



Dandelion-like cobalt oxide microsphere-supported RuCo bimetallic catalyst for highly efficient hydrogenolysis of 5-hydroxymethylfurfural

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ABSTRACT

Currently, renewable biomass-derived energy sources and related transformation technologies are attracting numerous attentions due to the rapid consumption of fossil fuels and resulting increasing environmental pollution. Herein, a new dandelion-like cobalt oxide (CoO_x) microsphere-supported bimetallic RuCo catalyst was fabricated by a simple one-pot embedding method and employed for the 5-hydroxymethylfurfural (HMF) hydrogenolysis to produce liquid 2,5-dimethylfuran (DMF) biofuel. It was found that bimetallic RuCo nanoparticles (NPs) with the average size of about 2.5 nm could homogeneously disperse on flower-like CoO_x microspheres possessing abundant surface defects (i.e. oxygen vacancies and Co^{2+} species) simultaneously constructed. As-fabricated RuCo/ CoO_x catalyst exhibited excellent catalytic performance in above reaction, along with a quite high DMF yield of 96.5% at a high HMF/Ru molar ratio of 252.7, which was correlated with the unique synergy between bimetallic RuCo NPs and abundant surface defects at the metal-support interface, as well as the enhanced hydrogen spillover effect and the dandelion-like superstructure of the catalyst. Additionally, the strong interactions between RuCo species and the CoO_x matrix in the RuCo/ CoO_x significantly prevented RuCo NPs from migration, aggregation, and leaching during the reaction. The present findings offer a new approach for designing other highly efficient and stable bimetallic catalysts applied in a variety of heterogeneous catalytic systems.

1. Introduction

Energy and environment have always been two essential elements for the development and survival of human society. Currently, non-renewable fossil fuels (i.e. coal, oil and natural gas) are rapidly depleted, which causes the emission of large quantities of toxic and hazardous substances in use [1,2]. To develop renewable alternatives to meet the growing energy demand and eliminate the resulting increasing environmental pollution, the innovation of new production routes and related technologies for transportation fuels through upgrading renewable biomass resources is attracting more and more attention in scientific and industrial communities [3–10]. For instance, 5-hydroxymethylfurfural (HMF), as one of the most important platform chemicals in the field of biomass transformation, can be obtained from biomass-derived carbohydrates [11–13]. Further, HMF can be converted to a variety of important chemicals, such as 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), 2,5-dihydroxymethylfuran (BHMF), 2,5-dihydroxymethyltetrahydrofuran (DHMTFH) and highly promising fuel additive 2,5-dimethylfuran

(DMF) [14–19]. Among these chemicals, DMF especially possesses unique properties including high energy density, high octane number and low boiling point, which are superior to those of ethanol. In a word, DMF is a more appropriate and promising renewable liquid transportation fuel than dominant ethanol liquid fuel.

At present, significant efforts have been made to explore catalytic hydrogenolysis of HMF to produce DMF using noble metal catalysts [15,20–25]. For example, Román-Leshkov et. al reported the HMF hydrogenolysis over CuRu/C catalysts, along with a 71% DMF yield using molecular hydrogen at 220 °C for 10 h [15], despite the easy deactivation of the catalyst. A Ru-doped hydrotalcite catalyst could afford a DMF yield of 58% at 220 °C for 4 h [20]. When using formic acid as hydrogen source and Pd/C catalysts, a high DMF yield of 95% could be achieved [21]. Recently, Abu-Omar et. al reported an effective bimetallic catalyst combination containing a Lewis-acidic Zn(II) and Pd/C components for this reaction [24]. In addition, the HMF hydrogenolysis was also conducted over copper-containing porous metal oxide (Cu-PMO) in supercritical methanol [26]. However, above most catalytic systems require harsh reaction conditions, such as high catalyst

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loading, high reaction temperatures and/or long reaction times, indicating that these catalysts are unfavorable for practical applications. Therefore, more efficient catalytic systems for HMF hydrogenolysis into DMF still need to be further explored.

As we know, surface geometric and electronic structures of catalysts have great influence on catalytic reactions [27]. In this regard, some reducible oxide supports (e.g. In_2O_3 [28], Co_3O_4 [29]) have been employed in hydrogenation reactions, thanks to the easy construction of surface oxygen vacancies (O_v). Recently, we also found that surface oxygen vacancies could be developed by the transformation of Mn^{3+} in supports to Mn^{2+} species [30]. Therefore, Mn^{2+} defects adjacent to oxygen vacancies could strongly interact with the oxygen atom in carbonyl group, thus resulting in the enhanced catalytic performance of Cu-based catalysts in the hydrogenation of dimethyl succinate. Therefore, to achieve the high efficiency of supported catalysts, finely controlling the microstructure of supports is of great importance.

Nowadays, bimetallic nanocatalysts are intensively investigated in a wide range of heterogeneous catalytic reactions [31,32], thanks to unique synergistic effects between two metals that can induce superior properties to their corresponding monometallic counterparts. In addition to the reduced cost of catalysts, the coordination of a base metal into precious metal can generate specific new active sites in bimetallic catalysts that originate from the unexpected electronic and geometrical effects between two metals. As for HMF hydrogenolysis to DMF, active hydrogen species need to selectively react with the formyl and hydroxyl groups without deep hydrogenation or ring-opening of furan. It was reported that bimetallic PtCo catalysts were effective for the reduction of C=O bond in α , β -unsaturated aldehydes, due to unique electronic and structural effects existing in PtCo nanoparticles (NPs) [33–35]. Moreover, in regards to supported bimetallic catalysts, the improvement in the dispersion and stability of bimetallic NPs remains a challenging task, despite successful synthesis of unsupported monometallic and bimetallic NPs [36–38].

Herein, we reported a facile one-pot embedding method (Scheme 1) for the synthesis of new bimetallic RuCo NPs embedded into dandelion-like CoO_x microspheres (RuCo/CoO_x). It was demonstrated that as-fabricated bimetallic RuCo catalyst with abundant surface $\text{Co}^{2+}-\text{O}_v-\text{Co}^{2+}$ defects could efficiently catalyze the HMF hydrogenolysis to produce DMF with a high DMF yield of 96.5% at a high HMF/Ru molar ratio of 252.7. Such high efficiency of the catalyst was correlated with the Ru-Co synergistic effect in RuCo NPs, favorable surface defects in proximal CoO_x sites, enhanced hydrogen spillover effect, as well as more active sites and reaction centers provided by the distinct dandelion-like nano/microstructure of CoO_x microspheres.

2. Experimental section

2.1. Synthesis of catalysts

RuCo/CoO_x sample with the theoretical Ru loading of 3 wt.% was prepared by our developed one-pot embedding method. Firstly, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (7 mmol), $\text{CO}(\text{NH}_2)_2$ (10.5 mmol) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.15 mmol) were dissolved in 80 mL of distilled water to form a red mixed solution. Then, the solution was transferred into an autoclave (100 mL) with a Teflon liner, followed by hydrothermal treatment at 165 °C for 6 h. The resulting dark red precipitate was separated by centrifugation and washed with distilled water and alcohol for several times until the pH = 7.0. The product was dried in a vacuum oven at 70 °C for 12 h and then calcined at 500 °C for 6 h with a ramp of 2 °C min^{-1} . Finally, the as-calcined $\text{RuO}_2/\text{Co}_3\text{O}_4$ sample was reduced in 10% H_2/N_2 atmosphere at 300 °C for 2 h at a ramp rate of 5 °C min^{-1} to obtain the resulting reduced sample (denoted as RuCo/CoO_x). In addition, pristine flower-like Co_3O_4 or $\text{Ru/Al}_2\text{O}_3$ sample was prepared by the above same method as that for $\text{RuO}_2/\text{Co}_3\text{O}_4$ in the absence of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ or as that for RuCo/CoO_x using $\text{Al}_2(\text{SO}_4)_3$ instead of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, respectively. And, Co/CoO_x sample was prepared using the same procedure as that for RuCo/CoO_x without the addition of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$.

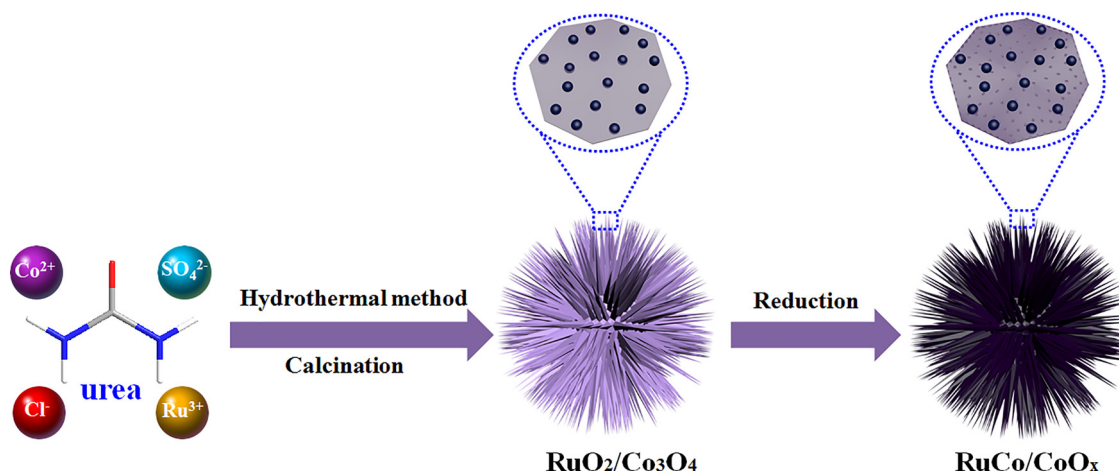
For comparison, $\text{Ru/Co}_3\text{O}_4\text{-B}$ and $\text{Ru/Co/CoO}_x\text{-B}$ samples with a Ru loading of 3 wt. % were prepared using NaBH_4 reducing agent. Firstly, Co/CoO_x (0.5 g) or flower-like Co_3O_4 (0.5 g) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ solution (0.15 mmol) were added into 100 mL of distilled water under ultrasonication for 1 h. Then, NaBH_4 aqueous solution was quickly added under vigorous stirring for 2 h. Afterwards, the obtained suspension was centrifuged, washed thoroughly and dried in a vacuum oven at 60 °C for 12 h.

2.2. Characterization

X-ray diffraction (XRD) data of samples were obtained at room time on a Shimadzu XRD-6000 diffractometer, using Cu K α radiation ($k = 0.154 \text{ nm}$) at 30 mA, 40 kV, a scanning rate of 10° min^{-1} , and a 2 θ angle ranging from 3° to 70°.

Elemental analysis of metal in samples was performed using a Shimadzu ICP-7500 inductively coupled plasma emission spectrometer (ICP-AES) after the samples were dissolved in nitrohydrochloric acid.

Low-temperature N_2 adsorption-desorption isotherms of the samples were obtained on a Micromeritics ASAP 2020 sorptometer apparatus. The total specific surface areas were evaluated with the multi-point Brunauer-Emmett-Teller (BET) method.



Scheme 1. The synthetic procedure for RuCo/CoO_x catalyst.

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