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ARTICLE

Reductive amination of triglycerides to fatty amines over a titanium oxide-supported Pt–Mo catalyst

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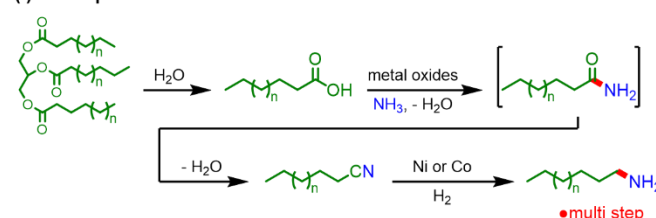
The reductive amination of naturally abundant triglycerides is a promising approach for the synthesis of fatty amines. However, existing catalytic systems for this transformation typically require harsh reaction conditions. Herein, we present a titanium oxide-supported platinum–molybdenum (Pt–Mo/TiO$_2$) catalyst that promotes the reductive amination of triglycerides to fatty amines. The Pt–Mo/TiO$_2$ catalyst exhibits a high activity under milder conditions, specifically at 1 MPa of H$_2$, surpassing the performance of previously reported catalysts. A wide range of triglycerides, including cooking oils, are successfully converted into the corresponding fatty amines in high yields. The Pt–Mo/TiO$_2$ catalyst is reusable and applicable to gram-scale reactions, demonstrating the high potential of Pt–Mo/TiO$_2$ for green and sustainable fatty amine production.
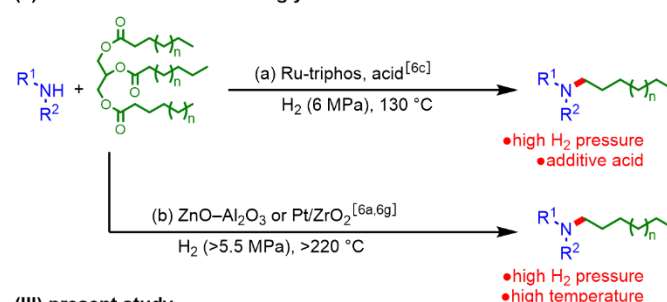
Introduction

The conversion of biomass-derived renewable carbon resources into valuable chemicals and fuels, instead of relying on fossil resources, has been recognized as a strategy to mitigate the global environmental burden caused by carbon dioxide emissions.[1] Among plant-based biomass resources, triglycerides, which are the main component of vegetable oils and fats, are used for the production of fatty acids, fatty alcohols, fatty acid alkyl esters, hydrocarbons, and fatty amines.[2] In this context, fatty amines are important due to their diverse applications, including use as fabric softeners, mineral processing reagents, corrosion inhibitors, and lubricants.[3] One of the well-known methods for producing fatty amines from triglycerides is the nitrile process.[1a,2a] This process involves multiple steps: hydrolysis to fatty acids, amidation followed by dehydration to form nitriles, and hydrogenation to produce fatty amines. It requires substantial amounts of solvent and energy for the synthesis and purification of intermediates (Scheme 1(I)). Therefore, the development of a more efficient and greener method for the direct conversion of triglycerides to fatty amines is desired.[4]

The reductive amination of triglycerides under H$_2$ is a straightforward method for producing fatty amines.[5,6] Beller *et al.* reported a homogeneous catalyst system consisting of a Ru-triphos complex with an additive acid working under 6 MPa H$_2$ at 130 °C (Scheme 1(IIa)).[6c] In addition, there have been two reports on heterogeneous catalyst systems (Scheme 1(IIb)). The
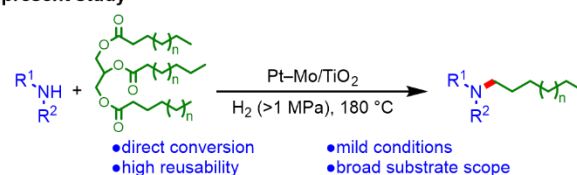
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Scheme 1 Fatty amine syntheses from triglycerides.

Table 1 Reductive amination of trilaurin (**2**) with piperidine (**1**) to 1-dodecylpiperidine (**3**) over various heterogeneous catalysts[a]

entry	catalyst	H_2 (MPa)	time (h)	conv. of 1^b (%)	yield[b] (%)		
					3	4	5
1	Pt–Mo/TiO$_2$	4	6	54	35	4	3
2	Pt–Mo/TiO$_2$	4	16	99	70	2	7
3	Pt–Mo/TiO$_2$	1	60	>99	61	1	11
4	Rh–Mo/TiO$_2$	4	6	35	17	2	1
5	Ru–Mo/TiO$_2$	4	6	62	8	24	<1
6	Pd–Mo/TiO$_2$	4	6	79	1	67	1
7	Pt–Re/TiO$_2$	4	6	61	26	21	1
8	Pt–W/TiO$_2$	4	6	95	14	53	1
9	Pt–V/TiO$_2$	4	6	67	14	41	<1
10	Pt–Mo/ZrO$_2$	4	6	53	32	3	2
11	Pt–Mo/γ-Al$_2$O$_3$	4	6	54	30	2	3
12	Pt–Mo/WO$_3$	4	6	23	7	6	<1
13	Pt–Mo/Nb$_2$O$_5$	4	6	21	4	2	0
14	Pt/TiO$_2$	4	6	80	16	49	1
15	Mo/TiO$_2$	4	6	59	0	47	0
16	TiO$_2$	4	6	70	0	61	0

[a] Reaction conditions: catalyst (0.15 g, Pt: 7 mol% and Mo: 2 mol%), **1** (1 mmol), **2** (0.5 mmol), *n*-hexane (3 mL), 180 °C. [b] Determined by gas chromatography-flame ionization detection (GC-FID) using an internal standard method. Yield was based on **1**.

ZnO–Al$_2$O$_3$ catalyst successfully promoted direct reductive amination at 25 MPa H$_2$ and 310 °C.[6a] Shimizu *et al.* reported a Pt/ZrO$_2$ catalyst capable of operating under 5.5 MPa H$_2$ and 220 °C.[6g] However, these catalytic systems require harsh reaction conditions, and their reusability has not yet been investigated. Hence, the development of highly active and reusable catalysts is desired to achieve the green and sustainable production of fatty amines.

Herein, we present the direct reductive amination of triglycerides to fatty amines using a titanium oxide-supported platinum–molybdenum (Pt–Mo/TiO$_2$) catalyst (Scheme 1(III)). The key features of the catalyst system include: (1) mild conditions, such as 1 MPa H$_2$ and 180 °C, in comparison with previously reported catalyst systems; (2) high reusability without loss of activity; and (3) a broad substrate scope, extending to real cooking oil.

## Results and discussion

Catalyst performance

Pt–Mo/TiO$_2$ and the other supported catalysts listed in Table 1 were prepared using the co-impregnation method. Catalytic activities were evaluated for the reaction between piperidine (**1**) and trilaurin (**2**) under 4 MPa H$_2$ at 180 °C for 6 h (Table 1 and Scheme S1). The Pt–Mo/TiO$_2$ catalyst afforded 1-dodecylpiperidine (**3**) in a 35% yield, 1-(1-piperidinyl)-1-dodecanone (**4**) in a 4% yield, and 1-propylpiperidine (**5**) in a 3% yield along with unidentified compounds (Table 1, entry 1 and Scheme S2). When the reaction time was prolonged to 16 h, **3** was obtained in a 70% yield (Table 1, entry 2). The combination

of other platinum-group metals (Rh, Ru, and Pd) with Mo, as well as Pt with other metals (Re, W, and V), resulted in lower yields of **3** compared with those of the Pt–Mo catalyst (Table 1, entries 4–9). The support materials for the Pt–Mo catalysts were also tested. ZrO$_2$ and γ-Al$_2$O$_3$ supports were effective in producing **3**, although the yields were slightly lower compared with those obtained with TiO$_2$ (Table 1, entries 10 and 11). The use of WO$_3$ and Nb$_2$O$_5$ resulted in a low yield of **3** (Table 1, entries 12 and 13). Single-metal catalysts (Pt/TiO$_2$ and Mo/TiO$_2$) and bare TiO$_2$ were ineffective in the reductive amination (Table 1, entries 14–16), with amide **4** being obtained as the major product. These results demonstrated that the combination of Pt, Mo, and TiO$_2$ was important for efficient reductive amination of triglycerides.

The solvents used in the reductive amination were also investigated (Table S1). Nonpolar *n*-hexane was effective for the reductive amination, while the use of tetrahydrofuran as a polar solvent resulted in poor yield of **3**. When ethanol was used as the solvent, **1** reacted with ethanol to give 1-ethylpiperidine in >99% yield. The high performance of the Pt–Mo/TiO$_2$ catalyst was further demonstrated in a reaction under 1 MPa H$_2$. The Pt–Mo/TiO$_2$ catalyst promoted the reductive amination under 1 MPa of H$_2$ to afford **3** in a 61% yield (Table 1, entry 3), outperforming previously reported catalysts (Table S2).[6a,6c,6g] The Pt–Mo/TiO$_2$ catalyst was applicable to the gram-scale reaction (Scheme 2); the reaction of 1.0 g of **1** with 3.5 g of **2** produced 1.9 g of **3** in a 62% isolated yield. Furthermore, the reusability of the heterogeneous catalysts is one of their key advantages over homogeneous catalysts. After reductive amination, the Pt–Mo/TiO$_2$ catalyst was recovered by
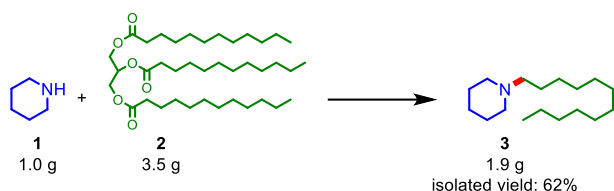
Scheme 2 Gram-scale reductive amination. Reaction conditions: Pt–Mo/TiO$_2$ (1.0 g, Pt: 4.1 mol% and Mo: 1.2 mol%), *n*-hexane (15 mL), 180 °C, H$_2$ (4 MPa), 60 h. Yield was based on **1**.
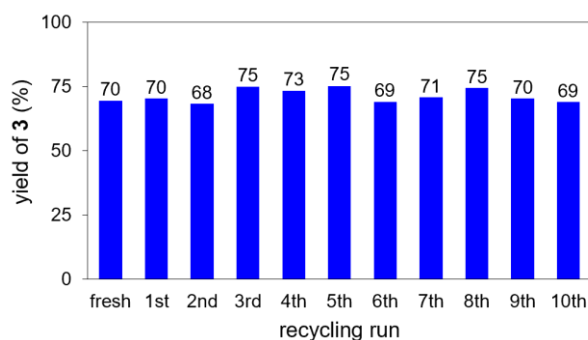
Fig. 1 Reusability of the Pt–Mo/TiO$_2$ catalyst in reductive amination reactions. Reaction conditions: Pt–Mo/TiO$_2$ (0.15 g, Pt: 7 mol% and Mo: 2 mol%), **1** (1 mmol), **2** (0.5 mmol), *n*-hexane (3 mL), 180 °C, H$_2$ (4 MPa), 16 h. Yield was determined by GC-FID using an internal standard method based on **1**.

centrifugation and reused in the next reaction without pretreatment. The high activity of the Pt–Mo/TiO$_2$ catalyst was maintained until the tenth cycle (Fig. 1 and Table S3). Inductively coupled plasma atomic emission spectroscopy analyses of the used Pt–Mo/TiO$_2$ catalyst showed similar Pt and Mo loadings to those of the fresh sample, confirming that the leaching of Pt and Mo into the reaction solution was negligible (Table S4). These results strongly support the high durability and reusability of the Pt–Mo/TiO$_2$ catalyst.

Substrate scope

The substrate scope of the Pt–Mo/TiO$_2$ catalyst was investigated using various amines and **2** (Table 2 and Table S5). Cyclic amines (**1** and azepane) were alkylated to afford the corresponding tertiary amines (**3** and 1-dodecylazepane) in yields of 70% and 60%, respectively (Table 2, entries 1 and 2). The Pt–Mo/TiO$_2$ catalyst could be applied to the reductive amination of **2** with primary amines; hexylamine and dodecylamine were alkylated to *N*-hexyldodecylamine and didodecylamine in 35 and 70% yields, respectively (Table 2, entries 3 and 4). Moreover, NH$_3$ gas was used for the reductive amination of **2**, and didodecylamine was obtained in a 74% yield (Table 2, entry 5). The reductive amination using pyridine and aniline proceeded along with hydrogenation of aromatic rings, providing **3** and *N*-dodecylcyclohexanamine as the major products in 44% and 46% yields, respectively (Table 2, entries 6 and 7).

The applicability of the Pt–Mo/TiO$_2$ catalyst in the reductive amination of triglycerides with different carbon chain lengths was explored. Pt–Mo/TiO$_2$ promoted the amination of triacetin, tricaprylin, tripalmitin, and tristearin, yielding *N*-alkylated

piperidine in over 61% yield (Table 2, entries 8–11). The utility of the Pt–Mo/TiO$_2$ system was also investigated in a reaction using real cooking oil, the composition of which is shown in Table S6, without pretreatment. The cooking oil was successfully aminated to the corresponding fatty amines (1-hexadecylpiperidine and 1-octadecylpiperidine) in a 65% total yield (Table 2, entry 12), demonstrating the versatility of Pt–Mo/TiO$_2$.

Reaction pathway

The reaction pathways in the Pt–Mo/TiO$_2$-catalyzed reductive amination of triglycerides were investigated. A time-course experiment was performed to obtain information on intermediates. The yield of 1-dodecanol (**7**) increased to 10% over 6 h and then decreased, whereas the formation of **4** was observed in a less than 4% yield throughout the reaction (Fig. S1). In addition, various TiO$_2$-supported catalysts and bare TiO$_2$ promoted the amidation of **2** with **1** to **4** (Table 1, entries 1–9 and 14–16). These results suggested that **7** and **4** were the potential intermediates in this reaction. Based on the above results, two reaction pathways were proposed: hydrogenation of triglycerides to aldehydes or alcohols followed by amination (path A), and amidation of triglycerides followed by hydrogenation of amides to amines (path B) (Fig. 2a).[6d,6f,6g]
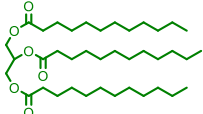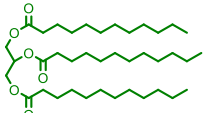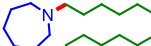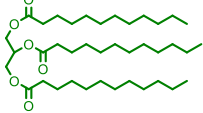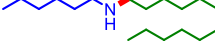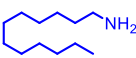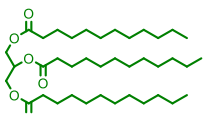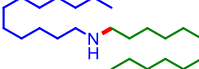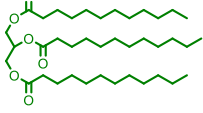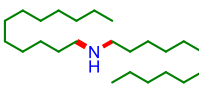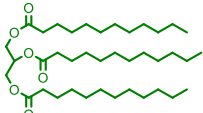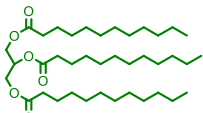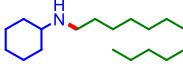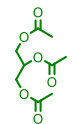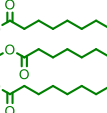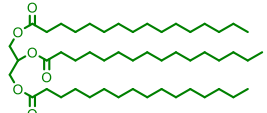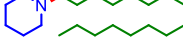
Catalysis by Pt–Mo

To gain insight into the high activity of Pt–Mo/TiO$_2$, its activity in each reaction step was evaluated and compared with that of Pt/TiO$_2$ as a reference (Fig. 2b and Table S7). The Pt–Mo/TiO$_2$ catalyst promoted the hydrogenation of **2** to afford **7** and *n*-dodecane (**8**) in yields of 15% and 63%, respectively, whereas Pt/TiO$_2$ afforded considerably lower yields than Pt–Mo/TiO$_2$ (Fig. 2b(i)). In the hydrogenation of **4**, the Pt–Mo/TiO$_2$ catalyst showed a higher activity towards **3** compared with using Pt/TiO$_2$. The yield of **3** was three times higher with Pt–Mo/TiO$_2$ (33%) than that obtained with Pt/TiO$_2$ (10%) (Fig. 2b(iv)). Other control experiments, such as the reductive amination of 1-dodecanal (**6**) (Fig. 2b(ii-1)), amination of **7** (Fig. 2b(ii-2)), and amidation of **2** (Fig. 2b(iii)), did not show significant differences in yields. Therefore, control experiments demonstrated that cooperative catalysis between Pt and Mo promoted the reaction steps of hydrogenation of triglycerides and amides more efficiently.

Furthermore, the structure of the catalyst during reductive amination was investigated. TEM images of the used Pt–Mo/TiO$_2$ and Pt/TiO$_2$ revealed the presence of Pt nanoparticles (NPs) with mean diameters of 3.5 and 4.2 nm, respectively, on the TiO$_2$ surface (Fig. 3a and S2). Elemental mapping using high-angle annular dark-field scanning TEM (HAADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDX), confirmed dispersion of Mo species in the used Pt–Mo/TiO$_2$ (Fig. S3). X-ray absorption near-edge structure (XANES) an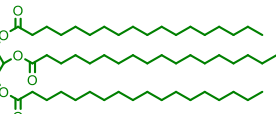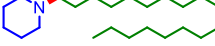alysis was used to investigate the chemical states of the Pt and Mo species (Fig. 3b, 3c, S4, and S5). The white-line intensities of the Pt L$_3$-edge XANES spectra of the used Pt–Mo/TiO$_2$ and Pt/TiO$_2$ were similar to those of the Pt foil, suggesting the presence of zero-valent Pt in both catalysts (Fig. 3b, S4, and S6). Fig. 3c shows the Mo K-

Table 2. Pt–Mo/TiO$_2$-catalyzed reductive amination of various triglycerides with amines[a]

entry	amine	triglyceride	product	time (h)	yield[b] (%)
1				16	70
2				36	60[c]
3				36	35
4				36	70
5[d]	NH$_3$			36	74
6				24	44
7				24	46
8				12	79
9				24	62[e]
10[f]				48	63[e]
11[f]				48	61[e]
12[f,g]		cooking oil		48	65[c]

[a] Reaction conditions: Pt–Mo/TiO$_2$ (0.15 g, Pt: 7 mol% and Mo: 2 mol%), amine (1 mmol), triglyceride (0.5 mmol), n-hexane (3 mL), 180 °C, H$_2$ (4 MPa). [b] Determined by GC-FID using an internal standard method. Yield was based on amine. [c] NMR yield. [d] Pt–Mo/TiO$_2$ (0.15 g, Pt: 4.8 mol% and Mo: 1.4 mol% with respect to the ester moiety), NH$_3$ (0.7 MPa). Yield was based on **2**. [e] Isolated yield. [f] n-Hexane (5 mL). [g] Cooking oil (0.5 g). The carboxylic acid contents of the cooking oil are shown in Table S6.
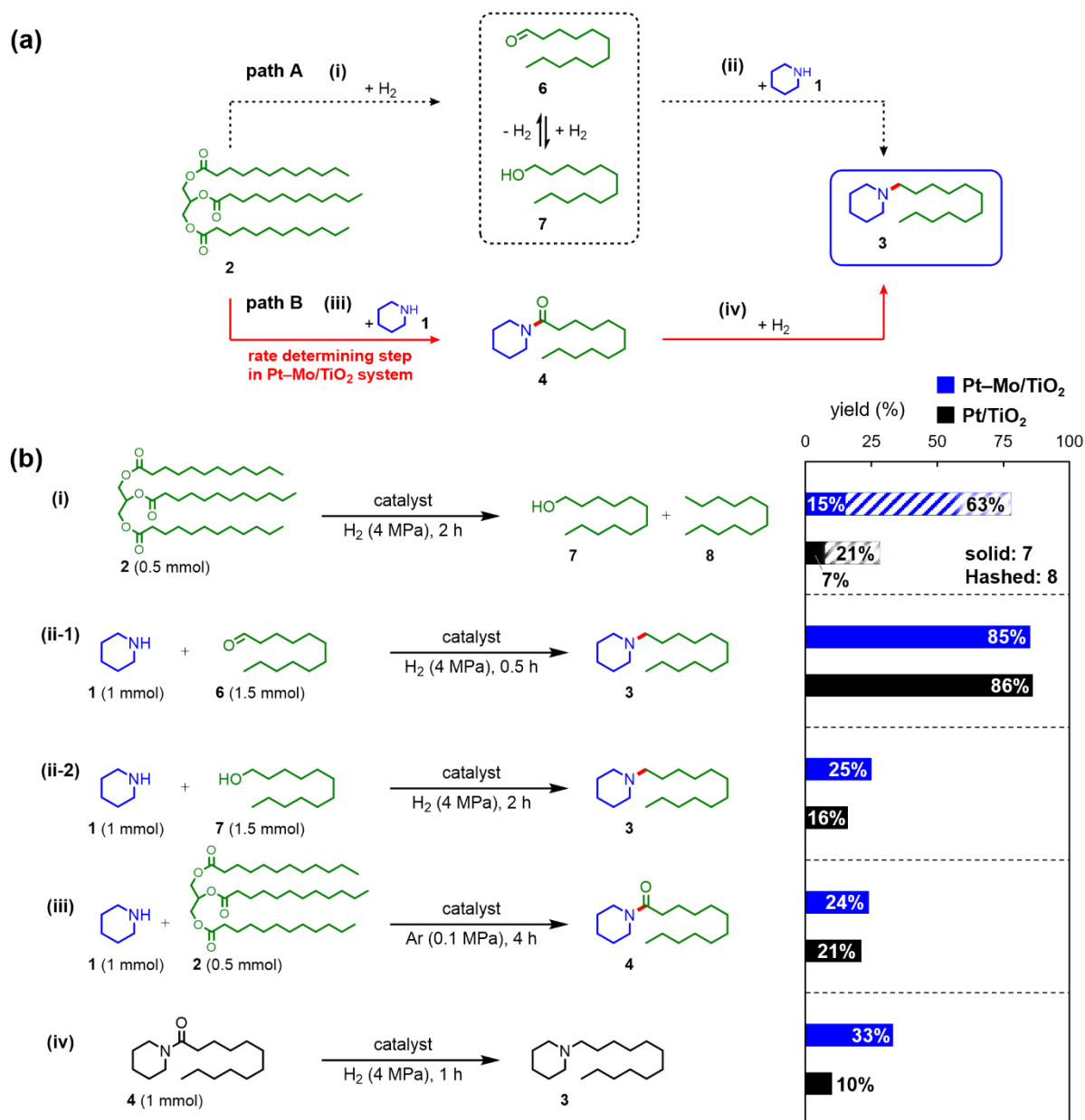
Fig. 2 (a) Reaction network in the reductive amination of triglycerides. (b) Comparison of the activities of Pt–Mo/TiO$_2$ and Pt/TiO$_2$. Reaction conditions: Pt–Mo/TiO$_2$ or Pt/TiO$_2$ (0.15 g; Pt: 4.8 mol% and Mo: 1.4 mol% with respect to the ester moiety for (i); Pt: 7 mol% and Mo: 2 mol% for (ii-1), (ii-2), (iii), (iv)), *n*-hexane (3 mL), 180 °C.

edge XANES spectra of fresh and used Pt–Mo/TiO$_2$. The absorption edge of the Mo K-edge XANES spectrum shifted towards a lower energy after reductive amination, indicating that the Mo species were reduced *in situ*. To obtain detailed information on the valence state of the Mo species, X-ray photoelectron spectroscopy (XPS) analysis of used Pt–Mo/TiO$_2$ was conducted. The deconvolution of the XPS spectrum of the used Pt–Mo/TiO$_2$ in the Mo 3d region displayed multiple peaks corresponding to Mo(0) and Mo oxides with valence states ranging from 4+ to 6+ (Fig. 3d and Table S8). These Mo K-edge XANES and XPS results demonstrated the formation of reduced Mo (MoO$_x$) species during the reaction (Fig. S7).

To investigate the interaction between MoO$_x$ and carbonyl compounds, temperature-programmed desorption infrared (TPD-IR) study was performed using acetone as a probe (Fig. S8). The C=O stretching vibration of acetone adsorbed on the Pt/TiO$_2$ and Pt–Mo/TiO$_2$ catalysts at 50 °C exhibited a peak at approximately 1690 cm^{-1}.[7] As temperature increased, the peak decreased in intensity and completely disappeared at 170 °C for Pt/TiO$_2$ (Fig. S8a). In contrast, the spectrum of Pt–Mo/TiO$_2$ showed a strong peak, and it retained even at 200 °C (Fig. S8b). Thus, the results of TPD-IR, Mo K-edge XANES, and Mo 3d XPS suggest that the carbonyl moieties of the substrates are strongly adsorbed and reduced on the MoO$_x$ sites.
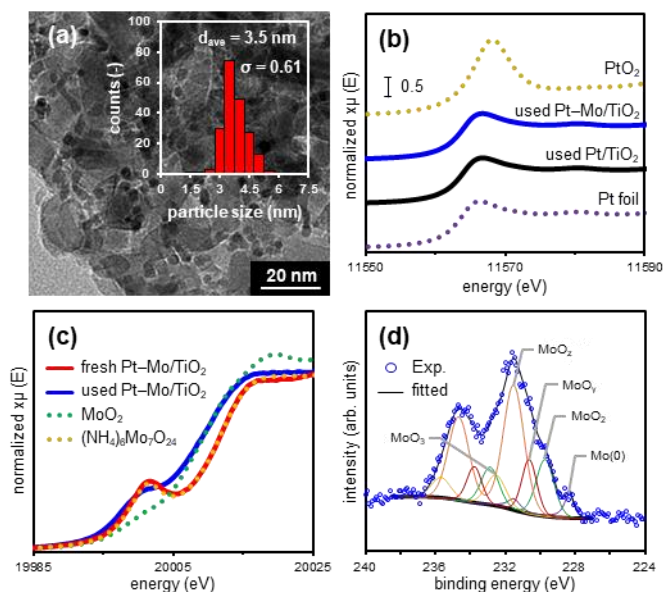
Fig. 3 (a) TEM image and size distribution histogram (inset) of used Pt–Mo/TiO$_2$. (b) Pt L$_3$-edge XANES spectra of PtO$_2$, used Pt–Mo/TiO$_2$, used Pt/TiO$_2$, and Pt foil. (c) Mo K-edge XANES spectra of fresh Pt–Mo/TiO$_2$, used Pt–Mo/TiO$_2$, MoO$_2$, and (NH$_4$)$_6$Mo$_7$O$_{24}$. (d) Mo 3d XPS spectrum of used Pt–Mo/TiO$_2$.

Support effect

The role of support materials was then investigated. Pt–Mo catalysts supported on TiO$_2$, ZrO$_2$, and γ-Al$_2$O$_3$ facilitated the reductive amination, whereas WO$_3$- and Nb$_2$O$_5$-supported catalysts showed a lower conversion of **1** (Table 1, entries 1 and 10–13). Moreover, bare TiO$_2$ efficiently converted **1** to **4** (Table 1, entry 16), indicating that the support materials are important for promoting amidation step (iii) in Fig. 2a. We further performed control experiments on the amidation of **2** under Ar; the Pt–Mo/TiO$_2$ and Pt–Mo/γ-Al$_2$O$_3$ catalysts provided **4** in 24% and 21% yields, respectively, which were much higher than that obtained with Pt–Mo/Nb$_2$O$_5$ (Table S9). NH$_3$-TPD measurements showed that the acid amount of Pt–Mo/TiO$_2$ and Pt–Mo/γ-Al$_2$O$_3$ were significantly higher than that of Pt–Mo/Nb$_2$O$_5$ (Fig. S9). It has been reported that acid property of metal oxides facilitates amidation reactions.[8] Hence, support materials with high acid amount effectively promote amidation, resulting in a high yield of **3** in the reductive amination of triglycerides. This result suggests that path B including amidation is likely to be a major reaction pathway.

Proposed reaction mechanism

In the time-course data shown in Fig. S1, **3** was formed without an induction period, and the yield of **4** was kept low (<4%) throughout the reaction. Moreover, control experiments on hydrogenation of amide using Pt–Mo/TiO$_2$ afforded **3** in 33% yield for 1 h (Fig. 2b(iv)), which is higher than the yield of **4** (24%) in the amidation for 4 h (Fig. 2b(iii)). These results reveal that the amidation is the rate-determining step in the present catalyst system. Based on the aforementioned results, including control experiments and physicochemical characterizations, the high catalytic activity of Pt–Mo/TiO$_2$ can be explained as follows: the carbonyl moiety of triglycerides is activated on the

acid site of the TiO$_2$ surface and transformed to amides, which is the rate-determining step.[8] H$_2$ is dissociated on the Pt NPs,[9] and spillover hydrogen reduces MoO$_3$ to form MoO$_x$[10] (Fig. S5). The carbonyl moiety of amides is then adsorbed onto MoO$_x$ and deoxygenated.[11] Thus, the combination of Pt NPs, MoO$_x$, and TiO$_2$ efficiently facilitated the reductive amination of triglycerides.

Conclusions

The direct synthesis of fatty amines by the reductive amination of triglycerides was achieved using a Pt–Mo/TiO$_2$ catalyst. The Pt–Mo/TiO$_2$ catalyst could be operated under milder reaction conditions, such as 1 MPa H$_2$ and 180 °C, compared with those reported in the previous studies. The high activity of Pt–Mo/TiO$_2$ was maintained even after being recycled ten times, demonstrating its excellent durability and reusability. A wide range of amines and triglycerides, including cooking oil, was applied to the catalytic system to afford the corresponding alkylated amines. The high activity of Pt–Mo/TiO$_2$ was attributed to cooperative catalysis of Pt NPs, MoO$_x$, and TiO$_2$, where TiO$_2$ facilitate amidation of triglycerides and Pt–Mo effectively hydrogenate amide intermediate. This study provides a green and sustainable method for fatty amine production.

Author contributions

K.S. and H.F. designed the experiments, conducted the catalytic activity tests, and characterized the catalysts. S. Y. and T. Mitsudome discussed the experiments and results. T. Mizugaki directed and conceived the project. K.S. and S.Y. co-wrote the manuscript with input from all authors. All authors commented on the manuscript and approved the final version.

Conflicts of interest

There are no conflicts to declare.

Data availability

The experimental data supporting this article have been included in the ESI.

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