Colloidal Co single-atom catalyst: a facile synthesis strategy and high catalytic activity for hydrogen generation

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Chemicals and materials

Potassium borohydride (KBH₄), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), nickel nitrate hexahydrate(Ni(NO₃)₂·6H₂O), iron nitrate nonahydrate (Fe(NO₃)₃·6H₂O), sodium hydroxide (NaOH), poly(N-vinyl-2-pyrrolidone) (PVP), starch, carboxymethylcellulose sodium (CMC-Na), polyvinyl alcohol (PVA), sodium polyacrylate (PAAS) and polyethylene glycol (PEG) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Rhodiumchloride (RhCl₃), chloroplatinic acid (H₂PtCl₆·6H₂O) and palladiumchloride (PdCl₂) were purchased from Aladdin. ISOBAM-104 (CAS.NO. 52032-17-4, average molecular weight of 55000~65000, see Figure S1 for its chemical structure) was purchased from KURARAY company, Japan. It is an amide-ammonium salt type of ISOBAM which is the trade name of a copolymer of isobutylene and maleicanhydride developed by KURARAY. All these raw materials were used directly without further purification. All glasswares and Teflon-coated magnetic stirring bars were cleaned with aqua regia, followed by copious rinsing with purified water. The water was purified by a PINGGUAN ultrapure water purification system (Wuhan, China). The hydrolysis tests of borohydride were carried out in an in-house designed device via measuring the mass of water displaced by the generated gas.

Instrumentation

Phases in samples were identified by powder X-ray diffraction (XRD) analysis using a Philips X’Pert PRO diffractometer (PANalytical, NETHERLANDS). Spectra were recorded at 40 mA and 40 kV, using Cu Ka radiation (λ=0.1542 nm) between 30° and 80° (20). UV-Vis absorption spectra were recorded at 200-800 nm by a Shimadzu UV-2550 spectrophotometer (Shimadzu company, Kobe, Japan). Transmission electron microscopy (TEM) was performed on a JEM-2100F(JEOL company, Tokyo, Japan) Field Emission High-resolution transmission electron microscope with an electron acceleration energy of 200 kV. The specimens were prepared by dropping 2-3 droplets of the prepared colloidal aqueous solution onto a copper micro grid covered with a thin amorphous carbon film, followed by atmosphere drying at an ambient temperature. To evaluate the mean diameter, at least 200 particles from different locations on the grid were examined for each sample. Fourier transform infrared (FTIR) spectra of samples (embedded in KBr pellet) were recorded within the frequency range of 4000–400 cm⁻¹ and with a resolution of 4 cm⁻¹ using an FTIR spectrometer (VERTEX 70, Germany). X-ray photoelectron
spectroscopy (XPS) was carried out on a VGMultilab 2000 instrument (Thermo Electron Co., USA) using 300 W Al Kα as the excitation source. Samples in this case were subjected to high vacuum before being introduced into the analysis chamber. The binding energies from XPS were referenced to the C1 s binding energy (284.6eV) of “adventitious” carbon contamination. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted on an FEI Titan Cubed Themis G2 300 with a spherical aberration corrector. Surface topography images of Co catalysts were taken using scanning probe microscopy (SPM, Keysight SPM 6500).

**Preparation of ISOBAM-104 stabilized Co catalysts and catalytic hydrolysis of borohydride**

The procedure used to prepare homogeneous ISOBAM-104 stabilized Co\(^{2+}\) colloidal catalysts was described as follows: a certain amount of ISOBAM-104 was added into a double-necked flask first, and then cobalt nitrate hexahydrate (Co(NO\(_3\))\(_2\)·6H\(_2\)O) precursor. 50 mL of the mixed solution were stirred for 24 hours to obtain the desired catalysts.

The hydrolysis tests were carried out in a 250-mL round bottom flask equipped with a constant pressure drop funnel and placed in a thermostatic bath. Catalytic hydrolysis reaction of borohydride for hydrogen generation was initiated by dropping the fresh aqueous solution of potassium borohydride from the drop funnel to the flask and stirring the mixed solution of KBH\(_4\) (10mL), Co(NO\(_3\))\(_2\)·6H\(_2\)O and ISOBAM-104 (50mL). The mass of the water replaced by the released hydrogen was measured by using an electronic balance and was automatically recorded at intervals of two seconds. Before entering the water-ejecting instrument, the generated gas was allowed to pass through a trap containing concentrated sulfuric acid to remove any possibly produced ammonia. The long-time activity (catalytic durability) of the ISOBAM-104 stabilized Co\(^{2+}\) solution was examined by repeating the batch tests, in which case the following batch test was started by adding the same amount of solid KBH\(_4\) into the ISOBAM-104 stabilized Co\(^{2+}\) solution upon the completion of the previous one.

It should be noted that the ISOBAM-104 used in this work contains NH\(_4^+\) group, which could act as a catalyst for hydrogen generation from hydrolysis of borohydride based on our previous work\(^1\). Therefore, to obtain the intrinsic catalytic activity of Co nanoparticles, the catalytic activities of ISOBAM-104 stabilized Co\(^{2+}\) and ISOBAM-104 (NH\(_4^+\) group) were respectively measured under the identical condition, and then
the catalytic activity value of ISOBAM-104 was subtracted from that of the ISOBAM-104 stabilized Co$^{2+}$.

In general, the hydrolysis experiment was carried out at ambient temperature (30 °C). The test conditions were varied to determine the kinetic parameters. All catalytic hydrolysis reactions were allowed to proceed for ~10 minutes and repeated at least three times under the identical conditions, and the mean values of the measured data were used to evaluate the catalytic activities. First, the optimum reaction conditions were determined by using a series of ISOBAM-104 solutions ($R_{\text{ISO}} = 10, 20, 30, 40, 50, 60$, $R_{\text{ISO}}$ is defined as the molar ratio of ISOBAM-104 in monomer units to the total metal ions) and Co(NO$_3$)$_2$·6H$_2$O solutions (0.30, 0.45, 0.60, 0.75, 0.90, 1.20, 1.50, 1.80 mmol/L). Second, the apparent activation energy of hydrolysis of borohydride catalyzed by ISOBAM-104 stabilized Co$^{2+}$ colloidal catalysts was evaluated based on several test runs at 20~40 °C. Third, the effects of different protective agents on the catalytic performance of Co$^{2+}$ solution in the hydrolysis of borohydride were examined and compared. Finally, the catalytic activities of ISOBAM-104 protected noble metal NPs (Pd, Pt and Rh NPs) were also studied and compared with those of the ISOBAM-104 protected Co NPs.

The hydrogen generation rate (HGR, mL-H$_2$·s$^{-1}$) was determined in terms of the slope of the hydrogen volume-time plot during the initial reaction stage. The experimental data in the first minute were used for the kinetic analysis (such as apparent activation energy). The catalytic activities (mL-H$_2$·min$^{-1}$·g-cat.$^{-1}$) were calculated in terms of the ratio of the hydrogen production rate to the catalyst. The intrinsic catalytic activity of Co NPs was calculated by subtracting the catalytic activity value of ISOBAM-104 from that of ISOBAM-104 stabilized colloidal Co$^{2+}$ catalysts.

**Quantum Chemical Calculations**

DFT calculations were carried out using spin-polarization DFT/GGA with the PBE exchange-correlation functional, as implemented in the DMol$^3$ package (BIOVIA company, San Diego, CA, USA). Double numerical basis set and polarization functions were carried out to describe the valence electrons, and an electron relativistic core treatment was used to perform full optimization of the investigated models without symmetry constraint. The convergence criteria were set to medium quality with a tolerance for self-consistent field (SCF), optimization energy, maximum force, and maximum displacement of $1\times10^{-5}$ Ha, $2\times10^{-5}$ Ha, 0.004
Ha/Å and 0.005 Å, respectively.

Figure S1 (a) The schematic diagram of proposed colloidal single-atom catalysts and (b) The chemical structure of ISOBAM-104.
Figure S2 (a) Color evolution of ISOBAM-104 stabilized Co$^{2+}$ solutions before and after reduction in air for various minutes, (b) UV-Vis spectra of Co$^{2+}$, ISOBAM-104, and ISOBAM-104 stabilized Co$^{2+}$ solutions before and after reduction in air for various minutes, and (c) the UV-Vis absorption intensity of ISOBAM-104 stabilized Co$^{2+}$ at 300 nm after addition of KBH$_4$ versus storing period. ([Co$^{2+}$]=0.9 mM, $R_{ISO}=40$, $V_{total}=50$ mL, 30 °C).
(c) Nanoparticle-3

![Graph showing nanoparticle diameter over time](image)

- 29 min
- 35 min
- 38 min
- 41 min
- 44 min
- 47 min
(d) Nanoparticle-4
(e) Nanoparticle-5
Figure S3 SPM images of ISOBAM-104 protected Co NPs and their size evolution with storing period.
(b) Starch

Sediment colloidal NPs

Supernatant colloidal NPs

Sediment colloidal NPs

Supernatant colloidal NPs

(c) CMC-Na
Supernatant colloidal NPs

Sediment colloidal NPs

(d) PVA

Supernatant colloidal NPs

Sediment colloidal NPs

(e) PAAS
Figure S4 TEM images and size distribution histograms of Co NPs synthesized with different types of protective agents (Samples both in supernatant and sediment were characterized by TEM for the Co NPs synthesized using PVP, Starch, CMC-Na, PVA, PAAS and PEG as protective agents for comparison.)

(f) PEG

\(D_{av}=2.3\ \text{nm}\)

\(S=0.6\ \text{nm}\)
Figure S5 HAADF-STEM images of ISOBAM-104-stabilized colloidal Co catalysts.

(a) Total Survey XPS spectra
(b) Co XPS spectra

(c) C XPS spectra

(d) N XPS spectra
Figure S6 Total survey, Co, C, N and O XPS spectra of ISOBAM-104-protected Co NPs

Figure S7 FT-IR spectra of ISOBAM-104, Co(NO$_3$)$_2$ and Co NPs/ISOBAM-104.
Figure S8 TEM images and size distribution histograms of ISOBAM-104 protected Pt, Pd and Rh NPs.

(a) Pt NPs

(b) Pd NPs

(c) Rh NPs

\(D_{av}: \text{average particle size}; \ S: \text{standard deviation}\)
Figure S9 TEM images and size distribution histograms of Co NPs synthesized with various $R_{ISO}$ values ([Co$^{2+}$]=0.6 mM, $V_{total}$=50 mL, 30 °C).
**Figure S10** Intrinsic catalytic activity of Co NPs synthesized with various $R_{ISO}$ values using Co(NO$_3$)$_2$·6H$_2$O as precursor ([Co$^{2+}$]=0.6 mM, V$_{total}$=50 mL, 30 °C).

(a) [Co$^{2+}$]=0.6 mM

(b) [Co$^{2+}$]=0.75 mM
Figure S11 TEM images and size distribution histograms of Co NPs synthesized with various Co(NO$_3$)$_2$·6H$_2$O concentrations ($R_{ISO}=40$, $V_{total}=50$ mL, 30 $^\circ$C).
**Figure S12** Intrinsic catalytic activity of Co NPs synthesized at various Co$^{2+}$ concentrations ($R_{\text{ISO}}=40$, $V_{\text{total}}=50$ mL, 30 °C).

**Figure S13** Effect of temperature on the catalytic performance of Co NPs: Linear fit of ln$k$ vs. 1/$T$ ($[\text{Co}^{2+}]=0.9$ mM, $R_{\text{ISO}}=40$, $V_{\text{total}}=50$ mL, 30 °C).
binding energy: -232.1 kJ/mol
(a1) Co$_4$ cluster on COO$^-$ site of ISOBAM-104

binding energy: -191.7 kJ/mol
(b1) Co single atom on COO$^-$ site of ISOBAM-104

binding energy: -198.2 kJ/mol
(a2) Co$_4$ cluster on CONH$_2$ site of ISOBAM-104

binding energy: 180.6 kJ/mol
(b2) Co single atom on CONH$_2$ site of ISOBAM-104

binding energy: -188.4 kJ/mol
(a3) Co$_4$ cluster on OCOCO site of ISOBAM-104

binding energy: -173.5 kJ/mol
(b3) Co single atom on OCOCO site of ISOBAM-104

binding energy: -113.1 kJ/mol
(a4) Co$_4$ cluster on PVP

binding energy: -91.1 kJ/mol
(b4) Co single atom on PVP
binding energy: -62.5 kJ/mol
(a5) Co$_4$ cluster on PVA

binding energy: -42.3 kJ/mol
(b5) Co single atom on PVA

binding energy: -72.7 kJ/mol
(a6) Co$_4$ cluster on PEG

binding energy: -52.6 kJ/mol
(b6) Co single atom on PEG

binding energy: -108.2 kJ/mol
(a7) Co$_4$ cluster on Starch

binding energy: -91.1 kJ/mol
(b7) Co single atom on Starch

binding energy: -91.0 kJ/mol
(a8) Co$_4$ cluster on CMC-Na

binding energy: -42.4 kJ/mol
(b8) Co single atom on CMC-Na
**Figure S14** Geometric structures and binding energies of $\text{Co}_4$ cluster and Co single atom on various stabilizing agents.

**Figure S15** Color evolution of CMC-NH$_4$ (Ammonium Caboxy Methyl Cellulose) stabilized $\text{Co}^{2+}$ solutions before and after reduction in air for various periods. ($[\text{Co}^{2+}]=0.9$ mM, $R_{\text{CMC-NH}_4}=40$, $V_{\text{total}}=50$ mL, 30 °C).

**Figure S16** Differential charge density and Mulliken charges of (a) Co single atom and (b) $\text{Co}_4$ cluster on ISOBAM-104.
(a) The first elementary step in the borohydride hydrolysis catalyzed by Co₄-ISO

(b) The first elementary step in the borohydride hydrolysis catalyzed by Pt₄-ISO
(c) The first elementary step in the borohydride hydrolysis catalyzed by Pd$_4$-ISO

(d) The first elementary step in the borohydride hydrolysis catalyzed by Rh$_4$-ISO

Figure S17 Geometric structures of the first elementary step of the borohydride hydrolysis catalyzed by Co$_4$-ISO, Pt$_4$-ISO, Pd$_4$-ISO and Rh$_4$-ISO.
Figure S18 (a) UV-Vis spectra of Co²⁺, ISOBAM-104, and ISOBAM-104 stabilized Co²⁺ solutions at “second addition” of KBH₄ in air for various minutes, and (b) the UV-Vis absorption intensity of ISOBAM-104 stabilized Co²⁺ at 300 nm at “second addition” of KBH₄ versus storing period. ([Co²⁺]=0.9 mM, $R_{ISO}$=40, $V_{total}$=50 mL, 30 °C).

Figure S19 TEM images of Co NPs synthesized at “second addition” of KBH₄ ($R_{ISO}$=40, [Co²⁺]=0.9 mM, $V_{total}$=50 mL, 30 °C).

Figure S20 Catalytic durability of as-prepared Co colloidal catalysts: intrinsic catalytic activity of Co NPs ([Co²⁺]=0.9 mM, $R_{ISO}$=40, $V_{total}$=50 mL, 30 °C).
<table>
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<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Catalytic Activity (mL H₂/min/g catalyst)</th>
<th>Ref.</th>
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<td>Co</td>
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<td>This work</td>
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<td>NH₄Cl (ammonium species)</td>
<td>KBH₄</td>
<td>4500</td>
<td>[1]</td>
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<td>Ru/Ni foam</td>
<td>NaBH₄</td>
<td>23030</td>
<td>[2]</td>
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<td>Co₃O₄ hollow fiber composed of nanoparticles array</td>
<td>NaBH₄</td>
<td>11120</td>
<td>[3]</td>
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<td>[5]</td>
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<td>Catalyst</td>
<td>Reactant</td>
<td>activation energy (kJ/mol)</td>
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<tr>
<td>----------------------------------</td>
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<td>-----------</td>
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<tr>
<td>Co</td>
<td>KBH₄</td>
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<td>Present work</td>
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<tr>
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<td>Raney Co</td>
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<td>Co/SiO₂</td>
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**Table S2** Comparison of apparent activation energy ($E_a$) values of Co-based catalysts from the literature.
Table S3 Calculated binding energies of Co single atom and Co$_4$ cluster on stabilizing agent.

<table>
<thead>
<tr>
<th>Co single atom</th>
<th>Binding energies (kJ/mol)</th>
<th>Co$_4$ cluster</th>
<th>Binding energies (kJ/mol)</th>
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<tr>
<td>PVA-Co</td>
<td>-42.3</td>
<td>PVA-Co$_4$</td>
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<tr>
<td>PEG-Co</td>
<td>-52.6</td>
<td>PEG-Co$_4$</td>
<td>-72.7</td>
</tr>
<tr>
<td>PVP-Co</td>
<td>-91.1</td>
<td>PVP-Co$_4$</td>
<td>-113.1</td>
</tr>
<tr>
<td>Starch-Co</td>
<td>-91.9</td>
<td>Starch-Co$_4$</td>
<td>-108.2</td>
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<tr>
<td>CMC-Na-Co</td>
<td>-42.4</td>
<td>CMC-Na-Co$_4$</td>
<td>-91.0</td>
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<td>PAAS-Co</td>
<td>-39.1</td>
<td>PAAS-Co$_4$</td>
<td>-90.1</td>
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<td>ISOBAM-Co$_4$-COO$^-$</td>
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<td>ISOBAM-Co$_4$-COO$^-$</td>
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<td>ISOBAM-Co$_4$-OCOCO</td>
<td>-173.5</td>
<td>ISOBAM-Co$_4$-OCOCO</td>
<td>-188.4</td>
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Table S4 Calculated activation energy ($E_a$) and reaction energy ($E_r$) of the first elementary step in the borohydride hydrolysis catalyzed by Co$_4$-ISO, Pt$_4$-ISO, Pd$_4$-ISO or Rh$_4$-ISO.

<table>
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<th>$E_a$ (kJ/mol)</th>
<th>$E_r$ (kJ/mol)</th>
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<tr>
<td>Co$_4$-ISO</td>
<td>31.0</td>
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<td>Pt$_4$-ISO</td>
<td>72.0</td>
<td>24.3</td>
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<td>Pd$_4$-ISO</td>
<td>80.3</td>
<td>28.9</td>
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<tr>
<td>Rh$_4$-ISO</td>
<td>46.4</td>
<td>-2.5</td>
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</table>

References

23 Irum, M., Zaheer, M., Friedrich, M. & Kempe, R. Mesoporous silica nanosphere supported platinum nanoparticles (Pt@MSN): one-pot synthesis and catalytic hydrogen generation. Rsc Adv. 6, 10438-10441 (2016).


40 Ding, X. L., Yuan, X. X., Jia, C. & Ma, Z. F. Hydrogen generation from catalytic hydrolysis of sodium borohydride solution using Cobalt-Copper-Boride (Co-Cu-B) catalysts. Int. J.