

Liquid phase transesterification of methyl salicylate and phenol over solid acids: Kinetic studies

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Abstract

The liquid phase transesterification of methyl salicylate and phenol to synthesize a value added ester, salol has been studied over the catalysts, ZrO₂ (Z), SO₄²⁻/ZrO₂ (SZ) and Mo(VI)/ZrO₂ (MZ). Physical and chemical characterization of the catalysts in the form of sulfur and Mo(VI) contents, BET surface area, total surface acidity and powder XRD were conducted. Effects of various parameters, such as speed of agitation of reaction mixture, mole ratio of reactants, catalyst weight, reaction temperature and reaction time were studied to optimize the reaction conditions. ZrO₂ and Mo(VI)/ZrO₂ were 100% selective towards the formation of salol, but in the case of SO₄²⁻/ZrO₂ diphenyl ether was also formed as a by-product. The conversion of phenol was correlated with surface acidity of the catalysts and the structure of ZrO₂. The conversion of phenol was found to increase with an increase in reaction temperature from 393 to 423 K and also increased with an excess of methyl salicylate in the reacting system. The kinetic studies suggested that the reaction follows the Eley–Rideal model and a possible reaction mechanism is proposed. The energy of activation of the catalysts in the reaction followed the order Z > MZ ≥ SZ.

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1. Introduction

Transesterification is one of the classic organic reactions that have enjoyed numerous laboratory uses and industrial applications. Organic chemists make use of this reaction quite often as a convenient means to prepare esters.

Transesterification is an equilibrium process, where a carboxylic ester is transformed into another through interchange of the alkoxy moiety in the presence of Brønsted acidic catalysts, such as sulfuric, sulfonic, phosphoric, hydrochloric acids or basic catalysts like sodium and potassium alkoxides, metal acetates, metal carbonates, etc. [1–4].

Although many effective and reliable methods for the preparation of aromatic esters exist, there is still an ample scope for research towards finding eco-friendly and economically viable processes. The use of the above-mentioned liquid catalysts is undesirable from the environmental point of view as these chemicals are corrosive and generally encounter the problems of

handling and transportation. Moreover, high product selectivity and reusability of the catalysts cannot be expected. Hence, there are numerous global efforts to replace these environmentally harmful chemicals with more eco-friendly and less expensive catalysts [5]. Solid acids, such as zeolites, cation exchange resins, metal oxides and AlPOs and their modified forms have been found to be safe alternatives for such conventional liquid acid catalysts used in synthetic organic chemistry in petroleum refining, fine chemicals synthesis, pharmaceutical industries, etc. [6–8].

The salicylate esters are an important group of esters used for the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, solvents, perfumes and cosmetics [9]. Generally, phenyl esters of salicylic acid, such as phenyl salicylate which has a commercial name 'salol' are prepared under liquid phase by refluxing the reactants (carboxylic acid and phenol) in the presence of small amount of concentrated H₂SO₄, HCl, POCl₃ or sulphonic acid as the catalysts [10]. Recently, we have used zeolites and sulfated oxides as catalysts in the synthesis of phenyl salicylate (salol) via esterification of phenol and salicylic acid. The catalysts showed a decrease in their activity when they were reused, due to the deactivation of the catalytic centers by the

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water formed as the by-product during esterification reaction [8]. Thus, the anhydrous condition prevalent in transesterification of methyl salicylate and phenol is an additional advantage.

A simple mechanism of transesterification of an ester with phenol includes the following steps. In the first step, the ester accepts a proton from the acid site of a solid acid. The second step is the nucleophilic attack of a phenol molecule to the carbonyl-carbon of ester to give an intermediate. In the final step, a proton is transferred from one oxygen to another to form another intermediate, which further loses a molecule of alcohol and proton to give a phenyl ester. All these steps are reversible.

The goal of the present work was to develop an environmentally benign catalyst system that combines good catalytic performance with satisfactory recovery of the catalysts used. ZrO_2 is an interesting catalytic material and can be prepared in many ways with various modifications. It possesses acidic, basic, oxidizing and reducing properties on the surface and these four properties, including phase modifications (monoclinic or tetragonal) change independently with the method of preparation and heat treatment. The acid–base properties of zirconia can be modified by the addition of anionic or cationic substances. Generally, it has been observed that the acidic properties of the modified forms of ZrO_2 will be higher than ZrO_2 itself [11].

Here, we report the use of zirconia and sulfate and molybdenum(VI) ions modified zirconia as catalysts in the liquid phase transesterification of methyl salicylate with phenol. The results obtained were very encouraging in the sense that the solid acids not only showed $\sim 100\%$ selectivity but also high activity towards the formation of salol. The effect of molar ratio of the reactants, catalyst weight, reaction temperature and reaction time on the yield of salol has been studied. Kinetic data on the transesterification reaction over solid acids are not widely available. In this work, we have tried to obtain various kinetic parameters in the transesterification of methyl salicylate and phenol. The Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) models are commonly used to correlate the kinetic data for the solid acid catalyzed reactions [12–14]. 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). We have tried to fit the kinetic data into LH and ER models and describe the reaction mechanism for the transesterification of methyl salicylate and phenol based on the best fit.

2. Experimental

2.1. Preparation of the catalytic materials

Hydrated ZrO_2 was obtained by the following precipitation method. Twenty-five grams of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in 250 mL deionised water. To this clear solution, aqueous ammonia was added drop-wise from a burette with constant stirring. Thus, obtained precipitate of $\text{Zr}(\text{OH})_4$ was washed thoroughly to remove the soluble ions and dried in an air oven at 393 K for 12 h.

Sulfate or Mo(VI) ion modified zirconia was prepared as follows:

- Sulfated zirconia was prepared by impregnating 3 g of hydrated zirconia with 1.5 mL of 3 M H_2SO_4 . The mixture was thoroughly mixed to form a paste which was then dried in an air oven at 393 K for 12 h [6].
- Similarly, 2%Mo(VI)/ ZrO_2 was prepared by impregnating 3 g of hydrated zirconia support with 0.2 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ [15].

The hydrated zirconia and their modified forms were calcined to 823 K for 5 h in a muffle furnace before their use as catalysts. Thus, prepared catalysts were denoted by (Z) for ZrO_2 , (SZ) for $\text{SO}_4^{2-}/\text{ZrO}_2$ and (MZ) for 2%Mo(VI)/ ZrO_2 .

2.2. Catalyst characterization

All the catalysts were analyzed for sulfur and molybdenum(VI) content, BET surface area, total surface acidity and powder XRD. The amount of sulfur in sulfated catalysts was obtained by conducting elemental analysis using an Elementar Vario EL III Carlo Erba 1108 instrument. The Mo(VI) content in MZ sample was determined by energy dispersive X-ray (EDX) analysis using a Stereo scan 440 apparatus. The BET surface area of the samples was measured using nitrogen as the adsorbent in a NOVA-1000 high speed gas sorption analyzer version 3.70. The total surface acidity was measured by NH_3 -TPD measurement on an AutoChem-2910 instrument and also by the *n*-butylamine back titration method [16], using dry benzene as solvent and bromothymol blue as indicator. The X-ray powder diffraction patterns of all the samples were collected on a Siemens-D5005 X-ray diffractometer with a Ni filtered $\text{Cu K}\alpha$ radiation (1.5418 Å).

2.3. Catalytic activity studies

The catalytic activity of all the catalysts was determined in liquid phase transesterification of methyl salicylate with phenol in a 100 mL round bottomed (RB) flask fitted with water-cooled condenser in an oil bath with continuous stirring. Methyl salicylate (MS), phenol (P) and the catalyst were taken in the RB flask and heated for a definite period. The total volume of the reaction mixture was kept constant at 15 mL in all the reactions. After a definite period of time, the reaction mixture was cooled to room temperature and filtered. The filtrate containing the reactants and the products was analyzed quantitatively by a gas chromatograph fitted with a (10%SE-30 chromosorb w-AW, 3 m \times 1/8 in.) column coupled with a FID detector and qualitatively by GC–MS (Varian). The various parameters, such as molar ratio of the reactants, amount of the catalyst, reaction temperature and reaction time were varied to optimize the reaction conditions.

The kinetic studies were conducted in a temperature range from 393 to 423 K. The reactions were carried out by following the procedure as mentioned in the previous paragraph, by varying the amount of catalysts (0.1–1.5 g) and reaction time (0.5–12 h). The reusability of the catalysts was also studied by using the spent catalyst in the next consecutive reaction cycles after washing them with acetone and calcining in a furnace for 2 h at 823 K.

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