Supplementary Figure 1.

Total oxygenates selectivity (without considering CO$_2$ formation) as a function of reaction temperature (A) and CO conversion (B). A total pressure of 40 bar with a H$_2$/CO ratio of 1.5 was adjusted. The detailed reaction conditions are identical to those in Figure 1 of the main text.

The rational behind calculating total oxygenates selectivities without consideration of CO$_2$ formation is that in industrial applications frequently H$_2$-lean syngas (from coal or biomass) is being employed. Since most FT catalysts display water gas shift activities, the H$_2$/CO ratio (and therefore the CO$_2$ amounts) can be favorably adjusted. According to Figure S1, a total oxygenates selectivity up to ~50 wt% can be obtained at a CO conversion of more than 40%.
Supplementary Figure 2.
Effect of different alkali metals on the catalytic performance of Co<sub>4</sub>Mn<sub>1</sub> catalysts in CO hydrogenation. Catalytic tests were carried out at \( p=40 \) bar, \( \text{H}_2/\text{CO}=1.5 \) and total gas flow=40 ml/min.
Supplementary Figure 3.
Selectivity of aldehydes in total oxygenates over different alkali containing Co$_4$Mn$_1$ catalysts.
Supplementary Figure 4.

$\alpha$-chain lengthening probabilities for oxygenates, alkanes and alkenes over various CoMnK catalysts. The $\alpha$-values were calculated based on the Anderson-Schulz-Flory equation $W_n = n \cdot (1-\alpha)^2 \cdot \alpha^{n-1}$ where $W_n$ stands for the mass fraction of products containing $n$ carbon atoms. The $\alpha$ values for oxygenates were calculated for C$_{4+}$ because C$_{1-3}$ fractions do not follow the Schulz-Flory distribution. The $\alpha$ values for alkanes and alkenes were calculated for C$_{2+}$ and C$_{3+}$, respectively.
Supplementary Figure 5.
(A) selectivity of C₄⁺ long chain oxygenates and (B) selectivity of C₂–C₄ short chain oxygenates over various catalysts and different temperature.
Supplementary Figure 6.

(A) and (B): Activity (CO conversion) and total oxygenates selectivity (without CO₂) as a function of time-on-stream for Co₄Mn₁K₀.₁ catalyst at 220°C (Panel A) and 260°C (Panel B), 40 bar, H₂/CO=1.5.

It is seen that at both temperatures, the selectivity of total oxygenates (without CO₂) is remarkably stable within the investigated ranges of time-on-stream (between 56 to 62 wt% at 220°C and 40 to 47 wt% at 260°C, respectively). The selectivity of hydrocarbons (sum of paraffins and olefins) and CO₂ are also stable. At 220°C, the CO conversion during the measurements was always between 5 and 10%, but never below 5% within 112 h time-on-stream. At 260°C, the CO conversion slightly decreased from 44 to 35% after 96 h time-on-stream, however, the total oxygenates yield (CO conversion * oxygenates selectivity) remained strikingly stable (between 15 to 17 wt%).

(C): XRD pattern of the Co₄Mn₁K₀.₁ catalyst after long-term stability testing for 96 h at 260°C. The XRD measurement was performed with the SiC-diluted catalyst as recovered from the reactor. The diffraction spectrum at 2 theta between 39-50° (typical diffraction region for Co metallic and Co carbides) shows clearly the occurrence of a Co₂C phase while the Co metallic phase as initially present in the virgin catalyst, is completely absent.
Supplementary Figure 7.

Kinetic analysis indicates that the rate of the reaction follows a first order dependence in the hydrogen pressure.

\[ r = k \frac{P_{H_2}}{P_{CO}^{0.5}} \]
Supplementary Figure 8.
Comparison of selectivity between traditional supported Co/MnO\textsubscript{x} catalyst (prepared by impregnation) with “unsupported” CoMn prepared through oxalate co-precipitation. To allow a comparison, the MnO\textsubscript{x} support was prepared by thermal decomposition of Mn-oxalate. The Co particle size was around 10 nm for Co/MnO\textsubscript{x}.
It is clearly seen that the selectivity of oxygenates is significantly higher for the Co\textsubscript{2}Mn\textsubscript{1} (oxalate co-precipitated) catalyst than for Co nanoparticle (prepared from hot-injection of Co\textsubscript{2}(CO)\textsubscript{8}, see reference [2]) supported on MnO\textsubscript{x} (x = ~1.6, close to Mn\textsubscript{5}O\textsubscript{8}, prepared by thermal decomposition of Mn-oxalate).
Supplementary Figure 9.
EDX chemical mapping of Co$_4$Mn$_1$K$_{0.1}$ catalyst (A) before and (B) after catalytic CO hydrogenation at 240°C for 24 h.
Supplementary Figure 10.
HRTEM images of the Co₄Mn₁K₀.₁ catalyst before reaction. Both fcc and hcp cobalt are identified (upper panel) through FFT of the selected regions. In the lower panel, Mn₅O₈ is observed as a “shell” of a big cobalt (hcp) particle.
Supplementary Figure 11.
TEM image of Co₄Mn₁K₀.₁ catalyst along with a particle size distribution histogram. More than 200 particles of the shown image as well as of other images were evaluated for their size so as to determine the percentage of each particle size range. These particles are composed of mainly cobalt with also certain amounts of manganese according to STEM-EDX (Figure S9).
Supplementary Figure 12.
XRD patterns of Co$_4$Mn$_1$, Co$_4$Mn$_1$Li$_{0.1}$, Co$_4$Mn$_1$Na$_{0.1}$ and Co$_4$Mn$_1$K$_{0.1}$ catalysts after reaction for 24 h: T=240°C, p=40 bar, H$_2$/CO=1.5/1. (#): cubic Co and (+): Co$_2$C.

For Co$_4$Mn$_1$, fcc metallic Co was identified as being the major diffraction peak; peaks of Co$_2$C were not clearly attributable. The presence of alkali metals promoted the formation of Co$_2$C during reaction. With Li and Na, both metallic Co and Co$_2$C were observed, but for the K doped catalyst, metallic Co was completely absent. Other diffraction peaks in Figure S12 are associated with the Mn-oxide phase, alkali manganese mixed oxide etc. and will be discussed elsewhere.
### Supplementary Table 1.
Catalytic performance of CoMn catalysts during CO hydrogenation.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO conv. (%)</th>
<th>Selectivity (wt%)</th>
<th>RCHO in RO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RH</td>
<td>R_</td>
<td>RO</td>
</tr>
<tr>
<td>Co&lt;sub&gt;1&lt;/sub&gt;Mn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4.5</td>
<td>36</td>
<td>34</td>
</tr>
<tr>
<td>Co&lt;sub&gt;2&lt;/sub&gt;Mn&lt;sub&gt;1&lt;/sub&gt;</td>
<td>4.9</td>
<td>37</td>
<td>32</td>
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<tr>
<td>Co&lt;sub&gt;2&lt;/sub&gt;Mn&lt;sub&gt;1&lt;/sub&gt;</td>
<td>6.5</td>
<td>39</td>
<td>30</td>
</tr>
<tr>
<td>Co&lt;sub&gt;4&lt;/sub&gt;Mn&lt;sub&gt;1&lt;/sub&gt;</td>
<td>6.6</td>
<td>45</td>
<td>26</td>
</tr>
</tbody>
</table>

Reaction conditions: 220°C, 40 bar, 4800 ml/g<sub>cat</sub>/h, H<sub>2</sub>/CO=1.5/1. RH: alkanes, R_: alkenes, RO: oxygenates, RCHO: aldehydes.
Supplementary Table 2.

BET surface area of CoMnK catalysts with different relative amount of metal atom ratio.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Co$_2$Mn$_1$</th>
<th>Co$_2$Mn$<em>1$K$</em>{0.1}$</th>
<th>Co$_2$Mn$<em>1$K$</em>{0.3}$</th>
<th>Co$_4$Mn$_1$</th>
<th>Co$_4$Mn$<em>1$K$</em>{0.1}$</th>
<th>Co$_4$Mn$<em>1$K$</em>{0.3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{BET}}$ (m$^2$/g)</td>
<td>74.5</td>
<td>47.0</td>
<td>37.6</td>
<td>69.2</td>
<td>46.1</td>
<td>33.2</td>
</tr>
</tbody>
</table>
**Supplementary Methods**

**Catalyst preparation.** Binary CoMn oxalates were co-precipitated by fast addition of a mixed solution of Co(NO$_3$)$_2$$\cdot$6H$_2$O and Mn(NO$_3$)$_2$$\cdot$4H$_2$O (100 ml) to an excess of H$_2$C$_2$O$_4$$\cdot$2H$_2$O solution (150 ml) under vigorous stirring using acetone as solvent. Stirring usually continued for at least 5 min until the color of the precipitates appeared homogeneous. The atomic ratios of Co to Mn were adjusted to 1/2, 1/1, 2/1 and 4/1. Then the slurries were kept overnight for aging. After removal of the supernatant acetone the precipitate was centrifuged, dried overnight at 110°C and finally crushed and sieved so as to obtain a size fraction between 125 and 250 µm for characterization and high-pressure catalytic investigations.

The mixed-metal oxalate or hybrid precursors were treated thermally in the presence of hydrogen either directly in the high-pressure flow reactor (0.1 MPa H$_2$, 30 ml min$^{-1}$ at 370 °C for 1 h) for catalytic testing, or in an atmospheric-pressure U-type flow reactor for characterization. Reduced catalysts were pyrophoric and had to be passivated (1% O$_2$ in Ar at 25 °C, for at least 30 min) before TEM and XRD characterization.

**Catalyst characterization.** X-ray diffraction (XRD) patterns of the catalysts were collected with a Cu Kα source using a Rigaku Miniflex-600 X-ray diffractometer operating at 40 mA and 35 kV in the continuous-scan mode with steps of 1 degree/min in a wide 2θ angle range from 20 to 80°.

(HR)TEM images and EDX chemical mapping of Co$_4$Mn$_1$K$_{0.1}$ before reaction were made at Zhejiang University of Technology using a Tecnai G2 F30 S-Twin TEM at an operating voltage of 300 kV. The HAADF STEM images for the Co$_4$Mn$_1$K$_{0.1}$ catalyst
after CO hydrogenation were collected at Pacific Northwest National Laboratory using a Titan 80-300™ scanning/transmission electron microscope S/TEM operating at 300 kV.

In-situ Brunauer-Emmett-Teller (BET) surface areas were measured using Ar as probe gas in a U-type flow reactor (made of quartz, ~5 cm³ inner volume, equipped with a dead-end orifice for temperature measurement and a frit for sample deposition) connected to a quadrupole mass spectrometer (Balzers-QMG 422) via a capillary. The cross-section for non-specific Ar atom adsorption (σ_{Ar}=19.2 Å) was determined in calibration experiments with N₂ (σ_{N₂}=16.2 Å) using Aerosil 200 (Degussa). Details of the methodological approach were described elsewhere.

**Catalytic tests.** For catalytic tests with varying H₂/CO pressure ratio, the H₂/CO flow rate was systematically changed while keeping the total pressure constant at p=40 bar. For each hydrogen incremental pressure increase, steady state conditions were first established before data were taken after 24 h time-on-stream.

The carbon balance has been double-checked by comparing the CO conversion (using an external standard) and the total carbon as detected in the products.
Supplementary References
