Disordered Manganese Oxide Nano-powder Prepared by Low-temperature Synthesis Followed by Acid Treatment

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ABSTRACT

Disordered manganese oxide, prepared by low-temperature synthesis followed by acid treatment is introduced. Aggregated nano-powder of disordered manganese oxide was obtained in this method. The disordered manganese oxide is suitable starting material for the preparation of efficient adsorbents for the removal of harmful metals from the environment.

INTRODUCTION

Crystal forms of manganese oxide are categorized into various phases such as the rock-salt-type MnO (cubic), spinel-type lambda-MnO_2 (cubic), ramsdellite lambda-MnO_2 (monoclinic), and hausmannite Mn_3O_4 (tetragonal). The crystal structures of manganese oxide contain fundamental building blocks of MnO_6 octahedron. However, the oxygen array of the crystal lattice usually features other octahedral and tetrahedral sites that may accommodate Mn and other cations via subtle distortion/tilting of the MnO_6 octahedra and/or formation of oxygen defects. These properties in conjunction with the variation of Mn^{2+} and Mn^{4+} valence states and the interactions with the Mn magnetic moments, give rise to a variety of very intriguing crystal morphology and structural transformations as well as magnetic ordering at low temperatures that are of fundamental interest. Technologically, once the properties of materials are understood, novel applications can be tailored. New batteries, ion exchangers for environmental decontamination, and magnetic spin-valve devices are such examples among many suggested potential applications.

The authors have studied manganese oxide-based materials for the research and development of efficient adsorbents in order to remove harmful metals from the environment. Recently, we synthesized the disordered phase of manganese oxide and discovered the exhibition of high adsorption capability of pollutants such as Cd and As ions and of rare metal such as Au [1]-[6]. These phenomena occur only in the disordered manganese oxide powder after protonation by acid treatments. The disordered-manganese oxide powder show the quantity of adsorption to be at least more than 10 times higher compared with the manganese oxide without the acid treatments.

EXPERIMENTAL

$MnCO_3$ powder (Wako, 99% purity) as the starting material was heated using an electric furnace at 200 ºC in air for 4.5 h. Acid treatment began by adding the powder into 0.5 mol/L of nitric or hydrochloric acid while stirring (using a magnetic stirrer) for a certain period of suspension time. Afterward the suspended particles were filtered from the solution using a glass filter (0.2 μm mesh), followed by washing with distilled water. This first stage processed with a 60 min suspension time for an initial acid treatment enabled the growth of nanometer-size crystalline Mn_2O_3 grains on the surfaces of micron-size crystalline $MnCO_3$ particles. Subsequent acid treatments, typically for 1 h suspension each, allowed the removal of $MnCO_3$ component and the self-assembly of adsorbed H^+ ions (protons) on the Mn_2O_3 nanoparticles. This second acid treatment resulted in substantial increase of the population of protonated sites. Furthermore, remaining $MnCl_2$ or $MnNO_3$ in the solution after the acid treatment and filtration of the adsorbent can be readily converted to MnO_2 powder with useful high surface area by adding an appropriate amount of $KMnO_4$ to the solution. This reduces the amount of waste and negative environmental impacts.

RESULTS AND DISSCUSSION

Fig. 1 shows the Variation of XRD pattern on the disordered-manganese oxide powder prepared by low-temperature synthesis followed by acid treatment. The XRD of the prepared sample (no acid treatment) heated less than 200 ºC showed similar pattern with the starting material ($MnCO_3$). However, the color was different from each other. The flesh-colored of $MnCO_3$ has changed the black of Mn_2O_3 [6]. The peaks on the XRD patterns have changed the broadness according to increase in the frequency of the acid treatment, and indicated the disordered crystal phase of the manganese oxide remarkably. We assume that this disordered phase is the result of acid treatment of the surface layer of Mn_2O_3.

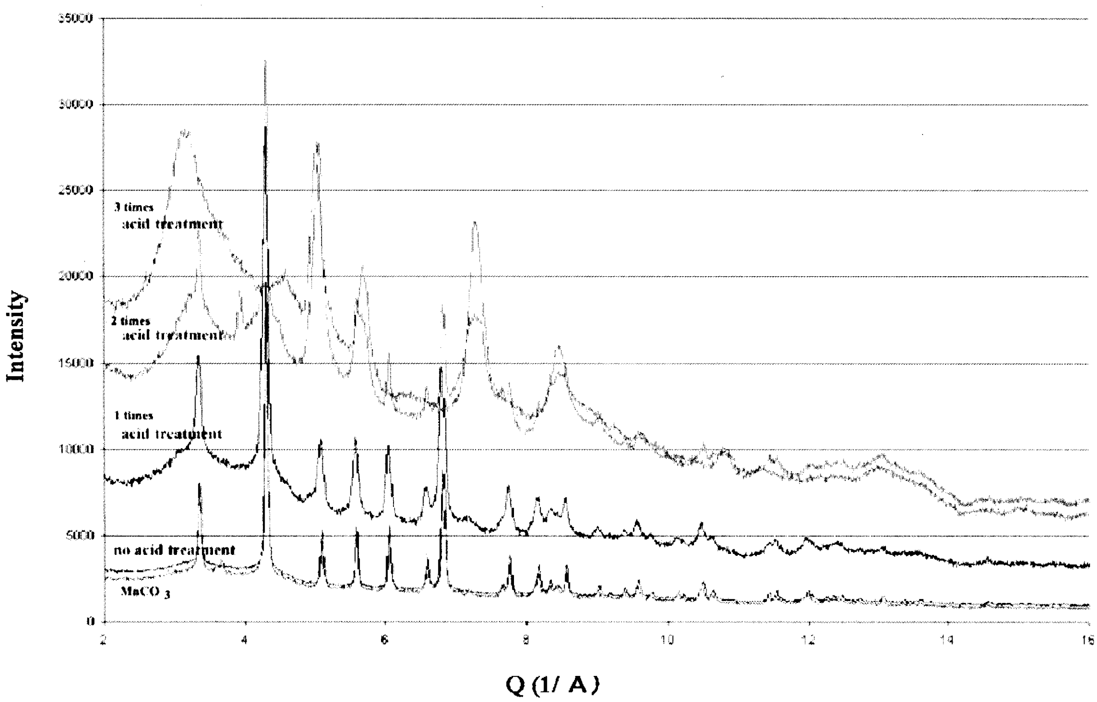

Fig. 1 Variation of XRD pattern on the disordered-manganese oxide powder prepared by low-temperature synthesis followed by acid treatment.

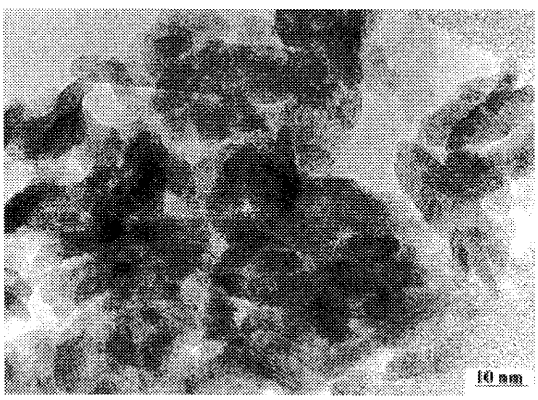

Fig. 2 TEM image of the disordered-manganese oxide powder.

Fig. 2 shows the TEM image of the disordered -manganese oxide powder obtained after 3 times of acid treatment. Aggregated nano powders were observed in the image. These powders construct aggregated powders in micro-meter size, and show remarkable adsorption ability for the complex ions such as gold, palladium, and silver in aqueous solution [4]-[6]. The electrons are supplied from the manganese oxide to each complex adsorbed according to the each redox potential. The adsorbed complex is deposited on the surface of the manganese oxide as the metallic nano-particles.

CONCLUSIONS

A new method to prepare nano-powders of the disordered-manganese oxide based on Mn_2O_3 was introduced in this report. In principle, this synthesis method can produce useful manganese oxide-based catalysts supporting different metallic nanoparticles such as Au, Pd, and Ag.

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