

Synthesis of some Polyol Esters and Diesters Catalyzed with SnO₂ and Nano-SnO₂

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ABSTRACT: Esterification reactions of some polyols and diols were investigated in the presence of SnO₂ and nano-SnO₂ and the results were compared with the catalyst-free conditions. High conversions were obtained for most of the reactions in the presence of SnO₂ and nano-SnO₂ which shows the high catalytic activity of SnO₂ and nano-SnO₂ for the esterification reaction. Low cost of the catalysts compared to alkyl tins, high safety compared to protic acids such as sulfuric acid and high chemical and thermal stability of the catalysts make the reactions interesting for the large-scale production of various polyol esters. Due to the important role of the polyol esters in various industries especially in the lubricant industry, the introduced approach can be interesting.

KEYWORDS: Esterification; Polyol esters; Diesters, SnO₂, Nanoparticles.

INTRODUCTION

Animal fats such as sperm oil, lard oil, or vegetable oil such as rapeseed or castor oil were the main classes of lubricants until the nineteenth century. Around 1937, the investigation into the preparation of synthetic oil was begun in Germany. During World War II a range of synthetic oils with low pour point was developed with application in cold conditions. The synthesized esters resolved the freezing problem of the lubricants in cold weather, but the superior properties of polyol esters such as high flash point and low viscosity encourage the researchers to develop new lubricants [1].

Today, a wide range of application was recognized for esters such as automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils, and grease formulations. Ester oils are interesting due to low pour point, high flash point, low viscosity, high breakdown voltage and high performance. Moreover, ester lubricants

are nontoxic and biodegradable, so their applications have been extended to the food and cosmetic industry [2-8].

The reaction of a multi-functional carboxylic acid with alcohol or multi-functional alcohol with carboxylic acids gave a diester or polyol ester [9]. The most important esters with a wide application in the lubricant, the industry can be synthesized from alcohols such as pentaerythritol (PE), trimethylol propane (TMP) and neopentyl glycol (NPG). A wide variety of carboxylic acids were introduced for the reaction, that the number of carbons of carboxylic acid determined the properties of the final product [10-12]. Various catalysts are able to catalyze the esterification reaction such as sulfuric acid, *p*-toluenesulfonic acid, sodium bisulfate, various phosphorus compounds, zinc oxide, ion-exchange resins, tin compounds, etc [13]. Some of these catalysts have disadvantages which cause many problems in the synthetic

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procedure. For example, sulfuric acid is a dangerous and corrosive acid which due to the increase of the acid number of the product is avoided. Increasing the acid number led to the corrosion in the instruments. There is a similar problem for *p*-toluenesulfonic acid and phosphoric acid. Various tin compounds were used as the catalyst for the esterification reactions. Among them, SnO₂ due to its high performance and the low cost is interesting. For improving the catalytic activity of SnO₂, various modified SnO₂ catalysts such as SnO₂/γ-Al₂O₃ [14], SnO₂-TiO₂/SiO₂ [14], SO₄²⁻/SnO₂-SiO₂ [15, 16], SnO₂/WO₃ [17], SO₄²⁻/Fe₂O₃-SnO₂ [18], SO₄²⁻/Fe₂O₃-SnO₂ [19] were introduced. These modifications led to the increase of the catalyst performance with respect to time consuming and cost for the modifications. Herein, we report a novel method for the high conversion of esterification reaction using nano-SnO₂ as the catalyst under the dean-stark system for removing of the produced H₂O from the reaction. To the best of our knowledge, this work is the first report about esterification reactions of PE, TMP, NPG, ethylene glycol (EG), diethylene glycol (DEG) and glycerol with SnO₂ and nano-SnO₂ as the catalyst. As part of our current studies on the catalytic reactions [20-25], we have investigated the synthesis of polyol esters using SnO₂ and nano-SnO₂. Various alcohols in the reaction with acetic anhydride or a carboxylic acid derivative gave diesters or polyol esters in the presence of SnO₂ and nano-SnO₂.

EXPERIMENTAL SECTION

General

The chemicals used in this work were purchased from Merck and Sigma-Aldrich Chemical Companies. ¹H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13. NMR spectra were obtained on the solution in CDCl₃.

The typical procedure for the esterification reaction of PE with acetic anhydride in the presence of nano-SnO₂

PE (10 mmol), acetic anhydride (44 mmol) and nano-SnO₂ (0.08 g) were added to a two-necked flask attached to a thermometer and a dean-stark apparatus. A reflux column was connected above the dean-stark apparatus. The reaction mixture was heated with a mantle heater at 80 °C for 3.5 h. Then, the temperature was elevated to 140 °C for 0.5 h under vacuum to remove the excess of

acetic anhydride and produced acetic acid. Finally, the catalyst was separated via filtration, and the product was characterized by ¹H NMR.

The typical procedure for the esterification reaction of NPG with 2-EHA in the presence of nano-SnO₂

NPG (10 mmol), 2-EHA (22 mmol) and nano-SnO₂ (0.08 g) were added to a two-necked flask attached to a thermometer and a dean-stark apparatus. A reflux column was connected above the dean-stark apparatus, and vacuum pump attached to the reflux column. The reaction mixture was vacuumed with vacuum pump (10⁻⁶ bar), and then heated with a mantle heater at 160 °C for 8 h. Then, the vacuum was removed, and the produced H₂O and the excess of 2-ethylhexanoic acid which collected in the dean-stark were discharged. The system was operated for again to complete removing of the 2-ethylhexanoic acid at 160 °C in vacuum for 1 h. Finally, the catalyst was separated via filtration, and the mixture was cooled to room temperature and characterized by ¹H NMR without any purification.

RESULTS AND DISCUSSION

Synthesis and characterization of nano-SnO₂

Nano-SnO₂ was synthesized from SnCl₄ via the sol-gel process [26-28]. For confirming the synthesis of nano-particles of SnO₂ SEM analysis was performed. SEM analysis showed that nano-SnO₂ with the particle size of about 30-40 nm were prepared.

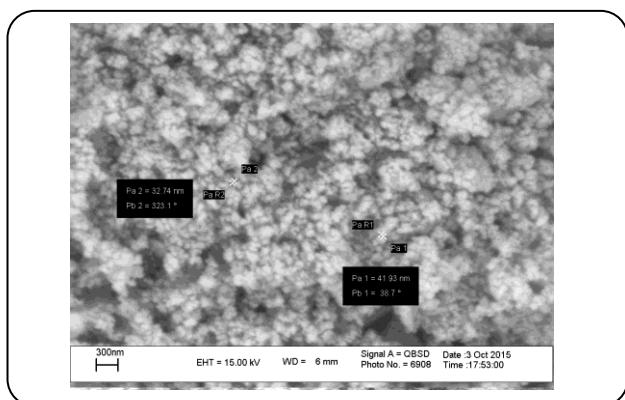
Esterification reactions of PE, TMP, NPG, EG, DEG, and glycerol with acetic anhydride

The esterification reaction of PE, TMP, NPG, EG, DEG, and glycerol with acetic anhydride were investigated to evaluate the catalytic activity of SnO₂ and nano-SnO₂. Since acetic anhydride is an active reagent, the esterification reaction can be performed even without the catalyst. So, the reaction was investigated in the catalyst-free conditions and in the presence of SnO₂ and nano-SnO₂. The catalyst amount was optimized for the esterification of PE and acetic anhydride. The best conditions for the esterification reaction of 10 mmol of PE were obtained using 0.08 g SnO₂ or 0.08 g nano-SnO₂ at 80 °C and ambient pressure. Table 1 shows the various examined reaction conditions for the esterification of PE with acetic anhydride. The reaction needs to prolong times

Table 1: Optimization of the reaction conditions for esterification of PE with acetic anhydride^a.

Entry	Catalyst amount (g)		Temp. °C	Time (h)		A	
	SnO ₂	nano-SnO ₂		SnO ₂	nano-SnO ₂	SnO ₂	nano-SnO ₂
1	0.07	0.07	80	4.5	4	Q ^b	Q ^b
2	0.08	0.08	80	4	3.5	Q ^b	Q ^b
3	0.09	0.09	80	4	3.5	Q ^b	Q ^b
4	0.08	0.08	70	6	4.5	Q ^b	Q ^b
5	0.08	0.08	90	4	3.5	Q ^b	Q ^b

a) Reaction conditions: PE (10 mmol), acetic anhydride (44 mmol), ambient pressure. A: esterification percent according to the determination with sampling and ¹H NMR study. ^bQ = quantitative yield

**Fig. 1: SEM image of nano-SnO₂.**

for completion in the presence of low catalyst amounts and low temperatures.

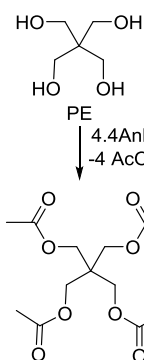
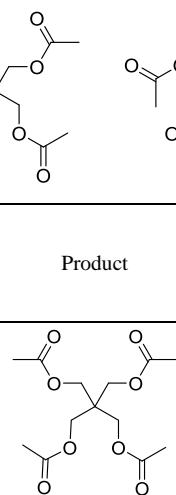
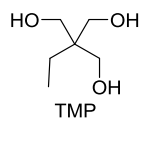
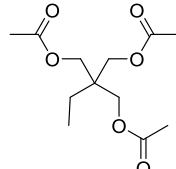
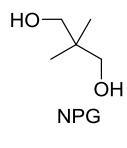
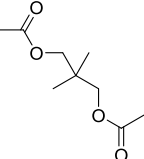
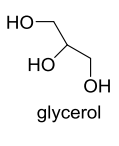
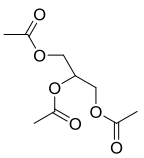
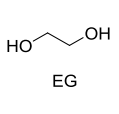
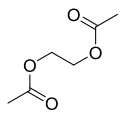
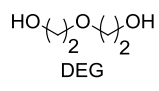
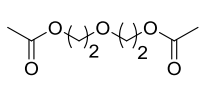
Table 2 shows the results of esterification reactions of PE, TMP, NPG, glycerol, EG, and DEG with acetic anhydride to afford polyol ester or diester. The reaction gave acetic acid as the only by-product. The products were assigned with ¹H NMR and the completion of reactions was determined with the investigation of the amount of polyol. For this propose, the sampling was performed in each 0.5 h during the reaction, impurity of acetic anhydride and acetic acid of the sample was removed with heating under vacuum, and ¹H NMR was prepared from the product. The completion of reactions cannot be determined with the produced H₂O, since H₂O and acetic anhydride are homogeneous. Excess amount of acetic anhydride for obtaining quantitative yield is necessary. The esterification reactions for all of the alcohols gave a quantitative yield. Short reaction time is needed for diols in comparison to triols and PE. The use of SnO₂ increase the reaction rate, but reducing of catalyst dimension to the nanometer did not decrease

the reaction duration for all of the reactions. For some of the alcohols including PE, TMP and glycerol the reaction times was decreased significantly. Also, the esterification reaction of PE with acetic acid instead of acetic anhydride was investigated which gave quantitative yield during 12 h in the presence of nano-SnO₂. Due to the high activity of acetic anhydride compared to acetic acid in the esterification reaction, we used acetic anhydride in the reactions.

Esterification reactions of PE, TMP, NPG, EG, DEG, and glycerol with 2-ethyl hexanoic acid (2-EHA)

The low impact of SnO₂ and nano-SnO₂ in the esterification reactions may be attributed to the high activity of the acetic anhydride, so the investigation of esterification reaction of a highly steric carboxylic acid such as 2-EHA is important for observing the catalytic efficiency of nano-SnO₂. Therefore, the esterification reactions were examined with 2-EHA instead of acetic anhydride in vacuum and refluxing conditions with the dean-stark system. Vacuum was used for reducing the reflux temperature since the boiling point of 2-EHA is about 228 °C at ambient pressure. High temperatures make the oil color darker, so the vacuum system assists to reduce the reaction temperature. Reflux conditions is necessary for removing of the produced H₂O, since 2-EHA as a H₂O carrier transferred the produced H₂O from the reaction vessel to the dean-stark tank. The progress of the reactions was monitored by the collected H₂O in dean-starks, and unlike the acetic anhydride did not need ¹H NMR study during the reaction. The collected H₂O for complete esterification transformation of each molecule of PE, triol and diol are four, three and two, respectively. So, the percent of esterification for alcohol is determined with the produced H₂O. As can be seen from Table 3, the esterification reaction of PE and 2-EHA

Table 2: The esterification reaction of alcohols with acetic anhydride.

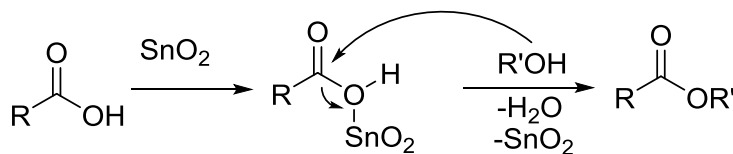
Entry	Alcohol	Product	Time (h)			A
			catalyst-free	SnO ₂	nano-SnO ₂	
1	 PE		5	4	3.5	Q ^b
2	 TMP		4.5	3	2.5	Q ^b
3	 NPG		3.5	2.5	2.5	Q ^b
4	 glycerol		4.5	3	2.5	Q ^b
5	 EG		2	1.5	1.5	Q ^b
6	 DEG		2	1.5	1.5	Q ^b

Reaction conditions: alcohol (10 mmol), acetic anhydride (22 mmol for diol, 33 mmol for triol, 44 mmol for PE), 80 °C, dean-stark. A: esterification percent determined with ¹H NMR. ^bQ = quantitative yield

Table 3: The esterification reaction of alcohols with 2-EHA^a.

Entry	Alcohol	Product	catalyst-free		SnO ₂		Nano- SnO ₂	
			Time (h)	A	Time (h)	A	Time (h)	A
1	PE		24	21	22	65	18	69
2	TMP		24	26	19	91	15	92
3	NPG		24	26	16	Q ^b	12	Q ^b
4	Glycerol		24	21	19	93	15	93
5	EG		24	29	13	Q ^b	8	Q ^b
6	DEG		24	27	16	Q ^b	12	Q ^b

^aReaction conditions: alcohol (10 mmol, except entries 5 and 6 with 11 mmol), 2-EHA (20 mmol for diol, 33 mmol for triol, 44 mmol for PE), 160 °C, dean-stark. A: esterification percent according to collected H₂O in dean-stark except entries 5 and 6 which they were determined with ¹H NMR. ^bQ = quantitative yield



Scheme 1: The proposed mechanism for the esterification reaction in the presence of SnO_2 .

did not complete in the catalyst free conditions, and 21% conversion was obtained in 24 h. The use of SnO_2 as the catalyst improved the reaction conversion to 65% for 22 h. Nano- SnO_2 decreased the reaction duration to 18 h with a little increasing in the reaction yield. Failure to achieve 100% efficiency for this reaction is related to the high steric repulsion of 2-ethyl hexanoate groups on the product. The esterification reaction was performed with TMP instead of PE in the catalyst free conditions. Again, the low yield was obtained in the catalyst free conditions which approve the necessity of the catalyst for esterification reactions. The reaction was examined in the presence of SnO_2 with 91% conversion during 19 h and nano- SnO_2 with 92% conversion during 15 h. For glycerol, 100% esterification reaction did not perform even in the presence of SnO_2 and nano- SnO_2 . NPG performed the esterification reaction with quantitative yield in the presence of SnO_2 and in shorter reaction time in nano- SnO_2 . For EG and DEG the esterification reactions were performed with an excess of them, regarding that their boiling points are lower than 2-EHA and they evaporated earlier from 2-EHA. Also, for these reactions due to homogeneous mixing of EG and DEG with H_2O , determination of the reaction progress with the produced H_2O is impossible, so, for these reactions, ^1H NMR study was performed in each 2 h during the reaction. The esterification reactions of EG and DEG with 2-EHA gave a quantitative yield in the presence of SnO_2 and nano- SnO_2 under a shorter time using nano- SnO_2 .

Esterification reactions of PE, TMP, NPG, and glycerol with isovaleric acid (IVA)

The esterification reactions of isovaleric acid with the alcohols were examined in the presence of SnO_2 and

nano- SnO_2 under vacuum at 110 °C (Table 4). The yield of esterification reaction of PE with IVA is significantly improved in the presence of SnO_2 and nano- SnO_2 in comparison to the catalyst-free conditions. The esterification reaction for TMP, glycerol, and NPG with IVA were performed completely in the presence of SnO_2 and nano- SnO_2 , with short reaction times in the presence of nano- SnO_2 .

Mechanism of the reaction

The esterification reaction mechanism in the presence of SnO_2 as a Lewis acid can be presented as Scheme 1. The hydroxyl group of carboxylic acid was activated for the leaving via coordination with SnO_2 . In continue, hydroxyl group of the carboxylic acid can be replaced with the nucleophilic attack of hydroxyl group of the alcohol.

CONCLUSIONS

In conclusion, we have developed an efficient and potentially useful SnO_2 and nano- SnO_2 catalyzed esterification reactions of some important polyols and diols. The importance of the work is due to broad applications of polyol esters especially polyol esters of PE, TMP, and NPG. The excellent catalytic activity of SnO_2 and nano- SnO_2 in these reactions was approved with the comparison of results with the catalyst-free esterification reactions. SnO_2 and nano- SnO_2 are the interesting catalysts for the esterification reaction due to high activity, chemically inert behavior, and nontoxic and noncorrosive properties.

Acknowledgement

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Table 4: The esterification reaction of alcohols with IVA^a.

Entry	Alcohol	Product	catalyst-free		SnO ₂		Nano- SnO ₂	
			Time (h)	A	Time (h)	A	Time (h)	A
1	PE		24	33	22	78	18	89
2	TMP		24	35	18	Q ^b	13	Q ^b
3	NPG		24	39	16	Q ^b	10	Q ^b
4	Glycerol		24	32	16	93	10	93

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