Communications In Catalysis
Vol. 1, No. 1, 2024, pp.11-19

Azarbaijan Shahid Madani University

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

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Received: 2024-02-25, Revised: 2024-03-11, Accepted: 2024-03-20

Abstract

The preparation of Neopenthylglycol (NPG) esters via esterification reaction of Neopenthylglycol by carboxylic acid in the presence of solid acidic catalysts has been investigated. The used catalysts were natural zeolite, acidic ion exchange resin catalyst (polyestyrendivinylbenzensulfated), synthetic zeolites (ZEOKAR-2, ASHNCH-3), heteropolyacid $H_4Si(W_3O_{10})_4$, and sulfated metal oxid 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 nonvolatilecompounds that are widely used in the polymerindustries [1]. Some commercially available plasticizers such asdibutyl phthalate (DBP), di-iso-butyl phthalate (DIBP), di-isopentylphthalate (DIPP), di-iso-heptyl phthalate (DIHP),and dioctyl phthalate (DOP) are normally prepared via theesterification reaction of phthalic anhydride by the correspondingalcohols in the presence of acidic catalysts [2-4]. Amongplasticizers, dioctyl phthalate (DOP), DOA (dioctyladipate),and dioctyl terephthalate (DOTP) have been found wideapplications due their biocompatibility [5-7]. And co-workers.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 AlPO4-12, etc. in the esterification reaction of propinic acid with n-butanol has been investigated [13]. Preparation of DOP (dioctylphetalat) 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°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

Neopenthylglycol,Ethylenglycol(99% purity),pentanoicacid (99% purity), caprice acid (98% purity), heptanoicacid (99% purity), were obtained from Merck Chemical Co. Heteropolyacid acid $H_4Si(W_3O_{10})_4$, CAS No. 12027-38-2, inthe form of white to light yellow crystalline solid),polyestyrendivinylbenzensulfated 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 hotwater until neutralization (filtrated was checked by pH paper), and then drying at 450–500°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°C for 3 h.

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

Physicochemical properties	ASHNCH-3	ZEOKAR-2	Natural Zeolit
%2 SiO	83.0-85.0	83.0-89	62.0-69
%Al_2O_3	9.0-11.0	9.0-15.0	10.0-12.0
%$_2O_3Fe$	-	0.2>	0.8-1.0
%CaO	-	-	0.3-1.0
%Na_2O	0.3	0.7>	5.0-6.5
%$_2OK$	-	-	2.0-4.0
sRare earthoxid	2.3	-	-
Density (^{3})dm/Kg	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	reenLightg

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. 100cc 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 hydratedsodiumsulphate 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

^{1}H-NMR ($CDCl_3$) and FT-IR (neat) spectra were recorded on a Bruker-spectrospin-Avance 400-ultra shield spectrumeter and a Shimadzu 200-91527 spectrophotometer, respectively.

Spectra data neopenthylglycoldicaproat ester

^{1}H-NMR:δ(ppm) 0.89 (t ,J=7.5Hz, 6H ,2 CH_3) ,0.96 (s ,6H 2CH_3), 1.30 (m,8 H , 4CH_2), 1.62 (quin , J= 7.2Hz ,4H , 2CH_2), 2.30 (t, J=7.5Hz, 4H ,2CH_2CO), 3.87(s, 4H, 2CH_2O), 3.87 (s , 4H , 2CH_2O).

^{13}C- NMR δ (ppm)13.77 , 21.67, 22.20, 24.58, 31.22 , 34.15 , 34.56 , 68.90 , 173.58.FT-IR: $\bar{\upsilon}$ (cm^{-1}) 2958 , 2869 , 1739 , 1466 , 1378 , 1244 , 1168 , 1104 , 1006 .

Spectra data neopenthylglycoldipentanoat ester

^{1}H-NMR:δ (ppm) 0.91 (t ,J=7.5Hz, 6H ,2 CH_3) ,1.33 (quin,J=7.2Hz, 4H, $2CH_2$), 1.60 (quin, J=7.5 Hz ,4H, $2CH_2$), 2.32 (t, J= 7.5, 4H , $2CH_2CO$), 4.26 (s, 4H, $2CH_2O$) FT-IR: $\bar{\upsilon}$ (cm^{-1}) 2955, 2867, 1741, 1459, 1378, 1241, 1167, 1105 ,1061 , 965

Spectra data ethylenglycoldicaproat ester

^{1}H-NMR : δ(ppm) 0.86 (t ,J=6.3Hz, 6H ,2 CH_3) ,1.29 (bs , 8H, $4CH_2$), 1.61 (quin, J=6.3Hz ,4H, $2CH_2$), 2.31 (t, J= 7.5, 4H , $2CH_2CO$), 4.26 (s, 4H ,$2CH_2O$).^{13}C NMRδ:(ppm)13.82 , 22.24 , 24.52 , 31.21 , 34.04 , 61.93 , 173.50.FT-IR: $\bar{\upsilon}$ (cm^{-1}) 2956 , 2868 , 1742 , 1450 ,1379 , 1347 ,1277 ,1242 , 1167 , 1105 ,1060 ,965.

Spectra data ethylenglycoldiheptanoat ester

^{1}H-NMR: δ(ppm) 0.86 (t ,J=7.5Hz, 6H ,2 CH_3) ,1.27 (m ,12H , 7.2Hz , $6CH_2$), 1.58 (quin, J=7.2 Hz ,4H, $2CH_2CO$), 2.30 (t, J= 7.5Hz ,4H , $2CH_2$), 4.25 (s, 4H ,$2CH_2O$) ^{13}C- NMR :δ (ppm) 13.93 , 22.42 , 24.81 , 28.72 , 31.39 , 34.10 , 61.95 , 173.54.FT-IR: $\bar{\upsilon}$ (cm^{-1}) 2955 , 2867 , 1741 , 1459 ,1378 , 1241, 1167, 1105 , 1061 , 965 cm^{-1}

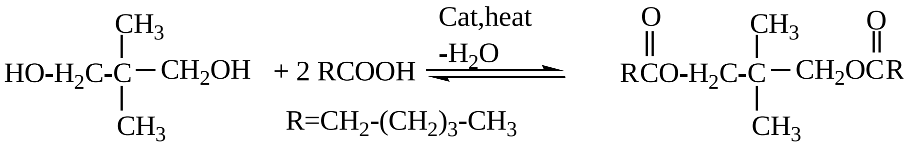
Spectra data trimethylolpropantricaproat ester

^{1}H-NMR ($CDCl_3$, 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}C NMR ($CDCl_3$, 400MHz) δ(ppm) 172.39, 62.59 , 39.5 , 33.09 , 30.18 , 23.52 , 21.93 , 21.19 , 12.78. FT-IR: $\bar{\upsilon}$ (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, ^{13C}-NMR, and ^{1}H-NMR spectroscopies. Reactions condition and conversions for the investigated catalysts are given in Table2. Using of p-toluenesulfonic acid, which is ahomogeneous catalyst was carried out for comparison.



$$HO\text{-}H_2C\text{-}C(CH_3)_2\text{-}CH_2OH + 2\,RCOOH \xrightleftharpoons[\;]{\text{Cat,heat}\;-H_2O} RCO(=O)\text{-}H_2C\text{-}C(CH_3)_2\text{-}CH_2OC(=O)R$$

$R=CH_2\text{-}(CH_2)_3\text{-}CH_3$

Scheme 1: Preparation of Neopenthylglycol ester

Table2: 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	$H_4Si(W_3O_{10})_4$	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.Neopenthylglycol.

c Calculated based on acid number.

d*p*-Toluene sulfonic acid

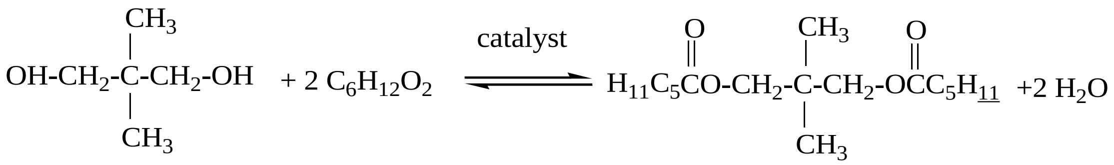
The important aspect of the present work is caring out the reaction under solvent free condition. This is very important points from economic and environmental views. Sulfatedzirconia showed the maximum reactivity among other catalysts within 4 h. The observed reactivity order of the investigated catalysts is as follow.

Sulfated ZrO_2~p-toluene sulfonic acid >natural zeolite> ASHNCH-3 > ZEOKAR-2> acidic ion exchange resin catalyst (polyestyrendivinylbenzensulfated)

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, heteropolyacidH4Si $(W_3O_{10})_4$ the neutralization and washing steps are omitted for heterogeneous catalysts. Removing of catalyst residue from the obtained product is a part of work-upwhen p-toluenesulfonic acid (entry 1) and heteropolyacid H_4Si $(W_3O_{10})_4$is preis used. The data given in Table 2 also show that increasing the amount of sulfated ZrO_2 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).

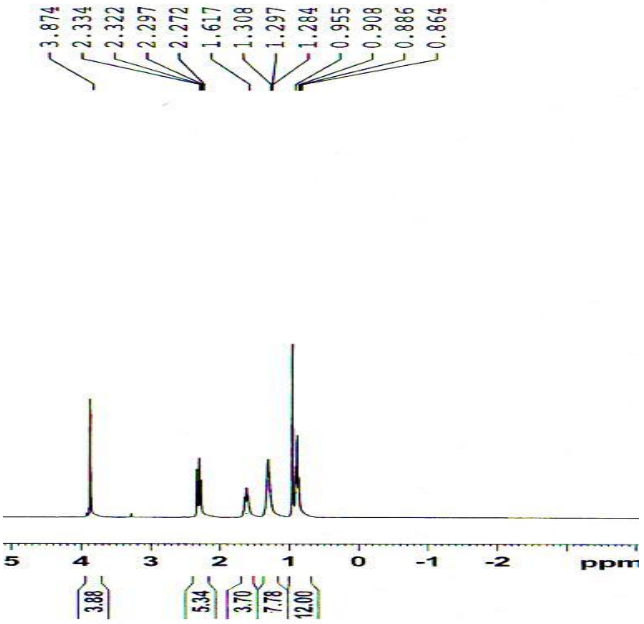
Neopenthylglycoldicaproateester, This ester was prepared according to the general procedure by using Neopenthylglycol (1 mole) and caproeic acid (2moles).

Its ^{1}H-NMR spectrum in chloroformshowed a triplet at δ = 0.89 ppm with J=7.5Hz for two methyl groups, a singlet at δ=0.96 ppm for two methylene groups, a multiplet at δ=1.30 ppm for four methylene groupsnext to carbonyl group,



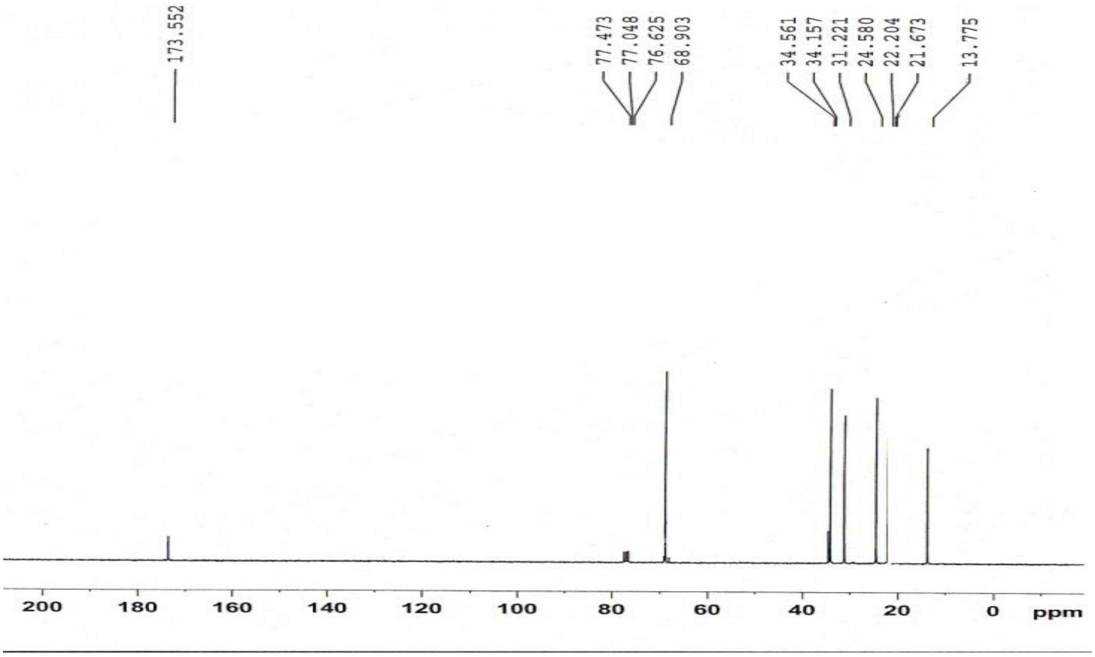
$$\mathrm{OH\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-}CH_2\text{-}OH} + 2\,\mathrm{C_6H_{12}O_2} \xrightleftharpoons{\text{catalyst}} \mathrm{H_{11}C_5\overset{\overset{\displaystyle O}{||}}{C}O\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-}CH_2\text{-}O\overset{\overset{\displaystyle O}{||}}{C}C_5H_{\underline{11}}} + 2\,\mathrm{H_2O}$$

Scheme 2: Preparation of Neopenthylglycoldicaproate ester



Scheme 3. ^{1}H-NMR Spectrum of Neopenthylglycoldicaproate ester

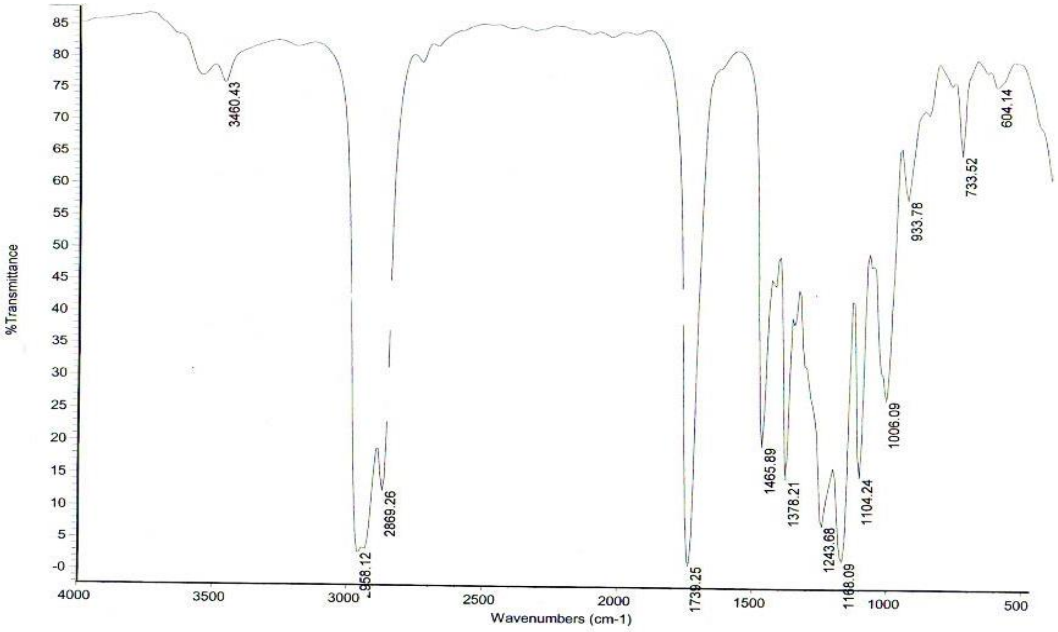
a quintet at δ=1.62 ppm with J=7.2 Hz for two methylene groups, and triplet at δ=2.30 ppm for next two methylene group , and singlet at δ=3.85-3.87 for four methylene groups next to oygene.



Scheme 4 .^{13}C-NMR Spectrum of Neopenthylglycoldicaproate ester

Its ^{13}C-NMR showed nine peaks for nine different carbons of which the peak at δ=173.58 ppm was due to carbonyl groups.

The peak at δ =68.97 ppm was due to carbon of methylene next to oxygene and other peaks are due to aliphatic alkyl chain.



Scheme 5. FT-IR Spectrum of Neopenthylglycoldicaproate 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(°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

^{a}Pentanoeic acid

^{b}.hexanoic acid

^{c}heptanoic acid

^{d} Calculated based on acid number

Conclusion

Esterification reactions of Neopenthylglycol 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 trimethylolpropane 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.

Acknowledgment

We are grateful to the research council of Urmia University for support of the present work.

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