



Transesterification of diethyl malonate with benzyl alcohol catalyzed by modified zirconia: Kinetic study



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ABSTRACT

Zirconia and its modified forms such as 10%Mo(VI)/ZrO₂, 10%V(V)/ZrO₂, 10%W(VI)/ZrO₂ and SO₄²⁻/ZrO₂ were prepared and characterized for their physico-chemical properties such as BET for surface area, NH₃-TPD and *n*-butylamine back titration method for total surface acidity, PXRD technique for crystallinity and ICP-OES technique for elemental analysis. These materials were used as catalysts in liquid phase transesterification reaction of diethyl malonate (DEM) with benzyl alcohol (BA). Optimization of reaction conditions such as reaction time, reaction temperature, weight of the catalyst and molar ratio of reactants were carried out to obtain highest possible transester yield. Dibenzyl malonate (DBM) and benzyl ethyl malonate (BEM) were obtained as major products. Highest total transester yield of (88%) was obtained in the presence of 0.75 g of SZ catalyst at a molar ratio of DEM: BA = 1:3, reaction temperature of 393 K and reaction time 5 h. Kinetic studies were carried out to find out the rate of the reaction and energy of activation values for zirconia catalysts, in order to identify a facile catalyst system for this reaction. A possible reaction mechanism was proposed based on the kinetic data and it was observed that Eley-Rideal mechanism fits well for this reaction. Reactivation and reusability studies of the catalysts were also taken up.

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1. Introduction

Solid acids are safe and eco-friendly than liquid acids such as, H₂SO₄, HCl, HF, AlCl₃, BF₃, ZnCl₂ and SbF₅ due to their specific features such as non-toxic, non-corrosive, easy to handle, easily recoverable, reusable and less expensive. Various solid acids such as zeolites, cation exchange resins, metal oxides and their modified forms, doped metal oxides, etc., have been successfully used as catalysts for many acid catalyzed organic transformations such as isomerization [1], dehydration [2], acylation [3], oxidation [4], transesterification [5,6], esterification reaction [7], etc.

Now-a-days metal oxide-based catalysts are active over a wide range of temperatures and having high resistance to thermal excursions. Over the past few years, the preparation, characterization and advantages of zirconia based solid acids have gained much attention in various organic transformations due to their non-toxicity, super acidity, simplified product isolation, high selectivity, reduction of wasteful byproducts and high activity at low temperatures [8–10].

Some modified oxides exhibit strong surface acidity due to generation of large number of positive or negative charge in the binary oxide model structure. Modified forms such as SO₄²⁻, Mo(VI), V(V) and W(VI) supported on ZrO₂ exhibit strong acidity and excellent catalytic activity towards various organic transformations in the liquid phase [5,6,11–17].

Esters, which are having wide range of category in organic compounds ranging from aliphatic to aromatic, are important intermediates in the synthesis of drugs, food preservatives, plasticizers, fine chemicals, cosmetics, perfumery, solvents, chiral-auxiliaries, agro chemicals and also as precursors for a number of pharmaceutical products. Especially, malonic esters are known for their importance either as starting materials or intermediates in organic fine chemical synthesis [18,19].

Keeping in view the importance of zirconia based solid acids and benzyl malonate esters, the goal of the present work has been set to explore the use of solid acids such as zirconia and its modified forms like Mo(VI)/ZrO₂ (MZ), V(V)/ZrO₂ (VZ), W(VI)/ZrO₂ (WZ) and SO₄²⁻/ZrO₂ (SZ) in acid catalyzed transesterification of DEM with BA. The total transester yield and percentage selectivity towards the desired product was optimized by varying reaction time, reaction temperature, weight of the catalyst and molar ratio of the reactants.

In order to find out the best catalyst for transesterification of DEM with BA among those used in the present study, kinetic studies

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were carried out to find out the data such as rate of the reaction and energy of activation.

The Langmuir-Hinshelwood (LH) model or an Eley-Rideal (ER) model is commonly used to correlate the kinetic data for the solid acid catalyzed reactions [20–22]. These two models are derived based on the assumption that the rate limiting step is the surface reaction between two adsorbed molecules (LH) or between an adsorbed molecule and a molecule in the bulk (ER). Attempt has been made to correlate the kinetic data into LH and ER models and describe the reaction mechanism for the transesterification of DEM and BA based on the best fit.

2. Experimental

2.1. Preparation of catalytic materials

2.1.1. Preparation of hydrated ZrO₂

Hydrated zirconia (Zr(OH)₄) was prepared by precipitation method. 100 g of zirconium oxychloride (ZrOCl₂·8H₂O) was dissolved in 250 ml of deionized water and the solution was heated to 353 K for about 10 min. To this 1:1 aqueous ammonia solution was added dropwise with constant stirring. Thus obtained precipitate of Zr(OH)₄ was filtered, washed with deionized water until it becomes chloride free. Thus obtained precipitate was dried in hot air oven at 393 K for 12 h.

2.1.2. Preparation of MZ, VZ and WZ

MZ, VZ and WZ were prepared by impregnation method. Typically, MZ was prepared by making a paste of 9.1 g of zirconyl nitrate (ZrO(NO₃)₂·H₂O) and 0.7 g of ammonium molybdate ((NH₄)₆Mo₇O₂₄·H₂O) with approximately 10 ml of deionized water. The paste was dried in hot air oven at 393 K for 12 h and made a fine powder. Similarly, VZ and WZ were prepared by using zirconyl nitrate, ammonium metavanadate and ammonium tungstate.

2.1.3. Preparation of sulfated zirconia (SZ)

SZ was prepared by making a fine paste of 10 g of previously prepared Zr(OH)₄ with 6 ml of 3 M H₂SO₄. The resulting paste was dried in a hot air oven at 393 K for 12 h and finely powdered.

Thus prepared samples were calcined in a muffle furnace at 832 K for 5 h before their use as catalytic material.

2.2. Characterization of catalytic materials

The specific surface area of all the prepared catalysts were measured by NOVA 1000 Quanta chrome high-speed gas sorption analyzer instrument. In this analysis, the catalytic material was degassed at 523 K for 5 h before measurements. Specific surface area of catalyst was determined by BET conventional method. The total surface acidity of the catalytic material was measured by NH₃-TPD method by using Plus Chemisorb 2705 from Micromeritics and also by *n*-butyl amine back titration method using dry benzene as a solvent. The zirconia catalysts were characterized for their powder XRD using Xpert Pro Philips diffractometer equipped with a Ni filtered Cu-K α radiation with $\lambda = 1.5418 \text{ \AA}$ using a graphite crystal monochromator in the range of scanning 25–60°. The amount of tungsten, vanadium and molybdenum present in WZ, VZ and MZ catalyst samples was estimated by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) analysis technique using Thermo-iCAP 6000 Series instrument.

2.3. Catalytic activity measurement

The liquid phase transesterification of diethyl malonate (DEM) with benzyl alcohol (BA) in presence of catalytic material was carried out in a 25 ml round bottomed flask on a hot plate cum

magnetic stirrer. The total volume of the reaction mixture was kept constant at 10 ml. After a definite period of time the reaction mixture was cooled, filtered and the filtrate was analyzed by gas chromatograph (GC) fitted with 10% carbowax column coupled with flame ionization detector and qualitatively by LCMS (Agilent).

To optimize the reaction conditions, parameters such as reaction time, reaction temperature, weight of the catalyst and molar ratio of the reactants were varied. Kinetic studies were conducted in the reaction time from 1 to 9 h, temperature ranging from 353 to 453 K, by varying catalyst weight in the range of 0.25–1.00 g and molar ratio of DEM: BA = 1:2–1:5 (with excess of BA) and with molar ratio of BA: DEM = 1:0.33–1:2 (with excess of DEM). The effect of nature of catalyst was also studied to find a facile catalyst desirable for transesterification of DEM with BA. Kinetic studies were carried out in presence of these short listed catalysts.

2.4. Reusability of catalytic materials

To study the reusability of the catalytic materials, used catalytic material was filtered from the reaction mixture, washed with acetone, dried at 393 K for 2 h and calcined at 832 K for 2 h. Thus obtained reactivated catalyst was subjected to transesterification of DEM with BA under similar reaction conditions. The re-usability of re-activated catalysts were carried out for 5 consecutive reaction cycles.

3. Results and discussion

3.1. Characterization of catalytic materials

Zirconia and its modified forms were characterized for their physico-chemical properties such as surface area, total surface acidity (along with acid site distribution) and % of metal ions and the data are given in Table 1.

The results obtained from ICP-OES indicated the modified forms of zirconia i.e., WZ, VZ and MZ consisted of 10.32%W(VI), 10.59%V(V) and 9.87%Mo(VI) respectively. The BET surface area of zirconia and its modified forms are presented in Table 1. The surface area is in the increasing order of ZrO₂ < WZ < VZ < MZ < SZ. The surface area of zirconia increases when impregnated with WO_x, VO_x, MoO_x or SO₄²⁻ ions. Among these, SZ is found to have higher surface area which is attributed to the cracking of ZrO₂ crystallinity into fine particles when treatment with sulfate ions [23]. In case of other modified forms, increase of the surface area is related to the formation of M–O–Zr (M = W or V or Mo) linkages resulting in a porous material [24]. The interaction of metal ions with zirconia also protects from sintering and hence bear the highest surface area. This phenomenon can again be directly correlated with tetragonal crystalline phase because tetragonal crystalline size is relatively smaller than monoclinic phases [25].

The total surface acidity (TSA) as well as acid site distribution of zirconia and its modified forms measured by NH₃-TPD method are given in Table 1. The TSA of the catalysts are in the order: ZrO₂ < WZ < VZ < MZ < SZ. It also indicates that the impregnated WO_x, VO_x, MoO_x and SO₄²⁻ ions have a strong influence on the acidic properties of zirconia. The TSA values of the catalysts were also determined by *n*-butylamine back titration method and their values are in good agreement with the TSA values obtained by NH₃-TPD method. When the values of acid site distribution of different zirconia catalysts were compared, pure zirconia consisted of only 'weak and medium' acid sites. Whereas, modified forms of zirconia i.e., WZ, VZ, and MZ consisted of 'medium and strong' acid sites. However, SZ was found to have 'strong and very strong' acid sites (super acid sites). Further, the acid site distribution values are in good agreement with the values provided in the literature [26].

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