



Short Communication

Catalytic ozonation of 2-ethoxy ethyl acetate using mesoporous nickel oxalates

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ABSTRACT

In this communication, synthesis of mesoporous nickel oxalate and its catalytic activity in ozonation of 2-ethoxy ethyl acetate (2-EEA) was reported. The mesoporous nickel oxalate was synthesized by simple method without using any template. The XRD and HR-TEM analyses indicated the formation of plate like nickel oxalate. The nitrogen adsorption–desorption analysis showed the mesopores over the catalyst surface with narrow pore size of 4.5 nm. About 0.125 g/L of dosage was found to be optimum for efficient removal of 2-EEA. The catalytic reusability studies demonstrated that nickel oxalate kept its catalytic activity in four consecutive cycles.

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1. Introduction

Recently, advanced oxidation processes (AOPs) have been used for water and wastewater treatment [1–3]. Among the various AOPs, catalytic ozonation process was found to be very effective for treating recalcitrant pollutants [4–8]. In the catalytic ozonation process, the ozone may decompose on the catalytic surface, which may yield hydroxyl radicals. Earlier studies have shown that metal ion catalyzed homogeneous and solid catalyzed heterogeneous catalytic ozonation processes were promising for the degradation [4–8]. Recently, various materials have been successfully used as catalysts in the catalytic ozonation processes and scientists are continuously searching for new and efficient catalysts for the application of catalytic ozonation processes. In our earlier studies, we have reported effective catalysts for the ozone decomposition as well as degradation of organic pollutants in catalytic ozonation [5,6,9]. In continuation of searching for new and efficient catalysts for catalytic ozonation processes, herein we report nickel oxalate as a catalytic material candidate for the first time.

Oxalic acid can form coordination complex with many metal ions under normal conditions, which have been well documented in the literature [10]. Moreover, these metal oxalate complexes had been used as a precursor for the preparation of respective metal oxides [11,12]. One of the notable advantages of the metal oxalates complex is that large amount of catalyst can be prepared via a simple procedure and are not expensive. The nickel oxalate was selected as a representative candidate in the metal-oxalate family due to its water insolubility and stability.

Although the nickel oxalate preparation method was reported in the literature, no reports are available for the preparation of mesoporous nickel oxalate [13–15]. To our best knowledge, this is the first report that a metal-oxalate is used as a catalyst for the environmental remediation process. 2-EEA was used as a model pollutant in this study. 2-EEA has widely been used as an industrial solvent in paints, adhesives, wood stains, and varnishes. Therefore, 2-EEA may be present as an environmental contaminant and thus important to be removed from the aqueous environment. In this communication, we have reported on the preparation of mesoporous nickel oxalate and degradation of 2-EEA by using the synthesized nickel oxalate. The effects of catalysts dosage, reusability, and various catalysts on the degradation of 2-EEA were investigated. The surface properties of the nickel oxalate before and after ozonation process were also studied and results were discussed.

2. Experimental section

Anhydrous oxalic acid, nickel nitrate hexahydrate, and 2-ethoxy ethyl acetate were purchased from Aldrich Chemical Co Ltd and TEDIA chemicals, respectively. All chemicals were of analytical grade and used as received without further purification. For all experimental work, Milli Q-Plus water (resistance = 18.2 M Ω) was used.

The nickel oxalate was prepared using nickel nitrate hexahydrate and oxalic acid as nickel and oxalate precursor, respectively. The nickel and oxalate precursors at 1:1.5 molar ratios were adopted and dissolved in water separately. Both the above-mentioned solutions were heated separately on a hotplate to 90 °C and then mixed under constant magnetic stirring (250 rpm). The precipitated nickel oxalate was harvested by filtration and washed several times with deionized water and

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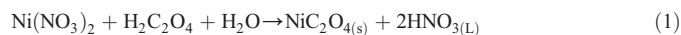
ethanol to remove possible impurities, before being dried in an oven at 120 °C for 2 h.

A 0.5 L semi-batch made of glass with the dimensions of 9 cm diameter and 15 cm height was used to facilitate the operation of all catalytic oxidation processes. Ozone was introduced through a porous fritted diffuser that can produce fairly fine bubbles. A 500 mL solution containing appropriate concentration of 2-EEA (1000 mg/L) and catalyst was placed in the reactor and in order to make homogeneous slurries the solution was magnetically stirred before ozone was introduced into the reactor. All experiments were operated at 25 °C using a water jacket around the reactor. Samples were withdrawn at regular intervals from the reactor and filtered through 0.45 µm membrane filter prior to the analysis. The experiments and analysis were done under similar conditions mentioned in the earlier report [5]. All the four reusability experiments were performed under similar condition mentioned above. After each cycle the catalysts were filtered by 0.45 µm membrane filter papers and then washed with plenty of water and dried at room temperature before being used for consecutive experiments. After fourth cycle the catalysts were recovered and washed, then XRD measurements were done.

The morphology of the nickel oxalate was performed on JSM-7401 and JEOL JSM-6700 field emission scanning electron microscopy (FESEM) at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) was performed using JEOL/JEM2010 model transmission electron microscope with an acceleration voltage of 120.0 kV. The X-ray diffraction (XRD) patterns were obtained in an X-ray diffractometer (type HZG41B-PC) using CuKα irradiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of $0.075^\circ (2\theta) \text{ min}^{-1}$. The Brunauer–Emmett–Teller (BET) surface area of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the samples were degassed at 120 °C for at least 12 h prior to nitrogen adsorption measurements.

3. Results and discussion

Nickel oxalate was prepared by using nickel nitrate with oxalic acid by a simple mixing method in water. The formation of nickel oxalate solid is shown in Eq. (1). A simple complex



formation method was used and developed for the preparation of mesoporous nickel oxalate which is one of the significant novelty presented in this paper. Most importantly these mesoporous nickel oxalate solid can be prepared without using any template. The XRD pattern of the synthesized nickel oxalate was studied and the result is presented in Fig. 1a. The XRD results presented in Fig. 1a clearly revealed the formation of nickel oxalate and are in good agreement with earlier XRD reports assigned for nickel oxalate [16–18]. No impurity peaks were noted, indicating the formation of high purity nickel oxalate. The morphology of the synthesized nickel oxalate was examined using FE-SEM and the results are presented in Fig. 2. The FE-SEM pictures in Fig. 2a indicate that the synthesized nickel oxalate does not possess any regular shape and appears to be aggregated particles. The particle sizes are in the range of 2 to 6 µm. In order to understand the morphology of nickel oxalate particles, the HR-TEM analysis was also done. Fig. 2b shows the HR-TEM pictures of the synthesized nickel oxalate and the results show plate like morphology and the plates are aggregated with non-uniform sizes.

The textural properties, such as surface area, pore size, and pore volume of the synthesized nickel oxalate, were studied using nitrogen adsorption–desorption analysis. The isotherm curve and pore size distribution curves are presented in Fig. 3a. The isotherm is classified as a typical type IV isotherm, which is attributed to the presence of mesoporous surface structure [19]. The mesopores could have formed by particle aggregation on the plate like surface. The surface area, pore

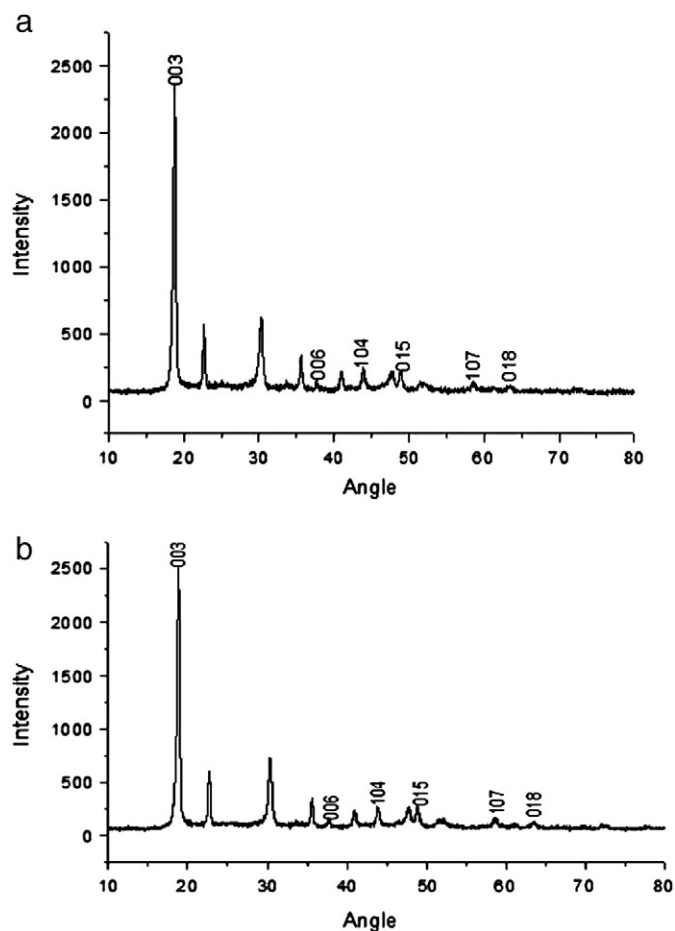


Fig. 1. The XRD pattern of (a) synthesized mesoporous nickel oxalate (unused) and (b) used nickel oxalate in four consecutive cycles.

size, and pore volume were found to be $30 \text{ m}^2/\text{g}$, 4.5 nm, and $0.0436 \text{ cm}^3/\text{g}$, respectively. The pore size curve presented in Fig. 3a insert has shown narrow pore size distribution of 4.5 nm. Although the synthesized nickel oxalate possesses mesoporous surface structure its surface area is small. This could be due to large particle size of the synthesized nickel oxalate and similar results were noted earlier in our studies [19,20]. Since we have not used any template for the synthesis process, the nickel oxalate should have been formed by a simple complex formation. Therefore, the particle assembly on the plates may induce mesoporous surface structure on the nickel oxalate plates.

The synthesized nickel oxalate was tested as a catalyst in catalytic ozonation process for the first time. The catalytic ozonation experiment was performed using 2-EEA as a model pollutant. We have already reported the degradation of 2-EEA by using ZnO nanobundles as a catalyst in catalytic ozonation process [5]. The direct reaction rate coefficient (k_D) of 2-EEA with ozone was found to be $0.675 \text{ M}^{-1} \text{ S}^{-1}$ which indicated that the ozonation process was not a potential treatment option for the degradation of 2-EEA containing wastewater [5]. Therefore, the hydroxyl radicals induced degradation is necessary for the effective removal of 2-EEA. Although the catalytic ozonation of 2-EEA was reported by ZnO nanobundles earlier, it is important to develop an environmentally benign and low cost catalyst for its removal [5]. Moreover, development of a low cost catalyst could reduce the cost of the treatment process appreciably. For comparison purpose, we have also studied NiO catalyzed ozonation of 2-EEA. The nickel oxide (NiO) was synthesized from nickel oxalate by thermal decomposition process at 400 °C for 2 h. Since the details of NiO preparation are not the scope of the manuscript, we didn't discuss the details about NiO catalyst in this manuscript. Fig. 4 shows the degradation of 2-EEA in the presence and

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