

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, ZrO_2 (Z), $\text{SO}_4^{2-}/\text{ZrO}_2$ (SZ) and Mo(VI)/ZrO_2 (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. ZrO_2 and Mo(VI)/ZrO_2 were 100% selective towards the formation of salol, but in the case of $\text{SO}_4^{2-}/\text{ZrO}_2$ 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 ZrO_2 . 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 $Z > \text{MZ} \geq \text{SZ}$.

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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 H_2SO_4 , HCl , POCl_3 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 $ZrOCl_2 \cdot 8H_2O$ 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 $Zr(OH)_4$ 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 $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [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 SO_4^{2-}/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 $Cu K\alpha$ radiation (1.5418 \AA).

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, $3 \text{ m} \times 1/8 \text{ in.}$) 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.

Table 1
Physico-chemical properties of solid acids

Catalyst	Total surface acidity (mmol/g)	BET surface area (m ² /g)	Sulfur (or) Mo(VI) (%)
Z	0.40 (0.44)	71	–
SZ	1.15 (1.09)	149	2.2
MZ	1.00 (1.01)	116	2.1

Note: Numbers in the parenthesis correspond to the total surface acidity values obtained by *n*-butyl amine back titration method.

3. Results and discussion

3.1. Characterization of catalysts

The sulfur and Mo(VI) contents, BET surface area and total surface acidity of all the catalysts used in this investigation are presented in Table 1. The sulfur and Mo(VI) contents showed good agreement with the theoretical values within an error of 2%. This error is due to the reduction in the weight as a result of dehydration of the support upon calcination.

The specific surface area of pure ZrO₂ was found to be 71 m²/g which was almost doubled on modification with sulfate or Mo(VI) ions. The increase in the surface area of sulfated zirconia was attributed by Arata [17] to cracking of ZrO₂ into fine particles upon treatment with sulfate ions, whereas for the MZ sample, the observed increase in the specific surface area was explained based on the formation of Mo–O–Zr linkages resulting in a porous material [18].

Temperature programmed desorption (TPD) of ammonia is a popular method for the determination of acidity of solid catalysts. The total acidity (total acid amount) of the catalysts which were used in our study follows the order; Z < MZ ≤ SZ. This order is in good agreement with the already published results [19]. The acid sites on zirconia have been classified as ‘medium’, ‘strong’ and ‘very strong’, based on the temperature at which NH₃ molecules desorbs from its surface [20]. It is observed that incorporation of either SO₄²⁻ or Mo(VI) ions on the surface of ZrO₂ results in a considerable increase in the total surface acidity. This increase in the acidity may be due to the creation of new acid sites with different strengths. It is also reported that presence of SO₄²⁻ ions on ZrO₂ results in the creation of acid sites that belong to ‘strong’ and ‘very strong’ categories [19]. However, Mo(VI) promotes the formation of sites with ‘medium’ and ‘strong’ acid strengths [15].

The powder X-ray diffractograms of Z, SZ and MZ are presented in Fig. 1. Zirconia is known to exhibit three well estab-

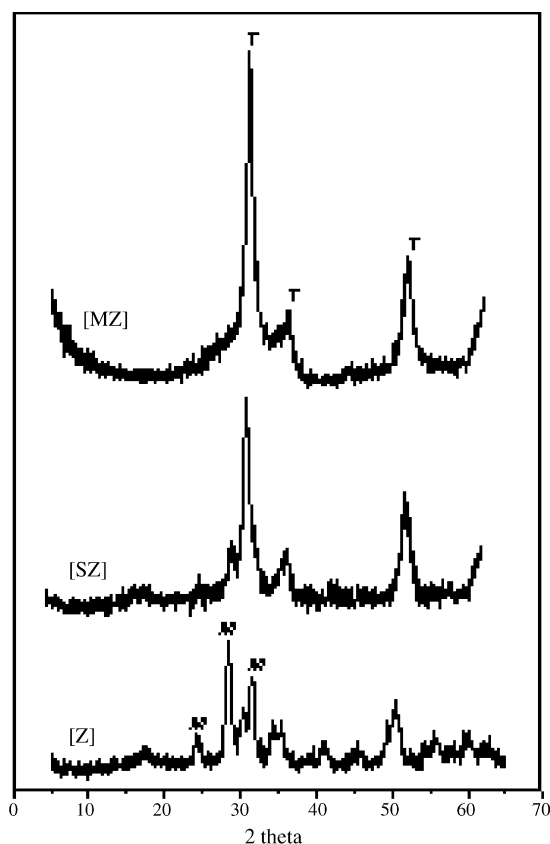


Fig. 1. Powder X-ray diffraction patterns of ZrO₂ (Z), SO₄²⁻/ZrO₂ (SZ) and Mo(VI)/ZrO₂ (MZ) samples calcined at 823 K: M—monoclinic ZrO₂ and T—tetragonal ZrO₂.

lished polymorphs; monoclinic, tetragonal and cubic phases [21]. The zirconia used in the present study found to exhibit monoclinic and tetragonal phases (Fig. 1). The sharp diffraction lines at ($2\theta = 24.7, 28.4, 31.6$) are due to the monoclinic form. The sulfate- or Mo(VI)-modified forms consist of more of the tetragonal phase than the monoclinic phase; it can be clearly observed in the figure that the peaks representing the monoclinic phase significantly decreases, whereas those of tetragonal phase ($2\theta = 30.3, 35.3, 50.7$) increases in intensity. We have reported a detailed study on the powder XRD phases of zirconia and its modified forms [22]. No diffraction lines corresponding to MoO₃ or any compound formation between MoO₃ and ZrO₂ (i.e., ZrMo₂O₈) are observed.

3.2. Catalytic activity studies

The catalytic activity of the calcined Z, SZ and MZ was examined in the transesterification reaction of methyl salicylate with phenol (Table 2). The GC and GC–MS analyses showed the presence of only four components, i.e., methyl salicylate, phenol, salol and methanol over Z and MZ catalysts. In the presence of SZ, in addition to salol and methanol, diphenyl ether was also formed as the by-product. The catalytic activity of a solid acid catalyst in the formation of a definite product in an organic reaction depends on the acid strength and concentration of active sites present on the solid acid.

Table 2
Activity of different catalysts for the synthesis of ester and ether

Catalyst	Conversion of phenol (%)	Selectivity for salol (%)	Selectivity for ether (%)
Z	36	100	0
SZ	54	91	9
MZ	50	100	0

Molar ratio of MS:P = 1:1; reaction temperature = 403 K; reaction time = 4 h; amount of catalyst = 1.0 g.

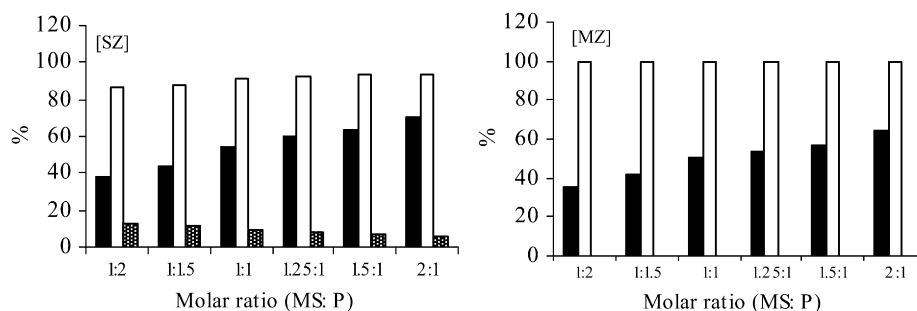


Fig. 2. Effect of methyl salicylate:phenol molar ratio. Catalyst weight = 1.0 g; reaction temperature = 403 K; reaction time = 4 h. (■) Conversion of phenol; (□) selectivity to salol; (▨) selectivity to diphenyl ether.

When the reaction was carried out without any catalyst, no conversion of phenol and methyl salicylate into salol was observed. This suggests that the reaction is a catalyzed reaction. All the catalysts were found to be active towards the formation of salol. It was further observed that the presence of SO_4^{2-} or Mo(VI) ions on ZrO_2 has increased the conversion of phenol to salol. A correlation of the surface area and surface acidity with the catalytic activity showed the same trend.

An attempt to identify the different phases of zirconia responsible for the formation of salol indicated that both monoclinic and tetragonal phases were associated with the catalytically active sites responsible for the formation of salol. However, the powder XRD suggests that an increase in the tetragonal phase of zirconia is responsible for higher transesterification activity [23]. Formation of diphenyl ether indicates that SZ is associated with active centers with ‘very strong’ acid strengths which are absent in Z and MZ catalysts. Thus, these studies have indirectly provided information that the ‘medium’ and ‘strong’ acid sites are present on the surface of Z, SZ and MZ, which are responsible for the salol formation and that the ‘very strong’ acid sites that

are associated only with SZ are catalytically active for diphenyl ether formation. As has already been reported [13,24], the formation of ether by acid catalyzed dehydration of an alcohol requires ‘very strong’ acid sites.

3.2.1. Effect of molar ratio of the reactants

The effect of molar ratio of reactants on the conversion of phenol and selectivity towards salol was studied by varying the molar ratio of methyl salicylate to phenol from 2:1 to 1:2. It was found that an increase in the concentration of methyl salicylate increased the conversion of phenol (Fig. 2). This may be due to the fact that transesterification is a reversible reaction and excess of methyl salicylate favors the forward reaction, leading to the formation of the desired product. On the other hand, it was found that an increase in the concentration of phenol decreases its conversion into salol, possibly because of the deactivation of the catalyst. Z and MZ catalysts were 100% selective towards the formation of salol. But in the case of SZ catalyst the selectivity towards salol was decreased accompanied with a decrease in the selectivity for diphenyl ether. However, the effect was only to an extent of ~4%.

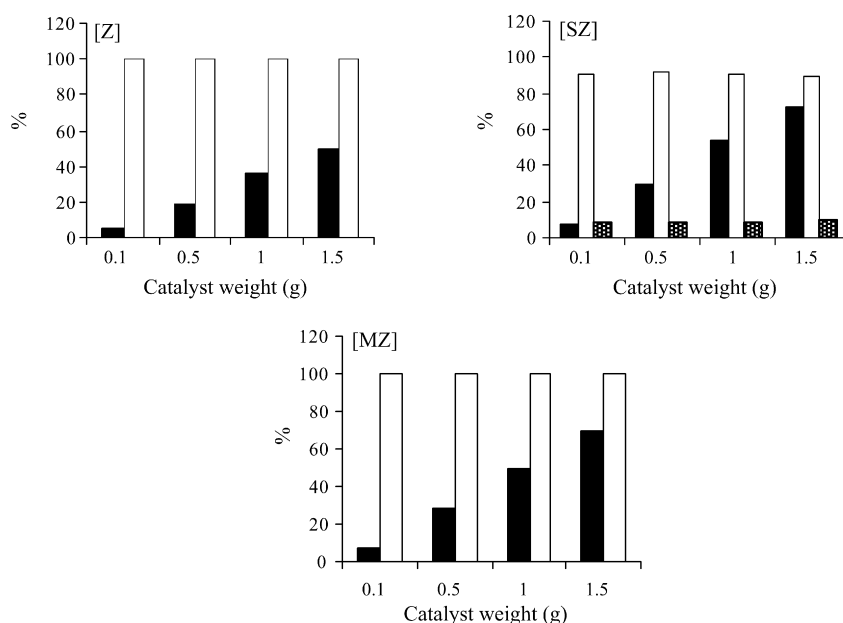


Fig. 3. Effect of catalyst weight. MS:P = 1:1; reaction time = 4 h; reaction temperature = 403 K. (■) Conversion of phenol; (□) selectivity to salol; (▨) selectivity to diphenyl ether.

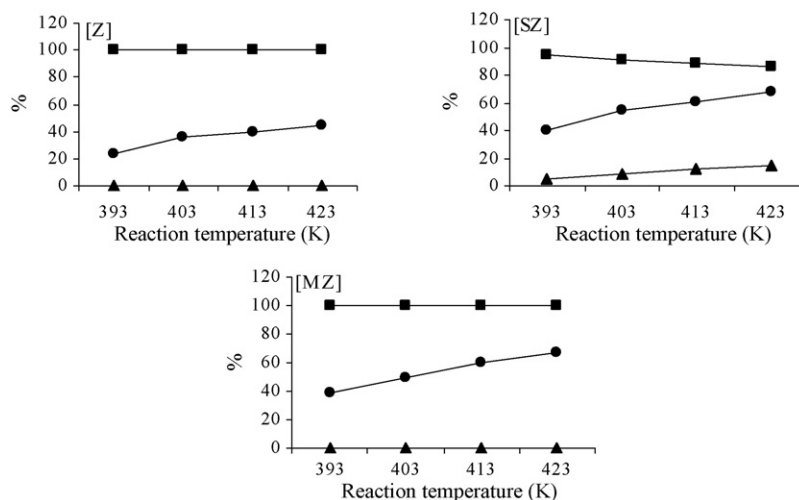


Fig. 4. Effect of reaction temperature. MS:P = 1:1; catalyst weight = 1.0 g; reaction time = 4 h. (●) Conversion of phenol; (■) selectivity to salol; (▲) selectivity to diphenyl ether.

3.2.2. Effect of amount of catalyst

The effect of catalyst weight on the conversion (%) of phenol was checked. The amount of catalyst was varied from 0.1 to 1.5 g. As illustrated in Fig. 3, an increase in the amount of catalyst substantially increased the conversion of phenol. The higher the catalyst loading, the greater the conversion of phenol. A maximum conversion of phenol (70%) with 100% selectivity towards salol was observed with 1.5 g (MZ) of the catalyst in 4 h at 403 K. In the case of SZ the conversion of phenol increased from 7 to 71% on increasing the weight of SZ from 0.1 to 1.5 g. But no reasonable change in the selectivity towards either salol or diphenyl ether was observed, i.e., the selectivity towards salol was ~91% and selectivity towards diphenyl ether was ~9%.

3.2.3. Effect of reaction temperature

The effect of reaction temperature on the conversion of phenol and the selectivity towards the ester or ether was studied over the temperature range from 393 to 423 K (Fig. 4). An increase

in the conversion of phenol was observed on increasing the reaction temperature over all the catalysts. Selectivity towards salol remains 100% over both Z and MZ catalysts. However, in the case of SZ catalyst, the selectivity towards salol decreased from 96 to 88% accompanied with an increase in the selectivity towards diphenyl ether from 4 to 12%. This suggests that over SZ, high temperatures favor the ether formation.

3.2.4. Effect of reaction time

Reactions were also carried out at different reaction (refluxing) times. The reaction time was varied from 0.5 to 12 h. The conversion of phenol increased rapidly in the beginning and gradually leveled off after 4 h (Fig. 5). For example, over MZ, the conversion increased from 15% in the first 0.5 h to around 54% in the next 4 h and the conversion increased only to an extent of 61% in 12 h. The selectivity towards the salol was 100% with both Z and MZ catalysts. In the case of SZ, the conversion increased from 16 to 55% in the first 4 h and the selectivity

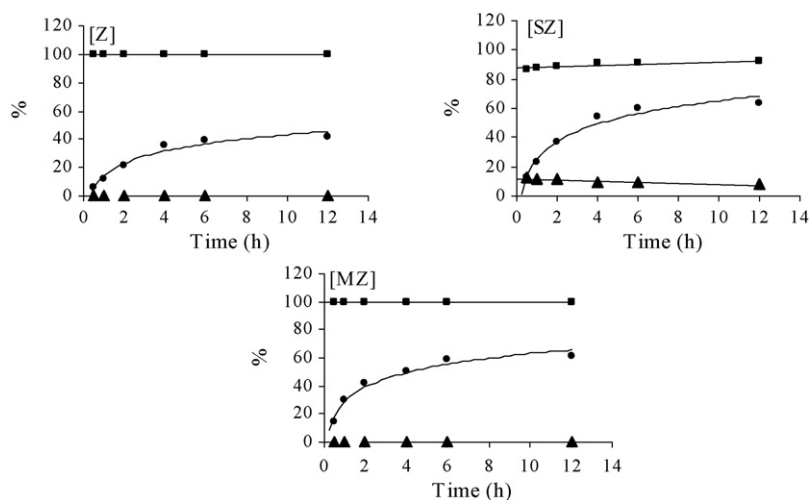


Fig. 5. Effect of reaction time. MS:P = 1:1; reaction temperature = 403 K; catalyst weight = 1.0 g. (●) Conversion of phenol; (■) selectivity to salol; (▲) selectivity to diphenyl ether.

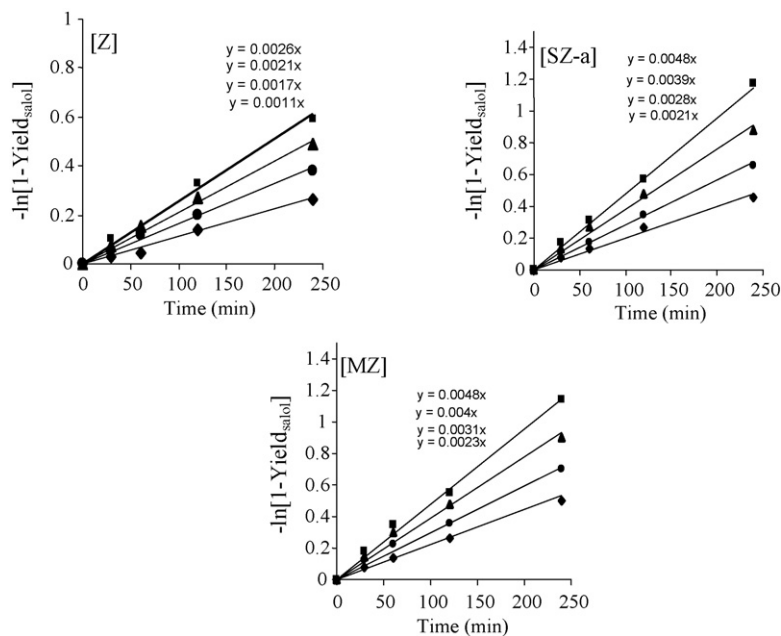


Fig. 6. Plot of first-order equation for the transesterification of methyl salicylate with phenol over ZrO_2 , SZ and MZ at 393 K (◆), 403 K (●), 413 K (▲) and 423 K (■).

towards either salol or diphenyl ether remained almost the same. The reaction period of 4 h seems to be good to get a reasonable conversion of phenol to salol.

3.3. Kinetic studies

Prior to the kinetic studies, experiments were conducted to establish the effect of heat and mass transfer limitations during the transesterification reaction.

The effect of heat transfer limitations was studied by carrying out the experiments at different agitation rates of the reaction mixture. Not much change in the conversion of phenol was observed when the rate of agitation was varied, i.e., conversion of phenol was independent of the rate of agitation. This indicates the absence of heat transfer limitation and therefore, it could be suggested that any external resistance to its transfer from the bulk liquid phase to the external surface of the catalyst is absent.

The reactions were carried out by varying the weight of catalyst. An increase in the conversion of phenol with an increase in the catalyst weight was observed (Fig. 3). This indicates that the resistance to mass transfer is negligibly small between liquid bulk of the reactant and the outer surface of the catalyst particles; according to Madon and Boudart [25] in the absence of all transport limitations, the rate of a reaction is proportional to the number of active sites, which in turn is proportional to the weight of the catalyst.

Plots of $-\ln[1 - \text{Yield}_{\text{salol}}]$ versus reaction time for the transesterification reactions carried out at different reaction temperatures ranging from 393 to 423 K over Z, SZ and MZ are given in Fig. 6. Since diphenyl ether was also formed over SZ, the transesterification and etherification were treated separately to get the kinetic data (Fig. 7). The first-order plot for the etherification in the presence of SZ is shown in Fig. 8. The plots are nearly linear in all the cases, indicating the transesterification

(and etherification in case of SZ only) to be a first-order reaction. The first-order rate constants obtained from the slopes of these plots, the energies of activation calculated from the Arrhenius equation and the temperature coefficients are given in Table 3. The energy of activation for transesterification are in the order;

$$Z > MZ \geq SZ$$

Zirconia has the highest energy of activation among the catalysts used in our case study. As far as SZ and MZ catalysts are concerned, the energy of activation are almost identical, which means that the reaction proceeds under the same kinetic mechanism, including the active sites required for the formation of salol. This indicates that transesterification is equally facile over SZ and MZ. The energy of activation for the formation of diphenyl ether over SZ catalyst was found to be 91 kJ mol^{-1} .

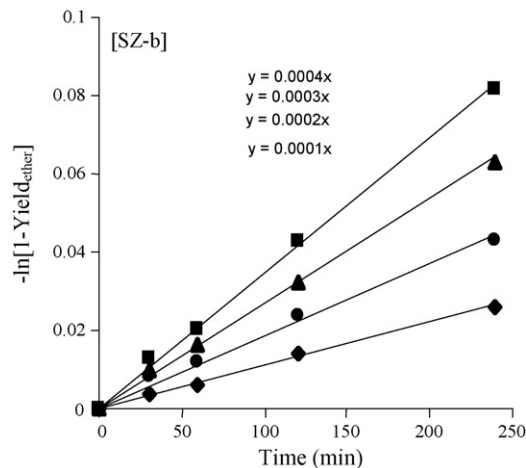


Fig. 7. Plot of first-order equation for the etherification of phenol over SZ at 393, 403, 413 and 423 K.

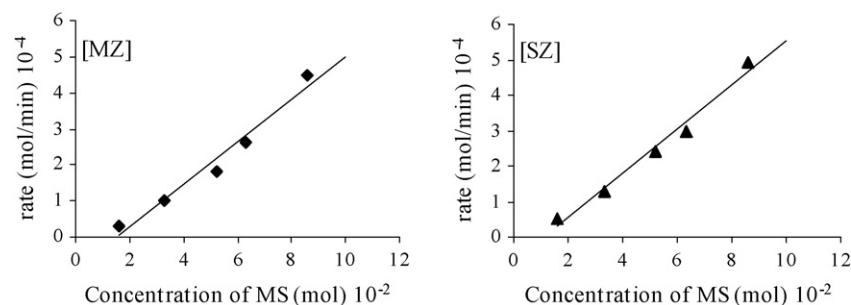


Fig. 8. Effect of methyl salicylate concentration on the initial reaction rate. Reaction temperature = 403 K; catalyst weight = 1.0 g.

Table 3

Reaction rate constants (10^{-3} min^{-1}), energy of activation (kJ/mol^{-1}) and temperature coefficients for transesterification and etherification

Catalyst	Rate constant (salol)		Rate constant (ether)		Energy of activation (E_a) for the formation of;		Temperature coefficient (k_2/k_1)	
	393 K (k_1)	403 K (k_2)	393 K (k_1)	403 K (k_2)	Salol	Ether	Salol	Ether
Z	1.1	1.7	–	–	57.31	–	1.54	–
SZ	2.1	2.9	0.1	0.2	37.87	91.28	1.33	2.00
MZ	2.3	3.1	–	–	39.31	–	1.35	–

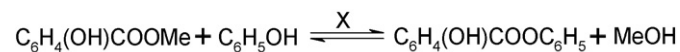
MZ is a preferred catalyst for salol synthesis due to its 100% selectivity towards the salol. This also suggests that, transesterification of methyl salicylate and phenol to prepare salol requires ‘medium’ or ‘strong’ acid sites which are present in all the catalysts used for our work.

3.4. Mechanism of reaction

In general, methyl salicylate reacts with phenol in the presence of an acid catalyst [X] to give the ester, salol as shown in Scheme 1. This acid catalyzed transesterification is an equilibrium chemical reaction.

The transesterification reaction can take place by following either a Langmuir–Hinshelwood model or an Eley–Rideal model. The kinetics of these two mechanisms does vastly differ. For example, LH kinetics involves a reaction between methyl salicylate adsorbed on the catalyst surface and phenol which is adsorbed on an adjacent site. In contrast, the reaction follows an ER mechanism, when only one of the reactant species (methyl salicylate or phenol) is bound on the catalyst surface and is converted to product when the other impinges upon it from the gas phase.

It has been reported in literature [26] that adsorbed phenol does not react, only poisons the catalytic sites. Therefore, it is assumed that phenol from the liquid phase reacts with adsorbed methyl salicylate. Furthermore, a decrease in the rate was observed with an increase in the concentration of phenol; this can be attributed to the poisoning of the active sites of the catalyst which was further proved by the change in the color of the catalyst from white to grey on increasing the concentration



Scheme 1. Transesterification of methyl salicylate with phenol in presence of an acid catalyst [X].

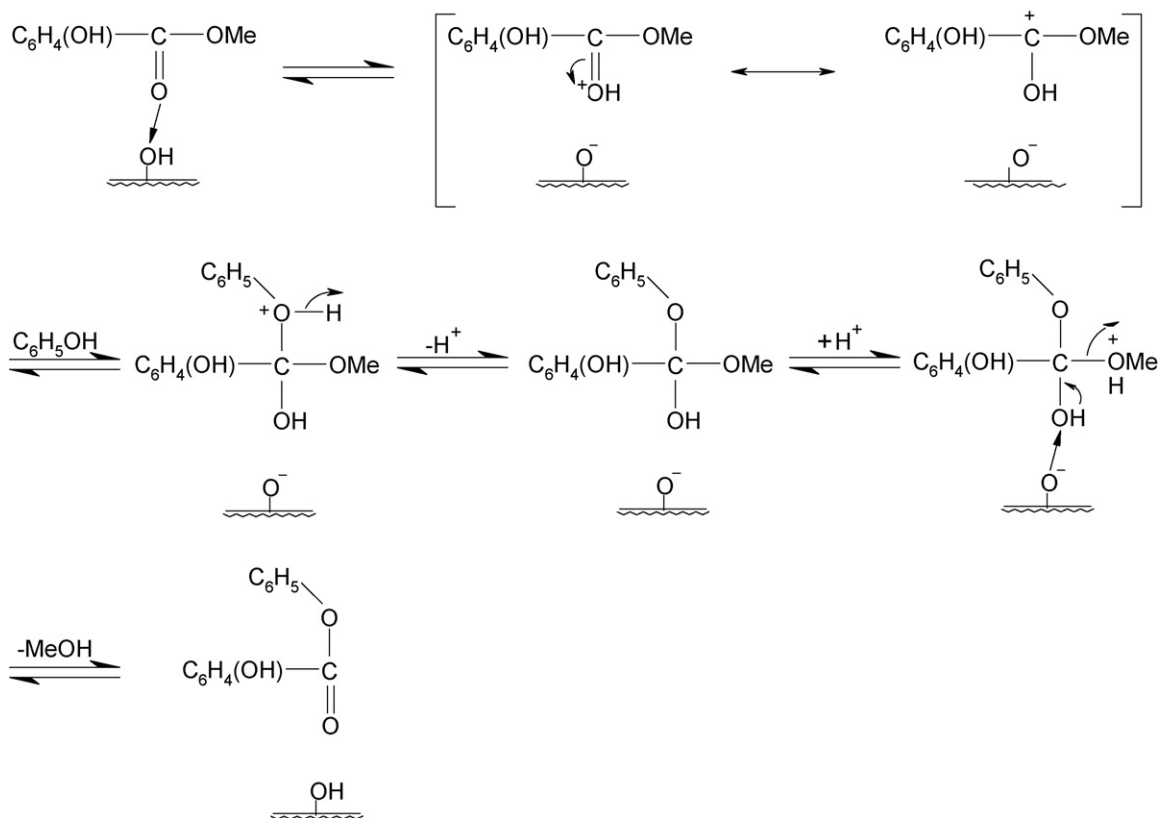
of phenol. On the other hand, an increase in the concentration of methyl salicylate increased the yield of salol with negligible deactivation (poisoning of active sites) of the catalyst. We did not observe any deactivation or color change of the catalyst even at a molar ratio of MS:P = 1:1. Thus, we can say that it is methyl salicylate which is adsorbing on the active sites of the catalyst and not phenol.

Since, there is no mass transfer limitation on the catalyst surface as mentioned already, the chemical step was assumed to be the rate limiting step. If the reaction proceeds through a LH mechanism, then a plot of rate versus concentration must pass through a maximum, according to Narayanan and co-workers [27], while if it follows an ER mechanism, no such maximum is encountered. Fig. 8 indicates that the initial reaction rate increases linearly with methyl salicylate concentration. This would suggest that the transesterification of methyl salicylate with phenol follows an ER mechanism.

Based on the above assumptions a possible mechanism for the transesterification of adsorbed methyl salicylate and phenol over solid acid catalysts is given in Scheme 2, which is similar to the mechanism of acid catalyzed Fischer esterification [28].

3.5. Reusability of the catalysts

In order to study the reusability of the catalysts, the solid catalyst recovered after the reaction by filtration was washed with acetone and calcined at 823 K in a furnace for 2 h. Thus, recovered catalyst was reused in the transesterification reaction. The experiments were repeated three times by following the same procedure and the variation in the conversion of phenol are given in Table 4. The data in the table shows that there is no considerable change in the catalytic activity of the Z and MZ catalysts. However, the SZ catalyst showed a substantial decrease in its activity after each cycle of the



Scheme 2. Transesterification of methyl salicylate and phenol over solid acids (protonic acid sites).

Table 4
Reusability of the catalysts in the transesterification reaction

Catalyst	Conversion (%) phenol			
	Fresh	First cycle	Second cycle	Third cycle
Z	36	34	33	33
SZ	54	50	45	36
MZ	50	47	47	46

Molar ratio of MS:P=1:1; reaction temperature=403 K; reaction time=4 h; amount of catalyst=1.0 g.

reaction. Thus, we can conclude that the Z and MZ catalysts are efficient and that they can be reused atleast upto three cycles.

4. Conclusion

The transesterification of methyl salicylate and phenol was studied over ZrO₂, SO₄²⁻/ZrO₂ and Mo(VI)/ZrO₂. Sulfate and Mo(VI) modified zirconia were found to be good catalysts. Mo(VI) modified zirconia was 100% selective towards the formation of salol (excluding the primary by-product methanol). But over SO₄²⁻/ZrO₂, in addition to salol, diphenyl ether was also formed to a small extent, thus decreasing the selectivity of salol. All the catalysts used in the present study have considerable reusability; however, SO₄²⁻/ZrO₂ showed a gradual decrease in the catalytic activity. Kinetic studies have shown that the transesterification followed an

Eley–Rideal mechanism. A possible mechanism for the transesterification of methyl salicylate and phenol over acid sites is proposed.

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