Electronic Supplementary Information for

Alkali α-MnO$_2$/Na$_x$MnO$_2$ collaboratively catalyzed ammoxidation-Pinner tandem reaction of aldehydes

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1. Additional Results

**Preparation of α-MnO$_2$.** α-MnO$_2$ was prepared according to the literature procedure (see below).[S1] A 100 mL aqueous solution containing 40 mmol KMnO$_4$ was added into another 100 mL aqueous solution containing 60 mmol Mn(NO$_3$)$_2$. After stirring at room temperature for 4 h, the resulting solid was collected by filtration, washed repeatedly with distilled water, and finally dried overnight in air at 60 °C and then calcined in air at 250 °C for 4 h.

**Preparation of β-MnO$_2$.** β-MnO$_2$ was prepared according to the literature procedure (see below).[S2] A 60 mL aqueous solution containing stoichiometric amount of MnSO$_4$ (18 mmol) and KMnO$_4$ (3 mmol) was loaded in a 100 mL Teflon-lined autoclave, which was sealed and maintained at 140 °C for 12 h. After naturally cooling to room temperature, the resulting solid was collected by centrifugation, washed repeatedly with distilled water, and finally dried overnight in air at 80 °C.

**Preparation of δ-MnO$_2$.** δ-MnO$_2$ was prepared according to the literature procedure (see below).[S3] An aqueous solution (A) was prepared by dissolving 0.04 mol of KMnO$_4$ and 1.2 mol of NaOH in 400 mL of water. Afterward, another aqueous solution (B) was prepared by dissolving 0.112 mol of MnCl$_2$·4H$_2$O in 400 mL of water. Solution B was added dropwise to solution A with vigorous stirring in an ice bath. The resulting precipitate was statically aged at room temperature for 1 day and then washed and dried at 90 °C.

**Preparation of OMS-2.** OMS-2 was prepared according to the literature
procedure (see below).\textsuperscript{[S4]} KMnO$_4$ (5.89 g) in water (100 mL) was added to a solution of MnSO$_4$·H$_2$O (8.8 g) in water (30 mL) and conc. HNO$_3$ (3 mL). The solution was refluxed at 100 °C for 24 h. Then, the dark brown solid was filtered off, washed with a large amount of water (ca. 3 L), and dried at 120 °C to afford 8.2 g of OMS-2.

**Preparation of Na$_x$MnO$_2$.** Na$_x$MnO$_2$ was prepared according to the literature procedure with some modification (see below).\textsuperscript{[S5]} A mixture of 10 mmol Na$_2$CO$_3$ and 30 mmol MnCO$_3$ was heated at 1000 °C for 15 h, followed by naturally cooling to room temperature.

\[\text{[S1]} \text{ E. Schleitzer (Ed.), Gmelin Handbook of Inorganic Chemistry 8th Edition} \]
\[\text{(Manganese), Verlag Chemie GmbH, Weinheim/Bergstrasse, 1973.}\]
\[\text{[S3]} \text{ O. Ghodbane, J.-L. Pascal, and F. Favier, } \textit{ACS Appl. Mater. Interfaces.} \textbf{2009}, \textit{1}, 1130.\]
Figure S1 XRD patterns of α-MnO$_2$. 

Figure S2 XRD patterns of β-MnO$_2$. 
Figure S3 XRD patterns of γ-MnO₂.

Figure S4 XRD patterns of δ-MnO₂.
Figure S5 XRD patterns of (a) fresh and (b) used $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C.
Figure S6 XRD patterns of Na$_x$MnO$_2$.

Figure S7 HRTEM image of $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C.
**Figure S8** XRD pattern of manganese oxide calcined at 500 °C with NaOH/Mn molar ratio of 1.2 and substituting NaMnO$_4$ for KMnO$_4$.

**Figure S9** TEM images of (a) fresh and (b) used $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C.
Figure S10 Catalytic conversion of furfural to methyl furan-2-carboximidate over different metal oxides. Reaction conditions: 0.5 mmol furfural, 0.1 g catalyst, 120 μL aq. NH$_3$ (3 equiv.), 5 mL MeOH, 0.5 MPa O$_2$, 30 °C, 12 h.

Table S1. Catalytic conversion of furfural at different temperatures.$^a$

<table>
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<th>Entry</th>
<th>T (°C)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
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<td></td>
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<td>2</td>
<td>3</td>
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<tr>
<td>1</td>
<td>30</td>
<td>&gt; 99</td>
<td>11</td>
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<tr>
<td>2</td>
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<td>3</td>
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<tr>
<td>3</td>
<td>120</td>
<td>&gt; 99</td>
<td>-</td>
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$^a$Reaction conditions: 0.5 mmol furfural, 0.1 g α-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C, 120 μL aq. NH$_3$ (3 equiv.), 5 mL MeOH, 0.5 MPa O$_2$, 12 h.
Table S2. ICP elemental analysis of $\alpha$-MnO$_2$/Na$_x$MnO$_2$.

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<th>Element</th>
<th>Weight%</th>
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<tr>
<td>Na</td>
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<tr>
<td>K</td>
<td>4.69</td>
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<tr>
<td>Mn</td>
<td>50.9</td>
<td>24.4</td>
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Table S3. EDS elemental analysis of $\alpha$-MnO$_2$/Na$_x$MnO$_2$.

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<th>Element</th>
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<td>K</td>
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<tr>
<td>Mn</td>
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<td>25.52</td>
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Table S4. ICP elemental analysis of manganese oxide prepared with KMnO$_4$ + KOH.

<table>
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<td>K</td>
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<tr>
<td>Mn</td>
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Table S5. ICP elemental analysis of manganese oxide prepared with NaMnO$_4$ + NaOH.

<table>
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<tr>
<td>Mn</td>
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<td>16.3</td>
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Scheme S1. Catalytic conversion of 5-bromofurfural over OMS-2.

Figure S11. α-MnO₂/NaₓMnO₂ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C oxidized synthesis of methyl furan-2-carboximidate from furfural. Reaction conditions: 0.5 mmol furfural, 120 μL aq. NH₃ (3 equiv.), 5 mL MeOH, 0.5 MPa N₂, 30 °C, 12 h. Note: The molar mass of α-MnO₂/NaₓMnO₂ was approximate to that of MnO₂.
**Figure S12.** XPS spectra of (a) fresh $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C, (b) $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C was treated with furfural and ammonia in MeOH at 30 °C under N$_2$ atmosphere for 48 h, (c) $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C in (b) was treated at 30 °C under O$_2$ atmosphere for 12 h.

**Figure S13.** EPR spectra of (a) fresh $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C, (b) $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C was treated with furfural and ammonia in MeOH at 30 °C under N$_2$ atmosphere for 48 h, (c) $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C in (b) was treated at 30 °C under O$_2$ atmosphere for 12 h.
Figure S14. Relationship of $\ln(C_0/C_t)$ and reaction time $t$ of 2-furonitrile conversion to methyl furan-2-carboximidate over $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 250 °C.

Figure S15. Relationship of $\ln(C_0/C_t)$ and reaction time $t$ of 2-furonitrile conversion to methyl furan-2-carboximidate over $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 400 °C.
Figure S16. Relationship of ln(C₀/Cₜ) and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO₂/NaₓMnO₂ with NaOH/Mn molar ratio of 1.2 calcined at 420 °C.

Figure S17. Relationship of ln(C₀/Cₜ) and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO₂/NaₓMnO₂ with NaOH/Mn molar ratio of 1.2 calcined at 450 °C.
**Figure S18.** Relationship of $\ln(C_0/C_t)$ and reaction time $t$ of 2-furonitrile conversion to methyl furan-2-carboximidate over $\alpha$-MnO$_2$/Na$_x$MnO$_2$ with NaOH/Mn molar ratio of 1.2 calcined at 500 °C.

**Figure S19.** Relationship of $\ln(C_0/C_t)$ and reaction time $t$ of 2-furonitrile conversion to methyl furan-2-carboximidate over Na$_x$MnO$_2$. 
2. GC, MS and NMR Traces

**Figure S20** GC spectrum of products from furfural (Figure 7 0.5 h in the main text).

MS: m/z (%): 95 (100) [M+], 64 (13), 44 (15), 39 (48), 32 (52)

**Figure S21** Mass spectrum of aldime.
Figure S22 GC spectrum of Table S1, entry 2.

MS: m/z (%): 111 (100) [M+], 95 (96), 44 (14), 39 (27), 32 (7)

Figure S23 Mass spectrum of 4.
**Figure S24** GC spectrum of Table 1, entry 3 in the main text.

MS: m/z (%): 93 (100) [M+], 64 (47), 38 (23)

**Figure S25** Mass spectrum of 2.

MS: m/z (%): 125 (41) [M+], 94 (100), 81 (41), 67 (57), 39 (41)

**Figure S26** Mass spectrum of 3.
Figure S27 $^1$H NMR (DMSO-$d_6$) of isolated methyl furan-2-carboximidate.

Figure S28 $^{13}$C NMR (DMSO-$d_6$) of isolated methyl furan-2-carboximidate.
Figure S29 $^1$H NMR (DMSO-$d_6$) of isolated methyl 5-methylfuran-2-carboximidate (Fig. 6 entry 1).

Figure S30 $^{13}$C NMR (DMSO-$d_6$) of isolated methyl 5-methylfuran-2-carboximidate.
Figure S31 $^1$H NMR (DMSO-d$_6$) of isolated methyl 5-ethoxymethylfuran-2-carboximidate (Fig. 6 entry 4).

Figure S32 $^{13}$C NMR (DMSO-d$_6$) of isolated methyl 5-ethoxymethylfuran-2-carboximidate.
**Figure S33** $^1$H NMR (DMSO-d$_6$) of isolated methyl 5-bromofuran-2-carboximidate (Fig.6 entry 5).

**Figure S34** $^{13}$C NMR (DMSO-d$_6$) of isolated methyl 5-bromofuran-2-carboximidate.
Figure S35 $^1$H NMR (DMSO-d$_6$) of isolated methyl 5-phenylfuran-2-carboximidate (Fig.6 entry 7).

Figure S36 $^{13}$C NMR (DMSO-d$_6$) of isolated methyl 5-phenylfuran-2-carboximidate.
Figure S37 $^1$H NMR (DMSO-$d_6$) of isolated methyl benzofuran-2-carboximidate (Fig.6 entry 8).

Figure S38 $^{13}$C NMR (DMSO-$d_6$) of isolated methyl benzofuran-2-carboximidate.