Enhanced Catalytic Hydrogenation Performance of Rh-Co₂O₃ Heteroaggregate Nanostructures by in Situ Transformation of Rh@Co Core–Shell Nanoparticles

Qiuyang Zhang,† Caiyun Xu,† Hongfeng Yin,*‡ and Shenghu Zhou*‡

†Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China
‡Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo, Zhejiang 315201, P. R. China

Supporting Information

ABSTRACT: In this work, poly(vinylpyrrolidone)-stabilized 3–5 nm Rh@Co core–shell nanoparticles were synthesized by a sequential reduction method, which was further in situ transformed into Rh-Co₂O₃ heteroaggregate nanostructures on alumina supports. The studies of XRD, HAADF-STEM images with phase mappings, XPS, TPR, and DRIFT-IR with CO probes confirm that the as-synthesized Rh@Co nanoparticles were core–shell-like structures with Rh cores and Co-rich shells, and Rh-Co₂O₃ heteroaggregate nanostructures are obtained by calcination of Rh@Co nanoparticles and subsequent selective H₂ reduction. The Rh-Co₂O₃/Al₂O₃ nanostructures demonstrated enhanced catalytic performance for hydrogenations of various substituted nitroaromatics relative to individual Rh/Al₂O₃ and illustrated a high catalytic stability during recycling experiments for o-nitrophenol hydrogenation reactions. The catalytic performance enhancement of Rh-Co₂O₃/Al₂O₃ nanocatalysts is ascribed to the Rh-Co₂O₃ interaction not only prevents the active Rh particles from agglomeration but also promotes the catalytic hydrogenation performance.

1. INTRODUCTION

Catalytic hydrogenation of substituted nitroaromatics has been widely used to manufacture the corresponding substituted anilines, the intermediates for syntheses of pharmaceuticals, pesticides, and dyes.1−14 Typically, supported noble metals such as Pd5,6 and Pt7−10 are efficient catalysts for hydrogenations of substituted nitroaromatics but with relatively low selectivity due to nonselective coordination of functional groups. To improve the catalytic performance of noble metals, bimetallic nanocatalysts are developed to exploit the metal–metal interaction to improve the catalytic selectivity.11−15 For example, bimetallic PtSn nanocatalysts exhibit enhanced selectivity of crotyl alcohol for hydrogenation of crotonaldehyde due to the Pt-Sn synergic effect.16

Among various bimetallic nanostructures with enhanced catalytic performances, nanostructures containing metals and metal oxides have been intensively studied because the metal–metal oxide interfaces are highly active for some hydrogenation reactions.7,17−21 In the traditional strong metal–support interaction catalysts (SMSI), reducible supports such as TiO₂,22−25 CeO₂,26−28 and ZrO₂,29−31 are usually employed, where reducible supports are partially reduced by H₂ at high temperatures and subsequently the partially reduced support species migrate onto metal surfaces to form metal–support interfaces that are highly active for some types of hydrogenation reactions.32,33 However, the requirement of reducible supports limits the use of readily available nonreducible Al₂O₃ or SiO₂ supports in this system. To apply alumina or silica in SMSI catalysts, one methodology is to prepare alumina- or silica-supported bimetallic nanoparticles (NPs) where those bimetallic NPs are further transformed into metal–metal oxide heteroaggregate nanostructures on supports.34−36

Here, we report the synthesis of alumina-supported Rh-Co₂O₃/Al₂O₃ heteroaggregate nanocatalysts by in situ transformation of Rh@Co NPs. Rh has demonstrated excellent chemical and electrochemical stability37,38 and has been widely used in many catalytic and electrocatalytic reactions.39−41 However, Rh is rarely used in the catalytic hydrogenation of substituted nitroaromatics due to its lower efficiency than those Pd or Pt catalysts. In this study, to enhance its activity for nitroaromatic hydrogenations, we prepared Rh-Co₂O₃ heteroaggregate nanostructures by transformation of Rh@Co NPs. The 3–5 nm Rh@Co NPs were prepared by a sequential reduction method, which was further in situ transformed into Rh-Co₂O₃ heteroaggregate nanostructures by calcination and following selective H₂ reduction. Scheme 1 illustrates the synthetic procedures of Rh-Co₂O₃ heteroaggregate nanostructures. Hydrogenations of various substituted nitroaromatics were chosen to investigate the correlation between catalytic performance and catalyst structures. Compared with individual

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Rh/Al\textsubscript{2}O\textsubscript{3} nanocatalysts, the Rh-Co\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts demonstrate enhanced catalytic activities as well as selectivity for hydrogenations of a series of substituted nitroaromatics. Characterization and catalytic results suggest that the synergistic effect between Co\textsubscript{2}O\textsubscript{3} and Rh not only stabilizes the active Rh particles but also promotes the hydrogenation activity and selectivity.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Various Materials. Rh@Co core-shell-like NPs were synthesized by a seed-mediated growth method. PVP-stabilized Rh NPs were synthesized by reduction of Rh\textsubscript{2}(COOCF\textsubscript{3})\textsubscript{4} using EG as a reduction agent and a solvent, which was further used as a seed to deposit Co onto Rh surfaces by reduction of Co(acac)\textsubscript{2} using NaBH\textsubscript{4} as the reduction agent. The Rh-Co\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} nanocatalysts were obtained by in situ transformation of Rh@Co/Al\textsubscript{2}O\textsubscript{3} through calcination at 500 °C followed by H\textsubscript{2} reduction at 250 °C.

Figure 1 presents XRD patterns of Rh NPs, Rh@Co NPs, and Rh-Co\textsubscript{2}O\textsubscript{3} NPs. The Rh-Co\textsubscript{2}O\textsubscript{3} NPs are obtained by calcination of Rh@Co NPs at 550 °C and following H\textsubscript{2} reduction at 250 °C. As shown in Figure 1a, the Rh NPs show well-defined fcc structures with characteristic diffractions at 41.0, 47.6, and 69.6°. While the Rh (111) diffractions in Rh@Co NPs are clearly observed in Figure 1b, the Co diffractions are not observed, which possibly suggests a core-shell-like structure with pure Rh cores and amorphous Co shells. After calcination of Rh@Co NPs and following H\textsubscript{2} reduction, the Rh diffractions in Rh-Co\textsubscript{2}O\textsubscript{3} NPs appear without Co\textsubscript{2}O\textsubscript{3} diffractions, indicating heteroaggregate nanostructures consisting of Rh and amorphous Co\textsubscript{2}O\textsubscript{3} phases. A similar phenomenon has been reported in the literature. The absence of Co diffractions in Rh@Co NPs and Co\textsubscript{2}O\textsubscript{3} diffractions in Rh-Co\textsubscript{2}O\textsubscript{3} is due to the small sizes of Co and Co\textsubscript{2}O\textsubscript{3} phases with less crystallization, and the enrichment of the Co element in outer layers will be confirmed by HAADF-STEM with phase mappings and XPS studies.

To further confirm the core–shell structure of Rh@Co NPs, HAADF-STEM studies with elemental phase mappings were performed. Figure 4a–d shows the HAADF-STEM images of Rh@Co NPs and their corresponding Rh mapping, Co mapping, and the combined Rh/Co mapping, respectively. It is apparent that the Co mapping (Figure 4c) is bigger than the Rh mapping (Figure 4b), indicating the presence of Co in the shells. Moreover, the combined Rh and Co mapping in Figure 4d clearly demonstrates a core–shell structure of Rh@Co NPs with Rh cores and Co shells and is consistent with the their corresponding particle size histograms are presented in Figure 3a–d, respectively. As shown in Figures 2a and 3a, the Rh NPs are relatively spherical with an average particle size of ~4.0 nm. The inset of Figure 2a shows a lattice spacing of 0.228 nm, which is consistent with 0.227 nm of Rh (111) planes. The Rh@Co NPs in Figure 2b are spherical with an average particle size of ~4.2 nm. The inset in Figure 2b presents the Rh (111) lattice of 0.229 nm for Rh@Co NPs, suggesting phase-pure Rh cores. The TEM images/particle size analyses of Rh/Al\textsubscript{2}O\textsubscript{3} and Rh-Co\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} are illustrated in Figures 2c/3c and 2d/3d, respectively. After calcination and following reduction, the Rh particle size of Rh/Al\textsubscript{2}O\textsubscript{3} increases from ~4.0 nm (Figure 3a) to ~5.2 nm (Figure 3c), suggesting a size increase after thermal treatment. In contrast, the average particle size changes from ~4.2 nm in Figure 3b to ~4.3 nm in Figure 3d. Due to the small contrast between Co\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}, the size analysis in Figure 3d is ascribed to the Rh size in Rh-Co\textsubscript{2}O\textsubscript{3} nanostructures. The nearly same particle size before and after high-temperature treatment suggests that the Rh-Co\textsubscript{2}O\textsubscript{3} interaction can prevent the Rh NPs from agglomeration.
sequential reduction method using Rh seeds. The EDS linescan of Rh@Co NPs is shown in Figure S1 and is consistent with the phase mapping, further confirming the formation of core−shell structures.

The XPS spectra of Rh@Co and Rh-Co2O3 are shown in Figure 5a,b, respectively, where Rh-Co2O3 is prepared by calcination and following reduction of as-synthesized Rh@Co NPs. The aforementioned samples were unsupported in order to obtain a better XPS signal/noise ratio. The method of Doniach and Sunjic was used for XPS curve fitting. The binding energy assignment is in accordance with those in the literature.43−45 As shown in Figure 5a, the binding energies at 307.1/311.8 and 308.1/312.8 eV in Figure 5a can be ascribed to 3d5/2/3d3/2 of metallic Rh and oxidized Rh 3+ species, respectively, while the binding energies at 778.1/793.1 and 780.3/795.8 eV could be assigned to 2p3/2/2p1/2 of Co0 and Co3+ species, respectively.46−48 In addition, a broad satellite peak at 783.6/802.0 eV is assigned to 2p3/2/2p1/2 of Co2O3.
suggesting that the Co ions are primarily in a high-spin electronic state.47,49,50

As for the XPS spectra of Rh-Co2O3 NPs in Figure 5b, the binding energies at 307.1/311.9 and 309.0/313.7 eV can be assigned to 3d5/2/3d3/2 of Rh0 and oxidized Rh3+ species, respectively. The Co binding energies at 781.2/796.7 and 784.7/802.4 eV are ascribed to 2p3/2/2p1/2 of Co3+ and Co3+ satellite peaks, respectively. The only presence of Co3+ species is observed in Figure 5b, suggesting that calcination at 550 °C results in the complete oxidation of Co species and the following 250 °C H2 reduction cannot reduce the Co3+ species.

Table 1 summarizes the atomic ratios for different species. For Rh@Co NPs, 29.3% of Rh3+ species is observed due to the air exposure, while 77.1% of Co atoms are in the oxidation state due to air exposure. It is well known that Co is an active metal and the metallic Co NPs will be oxidized to form cobalt oxide NPs due to air exposures. Therefore, it is reasonable that the oxidized cobalt accounts for the largest percentage in XPS studies. Similarly, 30.6% of Rh3+ species is present in Rh-Co2O3 due to the surface oxidation when NPs are exposed to air. The total Co/Rh ratios of Rh@Co and Rh-Co2O3 NPs by XPS analysis are 2.3/1.0 and 2.5/1.0, respectively, while those by EDS analysis are 1.1/1.0 (1/1 ratio of the starting materials). Since XPS is a surface-sensitive technique and EDS is a bulk technique, the significantly higher Co/Rh ratios for Rh@Co and Rh-Co2O3 suggest core−shell-like structures of Rh@Co and Rh-Co2O3 NPs with nearly pure Rh cores and Co-rich shells.

Figure 6a shows the TPO study of Rh@Co/Al2O3. The O2 consumption peaks appear below 500 °C, confirming the complete oxidation of Co and Rh in Rh@Co NPs by 500 °C calcination.51−53 H2-TPR profiles of Rh2O3-Co2O3/Al2O3 are presented in Figure 6b. A consumption peak at ~77 °C is due to the reduction of Rh2O3.52,54,55 Moreover, H2 consumption peaks at ~282, ~422, and ~658 °C are the reduction peaks of Co3O4, CoO36, and CoO, respectively.56,57 It is concluded that only Rh will be reduced to form Rh-Co2O3/Al2O3 in the reduction of Rh2O3-Co3O4/Al2O3 at 250 °C with H2, which is consistent with the XPS study of Rh-Co2O3 where only Co3+ species were observed for Rh-Co2O3 NPs.

Figure 7 shows DRIFT-IR spectra with CO probes of Rh/Al2O3, Rh@Co/Al2O3, and Rh-Co2O3/Al2O3. As shown in Figure 7a (Rh/Al2O3), two characteristic bands at 1906 and 2018 cm−1 are clearly observed: the former is ascribed to bridge CO on Rh sites, and the latter can be attributed to linear CO on Rh sites.58 Figure 7b shows the DRIFT-IR spectrum of Rh@Co/Al2O3. The 1885 cm−1 peak for bridge CO on Rh sites and 2019 cm−1 peak for linear CO on Rh sites are clearly observed, while the bands at 1652 and 2177 cm−1 are the characteristic bands of bridged and linear CO on Co sites, respectively.59−63 The copresence of CO bands on Co and Rh sites in Figure 7b indicates that the shells are Co-rich (not pure Co). Accordingly, as shown in Figure 7c, after calcination and subsequent reduction of Rh@Co/Al2O3, the Rh-Co2O3/Al2O3 shows the bands at 1640 and 2183 cm−1, which can be attributed to CO on Co sites, while the bands at 1885, 2019, and 2066 cm−1 are ascribed to CO on Rh sites.58 Again, the copresence of Co and Rh in Rh-Co2O3/Al2O3 by the DRIFT-IR study indicates Rh-Co2O3 heteroaggregate nanostructures with some naked Rh surfaces.

### Table 1. Atomic Ratios of Co/Rh by XPS and EDS Analysis

| samples     | Co0/Co3+ | Rh0/Rh3+ | Co/Rh (XPS) | Co/Rh (EDS) |
|-------------|----------|----------|-------------|-------------|
| Rh@Co       | 22.9/77.1| 70.8/29.3| 2.3/1.0     | 1.1/1.0     |
| Rh-Co2O3    | 0.0/100.0| 69.4/30.6| 2.5/1.0     | 1.1/1.0     |

Figure 7. DRIFT-IR spectra with CO probes: (a) Rh/Al2O3; (b) Rh@Co/Al2O3; (c) Rh-Co2O3/Al2O3.

2.2. Catalytic Performances of Rh-Co2O3/Al2O3 and Rh/Al2O3 Nanocatalysts. Catalytic hydrogenations of various substituted nitroaromatics over Rh-Co2O3/Al2O3 were carried out with vigorous magnetic stirring under the reaction conditions of 45 °C and atmospheric H2 pressure.
theoretical Rh loadings Rh-CoO₃/Al₂O₃ and Rh/Al₂O₃ are both 0.5 wt %, and the real Rh loadings of Rh-CoO₃/Al₂O₃ and Rh/Al₂O₃ are 0.40 and 0.47 wt %, respectively.

The hydrogenation of m-chloronitrobenzene (m-CNB) over Rh-CoO₃/Al₂O₃ nanocatalysts with Rh/Co ratios of 2/1, 1/1, and 1/2 is shown in Table S1, and we denote the abovementioned catalysts as 2/1-Rh-CoO₃/Al₂O₃, Rh-CoO₃/Al₂O₃, and 1/2-Rh-CoO₃/Al₂O₃, respectively. The major product in catalytic hydrogenation of m-CNB is m-chloroaniline (m-CAN) and the main by-products are the intermediates during the hydrogenation process as well as the aniline from the hydrodechlorination reactions. As shown in Table S1, compared with 2/1-Rh-CoO₃/Al₂O₃ and 1/2-Rh-CoO₃/Al₂O₃, the Rh-CoO₃/Al₂O₃ catalysts illustrate a significantly enhanced performance with an m-CNB conversion of 99.6% and m-CAN selectivity of 97.0%. The comparison suggests that a ratio of Rh/Co of 1/1 is desired, and higher or lower ratios of Rh/Co result in poor catalytic performance due to a weaker Rh-CoO₃ interaction or less exposed Rh surfaces, respectively. Therefore, Rh-CoO₃/Al₂O₃ catalysts were selected for hydrogenations of a series of substituted nitroaromatics. Moreover, as shown in Table S2, individual CoO₃/Al₂O₃ shows no activity, and the physical mixtures of Rh/Al₂O₃ and CoO₃/Al₂O₃ show a similar activity to that of individual Rh/Al₂O₃ indicating that any catalytic enhancement of Rh-CoO₃ should originate from the close-contact Rh-CoO₃ heteroaggregate nanostructures.

Table 2 presents the catalytic performance of Rh-CoO₃/Al₂O₃ catalysts. For o- and m-CNB hydrogenations, the Rh-CoO₃/Al₂O₃ nanocatalysts exhibit a high catalytic activity and selectivity. For hydrogenations of o- and m-CNB, Rh-CoO₃/Al₂O₃ shows a 99.9% o-CNB conversion with 99.8% of o-CAN selectivity even at a relatively low Rh loading, while the control Rh/Al₂O₃ presents 20.7% of conversion with 76.3% of selectivity. For hydrogenations of o- and p-NP, Rh-CoO₃/Al₂O₃ also demonstrates enhanced activities and selectivity relative to control Rh/Al₂O₃, confirming the beneficial effect of CoO₃/Al₂O₃ on the catalytic performance due to the Rh-CoO₃ interaction. This interaction could induce a blockage effect where the decoration of metal oxide onto active metals will selectively facilitate the coordination of the desired functional groups, resulting in enhanced selectivity.

The effects of reaction time on o-NP conversion and o-AP selectivity over Rh-CoO₃/Al₂O₃ nanocatalysts are shown in Figure S2. With increasing reaction time, the conversion of o-NP increases from 8.0% at 0.5 h to 100.0% at 4.0 h, while o-AP selectivity remains at nearly 100% during the hydrogenation process, suggesting a fast process from the intermediates to the final product o-aminophenol. The effects of temperatures and catalyst weights on catalytic hydrogenation of o-NP over Rh-CoO₃/Al₂O₃ are highly stable with 100% of o-NP conversion and above 98.7% of o-AP selectivity, strongly suggesting a good structural stability of Rh-CoO₃ heteroaggregate nanostructures.

3. CONCLUSIONS

In summary, Rh@Co core–shell-like NPs were successfully prepared by a sequential reduction method, and Rh-CoO₃/Al₂O₃ heteroaggregate nanocatalysts were synthesized by in situ transformation of Rh@Co NPs on Al₂O₃ supports. Various characterizations confirm that the Rh@Co NPs consist of pure Rh cores and Co-rich shells, and Rh-CoO₃ NPs are close-contact heteroaggregate nanostructures. The Rh-CoO₃/Al₂O₃ nanocatalysts show enhanced catalytic activity and selectivity for the hydrogenations of o-CNB, m-CNB, o-NP, m-NP, and p-NP relative to the control Rh/Al₂O₃ nanocatalysts, and the catalytic performance enhancement of Rh-CoO₃/Al₂O₃ is ascribed to the strong Rh-CoO₃ interaction.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Cobalt acetylacetonate (Co(acac)₃, 98%), rhodium(II) trifluoroacetic emitter (Rh₂(OOCOCF₃)₄ GR), sodium trifluoroacetate (NaOOCOCF₃, >98%), sodium borohydride (NaBH₄ >96%), o-nitrophenol (o-NP, >99%), m-nitrotoluene (m-NP, >98%), p-nitrophenol (p-NP, >98%), o-chloronitrobenzene (m-CN, 98%), and m-chloronitrobenzene (m-CN, 98%) were purchased from Aladdin. Poly(vinylpyrrolidone) (PVP-K30, GR), triethylglycol (TREG, AR), ethylene glycol (EG, AR), absolute ethyl alcohol (AR), and acetone (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aluminum oxide powders calcined at 500 °C for 3 h were purchased from Qingdao Haiyang Chemical Co., Ltd. All of the reagents were used as received without further purification.
round-bottom 277.5 mg of PVP-K30 were charged into a 50 mL three-necked solids (0.05 mmol Rh) dispersed in 10.0 mL of TREG and were synthesized by a sequential reduction method. Rh NP ° min, the system was further heated to and maintained at 155 reduction of Rh precursors. After maintaining at 115 °C for 15 min, the system was heated to 115 °C with vigorous magnetic stirring under a nitrogen atmosphere. The color of the solution gradually changed from light blue to black, indicating the formation of Rh nanoparticles. The mixture was further cooled to room temperature, 45 °C for 20 min at a gas flow rate of 20 mL/min followed by cooling down to 30 °C. After the samples were purged with Ar at 30 °C for 20 min, the DRIFT-IR background spectrum was recorded. The samples were further treated with CO at a gas flow rate of 20 mL/min at 30 °C for 20 min and subsequently purged with Ar to remove the sample.

Table 3. Cycle to Cycle o-NP Hydrogenations over Rh-Co2O3/Al2O3 Catalysts

| cycle index | catalyst (g) | o-NP (%) | conversion (%) | o-NP selectivity (%) |
|-------------|--------------|----------|---------------|----------------------|
| 1           | 0.0905       | 0.905    | 100.0         | 100.0                |
| 2           | 0.0756       | 0.756    | 100.0         | 99.4                 |
| 3           | 0.0621       | 0.621    | 100.0         | 99.3                 |
| 4           | 0.0555       | 0.555    | 100.0         | 98.7                 |
| 5           | 0.0465       | 0.465    | 100.0         | 99.5                 |

4.2. Catalyst Preparation. 4.2.1. Synthesis of Rh NPs. Rh NPs were synthesized by a reported method. In a typical synthesis, 0.050 mmol of Rh(COOCF3)3, 277.5 mg of PVP-K30, 1.0 mmol of NaCOOCF3, and 10.0 mL of EG were transferred into a 50 mL three-necked round-bottom flask. The system was heated to 115 °C with vigorous magnetic stirring under a nitrogen atmosphere. The color of the solution gradually changed from light blue to black, indicating the reduction of Rh precursors. After maintaining at 115 °C for 15 min, the system was further cooled to and maintained at 155 °C for 75 min. The mixture was cooled to room temperature followed by centrifugation with acetone and ethyl alcohol three times to collect black solids for further characterization.

4.2.2. Synthesis of Rh@Co Core–Shell NPs. Rh@Co NPs were synthesized by a sequential reduction method. Rh NP solids (0.05 mmol Rh) dispersed in 10.0 mL of TREG and 277.5 mg of PVP-K30 were charged into a 50 mL three-necked round-bottom flask with vigorous magnetic stirring under a N2 atmosphere. The mixture was further heated to 175 °C, and then 0.05 mmol of Co(acac)2 in 1.0 mL of absolute methanol was injected into the system using a syringe followed by addition of 1.0 mmol of solid NaBH4. The mixture was maintained at 175 °C for 2 h to complete the reduction of Co precursors. The mixture was further cooled to room temperature followed by centrifugation with acetone and ethyl alcohol three times to collect black solids for further characterization.

4.2.3. Synthesis of Rh-Co2O3/Al2O3 and Rh/Al2O3 Nanocatalysts. The collected Rh@Co solids were dispersed in absolute ethanol in a 100 mL three-necked round-bottom flask, and a calculated amount of alumina (a Rh theoretical loading of 0.5 wt %) was added to the abovementioned colloid. The resultant mixture was further heated to 60 °C and purged with N2 to remove ethanol to obtain the gray Rh@Co2O3/Al2O3 materials, which was then calcined at 500 °C in air for 3 h and subsequently reduced in H2 at 250 °C for 3 h with a 50 v/v H2/N2 gas to give Rh-Co2O3/Al2O3 nanocatalysts.

The synthesis of Rh/Al2O3 nanocatalysts with a Rh theoretical loading of 0.5 wt % was the same as that of Rh-Co2O3/Al2O3 nanocatalysts except that the dispersed Rh ethanol colloids are used. The real metal loadings of Rh/Al2O3 and Rh-Co2O3/Al2O3 were determined by ICP-OES.

4.3. Catalyst Characterizations. X-ray diffraction (XRD) patterns of Rh, Rh@Co, and Rh-Co2O3 NPs were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation in the 2θ range from 20 to 90°. Transmission electron microscopy (TEM) images with energy-dispersive X-ray spectroscopy (EDS) were obtained by using a JEOL 2100 transmission electron microscope operated at 200 kV. The high-angle annular dark-field scanning transmission electron microscopy images (HAADF-STEM) with phase mappings were obtained using a Talos F200x, which is operated at 200 kV with 0.16 nm resolution for STEM images. X-ray photoelectron spectra (XPS) were obtained on an AXIS ULTRA DLD multifunctional X-ray photoelectron spectroscopy with an Al source. The instrument was calibrated by C 1s (284.8 eV), and the XPS data were processed using a Casa XPS software. The studies of O2 temperature-programmed oxidation (TPO) of Rh@Co/Al2O3 and H2 temperature-programmed reduction (H2-TPR) of Rh2O3-Co2O3/Al2O3 were performed on an Auto ChemII 2920 instrument. The diffuse reflectance Fourier transform infrared spectra (DRIFT-IR) with CO probes were obtained using a Nicolet-6700 Fourier transform infrared spectrometer with a resolution of 4 cm−1 and the number of scans of 32. At first, the materials were pretreated with H2 at 100 °C for 20 min at a gas flow rate of 20 mL/min followed by cooling down to 30 °C. After the samples were purged with Ar at 30 °C for 20 min, the DRIFT-IR background spectrum was recorded. The samples were further treated with CO (99.99%) at a gas flow rate of 20 mL/min at 30 °C for 20 min and subsequently purged with Ar to remove the sample.
the free CO before the DRIFT-IR spectra were recorded. The product analyses of catalytic hydrogenations of substituted nitroaromatics over Rh-Co2O3/Al2O3 and Rh/Al2O3 were performed by a GC 2060 gas chromatograph equipped with a flame ionization detector.

4.4. Catalyst Activity Measurements. The atmospheric H2 pressure and a vigorous magnetic stirring at 500 rpm are employed for hydrogenations of various substituted nitroaromatics with H2. Various substituted nitroaromatics (1.0000 g), supported catalysts (0.1000 g), and absolute ethanol (25 mL) were charged into a 100 mL three-necked round-bottom flask. The system was heated to and kept at a desired temperature under 0.1 MPa H2 for the defined reaction time. After the reaction was done, the solid catalysts were collected by centrifugation, and the liquid products were analyzed by a gas chromatograph. For recycling experiments, after each cycle, the solid catalysts were collected by centrifugation, washed with ethyl alcohol several times, and further dried in an oven at 60 °C overnight. In the next cycle experiment, the amounts of substituted nitroaromatics and solvents were decreased according to the weights of recovered catalysts to keep the ratios of reactant/catalyst and reactant/solvent constant.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03340.

More synthesis, EDS linescan of Rh@Co NPs, and more comparison of different catalysts (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: yinhf@nmtme.ac.cn (H.F.).
*E-mail: zhoushenghu@ecust.edu.cn. Fax: (+86) 21-64253159 (S.Z.).

ORCID

Shenghu Zhou: 0000-0002-8203-6546

Notes

The authors declare no competing financial interest.

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