## Supporting Information

# Ni-Al/CoOx catalyzing hydrodeoxygenation of 5-hydroxymethyl furfural into 2,5-dimethylfuran at low-temperature without external hydrogen

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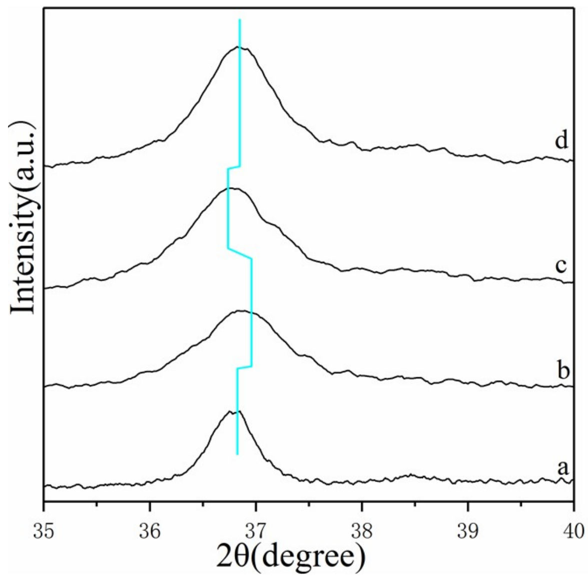



**Fig. S1** XRD patterns of CoOx (a), Ni/CoOx (b), Al/CoOx (c) and Ni-Al/CoOx-1 (d) samples after calcination in the 2θ ranges of 35-40°, respectively.

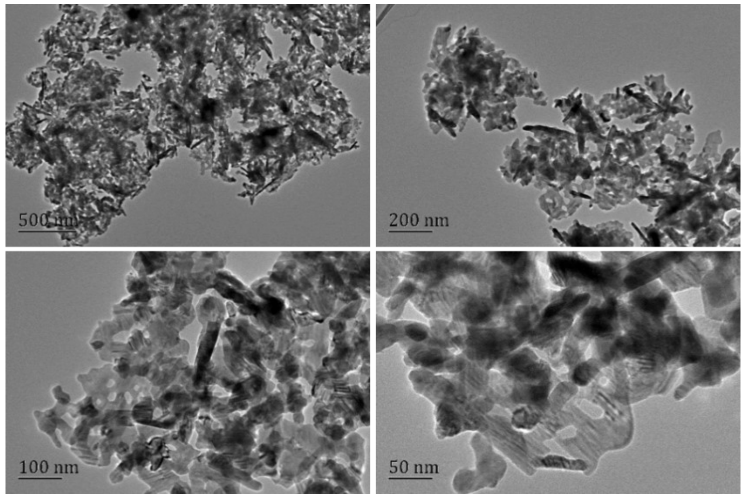



**Fig. S2** TEM images of the CoOx sample.

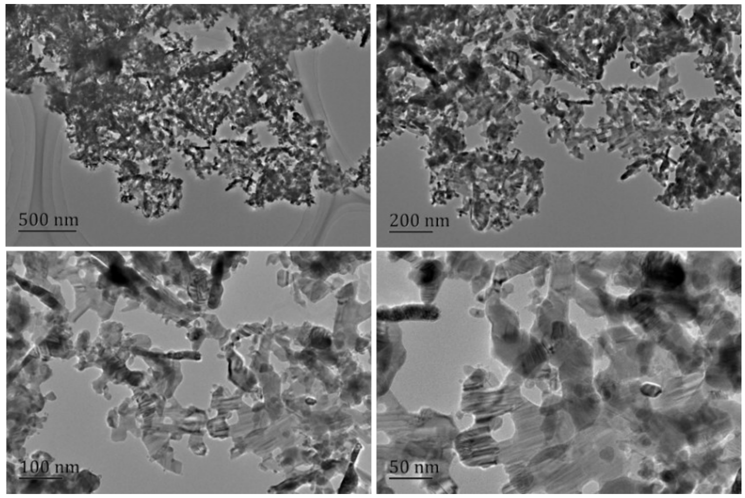



**Fig. S3** TEM images of the Ni/CoOx sample.

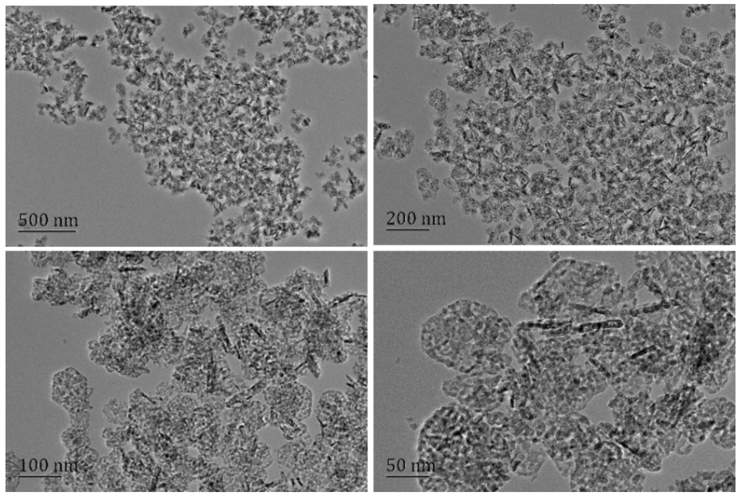



**Fig. S4** TEM images of the Al/CoOx sample.

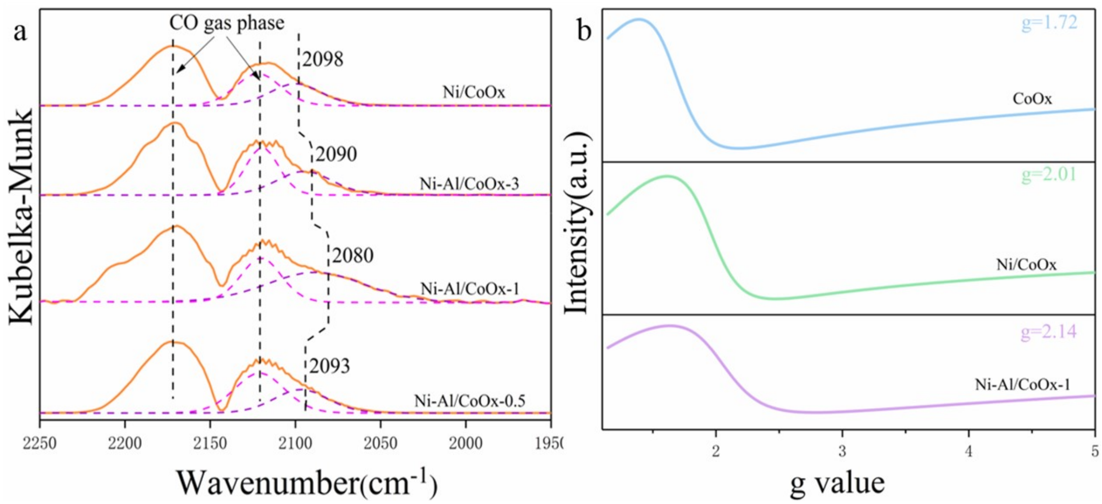



**Fig. S5** CO-DRIFTS spectra of Ni/CoOx, Ni-Al/CoOx-3, Ni-Al/CoOx-1 and Ni-Al/CoOx-0.5 samples at room temperature (a). EPR spectra of CoOx, Ni/CoOx and Ni-Al/CoOx-1 samples (b).

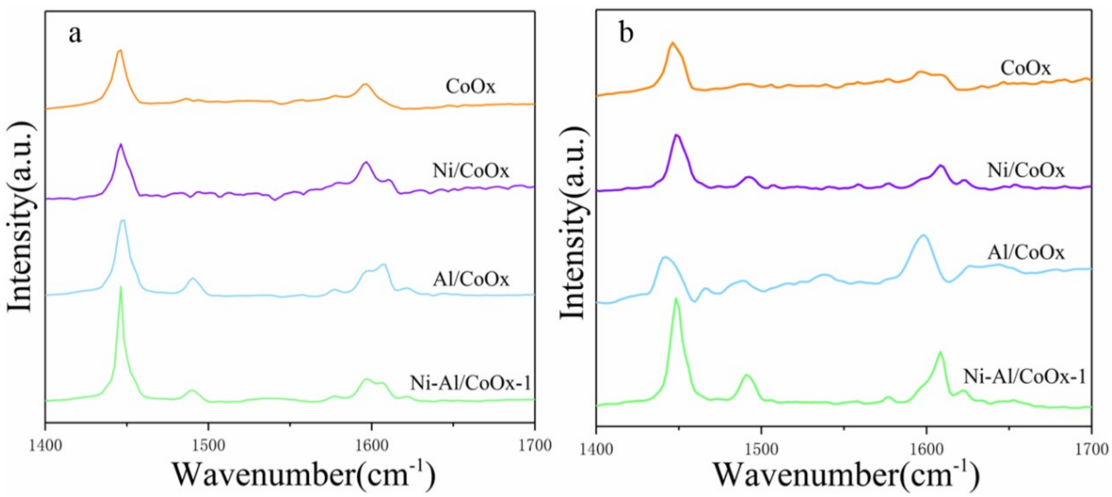



**Fig. S6** Pyridine-FTIR spectra for CoOx, Ni/CoOx, Al/CoOx and Ni-Al/CoOx-1 catalysts, recorded at (a) 200 °C and (b) 350 °C.

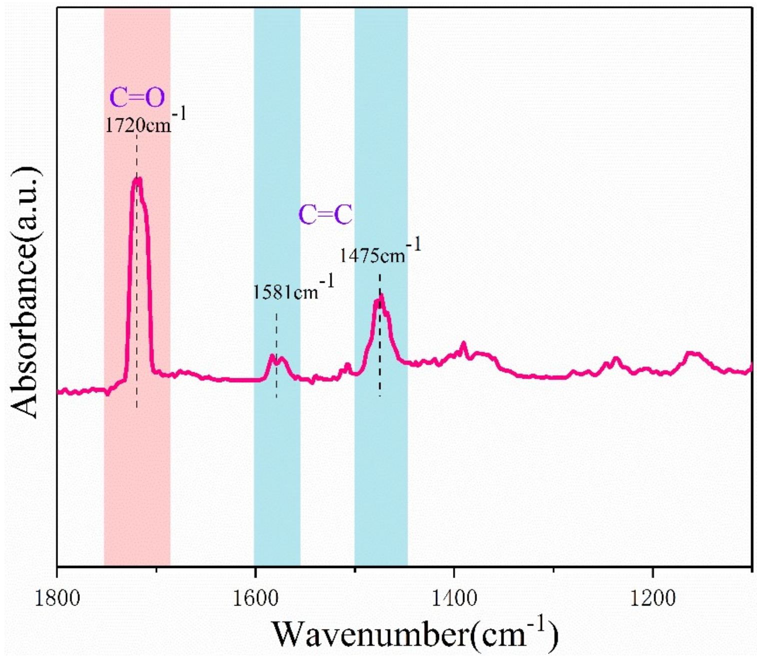



**Fig. S7** *In situ* DRIFT adsorption of furfural without catalysts.

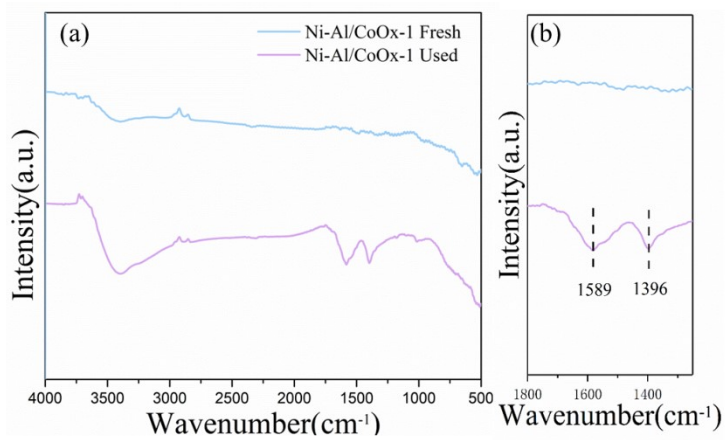



**Fig. S8** FT-IR spectra of the fresh and used Ni-Al/CoOx-1 catalyst in the wavenumber ranges of 500-4000cm$^{-1}$ (a) and 1250-1800cm$^{-1}$ (b) respectively.

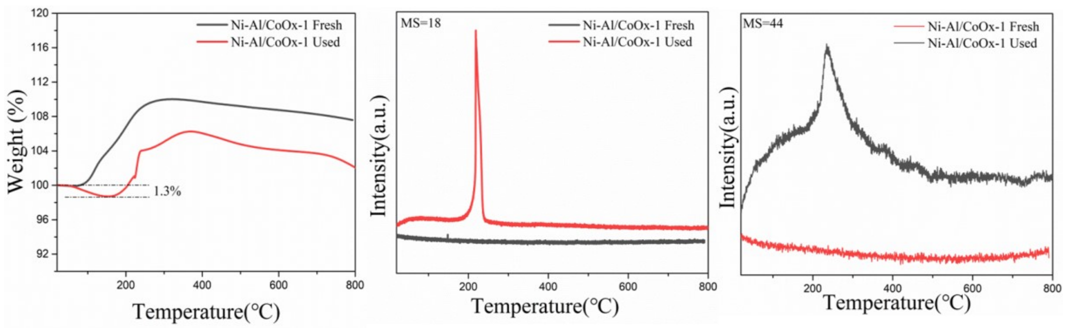



**Fig. S9** TG-MS of Ni-Al/CoOx-1 before and after 7 cycles of reaction.

**Table S1** ICP-OES data of Ni/CoOx, Al/CoOx, Ni-Al/CoOx-0.5, Ni-Al/CoOx-1 and Ni-Al/CoOx-3 samples.

| Catalysts | Theoretical | | | | Actual | | | |
|---|---|---|---|---|---|---|---|---|
| | Ni (wt%) | Al (wt%) | Co (wt%) | Ni/Al[b] | Ni (wt%) | Al (wt%) | Co (wt%) | Ni/Al[a] |
| Ni/CoOx | 20.0 | - | 80.0 | - | 24.9 | - | 75.1 | - |
| Al/CoOx | - | 10.5 | 89.5 | - | - | 6.9 | 93.1 | - |
| Ni-Al/CoOx-0.5 | 7.3 | 6.7 | 86.0 | 0.5 | 7.4 | 5.7 | 86.9 | 0.5 |
| Ni-Al/CoOx-1 | 10.7 | 4.9 | 84.4 | 1.0 | 11.1 | 4.4 | 84.5 | 1.1 |
| Ni-Al/CoOx-3 | 15.5 | 2.3 | 82.2 | 3.0 | 16.2 | 2.1 | 81.7 | 3.5 |

[a] The molar ratio of Ni/Al.

**Table S2** Gaussian fitting analysis of $H_2$-TPR patterns of the calcined catalysts.

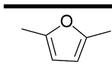
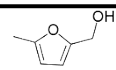
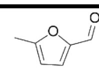
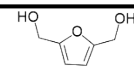
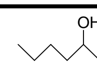
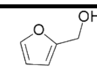
| Samples | Total $H_2$ Consumption(μmmol/g) | Reduction temperature(°C)/Relative content(%) | | | | |
|---|---|---|---|---|---|---|
| | | $Co_3O_4$ | α-CoO | γ-CoO | α-NiO | γ-NiO |
| CoOx | $1.859\times10^4$ | 272/23.3 | 347/76.7 | - | - | - |
| Ni/CoOx | $1.833\times10^4$ | 205/20.0 | 314/56.1 | - | 381/23.9 | - |
| Al/CoOx | $1.368\times10^4$ | 290/22.7 | - | 677/77.3 | - | - |
| Ni-Al/CoOx-1 | $1.559\times10^4$ | 245/20.9 | - | 580/60.0 | 325/2.1 | 734/17.0 |

**Table S3** Quantitative analysis of surface acid sites on different samples.

| Catalyst | Temperature(°C) | | | Contents of acid sites (μmol $NH_3/g_{catalyst}$)[a] | | | Total contents of acid sites (μmol $NH_3/g_{catalyst}$) |
|---|---|---|---|---|---|---|---|
| | T1 | T2 | T3 | T1 | T2 | T3 | |
| CoOx | 66 | 335 | - | 32.2 | 7.1 | - | 39.3 |
| Ni/CoOx | 66 | 338 | 555 | 38.5 | 24.8 | 61.1 | 124.4 |
| Ni-Al/CoOx-1 | 80 | 270 | 513 | 330.2 | 80.8 | 26.5 | 437.5 |
| Al/CoOx | 80 | 263 | - | 493.8 | 7.6 | - | 501.4 |

[a] Calculated from the Percentage of peak area.

**Table S4** Conversion and selectivity of liquid-phase HMF catalytic transfer hydrogenation on different samples.

| Catalyst | Conv. (%) | Sel.(%) | | | | | |
|---|---|---|---|---|---|---|---|
| | |  |  |  |  |  |  |
| CoOx | 21.8 | 0 | 4.6 | 18.3 | 77.1 | - | - |
| Al/CoOx | 69.3 | 0 | 1.6 | 7.5 | 90.9 | - | - |
| Ni/CoOx | 32.3 | 2.5 | 8.7 | 13.9 | 62.5 | 4.2 | 8.2 |
| Ni-Al/CoOx-0.5 | 95.6 | 47.2 | 31.4 | 2.4 | 13.3 | 2.3 | 3.4 |
| Ni-Al/CoOx-1 | 99.9 | 97.2 | 0 | 0 | 0 | 0.5 | 2.3 |
| Ni-Al/CoOx-2 | 99.9 | 74.5 | 0 | 0 | 3.5 | 10.1 | 11.9 |
| Ni-Al/CoOx-3 | 93.1 | 7.0 | 36.4 | 7.2 | 27.7 | 9.5 | 12.2 |

Reaction conditions: 210°C, 1 h, 0.21 g HMF,0.1 g catalyst,40 mL 2-propanol, 0.5 MPa $N_2$, 400 r/min.

**Table S5** Comparison of the catalytic performance of Ni-Al/CoOx with other reported catalysts for the hydrogenation of HMF.

| Entry | Catalyst | T(°C) | Time(h) | Hydrogen source | Conv.(%) | Yield（%） | DMF productivity ($mol_{DMF}/g_{catalyst}*h^{-1}$) | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | CuZnCoOx | 210 | 5 | ethanol | 100 | 99.0 | 0.00516 | [2] |
| 2 | NC-Cu/MgAlO | 220 | 0.5 | cyclohexanol | 100 | 96.1 | 0.076 | [3] |
| 3 | Ru/C | 190 | 6 | 2-propanol | 100 | 81.0 | - | [4] |
| 4 | $RuO_2$-Ru/C | 190 | 6 | 2-propanol | 100 | 72.0 | - | [5] |
| 5 | Cu−Pd@RGO | 200 | - | 2-propanol | 96 | 95 | 0.0388 | [6] |
| 6 | Pd/$Fe_2O_3$ | 180 | - | 2-propanol | 100 | 72.0 | - | [7] |
| 7 | Cu-PMO | 300 | 0.75 | methanol | 100 | 34.0 | 0.00359 | [8] |
| 8 | Cu/Al | 240 | 6 | methanol | 100 | 75.0 | - | [9] |
| 9 | Co-Ni/C | 210 | 24 | Formic acid | 99 | 90 | 0.00037 | [10] |
| 12 | Co@NGs | 200 | 6 | $H_2$ | 100 | 94.7 | 0.00394 | [11] |
| 13 | Co-Cu/C | 180 | 8 | $H_2$ | 100 | 99.4 | 0.12276 | [12] |
| 14 | NiZnAl | 180 | 15 | $H_2$ | 100 | 93.6 | 0.00492 | [13] |
| 15 | Fe-Co-Ni/h-BN | 180 | 4.5 | $H_2$ | 100 | 94 | 0.00208 | [14] |
| 16 | Ni/$LaFeO_3$ | 230 | 6 | $H_2$ | >99 | 98.3 | 0.00163 | [15] |
| 17 | NiFe/CNTs | 200 | 3 | $H_2$ | 100 | 91.3 | 0.02426 | [16] |
| 18 | Fe-L1/C | 240 | 5 | $H_2$ | 100 | 86 | 0.00086 | [17] |
| 19 | NiSi-PS | 150 | 3 | $H_2$ | 100 | 90.2 | 0.04464 | [18] |
| 20 | Cu−Ni/$TiO_2$ | 200 | 8 | $H_2$ | 100 | 84.3 | 0.00138 | [19] |
| **10** | **Ni-Al/CoOx** | **170** | **4** | **2-propanol** | **99.9** | **96.8** | **0.00416** | **This work** |
| **11** | **Ni-Al/CoOx** | **130** | **36** | **2-propanol** | **98.7** | **87.2** | **0.00040** | **This work** |

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