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Ozonation of oxalic acid with an effective catalyst based on mesoporous MCM-41 supported manganese and cerium oxides

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ABSTRACT

In this paper, mesoporous catalysts were prepared by deposition of various fractions of manganese and cerium oxides on MCM-41. The prepared catalyst samples presented uniform hexagonal pore structure in XRD, BET, and TEM characterization tests. The application of supported catalysts in the presence of ozone was found to be remarkably effective in elimination of oxalic acid in water with a conversion as high as 76–92%, compared to ozonation (10% removal), adsorption (20% removal), and catalytic ozonation using the support alone (56% removal). It was shown that the main portion of OA was degraded through reaction with hydroxyl radicals, which were generated by the application of the catalysts. In addition, the investigation of the activity of catalysts at various loadings of manganese and cerium oxides on the support showed that cerium oxide alone is a more effective than manganese oxide alone. However, the co-deposition of cerium oxide on a surface preloaded with fixed amount of manganese oxides led to mutual interactions, affecting the activity of the catalysts. At fixed loading of manganese oxides, the rate of degradation of oxalic acid was found to be much higher in the absence of any cerium oxide on the surface than high cerium oxide concentration. At optimum metal oxides proportions, the highest total organic carbon removal (90.3%) was achieved.

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1. Introduction

Various kinds of emerging pollutants such as pesticides, pharmaceuticals and personal care products (PPCPs), and endocrine disrupting chemicals (EDCs) have been detected in water at concentrations that may pose a risk to aquatic organisms and public health [1–4]. Therefore, it is important to devise an effective and feasible technology to remove the organic pollutants from water.

Ozonation treatment is one of the promising technologies, which has been used in oxidation and destruction of a wide variety of organic pollutants in water and wastewater [5,6]. However, ozonation can lead to partial oxidation of organic compounds [7] and accumulation of recalcitrant and possibly more toxic end-products [8]. Degradation of recalcitrant organic pollutants in water and wastewater requires the application of an advanced oxidation process (AOP) such as catalytic ozonation [9–11].

Catalytic ozonation enhances the oxidation of the aqueous organic compounds, which are difficult to oxidize using ozonation alone. Catalytic ozonation utilizes a catalyst to enhance the generation of free radicals through ozone decomposition. An increased free radical concentration yields higher removal of organic contaminants, compared with ozonation alone [12].

The efficiency of a heterogeneous catalytic ozonation substantially depends on the choice of the catalyst. Activity of a supported catalyst is strongly affected by the choice of the support, the active components of the catalysts, and the preparation of the catalysts.

Some of the catalyst supports that have commonly been used in catalytic ozonation are TiO_2, Al_2O_3, clay, MCM-41, SBA-15 and activated carbon (AC). The recent discoveries of various mesoporous molecular sieves such as MCM-41 have brought a new aspect to the design of catalysts due to the flexibility they offer in fine-tuning pore diameters during their synthesis. Their potential is currently under study in a variety of catalytic applications such as catalytic ozonation. In addition, the unique properties of the molecular sieve materials including high surface area, large and uniform mesoporous channels make them effective adsorbents [13] and catalysts [14,15] in the ozonation of organic compounds in water. Therefore, MCM-41, as a typical mesoporous molecular sieve, was selected as the support of the catalyst in this study.

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The active component also affects the efficiency of a heterogeneous catalyst significantly. The oxides of transition metals such as Fe, Co, Mn, Cu, Ni, and Ce have generally been used as the active component of a catalyst due to their low cost, high thermal stability, and moderate mechanical strength [16,17]. Among them, manganese and cerium oxides loaded on MCM-41 have presented improved activity during ozone decomposition [18,19]. However, the performance of the mesoporous MCM-41 supported combined manganese and cerium oxides in catalytic ozonation for the removal of organic contaminants in water has not been studied. In particular, it is unclear if the simultaneous introduction of the two metal oxides on the support would cause synergy leading to an enhancement or reduction of the catalytic activity of the catalyst.

Therefore, this study aims to evaluate performance of a modified-mesoporous material in degradation of aqueous organic pollutants by loading two transition metal oxides on a mesoporous support, and investigating the possible synergy of the two metal oxide loadings. Therefore, this study aims at preparation, characterization, and application of the supported catalysts (Mn, Ce/MCM-41) with different loadings of the active metal oxides in catalytic ozonation of a representative recalcitrant organic pollutant in water. The main objective of this study is to investigate the activity of the prepared catalysts in order to determine the optimum loadings of the metal oxides, which lead to the maximum removal of the organic pollutant. Response surface methodology (RSM) was applied in this study to facilitate the investigation of the simultaneous effect of the two metal oxides loadings on the activity of the catalyst.

2. Materials and methodology

2.1. Materials

Oxalic acid (OA) is one of the organic recalcitrant end-products of an ozonation process. Therefore, OA was selected as the representative organic contaminant in this catalytic ozonation study.

OA, tert-Butanol ($\geq$99%), ammonium hydroxide solution (28%), Ludox HS-40, and tetra-methyl-ammonium hydroxide solution (25%) were purchased from Sigma-Aldrich®. Sodium thiosulfate (anhydrous, 99%) was supplied by Alfa Aesar®. Cetyl-trimethyl-ammonium bromide (CTAB) was purchased from Fisher Scientific. Stock solutions were prepared in ultrapure Milli-Q water

($20.4\,M\Omega\,cm^{-1}$ at 25 °C). All of the materials were used as supplied without further purification.

2.2. Preparation of catalysts (Mn, Ce/MCM-41)

Mesoporous siliceous MCM-41 molecular sieve was prepared by aging Ludox HS-40 in cetyl-trimethyl-ammonium bromide (CTAB) under hydrothermal conditions as reported elsewhere [20,21].

Typically, 35 g of Ludox HS-40 was added to 14.55 mL of water under stirring, and 18.2 mL of 25% tetra-methyl-ammonium hydroxide solution was added. Independently, 18.25 g of CTAB was dissolved in 33 mL of water, and subsequently, 7 mL of 28% ammonium hydroxide solution was introduced. Finally, the above two solutions were mixed together, and the final mixture was stirred for 30 min and then transferred into a Teflon®-lined autoclave for hydrothermal treatment at 90 °C for 3 days. The resulting solids were filtered, washed, dried and calcined at 540 °C for 5 h under airflow at about 2 °C/min ramping rate. The synthesized MCM-41 was used as the support of the catalyst in this study.

Manganese-cerium loaded MCM-41 (Mn, Ce/MCM-41) was prepared by dry impregnation method using manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$) and cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) as manganese and cerium precursors, respectively. Appropriate amounts of the salts were dissolved in water for dry impregnation process. The solution was mixed with the support, air-dried, and calcined at 450 °C for 3 h under airflow at about 2 °C/min ramping rate.

2.3. Experimental set-up of catalytic ozonation

A schematic of the experimental set-up of catalytic ozonation reactions is presented in Fig. 1. The reactions were conducted in a semi-batch reactor. The reaction solution was stirred with a magnetic stirrer with agitation speed of 600 rpm.

A peristaltic pump (Model 72-320-000, Thermo-Scientific) was used to circulate water from the reactor to the aqueous ozone analyzer (Model UV-106-W, 2B Technologies, Inc.). A filter (stainless steel Tee-type particulate filter, 3/8 in. Swagelok tube fitting, 15 μm pore size) was used before the pump to avoid the entrainment of catalyst particles from the reactor. Ozone was generated by a laboratory ozone generator (Model OZV-8S, Ozone Solutions Co.) from pure oxygen and injected into the water in the reactor at a specific experimental condition (69.5 L h^{-1} gas flow rate and 21.8 ppm ozone concentration in the feed gas) in all experiments unless it is
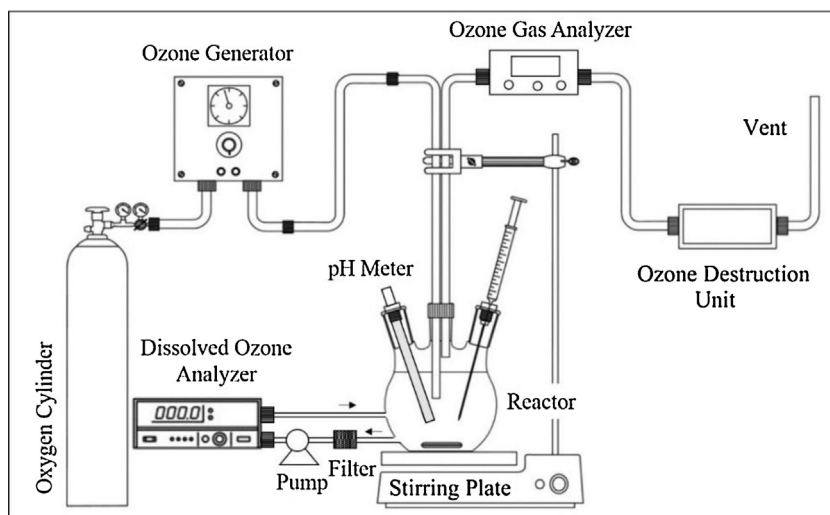

Fig. 1. A schematic diagram of the experimental setup for the catalytic ozonation experiments.