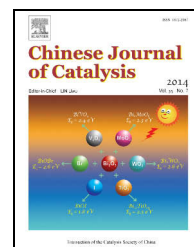


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## Article

# Study of catalytic activity and product selectivity of M/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (M = Pt-Ru, Ru, and Pt) in catalytic wet air oxidation of methylamine

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## ARTICLE INFO

## Article history:

Received 28 January 2014

Accepted 21 March 2014

Published 20 July 2014

## Keywords:

Dispersion

Hysteresis

Platinum

Ruthenium

Catalytic wet air oxidation

Methylamine

## ABSTRACT

M/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (M = Pt-Ru, Ru, and Pt) catalysts were prepared using an impregnation method. Their catalytic performance in catalytic wet air oxidation (CWAO) of methylamine was compared. The catalysts were characterized using temperature-programmed reduction, X-ray photoelectron spectroscopy, X-ray diffraction, transmission electron microscopy, N<sub>2</sub> adsorption, and CO chemisorption. The experimental results indicated that the dispersion of active species in the Pt-Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst was greatly improved by the introduction of Pt; therefore, its catalytic performance was significantly enhanced. Temperature-dependent activity showed hysteresis over the catalysts, indicating that CWAO of methylamine followed a chemisorption mechanism.

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## 1. Introduction

The release of large amounts of wastewater containing organic pollutants causes severe environmental problems. The development of highly efficient, green, environmentally friendly methods for treating wastewater is therefore an important challenge. To date, many techniques have been used to treat the organic pollutants in aqueous phases, such as physicochemical treatments, biological methods, and chemical oxidation processes [1–3]. Catalytic wet air oxidation (CWAO), which is an efficient and promising technique for wastewater treatment, can oxidize highly concentrated organic pollutants (chemical oxygen demand 10–100 g/L) to biodegradable intermediates

or completely to CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O with oxygen or with oxygen in the air at mild temperatures (80–300 °C) under pressure of 0.5–6 MPa. CWAO is thus considered an effective method for treating organic pollutants in water [4,5].

Homogeneous catalysts such as Cu, Fe, and Mn salts are generally efficient because they are in direct contact with the pollutants in reaction media [6]. However, these salts are difficult to separate from the treated effluent and recycle, which may cause secondary pollutions and increase the process cost. In contrast, heterogeneous catalysts can be easily recovered, regenerated, and reused. Heterogeneous catalysts have therefore attracted much attention in CWAO research in recent decades. The heterogeneous catalysts used in the CWAO process

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This work was supported by the National Basic Research Program of China (973 Program, 2013CB632404, 2009CB220003), the National Natural Science Foundation of China (21373245, 21173242, 2012AA051501), and the Project Support of Gansu Provincial Science & Technology Department (1304FKCA085).

DOI: 10.1016/S1872-2067(14)60091-7 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 7, July 2014

can be divided into transition-metal oxides and supported noble metals. Transition-metal oxides such as CuO, Co<sub>3</sub>O<sub>4</sub>, and NiO are cheap but not very active, and are quickly deactivated as a result of leaching of active species under the harsh reaction conditions [7–11]. Supported noble metals such as Pt, Ru, and Pd are expensive, but they are much more active and stable than transition-metal oxides; they show particularly good activity in the CWAO of refractory compounds [12].

It is well known that the catalytic activity of a heterogeneous catalyst can be tuned by appropriate selection of factors such as the synthetic approach, precursor, support, and second component [13–20]. Among these, the introduction of a second component is an effective and convenient method for promoting the catalytic activity; for example, Cuauhtémoc *et al.* [21] reported that the introduction of a Sn component enhanced the activity and selectivity of a Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst for the CWAO of *tert*-amyl methyl ether. Barbier *et al.* [22] found that introduction of Pd into a Ru/CeO<sub>2</sub> catalyst contributed to the formation of N<sub>2</sub> in the CWAO of ammonia.

In this work, catalysts Pt-Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> were prepared using an impregnation method, and their catalytic performance in the CWAO of methylamine (MA) was tested. The catalyst structures were determined using temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), N<sub>2</sub> adsorption, and CO chemisorption. Correlations of the structural properties and catalytic performance showed that Pt-Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> has the best catalytic activity for the CWAO of MA because it has the highest dispersion of active species and can be efficiently promoted by the introduction of a Pt component into the Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst.

## 2. Experimental

### 2.1. Preparation of Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and M/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalysts

All reagents were of analytical reagent grade. Commercial Al<sub>2</sub>O<sub>3</sub> (>95%, spherical, Kaixin Al<sub>2</sub>O<sub>3</sub> Co., Ltd., China) was crushed to about 25–45 mesh and calcined at 600 °C for 6 h prior to use. The Al<sub>2</sub>O<sub>3</sub> particles were modified with CeO<sub>2</sub> using an impregnation method. Al<sub>2</sub>O<sub>3</sub> particles (30 g) were impregnated overnight with an aqueous solution (30 mL) containing CeN<sub>3</sub>O<sub>9</sub> (2.85 g) and then dried at 120 °C for 12 h, followed by calcination in air at 600 °C for 6 h.

Pt-Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalysts were also prepared by impregnation using H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and RuCl<sub>3</sub>·xH<sub>2</sub>O as the Pt and Ru precursors, respectively. The total metal loadings on the three catalysts were fixed at 5 wt% with respect to Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>; for the preparation of the Pt-Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst, the mass ratio of Pt:Ru was 1:1. Briefly, after impregnation of the modified Al<sub>2</sub>O<sub>3</sub> particles (10 g) with a precursor solution (10 mL) containing the desired amount of H<sub>2</sub>PtCl<sub>6</sub> and/or RuCl<sub>3</sub>, the precursor catalysts were dried at 120 °C for 8 h, calcined at 300 °C for 8 h, and reduced in H<sub>2</sub> flow (40 mL/min) at 300 °C for 6 h. For simplicity, the prepared catalysts were denoted by Pt-Ru, Pt, and Ru for

Pt-Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and Ru/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, respectively.

### 2.2. Catalytic activity evaluation

The catalytic activity of the three catalysts was tested in an automated and computer-controlled continuous-flow catalytic evaluation apparatus specifically designed for heterogeneous catalysts (Pengxiang Technology Company, Tianjin, China); a schematic diagram is shown in Fig. 1. Briefly, a premixed MA solution (2400 ± 120 mg/L) was introduced into the vaporizing chamber using a peristaltic infusion pump (Lab Alliance Series I, USA). After vaporizing, the mixture of MA and steam was merged with an oxygen stream (300 mL/min) in a T-joint and then introduced into the reaction tube, which was charged with catalyst (10 mL). The gases and steam, which passed over the catalyst bed and reacted at the desired temperature, and then flowed out at the bottom of the reactor, were cooled with a cold trap and separated in a gas-liquid separator. The reaction liquid at the outlet was periodically extracted from the liquid collector and analyzed for total organic carbon (TOC), organic product, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> contents.

The TOC was measured using an Analytik Jena Multi N/C 2100 TOC analyzer (Analytik Jena, Germany). The organic products were determined by gas chromatography-mass spectrometry (GC-MS) using an Agilent 7890A system with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 mm), coupled with an Agilent 5975 mass spectrometer. The concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> in the collected liquid were determined colorimetrically according to the Chinese National Standard (GB/T 5750-2006) method. The concentration of N<sub>2</sub> was calculated from the material balance of N atoms. The TOC conversion (which indicates the catalytic activity) and the N species selectivity (which indicates the selectivity) are expressed as follows:

$$\text{Activity (\%)} = (1 - \text{TOC}_{\text{det}}/\text{TOC}_{\text{ini}}) \times 100\%$$

$$\text{Selectivity (\%)} = (n_{\text{liq}}(\text{N})/n_{\text{ini}}(\text{MA})) \times 100\%$$

$$\text{or Selectivity (\%)} = (2 \times n(\text{N}_2)/n_{\text{ini}}(\text{MA})) \times 100\%$$

where TOC<sub>ini</sub> is the initial TOC concentration, TOC<sub>det</sub> is the de-

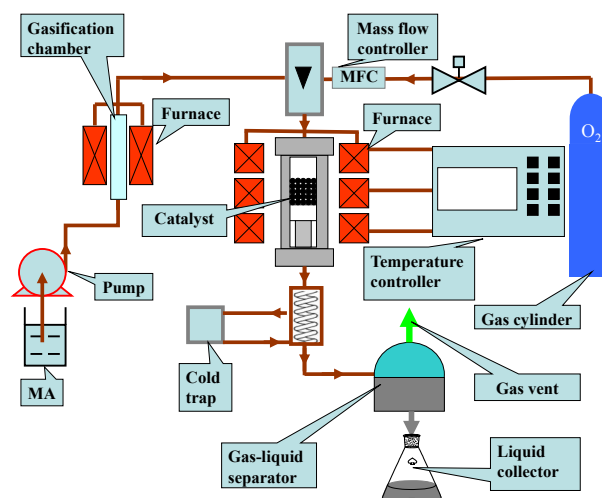


Fig. 1. Schematic diagram of setup for CWAO of MA.

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