



Bimetallic Ru–Cu as a highly active, selective and stable catalyst for catalytic wet oxidation of aqueous ammonia to nitrogen



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ARTICLE INFO

Article history:

Received 20 September 2015

Received in revised form

16 November 2015

Accepted 21 November 2015

Keywords:

Catalytic wet air oxidation

Aqueous ammonia

Bimetallic Ru–Cu/C catalyst

Oxygen property

ABSTRACT

Ru/C, Cu/C and bimetallic Ru–Cu/C catalysts are prepared via chemical reduction methods and investigated for catalytic wet oxidation of aqueous ammonia to nitrogen. It is found that the as-prepared bimetallic Ru–Cu/C catalyst is very active and selective as well stable as for selective oxidation of aqueous ammonia toward nitrogen at rather mild conditions. The results show that the Ru–Cu/C catalyst is much more efficient especially stable than the corresponding monometallic Ru/C and Cu/C catalysts, indicating the synergistic effect of Cu and Ru. These catalysts are characterized by XRD, XPS, TEM, and H₂–TPR, and the results are revealed that there is strong interaction between Ru and Cu over Ru–Cu/C catalysts and the co-presence of Ru and Cu can effectively adjust the reactivity and converge of oxygen species as well as protect the Ru and Cu from leaching. The strong interaction, synergistic effect, proper oxygen nature and ability against leaching could be attributed to the excellent catalytic property of Ru–Cu/C catalyst.

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1. Introduction

Ammonia in wastewater not only causes serious eutrophication problems but also has toxic and harmful effects on aquatic life and human beings. With the increasing environmental concerns, the abatement of aqueous ammonia has become a critical issue. Conventionally, biological and chemical treatment processes are adopted [1–5] to convert it to harmless nitrogen. Compared with these traditional methods, catalytic wet air oxidation (CWAO) is a much more efficient and environmental-friendly technology for ammonia wastewater treatment [6], in which ammonia can be directly and selectively converted to N₂ over proper catalysts.

Various types of catalytic materials have been investigated for catalytic wet oxidation of aqueous ammonia to N₂. Among these materials, noble metals such as Ru, Pd and Pt, were widely used as active catalysts due to their superior catalytic performance. Qin et al. obtained 99% ammonia removal with 2 g of Pd or Ru (3 wt%)/Al₂O₃ catalyst for 100 mL of ammonium chloride solution (NH₃: 1695 mg/L, pH 12.3) at 230 °C in a batch reactor, in which both

Pd and Ru/Al₂O₃ can convert 99% ammonia to N₂ at 230 °C with the addition of NaOH in order to adjust the pH [7]. In another work [8], Pt/TiO₂ catalyst could completely convert NH₄⁺ to N₂ at 200 °C and 36 bar of air. However, clearly the works on reported literature using precious metal catalysts can only be worked under rather severe conditions (temperature >150 °C and/or pressure >1.0 MPa) and the metal loading is usually as high as 3 wt% (as listed in Table 1), these limit their pave toward industrial applications. Transition metal based catalysts were also utilized due to much lower cost although they are usually at the same time much lower activity than precious metals. Using transition metal alone, e.g., a Ni/Al₂O₃ catalyst, only 21% of ammonia was removed even at 230 °C and 2.0 MPa [9]. Co/Ce, Mn/Ce composite oxides [10] and Mn, Co, Mo, Fe, Cr supported on activated carbon [11] or Al₂O₃ [12] have also been used in the CWAO of ammonia. The results show that these catalysts have no activity when reaction temperature below 250 °C, which further confirms the necessity of noble metals in the CWAO of ammonia if low reaction temperature is required. In order to reduce the costs of catalyst and operation to make the CWAO processes economical feasible and sustainable, more effective catalysts which can work under relative mild reaction conditions at the same time with precious metal loadings as less as possible are urgently needed. However, preparing such catalysts is a very challenging work.

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Based on the reported research works, the oxidizing capability of catalyst plays the crucial role to determine the catalytic performance to convert ammonia to nitrogen via CWAQ. Proper oxygen species is necessary not only for activation of ammonia but also for selective oxidation of ammonia to nitrogen, instead of nitrite and nitrate ions. Qin et al. reported that only those metals including Pd and Ru with moderate oxygen affinity can become the good catalysts for the CWAQ of ammonia [7]. Similarly, Lousteau et al. studied Pt, Pd, Ir, Rh and Ru supported catalysts in the CWAQ of ammonia [13] and established the relationship between the oxygen coverage at the catalyst surface and the catalytic performance, concluding that only the catalysts with appropriate values of metal oxygen bond energy had optimal activity and N₂ selectivity. Generally, surface oxygen over noble metals exhibit higher reaction activity than that over transition metals while transition metals present higher surface oxygen concentration than noble metals. It is reasonable to infer that the activity and concentration of the surface oxygen may be tuned by the coexisting of precious and transition metals if the structure is carefully designed. In fact, transition metals (Fe, Co, Ni, Cu et al) have often been used as promoters to enhance catalytic performances of noble metal catalysts for the reactions involving oxygen activation [14]. Our previous works also revealed that transition metal can tune Pt-based catalyst's oxophilicity (playing a role in maneuvering surface oxygenated species) and thus the catalytic performance of CO oxidation reaction [15,16]. Therefore, it can be expected that the combination of precious and transition metals would adjust the oxidizing capacity of surface oxygen and thus result in much better catalytic performance for CWAQ ammonia to nitrogen while significantly reducing the use of noble metals in the catalysts. However, for the best of our knowledge, there is virtually no such a report on the application of bimetallic catalysts for CWAQ of ammonia to nitrogen. As can also be seen in Table 1, the CWAQ catalysts used in literature either one noble or transition metal, or bi-noble metals or bi-transition metals, but never use of noble-transition metals together. Furthermore, it is hardly to find reported literature on catalyst stability in CWAQ of ammonia.

It was reported that supported-Ru catalyst presented excellent catalytic performance for CWAQ of ammonia to N₂ [7,13,17]. For the transition metals, Cu is one of the most prospective species to compete with noble metals for CWAQ [6]. Therefore, in this paper, Ru and Cu are combined to adjust the surface oxygen property with the purpose of obtaining more efficient and stable catalysts with much lower Ru loading for catalytic wet air oxidation of ammonia to nitrogen, and Ru/C and Cu/C monometallic catalysts were also studied for comparison. The results indicated that Ru–Cu/C bimetallic catalyst exhibited excellent catalytic performance under relative mild conditions. Characterizations including XRD, H₂ temperature-programmed reduction (H₂-TPR), XPS and TEM were performed to discover the relationship between the catalytic performance and physicochemical properties.

2. Experimental

2.1. Catalyst preparation

Ru–Cu bimetallic catalysts were prepared by a chemical reduction method, using CuCl₂•2H₂O, RuCl₃•3H₂O and BP2000 as active metal precursors and support, respectively. Typically, 0.5 g BP2000 was added into 150 mL solution of CuCl₂•2H₂O (containing the desired Cu). After adjusting the pH to 10 by ammonia, the mixture was stirred for 3.5 h at room temperature. Then desired hydrazine was added to reduce Cu²⁺ to Cu. Two hours later, the 7.65 mL solution of RuCl₃•3H₂O (containing the desired Ru) was added to the mixture. It is worth to point out that ammonia concentration is insufficient for the complexation of cupric ions if pH in the solution is lower than 8, and cuprous oxide, which will weaken the interaction between Cu and Ru, will be produced. After stirring 16 h at room temperature, the mixture was filtered and washed by deionized water. The resultant solid was dried at 60 °C for 24 h. Finally, the solid was calcined in a flow of pure H₂ at 250 °C for 4 h. The obtained catalyst was denoted as xRu–yCu/C, where x and y refer to the mass percent of Ru and Cu. 3Ru/C and 3Cu/C catalysts were prepared by a similar procedure but only Ru or Cu metal precursor was added.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were obtained with a Panalytical X'pert Pro diffractometer operated at 40 kV and 30 mV, using Cu K α radiation. The images of TEM were gained on a Tecnai F30 electron microscope (Phillips Analytical) operated at an acceleration voltage of 300 kV. X-ray photoelectron spectra (XPS) were recorded on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K α radiation (1846.6 eV) as the X-ray source. The metal leaching was measured by inductively coupled plasma mass spectrometry (ICP-MS).

For H₂-temperature programmed reduction (TPR), 50.0 mg sample was placed in a quartz reactor as a shallow packed bed, heated in a pure O₂ at 150 °C for 2 h and cooled down to room temperature. After the gas was switched to 7.0% H₂/Ar, the temperature was increased to 400 °C at the rate of with 10 °C/min.

2.3. Apparatus and procedure

The reaction procedure in this work is similar to Lee's work [24]. The difference is that the total volume of the reactor was 100 mL. Generally 0.5 g catalyst and 50 mL solution with 1000 ppm ammonia were added into the reactor for every reaction through this paper. All reactions were carried out in a stainless steel reactor with 100 mL capacity volume and a magnetic spin bar was used for stirring. The reactor was coated with Teflon liner 2 mm thick inside to avoid corrosion of the reactor wall. The pH of the

Table 1
Summary of reported studies on CWAQ of ammonia to N₂.

Catalyst	Metal loading	Reaction condition	Reference
Ru, Pd supported on Al ₂ O ₃	3%	200–230 °C, 1.5 MPa of O ₂	[7]
Ru/TiO ₂	3%	200 °C, 0.5 MPa of O ₂	[17]
Pt/TiO ₂ , Pt/ZrO ₂	3%	200 °C, 5.0 MPa of air	[8]
Pt, Ru, Pd, and Ru–Pd on CeO ₂	5% for Ru and Pd, 10% for Pt	120–230 °C, 2.0 MPa of O ₂	[18]
Pt–Pd–Rh composite washcoated on γ -Al ₂ O ₃	6.4%	150–230 °C, 2.0 MPa of O ₂	[19]
Pt, Pd, Ru, Rh, Ir supported on TiO ₂ and ZrO ₂	2.5%–3%	200 °C, 5.0 MPa total pressure	[13]
Cu–La–Ce composite coated on cordierite	15%–50%	150–200 °C, 3.0 MPa of O ₂	[20]
Cu/ACF	15%–25%	150–190 °C, 3.0 MPa of O ₂	[21]
Cu/ACF	15%–25%	150–190 °C, 2.0–5.0 MPa of O ₂	[22]
Co-precipitated transition metal–aluminium catalyst (transition metal: Cu, Ni, Co, Fe, and Mn)	No support	230 °C, 2.0 MPa of air	[23]
Ni/Al ₂ O ₃	20%	230 °C, 2.0 MPa of air	[9]
Cu, Co, Mo, Mn, Ru	3%–7%	200 °C, 0.42 MPa of O ₂	[11]

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