Entropy–Stabilized Metal Oxide Solid Solutions as CO Oxidation Catalysts with High–Temperature Stability

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Experimental

Materials and Chemicals

H$_2$PtCl$_6$·xH$_2$O (99.9%, ALDRICH, USA), MgCl$_2$·6H$_2$O (AR, ACROS, USA), ZnCl$_2$ (98%, Alfa Aesar, USA), CoCl$_2$ (97.0%, ACROS, USA), CuCl$_2$ (AR, ACROS, USA) and Ni(OOCCH$_3$)$_2$·4H$_2$O (99.0%, ACROS, USA) were purchased as received. Ammonium hydroxide (NH$_3$.H$_2$O, 28.0~30.0%) was brought from Avantor Performance Materials (USA) and cetyltrimethyl ammonium bromide (CTAB, AR) was purchased from MP Biomedicals, LLC (France).

Synthesis of entropy-stabilized metal oxide solid solutions

NiMgCuZnCoOx (mix)

MgCl$_2$·6H$_2$O, ZnCl$_2$, CoCl$_2$, CuCl$_2$ and Ni(OOCCH$_3$)$_2$·4H$_2$O are massed and physical mixed just using agate mortar. To ensure adequate mixing, all batches are milled for at least 2 h. Mixed powders are then calcinated in air under 800, 900 and 1000 °C for 4 h (5 °C/min) to obtain desired crystalline oxide phase.

NiMgCuZnCoOx (co-precipitation)

Equal molar ratio (0.02 M) of MgCl$_2$·6H$_2$O, ZnCl$_2$, CoCl$_2$, CuCl$_2$ and Ni(OOCCH$_3$)$_2$ are dissolved in 30 ml water followed by adding the 0.47 g CTAB. After stirring for 12 h at 60 °C, 2.5 ml NH$_3$.H$_2$O was added and continues stirring for 12 h at 60 °C. After filtering, the precipitate was dried at 120 °C for 4 h and finally calcined at 900 °C for 4 h (5 °C/min).
to obtain desired crystalline oxide phase.

**PtNiMgCuZnCoOx (co-deposition)**

Equal molar ratio (0.02 M) of MgCl$_2$$\cdot$6H$_2$O, ZnCl$_2$, CoCl$_2$, CuCl$_2$ and Ni(OOCCH$_3$)$_2$ are dissolved in 30 ml water followed by adding the 0.47 g CTAB. After stirring for 12 h at 60 °C, precalculated amount of H$_2$PtCl$_6$ (0.3, 0.6 and 1.0 wt%) in H$_2$O was added and then stirred constantly for 12 h. 2.5 ml NH$_3$.H$_2$O was added and continues stirring for 12 h at 60 °C. After filtering, the precipitate was dried at 120 °C for 4 h and finally calcined at 900 °C for 4 h (5 °C/min) to obtain desired crystalline oxide phase.

The reduced 0.3wt%PtNiMgCuZnCoOx were measured under 300 °C for 2 h using a mixture of 4% H$_2$ in 96% N$_2$.

**Characterization of the catalysts**

The powder X-ray diffraction (XRD) data were recorded with a PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA (scanning step: 0.02 ° per step). The diffraction patterns were recorded in the range of 10-80°. The nanoparticle size (dBa, nm) was estimated according to Scherrer equation: $S4 = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$ (K = 0.9, $\lambda$ = 0.1540598 nm).

The nitrogen adsorption and desorption isotherms were measured at 77 K under a Gemini VII surface area analyzer. Samples were degassed for 12 h under N$_2$ at 100 °C prior to the measurement.

High resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted on
an aberration-corrected FEI Titan S 80-300 TEM/STEM operated at 300 kV and a large active area (60mm²) EDAX silicon drift detector (SDD) for high-collection-efficiency energy dispersive x-ray spectroscopy (EDS).

X-ray photoelectron spectroscopy (XPS) experiments were performed with a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV.

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Temperature-programmed reduction of H₂ (H₂-TPR) experiments were conducted on a PX200 apparatus with a TCD. 50 mg of sample was pretreated at 450 °C (10 °C/min) in He for 1 h and then cooled to room temperature. Then the sample was directly heated from 60 °C to 700 °C at a rate of 10 °C/min in a flow of 5 vol % H₂/N₂ (40 mL/min). The hydrogen consumption was quantitatively evaluated by the TCD signal.

**Catalytic CO oxidation**

Catalytic CO oxidation was carried out in a fixed-bed reactor (straight quartz tube) at atmospheric pressure. For the measurement of CO light-off curves showing CO conversion as a function of reaction temperature, a 20 mg catalyst supported by quartz wool was loaded in the reactor. The feed gas of 1 % CO balanced with dry air (< 4 ppm water) passed though the catalyst bed at a flow rate of 10 ml/min corresponding to gas hourly space velocity (GHSV) of 30,000 mL (h g<sub>cat</sub>)⁻¹. The concentrations of CO and CO₂ in the
reactor effluent were analyzed by a Buck Scientific 910 gas chromatograph equipped with a dual molecular sieve/porous polymer column (Alltech CTR1) and a thermal conductivity detector. We controlled the reaction temperature through changing its discharge and maintained at each temperature point for 5 min to detect each experiment for two times.
Figure S1. TPR result of NiMgCuZnCoO$_x$ 900 and as–synthesized 0.3wt%PtNiMgCuZnCoO$_x$. 
Figure S2. HRTEM images of reduced 0.3 wt% PtNiMgCuZnCoOx.
Figure S3. TEM–EDS analysis of reduced 0.3wt%PtNiMgCuZnCoOₓ.
Figure S4. XPS results of Pt in reduced 0.3wt%PtNiMgCuZnCoO$_x$. 
Figure S5. XPS results of Ni, Mg Cu, Zn and Co in NiMgCuZnCoOₓ treated at 800 °C and 900 °C.
Figure S6. CO oxidation over NiMgCuZnCoOₓ and reduced 0.3wt%PtNiMgCuZnCoOₓ calcined at 600 and 800 °C.
Figure S7. The variation of LnK with the 1/T for (a) NiMgCuZnCoO\textsubscript{x} 900; (b) as-synthesized 0.3wt%PtNiMgCuZnCoO\textsubscript{x} and (c) reduced 0.3wt%PtNiMgCuZnCoO\textsubscript{x}. The relations between LnK and 1/T were all found to be in linearly.
Figure S8. CO oxidation over reduced PtNiMgCuZnCoO₉₀₀ with different Pt loading.
Figure S9. CO oxidation over 1 wt% Au/Al₂O₃ and Co₃O₄ (as-received and calculated at 900 °C).
Table S1. Calculated pre–exponential factor (A) and apparent activation energy (Ea) for NiMgCuZnCoOy 900, as–synthesized 0.3wt%PtNiMgCuZnCoOy and reduced 0.3wt%PtNiMgCuZnCoOy.

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<tr>
<th>Catalyst</th>
<th>$A$ (min$^{-1}$)</th>
<th>$E_a$ (KJ·mol$^{-1}$)</th>
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<tr>
<td>NiMgCuZnCoOy 900</td>
<td>2.78×10$^{10}$</td>
<td>91.5±3.57</td>
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<tr>
<td>as–synthesized 0.3wt%PtNiMgCuZnCoOy</td>
<td>1.12×10$^8$</td>
<td>57.2±6.07</td>
</tr>
<tr>
<td>reduced 0.3wt%PtNiMgCuZnCoOy</td>
<td>7.53×10$^8$</td>
<td>54.8±3.41</td>
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References: