

ESTERIFICATION BY ZrO_2 AND $Mo-ZrO_2$ ECO-FRIENDLY SOLID ACID CATALYSTS

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ABSTRACT: Esterification of mono- and dicarboxylic acids catalysed by single (ZrO_2) and mixed oxide ($Mo-ZrO_2$) eco-friendly solid acid catalysts is described. The $Mo-ZrO_2$ catalyst exhibits better catalytic performance than ZrO_2 .

Esters are useful as solvents and in making artificial flavours and essences. The conventional catalyst used in catalyzing esterification reaction is sulfuric acid.¹ However, it is toxic, corrosive, produces large amount of by-products and difficult to separate from the reaction medium. Sulfuric acid is replaced by p-toluene sulfonic acid in homogeneous catalysis and SO_3-H resins in heterogeneous catalysis.² Recycling of these catalysts is also often difficult, expensive and partial sulfonation of the product is possible. Non-acidic alkyl titanates are the new generation catalysts having the advantage of low by-product formation, however, require very high temperatures (>473 K).

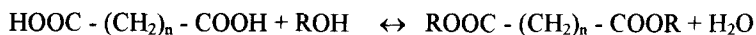
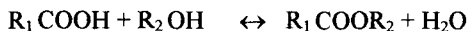
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In view of environmental concern, there is a global effort to replace the conventional catalysts by solid acids which are easily separable from the products, less toxic, and reusable. Esterification was carried out under batch and flow conditions over decaionized Y-zeolite,³ niobic acid,^{4,5} solid super acids,⁶ heteropoly acids,⁷⁻⁹ and heteropoly acids supported on carbon.^{10,11} Sulfated zirconia is another good catalyst for esterification, however, gets deactivated easily by loosing sulfate ions and thereby recycling of the catalyst is restricted. In case of heteropoly acids the separation is difficult and when supported on carbon the activity decreases. In this communication we report esterification of various mono- and dicarboxylic acids by single oxide (ZrO_2) and binary oxide ($Mo-ZrO_2$) solid acid catalysts. Zirconia is an interesting catalytic material possesses acidic, basic, oxidizing and reducing properties on the surface and these four surface properties including phase modifications change independently with the method of preparation and pre-treatment temperature.¹²⁻¹⁴

Alcohol or acid is taken in excess to make the reaction proceed in forward direction and also to see that the reaction is complete. The activity and selectivity results obtained are presented in Table I. After completion of the reaction, the reaction mixture was separated and the wet catalyst is used for recycling. No change in the activity was observed.

The acidic and basic properties of ZrO_2 can be modified by the addition of anionic or cationic substances. The $Mo-ZrO_2$ mixed oxide catalyst exhibited higher acidity than ZrO_2 single oxide catalyst which is due to electron deficient state formed by the introduction of Mo cations into the lattice of ZrO_2 solid. In

TABLE I : Catalytic esterification of mono- and dicarboxylic acids using ZrO₂ and Mo-ZrO₂ eco-friendly catalysts.



Entry	Catalyst	Carboxylic acid	Alcohol	Product	Yield ^a (%)
1	Mo-ZrO ₂	CH ₃ COOH	Bu-OH	CH ₃ COOBu	95
	ZrO ₂				94
2	Mo-ZrO ₂	CH ₃ COOH	$\text{>CH}_2\text{OH}$	$\text{CH}_3\text{COOCH}_2\text{<}$	85
	ZrO ₂				70
3	Mo-ZrO ₂	PhCOOH	BuOH	PhCOOBu	57
	ZrO ₂				30
4	Mo-ZrO ₂	CH ₃ COOH	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OCOCH}_3 \\ \\ \text{CH}_2\text{OCOCH}_3 \end{array}$	63
	ZrO ₂				21
5	Mo-ZrO ₂	CH ₃ COOH	PhCH ₂ OH	CH ₃ COOCH ₂ Ph	71
	ZrO ₂				52
6	Mo-ZrO ₂	CH ₃ COOH	C ₆ H ₁₁ OH ^b	c	-
	ZrO ₂				-
7	Mo-ZrO ₂	$\begin{array}{c} \diagup \text{COOH} \\ \text{CH}_2 \\ \diagdown \text{COOH} \end{array}$	CH ₃ OH	$\begin{array}{c} \diagup \text{COOCH}_3 \\ \text{CH}_2 \\ \diagdown \text{COOCH}_3 \end{array}$	95
	ZrO ₂				50
8	Mo-ZrO ₂	$\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$	CH ₃ OH	$\begin{array}{c} \text{COOCH}_3 \\ \\ \text{COOCH}_3 \end{array}$	77
	ZrO ₂				-

^a Based on GC analysis, ^b Cyclohexanol, ^c No reaction.

conclusion, the Mo-ZrO₂ is an efficient catalyst for esterification reactions. The advantages are the ease of operation and simplicity in work up which involves mere filtration of the catalyst and reusability.

Preparation of the Catalyst: To make ZrO₂ catalyst, about 5 g of ZrOCl₂.8H₂O (Loba Chemie, GR grade) was dissolved in 40 ml of doubly distilled water. The pH

of the solution was 2. Dilute ammonia solution was added slowly until the pH of the solution reached 7 with continuous stirring. The obtained precipitate was washed with distilled water several times until free from chloride ions and dried at 393 K for 48 h. The oven dried sample was calcined at 873 K in a flow of oxygen for 5 h. For the preparation of 9% Mo-ZrO₂ catalyst, 0.5459 g of ammonium heptamolybdate (JT Baker, England; GR grade) was dissolved in 20 ml of 1M oxalic acid solution. To this clear solution 3 g of Zr(OH)₄ was added and the excess water was evaporated on a water bath. Thus obtained sample was oven dried at 393 K for 48 h and finally calcined at 873 K for 5 h in a flow of oxygen. The X-ray powder diffraction profiles of both the samples show the presence of tetragonal ZrO₂ phase and ZrMo₂O₈ in the case of Mo-ZrO₂ sample.

General Procedure for Esterification: A mixture of acid (1 g), alcohol (excess) and catalyst (0.1 g) was heated at 358 K for 6 h in a round bottomed flask provided with condenser. After completion of the reaction conversion and selectivities are obtained quantitatively by using gas chromatography with a 10% OV-17 column and FID detector and qualitatively by NMR. After completion of the reaction, catalyst was filtered, NaHCO₃ solution was added to the filtrate and extracted with ether. The organic layer was dried with (anhydrous) Na₂SO₄, concentrated and chromatographed on SiO₂.

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