**Supporting information for**

# Chemoselective Nitrilation of Dimethyl Adipate with Ammonia over Carbon Encapsulated $WO_x$ Catalysts under Continuous Flow Conditions

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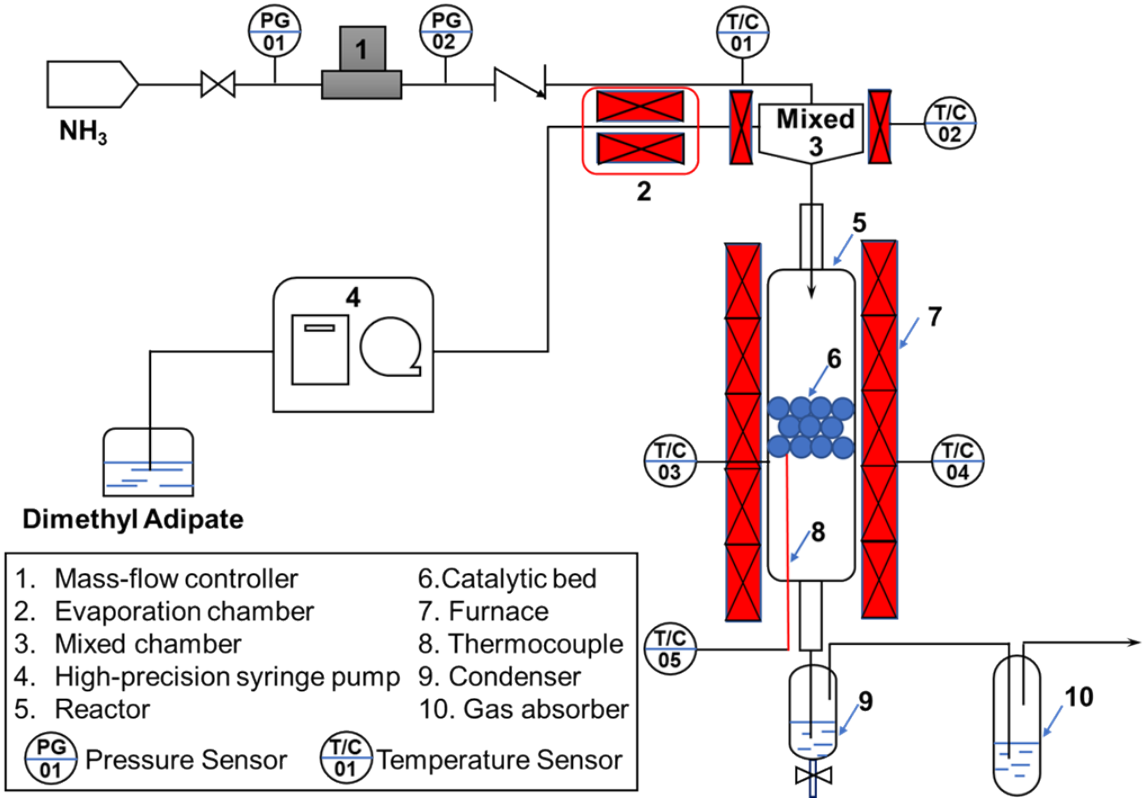
# 1. Experimental

## *Continuous-Flow Setup*

The catalysts evaluation experiments in dimethyl adipate nitrification have been performed on a homemade continuous-flow fixed bed stainless steel microreactor (Scheme S1), provided by controlled flow rates of reactants and connected vertical downstream with condensers using ethanol as absorbent in order to collect heavy products including adiponitrile, methyl 5-cyanopentanoate, dimethyl adipate and other by-products together. The microreactor consists of three main connected capacities: Upstream side is the evaporation chamber where liquid dimethyl adipate is fed into the heated volume by a high-precision syringe pump and blown downwards by a controlled nitrogen flow (mass flow meter, range 2-10 mL·min$^{-1}$), and the heating provided to the evaporation chamber and the flow parameters ensure full evaporation of the ester (>260 °C). Midstream core is a stainless steel tubular reactor (inner diameter = 6 mm, length = 320 mm), with the constant temperature zone contained catalytic bed of 1.50 ml volume, the tubular reactor is disposed inside a vertical furnace, ensuring a control over the catalytic bed's temperature (stability within 1 °C at 375 °C), the temperature was controlled by a K-type thermocouple placed in the middle of the catalyst bed. Ammonia flow is controlled (mass flow meter, range 2-10 mL·min$^{-1}$) and premixed with vaporized dimethyl adipate, delivered downstream at the top of the catalytic bed, ensuring that the reactants are thoroughly mixed before contacting the catalyst bed. The evaporation chamber, furnace and other pipeline are wholly put inside an oven maintaining temperature at 220 °C for preventing possible dimethyl adipate or products condensation. Downstream is condensers where the products at the reactor outlet dissolved in ethanol, which was collected with around a 1h interval and then mixed with biphenyl used as internal standard and analyzed by GC with FID detector and a DB-FFAP capillary column (Agilent, 30 m×0.32 mm×1.00 μm). The time of steam for is 8 h.




Scheme S1. Continuous-flow fixed bed setup for dimethyl adipate nitrification.

# 2. Supplementary figures and tables

**Table S1. Textural properties.**

| Entry | Samples | $S_{BET}$[a] ($m^2 g^{-1}$) | $S_{Exter}$[b] ($m^2 g^{-1}$) | $S_{micro}$[b] ($m^2 g^{-1}$) | $V_{micro}$[b] ($cm^3 g^{-1}$) | $V_p$[c] ($cm^3 g^{-1}$) | $D_p$[d] (nm) | $\rho_W$ (atoms·nm$^{-2}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | $WO_x$@C/C-400-0.25 | 58 | 51 | 7 | 0.003 | 0.14 | 9.63 | 17.79 |
| 2 | $WO_x$@C/C-500-0.25 | 121 | 58 | 63 | 0.027 | 0.18 | 5.88 | 8.84 |
| 3 | $WO_x$@C/C-600-0.25 | 320 | 116 | 204 | 0.085 | 0.31 | 3.91 | 3.43 |
| 4 | $WO_x$@C/C-700-0.25 | 366 | 91 | 275 | 0.112 | 0.30 | 3.26 | 3.07 |
| 5 | $WO_x$@C/C-800-0.25 | 358 | 86 | 272 | 0.111 | 0.27 | 3.05 | 3.44 |
| 6 | activated carbon | 813 | 396 | 416 | 0.208 | 0.65 | 3.2 | 0 |
| 7 | $SiW_{12}$@PIL/C | 51 | 47 | 3 | 0.001 | - | - | - |
| 8 | $WO_x$@C/C-600-0.25-C1 | 209 | 81 | 128 | 0.053 | 0.16 | 3.5 | 5.40 |
| 9 | $WO_x$@C/C-600-0.25-C2 | 282 | 96 | 185 | 0.077 | 0.27 | 3.80 | 4.01 |

[a] BET surface area.

[b] Microporous and external surface area, microporous volume estimated by the DFT method.

[c] Total pore volume.

[d] Average pore size.

[e] The W apparent density is calculated by the following equation: $\rho_W = \frac{n_W N_A}{m_{cat} S_{BET}}$

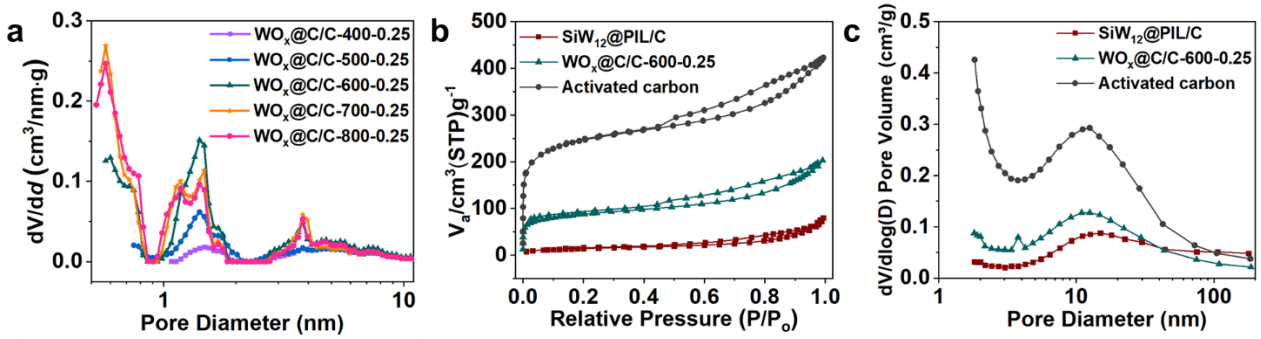



Figure S1. (a) the corresponding pore size distribution curves of $WO_x$@C/C-n-0.25 (n=400, 500, 600, 700, 800); (b) $N_2$ sorption isotherms and the (c) corresponding pore size distribution curves of $SiW_{12}$@PIL/C, $WO_x$@C/C-600-0.25 and activated carbon.

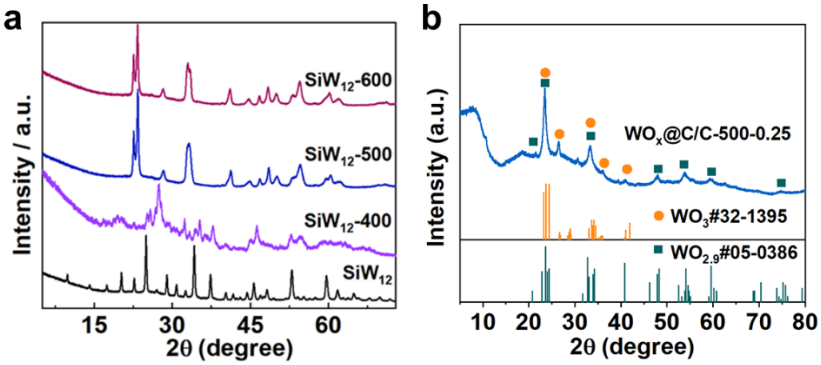



Figure S2. XRD spectra for a) tungstosilicic acid calcined at 400°C, 500°C, 600 °C under $N_2$ atmosphere; b) $WO_x$@C/C-500-0.25.

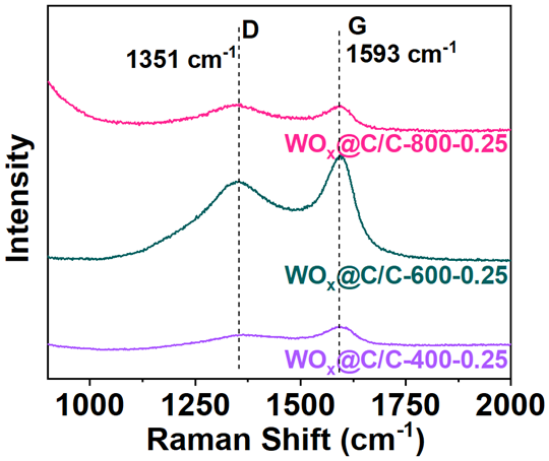



Figure S3. Characteristic D band and G band in Raman spectrum of $WO_x$@C/C-n-0.25 (n=400, 600, 800)

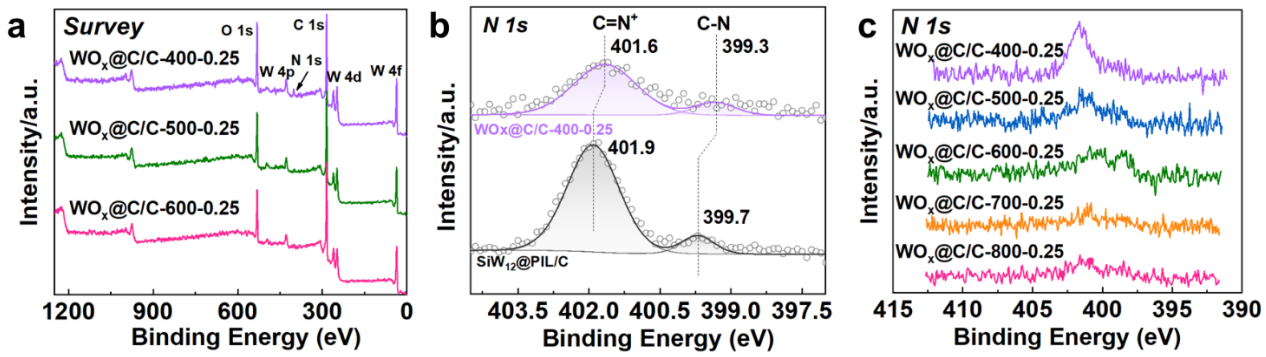



Figure S4 (a) XPS survey (b) Fitted N 1s XPS spectra of $SiW_{12}$@PIL/C and $WO_x$@C/C-400-0.25 (c) N 1s XPS spectra of $WO_x$@C/C-n-0.25 (n= 400, 500, 600, 700, 800)

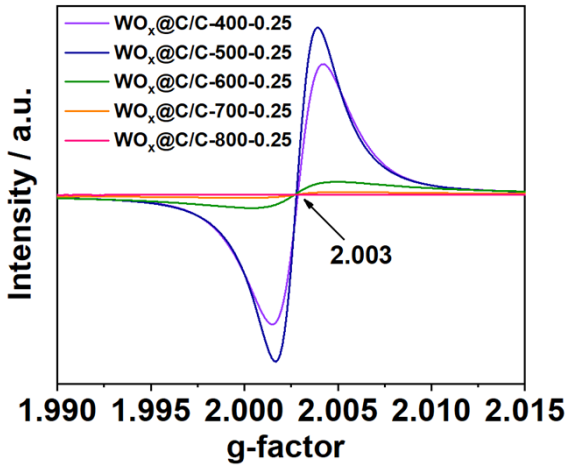



Figure S5 Room temperature EPR spectra of $WO_x$@C/C-n-0.25 (n = 400, 500, 600, 700, and 800)

**Table S2. Absolute Spins reports of EPR.**

| Samples | Spins ($\times 10^{17}$) | The test weight of sample (mg) |
|---|---|---|
| $WO_x$@C/C-400-0.25 | 1.430 | 10 |
| $WO_x$@C/C-500-0.25 | 1.328 | 10 |
| $WO_x$@C/C-600-0.25 | 1.215 | 10 |
| $WO_x$@C/C-700-0.25 | 0.930 | 10 |
| $WO_x$@C/C-800-0.25 | 0 | 10 |

**Table S3. Cyanation of Dimethyl Adipate over $WO_x$@C/C-n-0.25 (n = 400, 500, 600, 700, 800) [a]**

| Sample | Conversion | $STY_{ADN}$ mmol/($g_{cat}$ · h) | $STY_{MCP}$ mmol/($g_{cat}$ · h) | TON $mol_{ADN}/(mol_{WOx}·h)$ | TON $mol_{MCP}/(mol_{WOx}·h)$ | TON total | Selectivity |
|---|---|---|---|---|---|---|---|
| $SiW_{12}$@PIL/C | 33.55% | 0.22 | 0.09 | 0.17 | 0.07 | 0.23 | 34.88% |
| $WO_x$@C/C-400-0.25 | 38.59% | 0.46 | 0.28 | 0.27 | 0.16 | 0.43 | 51.60% |
| $WO_x$@C/C-500-0.25 | 38.73% | 0.47 | 0.45 | 0.26 | 0.26 | 0.52 | 67.54% |
| $WO_x$@C/C-600-0.25 | 50.63% | 0.93 | 0.94 | 0.51 | 0.52 | 1.03 | 92.10% |
| $WO_x$@C/C-700-0.25 | 50.54% | 0.78 | 0.83 | 0.42 | 0.45 | 0.86 | 86.67% |
| $WO_x$@C/C-800-0.25 | 49.96% | 0.68 | 0.91 | 0.33 | 0.44 | 0.77 | 77.61% |

[a]Reaction conditions: 375 °C, feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10 mL/min, WHSV 0.64 $h^{-1}$, TOS 8 h.

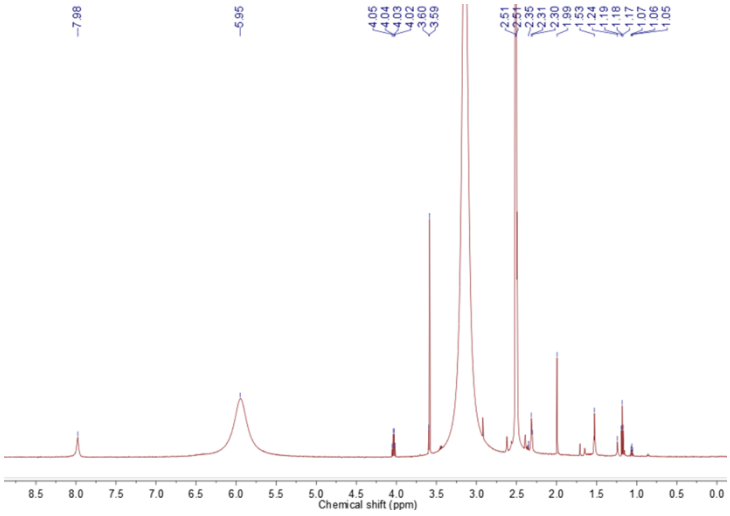



Figure S6. $^1H$ NMR spectrum of the solid mixture

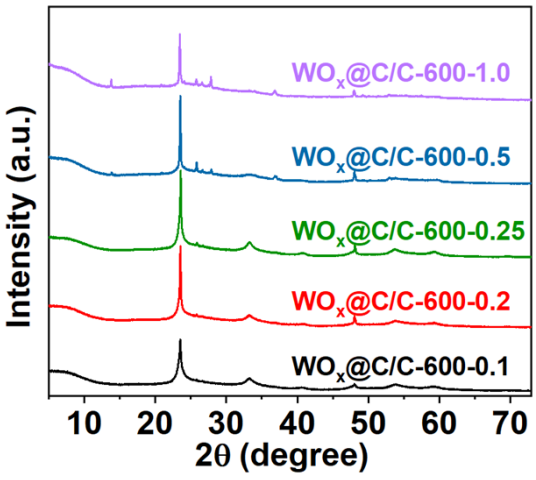



Figure S7. XRD spectra for $WO_x$@C/C-600-m (m = 0.1, 0.2, 0.25, 0.5, 1.0), showed similar main composition of $WO_{2.83}$

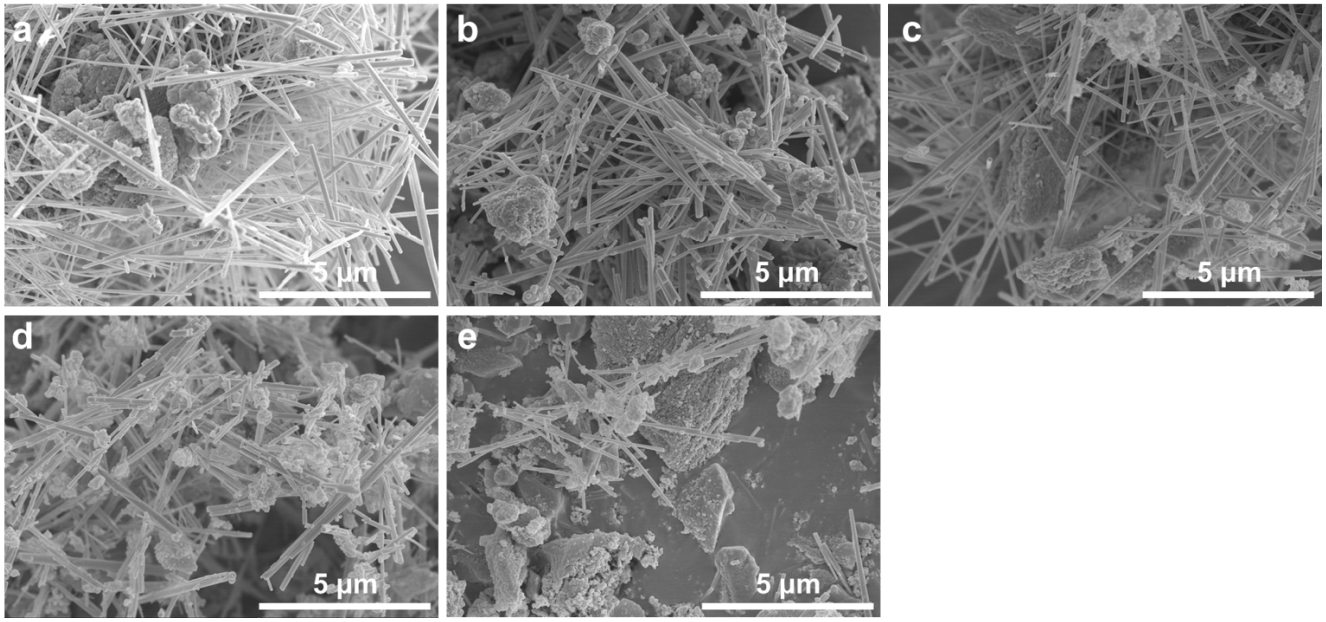



Figure S8. SEM images for a) $WO_x$@C/C-600-0.1, b) $WO_x$@C/C-600-0.2, c) $WO_x$@C/C-600-0.25, d) $WO_x$@C/C-600-0.5, e) $WO_x$@C/C-600-1.0, showed the better physical dispersion of $WO_x$ at the carbon support with increased dosage of active carbon.

**Table S4. Cyanation of Dimethyl Adipate over $WO_x$@C/C-600-m catalysts with different dosage of activated carbon.**

| Sample | Conversion | $STY_{ADN}$ $mmol/(g_{cat} \cdot h)$ | $STY_{MCP}$ $mmol/(g_{cat} \cdot h)$ | TON $mol_{ADN}/(mol_{WOx} \cdot h)$ | TON $mol_{MCP}/(mol_{WOx} \cdot h)$ | TON total | Selectivity |
|---|---|---|---|---|---|---|---|
| $WO_x$@C/C-600-0.1 | 16.41% | 0.12 | 0.38 | 0.05 | 0.15 | 0.20 | 61.34% |
| $WO_x$@C/C-600-0.2 | 44.46% | 0.64 | 0.94 | 0.31 | 0.46 | 0.76 | 87.72% |
| $WO_x$@C/C-600-0.25 | 50.63% | 0.93 | 0.94 | 0.51 | 0.52 | 1.03 | 92.10% |
| $WO_x$@C/C-600-0.5 | 66.24% | 0.86 | 0.54 | 0.65 | 0.41 | 1.07 | 82.82% |
| $WO_x$@C/C-600-1.0 | 82.73% | 0.67 | 0.15 | 0.83 | 0.19 | 1.02 | 70.97% |
| Reaction conditions: 375 °C, feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10mL/min, TOS 8 h. | | | | | | | |

**Table S5. Effect of WHSV of Dimethyl Adipate over $WO_x$@C/C-600-0.5**

| Sample | WHSV $(h^{-1})$ | Conversion | $STY_{ADN}$ $mmol/(g_{cat} \cdot h)$ | $STY_{MCP}$ $mmol/(g_{cat} \cdot h)$ | TON $mol_{ADN}/(mol_{WOx} \cdot h)$ | TON $Mol_{MCP}/(mol_{WOx} \cdot h)$ | TON total | Selectivity |
|---|---|---|---|---|---|---|---|---|
| $WO_x$@C/C-600-0.5 | 0.23 | 83.92% | 0.41 | 0.23 | 0.32 | 0.18 | 0.50 | 77.35% |
| | 0.44 | 66.24% | 0.84 | 0.53 | 0.65 | 0.41 | 1.07 | 82.82% |
| | 0.89 | 50.66% | 1.00 | 1.42 | 0.77 | 1.09 | 1.86 | 87.35% |
| | 1.77 | 35.07% | 1.08 | 2.09 | 0.83 | 1.61 | 2.43 | 80.52% |
| Reaction conditions: 375 °C, Feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10mL/min, TOS 8 h. | | | | | | | | |

**Table S6. Effect of Reaction Temperature for Cyanation of Dimethyl Adipate over $WO_x$@C/C-600-m (m=0.25, 0.5, 1.0)**

| Sample | Reaction temperature (°C) | Conversion | $STY_{ADN}$ mmol/($g_{cat}$ · h) | $STY_{MCP}$ mmol/($g_{cat}$ · h) | TON $mol_{ADN}$/($mol_{WOx}$·h) | TON $mol_{MCP}$/($mol_{WOx}$·h) | TON total | Selectivity |
|---|---|---|---|---|---|---|---|---|
| $WO_x$@C/C-600-0.25 | 350 | 49.71% | 0.65 | 0.93 | 0.35 | 0.50 | 0.84 | 80.24% |
| | 375 | 50.63% | 0.93 | 0.94 | 0.51 | 0.52 | 1.03 | 92.10% |
| | 385 | 57.91% | 0.89 | 0.77 | 0.48 | 0.41 | 0.88 | 83.20% |
| $WO_x$@C/C-600-0.5 | 350 | 61.99% | 0.60 | 0.50 | 0.47 | 0.39 | 0.86 | 67.70% |
| | 375 | 66.24% | 0.86 | 0.54 | 0.65 | 0.41 | 1.07 | 82.82% |
| | 385 | 72.23% | 1.23 | 0.73 | 0.95 | 0.57 | 1.52 | 78.23% |
| $WO_x$@C/C-600-1.0 | 350 | 82.04% | 0.59 | 0.23 | 0.73 | 0.29 | 1.02 | 60.66% |
| | 375 | 82.73% | 0.67 | 0.15 | 0.83 | 0.19 | 1.02 | 70.97% |
| | 385 | 81.55% | 0.78 | 0.16 | 0.98 | 0.20 | 1.18 | 65.50% |
| Reaction conditions: Feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10mL/min, TOS 8 h. | | | | | | | | |

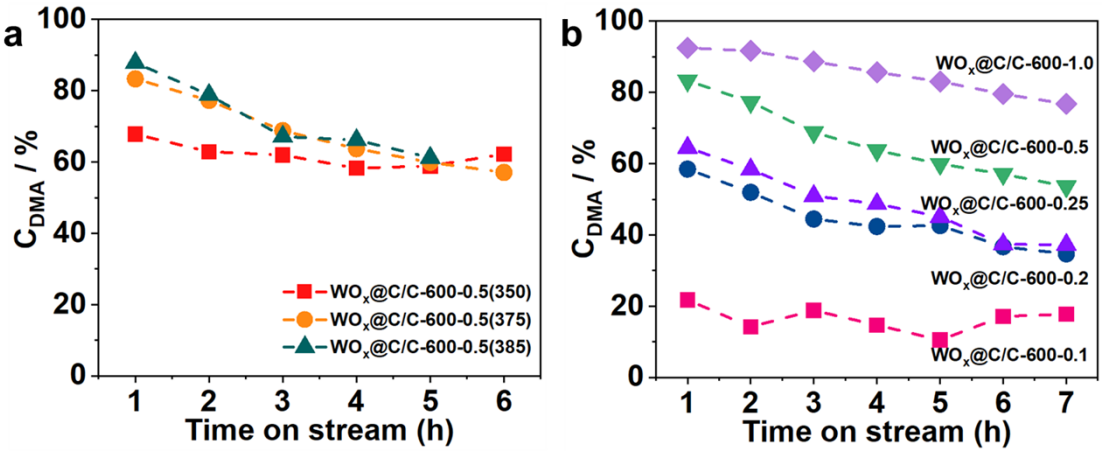



Figure S9. The catalyst durability of a) $WO_x$@C/C-600-0.5; reaction temperature: 350 °C, 375 °C, 385 °C, WHSV 0.44 $h^{-1}$, b) $WO_x$@C/C-600-m (m = 0.1, 0.2, 0.25, 0.5, 1.0), 375°C, common reaction conditions: feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10 mL/min.

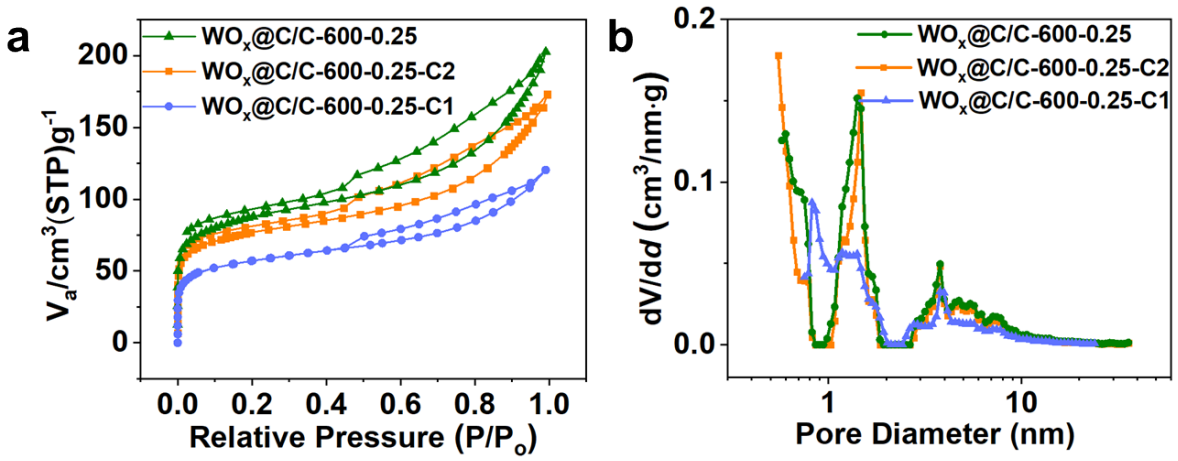



Figure S10. (a) $N_2$ sorption isotherms and the (b) corresponding pore size distribution curves of $WO_x$@C/C-600-0.25 and $WO_x$@C/C-600-0.25-C1, $WO_x$@C/C-600-0.25-C2.

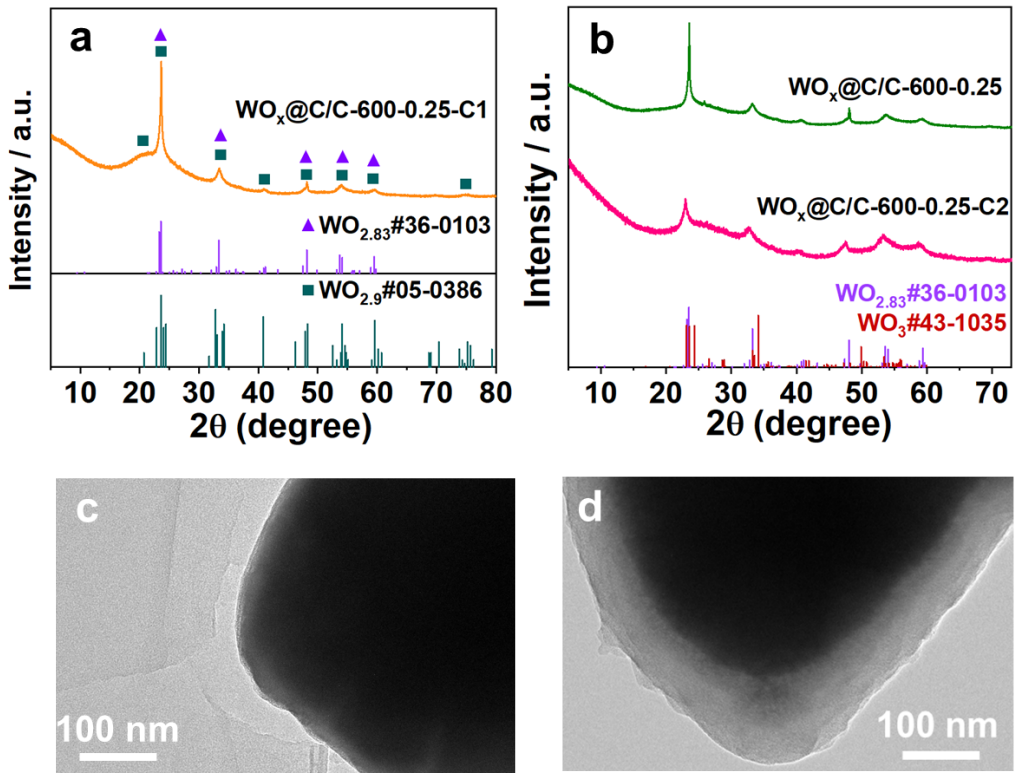



Figure S11. XRD spectra for (a) $WO_x$@C/C-600-0.25 and $WO_x$@C/C-600-0.25-C1, (b) $WO_x$@C/C-600-0.25-C2. TEM images of (c)$WO_x$@C/C-600-0.25-C1 and (d)WOx@C/C-600-0.25-C2, which showed that $WO_x$ is coated with thick carbon layer (~100 nm).

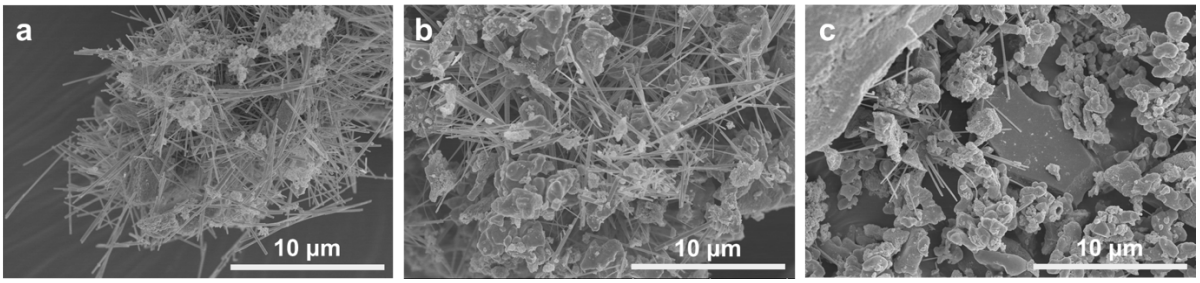



Figure S12. SEM images for a) for $WO_x$@C/C-600-0.25, nanowires structure of $WO_{2.83}$. b) for $WO_x$@C/C-600-0.25-C1, mixed $WO_{2.83}$ nanowires and $WO_{2.9}$ blocky structures and c) $WO_x$@C/C-600-0.25-C2, agglomerate blocky structure of $WO_3$.

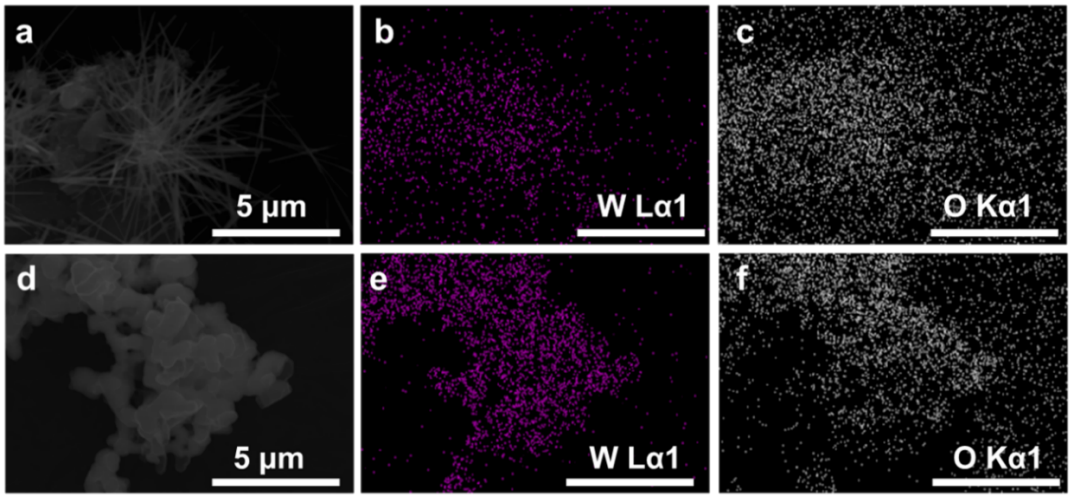



Figure S13. EDS images for a) nanowires structure of $WO_x$, b) and c) the distribution of W and O in $WO_x$@C/C-600-0.25; d) agglomerate blocky structure of $WO_x$, e) and f) the distribution of W and O in $WO_x$@C/C-600-0.25-C2.

**Table S7. Cyanation of Dimethyl Adipate over $WO_x$@C/C-600-0.25, $WO_x$@C/C-600-0.25-C1 and $WO_x$@C/C-600-0.25-C2.** [a]

| Sample | Conversion | $STY_{ADN}$ mmol/($g_{cat}$ · h) | $STY_{MCP}$ mmol/($g_{cat}$ · h) | TON $mol_{ADN}/(mol_{WOx}·h)$ | TON $mol_{MCP}/(mol_{WOx}·h)$ | TON total | Selectivity |
|---|---|---|---|---|---|---|---|
| $WO_x$@C/C-600-0.25 | 50.63% | 0.93 | 0.94 | 0.51 | 0.52 | 1.03 | 92.10% |
| $WO_x$@C/C-600-0.25-C1 | 49.26% | 0.63 | 0.9 | 0.34 | 0.48 | 0.82 | 84.31% |
| $WO_x$@C/C-600-0.25-C2 | 29.99% | 0.29 | 0.31 | 0.16 | 0.16 | 0.32 | 50.95% |

[a]Reaction conditions: 375 °C, feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10 mL/min, WHSV 0.64 $h^{-1}$, TOS 8 h.

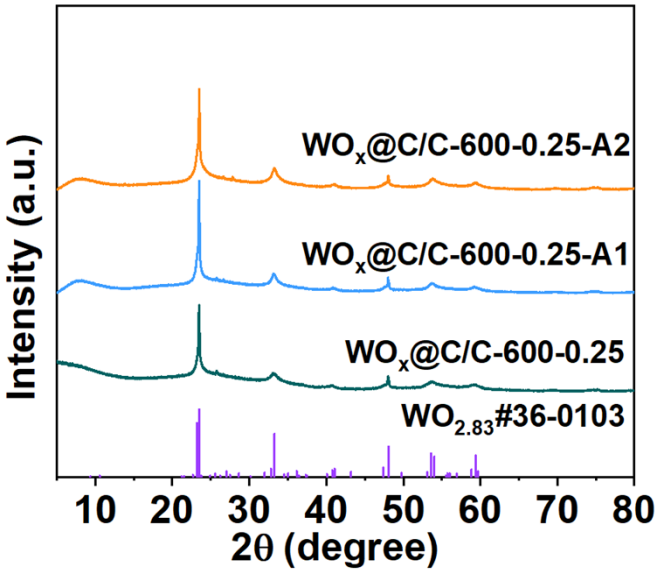



Figure S14. XRD spectra for (a) $WO_x$@C/C-600-0.25, $WO_x$@C/C-600-0.25-A1/A2

**Table S8. Cyanation of Dimethyl Adipate over $WO_x$@C/C-600-0.25, $WO_x$@C/C-600-0.25-A1 and $WO_x$@C/C-600-0.25-A2.** [a]

| Sample | Conversion | $STY_{ADN}$ mmol/($g_{cat}$ · h) | $STY_{MCP}$ mmol/($g_{cat}$ · h) | TON $mol_{ADN}/(mol_{WOx}·h)$ | TON $mol_{MCP}/(mol_{WOx}·h)$ | TON total | Selectivity |
|---|---|---|---|---|---|---|---|
| $WO_x$@C/C-600-0.25 | 50.63% | 0.93 | 0.94 | 0.51 | 0.52 | 1.03 | 92.10% |
| $WO_x$@C/C-600-0.25-A1 | 55.65% | 1.3 | 1.13 | 0.62 | 0.54 | 1.17 | 95.82% |
| $WO_x$@C/C-600-0.25-A2 | 65.33% | 1.6 | 1.35 | 0.68 | 0.57 | 1.26 | 95.26% |

[a]Reaction conditions: 375 °C, feed dimethyl adipate (DMA) 0.005 mL/min, $NH_3$ 10 mL/min, WHSV 0.64 $h^{-1}$, TOS 8 h.

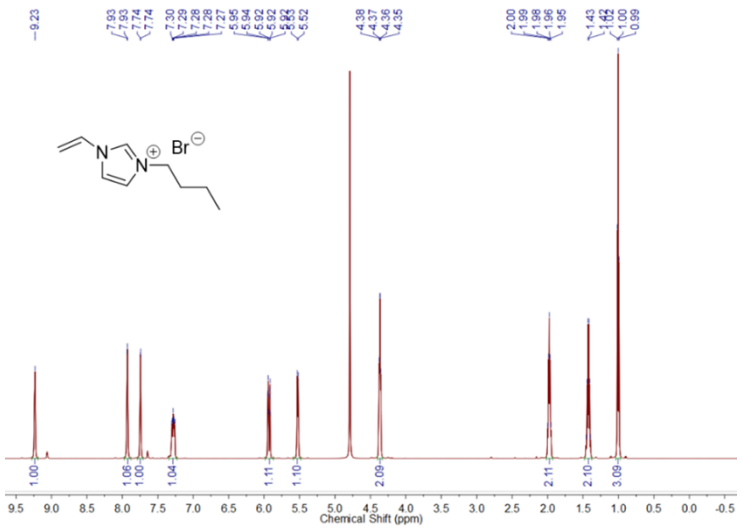



Figure S15. $^1$H NMR spectrum for [VBIM]Br