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Article

Study of catalytic activity and product selectivity of M/Al₂O₃-CeO₂ (M = Pt-Ru, Ru, and Pt) in catalytic wet air oxidation of methylamine

Aiying Song^{a,b,c}, Gongxuan Lü^{a,*}^aState Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China^bChemical Physics Laboratory, Gansu Provincial Center for Disease Control and Prevention, Lanzhou 730020, Gansu, China^cUniversity of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

M/Al₂O₃-CeO₂ (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, N₂ adsorption, and CO chemisorption. The experimental results indicated that the dispersion of active species in the Pt-Ru/Al₂O₃-CeO₂ 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 CO₂, N₂, and H₂O 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

*Corresponding author. Tel/Fax: +86-931-4968178; E-mail: gxlu@lzb.ac.cn

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can be divided into transition-metal oxides and supported noble metals. Transition-metal oxides such as CuO, Co₃O₄, 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/ γ -Al₂O₃-CeO₂ catalyst for the CWAO of *tert*-amyl methyl ether. Barbier *et al.* [22] found that introduction of Pd into a Ru/CeO₂ catalyst contributed to the formation of N₂ in the CWAO of ammonia.

In this work, catalysts Pt-Ru/Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂, and Ru/Al₂O₃-CeO₂ 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), N₂ adsorption, and CO chemisorption. Correlations of the structural properties and catalytic performance showed that Pt-Ru/Al₂O₃-CeO₂ 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/Al₂O₃-CeO₂ catalyst.

2. Experimental

2.1. Preparation of Al₂O₃-CeO₂ and M/Al₂O₃-CeO₂ catalysts

All reagents were of analytical reagent grade. Commercial Al₂O₃ (>95%, spherical, Kaixin Al₂O₃ Co., Ltd., China) was crushed to about 25–45 mesh and calcined at 600 °C for 6 h prior to use. The Al₂O₃ particles were modified with CeO₂ using an impregnation method. Al₂O₃ particles (30 g) were impregnated overnight with an aqueous solution (30 mL) containing CeN₃O₉ (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/Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂, and Ru/Al₂O₃-CeO₂ catalysts were also prepared by impregnation using H₂PtCl₆·6H₂O and RuCl₃·xH₂O as the Pt and Ru precursors, respectively. The total metal loadings on the three catalysts were fixed at 5 wt% with respect to Al₂O₃-CeO₂; for the preparation of the Pt-Ru/Al₂O₃-CeO₂ catalyst, the mass ratio of Pt:Ru was 1:1. Briefly, after impregnation of the modified Al₂O₃ particles (10 g) with a precursor solution (10 mL) containing the desired amount of H₂PtCl₆ and/or RuCl₃, the precursor catalysts were dried at 120 °C for 8 h, calcined at 300 °C for 8 h, and reduced in H₂ 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/Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂, and Ru/Al₂O₃-CeO₂, 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, NH₄⁺, NO₂⁻, and NO₃⁻ 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 NH₄⁺, NO₂⁻, and NO₃⁻ in the collected liquid were determined colorimetrically according to the Chinese National Standard (GB/T 5750-2006) method. The concentration of N₂ 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_{ini} is the initial TOC concentration, TOC_{det} is the de-

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

terminated TOC concentration, $n_{\text{q}}(\text{N})$ is the mole of nitrogenous products, $n_{\text{ini}}(\text{MA})$ is the initial mole of MA, and $n(\text{N}_2)$ is the mole of N_2 .

2.3. Catalyst characterization

XPS was performed on a K-Alpha-Surface Analysis System (Thermo Scientific) with Mg K_{α} radiation, and the binding energy was directly referenced to the C 1s peak at 284.6 eV. XRD patterns were recorded using a Rigaku B/Max-RB diffractometer with Ni-filtered Cu K_{α} radiation operated at 40 kV and 40 mA. TEM and high-resolution TEM (HRTEM) were performed using a Tecnai G² F30 field-emission transmission electron microscope operated at an accelerating voltage of 300 kV. The specific surface area, total pore volume, and average pore width of the supports and catalysts were determined from the N_2 adsorption and desorption isotherms at $-196\text{ }^{\circ}\text{C}$ using a Micromeritics ASAP 2010 instrument. H_2 -TPR experiments were performed by passing a stream of 5% H_2 -95% Ar (15 mL/min) through the catalysts (50 mg). The temperature was increased from 50 to 500 $^{\circ}\text{C}$ at a linearly programmed rate of 10 $^{\circ}\text{C}/\text{min}$. A thermal conductivity detector was used to determine the amount of H_2 consumed. The amounts of CO chemisorbed on the catalysts were measured using a Micromeritics Chemisorb 2750 automated system.

3. Results and discussion

3.1. Catalytic activity evaluation

3.1.1. Influence of temperature on catalytic activity

Figure 2(a) and (b) shows the changes in TOC conversion and N_2 selectivity with temperature over the Pt-Ru, Pt, and Ru catalysts. It can be seen that the TOC conversion and N_2 selectivity increased with increasing reaction temperature. Clearly, the catalytic activity of Pt-Ru and Ru were higher than that of Pt in the CWAQ of MA in the examined temperature ranges. MA was totally mineralized at 210 and 230 $^{\circ}\text{C}$ over Pt-Ru and Ru, respectively; however, the temperature required to decompose MA fully over Pt was 260 $^{\circ}\text{C}$. It can be seen from Fig. 2(b) that the temperatures required for $\sim 100\%$ N_2 selectivity over the catalysts were completely consistent with those for total degradation of MA. This indicates that high activity corresponds to high N_2 selectivity; a similar phenomenon was observed by Garcia *et al.* [23] during the CWAQ of aniline. These results suggest that Ru is much more efficient than Pt, and that Pt-Ru has the best catalytic activity in MA degradation. In addition, the turnover frequency (TOF) values for the Pt-Ru, Pt, and Ru catalysts were 51, 35, and 160 h^{-1} , respectively, at 210 $^{\circ}\text{C}$, indicating that the metal atoms in the Ru-based catalysts are much more active than those in the Pt-based ones.

The stability of the catalysts was investigated by performing endurance tests for 300 h at 210, 260, and 230 $^{\circ}\text{C}$, and at liquid hourly space velocity (LHSV) of 5.4 h^{-1} , for Pt-Ru, Pt, and Ru, respectively. The TOC conversions and N_2 selectivities basically remained at $\sim 100\%$ during the entire time on stream, showing that all the catalysts have good stability in the CWAQ of MA.

Interestingly, obvious temperature-dependent hysteresis of the TOC conversion and N_2 selectivity was observed over the three catalysts; for example, over the Pt-Ru catalyst, the TOC conversion decreased from 88% to 45% as the temperature decreased from 200 to 160 $^{\circ}\text{C}$, and it was only possible to achieve the same TOC conversion when temperature was increased from 175 to 205 $^{\circ}\text{C}$. These results indicate that the CWAQ of MA may follow a chemisorption-type mechanism. A possible explanation of the hysteresis is as follows: the concentration of activated oxygen species is high at high temperatures, and the adsorbed oxygen molecules may not be desorbed from the catalyst surface during cooling until the temperature has been at a certain temperature for a long time. The TOC conversion and N_2 selectivity on cooling are therefore higher than those on heating.

Figure 2(c) shows the influence of temperature on NH_4^+ selectivity over the three catalysts. It can be seen that NH_4^+ was formed as an intermediate by scission of the C–N bond in the medium-temperature regime; with further temperature increase, NH_4^+ was converted to N_2 . At the same time, the yields of over-oxidized products, namely NO_2^- and NO_3^- , also increased. In addition, with a steadily increasing temperature, N_2 may be directly generated by cleavage of the C–N bonds of MA. Figure 2(d) and (e) shows the influence of temperature on NO_2^- and NO_3^- , respectively. It can be seen that the NO_2^- yields first increased and then decreased, whereas the NO_3^- yields increased continuously in the high-temperature region with increasing temperature. It is worth mentioning that CO_2 and N_2 were the predominant products, and only traces of NO_2^- and NO_3^- were formed in the CWAQ of MA using our experimental procedures. In contrast, significant amounts of NO_2^- and NO_3^- are usually observed in the CWAQ of N-containing compounds performed in autoclaves at high temperatures and pressure [22]. Based on these facts, it is suggested that NO_2^- and/or NO_3^- byproducts are easily formed in high concentrations of activated oxygen species in aqueous media. Another possible explanation is that N_2 and CO_2 can be easily separated from the reaction system under our reaction conditions, which may cause the oxidation reaction to proceed toward the formation of N_2 and CO_2 . These results indicate that designing the CWAQ of N-containing compounds to proceed over the catalyst surface and/or timely separation of CO_2 and N_2 from the reaction system might avoid the formation of these undesired byproducts. These assumptions need further investigation.

3.1.2. Influence of LHSV on catalytic activity

The TOC conversion and nitrogenous product selectivity as a function of LHSV at two different temperatures are shown in Fig. 3. It is evident that the TOC conversion and N_2 selectivity declined with increasing LHSV (Fig. 3(a) and (b)); for example, at 200 $^{\circ}\text{C}$ the TOC conversion and N_2 selectivity decreased from an initial value of $\sim 100\%$ at 0.6 h^{-1} to $\sim 50\%$ at 5.4 h^{-1} over Pt-Ru. In addition, at the same LHSV, the TOC conversion and N_2 selectivity at high temperature were usually higher than those at low temperature, and the difference became greater with increasing LHSV. This shows that the effect of the LHSV is more obvious at low temperatures.

Fig. 2. Influence of temperature on (a) TOC conversion, (b) N₂ selectivity, (c) NH₄⁺ selectivity, (d) NO₂⁻ selectivity, and (e) NO₃⁻ selectivity in CWAO of MA over (1) Pt-Ru, (2) Pt, and (3) Ru catalysts.

It can be seen from Fig. 3(c) that the NH₄⁺ selectivity initially increased with increasing LHSV, and, after reaching a maximum, decreased with increasing LHSV over the Pt catalyst. The effect of LHSV on the NO₂⁻ selectivity (Fig. 3(d)) was similar to that on the NH₄⁺ selectivity, but the NO₃⁻ selectivity (Fig. 3(e)) declined with increasing LHSV. These observations indicate that the O₂/MA ratio plays an important role in product distribution in the MA oxidation process. A high O₂/MA ratio contributes to formation of N₂ and NO₃⁻, whereas a medium ratio

favors formation of NH₄⁺ and NO₂⁻.

3.2. MA oxidation pathway

In this work, GC-MS was used to identify the organic products in the collected liquids. Contrary to our expectations, no organic intermediates were found in the collected liquids; this is probably because of direct conversion of -CH₃ fragments to CO₂ and/or easy oxidation of organic intermediates to CO₂. On

Fig. 3. Influence of LHSV on (a) TOC conversion, (b) N_2 selectivity, (c) NH_4^+ selectivity, (d) NO_2^- selectivity, and (e) NO_3^- selectivity in CWAO of MA over (1) Pt-Ru, (2) Pt, and (3) Ru catalysts at different temperatures.

the basis of the analytical results, we propose a plausible reaction scheme for MA oxidation, shown in Scheme 1. Initially, the target MA molecule is mainly oxidized to CO_2 , N_2 , and NH_4^+ , and then NH_4^+ is further oxidized to N_2 , NO_2^- , and NO_3^- .

3.3. Textural properties of catalysts

The surface area, pore volume, and pore size of the support, Pt-Ru, Pt, and Ru catalysts are listed in Table 1. The surface area of Al_2O_3 was hardly changed after modification with CeO_2 , but there were slight decreases in the surface area and pore volume of the as-prepared catalysts, indicating that precious

metal particles were successfully supported on $\text{Al}_2\text{O}_3\text{-CeO}_2$ and that the textural properties of the support remained unchanged after impregnation.

Scheme 1. Plausible pathway for MA oxidation.

Table 1Textural properties of support, Pt-Ru/Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂, and Ru/Al₂O₃-CeO₂.

Sample	<i>A</i> _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Al ₂ O ₃	163	0.48	12
Al ₂ O ₃ -CeO ₂	162	0.49	12
Pt-Ru/Al ₂ O ₃ -CeO ₂	158	0.43	11
Pt/Al ₂ O ₃ -CeO ₂	153	0.45	12
Ru/Al ₂ O ₃ -CeO ₂	157	0.47	12

3.4. H₂-TPR results

The H₂-TPR profiles of the calcined samples are shown in Fig. 4. From Fig. 4(a) it can be seen that the main reduction peak for the Pt catalyst, attributed to reduction of PtO_xCl_y species, occurs at 225 °C, and there is no interaction between these species and the support [24]. For the Ru catalyst, a sharp reduction peak appears at about 200 °C and is assigned to RuO₂ [25], indicating that the RuCl₃ precursor was completely transformed into RuO₂ by calcination. In the case of the Pt-Ru catalyst, a peak maximum appears at 200 °C, with a shoulder at 225 °C; these temperatures are consistent with the reduction temperatures for RuO₂ and PtO_xCl_y species, respectively, in mono-metallic catalysts. These results indicate that Pt and Ru were separately deposited on the support and did not form alloys. The reduction temperatures of the metal oxides in this system

Fig. 4. TPR profiles of calcined (1) Pt-Ru, (2) Pt, and (3) Ru catalysts. (a) Al₂O₃-CeO₂ as support; (b) Al₂O₃ as support.

Fig. 5. (a) Pt 4d_{5/2} and (b) Ru 3p_{3/2} XPS spectra for (1) Pt-Ru, (2) Pt, and (3) Ru catalysts.

are lower than those of the corresponding metal oxides dispersed in the bare Al₂O₃ support (Fig. 4(b)), showing that the metal oxides can be easily reduced in the presence of CeO₂. In addition, the peaks for the former are much sharper than those for the latter, indicating that modification of the Al₂O₃ support with CeO₂ favors a narrow size distribution of metal particles.

3.5. XPS analysis

The surface oxidation states of the metal particles in the Pt-Ru, Pt, and Ru catalysts were investigated using XPS; the results are shown in Fig. 5. It can be observed that the Pt 4d_{5/2} XPS spectra of the Pt-Ru and Pt catalysts only have a peak centered at a binding energy of 315.0 eV, indicating that Pt existed in the metallic state in the Pt-based catalysts [26]. After deconvoluting the Ru 3p_{3/2} XPS spectra, two peaks centered at 461.4 and 463.8 eV, corresponding to Ru⁰ and Ru⁴⁺ species, can be observed for the bimetallic catalyst, but only a peak centered at 463.8 eV can be found for the Ru catalyst [26]. These results indicate that the Ru precursor can be more easily converted to metallic Ru in the presence of the Pt precursor. The XPS semi-quantitative surface composition results for the three catalysts indicate that Pt and Ru existed in metallic forms in the Pt-Ru and Pt catalysts, whereas Ru existed as Ru⁰ and Ru⁴⁺ on the Ru particle surfaces; the percentages of Ru⁰ and Ru⁴⁺ species were 51.4% and 48.6%, respectively.

3.6. XRD results

Figure 6 shows the XRD patterns of the support and Pt-Ru, Pt, and Ru catalysts. The peaks in Fig. 6(1) at $2\theta = 28.3^\circ$, 38.5° , 46.0° , 49.2° , and 67.3° are assigned to cubic Al_2O_3 structures (JCPDS 88-0107), no obvious diffraction peaks for crystalline CeO_2 can be observed, which indicates that CeO_2 is well dispersed in the support substrate. The Pt-Ru catalyst does not show any clear diffraction peaks for crystalline Pt (Fig. 6(2)), and the XRD pattern of the Pt catalyst shows diffuse diffraction peaks at $2\theta = 39.3^\circ$ and 46.0° , corresponding to the (111) and (200) planes of a face-centered cubic (fcc) structure for Pt (Fig. 6(3)), which indicates that the crystalline Pt particles are small. In contrast, in the XRD pattern of the Ru-based catalyst, there are obvious diffraction peaks at $2\theta = 44.0^\circ$, 42.0° , and 38.6° , corresponding to the (101), (002), and (100) planes, respectively, of primitive hexagonal close-packed (hcp) crystalline Ru (Fig. 6(2) and (4)).

3.7. TEM and CO chemisorption results

The TEM and HRTEM images and particle size distribution of the catalysts are presented in Fig. 7. The HRTEM images show that the Pt and Ru particles are highly crystalline. The d -spacings of 0.233 and 0.204 nm can be respectively indexed to the (111) plane of fcc Pt and the (101) plane of hcp Ru. The

Fig. 6. XRD patterns of (1) Al_2O_3 - CeO_2 support and (2) Pt-Ru, (3) Pt, and (4) Ru catalysts.

low-magnification TEM images and corresponding particle size distribution of all the catalysts show that small black metal particles are more uniformly dispersed in the bimetallic catalyst than in the monometallic catalyst, and sintering can be clearly observed in the Ru catalyst. The particle size of the Pt-Ru, Pt, and Ru catalysts range from 1.2 to 5.8, 1.3 to 8.7, and 3 to 25 nm, respectively. The average diameters of the metal particles in the Pt-Ru, Pt, and Ru catalysts are 2.2, 4.1, and 13.9

Fig. 7. (a) TEM and (c) HRTEM images and (b) histograms of particle size distribution of (1) Pt-Ru, (2) Pt, and (3) Ru catalysts.

Table 2

Dispersion and average particle size of Pt-Ru, Pt, and Ru catalysts determined by CO chemisorption.

Catalyst	Dispersion (%)	Average particle size (nm)
Pt-Ru	47.7	2.8
Pt	22.5	4.9
Ru	8.8	15.2

nm, respectively, which are consistent with those obtained using CO chemisorption (Table 2). The aggregation and/or sintering of Ru can therefore effectively be prevented by the introduction of Pt, probably as a result of interactions between the PtCl_6^{2-} and Ru^{3+} precursors in the impregnation solution and the different reducibility of the metal oxides in the calcined bimetallic samples. As a result, Pt-Ru has the highest dispersion of active species and therefore gives the best catalytic performance in the CWAO of MA. Based on these facts, we conclude that the catalyst activity and N_2 selectivity of the Ru catalyst in the CWAO of MA can be controlled by introducing a Pt component, which promotes the formation of active species in Pt-Ru catalysts.

4. Conclusions

Pt-Ru/ Al_2O_3 - CeO_2 , Pt/ Al_2O_3 - CeO_2 , and Ru/ Al_2O_3 - CeO_2 catalysts were prepared using an impregnation method. In the CWAO of MA, the temperatures required for ~100% TOC conversion and N_2 selectivity over the Pt-Ru, Pt, and Ru catalysts were 210, 230, and 260 °C, respectively. The bimetallic catalyst showed the best catalytic activity, mainly because it had the highest dispersion of active species. The temperature-dependent hysteresis for TOC conversion and N_2 selectivity in the heating and cooling process showed that CWAO of MA follows a chemisorption mechanism. In addition, only traces of NO_2^- and NO_3^- byproducts were formed in the experimental procedure, which indicates that designing the CWAO of N-containing

compounds to proceed over the catalyst surface and/or timely separation of CO_2 and N_2 from the reaction system might avoid formation of these undesired byproducts.

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Graphical Abstract

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Study of catalytic activity and product selectivity of M/ Al_2O_3 - CeO_2 (M = Pt-Ru, Ru, and Pt) in catalytic wet air oxidation of methylamine

Aiyong Song, Gongxuan Lü*

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; Gansu Provincial Center for Disease Control and Prevention; University of Chinese Academy of Sciences

The Pt-Ru/ Al_2O_3 - CeO_2 catalyst had the best catalytic activity because it had the highest dispersion of active species. The dispersion of bimetallic catalysts can be efficiently promoted by introduction of Pt into Ru/ Al_2O_3 - CeO_2 catalyst.

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M/Al₂O₃-CeO₂ (M = Pt-Ru, Ru, Pt)催化剂在甲胺催化湿式氧化中的活性与选择性

宋爱英^{a,b,c}, 吕功煊^{a,*}

^a中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室, 甘肃兰州730000

^b甘肃省疾病预防控制中心理化实验室, 甘肃兰州730020

^c中国科学院大学, 北京100049

摘要: 采用浸渍法制备了M/Al₂O₃-CeO₂ (M = Pt-Ru, Ru, Pt)催化剂, 并将其用于甲胺的催化湿式氧化反应(CWAO)。结果表明, Pt-Ru/Al₂O₃-CeO₂具有最佳活性和选择性。运用程序升温还原、X射线光电子能谱、X射线衍射、透射电子显微镜、N₂吸附和CO化学吸附等技术对催化剂的物化性质进行了表征。Pt组分的引入可有效提高双金属催化剂活性组分的分散度, 从而明显提高了其催化性能。升降温过程中总有机碳(TOC)转化率与N₂选择性迟滞效应表明, 甲胺CWAO遵循化学吸附-脱附机理。

关键词: 分散度; 迟滞效应; 铂; 钌; 催化湿法氧化; 甲胺

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*通讯联系人. 电话/传真: (0931)4968178; 电子信箱: gxl@lzb.ac.cn

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1. 前言

有机污水的大量排放造成了严重环境污染。对污水中有机污染物进行高效绿色无害化处理, 一直是一个具有挑战性的课题。目前, 有机污水净化处理方法主要有物化技术、生物技术和化学氧化技术等^[1-3]。其中催化湿式氧化(CWAO)作为新型高效的水处理净化技术, 可以使用氧气或空气为氧化剂, 在一定温度(80–300 °C)和压力(0.5–6 MPa)条件下可将较高浓度的有机污染物(化学需氧量COD约为10–100 g/L)氧化为易于微生物降解处理的中间产物或CO₂, N₂和H₂O。因此, CWAO是一种处理水中有机污染物的有效方法^[4,5]。

CWAO过程中, 由于均相催化剂(主要为Cu, Fe和Mn盐)在反应体系中可以直接与反应底物作用, 因而通常表现出很好的催化活性。此类催化虽然高效, 但存在反应后活性组分难以回收、易造成二次污染和操作成本提高等问题^[6]。相比之下, 由于多相催化剂具有易于回收、可再生和可重复利用等优点, 在过去几十年中受到了许多科研工作者的关注。多相催化剂可分为过渡金属氧化物和贵金属催化剂两类。过渡金属氧化物主要有

CuO, Co₃O₄和NiO等, 此类催化剂成本低廉, 但存在选择性较差, 在苛刻的CWAO反应条件下活性组分的流失易导致催化剂失活等缺点^[7-11]。贵金属催化剂(Pt, Ru和Pd等)虽然比较昂贵, 但它们的催化活性和稳定性远高于过渡金属氧化物, 尤其在难降解有机化合物的氧化降解过程中此类催化剂往往表现出优异的催化活性^[12]。

众所周知, 多相催化剂的性能可以通过选择合适的制备方法、前驱体、载体和第二添加组分等手段进行有效调控^[13-20]; 其中引入第二组分是提高催化剂活性便捷且行之有效的方法。Cuauhtémoc等^[21]报道向Rh/ γ -Al₂O₃-CeO₂催化剂中引入Sn组分会明显提高催化剂在甲基叔戊基醚CWAO反应中的活性与选择性。Barbier等^[22]发现向Ru/CeO₂中引入Pd组分有助于提高催化剂在氨氧化过程中的N₂选择性。

本文采用浸渍法制备了Pt-Ru/Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂和Ru/Al₂O₃-CeO₂催化剂, 并考察了催化剂在甲胺(MA) CWAO反应中的催化性能。同时, 通过程序升温还原(TPR)、X射线光电子能谱(XPS)、X射线衍射(XRD)、透射电子显微镜(TEM)、N₂吸附和CO化学吸附等技术对催化剂进行了表征。通过关联催化剂结构性质与其催化

性能后发现, Pt-Ru/Al₂O₃-CeO₂催化剂在甲胺的CWAO过程中表现出最佳的催化活性. 这主要是由于在Ru/Al₂O₃-CeO₂催化剂中引入Pt组分提高了双金属催化剂中活性物种的分散度.

2. 实验部分

2.1. 载体Al₂O₃-CeO₂和催化剂的制备

实验所用化学试剂均为分析纯. 将商用氧化铝小球(纯度大于95%, 中国凯信氧化铝有限公司生产)研磨成直径为25–45目的颗粒, 在修饰之前先将氧化铝颗粒在600 °C焙烧6 h, 然后将30 g氧化铝颗粒浸渍于30 ml含有CeN₃O₉·6H₂O (2.85 g)的溶液中, 过夜, 在120 °C下干燥6 h后再于600 °C下焙烧8 h即得Al₂O₃-CeO₂载体.

Pt-Ru/Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂ 和 Ru/Al₂O₃-CeO₂ 催化剂也利用浸渍法制备, 分别以H₂PtCl₆·6H₂O和RuCl₃·xH₂O作为Pt和Ru的前驱体. 所有催化剂中金属负载量均固定在5% (质量分数), 其中在双金属催化剂中Pt和Ru的质量比为1:1. 将10 g载体颗粒浸渍于10 ml含有所需浓度H₂PtCl₆和/或RuCl₃的溶液中浸渍过夜, 然后将催化剂前驱体于120 °C干燥8 h, 再于300 °C下焙烧6 h, 最后将催化剂在氢气氛(40 ml/min)中300 °C还原8 h. 为了简便起见, 三种催化剂分别以Pt-Ru, Pt和Ru表示.

2.2. 催化活性评价

催化剂的催化活性评价在电脑全自动数控式多相催化剂评价装置(中国天津鹏翔科技有限公司)上进行(见图1). 将稀释好的甲胺原料液(浓度为2400±120 mg/L)经蠕动泵(Lab Alliance Series I, 美国)输送至汽化室进行汽化, 让甲胺-水蒸气的混合物与氧气(流量为300 ml/min)在T接头处充分混合, 然后导入装有10 ml催化剂的反应管中在设定温度下进行反应. 反应后混合物经冷阱冷却, 气液分离器分离后, 液体从排液管底端导入收集瓶, 定期进行收集, 以供对反应液中的TOC, 有机产物, NH₄⁺, NO₂⁻和NO₃⁻含量进行分析测定.

TOC在总有机碳氮测定仪(Aanalytik Jena, 德国)上测定. 反应液中有有机物利用GC-MS分析仪(Agilent 7890A)测定, 所用毛细管柱为HP-5MS型(30 m × 0.25 mm × 0.25 mm). 反应液中的NH₄⁺, NO₂⁻和NO₃⁻含量按照GB/T 5750-2006方法中的比色分析法测定. N₂产率通过N原子守恒经计算得出. TOC转化率(活性)和含氮产物选择性(选择性)通过以下公式进行计算:

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

$$\text{选择性}(\%) = (n_{\text{iq}}(\text{N})/n_{\text{ini}}(\text{MA})) \times 100\%$$

$$\text{或 选择性}(\%) = (2 \times n(\text{N}_2)/n_{\text{ini}}(\text{MA})) \times 100\%$$

式中, TOC_{ini}为初始TOC浓度, TOC_{det}为测得TOC浓度, n_{iq}(N)为含氮产物的摩尔数, n_{ini}(MA)为初始MA摩尔数, n(N₂)为N₂摩尔数.

2.3. 催化剂表征

XPS分析在K-Alpha-Surface Analysis光电子能谱仪(热电科技公司)上进行(Mg 靶, C 1s校正到284.6 eV). XRD晶相分析在Rigaku B/Max-RB型X射线粉末衍射仪上进行(Cu K_α, 管电流40 mA, 管电压40 kV). 高、低分辨透射电子显微镜图片在Tec-nai-G²-F30型高分辨透射电镜(FEI公司, 美国)上拍摄, 加速电压为300 kV. BET比表面积、孔总体积和平均孔尺寸测定在-196 °C以N₂为吸附质在Micromeritics ASAP 2010型比表面仪上进行. 程序升温还原在自建装置上进行, 称取50 mg催化剂置于内径为4 mm的石英反应管中, 以5% H₂/95% Ar (流量15 ml/min)还原, 从50 °C程序升温至500 °C, 升温速率为10 °C/min, 以热导池为检测器. 催化剂表面的CO吸附量在Micromeritics ChemiSorb 2750型物理化学吸附仪上进行测定.

3. 结果与讨论

3.1. 催化性能评价

3.1.1. 反应温度的影响

图2(a)和(b)分别给出了温度对活性和N₂选择性的影响. 可以看出, 随着温度上升, TOC转化率和N₂选择性逐渐增大. 很明显, 在甲胺CWAO反应中, 在所考察温度范围内, Pt-Ru和Ru的催化活性明显高于Pt. 当甲胺被彻底矿化时, Pt-Ru和Ru所需最低温度分别为210和230 °C, 而Pt则需要260 °C. 从图2(b)可以看出, 当N₂选择性达到~100%时, 各催化剂所需温度与甲胺彻底降解时所需温度完全相同, 说明在本实验条件下催化剂的高活性对应于高的N₂选择性. Garcia等^[23]在苯胺的CWAO过程中也观察到类似现象. 以上结果充分说明Ru对甲胺CWAO的催化活性优于Pt, 向Ru中引入Pt组分可明显提高双金属催化剂的活性和选择性. 另外, 在210 °C时, Pt-Ru, Pt和Ru催化甲胺氧化反应的转化频率(TOF)分别为51, 35和160 h⁻¹, 说明Ru催化剂表面原子的活性明显高于Pt基催化剂中表面金属原子的活性.

为了考察催化剂的稳定性, 分别在210, 260和230 °C, 液时空速为5.4 h⁻¹条件下, 将催化剂Pt-Ru, Pt和Ru的反应时间延长至300 h. 结果发现, 在所考察反应时间内, 所有催化剂的TOC转化率和N₂选择性基本维持在

100%左右,说明所有催化剂在甲胺的CWAO过程均表现出良好的稳定性。

有趣的是,在升降温过程中TOC转化率和 N_2 选择性均表现出了明显的温度迟滞效应。以Pt-Ru为例,当温度从200降到160 °C时,TOC转化率从88%降到45%;但在升温过程中,要使TOC转化率重新从45%提高至88%,则需要将温度从175 °C升至205 °C。以上结果表明该反应遵循着化学吸附-脱附机理。合理的解释是:温度较高时,催化剂表面活化氧物种浓度较高,将温度下调至某一数值时,吸附在催化剂表面的活化氧物种脱附达到新的平衡还需要一定时间,因而可观察到降温过程中的TOC转化率和 N_2 选择性明显高于升温过程。

图2(c)为不同温度下催化剂上 NH_4^+ 的选择性。可以看出,在较低温度下,由于C-N键的断裂会形成大量 NH_4^+ ,随温度的逐渐升高, NH_4^+ 被进一步氧化为 N_2 ,且深度氧化产物 NO_2^- 和 NO_3^- 的含量也有所增加。另外,随反应温度升高,C-N断裂也可能会直接生成 N_2 。图2(d)和(e)是温度对 NO_2^- 和 NO_3^- 选择性的影响。可以看出,随温度升高, NO_2^- 选择性先升高后降低,而 NO_3^- 选择性在高温区随温度的升高一直都在增加。值得指出的是,在甲胺的CWAO过程中, CO_2 和 N_2 始终为主要产物,仅有极少量的 NO_2^- 和 NO_3^- 副产物生成。与此相反,在高压反应釜中进行的含氮有机物CWAO反应会在高温高压条件下产生大量的此类副产物^[22]。据此,我们推断水中溶解氧在高温条件下产生高浓度活化氧物种是导致大量 NO_2^- 和 NO_3^- 副产物形成的可能原因。此外,目标产物 CO_2 和 N_2 能够及时从反应体系中脱离,使反应向生成 N_2 的方向进行,也是有效降低 NO_2^- 和 NO_3^- 的可能原因。因此,设计含氮化合物的CWAO反应在催化剂表面进行或让 CO_2 和 N_2 及时从反应体系中脱离可能会有效降低 NO_2^- 和 NO_3^- 副产物的生成。这些推断还需进一步研究。

3.1.2. 液时空速的影响

图3为不同温度下液时空速对TOC转化率和 N_2 、 NH_4^+ 、 NO_2^- 和 NO_3^- 选择性的影响。从图3(a)和(b)可以看出,随着液时空速提高,TOC转化率和 N_2 选择性逐渐下降。例如在200 °C, Pt-Ru存在条件下,当液时空速从0.6增加到5.4 h⁻¹时,TOC转化率和 N_2 选择性则从~100%降到50%。另外,在液时空速一定的条件下,高温时的TOC转化率和 N_2 选择性总要高于低温时的,并且随着液时空速的增加,这种差别还会逐渐增大,表明温度越低,液时空速的影响将愈加明显。图3(c)较为典型地反映了随液时空速的提升, NH_4^+ 选择性先增大后减小的变化规律。

另外,液时空速对 NO_2^- 选择性的影响(图3(d))与此类似,而 NO_3^- 选择性随液时空速的提高呈下降趋势(图3(e))。以上结果表明, O_2/MA 比值对甲胺氧化过程中的产物分布具有十分重要的影响。较高的 O_2/MA 比值(高温低液时空速)有利于 N_2 和 NO_3^- 的形成,而较低的 O_2/MA 比值则有利于 NH_3 和 NO_2^- 的形成。

3.2. 甲胺降解途径

我们利用GC-MS对反应收集液中的有机物进行了检测分析。但出乎意料的是,在反应液中并未发现任何有机中间产物,说明在甲胺的CWAO过程中, $-CH_3$ 被完全转化成 CO_2 或产生的中间产物很容易被氧化为 CO_2 。基于对反应液中产物的分析结果,我们提出了甲胺氧化的可能途径(图式1)。首先目标分子被主要氧化为 CO_2 、 N_2 和 NH_4^+ , NH_4^+ 可被进一步氧化生成 N_2 、 NO_2^- 和 NO_3^- 。

3.3. 催化剂的组织性质

表1列出了 Al_2O_3 、 $Al_2O_3-CeO_2$ 和催化剂样品的比表面积、孔体积和平均孔径。可以看出, Al_2O_3 的比表面积经 CeO_2 修饰后基本没有变化,但催化剂样品的比表面积和孔体积与载体相比略有降低,说明金属颗粒被成功负载到载体 $Al_2O_3-CeO_2$ 表面,并且负载金属后催化剂载体的组织性质没有发生明显的变化。

3.4. H_2 -TPR结果

图4(a)为各催化剂的 H_2 -TPR曲线。可以看出,Pt催化剂在225 °C处出现一个耗 H_2 峰,对应于 PtO_xCl_y 物种,表明金属氯化物与载体之间没有明显的相互作用^[24]。Ru催化剂在200 °C处出现强锐峰,峰位置接近于 RuO_2 的还原温度^[25],说明焙烧后前驱体 $RuCl_3$ 基本完全转化成了 RuO_2 。Pt-Ru催化剂在200和225 °C处分别出现一尖锐峰和肩峰,其峰位置完全对应于单金属催化剂中的 RuO_2 和 PtO_xCl_y 物种,意味着在双金属样品中两种金属不能形成合金,仅完全独立分散在载体表面。图4(b)列出了Pt-Ru/ Al_2O_3 、Pt/ Al_2O_3 和Ru/ Al_2O_3 样品的TPR谱。比较图4(a)与(b)可以看出,金属氧化物在载体修饰后还原峰位置向低温区略有移动,表明 CeO_2 对载体的修饰可使金属氧化物更易于还原。另外当载体被修饰后,所有金属氧化物还原峰比未修饰之前更为尖锐,说明这种修饰会使金属颗粒的尺寸分布变窄。

3.5. XPS结果

催化剂颗粒表面的化学状态利用XPS技术进行了表征,结果如图5所示。从Pt 4d_{5/2}的信号峰可以看出,Pt-Ru和Pt催化剂中Pt 4d_{5/2}的结合能均为315.0 eV,表明催化剂中的Pt主要以单质形式存在^[26]。通过对Ru 3p_{3/2}

的信号峰进行解析后发现, 催化剂Pt-Ru分别在461.4和463.8 eV处出现了特征信号峰, 可分别归属于 Ru^0 和 Ru^{4+} 物种^[26]. 而Ru催化剂仅在463.8 eV处出现 Ru^{4+} 的特征信号峰, 意味着在Ru催化剂中金属颗粒表层金属以 RuO_2 形式存在, 从而说明双金属催化剂中Pt在一定程度上可促进金属颗粒表面单质Ru的形成. 通过对XPS数据进行半定量计算可知, 在Pt-Ru和Pt催化剂表面的 Pt^0 物种为100%, Pt-Ru表面的Ru物种也为100%, 而Ru催化剂表面 Ru^0 和 Ru^{4+} 物种分别为51.4%和48.6%.

3.6. XRD结果

图6是载体与各催化剂的XRD谱. 可以看出, 载体 $\text{Al}_2\text{O}_3\text{-CeO}_2$ 仅在 $2\theta = 28.3^\circ, 38.5^\circ, 46.0^\circ, 49.2^\circ$ 和 67.3° 处出现了氧化铝正交晶系的特征衍射峰(JCPDS 88-0107), 未见任何 CeO_2 的特征衍射峰, 说明 CeO_2 很好地分散在 Al_2O_3 表面. 在Pt-Ru催化剂的XRD谱中没有观察到任何Pt的特征衍射峰, 而Pt催化剂在 $2\theta = 39.3^\circ$ 和 46.0° 处出现了Pt的特征峰, 对应于Pt面心立方晶体的(111)和(200)晶面, 但该峰较为弥散, 说明在该样品中Pt晶粒较小. 与Pt有所不同, Ru的特征衍射峰可以在Pt-Ru和Ru的XRD谱中清楚观察到, 分别位于 $2\theta = 44.0^\circ, 42.0^\circ$ 和 38.6° 处, 对应于Ru原始六方堆积晶体的(101), (002)和(100)晶面.

3.7. TEM和CO化学吸附结果

图7是催化剂的高、低分辨透射电镜照片和金属颗粒尺寸分布图. 从HRTEM照片可以看出, Pt和Ru纳米粒子在所有样品中均具有良好的结晶性, 晶格条纹间距约为0.233和0.204 nm, 分别对应于面心立方晶相(fcc)Pt的(111)晶面和六方密堆积晶相(hcp)Ru的(101)晶面. 从TEM照片和金属颗粒尺寸分布图可以看出, 双金属样品中活性物种以纳米颗粒的形式均匀附着于载体表面, 纳米颗粒粒径为1.2–5.8 nm, 粒径分布范围较窄, 仅能观察到轻微的烧结现象; Pt样品中金属纳米颗粒径为1.3–8.7 nm, 粒径分布范围较宽, 有一定的烧结现象; Ru中金属

纳米颗粒在载体表面分散很不均匀, 粒径为3–25 nm, 分布范围很广, 可观察到十分明显的烧结现象.

为了进一步确定活性组分的分散度和平均粒径, 我们还对催化剂进行了CO化学吸附表征. 结果表明(见表2), Pt-Ru, Pt和Ru催化剂中活性组分的分散度分别为47.7%, 22.5%和8.8%, 对应的粒径分别为2.8, 4.9和15.2 nm, 该结果基本与TEM测定结果(2.2, 4.1和13.9 nm)一致, 表明向Ru中引入Pt能有效防止Ru活性组分的团聚或烧结. 其可能作用机理为: 在浸渍液中, 前驱体离子 Ru^{3+} 和 PtCl_6^{2-} 之间的静电作用使阴阳离子形成分散均匀的“离子团”, 在浸渍过程中, “离子团”会被吸附到载体表面. 另外, 在催化剂还原过程中, 由于两种金属氧化物没有同步被还原, 所以Pt与Ru之间并未形成合金. 以上作用可能抑制了双金属催化剂活性组分的团聚或烧结, 因此Pt-Ru催化剂中的活性组分具有最高的分散度, 该催化剂在甲胺的CWAO过程中表现出最佳的催化活性. 据此, 我们认为通过向Ru催化剂样品中引入Pt组分可以有效提高双金属活性组分的分散度, 从而实现Ru催化剂在甲胺CWAO反应过程中的活性与产物选择性控制.

4. 结论

以 $\text{Al}_2\text{O}_3\text{-CeO}_2$ 为载体, 采用浸渍法制备了Pt-Ru/ $\text{Al}_2\text{O}_3\text{-CeO}_2$, Pt/ $\text{Al}_2\text{O}_3\text{-CeO}_2$ 和Ru/ $\text{Al}_2\text{O}_3\text{-CeO}_2$ 催化剂. 在甲胺CWAO反应中, TOC转化率和 N_2 选择性达到100%时3种催化剂所需温度分别为210, 230和260 $^\circ\text{C}$. 双金属最佳的催化活性主要归因于其活性组分良好的分散度. 在升降温过程中, TOC转化率和 N_2 选择性出现明显的迟滞效应, 说明甲胺CWAO反应遵循化学吸附-脱附机理. 在本实验条件下, 仅有极少量的 NO_2^- 和 NO_3^- 副产物生成; 说明设计反应尽量在催化剂表面进行并及时对气体产物(CO_2 和 N_2)进行排放可有效降低 NO_2^- 和 NO_3^- 副产物在含氮化合物CWAO过程中的形成.