



Synthesis of Neopentylglycolesters using homogeneous and heterogeneous catalysts as synthetic lubricant base oils

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Abstract

The preparation of Neopentylglycol (NPG) esters via esterification reaction of Neopentylglycol by carboxylic acid in the presence of solid acidic catalysts has been investigated. The used catalysts were natural zeolite, acidic ion exchange resin catalyst (polystyren divinyl benzensulfated), synthetic zeolites (ZEOKAR-2, ASHNCH-3), heteropolyacid $H_4Si(W_3O_{10})_4$, and sulfated metal oxide 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. For this purpose esterification of ethylenglycol, trimethylolpropan using sulfated ZrO_2 by carboxylic acids has been investigated.

Keywords: Esterification; Solid catalyst; Zeolite; Sulfated zirconia; NPG.

Introduction

Plasticizers are important class of low molecular weight nonvolatile compounds that are widely used in the polymer industries [1]. Some commercially available plasticizers such as dibutyl phthalate (DBP), di-iso-butyl phthalate (DIBP), di-isopentylphthalate (DIPP), di-iso-heptyl phthalate (DIHP), and dioctyl phthalate (DOP) are normally prepared via the esterification reaction of phthalic anhydride by the corresponding alcohols in the presence of acidic catalysts [2-4]. Among plasticizers, dioctyl phthalate (DOP), DOA (dioctyladipate), and dioctyl terephthalate (DOTP) have been found wide applications due their biocompatibility [5-7]. Heteropolyacids are widely used in variety of acid catalyzed reactions such as esterification [8, 9] etherification hydration of olefin deesterification [10] dehydration of alcohol [11] and polymerization of THF [12] in homogenous and heterogeneous systems. Their application the production of DOP was also reported. The catalytic activity of some $AlPO_4$ molecular such as $AlPO_4-12$, etc. in the esterification reaction of propionic acid with n-butanol has been investigated [13]. Preparation of DOP (dioctylphthalat) using silicoaluminophosphate molecular sieve HSAPO-1 has also reported by Zhao [14].

Among various sulfated metal oxides, sulfated zirconia has attracted much attention and has been extensively investigated during the last two decades [15, 16] The major concern of this research still focuses on the acidity, in terms of types Sulfated zirconia catalyst, promoted with iron aluminum and manganese, has shown much higher

activity and could isomerize n-butane at $35^\circ C$ under normal pressure in a continuous-flow recirculation tank reactor. Zeolites are widely used within the petrochemical industry in acid catalyzed processes, and there are several reviews concerning recent developments in their use in the synthesis of fine and specialty chemicals [17-20]. For this purpose esterification of polyol alcohols by carboxylic acids has been investigated. It was observed that sulfated zirconia is an effective catalyst for this purpose. Zirconia is an effective catalyst for this purpose.

Experimental

General

Neopentylglycol, Ethylenglycol(99% purity), pentanoic acid (99% purity), capric acid (98% purity), heptanoic acid (99% purity), were obtained from Merck Chemical Co. Heteropolyacid acid $H_4Si(W_3O_{10})_4$, CAS No. 12027-38-2, in the form of white to light yellow crystalline solid), polystyrene divinyl benzene sulfated and p-Toluenesulfonic acid were purchased from Merck Chemical. 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 (filtrated was checked by pH paper), and then drying at $450-500^\circ C$ for 3 h. ZEOKAR-2 and ASHNCH-3 are synthetic zeolites and purchased from YUKOS Co. (Russian). They have been activated by heating at $550-600^\circ C$ for 3 h.

Table 1. Characteristics of the natural and synthetic Zeolites [21]

Physicochemical properties	ASHNCH-3	ZEOKAR-2	Natural Zeolit
%SiO ₂	83.0-85.0	83.0-89	62.0-69
%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
%KO ₂	-	-	2.0-4.0
sRare earth oxid	2.3	-	-
Density (dm/Kg ³)	0.69-0.7	0.62-0.7	0.85-1.0
size particle (mm)	2.5-5.0	2.5-5.0	1.46-2.46
Color	white	Gray	Green Light

Typical procedure for preparation of diol esters

Fatty acid and alcohol was transferred into a reaction flask. The reaction flask was equipped with a modified Dean – Stark distillation set-up, magnetic stirrer, condenser, dropping funnel and heating plate. 100 ml of toluene is added to the reaction mixture. Heating continued for not more than 5 hours. Water formed as by-product of the esterification reaction was removed continuously by means of distillation with the aid of toluene while toluene was recycled continuously back to the reaction mixture. After the reaction was completed, the crude product was cooled to ambient temperature. Then, heterogeneous acid catalyst was removed by simple filtration and excess solvent was removed from the crude product by means of rotary evaporation. The product was dried with anhydrous sodium sulphate and the hydrated sodium sulphate was removed from the dried product. The dried product was further

purified by using a column packed with silica gel. Trace solvent was further removed by a vacuum pump and finally unreacted fatty acid was removed by vacuum distillation. Unreacted fatty acid would remain as residue while Polyol esters would be collected as distillates.

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.

Spectra data neopentylglycoldicaproat ester

¹H-NMR:δ(ppm) 0.89 (t ,J=7.5Hz, 6H ,2 CH₃),0.96 (s ,6H 2CH₃), 1.30 (m,8 H , 4CH₂), 1.62 (quin , J= 7.2Hz ,4H , 2CH₂), 2.30 (t, J=7.5Hz, 4H ,2CH₂CO), 3.87(s, 4H, 2CH₂O), 3.87 (s , 4H , 2CH₂O).

¹³C- NMR δ (ppm)13.77 , 21.67, 22.20, 24.58, 31.22 , 34.15 , 34.56 , 68.90 , 173.58.FT-IR: $\bar{\nu}$ (cm⁻¹) 2958 , 2869 ,

1739 , 1466 , 1378 , 1244 , 1168 , 1104 , 1006 .

Spectra data neopentylglycoldipentanoat ester

$^1\text{H-NMR}$: δ (ppm) 0.91 (t ,J=7.5Hz, 6H ,2 CH₃) ,1.33 (quin,J=7.2Hz, 4H, 2CH₂), 1.60 (quin, J=7.5 Hz ,4H, 2CH₂), 2.32 (t, J= 7.5, 4H , 2CH₂CO), 4.26 (s, 4H, 2CH₂O) FT-IR: $\bar{\nu}$ (cm⁻¹) 2955, 2867, 1741, 1459, 1378, 1241, 1167, 1105 ,1061 ,965

Spectra data ethylenglycoldicaproat ester

$^1\text{H-NMR}$: δ (ppm) 0.86 (t ,J=6.3Hz, 6H ,2 CH₃) ,1.29 (bs , 8H, 4CH₂), 1.61 (quin, J=6.3Hz ,4H, 2CH₂), 2.31 (t, J= 7.5, 4H , 2CH₂CO), 4.26 (s, 4H ,2CH₂O). $^{13}\text{C NMR}$ δ :(ppm)13.82 , 22.24 , 24.52 , 31.21 , 34.04 , 61.93 , 173.50.FT-IR: $\bar{\nu}$ (cm⁻¹) 2956 , 2868 , 1742 , 1450 ,1379 , 1347 ,1277 ,1242 , 1167 , 1105 ,1060 ,965.

Spectra data ethylenglycoldiheptanoat ester

$^1\text{H-NMR}$: δ (ppm) 0.86 (t ,J=7.5Hz, 6H ,2 CH₃) ,1.27 (m ,12H , 7.2Hz , 6CH₂), 1.58 (quin, J=7.2 Hz ,4H, 2CH₂CO), 2.30 (t, J= 7.5Hz ,4H , 2CH₂), 4.25 (s, 4H ,2CH₂O) $^{13}\text{C-NMR}$: δ (ppm) 13.93 , 22.42 , 24.81 , 28.72 , 31.39 , 34.10 , 61.95 , 173.54.FT-IR: $\bar{\nu}$ (cm⁻¹) 2955 , 2867 , 1741 , 1459 ,1378 , 1241, 1167, 1105 , 1061 , 965 cm⁻¹

Spectra data trimethylolpropantricaproat ester

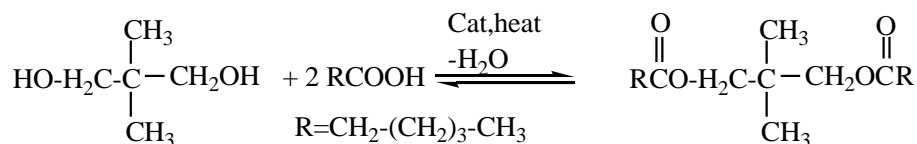
$^1\text{H-NMR}$ (CDCl₃ , 400MHz) δ (ppm) 3.98 (s, 6H) ,2.27 (t, 6H, J= 7.6Hz), 1.54(quin, 6H, J=7.4Hz), 1.44(q, 2H, J= 7.6), 1.26 (m, 12H), 0.86(t, 3H, J=7.2), 0.85(t, 9H, J =7.6 Hz). $^{13}\text{C NMR}$ (CDCl₃ , 400MHz) δ (ppm) 172.39, 62.59 , 39.5 , 33.09 , 30.18 , 23.52 , 21.93 , 21.19 , 12.78.

FT-IR: $\bar{\nu}$ (KBr) 2970, 2930, 2865, 1740,1465,1250,1100 cm⁻¹.

Result and discussion

Esterification of NPG by acid takes place in two stages. The first stage is so rapid that it can be carried out in the absence ofcatalyst. 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. (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 reactions conversions were determined by measuring the acid number of the obtained crude reaction mixture. The obtained products were characterized by FT-IR, $^{13}\text{C-NMR}$, and $^1\text{H-NMR}$ spectroscopies. Reactions condition and conversions for the investigated catalysts are given in Table 2. Using of p-toluenesulfonic acid, which is ahomogeneous catalyst was carried out for comparison.



Scheme 1: Preparation of Neopentylglycol ester

Table 2. Reaction conditions and conversions of NPG synthesis by various catalysts [22]

Entry	Catalyst	Catalyst (g/mol C6) ^a	NPG/C6 (molarratio) ^b	Toluene (ml/mol NPG)	Reaction Temperature(°C)	Reaction time (min)	Conversion ^c (%)
1	PTSA ^d	4.5	3.4	150	100	240	98.7
2	ZEOKAR-2	40.5	3.2	-	110-190	240	58.7
3	ASHNCH-3	40.5	3.2	-	110-190	240	63.5
4	Natural Zeolite	40.5	3.6	-	110-190	240	87.7
5	H ₄ Si(W ₃ O ₁₀) ₄	20.5	3.6	-	100-180	100	89.6
6	Sulfated ZrO ₂	30.3	3.6	-	100-200	240	98.7
7	Sulfated ZrO ₂	40.5	3.6	-	110-200	240	99.1
8	Sulfated ZrO ₂	48.0	3.6	-	110-200	240	99.1
9	Sulfated ZrO ₂	40.5	3.6	-	110-200	85	97.5
10	Sulfated ZrO ₂	40.5	3.6	-	110-200	105	98.6

aCaproic acid

b.Neopentylglycol.

c Calculated based on acid number.

dp-Toluene sulfonic acid

The important aspect of the present work is caring out the reaction under solvent free condition. This is very important points from economic 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.

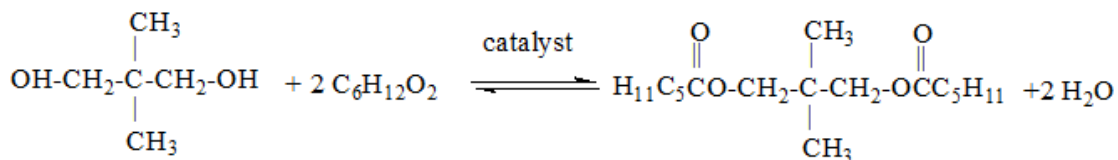
Sulfated ZrO₂~p-toluene sulfonic acid >natural zeolite> ASHNCH-3 > ZEOKAR-2> acidic ion exchange resin catalyst (polystyren divinyl benzensulfated) Although the reactivity of the remaining catalysts is lower than homogeneous p-toluene sulfonic acid, but it must be noted they have easy work-up and they use without any solvent. Except in entry 5, heteropolyacid H₄Si (W₃O₁₀)₄ the neutralization and washing steps are

omitted for heterogeneous catalysts. Removing of catalyst residue from the obtained product is a part of work-up when p-toluenesulfonic acid (entry 1) and heteropolyacid H₄Si (W₃O₁₀)₄ is used. The data given in Table 2 also show that increasing the amount of sulfated ZrO₂ up to 48.0 g/mol of caproic acid has not significant effect on the reaction conversion. Within 85min using this catalyst (entry 9), only small change takes place in the reaction conversions refer to other time (entries 10, 6).

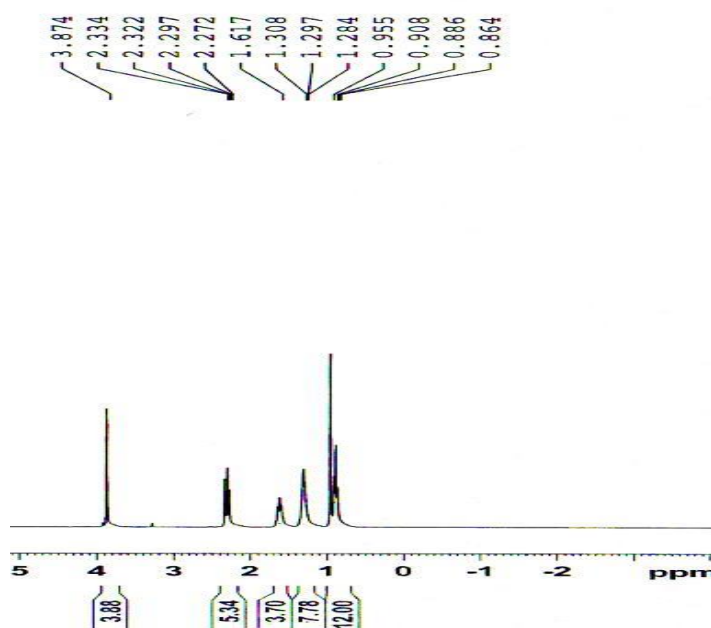
Neopentylglycoldicaproate ester, This ester was prepared according to the general procedure by using Neopentylglycol (1 mole) and caproic acid (2moles). Its ¹H-NMR spectrum in chloroform showed a triplet at δ = 0.89 ppm with

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J=7.5Hz for two methyl groups, a singlet at $\delta=0.96$ ppm for two methylene groups, a multiplet at $\delta=1.30$ ppm for four methylene groups next to carbonyl group,

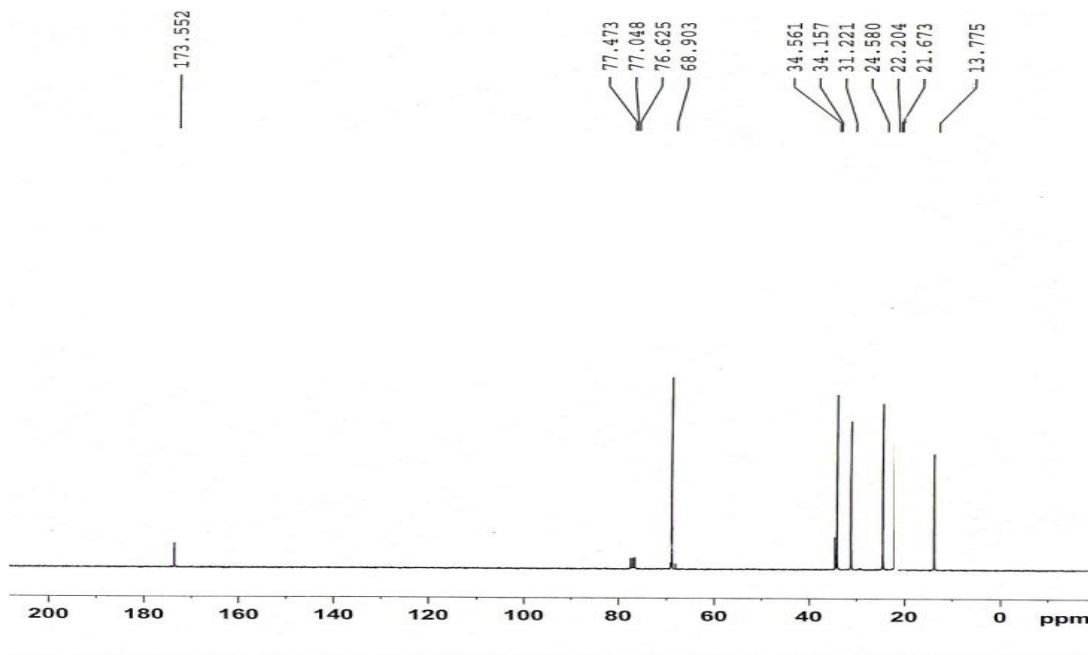


Scheme 2: Preparation of Neopentylglycoldicaprate ester



Scheme 3. ¹H-NMR Spectrum of Neopentyl glycoldicaprate ester

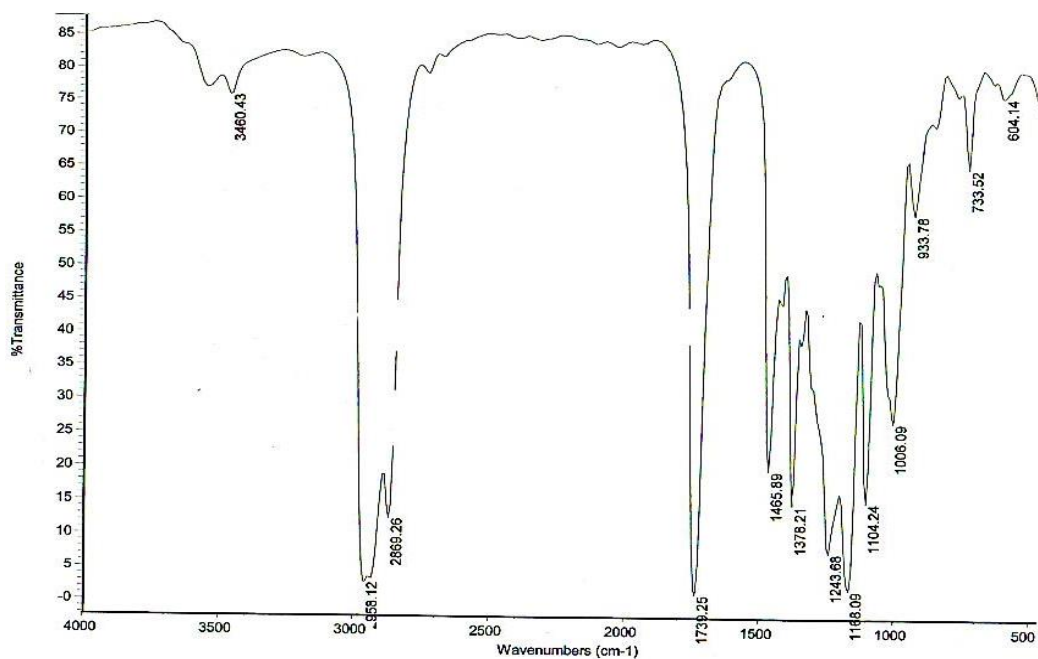
a quintet at $\delta=1.62$ ppm with J=7.2 Hz for two methylene groups, and triplet at $\delta=2.30$ ppm for next two methylene group, and singlet at $\delta=3.85$ - 3.87 for four methylene groups next to oxygen.



Scheme 4. ¹³C-NMR Spectrum of Neopentylglycoldicaproate ester

Its ¹³C-NMR showed nine peaks for nine different carbons of which the peak at $\delta=173.58$ ppm was due to carbonyl groups.

The peak at $\delta =68.97$ ppm was due to carbon of methylene next to oxygen and other peaks are due to aliphatic alkyl chain.



Scheme 5. FT-IR Spectrum of Neopentylglycoldicaproate ester

Its FT-IR showed strong absorption at 1739 cm^{-1} due to carbonyl groups.

Table 3. Reaction conditions and conversions of esterification reaction using sulfated ZrO_2

Acid	Alcohol	Catalyst %	lcoholA/acid	Reactio Temperature($^{\circ}\text{C}$)	Reaction time (min)	Conversion ^d (%)
5 ^a C	ethylenglycol	3.3	3.1	100-180	105	96
C6 ^b	ethylenglycol	3.3	3.1	110-190	125	98.1
C6	ethylenglycol	3.3	3.1	100-200	130	96.6
C7 ^c	trimethylolpropan	3.3	3.1	110-190	105	98.8

^aPentanoic acid

^bhexanoic acid

^cheptanoic acid

^d Calculated based on acid number

Conclusion

Esterification reactions of Neopentylglycol by caproic acid 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. ethylenglycol, and trimethylol propane 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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