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Catalysis Today 97 (2004) 271–276

www.elsevier.com/locate/cattod

Polyoxyethylene esters of fatty acids: an alternative synthetic route for high selectivity of monoesters

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Abstract

Esterification reaction of fatty acids with polyoxyethylenes has been studied in the presence of solid acid catalysts and the results are compared with those obtained with a classical homogeneous catalyst, *p*-toluene sulphonic acid. Solid acid catalysts showed very high selectivities for monoesters even under less favorable reaction conditions of 1:1 molar ratios of oleic acid to PEG. Excess amount of PEG is normally required to ensure high selectivity for monoesters in the presence of homogeneous catalysts. The yields for monoesters given by heterogeneous catalysts such as zeolites, HPA and nafion were comparable to that with *p*-toluene sulphonic acid after 24 h of reaction. Results suggest that solid acid catalysts are potential catalysts for selective synthesis of monoesters from oleic acids and PEG even under severe reaction conditions. A screening study of different solid acid catalysts showed ZSM-5, zeolite-β, and nafion to be better catalysts than zeolite USY and mordenite, the former giving higher selectivity and yield to monoesters. The results suggest that the most important parameters in optimization catalyst performance for monoesters production is the acid strength and less so on other properties such as shape selectivity and concentration of active sites.

Keywords: Esterification; Fatty acids; Monoesters; Catalyst; Zeolites; Acidity; Characterization; Oleic acids

1. Introduction

Fatty acid esters of polyoxyethylene are well recognized for their less toxicity and are widely used in textile, cosmetic and pharmaceutical industries as softeners, emulsifiers, dispersants, anti-static agents etc. These fatty acid esters are prepared either by ethoxylation or esterification reactions [1]. Esterification process is preferred as it is safer and as the degree of ethoxylation can be controlled more easily.

Recommended synthetic methods for increased selectivity of monoesters involve usage of large excesses of polyoxyethylenes over fatty acid. Even molar ratios of polyoxyethylene to fatty acid of 6–12 are generally used [2]. Excess polyoxyethylene is washed out after the reaction, using concentrated salt solution [3]. Synthetic methods using boric acid in order to selectively protect one of the two terminal ligands have been also reported [4]. Even though, esterification reaction can take place at room temperature, the rate is very slow. Hence, esterification is normally carried out at higher temperatures, between 323 and 523 K, in presence of homogeneous acidic, amphoteric or alkaline catalysts [5]. Sodium or potassium hydroxide or *p*-toluene sulphonic acid are the most preferred catalysts. In order to favorably shift the equilibrium, water produced is removed by applying vacuum or using a current of nitrogen.

There is a trend to use fats or oils directly for the industrial production of polyoxyethylene esters of fatty acids. Most of the accepted methods reported for this reaction include utilization of alkaline catalysts. The reaction product is normally a mixture of triglycerides, diglycerides, monoglycerides, free glycerol, unreacted

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2004.07.017

polyoxyethylene along with mono and disubstituted fatty acid esters [6,7]. As this reaction leads to a highly complex product mixture, it is not favored in many cases.

The esterification product is normally a mixture of monoesters and diesters. Diesters can be selectively synthesized in high yields taking appropriate molar ratios of reactants. However, preparation of monoesters, which are the true surface-active species, is highly demanding even though the formation of monoester is the first step of the esterification reaction. This is because of the equal activity of both the hydroxyl groups of polyoxyethylene, which results in the esterification at both ends. Another important factor that affects the reaction pathway is the higher miscibility of fatty acids with the monoesters, which promotes the reaction of fatty acids with the free hydroxyl group of the monoesters, rather than with that of polyoxyethylene. Moreover, disproportionation of monoester formed in the first step by transesterification also leads to increased amounts of diester as the reaction proceeds [8].

$$\begin{aligned}2\mathrm{RCO}\,(\mathrm{OCH_2CH_2})_x\mathrm{OH} &\rightleftharpoons \mathrm{RCO}\,(\mathrm{OCH_2CH_2})_x\mathrm{OCOR}\\ &\quad + \mathrm{H}\,(\mathrm{OCH_2CH_2})_x\mathrm{OH}\end{aligned}$$

p-Toluene sulphonic acid (PTSA) is widely used as a catalyst for this reaction. The main problem associated with these catalysts is the need for a final neutralization step. Moreover, homogeneous catalysts are being increasingly replaced by the more eco-friendly heterogeneous catalysts. In addition to other special advantages, which differ from case to case, ease of removal of catalyst after reaction is an important advantage expected out of this process change.

The present study explores the effectiveness of different types of heterogeneous catalysts [9,10] in the esterification reaction for the selective synthesis of monoesters. Considering the shape-selective properties, zeolites with four different types of topologies are used. The selection of catalysts [11,12] has been made in such a way that in addition to pore structure, important insights regarding the role of acid strength and the role of concentration of Bronsted acid sites on the selective synthesis of monoesters can be obtained. The effect of acid strength is further explored by choosing Nafion and HPA catalysts, which are categorized as strong acid catalysts [12]. The results are compared with that in presence of representative homogeneous catalyst, PTSA. Oleic acid is chosen as the feedstock for the study, which has been esterified with polyethylene glycol (PEG).

2. Experimental section

2.1. Materials

Oleic acid, technical grade (90%, Aldrich), polyoxyethylene of molecular weight 600 (PEG 600) (Aldrich) were used for the reaction studies. Prior to reaction, both reactants, oleic acid and polyoxyethylene, were dehydrated by heating at 363 K under vacuum for 2 h. The experiments were conducted in a standard-design glass apparatus where the temperature is regulated with silicon oil bath equipped with a temperature controller.

The zeolite catalysts used were supplied by Zeolyst and the physicochemical properties of the catalysts are as summarized in Table 1 [13]. They were activated by calcination at 523 K under vacuum before the reaction. Nafion and HPA were synthesized and activated as per reported procedures [14,15].

HPLC grade acetonitrile and acetone (Merck) were used for HPLC analysis. Stearic acid (99%, Aldrich) was used as an internal standard for HPLC analysis.

2.2. Catalyst characterization

X-ray diffraction measurements were carried out using Bruker D8 Advance Powder X-ray diffractometer (θ–2θ mode, Cu–Kα radiation at λ = 1.5405 A, scintillation detector) equipped with EVA diffract software for data acquisition and analysis. The diffractogram were recorded

Table 1
Physico–chemical characteristics of the solid acid catalysts used

Catalyst	Si/Al	Nominal cation	Na_2O weight	Surface area (m^2/g)	Molecular formula	Channel
Zeolite β CP 811	13	H^+	0.05	~650	Na^{7+} [$Al_7Si_{57}O_{128}$] BEA	[0 0 1] **12** 6.5 × 7.0 ↔ {[0 1 0] **8** 3.4 × 4.8 ↔ [0 0 1] **8** 2.6 × 5.7}
Zeolite USY CBV400	2.55	H^+	2.8	~730	$(Ca^{2+}, Mg^{2+}Na^{2+})_{29}(H_2O)_{240}$ [$Al_{58}Si_{134}O_{384}$]-FAU	[1 1 1] **12** 7.4 × 7.4
Mordenite CBV20A	10	NH_4^+	0.08	~500	Na^{8+} $(H_2O)_{24}$[$Al_8Si_4O_{96}$]–MOR	[0 0 1] **12** 6.5 × 7.0 ↔ {[0 1 0} **8** 3.4 × 4.8 ↔ [0 0 1] **8** 2.6 × 5.7}
ZSM-5 CBV3020	18	NH_4^+	0.05	~425	$Na^{n+}(H_2O)_{16}$ [$Al_nSi_{96-n}O_{192}$] MFI, $n < 27$	{[1 0 0] **10** 5.1 × 5.5 ↔ [0 1 0] **10** 5.3 × 5.6}
HPA Cs2.5	NA	NA	NA	348	$Cs_{2.5}$ $H_{0.5}PW_{12}O_{40}$	NA
HPA Cs1.87	NA	NA	NA	348	$Cs_{1.87}$ $H_{1.13}PW_{12}O_{40}$	NA
Nafion	NA	NA	NA	–		NA
PTSA	NA	NA	NA	NA	$C_7H_8O_3S.H_2O$	NA

NA: not applicable.

over 2θ values ranging from 2–60° with a scanning rate of 0.04 s/step at ambient temperature. The crystal phases of the sample were identified by overlaying the standard JCPDS diffraction pattern matching both peak positions and relative intensity.

Both, −OH groups and acidity, were monitored by infrared spectroscopy. FT–IR spectra were recorded in the transmission mode using Bruker IFS66V/S spectrometer. The catalysts were ground well into uniform fine particle size and were compressed into KBr pellets of 12 mm diameter at 20000 psi. Infra-red spectra of 400–4000 cm^{-1} ranges was recorded by a 32 scan data accumulation at a resolution of 4.0 cm^{-1} under ambient temperature and pressure. For acidity measurements, catalysts were outgassed overnight at 673 K and 10^{-3} Pa dynamic vacuum using self-supported wafers of 10 mg cm^{-2}; then pyridine was admitted into the cell at room temperature. After saturation, the samples were outgassed at different temperatures (523 and 623 K) for 1 h under vacuum, cooled to room temperature, and the spectra were recorded.

2.3. Reaction procedure

The zeolite catalysts (13 wt.%) were activated in situ in a 25-ml two-necked flask at 523 K under vacuum for 2 h. Nafion (2 wt.%) and HPA (3 wt.%) were activated by heating under vacuum at 373 K (overnight) and at 623 K (3 h), respectively. The amount of homogeneous catalyst, *p*-toluene sulphonic acid (PTSA) used for the reaction was 0.5 wt.%.

Dehydrated oleic acid (0.28 g; 1 mmol) was added to the activated catalyst using a syringe until the catalyst surface was well covered by the reactant. At this point, the vacuum was disconnected and PEG 600 (0.62 g; 1 mmol) was subsequently added to the reaction flask. Two different molar ratios of oleic acids to Peg 600 were used, namely 1:1 and 1:4. Esterification reaction was carried out at 403 K under vigorous stirring conditions in inert atmosphere by bubbling nitrogen gas into the reaction mixture. This also helped to remove water produced during the reaction so that the reaction equilibrium can be favorably shifted in favor of esterification reaction as opposed to hydrolysis. The progress of the reaction was monitored by continuous sampling of 50 μl reaction mixture after 1, 3, 7 and 24 h, then analysed using HPLC. The reactions using HPA catalysts were monitored only during the first 7 h. Samples collected were centrifuged at 15,000 rpm for 3 min to separate the solid catalysts from the liquid fractions. A known quantity of stearic acid was used as internal standard. At the end of the reaction, the mixture was filtered and cooled to room temperature. Excess PEG600 was removed by repeated washing with saturated brine solution.

HPLC analyses were performed on a Waters 1525 system consisting of ELSD detector using a reverse phase C_{18} column (Symmetry® 5 μm 4.6 mm × 159 mm). The analysis was conducted under gradient conditions using an appropriate mixture of acetonitrile and acetone.

3. Results and discussion

3.1. Selection of heterogeneous catalysts and their properties

Established esterification process uses homogeneous catalysts like *p*-toluenesulfonic acid (PTSA), sulfuric acids etc., to catalyze the reaction [5]. These catalysts are highly active and are able to convert oleic acid and PEG 600 to their corresponding esters. However, this reaction proceeds without showing any selective preference for the formation of monoesters.

Heterogeneous catalysts on the other hand, have been known to have the flexibility to modify the acidic nature, number and strength of acid sites. They can be tuned within a certain range by modifying their composition and in this way, one most appropriate acidity to maximize the conversion and selectivity for a given reaction can be determined. Structure, pore size and surface area are also important parameters contributing to conversion and selectivity. For example, selection of an appropriate pore size of a porous catalyst system could limit the formation of bulkier diesters in the esterification reaction. Following this idea, representative catalysts from different families were appropriately identified to study the effectiveness and influence of their properties on the selectivity for the formation of monoesters in the esterification of fatty acids with PEG 600. The three different families of heterogeneous catalyst systems chosen were zeolites, heteropolyacids (HPA Cs 1.87 and HPA Cs 2.5) and Nafion.

In Table 1, the library of used catalysts is summarized. Four different types of zeolites were used: Mordenite, USY, Beta, and ZSM-5, all having different topologies: a 12-membered ring (MR), large-pore unidirectional zeolite (Mordenite), a 12-MR large-pore tridirectional zeolite with cavities (Y), a large-pore tridirectional 12-MR zeolite but without cavities (Beta) and one medium pore bi-directional zeolite (ZSM-5). All of them exhibit very high surface area of 425–730 m^2/g. The acid properties of zeolite catalysts used for the study are compiled in Table 2.

As mentioned earlier, other solid acid catalysts used for this study include Nafion and HPA, which are categorized as strong bronsted acids [11,12,16]. These catalysts were

Table 2
Acid properties of zeolite catalysts used

Catalyst	Si/Al	Bronsted acidity[a]	
		523 K	623 K
Beta (CP-811)	13	42	22
USY (CBV-400)	2.5	23	5
MOR (CBV-20 A)	10	67	38
ZSM-5 (CBV-3020)	18	42	25

[a] Acidity (μmoles of pyridine/g catalyst) of the zeolite catalysts at 523 and 623 K; calculated using the extinction coefficients given in reference [18].

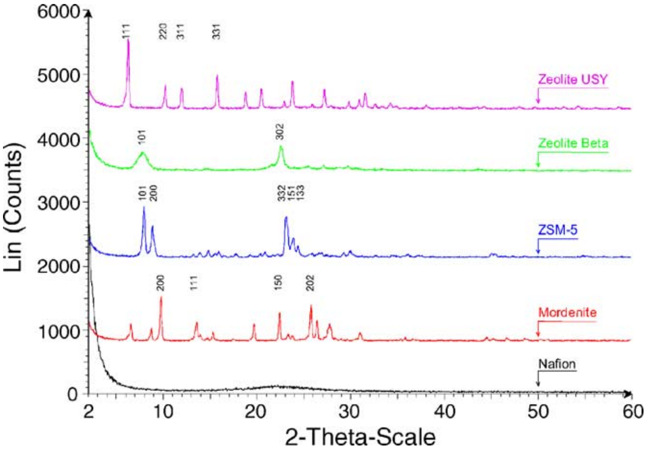

Fig. 1. Phase identification of catalysts determined by X-ray diffraction technique (XRD).

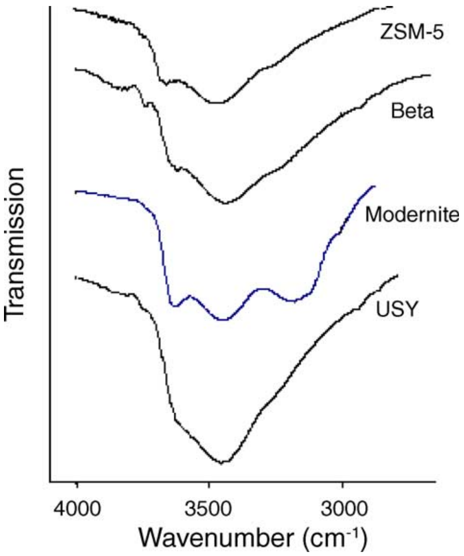

Fig. 2. Infrared spectra of the OH stretching vibration region of zeolites.

chosen in order to gain further insights regarding the effect of acid strength in restricting the disproportionation reaction of monoesters formed in the first step, which can lead to formation of higher amounts of diesters. There are two different grades of heteropolyacids used 1.87 and 2.5 Cs-exchanged rendering solids with relatively enhanced acid strength.

The various phases of zeolites used have been confirmed using XRD technique shown in Fig. 1. Based on the XRD spectra, it can be deduced that the zeolites are highly crystalline with minimal impurities as shown by the absence of foreign peaks (Table 3).

Fig. 2 presents FT–IR spectra of zeolite samples between the 4000–3000 cm^{-1} region and the corresponding data are summarized in Table 4. The strong intensity −OH stretching vibrations in the region of 3400–3500 cm^{-1} due to bridging −OH groups [17] confirm that the active centres of the zeolite catalysts are predominantly bronsted acidic in nature. The intensities due to terminal −OH stretch vibrations in the region of 3600–3700 cm^{-1} [17], which can be attributed to Lewis acidity, are much less prominent compared to that from the bridging −OH groups.

3.2. Catalyst performances studies

Experiments were conducted using oleic acid:PEG ratio of 1:1 in the presence of different catalysts at 403 K. The esterification reaction normally results in a mixture of monoesters and diesters as shown below:

$$3RCOOH + 2H\,(OCH_2CH_2)_xOH \rightleftharpoons RCO(OCH_2CH_2)_xOH + RCO\,(OCH_2CH_2)_xOC\,OR + 3H_2O$$

The free OH groups of polyoxyethylenes of monoesters further react to give diesters, resulting in an equilibrium mixture of mono- and diesters.

In Fig. 3, the conversion (%) of oleic acid in the presence of different catalysts used in this study is shown. A comparison based on the performance of these catalysts, based on this figure, shows that the order of activity is: PTSA > HPA-Cs2.5 > HPA-Cs1.9 > Mordenite > Nafion > ZSM-5 ∼ Beta > USY.

Among the solid catalysts chosen in this study, HPA-Cs2.5 and HPA-Cs1.9 and Nafion are the best catalysts. This clearly shows the importance of acid strength of the catalysts in the overall activity. Among the zeolite catalysts, Mordenite exhibits the highest initial reaction rate, which can be attributed to their higher concentration of acid sites, compared with the others zeolite samples (see Table 2). However, despite the higher initial reaction rate (even more than Nafion), the maximum attainable conversion is 67%, which is achieved after 7 h reaction time, and this conversion remains constant with time. The behaviour of the reaction with time indicates that a fast deactivation of the catalyst is

Table 3
Infrared spectral data for terminal and bridging OH groups present in zeolites used as catalysts in the study

Catalyst	Terminal OH (cm^{-1})	Bridged OH (cm^{-1})
ZSM-5	3648	3460
Beta	3620	3437
Mordenite	3628	3454
USY	3600 (shoulder)	3450

Table 4
Effect of oleic acid to PEG 600 molar ratios on the selectivity (%) of monoesters after 24 h at 403 K

Catalyst	Selectivity of monoesters (% mole)	
	Oleic acid:PEG 600 = 1:4	Oleic acid:PEG 600 = 1:1
PTSA*	100	33.49
Zeolite-β	100	96.58
Nafion	100	93.89

* @373 K reaction temperature.

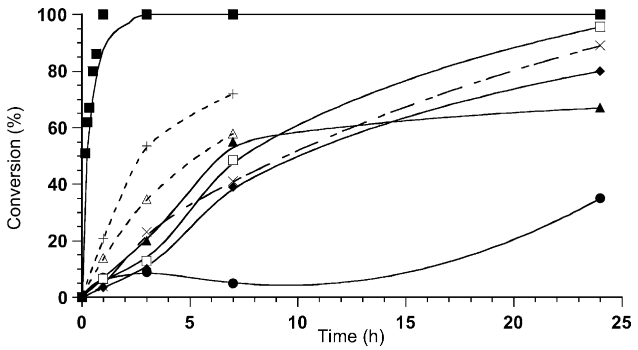

Fig. 3. Conversion (%) of monoesters in the presence of different catalysts used for the screening of esterification reaction between oleic acid and polyoxyethylene. Reaction conditions: 403 K, 1:1 molar ratio of oleic acid:PEG. PTSA(■):HPA-Cs2.5(+); HPA-Cs1.87(△);Mordenite (▲); Nafion (□); ZSM-5(×); Beta (◆); USY (●).

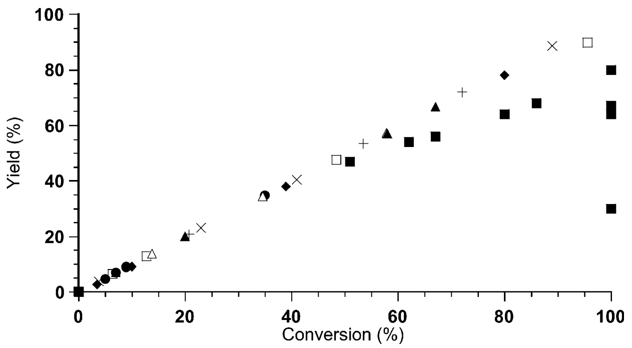

Fig. 4. Yield (%) of monoesters vs. oleic acid conversion in presence of different catalysts used for screening the reaction. Reaction conditions: 403 K, 1:1 molar ratio of oleic acid:PEG. PTSA(■):HPA-Cs2.5(+); HPA-Cs1.87(△); Mordenite (▲); Nafion (□); ZSM-5(×); Beta (◆); USY (●).

occurring during the process. This higher rate of deactivation observed for Mordenite catalyst can be attributed to its unidirectional system of channels, thus reactants and/or products could remain strongly adsorbed blocking channels and active sites. Except for Mordenite catalyst, the increase in the conversion with reaction time indicates that that there is no loss of catalyst activity with time. With reference to Zeolite Beta and ZSM-5, they both have comparable acid strength and number of active sites and therefore both catalysts exhibit similar activities. USY zeolite exhibits very low activity, which can be explained taking into account their lower acidity compared with the other zeolite samples.

Other information that can be garnered from Fig. 3 was that Nafion and ZSM-5 required higher induction periods compared to other catalysts. However, despite this, the results after 24 h of reaction showed that both catalysts are able to achieve excellent conversions (between 85 and 95%).

In Fig. 4, the yield of monoesters versus conversion of oleic acid obtained for all catalysts tested is displayed. As can be observed, selectivity of all the solid acid catalysts is very similar (between 95 and 99%) and it is independent on the level of conversion of oleic acid. In clear contrast, PTSA showed a decrease in the selectivity of monoesters with the level of conversion due to the further reactions of the monoesters, which resulted in the formation of diesters. In fact, at conversions higher than 50%, the selectivity to monoesters is remarkably higher with the solid catalysts than with the homogeneous PTSA. The fact that the selectivity of all the solid acid catalysts was comparable leads to the conclusion that the nature of active sites is similar in all these solid catalysts. The nature of acid sites of solid catalysts is different from that of PTSA, which promotes consecutive and competitive reactions. Interestingly, in Fig. 4, it is shown that although ZSM-5 has smaller pore size, very high selectivity is also observed for this catalyst. This further emphasizes the importance of acid strength over diffusion for this reaction. However, the role of shape selectivity as well as steric constraints cannot be completely ruled out in the case of zeolites. In general, solid acid catalysts lower the activation energy required for the formation of products. This is because reactant molecules are adsorbed onto the surface of catalysts, unlike the case for homogeneous catalysts where solubility of reactants is a requisite for the reaction. Thus, the lower miscibility of PEG 600 with the fatty acid compared to that of monoesters leads to the formation of diesters when homogeneous catalysts are used. On the other hand, heterogeneous catalysts form strong interaction between the active sites and the un-reacted hydroxyl group of PEG. This could be the main factor restricting the consecutive esterification reactions leading to the formation of diesters.

The results of the study suggest that heterogeneous catalysts selectively promote the synthesis of monoesters compared to diesters even in the absence of excess of PEG, which is considered as a less favorable reaction condition for monoester synthesis.

3.3. *Influence of oleic acid/PEG ratio*

The reaction conditions, in terms of reactants ratio of 1:1 (oleic acid:PEG600), are less favorable for monoester formation. The most favorable condition for the formation of monoesters is when excess of PEG is used. This can be seen from Table 4, which shows that selectivity is much higher when 1:4 molar ratio of oleic acid to PEG 600 was chosen compared to 1:1 molar ratio. The results of the reactions using solid acid catalysts are compared with the results obtained using a representative homogeneous catalyst, PTSA. Table 4 also shows that the drop in selectivity of monoesters in the presence of PTSA with 1:1 molar ratio of oleic acid to PEG is much higher compared to that in the presence of solid acid catalysts.

4. Conclusions

It has been shown that solid acid catalysts are active and selective catalysts for the synthesis of fatty acid monoesters of polyoxyethylenes. Acid strength of the catalysts seems to be the most important factor in determining the yield of monoesters. Hence, optimization efforts should focus on acid strength rather than shape selectivity or concentration of bronsted acid sites. All the solid acid catalysts showed superior selectivity for the formation of monoesters compared to homogeneous acid catalysts.

Acknowledgement

Financial support from Ministry of Science Environment and Technology (MOSTE), Malaysia and the technical support from Institute of Chemical Technology, Spain are gratefully acknowledged.

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