Shi, J. Yu, L.Z. Wang and D.S. Yan, *Micropor. Mesopor. Mater.*, **39**, 171 (2000); [https://doi.org/10.1016/S1387-1811\(00\)00193-1](https://doi.org/10.1016/S1387-1811(00)00193-1)
- 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>
- J.R. Sohn and M.Y. Park, *Langmuir*, **14**, 6140 (1998); <https://doi.org/10.1021/la980222z>
- K.V. Bineesh, D.K. Kim and D.W. Park, *Nanoscale*, **2**, 1222 (2010); <https://doi.org/10.1039/C0NR00108B>