

Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition

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Abstract

The preparation of di-2-ethylhexylphthalate (DOP) via esterification reaction of phthalic anhydride by 2-ethylhexanol in the presence of solid acidic catalysts has been investigated. The used catalysts were natural zeolite, synthetic zeolites (ZEOKAR-2, ASHNCH-3), heteropolyacid $H_4Si(W_3O_{10})_4$ and sulfated ZrO_2 . The reactions were carried out under solvent-less conditions. It was observed that sulfated ZrO_2 has higher reactivity and efficiency among the investigated catalysts. In the next part of the work, important plasticizers and ester base oils have prepared through esterification reaction of anhydrides and acids by alcohols in the presence of sulfated zirconia.

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1. Introduction

Plasticizers are important class of low molecular weight non-volatile compounds that they widely use in the polymer industries. Some commercially available plasticizers such as dibutylphthalate (DBP), dioctylphthalate (DOP), dioctyladipate (DOA), di-*iso*-pentylphthalate (DIPP), and di-*iso*-heptylphthalate (DIHP) are usually prepared via esterification reaction between corresponding acids/anhydrides and alcohols in the presence of acidic catalysts [1,2].

Sulfuric acid, methane sulfonic acid, *p*-toluene sulfonic acid, and sodium hydrogen sulfate are the most conventional homogeneous used catalysts. Titanium alkylates and organo tin compounds are also used as amphoteric catalysts at elevated temperatures (200 °C). The applications of these catalysts cause some problems such as corrosion, loss of catalyst, and environment problems. Therefore, development of more efficient catalysts will be interesting and useful. It is

well known that the use of heterogeneous catalysts for liquid phase organic synthesis reactions can give a lot of benefits [3], for example, a clean reaction product solution can be obtained after simple filtration, the catalyst is easy to be recovered and reused, and avoidance of corrosion, etc. Hence, some attention has been paid to the use of heterogeneous catalysts in the esterification reactions of carboxylic acids [4–7].

Heteropolyacids are widely used in variety of acid-catalyzed reactions such as esterification [8], etherification [9], hydration of olefin [10], deesterification [11], dehydration of alcohol [12] and polymerization of THF [13] in homogenous and heterogeneous systems. Their application in the production of DOP was also reported [14,15].

The catalytic activity of some $AlPO_4$ molecular sieves such as $AlPO_4-12$, etc. in the esterification reaction of propionic acid with *n*-butanol has been investigated [16]. Preparation of DOP using silicoaluminophosphate molecular sieve CHSAPO-1 has also reported by Zhao [17].

Among various sulfated metal oxides, sulfated zirconia has attracted much attention and has been extensively investigated during the last two decades [18,19]. The major concern of this research still focuses on the acidity, in terms of types and strength. Sulfated zirconia catalyst, promoted with iron,

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aluminum and manganese, has shown much higher activity and could isomerize *n*-butane at 35 °C under normal pressure in a continuous-flow recirculation tank reactor [20,21]. Also, it was proposed that iron-oxy species were the active sites [22]. It was also claimed sulfated zirconia is a solid superacid which can catalyze the skeletal isomerization of *n*-butane to *iso*-butane at room temperature and change the color of Hammett indicator at $pK_a < -11.9$ [23,24]. Furthermore, it shows remarkable activity in many catalytic reactions [25–27]. Lots of papers suggested that the superacidity is responsible for its unique catalytic properties. However, many authors gave different opinions that sulfate zirconia is not a superacid [28–32], and its acidity is even weaker than the zeolite HZSM-5 [33]. Recent progresses in the sulfated zirconia have been reviewed by Song and Sayari [18], Arata [34], Cheung and Gates [35], Adeeva et al. [29], Farcasiu and Li [36], Hong et al. [37], and Yadav et al. [38].

Here, we report the esterification reaction of phthalic anhydride by 2-ethylhexanol in the presence of several solid acid catalysts such as zeolites, Heteropolyacid $H_4Si(W_3O_{10})_4$, and sulfated zirconia under solvent-less condition. This work was originally performed in the aim of simplification of the esterification process, easier work-up, cleaner reaction, lower cost, and lowering the acidic wastes, which is environmentally favored. In this way, the reactivity of solid superacidic catalysts such as sulfated zirconia, heteropolyacid $H_4Si(W_3O_{10})_4$, and a few types of zeolites have been studied and compared in the preparation of DOP. Showing the ability of sulfated zirconia under solvent-free condition in the preparation of important ester compounds, which have been found wide applications as plasticizers and ester base fluids, was also aimed. For this purpose esterification of mono- and di-carboxylic acids by mono and polyols has been investigated. It was observed that sulfated zirconia is an effective catalyst for this purpose.

2. Experimental

2.1. General

Phthalic anhydride (99% purity) was obtained from Farabi Petrochemical Co. (Iran). Diethyleneglycol and 2-ethylhexanol (98.8% purity) were purchased from Arak Petrochemical Co. (Iran). Caproic acid (98% purity) was obtained from Chem Reactive (Russia). Pentaerythritol was product of BASF (Germany). Heteropolyacid tungstosilicic acid $H_4Si(W_3O_{10})_4$, CAS No. 12027-38-2, in the form of white to light yellow crystalline solid, and *p*-toluenesulfonic acid were purchased from Merck Chemical Co. and used without further purification. Natural Zeolite (Clinoptilolite) was obtained from “Iran Zeolite Co.” (Tehran, Iran). It was activated before use by refluxing in 60% H_2SO_4 solution for 2 h, washing with hot water until neutralization (filtrate was checked by pH paper), and then drying at 450–500 °C for 3 h. ZEOKAR-2 and ASHNCH-3 are synthetic zeolites

Table 1
Characteristics of the natural and synthetic Zeolites

Physicochemical properties	ZEOKAR-2	ASHNCH-3	Natural zeolite
%SiO ₂	83.0–85.0	83.0–89.0	62.0–64.0
%Al ₂ O ₃	9.0–11.0	9.0–15.0	10.0–12.0
%Fe ₂ O ₃	–	≤0.2	0.8–1.0
%CaO	–	–	0.3–1.0
%Na ₂ O	0.3	≤0.7	5.0–6.5
%K ₂ O	–	–	2.0–4.0
%Rare earth oxides	2.3	–	–
Bulk density (kg/dm ³)	0.69–0.70	0.62–0.70	0.85–1.00
Particle size (mm)	2.50–5.00	2.50–5.00	1.46–2.46
Color	White	Gray	Light green

and purchased from YUKOS Co. (Russian). They have been activated by heating at 550–600 °C for 3 h. The characteristic features of natural and synthetic zeolites are given in Table 1. Sulfated ZrO₂ was prepared according to literature [31].

2.2. Instrumentation

¹H-NMR (CDCl₃) and FT-IR (neat) spectra were recorded on a Bruker-spectrospin-Avance 400-ultra shield spectrometer and a Shimadzu 200-91527 spectrophotometer, respectively.

2.3. *Trans*-(2-hexenyl)succinic anhydride

The ene-reaction was taken place according to reference [39]. An autoclave equipped with an agitator, internal and external thermometers, a manometer, and safety valve has been charged with 1-hexene (328 g, 4 mol), maleic anhydride (98 g, 1 mol) and phenothiazine (0.001 g). Temperature has been raised to 210 °C in a period of 1 h and maintained at this temperature for additional 11 h. The reaction mixture was subjected to distillation under atmospheric pressure in order to remove excess of 1-hexene and followed by vacuum distillation to separate the main product, *trans*-(2-hexenyl)succinic anhydride, (b.p. 165 °C/1 mmHg, 66% yield).

2.4. General procedure for esterification reaction

In a round-bottom flask equipped with an efficient mechanical stirrer, reflux condenser, and Dean-Stark trap acid/anhydride, and alcohol were placed and heated at the defined temperature for the defined time (Tables 2 and 3). The reactions progress was followed by measuring the amount of collected water. After completion of reaction, the mixture was allowed to settle down and then decanted. The reaction mixture was distilled under reduced pressure for removing the excess of alcohol and distillation continued to obtain the main product. The reactions conversions were calculated by determination of acid numbers of the crude reactions mixture.

Table 2
Reaction conditions and conversions of DOP synthesis by various catalysts

Entry	Catalyst	Catalyst (g/mol PA) ^a	EA/PA (molar ratio) ^b	Toluene (ml/mol PA)	Reaction temperature (°C)	Reaction time (min)	Conversion (%) ^c
1	PTSA ^d	3.2	2.4	150	90	240	98.2
2	ZEOKAR-2	40.5	2.9	–	110–180	240	62.0
3	ASHNCH-3	40.5	2.9	–	110–180	240	67.5
4	Natural Zeolite	40.5	2.3	–	110–180	240	87.1
5	H ₄ Si(W ₃ O ₁₀) ₄	10.5	2.3	–	110–170	100	88.5
6	Sulfated ZrO ₂	20.3	2.3	–	110–190	240	98.4
7	Sulfated ZrO ₂	40.5	2.3	–	110–190	240	98.9
8	Sulfated ZrO ₂	48.0	2.3	–	110–190	240	98.9
9	Sulfated ZrO ₂	40.5	2.3	–	110–190	85	96.4
10	Sulfated ZrO ₂	40.5	2.3	–	110–190	105	97.3

^a Phthalic anhydride.

^b 2-Ethylhexanol.

^c Calculated based on acid number.

^d *p*-Toluene sulfonic acid.

2.5. Determination of reactions conversion by acid number measurements

The extent of conversion for synthesis of DOP was calculated from the following equation:

$$\text{conversion (\%)} = [(200.87 - a) \times 100] / 200.87$$

where “*a*” is the acid number (mg KOH/g) of the crude reaction mixture after completion of the reaction, corrected by amount of KOH required for the catalyst. The number 200.87 is the obtained acid number (mg KOH/g) of the half esterified phthalic anhydride, (C₆H₄)COOC₈H₁₇·COOH. The half esterification of phthalic anhydride is taking place in the absence of catalyst. This is the acid number (mg KOH/g) of the reaction mixture obtained from refluxing of equimolar mixture of phthalic anhydride and 2-ethylhexanol for 2 h in the absence of solvent and catalyst (theoretical value is 201.59). The extent of conversion for esterification of *trans*-(2-hexenyl)succinic anhydride was calculated from same equation in which 178.54 was used in place of 200.87. The number was obtained same as for phthalic anhydride (theoretical value is 179.58). This number is acid number (mg KOH/g) of the half esterified anhydride. The extent of conversions for esterifications of mono- and di-carboxylic

acids was calculated by the following equation:

$$\text{conversion (\%)} = [(a_1 - a_2) \times 100] / a_1$$

where “*a*₁” is the acid number (mg KOH/g) of the reaction mixture at the beginning, and “*a*₂” is the acid number (mg KOH/g) of the crude reaction mixture after completion of the reaction. Both values are corrected by amount of KOH required for catalyst. The obtained values for extent of conversions were in accordance with the values obtained based on collected water.

3. Results and discussions

Esterification of phthalic anhydride by alcohol takes place in two stages. The first stage is so rapid that it can be carried out in the absence of catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by acid catalyst and the resulting water must be removed from the reaction mixture. In this work, various acidic catalysts and zeolites were used for preparation of dioctylphthalate, DOP (Scheme 1). The characteristics features of the used natural and synthetic zeolites are given in Table 1. The investigated catalysts were easily separated from the product by simple decantation. The excess of 2-ethylhexanol was

Table 3
Reaction conditions and conversions of esterification reaction using sulfated ZrO₂

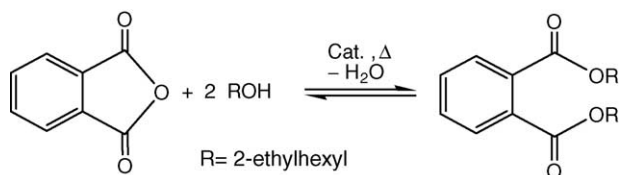
Acid	Alcohol	Catalyst (mass %) ^a	Alcohol/acid (molar ratio)	Reaction temperature (°C)	Reaction time (min)	Conversion (%) ^b	b.p. (°C) ^c
Sebacic acid	2-Et-Hexanol	2.3	2.2	110–170	90	96.4	210–220
<i>Trans</i> -(2-hexenyl)succinic anhydride ^d	2-Et-Hexanol	2.3	2.2	110–180	120	97.3	190–200
Adipic acid	2-Et-Hexanol	2.3	2.2	110–160	120	95.6	165–175
Caproic acid	Diethyleneglycol	2.3	2.2	110–160	90	97.7	200–210
Caproic acid	Pentaerythritol	2.3	4.4	110–190	150	96.5	210–220

^a Based on acid or anhydride.

^b Calculated based on acid number.

^c At 1–2 mmHg.

^d See Section 2.



Scheme 1.

removed under reduced pressure and the reactions conversions were determined by measuring the acid number of the obtained crude reaction mixture. The obtained products were characterized by FT-IR and $^1\text{H-NMR}$ spectroscopies. The refractive indices of the products were also measured and compared with those for DOP. Reactions condition and conversions for the investigated catalysts are given in Table 2.

Using of *p*-toluene sulfonic acid, which is a homogeneous catalyst was carried out for comparison. The important aspect of the present work is caring out the reaction under solvent-free condition. This is very important points from economical and environmental views. Sulfated zirconia showed the maximum reactivity among other catalysts within 4 h. The observed reactivity order of the investigated catalysts is as follow.

Sulfated $\text{ZrO}_2 \sim p$ -toluene sulfonic acid > natural

zeolite > ASHNCH-3 > ZEOKAR-2

Although the reactivity of the remaining catalysts is lower than homogeneous *p*-toluene sulfonic acid, but it must be noted they have easy work-up and they use without any solvent. Except in entry 5, heteropolyacid $\text{H}_4\text{Si}(\text{W}_3\text{O}_{10})_4$, the neutralization and washing steps are omitted for heterogeneous catalysts. Removing of catalyst residue from the obtained product is a part of reaction work-up when *p*-toluene sulfonic acid (entry 1) and heteropolyacid $\text{H}_4\text{Si}(\text{W}_3\text{O}_{10})_4$ (entry 5) use as catalyst.

The data given in Table 2 also show that increasing the amount of sulfated ZrO_2 up to 48.0 g/mol of phthalic anhydride has not significant effect on the reaction conversion (entries 6–8). Reaction conversion reaches to about 96.4% conversion within 85 min using this catalyst (entry 9), and only small change takes place in the reaction conversions after this time (entries 10, 6). In order to ensuring the absence of any acid and sulfate anion in the obtained product, about 2 ml of the obtained DOP was well stirred with 2 ml of water. The Aqueous phase had pH of about 7.0 and no precipitate was observed when the barium chloride solution was added.

The effectiveness of sulfated zirconia was also shown by performing a series of esterification reactions of acids/anhydrides by different alcohols. The reactions conditions and conversions as well as boiling points are given in Table 3. Boiling points are in accordance with the literature reported values. The reactions conversions, which calculated by measuring the acid number of the crude reactions mixture, were higher than 96% in all cases. All obtained products are important materials and they have wide applications as plas-

ticizer and synthetic base oil. For example, dioctyladipate (DOA) is an environmentally friendly plasticizer and found wide applications due its biocompatibility [40]. Dioctylsebacate (DOS) is an important synthetic diester base oil, which was chosen as calibration fluid for the viscosity measurements of ester base oils, since its viscosity–pressure relationship is well known [41].

Trans-(2-hexenyl)succinic anhydride was prepared via ene-reaction between succinic anhydride and 1-hexene in the presence of phenothiazine [39]. We have previously reported the preparation of synthetic ester base oil from *trans*-(2-hexenyl)succinic acid [42]. The catalytic condensation reaction of *trans*-(2-hexenyl)succinic anhydride by with tri-, tetra-ethylene glycols leading to the formation of macrocyclic crown esters base oil is also under investigation in our group. In the present study, esterification reaction of *trans*-(2-hexenyl)succinic anhydride by 2-ethylhexanol in the presence of sulfated zirconia performed in high conversion (97.3%).

The point, which would be noted in Tables 2 and 3 is reaction temperatures. In contrast to entry 1, which was carried out at a fixed temperature, the remaining reactions were performed at a wide temperature range. The lower limit observed when the reaction started (beginning of water separation). The upper limit observed when the reaction terminated (cessation of water separation). The reactions temperatures were gradually raised from lower limit to upper limit during reaction progress. This is because of performing the reactions in the absence of solvent. Under this condition, the reaction composition will dramatically change as the reaction progress, in compared when using solvent (Table 2, entry 1), and temperature changes will be sever. At the beginning of the reaction, the mixture includes anhydride/carboxylic acid, 2-ethylhexanol (which play the solvent role), and catalyst. As the reaction progress, anhydride/carboxylic acid and the alcohol were gradually consumed and ester (product) formed. At the end of the reaction we have large amount of ester (which now play the solvent role), catalyst, and small amounts of reactants. In fact, because of lack of solvent, the reaction temperature is controlled by reaction mixture composition.

In summary, the investigated heterogeneous catalysts showed high efficiency for esterification reactions. They have many advantages over homogeneous catalysts e.g., (a) high reaction yield, (b) not requiring for solvent and therefore low cost, (c) readily availability and (d) not requiring for neutralization and washing steps which produce large amounts acidic waste (environmentally friendly). Among the investigated catalysts, sulfated zirconia was showed the best reactivity and efficiency. In addition, these catalysts can be ecologically and economically preferred over homogeneous catalysts. Using these types of catalysts in the production of esters like DOP, DOA, DOS and also polyol esters will make the industrial processes easier, cleaner, and less complicated. They also will have less corrosion problem than homogeneous catalysts.

4. Conclusion

Esterification reactions of phthalic anhydride by 2-ethylhexanol in the presence of solid acidic catalysts have been investigated under solvent-less condition. The results were compared with the case of homogeneous catalyst, *p*-toluene sulfonic acid. Sulfated zirconia was showed the best reactivity and efficiency among the investigated heterogeneous catalysts. Effectiveness of the sulfated zirconia in the preparation of important ester compounds, which have found wide applications as plasticizer and ester base fluids, e.g. dioctyladipate (DOA) and dioctylsebacate (DOS), and polyol esters was also investigated. Using of these catalysts make the industrial processes easier, cleaner, and less complicated. The reaction work-up is also simplified. These catalysts are environmentally friendly and cleaner than conventional homogeneous catalysts, because they do not need solvent and they have very low waste. These parameters also make them economically preferred.

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