

# Selective synthesis of phenyl salicylate (salol) by esterification reaction over solid acid catalysts

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Received 8 July 2003; received in revised form 10 July 2003; accepted 1 March 2004

Available online 1 October 2004

## Abstract

Esterification of salicylic acid with phenol to synthesize phenylsalicylate over solid acids as catalysts has been studied. Catalytic activity of different oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and their sulfated forms and zeolites such as Na-Y, Na- $\beta$ , ZSM-5 and their protonated forms have been investigated. Catalytic activity studies have been conducted in liquid phase under refluxing conditions. A systematic study has been made to find the effect of amount of the catalyst, the molar ratio of alcohol to acid and the duration of reaction on the synthesis of the ester. Product analysis has been done on gas chromatograph and further characterized by GC-MS, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. All the catalysts have been found to be active and exhibit 100% selectivity towards the formation of phenylsalicylate as the reaction product. The catalytic activities of sulfated oxides and protonated forms of zeolites are found to be higher than their parent forms. The catalysts have been characterized for their surface acidity and BET surface area.

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**Keywords:** Esterification; Salol; Oxides; Zeolites; Sulfated oxides and catalysts.

## 1. Introduction

Selective esterification of bifunctional carboxylic acids in the presence of aromatic alcohol is a useful organic synthesis reaction. The esters thus obtained are utilized to prepare fine chemicals used in the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, solvents, perfumes and cosmetics [1–3]. Generally phenylesters of salicylic acid are prepared under liquid phase, refluxing the reactants (carboxylic acid and phenol) in the presence of small amount of conc.  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{POCl}_3$  or sulfonic acid as the catalyst [4]. Although many effective and reliable methods for the preparation of aromatic esters exist, there is still a good scope for research towards finding eco-friendly and economically viable processes. The use of the above mentioned catalysts is undesirable from the environmental point of view as these chemicals are corrosive and generally encounter the prob-

lems of handling and transportation. Moreover reusability of the catalysts cannot be expected. Hence there are numerous global efforts to replace these environmentally harmful chemicals with more ecofriendly and less expensive catalysts.

Solid acids such as zeolites, oxides, aluminophosphates and their modified forms have been extensively studied as possible alternatives to conventional Lewis/Bronsted acid catalysts [5–10]. The oxides and zeolites possess on their surface and/or in the pores acidic sites. This property has been exploited in the synthesis of several organic fine chemicals via acid catalyzed reactions. Acidity of oxides found to increase on sulfate ion treatment [11] and that of zeolites by protonation [12]. The increase in acidity is found due to an increase in the number and the strength of acid sites. In several reactions it is observed that the yield and selectivity of a product depends not only on the concentration but also on the strength of the acid sites on these solid acids.

We have earlier [13–18] observed that solid acids such as modified forms of zeolites and oxides catalyze very efficiently esterification and alkylation reactions.

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Phenylsalicylate, the phenyl ester of salicylic acid is an important chemical. It is used in medicine as internal antiseptic under the name salol. It also finds applications in paints, waxes, varnishes due to its ability to absorb UV light in the range of 290–325 nm. Esterification of salicylic acid with phenol in the presence of  $\text{POCl}_3$  as the catalyst or transesterification of methyl salicylate with phenol in the presence of alkali or alkaline earth phosphates are the existing routes for the synthesis of phenyl salicylate [19].

The present investigation is aimed to find out the catalytic activity and the effect of sulfate ion treatment of oxides and protonation of zeolites in a reaction between phenol and salicylic acid to synthesize phenyl salicylate (salol). Here we report that the solid acids such as alumina, silica, zirconia, zeolites (Y,  $\beta$  and ZSM5) and their modified forms exhibit good catalytic activity in the esterification reaction between salicylic acid and phenol. The results obtained are very encouraging in the sense that solid acids not only show 100% selectivity but also high activity towards the formation of phenyl salicylate.

## 2. Experimental

### 2.1. Preparation of hydrated $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ , $\text{ZrO}_2$ and their sulfated forms

Initially  $\text{Al}(\text{OH})_3$  gel was prepared by adding drop wise liquor ammonia into  $750 \text{ cm}^3$  of a hot ( $\approx 80^\circ\text{C}$ ) aqueous solution of aluminum nitrate containing 100 g of the salt. The precipitate was separated by filtration, washed free from anions, dried overnight at  $120^\circ\text{C}$  in an air oven and calcined at  $550^\circ\text{C}$  for 5 h to obtain hydrated alumina. Similarly hydrated  $\text{ZrO}_2$  was obtained starting from zirconium oxychloride, 25 g of  $\text{ZrOCl}_2$  were dissolved in 250 ml deionised water, and liquor ammonia was used as the precipitating agent. Hydrated  $\text{SiO}_2$  was obtained starting from sodium silicate solution containing 25 g of the salt in 250 ml of deionised water using conc.  $\text{HNO}_3$  as the precipitating agent.

Hydrated oxides i.e., hydroxides of Al, Si and Zr dried at  $120^\circ\text{C}$  were modified by adsorbing sulfate ions on their surface by mixing the individual solid sample at room temperature with 1 M  $\text{H}_2\text{SO}_4$  (1 ml/g) for 1 h. The solid was then separated by filtration dried at  $120^\circ\text{C}$  for 24 h and further calcined at  $550^\circ\text{C}$  for 6 h. The samples were designated as SAl, SSi and SZr, respectively.

### 2.2. Preparation of protonated forms of zeolites

Zeolites  $\beta$ , Y and ZSM-5 were obtained in their sodium form from UCL (United Catalyst India Ltd.). These zeolites were modified by exchanging the  $\text{Na}^+$  ions of the parent zeolite by  $\text{H}^+$  ions. The protonated forms of the zeolites were prepared by the standard method reported in the literature [20,21]. Briefly the procedure followed is as follows: 20 g of the zeolite calcined at  $550^\circ\text{C}$  was immersed in  $250 \text{ cm}^3$  of

ammonium nitrate solution (1 M) containing 20 g of the salt. The mixture was stirred overnight, filtered and washed with deionised water. The solid was then dried at  $120^\circ\text{C}$  in an air oven overnight and calcined at  $550^\circ\text{C}$  for 5 h to obtain the protonated forms viz., H- $\beta$ , H-Y and H-ZSM5.

### 2.3. Characterization of the catalysts

All the oxides, zeolites and their sulfated and protonated forms as prepared by the procedures given under the above section have been characterized for their total surface acidity by TPD of  $\text{NH}_3$  and *n*-butylamine back titration method [22] using dry benzene as the solvent. BET surface area of the samples was also measured at liquid nitrogen temperature (using NOVA-100VER: 3.7 instrument).

### 2.4. Catalytic activity studies

The catalytic esterification reactions were carried out in liquid phase in a  $250 \text{ cm}^3$  RB flask equipped with reflux condenser. In each reaction 1 g of the catalyst was added to a mixture of salicylic acid and phenol (1:1.5 molar ratio). The mixture was refluxed on a heating mantle. The temperature of the reaction mixture was maintained in between 150 and  $160^\circ\text{C}$  for a predetermined time. Different reaction-runs were conducted by varying the reaction parameters such as molar ratio of the reactant, weight of the catalyst, reaction period and the catalyst type in order to optimize the reaction conditions to get good yield and high selectivity of the product, salol. After a stipulated time the reaction mixture was cooled to room temperature, acetone was added to dissolve the unreacted salicylic acid in the reaction mixture and filtered to separate out the catalyst. The filtrate was analyzed by gas chromatograph using 20% SE-30 column coupled with FID. The ester was identified by comparing with a standard and further confirmed by GC-MS, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The % yield of phenyl salicylate was calculated based on the conversion of salicylic acid using the following expression (14):

Conversion of salicylic acid (SA) (%)

$$= 100 - \frac{100 \times [\text{salicylic acid}]}{[\text{salicylic acid}] + [\text{phenyl salicylate}]}$$

## 3. Results and discussions

The catalysts used and their physicochemical properties such as BET surface area, total surface acidity are listed in Table 1. The data in this table indicate that in general sulfation or protonation of oxides and zeolites exhibited a moderate increase in their surface area. The surface area of the zeolites and their protonated forms are quite in agreement with reported values [21]. The total acidity measured by TPD shows that, both sulfated oxides and protonated forms of zeolites have stronger acidic sites than their parent forms. The

Table 1  
Physico chemical properties of the catalysts used

Catalyst (oxides)	Surface area (m <sup>2</sup> /g)	A	B	Catalyst (zeolites)	Surface area (m <sup>2</sup> /g)	A	B
Al <sub>2</sub> O <sub>3</sub>	180	0.41	0.37	Na-Y	295	0.52	0.44
SiO <sub>2</sub>	125	0.51	0.48	Na-β	445	0.69	0.52
ZrO <sub>2</sub>	95	0.55	0.49	Na-ZSM5	290	0.54	0.50
SAI	210	0.65	0.62	H-Y	320	0.85	0.79
SSi	135	0.78	0.79	H-β	450	1.12	1.01
SZ	130	0.98	0.89	H-ZSM5	280	0.81	0.75

A—surface acidity by TPD of NH<sub>3</sub> (mmol/g); B—surface acidity by *n*-butylamine titration method (mmol/g).

decreasing order of the catalyst acidity observed is as given below:

Oxides : SZr > SSi > SAI > ZrO<sub>2</sub> > SiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub>,

zeolites : H-β > H-Y > H-ZSM5 > Na-ZSM5  
> Na-Y > Na-β.

The above order of acidity of oxides clearly indicate that the interaction of sulfate ion during sulfating depends on the acidic and/or basic nature of the surface of the oxide used.

### 3.1. Catalytic activity studies

The GC analysis of the products from the catalytic esterification reactions indicated the presence of only three components in the reaction mixture. A comparison of the retention times of these components with authentic samples and GC-MS, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR confirmed the presence of only phenol, salicylic acid and phenyl salicylate in the product mixture. At the outset it is noticed from these experiments that the oxides, zeolites and their modified forms are found to exhibit 100% selectivity towards salol formation. The results of the experiments carried out in the presence of various catalysts and the percentage yield of phenyl salicylate obtained are given in Table 2. It is clear from the data that sulfated oxides and protonated forms of zeolites are much better catalysts for phenyl salicylate formation than their simple oxides and sodium forms of zeolites. The following order of catalytic activity towards the formation of salol was observed in

Table 2  
Comparison of catalytic activity of various catalysts

Catalyst	Yield of salol (%)	Catalyst	Yield of salol (%)
Al <sub>2</sub> O <sub>3</sub>	25	Na-Y	11
SiO <sub>2</sub>	26	Na-β	20
ZrO <sub>2</sub>	29	Na-ZSM 5	22
SAI	34	H-Y	58
SSi	37	H-β	70
SZ	59	H-ZSM5	52

Salicylic acid:phenol—0.1 mol:0.15 mol; amount of the catalyst—1 g.

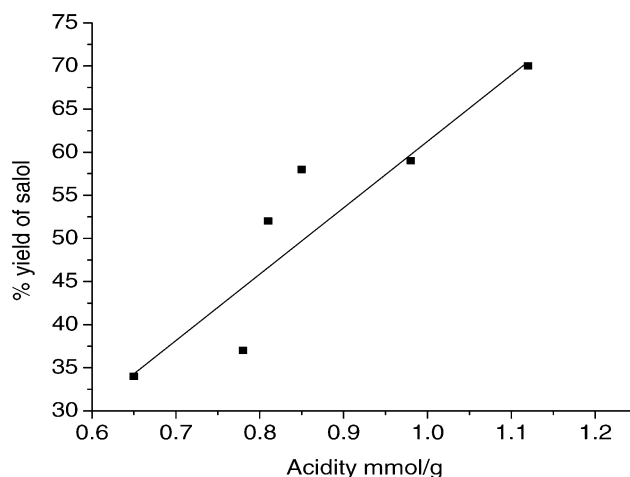


Fig. 1. Percentage yield of salol as a function of acidity.

the case of modified oxides and zeolites:

Sulphated oxides : SZr > SSi > SAI,

zeolite : H-β > H-Y > H-ZSM-5.

The catalytic activity towards conversion of salicylic acid was found to increase with increase in total acidity of the catalysts (Fig. 1). The data in the Table 2 also indicate that the simple oxides are more active than the sodium forms of zeolites though the latter possess higher acidity than the former. It confirms that it is not just the concentration of the acid sites but their strength also plays an important role in catalyzing a particular reaction [23]. Further investigations of these reactions were carried out on zeolite H-β and sulfated zirconia as these catalysts exhibited good yield and selectivity, to optimize the reaction conditions to get good conversions.

#### 3.1.1. Effect of amount of catalyst

Experiments were conducted by varying the amount of the catalyst between 0 and 2 g keeping phenol and salicylic acid molar ratio 1.5:1 and the reaction temperature 150–160 °C. The reactions were carried out for 6 h and the products were analyzed as explained earlier. The results are represented by plotting the amount of catalyst versus percentage yield of phenyl salicylate in Fig. 2. It is noticed that without catalyst the reaction did not occur to yield salol. This indicates that the oxides and zeolite are catalyzing the esterification reaction. An increase in the conversion of SA to phenyl salicylate from 39 to 72% was noticed when the amount of H-β increased from 0.25 to 1.5 g. For sulfated zirconia this increase has been found to be from 31.4 to 60% only. The increase in conversion of SA with the amount of the catalyst may be attributed to an increase in the number active sites available for the esterification reaction. However beyond 1 g of the catalyst % yield of salol remained almost constant.

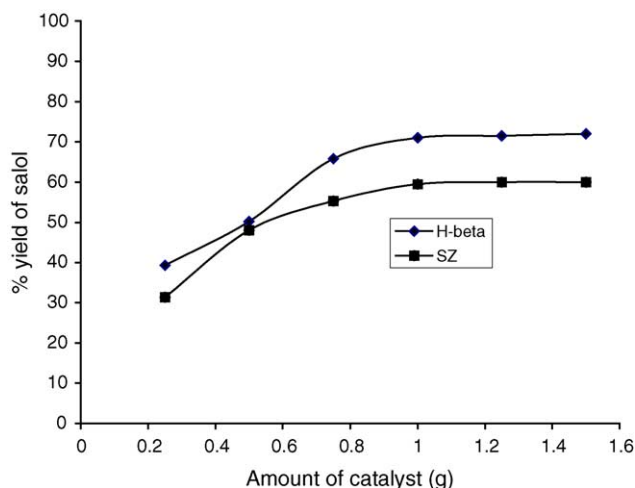


Fig. 2. Effect of amount of H- $\beta$  and SZ catalysts on salol formation.

### 3.1.2. Effect of phenol to salicylic acid molar ratio

The reactions were carried out using different phenol to salicylic acid molar ratio by increasing the amount of phenol only. However, studies with higher concentration of salicylic acid could not be conducted due to solubility restrictions. The results are summarized in Fig. 3. The % of phenyl salicylate increases from 61 to 70% on varying phenol to SA ratio from 1:1 to 2:1 for H- $\beta$ . In the case of SZ, for the same molar ratio region the % yield of phenyl salicylate is lower than that of H- $\beta$  and remained between 45 and 59%. The above results show that the yield of product increased with increasing the molar ratio of phenol to acid. This is mainly due to the fact that the esterification reaction of carboxylic acid with phenol is reversible and an increase in the molar ratio of phenol to acid leads to a shift of the equilibrium to the direction of producing the ester. However after, a particular concen-

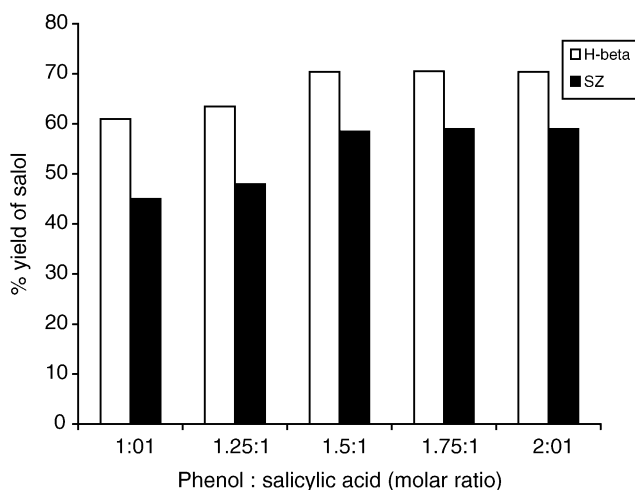


Fig. 3. Effect of the molar ratio of phenol to salicylic acid on salol formation over H- $\beta$  and SZ catalysts (amount of catalyst used—1 g; reaction time—6 h).

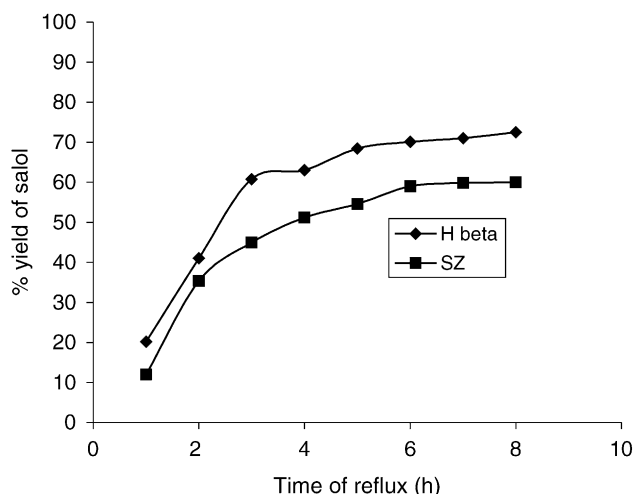


Fig. 4. Variation of the % yield of salol formed with reflux time over H- $\beta$  and sulfated zirconia (amount of catalysts used—1 g; phenol:salicylic acid—1.5:1).

tration of phenol no significant increase in the product was noticed.

### 3.1.3. Effect of reaction time

The effect of reaction time on the % yield of phenyl salicylate in the esterification reaction between salicylic acid and phenol is represented in Fig. 4. There is an increase in the amount of product with increase in reaction time in the presence of both H- $\beta$  and SZ catalysts. The optimum reaction time has been found to be 6 h. At all reaction times zeolite sample was found to be more active than the oxide. The selectivity towards phenyl salicylate remains 100% in all cases.

### 3.1.4. Reusability of the catalyst

In order to know whether the catalysts would succumb to poisoning and lose catalytic activity during the esterification reaction, the solid catalyst was recovered after the reaction by filtration and dried at 120 °C to remove acetone used for dissolving the reactants and products and reused as catalyst in the reaction between salicylic acid with phenol without any activation of catalyst. Such studies are conducted with H- $\beta$  and SZ. The experiments were repeated and the results obtained are given in Table 3. This data show that the recovered H- $\beta$  essentially retained all its catalytic activity, whereas sulfated zirconia shows considerable decrease in catalytic activity during the period of its reuse.

Table 3  
Reusability of H- $\beta$  and SZ catalysts in the esterification reaction

Number of cycles of the catalyst	% Yield of salol over H- $\beta$	% Yield of salol over SZ
Fresh	71	59.5
1	68.9	41
2	68	40
3	67.5	39

### 3.2. Conclusion

A liquid phase esterification reaction between salicylic acid and phenol in the presence of hydrated oxides (alumina, silica and zirconia) and zeolites ( $\gamma$ , ZSM5 and  $\beta$ ) and the sulfated forms of oxides and protonated forms of zeolites as catalysts yield salol with 100% selectivity. Of all the catalysts used H- $\beta$  and sulfated zirconia exhibited good conversion of salicylic acid, 70 and 59%, respectively. It is also noticed that  $\beta$  zeolite catalyst can be reused to get good selectivity and activity.

### Acknowledgements

The authors are grateful to the Department of Science and Technology (DST), New Delhi, India for financial support, to IISc, Bangalore, India for providing library facilities and to Dr. A.B. Halgari and Dr. J. Das (IPCL, Baroda, India) for useful scientific discussions.

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