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Selective Transformations of Triglycerides into Fatty Amines, Amides, and Nitriles using Heterogeneous Catalysts

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Abstract

The use of triglycerides as an important class of biomass is an effective strategy to realize a more sustainable society. Herein, we present three types of heterogeneous catalytic methods for the selective one-pot transformation of triglycerides into value-added chemicals: (i) the reductive amination of triglycerides to fatty amines with aqueous NH₃ under H₂ promoted by ZrO₂-supported Pt clusters; (ii) the amidation of triglycerides under gaseous NH₃ catalyzed by high-silica H-beta (Hβ) zeolite at 180 °C; (iii) the Hβ-promoted synthesis of nitriles from triglycerides and gaseous NH₃ at 220 °C. These methods are widely applicable to the transformation of various triglycerides (C4-C18 skeletons) into the corresponding amines, amides, and nitriles.

KEYWORDS: Biomass, triglycerides, heterogeneous catalysis, amines, amides, nitriles.

Introduction

The alarming predictions for the rapid depletion of fossil-fuel resources have inspired researchers to develop alternative technologies that exploit renewable energy sources.^[1-13] Many studies have focussed on the conversion of lignocellulosic biomass^[14-21] and triglycerides^[14,22,23] into various platforms of value-added chemicals.^[24-33] Industrially, triglycerides in oils and fats have been used as feedstocks for the synthesis of fatty amines, amides, nitriles, and alcohols, which in turn are used for the production of surfactants, polymers, and other useful commodity chemicals.^[34]

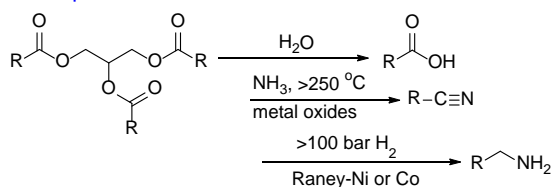
Currently, fatty amines are produced industrially from triglycerides via fatty nitriles or fatty alcohols.^[1,34] In the former method ('nitrile process' in **Scheme 1**), triglycerides extracted from oilseeds undergo hydrolysis to afford fatty acids, which are then treated with NH₃ in the presence of metal-oxide catalysts at high temperature to yield fatty nitriles; a subsequent metal-catalyzed high-temperature hydrogenation of the nitriles under high pressure of H₂ furnishes the targeted fatty amines.^[14,34,35] In the latter method, fatty acids or their methyl esters are hydrogenated to generate fatty alcohols, which are then treated with NH₃ to produce fatty amines.^[36] Henkel & Co Ltd. have reported a direct conversion of triglycerides into amines using Zn-Al₂O₃ or Zn-Cr₂O₃ catalysts with NH₃ or short-chained alkyl amines. However, this method suffers from serious drawbacks, which include harsh reaction conditions (200-400 °C; 50-400 bar H₂) and the use of sub-stoichiometric amounts of catalysts.^[37] Recently, Beller and co-workers have reported the first homogenous catalytic method for the direct synthesis of *N*-alkylated amines from triglycerides and amines under a H₂ pressure of 60 bar,^[38] which employs the [Ru(acac)₃]/Triphos/HNTf₂ catalytic system (acac = acetylacetonate; Triphos = 1,1,1-tris(diphenylphosphinomethyl)-ethane; HNTf₂ = triflimide). Although this study represents a significant step forward in this area, this catalytic system still requires additives and suffers from difficulties associated with catalyst/product separation. In addition, the use of NH₃ as a nitrogen source was not addressed in this report.

Fatty amides are widely used as/in surfactants, lubricants, cosmetics, shampoos, foam-control agents, fungicides, corrosion inhibitors, water repellents, detergents, and anti-blocking agents in the plastics-processing industry.^[39-41] Industrially, fatty amides are currently produced using a two-step process (**Scheme 2**): the conversion of triglycerides into fatty acid esters, followed by a high-temperature aminolysis to produce fatty amides.^[42] Several studies have reported the direct amidation of triglycerides with amino alcohols or isopropylamine using basic promoters such as methoxides,^[43] NaOH/CaO,^[44] Na-doped Ca(OH)₂,^[45] and Li-doped CaO,^[46] or using solid acid or biocatalysts.^[47] However, reports on the direct amidation of triglycerides with NH₃ remain scarce. To the best of our knowledge, only one report discusses the direct amidation of triglycerides to amides using NH₃-saturated *t*-butyl alcohol and lipase (Novozym 435).^[48] An environmentally benign method for the synthesis of fatty amides based on reusable heterogeneous catalysts thus represents an attractive research target.

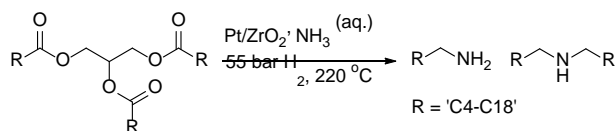
Reports on the direct synthesis of fatty nitriles from triglycerides and NH₃ remain equally scarce. As summarized by Corma,^[1] fatty nitriles are generally obtained from triglycerides via fatty acids or their esters (**Scheme 3**).^[1,49,50] Even though the direct synthesis of nitriles from renewable triglycerides is highly desirable, only one method has been reported so far, and that method requires high temperatures (400 °C).^[51] Thus, the development of more viable catalytic methods for the direct synthesis of nitriles from triglycerides is also desirable.

In general, benign manufacturing processes for the direct transformation of triglycerides into fatty amines, amides, and nitriles are relatively rare.^[1] Herein, we report three types of selective heterogeneous catalytic methods for the direct transformation of triglycerides into amines, amides, and nitriles. First, we show the direct synthesis of amines from triglycerides and aqueous NH₃ under H₂ using a Pt-loaded ZrO₂ (Pt/ZrO₂) catalyst. Then, we demonstrate the direct conversion of triglycerides with gaseous NH₃ into the corresponding amides or nitriles using a commercially available H-beta zeolite (Hβ) catalyst.

Nitrile process

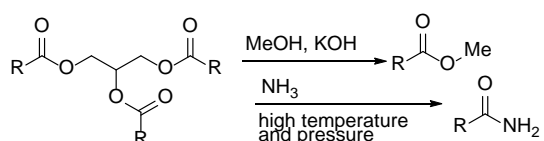


This work

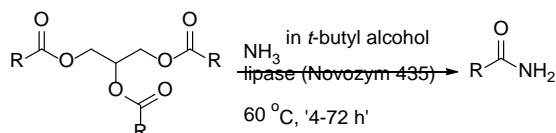


Scheme 1. The currently used multi-step industrial pathway to fatty amines (nitrile process) and the direct route presented in this study.

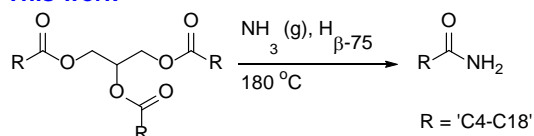
Industrial process



Direct amidation of triglycerides^[48]

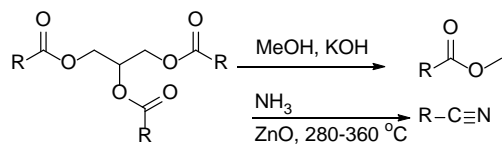


This work

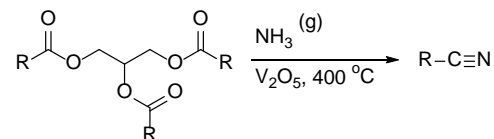


Scheme 2. Comparison of the amidation of triglycerides: the currently favored industrial multistep process, the direct lipase (Novozym 435) catalyzed amidation using ammonia-saturated *t*-butyl alcohol, and the Hβ-75-catalyzed direct amidation with gaseous NH₃ (this work).

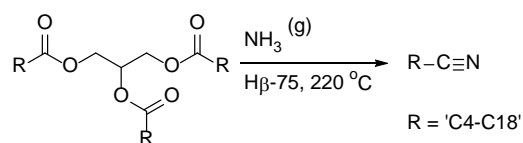
Current process



Direct nitrilation of triglyceride^[51]



This work



Scheme 3. Comparison of different nitrilation processes and this work (Hβ-75-promoted one-pot nitrilation with NH₃).

Results and Discussion

Characterization of Pt/ZrO₂

Figure 1 shows the results of the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements for pre-oxidized PtO_x/ZrO₂, pre-reduced Pt/ZrO₂, and the corresponding reference compounds (Pt foil and PtO₂). The distances and coordination numbers for the Pt–O and Pt–Pt shells were determined by a curve-fitting analysis of the EXAFS data (**Table 1**). The XANES spectrum of PtO_x/ZrO₂ shows an intense white-line peak that is quite similar to that of PtO₂. The EXAFS spectrum of PtO_x/ZrO₂ consists of a single Pt–O contribution at 2.02 Å with a coordination number of 5.5. The XANES and EXAFS results show that the Pt species in PtO_x/ZrO₂ are platinum oxides. The XANES spectrum of the reduced Pt/ZrO₂ is basically identical to that of Pt foil. The EXAFS analysis of Pt/ZrO₂ shows 4.5 Pt–Pt bonds at 2.65 Å. This distance is shorter than the Pt–Pt distance in bulk Pt metal (2.76 Å), and the Pt–Pt coordination number (4.5) is lower than that of bulk Pt metal (12). These features are similar to those of previously reported small Pt metal clusters.^[52]

Figure 2 shows the annular bright field scanning transmission electron microscopy (ABF-STEM) image and high-angle annular dark-field STEM (HAADF-STEM) images of Pt/ZrO₂, which show small Pt particles (diameter < 2 nm). In their entirety, the characterization data of the unreduced precursor (PtO_x/ZrO₂) and of reduced Pt/ZrO₂ suggest that the former is composed of platinum oxides on ZrO₂, while the latter consists of small Pt nanoparticles on ZrO₂.

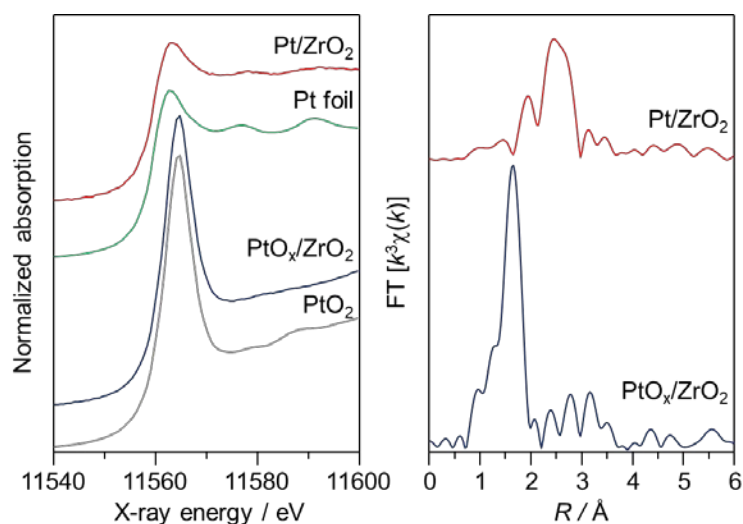


Figure 1. Pt L₃-edge XANES (left) and EXAFS Fourier transforms (right) of the Pt catalysts and the reference compounds.

Table 1. Curve-fitting analysis of the Pt L₃-edge EXAFS of the supported Pt catalysts.

Sample	Shell	N ^a	R (Å) ^b	σ (Å) ^c	R _f (%) ^d
PtO _x /ZrO ₂	O	5.5	2.02	0.061	0.8
Pt/ZrO ₂	Pt	4.5	2.65	0.078	0.3

^a Coordination number. ^b Bond distance. ^c Debye-Waller factor. ^d Residual factor.

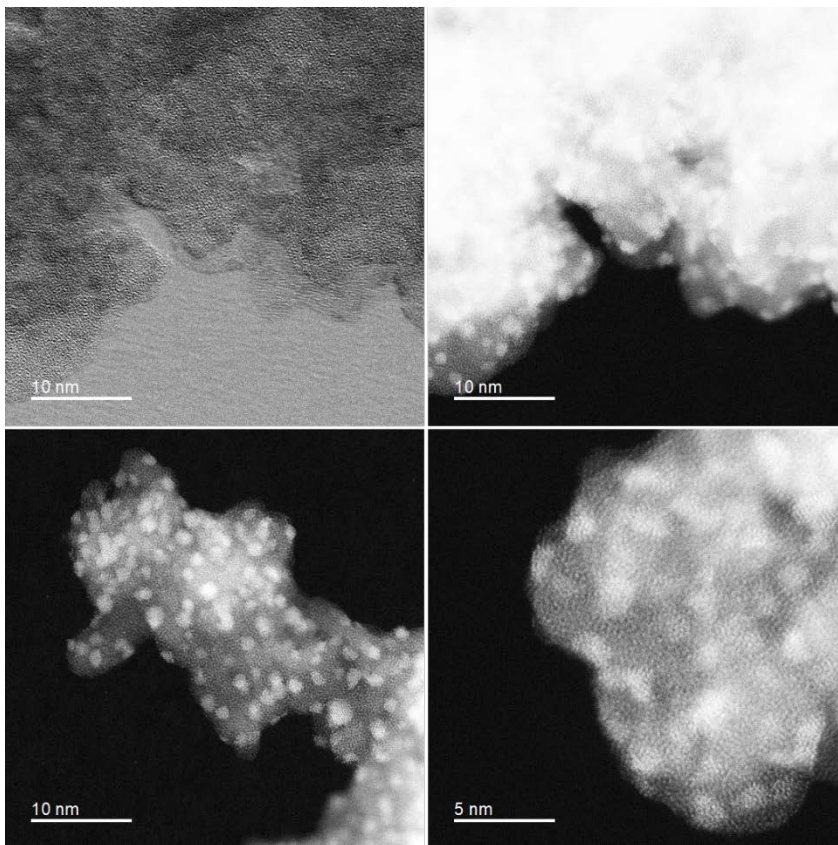


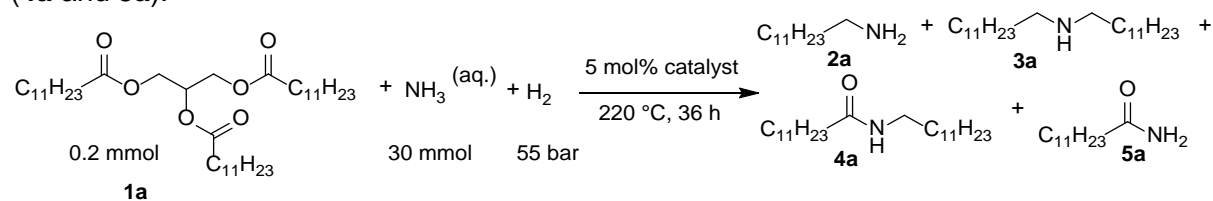
Figure 2. ABF- and HAADF-STEM images for Pt/ZrO₂.

Transformation of triglycerides into amines

To optimize the catalysts and reaction conditions for the reductive amination of triglycerides, we carried out a benchmark reaction, in which trilaurin (**1a**) was treated with aqueous ammonia under H₂ in a stainless-steel autoclave (dead space: 9.7 cm³). Catalyst screening tests (**Table 2**) were carried out using a series of supported metal nanoparticle catalysts that were pre-reduced under a flow of H₂ at 300 °C: a mixture of **1a** (0.2 mmol), 28% aqueous ammonia (30 mmol NH₃), and the catalyst containing 0.01 mmol of Pt (5 mol% with respect to **1a**) was stirred for 36 h at 220 °C under 55 bar H₂. **Table 2** summarizes the yields of dodecylamine (**2a**) and *N,N*-didodecylamine (**3a**) together with those of the undesired side products *N*-dodecyl-dodecanamide (**4a**) and dodecylamide (**5a**). In the first screening tests (entries 2-10), we tested 5 wt% Pt on various support materials. In the absence of a catalyst (entry 1), only **5a** was obtained in 72% yield. Using PtO_x/ZrO₂ also furnished only **5a** (80% yield) as an unreduced side product (entry 2). However, when using the pre-reduced metallic catalyst Pt/ZrO₂ (entry 3), amines were observed as the major products (**2a**: 43% yield; **3a**: 20%), together with unreduced side products (**4a**: 18%; **5a**: 17%). These results indicate that metallic Pt is the active species for the present reductive amination, while Pt oxides are inactive. Exposure of the reduced Pt/ZrO₂ catalyst to air at room temperature for 0.5 h (entry 4) resulted in lower amine yields (**2a**: 17%; **3a**: 3%). The lower yields could potentially be attributed to a decrease in the superficial amount of Pt⁰ species due to a re-oxidation by O₂. The reactions using metallic Pt on carbon (entry 5) and various other metal oxides (Al₂O₃, CeO₂, TiO₂, Nb₂O₅, and MgO; entries 6–10) afforded mixtures of **2a**, **3a**, **4a**, and **5a**, and the yields of amines **2a** and **3a** were lower than those obtained from Pt/ZrO₂. Interestingly, the yields of the amines increased upon decreasing the Pt load from 5 wt% to 1 wt% (entries 12-20). The yield of **2a** obtained from using 1 wt% Pt on ZrO₂ (entry 12) was higher than those obtained from other transition-metal-loaded ZrO₂ catalysts (entries 13-20), which furnished the unreduced amides **4a** and **5a** as the major products. The yield of **2a** decreased in the order Pt > Pd > Ru > Rh > Ni > Ir > Re > Cu > Ag. Based on the screening results, we identified 1 wt% Pt/ZrO₂ (entry 12) as the most suitable catalyst for the selective amination of **1a** to amines (**2a** and **3a**).

In separate catalytic experiments using Pt/ZrO₂ catalysts with different Pt loadings (1, 3, and 5 wt%), we estimated the initial formation rates for the conversion of **1a** into amines **2a** and **3a** under those conditions where the conversion of **1a** was < 40%, and we calculated the rates per total number of Pt atoms in the catalysts. We also carried out CO-adsorption experiments for the Pt/ZrO₂ catalysts in order to estimate the number of superficial Pt⁰ sites. The reaction rates per total number of Pt atoms and the fraction of surface Pt⁰ sites per total number of Pt atoms in Pt/ZrO₂ (**Figure 3**) show similar trends as a function of the Pt loading, and the catalyst with the lowest loading exhibits the highest conversion rate and the highest fraction of superficial Pt⁰ sites. These results show that the high activity of the 1 wt% Pt/ZrO₂ catalyst is due to the high dispersion of Pt⁰ in the catalyst.

Table 2. Catalyst screening for the amination of triglyceride **1a** into amines (**2a** and **3a**) and amides (**4a** and **5a**).



Entry	Catalyst	2a Yield [%] ^a	3a Yield [%] ^a	4a Yield [%] ^a	5a Yield [%] ^a
1	none	0	0	0	72
2	PtO _x /ZrO ₂	0	0	0	80
3	Pt/ZrO ₂	43	20	18	17
4	Pt/ZrO ₂ -air ^b	17	3	1	77
5	Pt/C	3	0	5	79
6	Pt/Al ₂ O ₃	6	2	7	82
7	Pt/CeO ₂	14	26	11	46
8	Pt/TiO ₂	21	8	7	60
9	Pt/Nb ₂ O ₅	9	6	4	79
10	Pt/MgO	6	1	1	87
11	Pt/ZrO ₂	48	24	17	9
12	Pt/ZrO ₂	59	32	7	2
13	Pd/ZrO ₂	28	9	7	45
14	Rh/ZrO ₂	19	6	2	57
15	Ir/ZrO ₂	11	7	1	69
16	Ni/ZrO ₂	13	5	3	71
17	Ru/ZrO ₂	21	8	5	53
18	Re/ZrO ₂	9	6	2	73
19	Cu/ZrO ₂	1	2	1	86
20	Ag/ZrO ₂	0	0	0	85

^a Yields were determined by GC (error range: $\pm 1.5\%$) Metal loading: 5 wt% for entries 2-10; 3 wt% for entry 11; 1 wt% for entries 12-20. ^b A pre-reduced Pt/ZrO₂ catalyst was exposed to air for 0.5 h at room temperature prior to use.

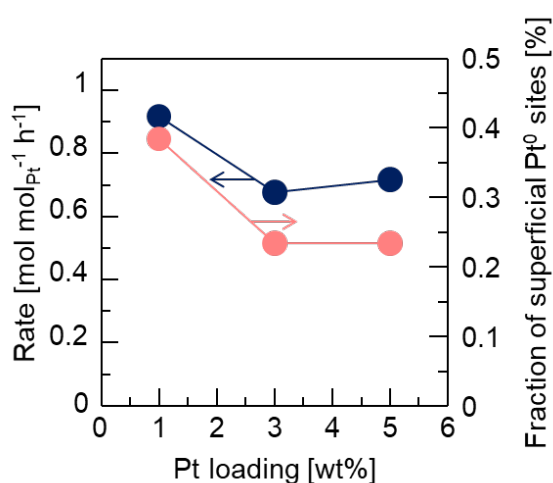
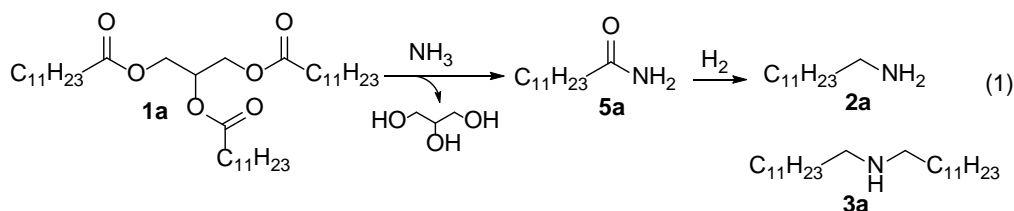
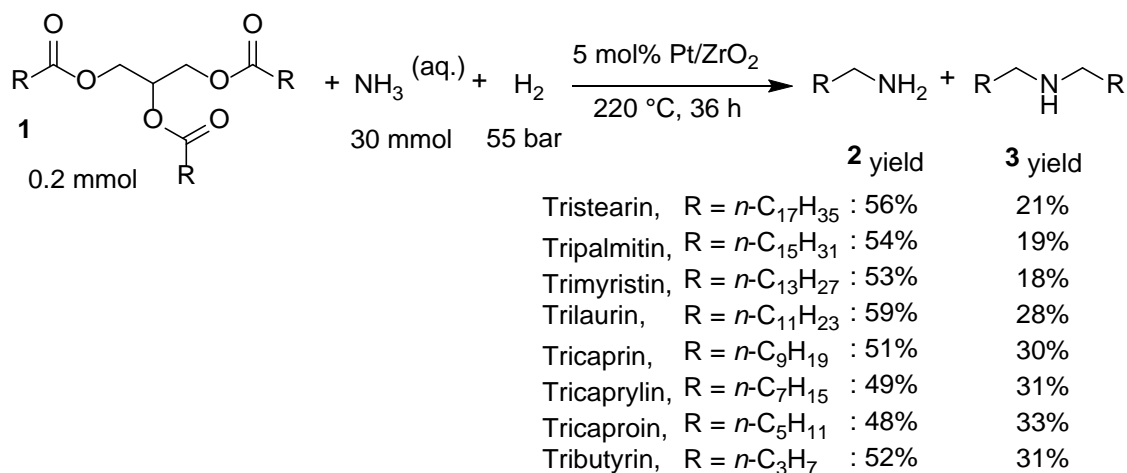


Figure 3. Conversion rate for the amination of **1a** into **2a** and **3a** per total number of Pt atoms in the catalyst and fraction of the superficial Pt⁰ sites per total number of Pt atoms in Pt/ZrO₂ as a function of the Pt loading in the catalyst.

Using the most effective catalyst, 1wt% Pt/ZrO₂, we then optimized the reaction conditions. **Figure 4** shows plots of the yields of amines **2a** and **3a** and amides **4a** and **5a** as a function of (A) the reaction temperature (150-240 °C), (B) the H₂ pressure (10-55 bar), (C) the amount of catalyst (0.5-5.0 mol%), and the reaction time (0-36 h) for the Pt/ZrO₂-catalyzed reductive amination of **1a** with aqueous NH₃. The temperature dependence of the yields under otherwise optimized conditions (55 bar H₂, 36 h, 5 mol% catalyst) in **Figure 4A** shows that increasing the temperature (up to 220 °C) results in a decreased yield of dodecylamide (**5a**) and an increased yield of amines (**2a** and **3a**); accordingly, 220 °C was identified as the optimal temperature. The effect of the H₂ pressure on the yields under otherwise optimized conditions (220 °C, 36 h, 5 mol% catalyst) in **Figure 4B** shows that increasing the H₂ pressure leads to a decreased yield of amide **5a**, while the yield of the amines (**2a** and **3a**) is increased; accordingly, 55 bar was identified as the most suitable pressure. The effect of the amount of catalyst on the yields under otherwise optimized conditions (220 °C, 55 bar H₂, 36 h) in **Figure 4C** shows that increasing the amount of catalyst decreases the yield of amide **5a** and increases that of the amines (**2a** and **3a**); accordingly, 5 mol% of the catalyst affords the highest yield of the amines (**2a** and **3a**). The time course of the reaction under the optimal conditions (**Figure 4D**) shows the typical kinetic pattern of a consecutive reaction. In the early stages of the reaction ($t < 5$ h), the amount of unreacted trilaurin (**1a**) decreases with time, accompanied by the formation of dodecylamide (**5a**) and then *N*-dodecyl-dodecanamide (**4a**). The yields of **5a** and **4a** reach a maximum at 5 h and 8 h, respectively, before they decrease with time, accompanied by the formation of the amines (**2a** and **3a**). After 36 h, the yields of the amines do not increase anymore. It should be noted that the formation of glycerol was not observed during the time-course analysis of the amination reaction. The kinetic results indicate that **2a** and **3a** are produced via the consecutive pathways shown in eqn. (1): **1a** undergoes a direct amidation with NH₃ to give **5a**, which is then hydrogenated to give **2a**; part of **2a** can react with free lauric acid to give the *N*-dodecyl-dodecanamide **4a**. Dodecylamine **2a** partly can also undergo a self-coupling reaction to form *N,N*-didodecylamine **3a**, which could also partly be produced by the hydrogenation of *N*-dodecyl-dodecanamide **4a**.



In order to demonstrate a gram-scale synthesis of an amine (eqn. 2), we treated 1 mmol of **1a** and 150 mmol of NH₃ (aq.) for 96 h under 55 bar of H₂ using 1 mol% of Pt/ZrO₂, which resulted in the formation of dodecylamine (51%) and *N,N*-didodecylamine (36%). This result implies that the developed method can most likely be applied to up-scaled conversions of triglycerides into corresponding amines.

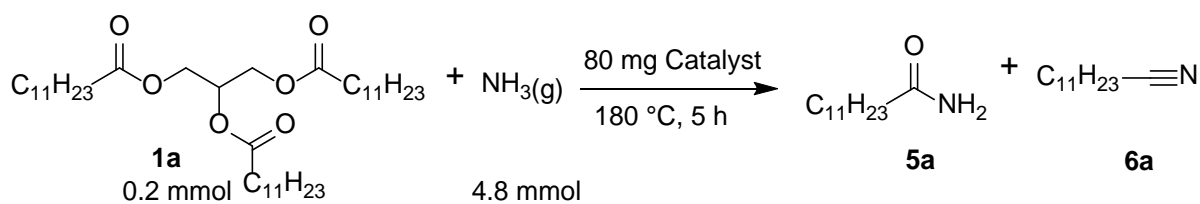


Scheme 4. Examination of the substrate scope for the reductive amination of various triglycerides using 5 mol% of 1 wt% Pt/ZrO₂.

Transformation of triglycerides into amides and nitriles.

Potentially, the reactions of triglycerides with NH₃ could also represent useful synthetic routes to fatty amides and nitriles. However, catalytic methods that afford fatty amides and nitriles in high yield remain rare, mostly due to the low reactivity of triglycerides and the difficulties associated with controlling the selectivity, i.e., the difficulties associated with preventing an over-dehydration to nitriles. Classically, multi-step methods with low atom efficiency are used for the synthesis of fatty amides and nitriles.^[12] Thus, an operationally simple heterogeneous catalytic method for the selective synthesis of primary fatty amides from triglycerides and ammonia represents an attractive research target.

To establish high-yield catalytic methods for the transformation of triglycerides into fatty amides and nitriles, we carried out a catalyst screening on the model substrate trilaurin **1a** (4 bar/ 4.8 mmol NH₃; 180 °C; 5 h). **Table 3** summarizes the yields of dodecylamide **5a** and dodecanenitrile **6a**. Under the applied conditions and in the absence of any catalyst, **5a** and **6a** were not obtained (entry 1). Various acid or base catalysts, including various types of heterogeneous catalysts (entries 2-17) and three types of homogeneous catalysts (entries 18-20) were also tested for this reaction. Among various single-metal oxides, ZrO₂ (entry 6) and SiO₂ (entry 8) afforded **5a** in relatively high yield (67-68%). We also screened Hbeta (Hβ) zeolites with different Si/Al ratios; Hβ-75, a zeolite with an intermediate Si:Al ratio of 75:1, furnished the highest yield of **5a** (95%). Among commercially available acidic resins, Amberlyst-15 afforded **5a** in higher yield (82%) than a Nafion/SiO₂ composite (32%). The water-tolerant homogeneous Lewis acid Sc(OTf)₃ and the homogeneous Brønsted acids *p*-toluenesulfonic acid (PTSA) and H₂SO₄ furnished **5a** in moderate to low yields (8-41%). Thus, Hβ-75 was identified as the best catalyst for the selective synthesis of amide **5a** from trilaurin **1a** and NH₃.

Table 3. Catalyst screening for the selective amidation of trilaurin (**1a**) to dodecylamide (**5a**).

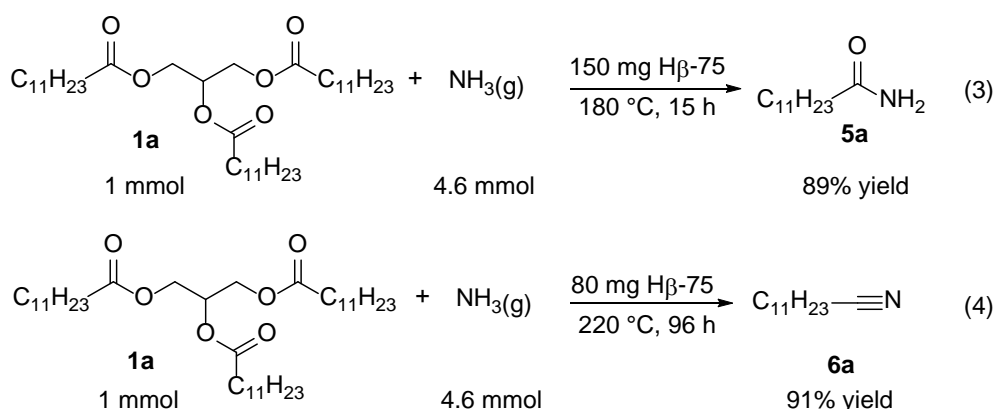
Entry	Catalysts	5a Yield [%] ^a	6a Yield [%] ^a
1	none	0	0
2	Nb_2O_5	28	10
3	TiO_2	19	6
4	CeO_2	16	3
5	Al_2O_3	24	4
6	ZrO_2	67	5
7	MgO	9	4
8	SiO_2	68	7
9	H β -12.5	62	5
10	H β -20	66	6
11	H β -75	95	4
12	H β -255	78	4
13	HZSM5-75	52	3
14	HY-50	61	5
15	HMOR-45	59	2
16	Amberlyst-15	82	7
17	Nafion/ SiO_2	32	5
18	$\text{Sc}(\text{OTf})_3$	41	7
19	PTSA	32	3
20	H_2SO_4	8	1

^a Yields were determined by GC (error range: $\pm 1.5\%$)

Subsequently, we tested the effect of various reaction parameters on the yields of **5a** and **6a** for this reaction (**Figure 5**). The effect of the reaction temperature on the yields of **5a** and **6a** shows that the yield of **5a** is highest at 180 °C (**Figure 5A**). The effect of the initial NH_3 pressure on the yields of **5a** and **6a** were tested by carrying out the reaction at 180 °C using different initial amounts of NH_3 (mmol) in the reactor. The results (**Figure 5B**) show that increasing amounts of NH_3 afford higher yields of **5a**. The time course of the reaction under 4 bar NH_3 (4.8 mmol NH_3) at 180 °C (**Figure 5C**) shows that the yield of **5a** reaches a maximum after 5 h. Based on these results, the optimal conditions for the selective synthesis of fatty amides were determined as: 4 bar NH_3 , 180 °C, 5 h, H β -75 (80 mg).

The H β -75-catalyzed reaction of triglycerides with gaseous ammonia is time-dependent, and produces nitriles after prolonged reaction times. In order to demonstrate a gram-scale synthesis of dodecanamide (eqn. 3), we treated 1 mmol of trilaurin **1a** for 15 h with 4.6 mmol (considering 29.3

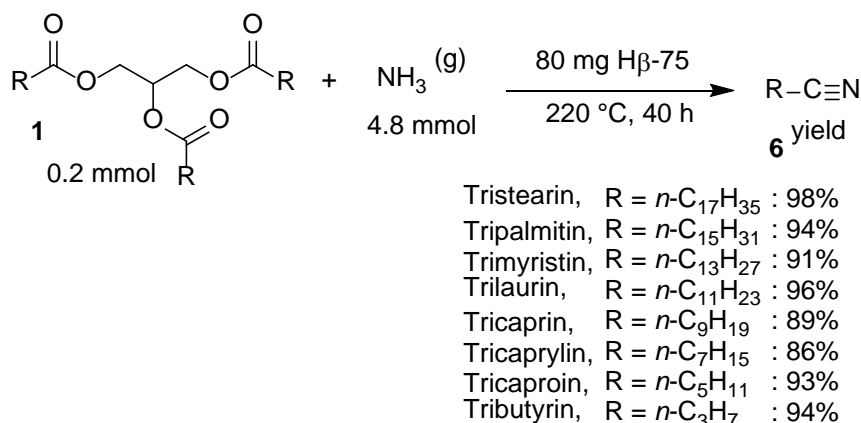
cm³ of dead space) of NH₃(g) using 150 mg of H β -75 (optimized conditions for the complete conversion of trilaurin to produce a minimum of the corresponding nitrile), which furnished dodecanamide (89%) and dodecanenitrile (5%). Moreover, we have conducted a gram-scale reaction for the synthesis of nitriles from trilaurin (eqn. 4). Using 80 mg of H β -75, the reaction between trilaurin (1 mmol) and NH₃(g) 4.6 mmol (considering 29.3 cm³ of dead space) for 96 h at 220 °C resulted in the formation of dodecanenitrile (91%) and dodecanamide (3%).



Under the optimized conditions, we examined the substrate scope of this catalytic amidation using various triglycerides (**Scheme 5**). Triglycerides with different chain lengths (C4-C18) were selectively transformed into the corresponding fatty amides in high yield (82-95%). A slightly longer time (6 h) was required for the optimal transformation of the long-chain triglycerides (C13, C15, and C17).

The time course data at 180 °C (**Figure 5C**) after 5 h shows that amide **5a** is converted into **6a** in up to 78% yield (after 36 h). This indicates that **5a** undergoes dehydration to form dodecanenitrile **6a**. This result motivated us to investigate the optimal conditions for the selective conversion of triglycerides into nitriles using H β -75 as a catalyst. **Figure 5D** shows the time course of the same reaction at higher temperature (220 °C). The formation rate of **6a** and the final yield of **6a** were higher than those at 180 °C, i.e., the yield of nitrile **6a** reached 96% after 40 h. It is interesting to note that only by tuning the reaction conditions, the same zeolite works as a catalyst for the selective synthesis of amides and nitriles.

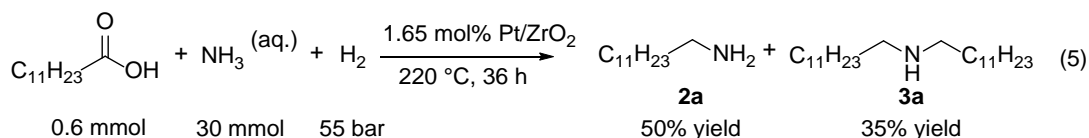
Under the conditions stipulated in **Figure 5D** (40 h), we studied the substrate scope of the direct nitrile synthesis using various triglycerides (**Scheme 6**). The C4-C18 triglycerides were transformed into the corresponding fatty nitriles in high yield (86-98%). Conventionally, fatty nitriles are produced from triglycerides via methyl esterification, followed by amidation with ammonia and dehydration of the amides to the corresponding fatty nitriles.^[1,49,50] This reaction represents a rare example of a direct catalytic reductive nitrilation of various triglycerides with NH₃.



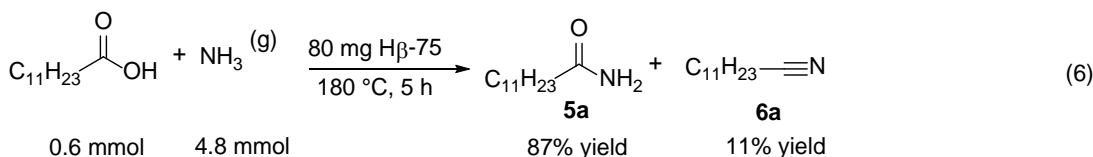
Scheme 6. H β -75 catalyzed direct nitrilation of triglycerides with NH₃.

We have also demonstrated the applicability of our catalytic systems to lauric acid as a homologue of fatty acids. We carried out the amination, amidation, and nitrilation of lauric acid using a Pt/ZrO₂ catalyst as outlined in eqn. (5) and the H β -75 catalyst as outlined in eqns. (6) and (7), respectively. In these reactions, the amount of lauric acid (0.6 mmol) was adjusted to that theoretically generated from trilaurin (0.2 mmol) used in the respective model reactions, while the other reaction parameters were kept identical to those of the model reactions. The reductive amination of lauric acid produced dodecylamine **2a** and *N,N*-didocecylamine **3a** in 50% and 35% yield, respectively. The amidation and nitrilation of lauric acid also afforded the corresponding amide **5a** and nitrile **6a** in high yields as shown in eqns. (6) and (7).

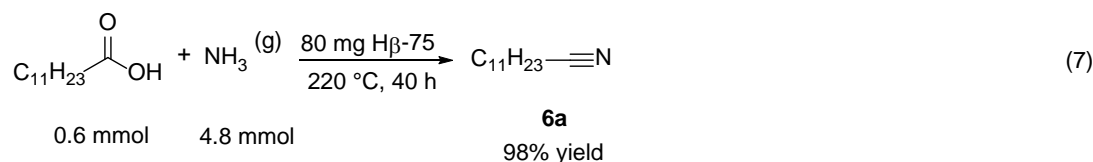
Amination of lauric acid



Amidation of lauric acid



Nitrilation of lauric acid



Finally, we would like to discuss the factors affecting the catalytic activity of H β for the direct conversion of triglyceride **1a** into amides and nitriles using NH₃. Employing H β catalysts with different Si/Al ratios, we estimated the initial formation rates of amide **5a** and nitrile **6a** at 180 °C and 220 °C,

respectively, under conditions where the conversion of **1a** was < 40%. As shown in **Figure 6**, the reaction rate per catalyst weight shows a volcano type dependence on the Si/Al ratio, in which H β with a moderate Si/Al ratio (H β -75) gives the highest rate. Recently, we have studied the hydrophilicity and acidity of such H β catalysts; [64-65] the number of acid sites was estimated by NH₃-TPD (temperature programmed desorption) and the hydrophobicity was estimated by the number of *n*-dodecane adsorbed on H β in water. The number of acid sites decreases with increasing Si/Al ratio, while the hydrophobicity of H β increases with the Si/Al ratio (**Figure 6**). Using the number of the acid sites, we calculated the turnover frequency (TOF) per acid site. The TOF for the formation of amides and nitriles increases with increasing Si/Al ratio, i.e., similar to the trend observed for the hydrophobicity of the zeolites.[66] These results indicate that the acidity and hydrophobicity are two important factors affecting the activity of the H β catalysts in this direct and selective catalytic reductive amidation/nitrilation of various triglycerides with NH₃. A larger number of acid sites and high hydrophobicity can increase the reaction rates (relative to the weight of the catalyst), which is the reason why the H β catalyst with a moderate Si/Al ratio (H β -75) exhibits the highest catalytic activity.

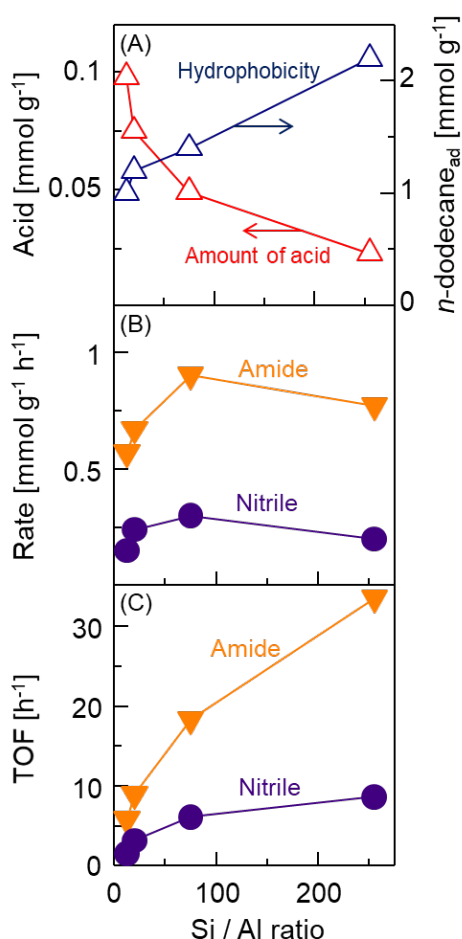


Figure 6. (A) Number of acid sites and amount of *n*-dodecane adsorbed in H β (hydrophobicity); (B) formation rates of amide **5a** and nitrile **6a** in the reactions of **1a** with NH₃ at 180 °C and 220 °C, respectively; (C) TOF per number of acid sites for the formation of amide **5a** and nitrile **6a** as a function of the Si/Al ratio in H β .

Conclusions

This study presents three heterogeneous catalytic methods for the selective one-pot transformation of triglycerides to value-added chemicals: (i) a reductive amination of triglycerides into fatty amines with aqueous NH_3 under an atmosphere of H_2 using ZrO_2 -supported Pt metal nanoparticles, (ii) an amidation of triglycerides under gaseous NH_3 using a high-silica $\text{H}\beta$ zeolite at 180 °C, and (iii) a direct synthesis of nitriles from triglycerides and gaseous NH_3 using a high-silica $\text{H}\beta$ zeolite at 220 °C. These methods selectively transform a wide variety of triglycerides (C4-C18) into the corresponding amines, amides, and nitriles, and thus represent a milestone in chemical transformation of triglycerides. A systematic analysis of reaction (ii) and (iii) reveals that the acidity and hydrophobicity of the zeolites are two important factors that affect the catalytic activity of the $\text{H}\beta$ catalysts. Specifically, increasing the number of acid sites and increasing the hydrophobicity may lead to higher reaction rates per weight of the catalyst.

Experimental

General

Chemical reagents were purchased from common commercial suppliers (Tokyo Chemical Industry, Wako Pure Chemical Industries, Kishida Chemical, or Mitsuwa Chemicals) and used as received. GC-FID (Shimadzu GC-2014) and GC-MS (Shimadzu GCMS-QP2010) analyses were performed using an Ultra ALLOY capillary column UA⁺-1 (Frontier Laboratories Ltd.) with N₂ or He as the carrier gas. ¹H and ¹³C NMR measurements were conducted on a JEOL-ECX 600 spectrometer operating at 600.17 (¹H) and 150.92 MHz (¹³C), or on a JEOL-ECX 400 spectrometer operating at 399.78 (¹H) and 100.52 MHz (¹³C), using tetramethylsilane as the internal standard.

Catalyst preparation

In the zeolites H β -x, x denotes the Si/Al ratio. The catalysts H β -75 (JRC-Z-HB150; originally supplied from Clariant), H β -12.5 (JRC-Z-HB25), HMOR-45 (JRC-Z-HM90; originally supplied from Clariant), ZrO₂ (JRC-ZRO-5; 193.7 m² g⁻¹), TiO₂ (JRC-TIO-4), CeO₂ (JRC-CEO-3), and MgO (JRC-MGO-3) were supplied by the Catalysis Society of Japan. Nb₂O₅ was prepared by calcination (500 °C; 3 h) of Nb₂O₅·*n*H₂O (kindly supplied by CBMM). SiO₂ (Q-10; 300 m² g⁻¹) was kindly supplied by Fuji Silysia Chemical Ltd. The carbon support (296 m² g⁻¹; Kishida Chemical) was commercially obtained. γ -Al₂O₃ was prepared by calcination of γ -AlOOH (Catapal B Alumina kindly supplied by Sasol; 900 °C; 3 h). H β -20 (HSZ-940HOA), H β -255 (HSZ-980HOA) and HY-50 (HSZ-385HUA) were purchased from Tosoh Co. HZSM5-75 was supplied from N.E. CHEMCAT Co.

Pt/ZrO₂ catalysts with a Pt loading of 1, 3, and 5 wt% were prepared by evaporating a mixture of ZrO₂ and an aqueous HNO₃ solution of Pt(NH₃)₂(NO₃)₂ at 50 °C, followed by consecutive drying (110 °C; 12 h) and reduction in a Pyrex tube under a flow of H₂ (20 cm³ min⁻¹) at 300 °C (0.5 h). Other supported Pt catalysts with Pt loadings of 5 wt% were prepared by the same method. M/ZrO₂ (M = Rh, Ir, Ru, Pd, Re, Cu, Ni, Ag) catalysts with a metal loading of 1 wt% were prepared by a similar method as for Pt/ZrO₂ using aqueous HNO₃ solutions of Rh(NO₃)₃ or Pd(NH₃)₂(NO₃)₂, aqueous solutions of metal nitrates (Ni, Cu, Ag), IrCl₃·*n*H₂O, RuCl₃, or NH₄ReO₄. Platinum-oxide-loaded ZrO₂ (PtO_{*x*}/ZrO₂) was prepared by calcination of the Pt(NH₃)₂(NO₃)₂-loaded ZrO₂ (300 °C; 0.5 h; in air).

Characterization. ABF- and HAADF-STEM images for 1 wt% Pt/ZrO₂ were recorded on a JEM-ARM200F microscope (JEOL) using an acceleration voltage of 200 kV. The Cs-corrector CESCOR (CEOS) was used in the STEM mode. The pre-reduced catalyst powder that was exposed to air at room temperature, was mixed with ethanol, and this ethanolic suspension of the sample was dropped on a carbon-supported copper grid.

Pt L₃-edge X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were carried out in transmittance mode at the BL14B2

beamline of SPring-8 (8 GeV), using a Si(311) double crystal monochromator. The Pt/ZrO₂ catalyst, pre-reduced under a flow of H₂ (20 cm³ min⁻¹) for 0.5 h at 300 °C, was cooled to room temperature under the flow of H₂ and sealed in a polyethylene-cell under N₂, before the EXAFS spectrum was recorded at room temperature. The curve-fitting EXAFS analysis was carried out using the REX ver. 2.5 program (RIGAKU) and the parameters for the Pt–O and Pt–Pt shells provided by FEFF6.

Catalytic reactions.

Before the catalytic tests for the amine synthesis, the metal catalysts were deposited in a glass tube (6.5 cm³) and reduced for 0.5 h under a flow of H₂ at 300 °C. Catalytic experiments were carried out without exposing the reduced catalyst to air. Hexadecane (1 mmol) was added to the reduced catalyst via a septum inlet; thus, the catalyst was covered with the hexadecane layer to avoid exposure to air. After removal of the septum in air, triglycerides (0.2 mmol), an aqueous solution of 28 wt% NH₃ (30 mmol) and a magnetic stirrer bar were added to the tube. The tube was then inserted into a stainless-steel autoclave (dead space: 9.7 cm³) and pressurized with H₂ (55 bar), followed by heating the autoclave to 220 °C for 36 h.

For the syntheses of amides and nitriles, triglycerides (0.2 mmol), *n*-hexadecane (0.25 mmol), and a magnetic stirrer bar were deposited in a reaction tube (30 cm³) in air. The glass tube was then inserted in a low-pressure autoclave (dead space: 30 cm³). Then, NH₃ (gas; 4.8 mmol) was added into the closed autoclave, which was subsequently heated for 5 h to 180 °C to yield the amide, and for 40 h to 220 °C to yield the nitriles.

After completion of the reaction, ethyl acetate (3 mL) was added and the products were analyzed by GC (Shimadzu GC-14B; Ultra ALLOY capillary column UA⁺-1 from Frontier Laboratories Ltd.; N₂) and GC-MS (SHIMADZU GCMS-QP2010; Ultra ALLOY capillary column UA⁺-1 from Frontier Laboratories Ltd.; He). The products were isolated by column chromatography on silica gel 60 (spherical; 50-100 μm; Kanto Chemical Co. Ltd.) using hexane/ethyl acetate (75/25, v/v) as the eluent. The isolated products were then analyzed by GC and GC-MS, as well as ¹H and ¹³C NMR spectroscopy. Isolated yields were determined relative to the starting triglycerides. Product yields based on the amount of ester groups in the triglycerides were determined by GC analysis, where GC sensitivities were estimated in comparison to the isolated products or to the commercial products using *n*-hexadecane as an internal standard. Further careful analyses of GC conversions and yields were also carried out affording an error range (±1.5 %) by exploiting the duplicated yields or conversions of the same reaction. In the substrate-scope studies (**Schemes 4-6**), the product yields are based on GC analysis, while the product identification was accomplished by GC-MS analysis.

To ensure the presence of glycerol in the reaction mixture of all three types of the reactions, we worked-up each model reaction by adding ethyl acetate (3 mL) and D₂O (2 mL). Then, the aqueous layer was analyzed by ¹H NMR spectroscopy. The amination reaction did not show the presence of glycerol using this reductive catalytic system, whereas the presence of glycerol was confirmed in the

reaction mixtures of the amidations and nitrilations. The formed glycerol could be separated from the desired products simply by washing with water.

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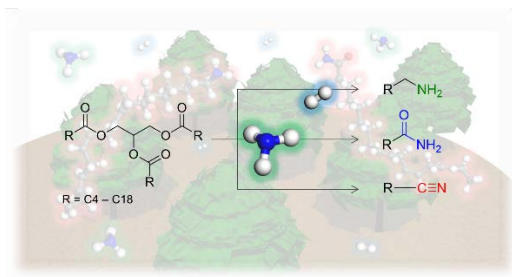
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Entry for the Table of Contents

FULL PAPER

Three heterogeneous catalytic methods for the selective one-pot transformation of triglycerides into value-added chemicals are presented: (i) the reductive amination of triglycerides into fatty amines with aqueous NH_3 and H_2 , (ii) the amidation of triglycerides with gaseous NH_3 , and (iii) the direct synthesis of nitriles with gaseous NH_3 .



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Selective Transformations of Triglycerides into Fatty Amines, Amides, and Nitriles using Heterogeneous Catalysts