

A comparison between Ce(III) and Ce(IV) ions in photocatalytic degradation of organic pollutants

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Abstract: Nano cerium oxides are efficient photocatalysts for pollutants degradation with highly dispersed Ce(III) ions as the suggested active species to promote the reaction, while Ce(IV) species do not behave as a catalyst. In this paper, to understand the mechanism of Ce-based photocatalysts, we studied the comparison of simple cerium ions, Ce(III) and Ce(IV) in aqueous solution for organic pollutants degradation under UV irradiation. Orange II (AOII), methyl orange, and *p*-nitrophenol were selected as the target pollutants. The formation and contribution of reactive oxygen species, the kinetics of Ce(IV) photoreduction and Ce(III) photooxidation, and the influence of solution pH were investigated in detail. It was found that at low pH Ce(IV) ions showed a higher activity for hydroxyl radicals production and AOII degradation than Ce(III) ions, which could be attributed to its fast reduction rate to Ce(III). However, its activity dramatically decreased when solution pH increased, and was also strongly influenced by the type of pollutants; while Ce(III) exhibited high degradation efficiency of all the tested pollutants over a wide pH range.

Keywords: cerium ions; photodegradation; hydroxyl radical; organic pollutants; rare earths

Cerium is the most abundant rare earth oxide and one of the most interesting elements^[1–3]. The photocatalytic degradation of organic pollutants with CeO₂ has become a very active research, due to its several intrinsic advantages, such as high chemical stability, non-toxicity, high thermal stability, redox properties and photoabsorption properties^[4–9]. Valente et al. have prepared the supported CeO₂ catalyst on MgAl layered double hydroxides, and tested its activity in the photocatalytic degradation of phenol and chlorinated phenols under UV irradiation^[7]. Ji et al. have tested CeO₂ for the photocatalytic degradation of acid orange 7, an azo dye, under visible light irradiation^[8].

The photo activity of CeO₂ is strongly influenced by its particle size or loading, and the Ce(III) species are considered to be important in the reactions^[10–12]. For example, the degradation of phenol by CeO₂ impregnated on Al-MCM-41 was reported and it highlights that cerium at lower loadings with high dispersion is in +3 oxidation state and shows good photocatalytic activity in comparison with pure ceria^[10]. The highly dispersed cerium oxide species on silica and alumina, which mainly exist as Ce(III) cations, were found to promote non-oxidative direct methane coupling photocatalytically. On the other hand Ce(IV) species would inhibit the formation of H₂ and would not catalyse this photoreac-

tion^[11]. The surface Ce³⁺ species in nano CeO₂ was also suggested to play a significant role in production of reactivity oxygen species under visible light irradiation^[12]. In addition, we have shown that the simple cerium salt Ce(NO₃)₃ can be used as an efficient photocatalyst for many pollutants degradation under UV irradiation^[13,14].

Although there are many reports about the photocatalytic ability of Ce(III) species and inactivity of Ce(IV) species, in this paper it was found that the simple Ce(IV) ions showed high photocatalytic efficiency for pollutants degradation under UV irradiation. As toxic organic compounds such as phenols and dyes, are predominant in wastewater effluent, the azo dyes orange II and methyl orange, and *p*-nitrophenol were selected as the target pollutants. The comparison of Ce(III) and Ce(IV) ions, the reaction mechanism and the influence of solution pH were discussed in detail. These results will be helpful for designing highly active Ce-based photocatalyst and understanding its mechanism.

1 Experimental

1.1 Chemicals

Ce(NO₃)₃·6H₂O, Ce(SO₄)₂, benzoquinone (BQ), *p*-nitrophenol (PNP), methyl orange (MO), terephthalic acid

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(TA), methanol, H_2SO_4 and NaOH were of analytical grade. Orange II (AOII) from Sigma Chemical Co. was used without further purification (>85%) for all experiments. The sample solutions were prepared using deionized water throughout the experiments. The solution pH was adjusted by H_2SO_4 (0.05 mol/L) or NaOH (0.05 mol/L).

1.2 Degradation experiments

The diagram of the photoreaction system is presented in Fig. 1. A 120 W high-pressure mercury lamp with primary wavelength distribution at approximately 365 nm was used as the irradiation source. The lamp was across the reactor with a light path of 2.0 cm. The whole reaction system was forced draft cooling and the reaction temperature was kept at about 25 °C. For all of the photoreactions unless especially noted, the experimental solution was prepared as follows: 50 mL aqueous solution with a concentration of organic pollutant of 37.5 $\mu\text{mol/L}$ (15 mg/L) and 0.25 mmol/L cerium ions was put into the reactor. The reaction was initialized by turning the light on.

1.3 Analysis methods

To monitor the pollutants degradation process, solution samples taken at different time intervals were measured on an UV-Vis spectrophotometer at the maximum characteristic absorption wavelength (Beijing Rayleigh Analytical Instrument Co. Ltd., China). The detection of hydroxyl radical formation was carried out on a Hitachi F-4500 fluorescence spectrophotometer at an excitation wavelength of 315 nm and an emission wavelength of 425 nm. TA was used as a probe molecule and before analysis it was dissolved in aqueous solution with twice the molar quantity of NaOH . The fluorescence spectra of Ce(III) and Ce(IV) ions during photoreaction were also performed on the same fluorescence spectrophotometer with an excitation maximum at 303 nm and a fluorescence emission maximum at 353 nm.

2 Results and discussion

2.1 Photocatalytic degradation of AOII with Ce(IV) and Ce(III) ions

The initial pH of the reaction solution containing Ce(IV) ions and AOII was 3.5, while for Ce(III) ions and the dye was 5.6. In order to compare their photocatalytic activity under the same conditions, the pH for Ce(III) solution was adjusted to 3.5 by H_2SO_4 . The precipitation was not observed under these conditions as the dye AOII is a good ligand and can form complex with the metal ions, which can be helpful to stabilize the metal ions. Fig. 2(a) shows the decolorization efficiency of AOII under different reaction conditions. From the figure it can be seen that when AOII was irradiated with a UV lamp,

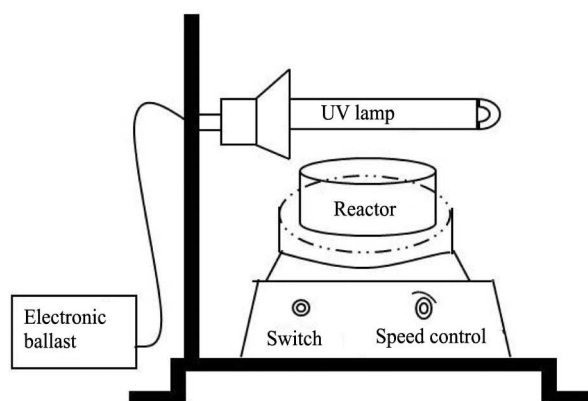


Fig. 1 Diagram of the photoreaction system

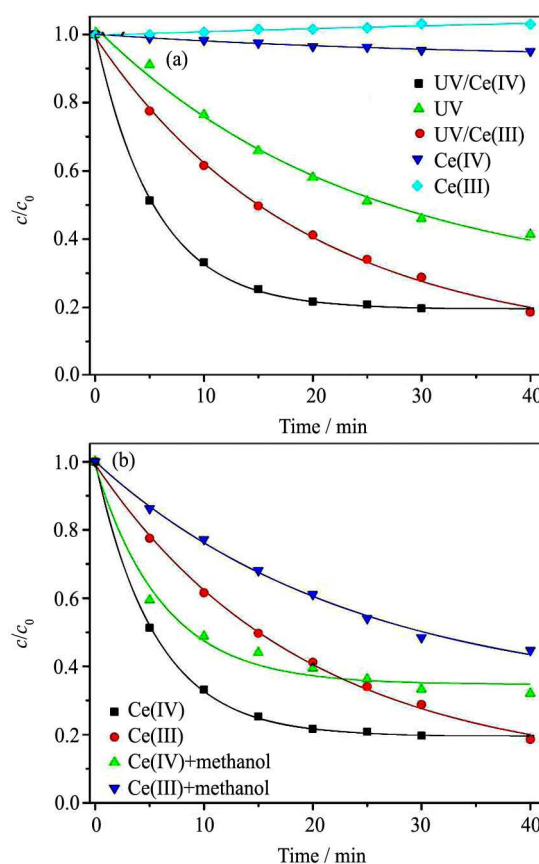


Fig. 2 Degradation of AOII with different systems (a) and Influence of methanol on photocatalytic degradation of AOII with Ce(IV) and Ce(III) ions (b) (Conditions: AOII 37.5 $\mu\text{mol/L}$, Ce(III) 0.25 mmol/L, Ce(IV) 0.25 mmol/L, Methanol 2.5 mol/L, pH 3.5)

about 60% of the dye was decolorized over a period of 40 min. The reaction rate was tremendously accelerated by the addition of simple Ce(III) salt to the UV system, and 80% of the dye was removed after 40 min. When Ce(IV) was used as the catalyst, a higher reaction rate was obtained with 80% removal of AOII within 20 min. These results clearly indicated that UV/ Ce(IV) system was much more efficient for remediation of pollutants than UV/ Ce(III) system. In addition, there was almost no decrease of the dye concentration in the presence of only 0.25 mmol/L Ce(III) ions. According to Ref. [15], the

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