

Solid acids in liquid phase esterification

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Catalytic activity of different protonated zeolites such as HY, H β , HZSM5 and sulfated oxides such as SO₄²⁻/Al₂O₃, SO₄²⁻/SiO₂, SO₄²⁻/ZrO₂ in the esterification of propionic acid with various alcohols (C₁-C₅) over solid acids as catalysts has been investigated. The catalysts have been characterized for their total surface acidity, BET surface area and sulfur content in sulfated catalysts. Catalytic activity studies have been conducted in liquid phase under refluxing conditions. A systematic study has been made to find out the effects of nature of alcohols, amount of the catalyst and the duration of reaction in the synthesis of propionate esters. Product analysis has been done quantitatively by gas chromatography and qualitatively by GC-MS. All the catalysts have been found to be active towards the formation of propionate esters as the major reaction product. A good correlation between the concentration of acid sites and the catalytic activity of the catalysts has been observed.

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Organic esters are a very important class of compounds having applications in a number of areas such as perfumery, artificial flavors, essences, pharmaceuticals, plasticizers etc^{1,2}. Different approaches have been employed on both laboratory and commercial scales to prepare esters, and the traditional homogenous catalyzed reactions which require acids such as sulfuric acid, hydrochloric acid, phosphoric acid etc.^{3,4} being less favored due to (i) several side reactions leading to the formation of toxic by-products and decrease the yield of ester (ii) corrosion of the equipment used and (iii) tedious procedure in separation of the catalyst and its reusability⁵.

Considering the impact of these chemicals on the environment, it is very essential to introduce new efficient catalysts for the production of esters. The use of solid acids such as metal oxides, zeolites, heteropoly acids, aluminophosphates and their modified forms in organic transformations in place of traditional catalysts is on the rise. These catalysts have been extensively used in many industrially important reactions such as alkylation, hydrogenation, dehydration, rearrangement, condensation, esterification and *trans*-esterification⁶⁻¹². The main advantages of using solid acids are that they are environmentally benign, cheaper, selective, easily separable from the products and reusable. In contrast to liquid acids, which possess well-defined acidic properties, solid acids may contain a variety of acid

sites. Generally they are categorized by their Brönsted and/or Lewis acidity, the strength and number of these acid sites and the textural properties of the support (surface area and porosity).

We have earlier reported the use of solid acids in alkylation and esterification reactions^{9,10,12}. Esterification being an acid catalyzed reaction requires efficient acid catalysts to get good yield of ester with better selectivity. Protonated zeolites and sulfated oxides, being strong solid acids, can be used in esterification reaction. In our earlier investigations⁸⁻¹² we have used protonated zeolites (HY, H β , HZSM5) and sulfated oxides (SO₄²⁻/Al₂O₃, SO₄²⁻/SiO₂, SO₄²⁻/ZrO₂) in acid catalyzed reactions and observed them to be very selective in the formation of the desired product.

The present investigation is aimed to find out the comparative catalytic activity of protonated zeolites and sulfated oxides in the liquid phase esterification reaction of propionic acid with different alcohols (C₁-C₅). The results have revealed that solid acids not only show good selectivity but also high activity towards the formation of the esters.

Materials and Methods

Preparation of protonated forms of zeolites

Zeolites Y, β , and ZSM5 were obtained in their sodium form from UCL (United Catalyst India Ltd.) and modified by exchanging the Na⁺ ions of the parent zeolite by H⁺ ions. The protonated forms of the

zeolites were prepared by following a standard method reported in the literature¹³. Briefly, the procedure followed is as follows: 20 g of the parent zeolite was immersed in 250 mL of ammonium nitrate solution containing 20 g of the salt (1 M). The mixture was stirred overnight, filtered and washed with deionised water. The solid was dried at 120°C in an air oven overnight.

Preparation of hydrated Al_2O_3 , SiO_2 and ZrO_2 in their sulfated forms

Initially $\text{Al}(\text{OH})_3$ gel was prepared by adding liquor ammonia dropwise into 750 mL of a hot aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ containing 100 g of the salt. In the case of hydrated zirconia preparation, the precipitation from an aqueous solution containing 25 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ per 250 mL was carried out by dropwise addition of liquor ammonia. Similarly, SiO_2 gel was prepared by the precipitation from a hot 1 M aqueous solution of Na_2SiO_3 with 1:1 HNO_3 . The precipitates of the respective metal hydroxides were filtered, washed thoroughly with deionised water and dried at 120 °C for 12 h in an air oven.

Thus obtained hydrated alumina, silica and zirconia were impregnated with sulfate ions. For this purpose, 1.5 mL of 3 M H_2SO_4 was added to 3 g of the support and mixed thoroughly to get a homogenous paste. The paste was dried in an air oven at 120°C for 12 h¹¹.

The protonated zeolites and sulfated oxides were ground to get a fine powder. The resulting fine powders were calcined at 550°C for 5 h in a muffle furnace just before using them as catalysts in the title reaction. Sulfated oxides were abbreviated as sulfated alumina (SA), sulfated silica (SS) and sulfated zirconia (SZ).

Catalyst characterization

All the catalysts were characterized for their total surface acidity, BET surface area and sulfur content in the sulfated samples. The total surface acidity of protonated zeolites and sulfated oxides was estimated by NH_3 -TPD technique¹⁴ and also by *n*-butylamine back titration method¹⁵ using bromothymol blue as the indicator. In the temperature programmed desorption (TPD) method gaseous base molecules like NH_3 are made to adsorb on the acidic sites of the solid and desorbed at different elevated temperatures. Molecules that are adsorbed on weak sites will be evacuated preferentially at lower temperatures compared to those adsorbed on the strong acid sites. Thus the proportion of adsorbed base evacuated gives

a measure of the acidity of the catalyst.

In a typical procedure for the estimation of acidity by *n*-butylamine back titration method, about 0.5 g of the solid acid was suspended in 25 mL of benzene solution of 0.05 M *n*-butylamine and the mixture was left for 24 h. During this period, presumably all the acid sites on the surface of the solid are neutralized. The unreacted *n*-butylamine was estimated by titrating against 0.05 M HCl using bromothymol blue as indicator. The surface acidity was calculated from the decrease in the concentration of *n*-butylamine when a known weight of the catalyst was treated with a known volume of *n*-butylamine of definite concentration.

The BET surface area of the samples was measured by using nitrogen as the adsorbent in a NOVA-1000 high speed gas sorption analyzer version 3.70. The amount of sulfur in sulfated samples was obtained by conducting elemental analysis using Elementar Vario EL III Carlo Erba 1108 instrument.

General procedure for esterification

A mixture of propionic acid, an alcohol (methyl alcohol or ethyl alcohol or iso-propyl alcohol or iso-butyl alcohol or iso-pentyl alcohol) and the catalyst was heated at refluxing temperature (~120°C) for a specified period of time in a round bottomed flask provided with an ice cold water cooled condenser. The total volume of the reaction mixture without the catalyst was kept constant at 15 mL and the molar ratio of alcohol: acid was 1:2. After the stipulated time of the reaction, the reaction mixture was cooled to room temperature and filtered.

The qualitative analysis of the filtrate containing reactants and the products was made by chromatography fitted with a 20%SE-30 (chromosorb w-AW, 3m $\times$ 1/8") column coupled with FID detector. The product identity was got by GC-MS (Varian) analysis.

Results and Discussion

The catalysts used and their physicochemical properties such as total surface acidity, BET surface area and amount of sulfur in sulfated samples are listed in Table 1. The decreasing order of the total surface acidity observed is as follows:

Protonated zeolites: $\text{H}\beta > \text{HZSM5} > \text{HY}$;

Sulfated oxides: $\text{SZ} > \text{SS} > \text{SA}$.

This order is in good agreement with that given in the literature^{9,12}. Among the zeolites studied, $\text{H}\beta$ and HZSM5 were found to have higher concentration of

acid sites and HY had much less of the same⁹. However, among the sulfated oxides, sulfated zirconia (SZ) was found to be more acidic than sulfated alumina and sulfated silica indicating that, the interaction of sulfate ions is more with zirconia than with alumina or silica¹². Treatment of zirconia with sulphate ions is known to increase its surface acidity. The BET surface area of the protonated zeolites and sulfated oxides are in agreement with reported values^{16,17}. Zeolites exhibited larger surface area than sulfated oxides due to the presence of channels and pores which are absent in sulfated oxides. Among the sulfated oxides, SZ was found to have larger surface area when compared to SA and SS. The higher surface area of SZ was attributed to the cracking of zirconia support into fine particles on treatment with sulfate ions¹⁸. This effect was found to be absent in the case of alumina and silica supports.

The amount of sulfur in the form of SO_4^{2-} retained on the surface of various hydrated oxides were found to be in good agreement with the theoretically calculated values within the experimental error (6%) indicating that most of the sulfuric acid, which was used as a source of SO_4^{2-} , was retained on the hydrated oxides.

Catalytic activity studies

The GC analysis of the products obtained from the catalytic esterification reactions indicated the presence of only three components in the reaction

mixture when the reaction was carried out in presence of zeolites H β , HZSM5, HY and sulfated oxides SA and SS (these catalysts are here onwards represented as Set-1). But when SZ was used as the catalyst four components were detected. GC-MS analysis of the reaction mixture confirmed the presence of only alcohol, propionic acid (PA) and the appropriate ester in the product mixture when Set-1 was used as catalysts. However, in presence of SZ, in addition to alcohol, propionic acid and ester, a small amount of ether (2% to 4%) was also observed. It is reported that over solid acid catalysts, ether is formed by the dehydration of alcohols in presence of 'very strong' acidic sites¹⁹. Formation of ether over SZ indicates the presence of 'very strong' acid sites on its surface²⁰.

The selectivity towards the formation of an ester was 100% in presence of Set-1 catalysts. When SZ catalyst was used, although the conversion (%) was good, the selectivity towards the formation of an ester was less (~96%) due to the formation of ether as the by-product. The results of the experiments carried out in the presence of various catalysts are given in Table 2. The following order of catalytic activity towards the conversion of PA was observed in the case of zeolites and sulfated oxides:

zeolites: H β > HZSM5 > HY;

sulfated oxides: SZ > SS > SA.

The catalytic activity towards conversion of propionic acid was found to increase with increase in

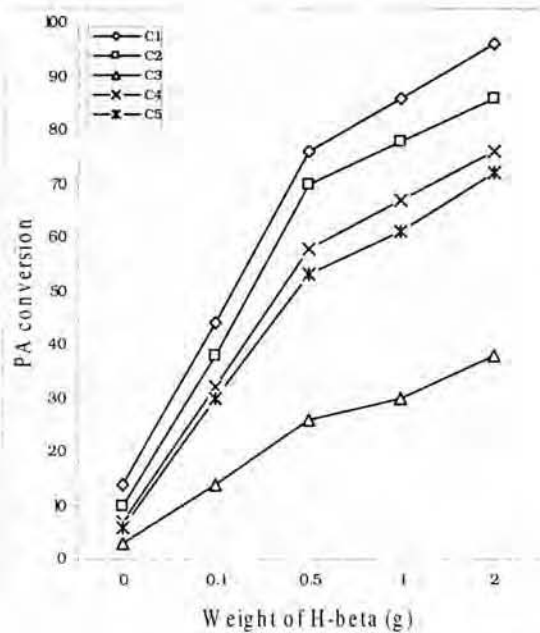
Table 1—Physico-chemical properties of solid acids used

Catalyst	Total surface acidity ^a (mmol/g)	BET surface area (m ² /g)	Sulfur content (%)
HY	0.85(0.79)	320	-
H β	1.12(1.01)	450	-
HZSM5	1.01(0.95)	280	-
SA	0.42(0.39)	208	2.21
SS	0.53(0.50)	215	2.18
SZ	1.08(1.02)	149	2.19

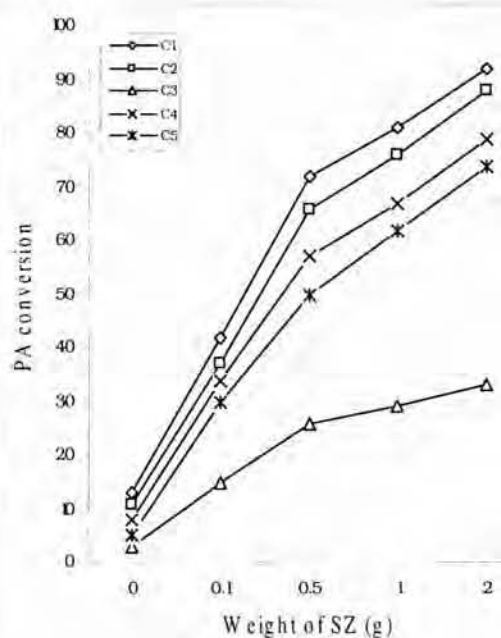
^aNumbers in the parentheses correspond to the total surface acidity values obtained by *n*-butyl amine back titration method and the values outside the parentheses correspond to the total surface acidity values obtained by NH_3 -TPD method.

Table 2—Esterification of different alcohols (C_1 - C_5) with propionic acid (PA) over solid acids [Molar ratio of alcohol:propionic acid = 1:2 ; catalyst amount = 0.5 g; refluxing time = 6 h]

Alcohols	PA conversion					
	HY	H β	HZSM5	SA	SS	SZ
Methyl alcohol (C_1)	65	76	71	53	61	72
Ethyl alcohol (C_2)	60	70	66	47	52	66
Iso-propyl alcohol (C_3)	19	26	23	12	14	26
Iso-butyl alcohol (C_4)	46	58	52	36	41	57
Iso-amyl alcohol (C_5)	41	53	46	31	36	50



(a)



(b)

Fig. 1—(a) Effect of amount of zeolite-H β on the conversion of PA; (b) Effect of amount of sulfated zirconia (SZ) on the conversion of PA.

total acidity of the catalysts. Among the zeolites H β and among sulfated oxides SZ were found to be highly active in the esterification reaction because they are much more acidic than their other group members. All the esterification reactions in our

present work were carried out with an alcohol to propionic acid molar ratio of 1:2 i.e., at higher concentration of propionic acid than alcohol. The use of higher concentration of organic acid in the reaction mixture enhances the yield of an ester. This is because of the fact that, esterification is a reversible reaction, an excess of organic acid favours forward reaction leading to the formation of more of the ester¹².

Effect of nature of alcohols

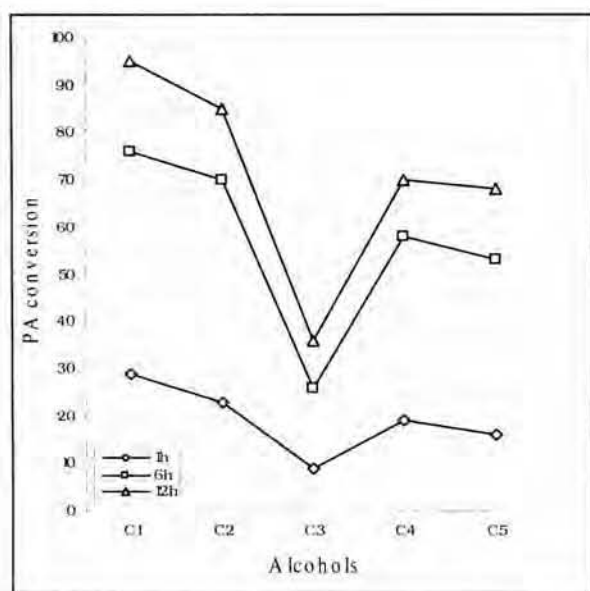
The esterification of propionic acid was carried out with various alcohols such as methyl alcohol, ethyl alcohol, iso-propyl alcohol, iso-butyl alcohol and iso-pentyl alcohol and the results of which are presented in Table 2. Except isopropyl alcohol all other alcohols used in our work were primary alcohols. The reactivity of alcohols was found to be in the order; Pri > Sec > Ter²¹. Further, since iso-propyl alcohol is a secondary alcohol it showed less conversion due to more steric hindrance compared to the primary alcohols used.

Therefore, the order of reactivity of alcohols with propionic acid in the esterification reaction was found to be, methyl alcohol > ethyl alcohol > iso-butyl alcohol > iso-pentyl alcohol > iso-propyl alcohol.

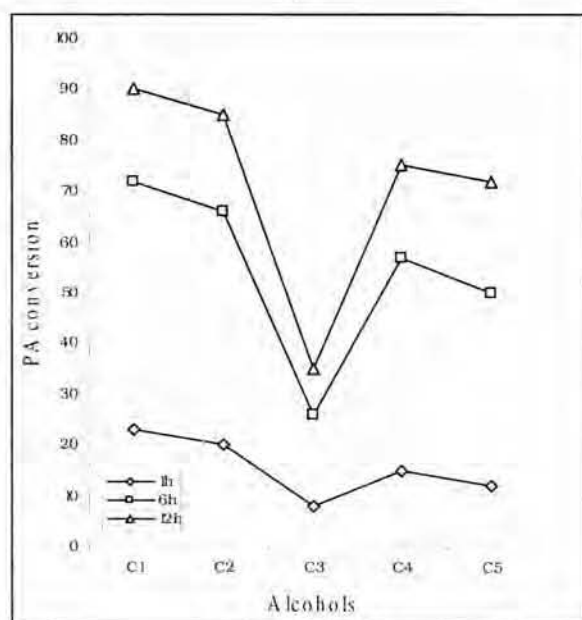
Effect of amount of catalyst

In order to optimize the reaction conditions zeolite-H β and sulfated zirconia (SZ) were selected as catalysts because, these catalysts showed good catalytic activity in esterification when compared to their other respective group members.

The amount of H β or SZ was varied between 0 and 2 g keeping alcohol to propionic acid molar ratio 1:2. The reactions were carried out for 6 h and the products were analyzed as explained in the experimental section. The results are represented in Fig 1(a) and (b). In the absence of any catalyst, only a mild conversion (3 to 11%) took place. When the amount of H β was increased from 0 to 2 g, an increase in the conversion of propionic acid to iso-propyl propionate from 3 to 38% and propionic acid to methyl propionate from 14 to 96% was observed. Similarly over sulfated zirconia, increase in the conversion of propionic acid to iso-propyl propionate was from 3 to 33% and propionic acid to methyl propionate was 13 to 92%. This indicates that the presence of a catalyst in the reaction mixture is enhancing the conversion of propionic acid. The increase in conversion of PA with the amount of the



(a)



(b)

Fig. 2—(a) Effect of refluxing time on the conversion of PA in presence of zeolite-H β ; (b) Effect of refluxing time on the conversion of PA in presence of sulfated zirconia (SZ).

catalyst may be attributed to an increase in the number of active sites (acid sites) available for the esterification reaction. In all the reactions, the selectivity towards ester formation remains 100% in presence of H β and >96% over sulfated zirconia.

Effect of reaction time

The effect of reaction time (refluxing time) on the conversion of propionic acid over H β and SZ is

represented in Fig 2(a) and (b) respectively. The conversion increases with reaction time over both H β and SZ. The optimum reaction time was found to be 6 h because a maximum conversion of PA has been observed in this time period of the reaction. The selectivity towards ester formation remains 100% in presence of H β and >95% over sulfated zirconia. For a 12 h reaction, H β gave a maximum conversion of 95%, while sulfated zirconia gave 90%.

Reusability of the catalyst

In order to know whether the catalysts would succumb to poisoning and lose their catalytic activity during the esterification reaction, the solid catalysts were recovered from the reaction mixture by filtration, dried at 120°C and reused as catalysts in the reaction between propionic acid with alcohols without any reactivation of catalyst. Experiments were repeated with H β and SZ and the results showed that the catalytic activity was reduced to a small extent, 2 to 4% in case of H β and 6 to 12% in the case of SZ which infers that the recovered H β essentially retained all its catalytic activity, whereas sulfated zirconia showed considerable decrease in catalytic activity during the period of its reuse. The decrease in the catalytic activity of SZ can be attributed to the deactivation of SZ by the water formed during the esterification reaction. The water formed during the reaction gets adsorbed on the surface of SZ and converts some of the strong Lewis acid sites into Brönsted acid sites, which are not catalytically active²². Due to the formation of non-catalytically active sites on the surface of SZ the conversion of propionic acid got reduced.

Conclusions

From the studies on the esterification of propionic acid with various alcohols (C₁-C₅), the following conclusions may be drawn. A liquid phase esterification reaction in the presence of zeolites (H β , HZSM5 and HY) and sulfated oxides (sulfated alumina, sulfated silica and sulfated zirconia) as catalysts, showed excellent activity in the formation of propionate esters with 100% selectivity. However, in presence of sulfated zirconia, the selectivity towards propionate ester decreased due to the formation of ether in small quantities (2-4%). The difference in the catalytic activity of different catalysts has been attributed to the acid site concentration. Of all the catalysts used zeolites H β , HZSM5 and sulfated zirconia exhibited good

conversion of propionic acid because of the presence of more number of acid sites. It is also noticed that zeolite-H β can be reused as catalyst.

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