

Supporting Information

Synergism of ultrafine RuCo alloy nanoparticles on graphite carbon nitride for efficient ammonia borane hydrolysis

Yating He, Ziqian Wang, Mingyue Mao, Qianggen Li* and Guangyin Fan*

College of Chemistry and Materials Science, Sichuan Normal University, Chengdu

610068, China

* Corresponding author

Email: liqgen@sicnu.edu.cn (Q. Li); fanguangyin@sicnu.edu.cn (G. Fan)

Experimental

Materials and Reagents

Ruthenium chloride hydrate (Ru wt%: 38.5%), cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and urea were purchased from Aladdin Bio-Chem Technology Co., Ltd (China). AB complex (90%) was obtained from Aldrich.

Characterization

Transmission electron microscope (TEM) images were obtained on a JEOL JEM-2100 FEGTEM under 200 Kv FE. Powder X-ray diffraction (XRD) was performed on Rigaku D/Max-2400X with Cu Ka radiation. X-ray photoelectron spectrometry (XPS) analysis was carried out on an ESCALABMKLL X-ray photoelectron spectrometer using an Al Ka source. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 870 instrument. The concentration of metals in the catalyst was measured via inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 8000 equipment).

Preparation of g-C₃N₄

The matrix g-C₃N₄ was prepared as the following procedure. A covered crucible loaded with 10g urea (10 g) was calcined at 773 K for 4 h in air atmosphere in a muffle furnace, with a heating rate of 2.5 K/min. The obtained yellow solid powder was used as matrix to encapsulate the bimetallic RuCo alloy NPs to catalyze AB hydrolysis with the in-situ reduction method.

Catalytic procedure

10 mg matrix was added into a 25 mL double neck flask containing 4 mL deionized water and then a certain volume of the precursors of Ru^{3+} (5mg/mL) and Co^{2+} (5mg/mL) were put into the flask. Then the mixture was treated by ultrasonication for 30 mins to get a uniform suspension. 1mL AB solution (1 mM) was injected into the flask to start the hydrolysis reaction while keeping the temperature at 298 K in water bath. The hydrogen released was collected and recorded by water-displacement method. The hydrolysis conditions of the contrast catalysts with different matrixes are consistent with the above conditions.

The various catalysts of $\text{Ru}_x\text{Co}_{1-x}/\text{g-C}_3\text{N}_4$ were prepared by changing the volume of the precursors. Considering the $\text{Ru}_{0.1}\text{Co}_{0.9}/\text{g-C}_3\text{N}_4$ catalyst has the highest catalytic activity, the study of mechanism of AB concentration was conducted at 298 K while the other conditions unchanged. The influence of temperature was explored at different temperatures (298, 303, 308, and 313 K) and further calculating the activation energy of AB hydrolysis over the $\text{Ru}_{0.1}\text{Co}_{0.9}/\text{g-C}_3\text{N}_4$ catalyst while controlling other conditions unchanged. Durability testing was carried out for AB hydrolysis over the optimal $\text{Ru}_{0.1}\text{Co}_{0.9}/\text{g-C}_3\text{N}_4$ for four times. Another fresh 1 mL AB solution (1 mM) was injected to begin another run of AB hydrolysis after finishing the previous run.

Calculation

The TOF value was determined on the basis of the reported literature using the eq.(S1)

$$TOF = \frac{P_{atm} V_{H_2} / RT}{n_{Ru} t} \quad (S1)$$

where P_{atm} is the atmospheric pressure (101325 Pa), V_{H_2} is the volume of generated hydrogen when conversion rate of 50%, R represents the ideal gas constant (8.314 J

$\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the reaction temperature (K), n_{Ru} is the total mole number of Ru atoms in catalyst, and t is the reaction time.

Table S1. Comparison of the catalytic efficiency of nanocatalyst.

Catalysts	Atomic ratios ^a	Initial TOF (min ⁻¹)	Revised TOF (min ⁻¹)
Ru/g-C ₃ N ₄	-	701	732
Ru _{0.05} Co _{0.95} /g-C ₃ N ₄	5:92	784	817
Ru _{0.1} Co _{0.9} /g-C ₃ N ₄	9:87	1210	1260
Ru _{0.15} Co _{0.85} /g-C ₃ N ₄	14:81	1090	1135
Ru _{0.2} Co _{0.8} /g-C ₃ N ₄	19:76	812	845
Co/g-C ₃ N ₄	-	-	-

^a Measured by ICP-OES