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Excellent Catalytic Performance of ISOBAM Stabilized Co/Fe Colloidal Catalysts toward KBH₄ Hydrolysis

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Abstract: Recently, developing a cost-effective and high-performance catalyst is regarded as an urgent priority for hydrogen generation technology. In this work, ISOBAM-104 stabilized Co/Fe colloidal catalysts were prepared via a co-reduction method and used for the hydrogen generation from KBH₄ hydrolysis. The obtained ISOBAM-104 stabilized Co₁₀Fe₉₀ colloidal catalysts exhibit an outstanding catalytic activity of 37,900 mL-H₂ min⁻¹ g-Co⁻¹, which is far higher than that of Fe or Co monometallic nanoparticles (MNPs). The apparent activation energy (Eₐ) of the as-prepared Co₁₀Fe₉₀ colloidal catalysts is only 14.6 ± 0.7 kJ mol⁻¹, which is much lower than that of previous reported noble metal-based catalysts. The X-ray photoelectron spectroscopy results and density functional theory calculations demonstrate that the electron transfer between Fe and Co atoms is beneficial for the catalytic hydrolysis of KBH₄.

Keywords: ISOBAM-104; Co/Fe colloidal catalysts; hydrogen generation; KBH₄ hydrolysis; catalytic activity

1. Introduction

Recently, hydrogen has been widely considered as a promising clean energy source to replace the traditional fossil fuels. Chemical hydrogen storage materials have aroused tremendous interest because of their inherent advantages such as high content of hydrogen, no toxicity, low hydrogen releasing temperature, and an easily controllable hydrogen generation process [1–8]. Among those materials, potassium borohydride (KBH₄) stands out owing to its safe production process, harmless hydrolysis product, low activation energy and enthalpy [9–14]. Unfortunately, the low hydrogen production rate of KBH₄ self-hydrolysis hinders its large-scale practical application.

Many researchers found that metal nanoparticles (NPs) could catalyze the hydrolysis of KBH₄ and accelerate the generation rate of hydrogen [7,15,16]. For example, Kilinc et al. [7] successfully prepared the Pd complex catalysts for promoting the KBH₄ hydrolysis. The catalytic activity of the as-prepared catalysts was up to 37,900 mL-H₂ min⁻¹ g-catalyst⁻¹. Recently, a series of colloidal metal catalysts were synthesized and used for catalyzing the hydrolysis of KBH₄ [17–20]. For instance, Wang et al. [19] successfully synthesized colloidal Co single-atom catalysts for the effective production of hydrogen from KBH₄ hydrolysis by using ISOBAM (isobutylene-alt maleic anhydride) as a protectant. The synthesized colloidal metal catalysts possess a clearly intrinsic catalytic activity of metal without the influence of support. Besides, those colloidal metal catalysts are stabilized by protective agents and present excellent catalytic activity and recyclability.
It has been widely accepted that the bimetallic catalysts exhibited a high catalytic activity for hydrogen production owing to the synergistic effects between different constituents [21–25]. In detail, the addition of another metal component could modify the electronic structure and then improve the catalytic activity [25,26]. For example, a previous report displayed that the Rh$_{10}$Ni$_{90}$ bimetallic nanoparticles (BNPs) possessed a higher catalytic activity for the KBH$_4$ hydrolysis than that of Rh or Ni MNPs [27]. The catalytic activity of the reported Au/Ni BNPs was several times higher than their corresponding monometallic counterparts [28]. In addition, some non-noble metal catalysts (including Fe [29–31], Ni [18,32,33], Co [19,34], and Cu [35,36]) attract increasing attention owing to their considerable natural abundance, low cost, and competitive catalytic activity. However, the preparation of bimetallic catalysts with noble-free metal constituents is scarcely retrieved.

Herein, we reported a co-reduction method to prepare the ISOBAM-104 stabilized Co/Fe colloidal catalysts, which were then used for the hydrogen production from KBH$_4$ hydrolysis. The effects of the molar ratio of ISOBAM-104 to metal ion, concentration of metal ion, and molar ratio of Co/Fe were investigated. The as-synthesized ISOBAM-104 stabilized Co$_{10}$Fe$_{90}$ colloidal catalysts possess an unexpected catalytic activity for hydrogen production from KBH$_4$ hydrolysis at room temperature. The activation energy of the as-prepared Co$_{10}$Fe$_{90}$ colloidal catalysts towards KBH$_4$ hydrolysis was calculated by the Arrhenius formula. In addition, the electronic property of metal atoms was investigated based on the DFT calculations.

2. Experimental Section

2.1. Materials

Potassium borohydride (KBH$_4$), sodium hydroxide (NaOH), iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) and cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. ISOBAM-104 (NO. 52032-17-4, Figure S1) was purchased from Kuraray Co., Ltd., Tokyo, Japan. The deionized water was produced via a PINGGUAN ultrapure water purification system (Wuhan, China).

2.2. Preparation of Co/Fe Colloidal Catalysts and Hydrogen Generation

Firstly, certain concentrations of Co(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O solution were mixed together in a three-neck flask (Figure S2). Next, a certain amount of ISOBAM-104 was added into the flask and it was then filled with deionized water to 50 mL. After that, the mixed solution was continuously stirred for 24 h at room temperature. Subsequently, the configured KBH$_4$ and NaOH solution were rapidly added into the above solution to obtain ISOBAM-104 protected Co/Fe BNPs.

The influence of the molar ratio of ISOBAM-104 to metal ion concentration (denoted as $R_{ISO}$, from 10 to 80), metal ion concentration (from 0.6 to 1.5 mM), and chemical composition (Fe, Co$_{10}$Fe$_{90}$, Co$_{30}$Fe$_{70}$, Co$_{50}$Fe$_{50}$, Co$_{70}$Fe$_{30}$, Co$_{90}$Fe$_{10}$, and Co) were investigated. The detailed batch compositions are shown in the Table S1. The volume of generated H$_2$ was measured by an electronic balance, which was automatically recorded based on the displacement level of water every two seconds. During this process, the generated gas was passed through a trap containing concentrated H$_2$SO$_4$ to remove H$_2$O and any NH$_3$ that might have been generated. The rate of hydrogen generation ($k$, mL-H$_2$·min$^{-1}$) could be obtained from the slope of H$_2$ volume–time curve in the initial stage of the reaction.

The catalytic activity (mL-H$_2$·min$^{-1}$·g·cat$^{-1}$) could be calculated by the ratio of the hydrogen generation rate ($k$) to the mass of catalyst (m). It should be noted that the ISOBAM-104 used in this work contains the NH$_4^+$ group, which also possesses a catalytic effect for KBH$_4$ hydrolysis [19,37]. Therefore, under the same condition, the catalytic activities of ISOBAM-104 stabilized Co/Fe colloidal catalysts and ISOBAM-104 (NH$_4^+$ group) were measured. The intrinsic catalytic activity value of Co/Fe colloidal catalysts were obtained by subtracting the value of ISOBAM-104 from that of ISOBAM-104 stabilized catalysts. All the catalytic experiments were repeated no less than three times under the identical condition. The average values, which were normalized to mL-H$_2$·min$^{-1}$·g·Co$^{-1}$, were
used to determine the catalytic activity (detailed calculation procedures are provided in the
supporting information).

2.3. Material Characterization

UV-vis absorption spectra were recorded at 200–800 nm by a Shimadzu UV-2550
spectrophotometer (Shimadzu Company, Kobe, Japan). Transmission electron microscopy
(TEM) and high-resolution transmission electron microscopy (HRTEM) images were col-
clected by using a JEM-2100F (JEOL Company, Tokyo, Japan). The average size of the
nanoparticles in each sample was estimated by measuring at least 200 particles from differ-
ent parts of the grid. Fourier transform infrared (FTIR) spectra were obtained on a FTIR
spectrometer (VERTEX 70, Bruker Corporation, Karlsruhe, Germany), and the samples
were embedded in KBr pellet. X-ray photoelectron spectroscopy (XPS) measurements
were performed on a VG MultiLab 2000 instrument (Thermo Electron Corporation, Mas-
sachusetts, USA) equipped with a 300 W Al Ka excitation source. The obtained XPS spectra
were calibrated using a reference energy of 284.6 eV for the C 1s level and analyzed by
Avantage software.

2.4. Density Functional Theory (DFT) Calculation

The spin-polarized density functional theory (DFT) calculations were carried out
using a generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE)
exchange-correlation functional [38], as implemented in the DMol³ package (BIOVIA Com-
pany, San Diego, CA, USA) [39]. The double numerical basis set and polarization functions
(DNP) were carried out to describe the valence electrons, and an electron relativistic core
treatment was used to perform full optimization of the investigated cluster model of
Co₆Fe₄₉ BNP without symmetry constraint. The convergence criteria were set to medium
quality with a tolerance for the self-consistent field (SCF), optimization energy, maximum
force, and maximum displacement of 10⁻⁵ Ha, 2 × 10⁻⁵ Ha, 0.004 Ha/Å and 0.005 Å,
respectively. The charge analysis was performed on the basis of the Mulliken population
distribution scheme [40,41].

3. Results and Discussion

3.1. Effect of R_ISO on the Activity of Co/Fe Colloidal Catalysts

To explore the optimized reaction condition, the effect of R_ISO on the preparation and
catalytic activity of the Co/Fe BNPs was systematically investigated. The TEM images
(Figure 1) and size distribution histograms (Figure S3) indicate that the average particle
sizes of Co₅₀Fe₅₀ BNPs are about 4.6 nm (R_ISO = 10), 3.7 nm (R_ISO = 30), 3.2 nm (R_ISO = 50),
and 2.3 nm (R_ISO = 80), respectively. Obviously, the average particle size decreases with
the increase of R_ISO value, which may be ascribed to the fact that the increase of the
protective agents could provide a large number of −COO⁻ and −NH₂ groups to prevent
the agglomeration of particles. Figure 2 displays the catalytic activities of the obtained
Co₅₀Fe₅₀ colloidal catalysts for hydrogen production at different R_ISO. It can be clearly
observed that the Co₅₀Fe₅₀ colloidal catalysts with R_ISO = 50 possess a higher catalytic
value (17,500 mL-H₂ min⁻¹ g-Co⁻¹) than those synthesized at R_ISO = 10, 30, and 80 (6800,
6600, and 5500 mL-H₂ min⁻¹ g-Co⁻¹, respectively). This result may be attributed to the
fact that Co₅₀Fe₅₀ nanoparticles cannot receive effective protection at low R_ISO and are
prone to agglomeration, leading to a low catalytic activity. Comparatively, when R_ISO was
superfluous, the surface of the nanoparticles would be covered by ISOBAM-104, resulting
in the decrease of active sites and catalytic activity [28]. Thus, based on the above results,
the Co₅₀Fe₅₀ catalysts with moderate particle size and high catalytic activity could be
synthesized when R_ISO = 50.
Figure 1. TEM images of Co$_{50}$Fe$_{50}$ colloidal catalysts with various $R_{ISO}$ ([Co$^{2+}$ + Fe$^{3+}$] = 0.9 mM; $R_{ISO} = 10$ (a), 30 (b), 50 (c), and 80 (d)). (D$_{av}$: average particle size; S: standard deviation).

Figure 2. Comparison of catalytic activity of Co$_{50}$Fe$_{50}$ colloidal catalysts with varied $R_{ISO}$ ([Co$^{2+}$ + Fe$^{3+}$] = 0.9 mM).

3.2. Effect of Metal Ion Concentration on the Activity of Co/Fe Colloidal Catalysts

The effect of ion concentration on the preparation and catalytic activity of Co$_{50}$Fe$_{50}$ colloidal catalysts was also investigated. TEM morphologies and size distribution histograms of the as-prepared Co$_{50}$Fe$_{50}$ BNPs are presented in Figure 3 and Figure S4. The average particle sizes are about 2.3, 3.2, 2.6, and 3.4 nm at the metal ion concentrations of 0.6, 0.9, 1.2, and 1.5 mM, respectively. It is found that the metal ion concentration exerts a significant influence on the particle size of the obtained catalysts. Although the Co$_{50}$Fe$_{50}$ BNPs with the smaller particle sizes are obtained at the metal ion concentrations of 0.6 mM, the low concentration of metal ion impedes the large-scale preparation of catalysts. Hence, the concentration of metal ion is set as 1.2 mM in the following discussion.
Figure 3. TEM images and size distribution histograms of Co\textsubscript{50}Fe\textsubscript{50} colloidal catalysts synthesized with different ion concentrations ([Co\textsuperscript{2+} + Fe\textsuperscript{3+}] = 0.6 (a), 0.9 (b), 1.2 (c), and 1.5 (d) mM). (D\textsubscript{av}: average particle size; S: standard deviation).

3.3. Effect of Chemical Composition on the Activity of Co/Fe Colloidal Catalysts

The UV-vis spectra of the obtained Co/Fe BNPs with various compositions are shown in Figure S5. It was found that no surface plasma resonance peak of Fe or Co nanoparticles could be detected, which agrees with the previous reports [26,27,42]. The spectra of the dispersed Co/Fe nanoparticles BNPs with a featureless absorbance were located between the spectra of single Co and Fe nanoparticles, exhibiting a featureless absorbance. These obvious differences of the absorbance at various Fe content suggest the formation of alloy-structured Co/Fe BNPs. Figure 4 presents the TEM images of the obtained Co/Fe BNPs at various Co/Fe atomic ratios. It can be clearly seen that the particles possessed a sphere-like morphology. The average sizes of ISOBAM-104 stabilized Fe, Co\textsubscript{10}Fe\textsubscript{90}, Co\textsubscript{30}Fe\textsubscript{70}, Co\textsubscript{50}Fe\textsubscript{50}, Co\textsubscript{70}Fe\textsubscript{30}, Co\textsubscript{90}Fe\textsubscript{10}, and Co colloidal catalysts are respectively about 3.0, 3.2, 2.6, 2.6, 2.2, 2.5, and 1.8 nm (Figure S6). The corresponding catalytic activities of the above colloidal catalysts are displayed in Figure 5. By comparison, the above-mentioned Co/Fe BNPs presented a superior catalytic activity than that of Co or Fe MNPs. More importantly, the catalytic activity of the Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts reaches up to 37,900 mL-H\textsubscript{2} min\textsuperscript{-1} g-Co\textsuperscript{-1}, which is about 5 and 4 times higher than that of Fe (7400 mL-H\textsubscript{2} min\textsuperscript{-1} g-Fe\textsuperscript{-1}) and Co (9600 mL-H\textsubscript{2} min\textsuperscript{-1} g-Co\textsuperscript{-1}), respectively. Based on the above results, the desirable Co/Fe colloidal catalysts with high catalytic performance can be synthesized at the chemical composition of Co\textsubscript{10}Fe\textsubscript{90}, R\textsubscript{ISO} = 50, and ion concentrations of 1.2 mM.
Figure 4. TEM images of Co/Fe colloidal catalysts synthesized with various chemical compositions ($R_{ISO} = 50$, $[\text{Co}^{2+} + \text{Fe}^{3+}] = 1.2 \text{ mM}$). ($D_{av}$: average particle size; $S$: standard deviation).

Figure 5. Comparison of catalytic activity of Co/Fe colloidal catalysts with various chemical compositions ($R_{ISO} = 50$, $[\text{Co}^{2+} + \text{Fe}^{3+}] = 1.2 \text{ mM}$).
The structure of the obtained Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts was further characterized by the high-resolution transmission electron microscope (HRTEM). As shown in Figure 6, the interplanar spacings of the four individual randomly-chosen Co/Fe BNPs are measured as 0.168, 0.172, 0.174, and 0.169 nm, respectively. These values are inconsistent with the theoretical interplanar spacing values of Co and Fe (Table S2). However, it is worth noting that this measured interplanar spacing located between the interplanar distance of Co (200) and Fe (200) (Table S3), suggests the alloy structure of the formed Co/Fe BNPs.

Figure 6. HRTEM images (a–d) of Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts (R\textsubscript{ISO} = 50, [Co\textsuperscript{2+} + Fe\textsuperscript{3+}] = 1.2 mM). (HRTEM images of a–d correspond to four individual randomly-chosen Co/Fe bimetallic nanoparticles.).

In order to understand the protecting role of ISOBAM-104 in the catalysts stabilization, the FTIR spectra of ISOBAM-104 stabilized Co/Fe catalysts, ISOBAM-104, Co(NO\textsubscript{3})\textsubscript{2}, and Fe(NO\textsubscript{3})\textsubscript{3} are displayed in Figure S7. The absorption peak at 1400, 1680, 2300, and 3400 cm\textsuperscript{-1}, respectively, correspond to the stretching vibration of –OH, –COOH, –CO\textsubscript{2}, and the –NH\textsubscript{2} group of ISOBAM-104. By comparison, it can be clearly seen that the –COOH group of ISOBAM-104 disappeared, while the –OH and –NH\textsubscript{2} group still appeared in the ISOBAM-104 stabilized Co/Fe catalysts, demonstrating that the –NH\textsubscript{2} group in ISOBAM-104 should play a protective role on the as-prepared metal catalysts\cite{18}.

3.4. Kinetic Study and Catalytic Mechanism of Co/Fe Colloidal Catalysts

To calculate the apparent activation energy (\(E_a\)), the catalytic performance of Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts were evaluated under the perturbation of the reaction temperature. As shown in Figure S8, it can be seen that the catalytic activity of the Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts increases from 8400 to 15,200 mL-H\textsubscript{2} min\textsuperscript{-1} g-catalyst\textsuperscript{-1} as the temperature increases from 293 to 308 K. The \(E_a\) is calculated by using the Arrhenius method\cite{43}. As shown in Figure 7, the slope of the linear curve between the natural logarithm of catalytic activity and the reciprocal of temperature is \(-E_a/R\), where R is the universal gas constant. The calculated \(E_a\) of Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts is 14.6 ± 0.7 kJ mol\textsuperscript{-1}, which is much lower than most of the reported metal-based catalysts (Table 1). Interestingly, the corresponding catalytic activity of the Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts is much higher than these metal-based catalysts. Thus, it can be confirmed that the excellent catalytic activity of Co\textsubscript{10}Fe\textsubscript{90} colloidal catalysts is closely related to the lower activation energy towards KBH\textsubscript{4} hydrolysis.
Figure 7. The apparent activation energy ($E_a$) of Co$_{10}$Fe$_{90}$ colloidal catalysts for KBH$_4$ hydrolysis at 293–308 K.

Table 1. Comparison of the apparent activation energy between the Co$_{10}$Fe$_{90}$ colloidal catalysts and other catalysts in the previously reported literature.

| Catalyst | Reactant | Activation Energy (kJ mol$^{-1}$) | Catalytic Activity (mL-H$_2$ min$^{-1}$ g-cat.$^{-1}$) | Reference |
|----------|----------|----------------------------------|--------------------------------------------------|-----------|
| Co/Fe    | KBH$_4$  | 14.6                             | 37,900                                           | Present work |
| Ni       | KBH$_4$  | 41.3                             | 12,400                                           | [18]       |
| Rh/Ni    | KBH$_4$  | 47.2                             | 11,580                                           | [27]       |
| Co-O-P   | NaBH$_4$ | 63                               | 4880                                             | [44]       |
| Ag/Ni    | NaBH$_4$ | 16.2                             | 2333                                             | [45]       |
| Co-Ni-P  | NaBH$_4$ | 31.2                             | 6681                                             | [46]       |
| Co-B     | NaBH$_4$ | 37.57                            | 2649                                             | [47]       |
| Co-B     | NaBH$_4$ | 30                               | 5310                                             | [48]       |
| CoO–Co$_2$P | NaBH$_4$ | 27.4                             | 3940                                             | [49]       |

An XPS measurement was subsequently carried out to clarify the elemental composition and valence state of the Co$_{10}$Fe$_{90}$ BNP s. In Figure S9a, the element of Co, Fe, O, N, C, and B are detected in the obtained Co/Fe colloidal catalysts. The high-resolution XPS spectra of Co 2p (Figure S9b) shows that the electron binding energy of Co$^{0}$ 2p$_{3/2}$ (776.0 eV) is about 2.3 eV lower than that of the bulk Co (778.3 eV), indicating a negatively-charged characteristic of Co atoms in Co$_{10}$Fe$_{90}$ BNP s. Meanwhile, the electron binding energy of Fe$^{0}$ 2p$_{3/2}$ (708.5 eV) was about 1.8 eV higher than that of the bulk Fe (706.7 eV), suggesting that the Fe atoms were positively charged (Figure S9c). The negative shift of the Co$^{0}$ 2p$_{3/2}$ binding energy and positive shift of the Fe$^{0}$ 2p$_{3/2}$ binding energy might be ascribed to the electron charge transfer occurring between Fe and Co atoms [23,24,26,50,51]. To further confirm the electron transfer effect, DFT calculations were employed to investigate the electronic states of each atom in the Co$_{6}$Fe$_{49}$ alloy nanoparticles [52]. As shown in Figure 8a, the Co atoms are negatively charged (−0.091 eV), while the Fe atoms are positively charged (0.029 or 0.021 eV), which is matched well with the above XPS result. Based on above discussions and the related literature [23,27], a plausible mechanism for the high catalytic performance of Co/Fe colloidal catalysts could be proposed. Due to the charge transfer between Fe atoms and Co atoms (Figure 8b), the negatively charged Co atoms are conducive to the fracture of H–O bonds in H$_2$O molecules, and the positively charged Fe atoms could promote the B–H bond breaking in KBH$_4$ molecules. As a result, the catalytic activity of Co/Fe colloidal catalysts for KBH$_4$ hydrolysis could be markedly enhanced under the synergistic effect of Fe and Co atoms.
4. Conclusions

In summary, the ISOBAM-104 stabilized Co/Fe colloidal catalysts are successfully synthesized for hydrogen generation by a simple co-reduction method via using ISOBAM-104 as a protective agent, and Co(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and KBH$_4$ as starting materials. The catalytic activities of the obtained Co/Fe colloidal catalysts could reach up to 37,900 mL-H$_2$ min$^{-1}$ g-Co$^{-1}$ at the chemical composition of Co$_{10}$Fe$_{90}$, $R_{ISO} = 50$, and ion concentrations of 1.2 mM, which is superior to their corresponding monometallic nanoparticles. The excellent catalytic activity of Co$_{10}$Fe$_{90}$ colloidal catalysts is mainly attributed to their lower activation energy towards KBH$_4$ hydrolysis, and the charge transfer effect between Fe and Co atoms. This finding could provide a deeper insight for developing the economic, highly active, and recyclable bimetallic catalysts.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12172998/s1, Figure S1: The chemical structure of ISOBAM-104; Figure S2: The schematic diagram of experimental device for KBH$_4$ hydrolysis reaction; Figure S3: Particles size distribution histograms of Co$_{50}$Fe$_{50}$ colloidal catalysts with various $R_{ISO}$ ([Co$^{2+}$ + Fe$^{3+}$] = 0.9 mM; $R_{ISO} = 10$ (a), 30 (b), 50 (c), and 80 (d)); Figure S4: Particles size distribution histograms of Co$_{50}$Fe$_{50}$ colloidal catalysts synthesized with various ion concentrations ($R_{ISO} = 50$; [Co$^{2+}$ + Fe$^{3+}$] = 0.6 (a), 0.9 (b), 1.2 (c), and 1.5 (d) mM); Figure S5: UV–vis spectra of Co/Fe BNPs, Co and Fe nanoparticles; Figure S6: Particles size distribution histograms of Co/Fe colloidal catalysts synthesized with various chemical compositions ($R_{ISO} = 50$; [Co$^{2+}$ + Fe$^{3+}$] = 1.2 mM); Figure S7: FTIR spectra of ISOBAM-104, Co(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and Co$_{10}$Fe$_{90}$ colloidal catalysts; Figure S8: Effect of temperature on the catalytic performance of Co$_{10}$Fe$_{90}$ colloidal catalysts; Figure S9: XPS spectra of Co$_{50}$/Fe$_{50}$ colloidal catalysts: (a) total spectra, (b) Co 2p, and (c) Fe 2p; Table S1: Batch compositions and processing conditions for the preparation of ISOBAM-104 stabilized Co/Fe colloidal catalysts; Table S2: Lattice spacing and indexed reflection planes of Co and Fe; Table S3: Lattice spacing and indexed reflection planes of Co/Fe colloidal catalysts determined by HRTEM.

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