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ORIGINAL PAPER

Mesoporous Silica-Supported Diarylammonium Catalysts for Esterification of Free Fatty Acids in Greases

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Abstract Biodiesel (BD), typically consisting of fatty acid methyl esters (FAME), has received much attention because it is a renewable biofuel that contributes little to global warming compared to petroleum-based diesel fuel. The most common method used for BD production is based on the alkali-catalyzed transesterification of first-use refined oils and fats with an alcohol (e.g. methanol). These technologies, however, require significant modification when applied to second use materials such as greases because of their higher free fatty acid (FFA) content. Recently, we reported a series of insoluble porous polymer grafted diphenylammonium salts that efficiently esterified the FFA in greases to FAME. In this work, the diphenylammonium salts were supported onto two robust mesoporous silicas. The resulting catalysts had high esterification activity with >99% of the FFA in greases converted to FAME, and the FFA content in the treated greases was reduced to <1 wt%. The mesoporous silica-supported catalysts displayed minimal transesterification activity.

Keywords Biodiesel · Brown grease · Diphenylammonium salts · Esterification · Fatty acid methyl esters · Free fatty acid · Heterogeneous catalysts · Yellow grease

Introduction

The increasing public concern about the emission of greenhouse gases and other environmental pollutants from fossil fuel combustion has rekindled research interests in the development of alternative fuels [1]. Biodiesel (BD), which is defined as the simple alkyl esters of fatty acids derived from natural fats and oils, is an alternative diesel fuel that has additional environmental benefits such as a reduction in total harmful emissions and no net increase in greenhouse gases. The first generation transesterification technologies used in the production of BD utilized refined oil and fat as the lipid feedstock, a homogeneous inorganic base (e.g. sodium hydroxide or sodium methoxide), and methanol to generate fatty acid methyl esters (FAME) and glycerol (Fig. 1) [2]. There are economic concerns, however, associated with this technology. First, the relatively high cost of the refined oil or fat feedstock, which constitutes as much as 75% of the final BD cost, can render BD economically uncompetitive with petrodiesel [3]. Second, the basic catalyst used in the BD production needs to be neutralized with aqueous acid or removed with an absorbent aid, which generates significant quantities of aqueous and/or solid wastes. Third, the use of refined edible fats and oils as BD feedstocks competes with their use as human foods and/or animal feeds. To address these concerns, we have sought to develop efficient immobilized catalysts for BD production that utilize second use lipid feedstocks such as greases that have a high free fatty acid (FFA) content [4,

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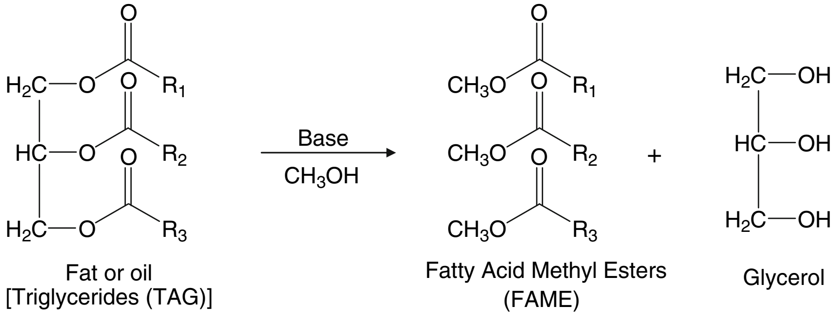

Fig. 1 Production of fatty acid esters for use as biodiesel fuels

5]. It has been shown that BD derived from yellow and/or brown greases has good fuel quality and acceptable engine performance [4–7]. The use of these alternative feedstocks not only offers an economic advantage over first-use feedstocks in producing BD but also does not compete with food grade lipids. The use of heterogeneous catalysts may lower processing costs in converting second use lipids to BD since it can reduce processing wastes.

Despite the feedstock cost advantage of greases over refined fats and oils, the additional processing steps, such as treatments to esterify the FFA can negatively impact the economics of BD production [8]. To circumvent these problems, several recyclable and re-usable solid acid catalysts have been reported for converting FFA to FAME. For instance, Kiss et al. [9–11] observed that metal oxides such as sulfated zirconia, sulfated titania and sulfated tin oxide efficiently catalyzed the esterification of FFA to FAME. Chung et al. [12] reported a series of modified microporous zeolites for esterifying the FFA in oils to FAME. These authors found that at 60 °C, the modified zeolites converted oleic acid in waste frying oil to methyl oleate in conversions between 60 and 80%. We recently reported a series of heterogeneous diarylammonium salts supported on highly porous cross-linked polymers for esterifying the FFA feedstocks to FAME. The heterogeneous catalysts were highly effective in converting the FFA in yellow (12 wt% FFA) and brown (21 and 40 wt% FFA) greases into FAME at conversions between 95 and 99% [13, 14]. The heterogeneous acid catalysts were easily removed by filtration and the pretreated greases now composed of FAME and glycerides were successfully transesterified with sodium methoxide to give FAME and glycerol. The heterogeneous catalysts could be used at least three times [13, 14]. To further explore the utility of diarylammonium salts as heterogeneous acid catalysts, we have now grafted them onto highly porous and robust mesoporous silica materials.

Since their discoveries by Kresge et al. in 1992 [15], mesoporous silicas have emerged as one of the more versatile solid catalyst supports. A number of catalytically active species have been grafted onto mesoporous silicas via siloxane linkages. The high surface areas of the mesoporous silicas allow high catalyst loadings and the large, regular, and tunable channels contained therein facilitate reagent and product transport. For example, Mbaraka et al. [16, 17] demonstrated that highly ordered mesoporous silica integrated with sulfonic acid functional groups were effective esterification catalysts for reducing 15 wt% palmitic acid in soybean oil to <0.5 wt% at 85 °C. More recently, Lin et al. [18, 19] developed novel mesoporous silica/calcium oxide composites as bifunctional catalysts for converting high FFA-containing feedstocks into BD in one step.

In this work, we supported diarylammonium salts onto two mesoporous silicas, mesoporous crystalline material MCM-48 and SBA-15, and evaluated their catalytic esterification activity. These solid acid catalysts were found to be effective for the esterification of FFA in greases with a conversion to FAME of 95–99%, resulting in a pretreated grease with a final FFA content of <1 wt%. The present system has the potential to exhibit enhanced catalyst activity and reusability and lower catalyst cost than the previously reported polymer supported diarylammonium salts.

Materials and Methods

4-Bromostyrene was purchased from Alfa Aesar (Ward Hill, MA). Cetyltrimethylammonium bromide, ammonium hydroxide (NH_4OH), tetraethyl orthosilicate (TEOS), 4-(trimethoxysilyl)aniline, sodium *tert*-butoxide (NaO^tBu), bromobenzene, toluene, oleic acid (90%), methanol, trifluoromethanesulfonic acid (triflic acid, TfOH), dichloromethane and 1,4-dioxane were purchased from Aldrich Chemical (Milwaukee, WI), tris[dibenzylideneacetone] dipalladium chloroform ($Pd_2(dba)_3{\cdot}CHCl_3$) and (*R*,*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (*rac*Binap) were obtained from Strem Chemical (Newburyport, MA). The yellow (12% FFA) and brown (21 and 40% FFA) greases were gifts from Kaluzny Bros. Inc. (Joliet, IL). All of these materials were used without further purification.

Catalyst preparations and manipulations were carried out under argon (to prevent moisture from contaminating the reactions) with the use of standard inert atmosphere and Schlenk techniques. Solvents used in the reactions were dried by standard procedures such as distillation with calcium hydride. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker NMR 400 DRX spectrometer. ^{1}H-NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated chloroform (δ 7.26). Microwave reactions were performed in a CEM Discover-LabMate (CEM, Mattews, NC) microwave reactor under the conditions described herein. Nitrogen adsorption experiments for Brauner-Emmett-Teller (BET) surface area results were performed on a Quantachrome-1C (Quantachrome, Boynton Beach, FL) surface area analyzer at liquid nitrogen temperature. The pore sizes were calculated by the Barrett, Joyner and Halenda (BJH) method [20]. Thermogravimetric analyses (TGA) were carried out on a Shimadzu TGA-50 (Columbia, MD) thermogravimetric analyzer in air at 3 °C/s.

Experimental Procedures

4-(*tert*-Butoxydimethoxysilyl)-*N*-phenylaniline (**2**, Fig. 2)

In a glove box, a 10 mL thick-walled pressure vial equipped with a silicone seal cap was charged with 4-(trimethoxysilyl)aniline (**1**, Fig. 2, 593.0 mg, 2.50 mmol), NaO^t-Bu (347.0 mg, 3.5 mmol), $Pd_2(dpa)_3 \cdot CHCl_3$ (23.0 mg, 0.0025 mmol), and *rac*BINAP (46.7 mg, 0.075 mmol). Bromobenzene (0.26 mL, 2.5 mmol) and distilled toluene (6 mL) were added via syringe to the sealed tube, and the mixture was sonicated for 30 min. The reaction vessel was then subjected to microwave irradiation under the following conditions: power, 300 W; pressure, 100 psi; temperature, 140 °C; reaction time, 10 min. The color of the reaction mixture changed from dark brown to dark red. The mixture was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo, and the residue purified by flash column chromatography on silica (20 g) using hexane (500 mL) and 50:1 hexane:ethyl acetate (500 mL) to give **2** as a yellow liquid (535.8 mg, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, 2H), 7.27 (t, 2H), 7.11 (d, 2H), 7.04 (d, 2H), 6.95 (t, 1H), 5.28 (broad s, 1H), 3.55 (s, 6H), 1.33 (s, 9H).

Synthesis of MCM-48/DPA-OTf (**4**, Fig. 2)

A solution of cetyltrimethylammonium bromide (CTAB, 7.8 g), H_2O (360 mL), ethanol (150 mL), and ammonium hydroxide (39 mL) was stirred for 10 min at room temperature (r.t.). To this solution tetraethyl orthosilicate

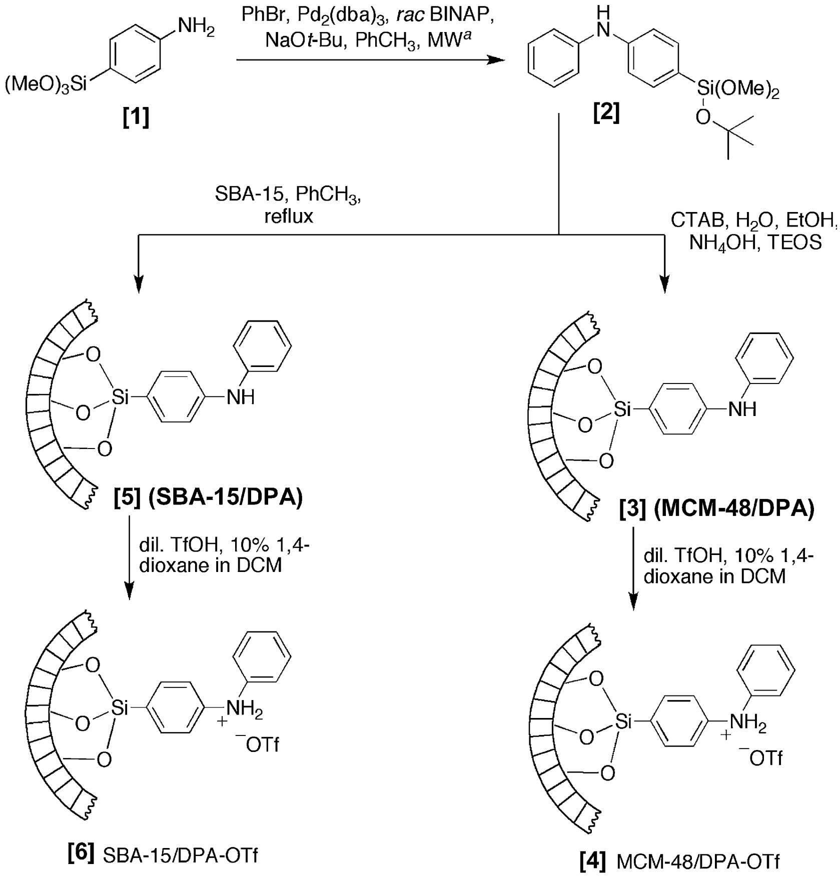

Fig. 2 Synthetic routes for the immobilization of diphenylammonium salt onto mesoporous silicas

(TEOS, 10.2 g) and 4-(*tert*-butoxydimethoxysilyl)-*N*-phenylaniline (**2**, Fig. 2) (250 mg, 0.75 mmol) were added and allowed to stir for 4 h at r.t. The resulting solid was filtered and rinsed sequentially with water (250 mL) and ethanol (250 mL). Surfactant was removed by triturating the solid with 1 wt% NaCl in methanol (3 × 200 mL) for 6 h at r.t. The solid was filtered, rinsed thoroughly with water and ethanol, and air dried (after each extraction) to afford 2.5 g of MCM-48/DPA (**3**, Fig. 2). Dried **3** (2.2 g) with DPA concentration of 0.44 mmol/g as determined by TGA based on the weight loss due to the organic moieties was treated with TfOH solution (10 equiv., 0.5 M in 10% 1,4-dioxane in dichloromethane). The suspension was stirred for 2 h at r.t. and the mixture was centrifuged (1,500×*g*; 10 min) and the solvent decanted. The solid residue was rinsed with 1,4-dioxane (50 mL) and centrifuged (1,500×*g*; 10 min) to remove excess TfOH to give activated MCM-48/DPA-OTf, (**4**, Fig. 2). Typically, after each wash, the supernatant was tested with pH paper and after five washes, the pH of the supernatant solution would be neutral. The solid was air dried overnight before use. Elemental analysis data for $C_{13}H_{12}F_3NO_3S$ on the MCM-48 support: calculated for 0.44 mmol/g catalyst loading, C, 6.86; H, 0.53; N, 0.16%; Found, C, 5.41; H, 1.70; N, 0.16%.

Synthesis of SBA-15/DPA-OTf (**6**, Fig. 2)

Silica SBA-15 was prepared following a previously reported synthesis and calcined at 400 °C overnight in air before use [21]. A 25-mL round bottom flask was charged with SBA-15 silica (3.2 g), 4-(*tert*-butoxydimethoxysilyl)-*N*-phenylaniline (**2**, Fig. 2, 0.321 g, 0.97 mmol), and toluene (10 mL) and set to reflux for 18 h under inert atmosphere. After reaction, the flask contents were brought to r.t. and centrifuged (1,500×*g*; 10 min). Solvents were decanted and the residual solid was rinsed with toluene (10 mL × 3) and ethyl acetate (10 mL × 3) to afford 3.5 g of SBA-15/DPA with DPA concentration of 0.28 mmol/g (**5**, Fig. 2) in quantitative yield. Concentration of DPA supported onto SBA-15 was confirmed by TGA based on the weight loss due to the organic moieties. SBA-15/DPA (1.8 g) was activated with TfOH (10 equiv., 0.5 M in 10% 1,4-dioxane in dichloromethane) by stirring at r.t. for 2 h. The reaction mixture was centrifuged and the solvent decanted. The activated solid SBA-15/DPA-OTf (**6**, Fig. 2) was triturated, centrifuged (1,500×*g*; 10 min) from 1,4-dioxane (50 mL) and solution was tested with pH papers. This procedure was repeated 5× to remove excess TfOH. The solid was air dried before use. Elemental analysis data for $C_{13}H_{12}F_3NO_3S$ on SBA-15 support: calculated for 0.28 mmol/g catalyst loading, C, 4.37; H, 0.34; N, 0.39%; found, C, 5.48; H, 1.31 N, <0.02%.

Esterification of Oleic Acid

A mixture of oleic acid (100 mg, 0.35 mmol), methanol (0.11 g, 3.4 mmol), and catalyst **6** (32 mg, 9.0 μmol) was mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2 h. The reaction mixture was allowed to cool to r.t. and 5 mL of hexane was used to transfer the mixture to a 25 mL one neck round bottom flask. The solvents were evaporated under reduced pressure. The crude product (10 μL) was taken via a 20-μL micropipette, diluted with hexane (1.5 mL), filtered through a 4-mm nylon syringe filter 0.45 μm (National Scientific) to remove the catalyst and the solution was analyzed by Hewlett Packard Series 1050 High Performance Liquid Chromatography (HPLC) equipped with a Varex (Minneapolis, Minnesota) Evaporative Light Scattering Detector IIA (ELSD) using a method developed previously [13, 14].

Conversion Curve for Esterification of Oleic Acid

A mixture of oleic acid (0.5 g, 1.8 mmol), methanol (0.57 g, 17.8 mmol), and catalyst **6** (158 mg, 0.044 mmol) was mixed in a two-neck flask attached to a reflux condenser and heated at 95 °C. At selected time intervals an aliquot (25 μL) was removed from the mixture via a syringe, placed into a 2-mL vial and dried under vacuum for 5 min to remove the excess methanol. The crude product (10 μL) was taken via a 20-μL micropipette, diluted with hexane (1.5 mL), filtered through a 4-mm nylon syringe filter 0.45 μm (National Scientific) to remove the solid catalyst and the solution was analyzed by HPLC [13, 14].

Esterification of Free Fatty Acid in Greases with Heterogeneous Catalysts

A typical procedure is given. A mixture of grease (12 wt% FFA (molecular weight = 282 g/mol), 0.5 g, 0.21 mmol of FFA), methanol (0.14 g, 4.4 mol), and catalyst **6** (57 mg, 0.016 mmol) was mixed in a 4-mL vial with a tightly sealed Teflon cap and heated at 95 °C for 2 h. The reaction mixture went from light yellow to dark brown in color. The mixture was allowed to cool to r.t., filtered to remove the catalyst, and a 10-μL sample was taken using a micropipette for analysis by HPLC [13, 14].

Results and Discussion

A diphenylammonium triflate acid catalyst was immobilized onto two robust and highly porous solid silica supports (MCM-48 and SBA-15, Fig. 2). MCM-48 is mesoporous silica with a network of interconnected threedimensional channels that has an extremely high surface area with a regular pore size of 2–3 nm. SBA-15 also was used in this study because of its high surface area and more importantly its larger pore size of 5–9 nm, which was anticipated to facilitate the transport of substrates to the catalytic sites throughout its larger channels.

To immobilize the diphenylammonium salt onto the surfaces of silicas MCM-48 and SBA-15, an alkoxysilyl substituted derivative of diphenylamine was synthesized. Pd-catalyzed *N*-arylation of 4-(trimethoxysilyl)aniline (**1**, Fig. 2) with 4-bromostyrene afforded 4-(*tert*-butoxydimethoxysilyl)-*N*-phenylaniline (**2**, Fig. 2). Several attempts at synthesizing product **2** using conventional heating resulted in low yields of the desired product. It was found that during the three-day reaction at refluxing temperature, the *tert*-butoxide anion of sodium *tert*-butoxide, which is required for the Pd-catalyzed coupling cycle of **1** to **2**, favored displacement of the methoxide groups of **1** to its mono-, di- and tri-*tert*-butoxy silyl aniline derivatives as confirmed by thin layer chromatography (TLC) and NMR. The use of microwave chemistry for the Pd-catalyzed transformation of **1** to **2**, however, as observed in most C–C and C–N coupling reactions, proved more successful in converting the relatively labile **1**, to the desired diphenylamine derivative **2** (Fig. 2). The time scale of a microwave reaction is on the order of minutes, which is believed to yield the N-arylation product at a faster rate than catalytic cycle deactivation, namely trimethoxy substitution by *tert*-butoxy anion. This explains the favored production of the desired mono-*tert*-butoxy dimethoxysilyl diphenylamine (**2**), which was required for the silica immobilization of **2** using either co-condensation or grafting method.

Co-condensation of **2** with a solution containing CTAB, H_2O, ethanol, NH_4OH and TEOS at a weighted ratio of 0.76:35.3:11.6:3.5:1.0:0.025 gave diphenylamine substituted mesoporous silica MCM-48/DPA (**3**, Fig. 2) in modest yields. After mesoporous silica **3** was formed, the surfactants and co-solvents were removed by a mild neutral extraction in a basic solution which resulted with diphenylamine substituted MCM-48 silica (MCM-48/DPA, **3**) with a concentration of 0.44 mmol DPA/g as confirmed by TGA. **3** was then subsequently treated with a dilute solution of TfOH in solvent to afford the active MCM-48/DPA-OTf (**4**, Fig. 2). The catalyst loading estimated from TGA was confirmed by the elemental analysis results of **4**.

On the other hand, preparation of diphenylamine substituted mesoporous silica SBA-15/DPA-OTf (**6**, Fig. 2) was conducted by utilizing the pre-synthesized silica SBA-15, which was made as previously reported [19]. **2** was then grafted onto SBA-15 to give silica SBA-15/DPA (**5**, Fig. 2) where the silanol groups on the surface of silica SBA-15 quantitatively reacted with **2** to form siloxane linkage in toluene (Fig. 2). TGA analysis indicated that **5** has a DPA concentration of 0.28 mmol/g. The active catalyst, SBA-15/DPA-OTf (**6**) was formed by treating **5** with a solution of TfOH. The catalyst loading estimated from TGA was confirmed by the elemental analysis results of **6**.

Nitrogen sorption isotherms (i.e. the adsorption and desorption curves) were measured on each of the mesoporous silicas to estimate their BET (i.e. specific surface area) and pore sizes (by BJH method) (Fig. 3). Both diphenylamine functionalized silicas **3** and **5** exhibited very high surface areas (Fig. 3; Table 1). Protonation of silica **3** with TfOH resulted in a specific surface area from 274 to 281 m^2/g (the small change is probably due to experimental error) and a decrease in pore size from 2.5 nm to 1.4 nm. The starting SBA-15 silica had a specific surface area of 860 m^2/g, but after conversion to SBA-15/DPA-OTf (**6**) exhibited a specific surface area of 505 m^2/g. Its pore size as determined by BJH method was not affected by conversion to **6**. The diphenylammonium groups of both mesoporous silicas **4** and **6** were expected to be readily accessible to catalyze heterogeneous esterification reactions.

The catalytic activities of the mesoporous silica-supported diphenylammonium salts were evaluated using oleic acid as a model substrate for the esterification of crude mixtures of FFA to FAME. Such control experiments are important since the greases used in this study are not refined materials, which can affect the catalysts performance. Control experiment with nonfunctionalized SBA-15 was also performed to ensure that the catalytic activity is not from the SBA-15 support since the acidity in SBA-15 maybe high enough to catalyze the reaction. The experiment was done with oleic acid, methanol (10 equiv. to oleic

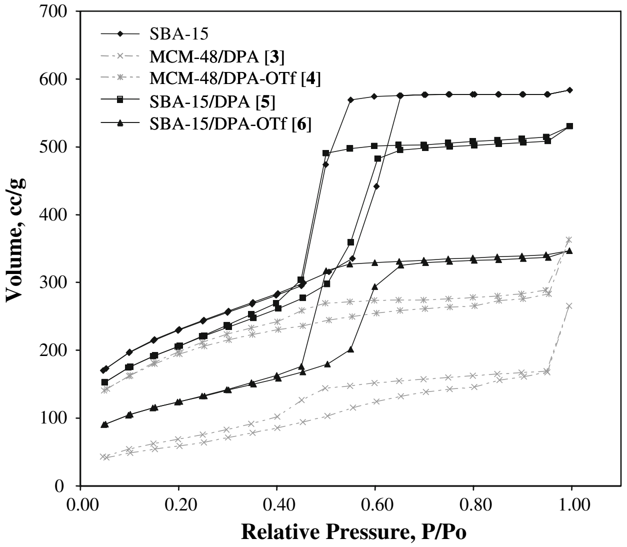

Fig. 3 Nitrogen sorption isotherms of mesoporous silicas after 6 h of heating at 100 °C

Table 1 Nitrogen sorption isotherm data for mesoporous silica materials

	BET surface area (m^2/g)	BJH pore size (nm)
MCM-48/DPA [3]	274	2.5
MCM-48/DPA-OTf [4]	281	1.4
SBA-15/DPA [5]	860	4.9
SBA-15/DPA-OTf [6]	505	4.9

acid) and SBA-15 (two times the amount of the functionalized SBA-15 by weight) at 95 °C for 2 h. <3% of oleic acid was converted to methyl oleate. The reaction conditions used in this control experiment is the same as the experiments in Fig. 4. As listed in Table 2 (entries 1 and 2), both heterogeneous catalysts **4** and **6** were effective in converting oleic acid to methyl oleate at conversions of >98.1 and 99%, respectively, after 2 h reaction. This suggested that both catalysts had similar activity but time-dependent conversion curves for oleic acid to methyl oleate indicated minor differences in their activities. The conversion curves showed that at comparable catalyst loadings, catalyst **6** had slightly higher activity than did catalyst **4** (Fig. 4). This was not totally unexpected, however, since as shown in Table 1 catalyst **6** had a larger pore size than catalyst **4**; this would allow for a more uniform grafting of the active diphenylamine moiety onto the silica surface. The larger pore size of catalyst **6** also allows for a more efficient transport of the substrates within its channels. For comparison purposes, the diphenylammonium triflate (DPAT) salt not immobilized onto the silica supports (synthesized using developed method) [13, 14] and liquid H_2SO_4 were used as homogeneous catalysts for the esterification of oleic acid with methanol. It appears that silica-supported catalysts **4** and **6** do not catalyze esterification of oleic acid as rapidly as do DPAT, H_2SO_4 and TfOH but this result was not unexpected given the heterogeneous nature of the mesoporous silica-supported catalysts. The conversion curve for DPAT further confirms this information, as it performed similarly to the H_2SO_4 catalyst but not as well as TfOH (Fig. 4). The TfOH catalyst was expected to perform much better than H_2SO_4 as TfOH has much higher acidity.

Although both catalysts **4** and **6** have good catalytic esterification activities with pure fatty acids, it is more important to evaluate the potential of these solid catalysts with greases. Greases are typically rendered fats and used frying oils or mixtures thereof and these second use lipids are ideal candidates for conversion to BD fuels because of their lower cost compared to first-use, refined oils and fats. Typically, greases are composed of varying amounts of FFA, triglycerides (TAG), diglycerides (DAG) and monoglycerides (MAG) as well as other minor constituents. It is the unknown nature of the latter materials that could adversely affect the esterification activity of the mesoporous silica catalysts **4** and **6**. Three different greases were selected and examined without further purification: yellow grease with 12 wt% FFA and brown greases with 21 and 40 wt% FFA. Table 2 (entries 3–8) lists the difference in performances for catalyst **4** with 5 and 15 mol% solid loading (mol of DPA per mol of FFA). Table 2 (entries 3–5 and 6–8) show two sets of three replicate analyses; this is done to show the reproducibility of the reactions. We have chosen to do the replicate experiments with the yellow grease because of its low FFA content, which requires only small amounts of solid catalysts. These results showed that the reactions are reproducible. 15 mol% of catalyst successfully reduced the FFA content in the starting grease from 12 to 0.52 wt% after reaction with 20 equiv. of methanol at 95 °C for 2 h (Table 2, entries 6–8). Interestingly, under similar reaction conditions, less than 5 mol% of catalyst **6** was needed to reduce the FFA content from 12 to <1 wt% FFA (Table 2, entries 9 and 10). The results obtained further confirmed that catalyst **6** works better than catalyst **4**. As shown in Table 2, catalysts **4** and **6** also were capable of reducing the FFA content in brown greases. In the presence of 15 mol% **4** or **6**, the 21 and 40 wt% FFA in the brown greases were converted to FAME. Interestingly, the conversions obtained for the 21 wt% greases were 94 and 91% for catalysts **4** and **6**, respectively (Table 2, entries 11 and 12). These results were not as good as the 40 wt% grease reactions which have conversions of 98% (Table 2, entries 13 and 14). This could be due to unknown impurities in the 21 wt% brown greases which could poison the catalysts. However, in general, as expected, catalyst **6** was more active than

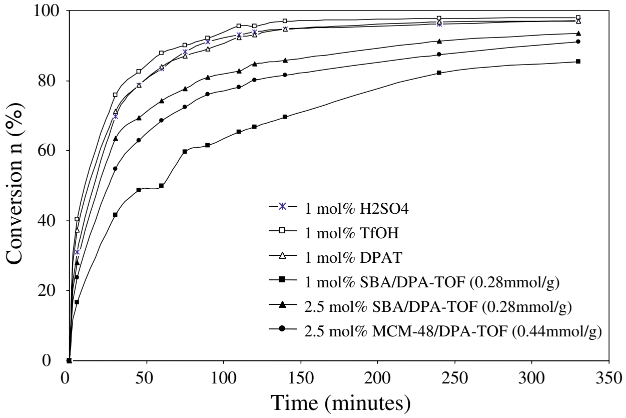

Fig. 4 Conversion curves for esterification of oleic acid with methanol (1:10 molar ratio) by liquid and solid catalysts at 95 °C

Table 2 Esterification of oleic acid and FFA in greases using heterogeneous catalysts

Entry	Substrate	Catalyst[a] (mol DPA per mol FFA)	MeOH (eq.)[a]	HPLC (wt%)			TAG	DAG	MAG
				FAME	FFA	% Conv.[d]			
1	Oleic acid (90%)	4 (2.5)	10	98.1	1.89	98.1	–	–	–
2	Oleic acid (90%)	6 (2.5)	10	>99	0	>99	–	–	–
	Grease (12% FFA)		–	0	12.0	–	66.1	20.4	1.66
3	Grease (12% FFA)	4 (5)b	20	13.4	1.42	88	58.1	24.4	2.68
4	Grease (12% FFA)	4 (5)b	20	11.7	2.00	83	64.7	21.6	0
5	Grease (12% FFA)	4 (5)b	20	15	1.24	89.7	64	19.8	0
6	Grease (12% FFA)	4 (15)c	20	16.6	0.52	96	63.1	19.8	0
7	Grease (12% FFA)	4 (15)c	20	25.9	0	>99	52.5	19.8	1.80
8	Grease (12% FFA)	4 (15)c	20	26.8	0.38	96.8	50.7	18.8	3.32
9	Grease (12% FFA)	6 (5)	15	16.4	0.72	94	60	21.5	1.47
10	Grease (12% FFA)	6 (5)	20	18.4	0.45	96	60	19.2	2.04
	Grease (21% FFA)		–	0	21.0	–	41.7	31.3	5.78
11	Grease (21% FFA)	4 (15)	20	28.2	1.36	94	41.0	27.6	1.72
12	Grease (21% FFA)	6 (15)	20	30.6	1.91	91	40.3	27.0	0
	Grease (40% FFA)		–	0	40.0	–	31.5	25	3.35
13	Grease (40% FFA)	4 (15)	20	51.9	0.77	98	22.9	19.5	5.87
14	Grease (40% FFA)	6 (15)	20	56.1	0.59	98	25.5	17.7	0

Reactions were performed at 95 °C for 2 h. FAME – fatty acid methyl esters, FFA – free fatty acids, TAG – triglycerides, DAG – diglycerides, MAG – monoglycerides. Catalyst **4** is mesoporous silica MCM-48/DPA-OTf shown in Fig. 2; diphenylammonium triflate concentration = 0.44 mmol/g. Catalysts **6** is mesoporous silica SBA-15/DPA-OTf shown in Fig. 2; diphenylammonium triflate concentration = 0.28 mmol/g

[a] Number of equivalents relative to FFA that are present in the substrates

[b] Mean % conversion is 86.9 ± 3.48 for three replicate analyses

[c] Mean % conversion is 97.3 ± 1.55 for three replicate analyses

[d] % conversion = $[({}^{i}\mathrm{FFA} - {}^{f}\mathrm{FFA})/({}^{i}\mathrm{FFA})]$

catalyst **4** (with the exception of the 21 wt% brown grease system) presumably due to more facile transport of the substrates and products through larger channels of silica SBA-15. For both catalysts **4** and **6** there were only minor changes observed in the distribution of the mono, di, and triglyceride compositions of the grease from that found for the starting greases, which indicated that under the conditions used in this work both of the heterogeneous catalysts exhibited only minimal transesterification activity. We have demonstrated previously [13, 14] that only the FFA in greases were esterified using polymer supported diphenylammonium salts. The glycerides in the resulting treated greases were efficiently transesterified by alkali yielding FAME preparations that were potentially suitable for use as BD (data not shown). Although polymer supported diphenylammonium salts present a potential sustainable solution for BD synthesis using readily available high fatty acid feedstock, the limited recovery and reusability of the catalysts are still a problem. The robustness of the silica-immobilized diphenylammonium salts **4** and **6** should potentially aid in catalyst recycle and reuse to increase the efficiency of BD production from greases.

Conclusions

Diphenylammonium salts were immobilized onto mesoporous silicas using either co-condensation or grafting technique. The resulting heterogeneous diphenylammonium catalysts were highly effective in esterifying the FFA in greases (12–40 wt% FFA) to FAME but display only minimal activity in transesterifying glycerides. Using these catalysts it was possible to reduce the FFA content in the greases to <1 wt% under mild reaction temperature (95 °C) and short reaction time (2 h). These catalysts have the potential to reduce salt wastes during BD production and will be further tested in continuous reactor systems.

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