

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

Firdovsi Tataroglu Sejidov^{a,*}, Yagoub Mansoori^{b,**}, Nadereh Goodarzi^a

^a Chemistry Department, Azad Islamic University of Tabriz, Darvaze Tehran, Tabriz, Iran

^b Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran

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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,

* Corresponding author. Tel.: +98 411 331 21 50; fax: +98 411 331 86 81.

** Corresponding author. Tel.: +98 21 7391 2703; fax: +98 21 749 1204.

E-mail addresses: firdovsi5@yahoo.com (F.T. Sejidov),
ya_mansoori@yahoo.com (Y. Mansoori).

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.

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