Nano Sulfated Titania Solid Acid Catalyst in
Direct Synthesis of Fatty Acid Amides

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Contents

Title, Author name, address………………………………………………………………........S1  
General methods and characterization data………………………....S2-S11  
Copies of $^1$H NMR and $^{13}$C NMR of Compounds *3a-3l*…………….S12-S22  
XRD, SEM, TEM, FT-IR, Theromogram, and Nitrogen adsorption isotherms of Nano sulfated titania………………………………….S23-S25  
References………………………………………………………………..............S26
**Experimental Section:**

**Materials and Instruments**

Titanium isobutoxide (C₁₆H₃₆O₄Ti), purchased from Fluka Company.

Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Ka (λ = 1.54178 Å) radiation. The FT-IR spectra were recorded on an impact 400D Nickolet FT-IR spectrophotometer. The morphology of the products were determined by using Leica Cambridge, model s360, version V03.03 Scanning electron microscopy (SEM) performed at accelerating voltage of 25 Kv. The size of nano flakes were confirmed by Philips CM10 TEM instrument. ¹H NMR and ¹³C NMR spectra were measured on Bruker Advance DPX FT 250 and 62.9 MHz spectrometry with TMS as an internal standard. Mass spectra were obtained on a Shimadzu GCMSQP 1000EX at 20 and/or 70 eV. Elemental analyses were performed on Thermo Finnigan, Flash EA 1112 series microanalyzer by the head of the CHN lab.

**Catalyst preparation**

Sulfated-TiO₂ nano powder was prepared by sol-gel process. Titanium isobutoxide (98% Fluka) was used as the source of TiO₂. An amount, 14.3 mL, of Ti (OC₄H₉)₄ was hydrolyzed in 150 mL water containing 1.25 mL nitric acid (65% Merck) and then the aqueous solution was stirred continuously at room temperature for 2 h to form a highly dispersed sol, and then sol was concentrated and dried at 60°C. Sulfation was done using 0.5 M sulfuric acid solution (2.0 g ml⁻¹). The samples, after 2 h drying at 110 °C, were calcined for 5 h at 500 °C.
Amidation of carboxylic acids with amines

Amidation reaction was performed in a flux at atmospheric pressure equipped with a Teflon-coated magnet-stirring bar. A mixture of carboxylic acid (1.0 mmol), amine (1.0 mmol) and nano sulfated-TiO$_2$ (0.2g, 0.011 mol %) were stirred magnetically at 115 °C and monitored by TLC or GC. The reaction mixture was diluted with EtOAc (10 mL) and centrifuged to remove the catalyst. The filtrate was washed with satd. aq. NaHCO$_3$ (3×10 mL) and water (3×10 mL), to afford the crude product, dried over CaCl$_2$, and concentrated in a rotary vacuum evaporation to afford the crude product, which was further purified by column chromatography using petroleum ether and EtOAc as solvent to yield the expected products. All products were characterized by NMR, IR, mass spectral, and CHN analysis data which for known compounds were found to be identical with those described in the literature and only $^1$H and $^{13}$C NMR are shown and for new compounds the complete spectroscopic data are described as bellow.

**N-Phenyl stearamide (3a)**

![N-Phenyl stearamide](image)

White solid; mp: 85-87°C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta= 0.85$ (3H, t, $J=6.59$ Hz), 1.25 (28H, m), 1.69-1.71 (2H, m), 2.21 (2H, t, $J=7.46$ Hz), 7.09 (1H, m), 7.26 (1H, s), 7.33 (2H, m), 7.50-7.53 (2H, m); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta= 14.1$, 22.7, 25.5, 29.3, 29.4, 29.5, 29.7, 31.9, 37.8, 119.8, 124.1, 128.9, 138.7, 173.5 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1657, 2912, 3342; MS: m/z (%)= 359 (0.4) [M$^+$]; Anal.
Calcd for molecular formula C_{24}H_{41}NO: C, 80.16; H, 11.49%; found: C, 80.02, H, 11.33%.

*N*-**P**-*Tolyl srearamide (3b)

\[
\begin{align*}
\text{White solid; mp: 70-71}^\circ\text{C; }^1\text{H NMR (250 MHz, CDCl}_3\text{): }\delta & = 0.88 (3\text{H, t, } J=6.92 \text{ Hz),} \\
& 1.25 (28\text{H, m), 1.68-1.74 (2H, m), 2.30 (3\text{H, s), 2.33 (2H, t, } J=7.54 \text{ Hz), 7.11 (2H, d, } J=8.17 \text{ Hz), 7.26 (1H, s), 7.39 (2H, d, } J=8.30 \text{ Hz); }^13\text{C NMR (62.9 MHz, CDCl}_3\text{): }\delta & =14.1, 20.8, 22.7, 25.7, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 37.8, 119.9, 129.4, 135.0, 173.0 \text{ some peaks were overlapped.}
\end{align*}
\]

*N**-(2-Chlorophenyl) stearamide (3c)

\[
\begin{align*}
\text{White solid; mp: 68-70}^\circ\text{C; }^1\text{H NMR (250 MHz, CDCl}_3\text{): }\delta & = 0.87 (3\text{H, t, } J=6.30 \text{ Hz), 1.25} \\
& (28\text{H, m), 1.62-1.73 (2H, m), 2.3 (2H, t, } J=7.42 \text{ Hz), 6.98-7.04 (1\text{H, m), 7.20-7.35 (2H, m), 7.68 (1\text{H, s), 8.37 (1\text{H, d, } J=8.05 \text{ Hz); }^13\text{C NMR (62.9MHz, CDCl}_3\text{): }\delta & =14.1, 22.7, 24.7, 24.9, 25.5, 27.9, 29.1, 29.2, 29.3, 29.4, 29.4, 29.5, 29.5, 29.6, 29.7, 31.9, 37.9, 121.8, 122.7, 124.5, 127.6, 128.9, 134.5, 171.6.}
\end{align*}
\]

*N**-(3-Chlorophenyl) stearamide (3d)
White solid; mp: 51-53 °C; 1H NMR (250 MHz, CDCl₃): δ= 0.87 (3H, t, J=6.30 Hz), 1.25 (28H, m), 1.62-1.73 (2H, m), 2.3 (2H, t, J=7.42 Hz), 7.04 (1H, m), 7.22-7.28 (2H, m), 7.37 (1H, d, J=8.05 Hz), 7.64 (1H, s); ¹³C NMR (62.9 MHz, CDCl₃): δ= 14.1, 22.7, 25.6, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 37.7, 117.9, 120.1, 124.2, 129.8, 134.5, 139.2, 172.1 some peaks were overlapped.

**N-(4-Clorophenyl) stearamide (3e)**

![N-(4-Clorophenyl) stearamide (3e)](image)

White solid; mp: 56-58 °C; ¹H NMR (250 MHz, CDCl₃): δ= 0.86 (3H, t, J=6.86 Hz), 1.25 (28H, m), 1.47 (2H, m), 2.18 (2H, t, J=7.40 Hz), 7.24 (1H, d, J=8.83 Hz), 7.38 (1H, s), 7.45 (1H, d, J=8.89 Hz); ¹³C NMR (62.9 MHz, CDCl₃): δ= 14.1, 22.7, 25.5, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9, 37.7, 120.9, 128.9, 136.6, 173.1 some peaks were overlapped.

**N-(4-(4-Aminophenoxy) phenyl) stearamide (3f)**

![N-(4-(4-Aminophenoxy) phenyl) stearamide (3f)](image)

Yellow solid; mp: 116-118 °C; ¹H NMR (250 MHz, DMSO-d₆): δ= 0.82 (3H, t, J=6.75 Hz), 1.20 28H, m), 1.46-1.53 (2H, m), 2.3 (2H, t, J=7.20 Hz), 5.10 (1H, s), 6.56 (2H, d, J=7.73 Hz), 6.69 (2H, d, J=7.67 Hz), 6.77 (2H, d, J=7.98 Hz), 7.47 (2H, d, J=8.81 Hz), 9.74 (2H, s); ¹³C NMR (62.9 MHz, CDCl₃): δ = 14.1, 22.7, 24.9, 25.4, 29.2, 29.4, 29.5, 29.7, 31.9, 34.4, 37.5, 103.3, 104.2, 141.5, 149.2, 156.0, 172.5 some peaks were overlapped.
N-(6-Aminopyridin-2-yl) stearamide (3g)

![Chemical Structure of N-(6-Aminopyridin-2-yl) stearamide (3g)]

White solid; mp=70.5-72 °C; \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.62\) (3H, t, \(J = 6.00\) Hz), 0.99 (28 H, m), 1.35-1.44 (2H, m), 2.09 (2H, t, \(J = 7.32\) Hz), 4.36 (2H, s), 5.96 (2H, d, \(J = 7.92\) Hz), 7.13-7.32 (1H, m), 8.94 (1H, s); \(^13\)C NMR (62.9 MHz, CDCl\(_3\)): \(\delta = 14.1, 22.7, 25.4, 27.9, 29.3, 31.9, 34.7, 37.5, 140.6, 149.8, 156.8, 172.2\) some peaks were overlapped; IR cm\(^{-1}\): (KBr) 1667, 2912, 3310.60, 3495.20; MS: m/z (%)= 375 (0.10) [M\(^+\)]; Anal. Calcd for molecular formula C\(_{23}\)H\(_{41}\)N\(_3\)O: C, 73.55; H, 11.00%; found: C, 73.46; H, 10.97%.

1-(Piperidin-1-yl) octadeca-1-one (3h)

![Chemical Structure of 1-(Piperidin-1-yl) octadeca-1-one (3h)]

Viscose liquid; \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.86\) (3H, t, \(J = 6.03\) Hz), 1.24 (28 H, m), 1.55-1.60 (8 H, m), 2.31 (2H, t, \(J = 7.14\) Hz), 3.46 (4H, m); \(^13\)C NMR (62.9 MHz, CDCl\(_3\)): \(\delta = 14.1, 22.7, 24.5, 24.8, 25.5, 26.1, 29.1, 29.3, 29.4, 29.5, 29.7, 31.9, 33.4, 33.9, 171.5\) some peaks were overlapped; IR cm\(^{-1}\): (KBr) 1644.70, 2923.40, 3456; MS: m/z (%)= 351 (0.90) [M\(^+\)]; Anal. Calcd for molecular formula C\(_{23}\)H\(_{45}\)NO: C, 78.57; H, 12.90%; found: C, 78.69; H, 12.84%.

1-Morpholineoctadeca-1-one (3i)
White solid; mp=42-44 °C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 0.84 (3H, t, $J$=6.17 Hz), 1.22 (28 H, m), 1.57-1.62 (2H, m), 2.29 (2H, t, $J$=7.36 Hz), 3.44 (4H, m), 3.62-3.64 (4H, m); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 14.1, 22.7, 24.8, 25.3, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 29.9, 31.9, 33.1, 34.0, 41.8, 46.1, 66.8, 172.1 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1628, 2922, 3457; MS: m/z (%)= 353 (0.80) [M$^+$]; Anal. Calcd for molecular formula C$_{22}$H$_{43}$NO$_2$: C, 74.73; H, 12.26%; found: C, 74.68; H, 12.20%.

$N$-(3-Morpholinopropyl) stearamide (3j)

White solid; mp=59-61 °C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 0.85 (3H, t, $J$=6.39 Hz), 1.22 (28H, m), 1.59-1.68 (4H, m), 2.14 (2H, t, $J$=7.16 Hz), 2.42 (6H, m), 3.33 (2H, t, $J$=6.80 Hz), 3.67-3.69 (4H, m), 6.29 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 14.1, 22.6, 24.9, 25.2, 25.9, 29.3, 29.4, 29.5, 29.7, 31.9, 34.8, 36.9, 38.9, 53.5, 57.5, 66.7, 173.1 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1638, 2923, 3331; MS: m/z (%)= 411 (2.4) [M$^+$+1]; Anal. Calcd for molecular formula C$_{25}$H$_{50}$N$_2$O$_2$: C, 73.12; H, 12.27%; found: C, 73.07; H, 12.21%.

$N$-Dodecy stearamide (3k)

S7
Brown solid; mp=90-91°C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$= 0.63 (6H, t, $J$=6.99 Hz), 0.99 (46H, m), 1.22-1.32 (4H, m), 1.93 (2H, t, $J$=7.35 Hz), 2.60 (2H, t, $J$=7.48 Hz), 5.40 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 14.1, 22.7, 24.7, 25.8, 26.9, 29.1, 29.3, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 31.9, 34.1, 36.9, 39.5, 173.4 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1633, 2912, 3320; MS: m/z (%)= 451 (5.8) [M$^+$]; Anal. Calcd for molecular formula C$_{30}$H$_{61}$NO: C, 79.75; H, 13.61%; found: C, 79.70; H, 13.58%.

$N$-Hexadecyl searamide (3l)

Brown solid; mp=98-100°C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$= 0.63 (6H, t, $J$=6.99 Hz), 1.23 (56H, m), 1.37 (4H, m), 2.07 (2H, t, $J$=7.35 Hz), 2.99 (2H, t, $J$=7.48 Hz), 5.32 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 14.1, 22.7, 24.7, 25.8, 26.9, 28.1, 29.3, 29.4, 29.5, 29.7, 31.9, 33.9, 39.5, 173.4 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1638, 2912, 3331; MS: m/z (%)= 506 (3) [M$^+$-1]; Anal. Calcd for molecular formula C$_{34}$H$_{69}$NO: C, 80.40; H, 13.69%; found: C, 80.36; H, 13.57%.

$N$-Phenyl octanamide (4a)

White solid; mp=82-84°C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$= 0.88 (3H, t, $J$=6.46 Hz), 1.26 (10H, m), 2.24 (2H, t, $J$=7.46 Hz), 7.15 (1H, m), 7.32 (1H, s), 7.43-7.52 (2H, m), 7.63
(2H, d, J=8.21 Hz); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 14.0, 22.6, 24.9, 29.1, 31.6, 34.4, 119.8, 124.1, 128.9, 138.5, 173.3 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1655, 2917, 3337; MS: m/z (%)= 219 (12) [M$^+$]; Anal. Calcd for molecular formula C$_{14}$H$_{21}$NO: C, 76.67; H, 9.65%; found: C, 76.61, H, 9.53%.

$\text{N-Phenyl dodecanamide (4b)}$

\[
\text{H} \quad \text{O} \quad \text{N}
\]

White solid; mp=93-86°C; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$= 0.71 (3H, t, J=6.07 Hz), 0.95 (18H, m), 1.99 (2H, t, J=7.48 Hz), 7.07 (1H, m), 7.36 (1H, s), 7.46-7.60 (2H, m), 7.72 (2H, d, J=8.40 Hz); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 13.8, 22.5, 24.8, 28.7, 29.0, 29.5, 29.8, 31.8, 36.1, 173.4 some peaks were overlapped; IR cm$^{-1}$: (KBr) 1656, 2912, 3331; MS: m/z (%)= 275 (1.9) [M$^+$]; Anal. Calcd for molecular formula C$_{18}$H$_{29}$NO: C, 78.49; H, 10.61%; found: C, 78.40, H, 10.54%.

$\text{N-Phenyl benzamide (6a)}$

\[
\text{H} \quad \text{O} \quad \text{N}
\]

White solid; mp=162-164°C (lit.$^7$ 162-163°C); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 7.33-7.43 (3H, m), 7.49-7.54 (3H, m), 7.65 (2H, d, J=8.17 Hz), 7.85 (2H, d, J=8.30 Hz), 7.87 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$= 120.3, 124.6, 127.1, 128.7, 129.1, 131.8, 134.9, 137.9, 165.9 some peaks were overlapped.

$\text{4-Methyl-N-Phenyl benzamide (6b)}$

\[
\text{H} \quad \text{O} \quad \text{N}
\]
White solid; mp=155-157°C (lit. 149-150°C); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 2.43$ (s, 3H), 7.22 (2H, d, $J=8.17$ Hz), 7.35-7.52 (5H, m), 7.78 (2H, d, $J=8.30$ Hz), 7.93 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 23.2, 120.4, 127.6, 128.9, 129.5, 131.5, 134.5, 135.9, 134.0, 165.9$ some peaks were overlapped.

3-Chloro-N-Phenyl benzamide (6c)$^4$

White solid; mp=186-188°C (lit. 187-188°C); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.11-7.20$ (2H, m), 7.24-7.35 (2H, m), 7.39 (1H, m), 7.53 (1H, d, $J=8.01$ Hz), 7.65 (2H, d, $J=8.40$ Hz), 7.87 (1H, d, $J=8.14$Hz), 7.94 (1H, s), 8.06 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 121.4, 124.4, 125.8, 127.5, 129.0, 130.2, 132.5, 134.1, 135.9, 135.9, 164.6$ some peaks were overlapped.

4-Chloro-N-Phenyl benzamide (6d)$^5$

White solid; mp=201-202°C (lit. 195-196°C); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.34$ (2H, d, $J=8.20$ Hz), 7.42-7.59 (5H, m), 7.82 (2H, d, $J=8.14$ Hz), 7.95 (1H, s); $^{13}$C NMR
(62.9 MHz, CDCl$_3$): δ= 121.6, 124.3, 128.9, 129.2, 129.2, 132.1, 135.9, 137.7, 165.3 some peaks were overlapped.

**2-Chloro-N-Phenyl benzamide (6e)**

![Structure of 2-Chloro-N-Phenyl benzamide (6e)]

White solid; mp=184-186°C (lit.$^6$ 180-182 °C); $^1$H NMR (250 MHz, CDCl$_3$): δ = 7.13-7.19 (1H, m), 7.32-7.39 (3H, m), 7.56 (2H, m), 7.73 (2H, d, $J$=8.32 Hz), 7.85 (1H, d, $J$=8.45 Hz), 8.24 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 120.9, 124.4, 127.1, 128.9, 129.0, 132.6, 132.7, 134.1, 136.3, 165.8 some peaks were overlapped.

**4-Nitro-N-Phenyl benzamide (6f)**

![Structure of 4-Nitro-N-Phenyl benzamide (6f)]

Pale yellow solid; mp=198-199°C (lit.$^8$ 217-218 °C); $^1$H NMR (250 MHz, CDCl$_3$): δ= 7.55 (2H, d, $J$=8.23 Hz), 7.58-7.65 (5H, m), 7.74 (2H, d, $J$=8.14 Hz), 7.90 (1H, s); $^{13}$C NMR (62.9 MHz, CDCl$_3$): δ= 121.3, 121.7, 124.5, 128.6, 129.1, 135.8, 140.2, 151.7, 164.9 some peaks were overlapped.
Figure 1: $^1$H-NMR, and $^{13}$C-NMR of N-Phenyl stearamide (3a)
Figure 2: $^1$H-NMR, $^{13}$C-NMR of N-P-Tolyl sarcamide (3b)
Figure 3: $^1$H-NMR, $^{13}$C-NMR of N-(2-Chlorophenyl) stearamide

$N-P$-Tolyl stearamide (3c)
Figure 4: $^1$H-NMR, $^{13}$C-NMR, IR and Mass Spectroscopy of $N$-(3-Chlorophenyl) stearamide (3d)
Figure 5: $^1$H-NMR, and $^{13}$C-NMR Spectroscopy of N-(4-Chlorophenyl) stearamide (3e)
Figure 6: $^1$H-NMR, and $^{13}$C-NMR, Spectroscopy of $N$-(4-(4-Aminophenoxy) phenyl) stearamide (3f)
Figure 7: $^1$H-NMR, and $^{13}$C-NMR, Spectroscopy of $N$-(6-Aminopyridin-2-yl) stearamide (3g)
Figure 8: $^1$H-NMR and $^{13}$C-NMR of 1-(Piperidin-1-yl) octadeca-1-one (3h)
Figure 9: $^1$H-NMR, and $^{13}$C-NMR, Spectroscopy of N-(3-morpholino propyl) stearamide (3j)
Figure 10: $^1$H-NMR, and $^{13}$C-NMR, Spectroscopy of N-Dodecy srearamide (3k)
Figure 11: $^1$H-NMR, and $^{13}$C-NMR, Spectroscopy N-Hexadecyl srearamide (3l)
Figure 12. XRD pattern of nano sulfated-TiO$_2$

![XRD pattern of nano sulfated-TiO$_2$]

Figure 13. SEM image of nano sulfated-TiO$_2$

![SEM image of nano sulfated-TiO$_2$]
Figure 14. TEM image of nano sulfated -TiO$_2$

Figure 15. FT-IR spectrum of nano sulfated-TiO$_2$
Figure 16. Thermograms revealing the thermal stability of A) Pure TiO$_2$ and B) sulfated-TiO$_2$.

Figure 17. Nitrogen adsorption isotherms of A) Pure TiO$_2$ and B) sulfated-TiO$_2$. 

References:


