



Catalytic ozonation not relying on hydroxyl radical oxidation: A selective and competitive reaction process related to metal–carboxylate complexes



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ABSTRACT

Catalytic ozonation following non-hydroxyl radical pathway is an important technique not only to degrade refractory carboxylic-containing organic compounds/matter but also to avoid catalyst deactivation caused by metal–carboxylate complexation. It is unknown whether this process is effective for all carboxylates or selective to special molecule structures. In this work, the selectivity was confirmed using $O_3/(CuO/CeO_2)$ and six distinct ozone-resistant probe carboxylates (i.e., acetate, citrate, malonate, oxalate, pyruvate and succinate). Among these probe compounds, pyruvate, oxalate, and citrate were readily degraded following the rate order of oxalate > citrate > pyruvate, while the degradation of acetate, malonate, and succinate was not promoted. The selectivity was independent on carboxylate group number of the probe compounds and solution pH. Competitive degradation was observed for carboxylate mixtures following the preference order of citrate, oxalate, and finally pyruvate. The competitive degradation was ascribed to competitive adsorption on the catalyst surface. It was revealed that the catalytically degradable compounds formed bidentate chelating or bridging complexes with surface copper sites of the catalyst, i.e., the active sites. The catalytically undegradable carboxylates formed monodentate complexes with surface copper sites or just electrostatically adsorbed on the catalyst surface. The selectivity, relying on the structure of surface metal–carboxylate complex, should be considered in the design of catalytic ozonation process.

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1. Introduction

Heterogeneous catalytic ozonation is a potential oxidation technique to improve organic pollutant degradation or mineralization for surface water and wastewater treatment [1]. According to studies performed on a number of transition metal oxides and noble metals, catalytic ozonation follows either hydroxyl radical oxidation or non-hydroxyl radical oxidation pathways [1–7]. Hydroxyl radical has high reaction rate constants with most organic pollutants [8]. However, its reaction rates with saturated carboxylic-containing compounds are relatively low compared to its reaction with ozone molecule ($k_{OH} = 1 \times 10^8 - 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [8] (ineffective hydroxyl radical consumption). Ozonation and hydroxyl radical oxidation produce hydrophilic byproducts from organic matter present in water. For instance, high concentrations of carboxylates (e.g., acetate and oxalate) and keto carboxylates (e.g., pyruvate and ketomalonnate) are usually detected in natural

water subjected to ozonation and hydroxyl radical oxidation [9,10]. Carboxylates such as citrate and succinate universally present in surface water (as high as 10 mg L^{-1} have been reported), which originate from industrial wastewater effluent discharge or natural metabolites of plants, animals, and microorganisms [11–15]. Citrate is also a chloroform precursor [11] and a good analog for functional groups of humic acids to study the mechanisms of their adsorption on minerals [16]. Usually, carboxylates in water form complexes with surface metal sites of metal oxides [17]. The efficiency of catalytic ozonation relying on hydroxyl radical generation can be reduced in long term-operation, due to the formation of metal–carboxylate complexes that significantly hinder ozone–surface interaction. Therefore, the degradation of carboxylates is not only important to reduce hydrophilic byproducts [18], but also critical to avoid deactivation of the catalytic ozonation for successive operations.

Previous studies showed that non-hydroxyl radical oxidation is the major degradation pathway of carboxylates during catalytic ozonation [18–22]. The pathway relies on surface complex formation of carboxylates with active metal sites. Noble metals seem to be the most efficient in the activation of surface carboxylate complexes for ozone oxidation but low pH is always necessary to achieve efficient degradation [6]. MnO_2 , Fe_2O_3 and Co_3O_4 are

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also active oxides in this process, but the low pH condition (≤ 3) is again required for efficient reaction [19,20,23], because H^+ is consumed during the reaction [18,21]. In our recent work, ceria significantly improved the activity of copper oxide in catalytic ozonation of oxalate at neutral pH values [7]. Moreover, it showed low metal leaching (less than $0.2 \mu\text{g L}^{-1}$ of copper was leached at the catalyst dosage of 100 mg L^{-1} at neutral pH) and high stability in repeated using. This catalyst does not promote hydroxyl radical generation from ozone, because (1) bicarbonate (a hydroxyl radical scavenger) promoted the catalytic ozonation, and (2) the degradation of atrazine (a hydroxyl radical probe compound) in the catalytic ozonation was even lower than that in ozonation alone. The ceria-supported copper oxide (CuO/CeO_2) could be a potential low cost and high efficient catalyst to promote carboxylate degradation in combination with ozone for surface water and wastewater treatment.

Thus far, all of studies on catalytic ozonation with non-hydroxyl radical pathway focused on single probe carboxylate. There is a lack of investigation on the selectivity of this oxidation process for different kinds of compounds. It is also unknown whether or not competitive reactions exist among different carboxylates during catalytic ozonation. Answering these questions would significantly improve our understanding on catalytic ozonation and help to better elaborate durable and multi-functional catalytic ozonation process for applications.

In this work, the selectivity of catalytic ozonation not relying on hydroxyl radical oxidation was studied using CuO/CeO_2 as catalyst and six ozone-resistant carboxylates (i.e., acetate, citrate, malonate, oxalate, pyruvate and succinate) as probe compounds. Additional experiments were performed to investigate competitive degradation of the probe carboxylates during catalytic ozonation. Competitive degradation was ascribed to competitive adsorption of the probes on the catalyst. The selectivity of the catalytic ozonation was correlated to the structure of surface metal-carboxylate complex. To the best of our knowledge, this is the first study showing selective and competitive reactions for catalytic ozonation.

2. Experimental

2.1. Materials and characterization

Ceria supported copper oxide (CuO/CeO_2) was prepared by immersing CeO_2 particles (prepared with a urea-hydrothermal method [6]; BET surface area of $94 \text{ m}^2 \text{ g}^{-1}$ and average particle size of $10 \mu\text{m}$) into $\text{Cu}(\text{NO}_3)_2$ solution for 24 h, drying at 120°C for 12 h, and then calcinating at 550°C for 4 h. The CuO weight percentage of the CuO/CeO_2 was determined to be 12% by ICP-MS (Agilent 7500) analysis after digestion of the catalyst with $\text{HCl} + \text{HNO}_3$ (v/v, 3:1) and HF in sequence. Energy-dispersive X-ray spectroscopy (EDX) taken on a Titan 80-300 transmission electronic microscope showed that copper dispersed well on the ceria support with surface Cu/Ce atom ratio of approximately 1:3 to 1:4 [7]. X-ray photoelectron spectroscopy (XPS) (Kratos AMICUS/ESCA 3400 spectrometer) characterization shown in our previous work [7] indicated that the oxidation state of copper on the ceria support was mainly Cu(II). The catalyst has a specific surface area of $64 \text{ m}^2 \text{ g}^{-1}$ (determined on a Micromeritics ASAP 2420 analyzer), an average particle size around $10 \mu\text{m}$ (measured on a Mastersizer 2000 laser particle size analyzer), and a pH_{pzc} of 9.1 (determined with acid-base titration). Copper oxide was prepared through calcination of copper nitrate at 550°C (same temperature as CuO/CeO_2 preparation) for 4 h. It has a specific surface area of $8.4 \text{ m}^2 \text{ g}^{-1}$, an average particle size of $6 \mu\text{m}$, and a pH_{pzc} of 9.5.

Acetic, malonic, oxalic, pyruvic, succinic and citric acids having relatively low reactivity toward ozone, were used in this

study. Their molecule structures, molecular weights, dissociation constants ($\text{p}K_a$) and second order reaction rate constants with ozone and hydroxyl radical were listed in Table 1.

2.2. Experimental procedure

A mass of 20 mg of catalyst was introduced into 200 mL of carboxylate solution (pH adjusted) in a 500 mL magnetically stirred glass reactor. Gaseous ozone ($27 \text{ mg O}_3 \text{ L}^{-1}$) produced from dried oxygen gas with an ozone generator (3S-A5, Tonglin Technology), was continuously introduced into the reactor through a stainless steel syringe needle (no dispenser was used to avoid any potential adsorption on the dispenser) at a flow rate of 2.0 L min^{-1} . Samples taken at predetermined time intervals were immediately filtered with $0.45 \mu\text{m}$ acetate-fiber syringe filters and then purged with pure N_2 to remove residual ozone. Filtration and purging had no impact on the carboxylate concentration.

Isothermal (20°C) adsorption was conducted at pH 7.5 without buffer addition to avoid any interference of other anions on carboxylate adsorption. Carboxylic acid solution was prepared by directly dissolving the organic acid into Milli-Q water ($18 \text{ M}\Omega \text{ cm}$, Millipore). Alkaline carboxylate solution was prepared by adding NaOH pellet into the carboxylic acid solution. Carboxylate solution of pH 7.5 was prepared by slowly dropping the alkaline carboxylate solution into the carboxylic acid solution with magnetic stirring and online pH measuring. Series of initial concentrations ($0.025\text{--}0.5 \text{ mM}$ for individual adsorption and $0.015\text{--}0.18 \text{ mM}$ for competitive adsorption) of each carboxylate and fixed catalyst dose (2 g L^{-1}) were used for adsorption experiments. The suspension was mixed with a rotator for 36 h, and then centrifuged at 4000 rpm for 5 min. The supernatant was analyzed for residual carboxylate concentration.

2.3. Analysis

Ozone concentration in gas phase was determined with iodometric method. Aqueous ozone concentration was analyzed with a UV spectrometer (Hach 500) at 258 nm (molar adsorption coefficient = $3000 \text{ M}^{-1} \text{ cm}^{-1}$). Acetate, pyruvate and oxalate were analyzed on a Dionex ICS-3000 IC equipped with an AS-11 column (2 mm i.d.). The mobile phase, i.e., 10 mM KOH , was pumped through at a flow rate of 0.35 mL min^{-1} . Malonate, succinate, and citrate were determined on a Waters HPLC equipped with an X-Bridge column at UV wavelength of 210 nm. Diluted phosphoric acid solution ($300 \mu\text{L}$ concentrated phosphoric acid in 1 L of Milli-Q water) was used as mobile phase at a flow rate of 0.4 mL min^{-1} .

To characterize surface carboxylate complex, 150 mg of pre-ozonated oxide was mixed with 25 mL of carboxylate solution (100 mM ; pH 7.5) for 24 h. The suspension was centrifuged at 4000 rpm. The supernatant was replaced by 1 mL of Milli-Q water. After mixing, the new suspension was dropped on the crystal of a Universal ATR accessory and scanned 50 times at a resolution of 2 cm^{-1} on a PerkinElmer FTIR spectrometer (Spectrum 100). Milli-Q water was used to scan the background. It was automatically subtracted from the spectra of the samples.

3. Results and discussion

3.1. Selectivity of catalytic ozonation

Fig. 1A and B show the removal of six carboxylates in separate solutions during ozonation alone and catalytic ozonation with CuO/CeO_2 at pH 7.5. For ozonation alone, the degradation rate of citrate was the highest (33% in 25 min) among the six compounds studied, followed by pyruvate (17%). The degradation rate of the other four carboxylates in ozonation alone ranged from 8% to 15%. In

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