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Synthesis of manganese oxide octahedral molecular sieves containing cobalt, nickel, or magnesium, and the catalytic properties for hydration of acrylonitrile

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Abstract

An octahedral molecular sieve known as OMS-1 has todorokite structure composed of magnesium and manganese oxides, which was named as Mg-todorokite here. Octahedral molecular sieves containing cobalt (Co-todorokite) or nickel (Ni-todorokite) without magnesium were prepared by a sequential method under optimum conditions and compared with the Mg-todorokite by powder XRD, ICP, FESEM, and catalytic reactions. The compositions of Co-todorokite, Ni-todorokite, and Mg-todorokite are $Co_{0.37}MnO_{2.3}(H_2O)_{2.1}$, $Ni_{0.24}MnO_{2.0}(H_2O)_{2.1}$, and $Mg_{0.22}MnO_{2.0}(H_2O)_{2.2}$, respectively. The Co-todorokite and Ni-todorokite are comparable in crystallinity with the highly crystalline Mg-todorokite. The catalytic properties were examined for the hydration of acrylonitrile. The apparent activation energies depend on the foreign metals. The order is Co-todorokite < Ni-todorokite < Mg-todorokite. The four products of the Mg-todorokite catalysis are 3-hydroxy-propionitrile, and bis-2-cyano-ethylether, succinonitrile, and acrylamide. The acid treatments for Mg-todorokite suppress the formations of 3-hydroxy-propionitrile and bis-2-cyano-ethylether, which would be due to the weakening of the basicity with the removal of magnesium ions. The only product of the Co-todorokite and the Ni-todorokite catalysis is acrylamide because of not containing magnesium.

Keywords: Todorokite; Octahedral molecular sieves; Manganese oxides; Catalysts; Acrylonitrile hydration

1. Introduction

Todorokite-type manganese oxide is one of the materials with edge- and corner-shared MnO_6 octahedra that form one-dimensional tunnel structures of various sizes, and it has tunnels of a (3 × 3) framework structure [1–4]. The framework is composed mainly of Mn (4+) O_6 octahedra. However, some of the central ions of the octahedra are trivalent and/or divalent manganese ions and foreign metal ions. Therefore, it has cation sites [3]. It was reported that some metal cations not only exist at cation sites but also are incorporated into the framework by isomorphous substitutions for parts of the skeletal MnO_6 octahedra in layered and tunnel manganese oxides [3,5,6].

Naturally occurring todorokite and todorokite-like manganese oxides include some inorganic cations, such as calcium, magnesium, and sodium, although their cation content differs from one locality to another [7–9]. Although todorokite in the natural form is a hydrated manganese oxide with impurities, the todorokite-type manganese oxide has been synthesized hydrothermally as a single-phase material [10–13]. Golden et al. have reported a synthetic todorokite-type manganese oxide that was prepared by the hydrothermal treatment of Mg^{2+}-exchanged birnessite-type manganese oxide [10]. Shen et al. have developed a thermally stable todorokite-type manganese oxide containing magnesium, called OMS-1, and found that it can be used as a molecular sieve with a pore size of 0.69 nm estimated by adsorption of various kinds of organic compounds [11].

These materials have many applications, such as ion sieves [4], cathodic materials for batteries [14–16], and as catalysts [17–26]. Todorokite and todorokite-like manganese oxides are expected to have unique catalytic properties because of the manganese oxide framework, cations, and the tunnel opening [9,10]. Some promising examples are the oxidations of carbon monoxide [17,18], alcohols [19,20] and hydrocarbons [21–24], the decomposition of hydrogen peroxide [25], and the cracking of propane [26].

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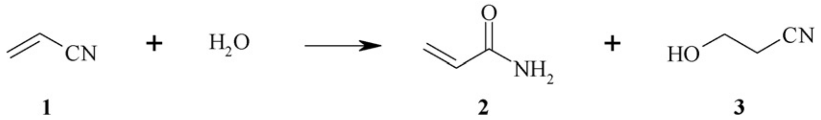

Scheme 1. The hydration of acrylonitrile: (1) acrylonitrile; (2) acrylamide; (3) 3-hydroxy-propionitrile.

Manganese dioxide shows good catalytic activity not only for the oxidation reactions but also for hydration reactions [27–30]. As shown in Scheme 1, the hydration of acrylonitrile can result in two products, acrylamide via hydration of C≡N bonds in the 1,2 addition, and 3-hydroxy-propionitrile and its derivatives via hydration of C═C double bonds in the 1,4 addition [28]. It was interesting to note the activity and the selectivity of todorokite catalysts for the hydration.

In the last two decades, there have been many reports of todorokite-type octahedral molecular sieves prepared by using magnesium salts and/or Mg $(MnO_4)_2$ [2,10–12]. Some of divalent magnesium cations exist in the framework and play a role in maintaining the stable structure of these manganese oxide compounds [31]. However, the todorokite catalysts with magnesium ions can result in undesired by-products for some reactions because of the base catalysis of magnesium species. On the other hands, there have been few reports of synthetic todorokite samples not containing magnesium [5,32], whose catalytic properties were not reported. For the development of todorokite catalysts, it is required the synthesis of crystalline todorokites containing the other metal ions from magnesium and the clarification of catalytic properties of the todorokites.

Here in, we report the synthesis of Co-todorokite and Ni-todorokite comparable in crystallinity to the highly crystalline Mg-todorokite, and, for the first time, the catalysis for the hydration of acrylonitrile. The effects of cobalt and nickel ions on the formation of todorokite and the catalytic properties are compared to those of magnesium ions by characterizations of the powder X-ray diffraction patterns, ICP elemental analysis, Mn average oxidation state determinations, and field emission scanning electron microscopy (FESEM) observations and the catalytic reactions.

2. Experimental

2.1. Synthesis procedure

Synthesis of todorokite-type manganese oxides containing a ‘‘foreign cation’’ Co^{2+}, Ni^{2+}, or Mg^{2+}, involved three major steps, as shown in Fig. 1 [11,33]. (1) Synthesis of the layered precursor, birnessite, by the slow addition of a homogeneously mixed solution of divalent manganese ions and foreign divalent metal ions into an alkali solution including heptavalent manganese ions, and by aging under alkaline conditions. (2) Ion-exchange with a solution of the same foreign cation to expand the interlayer distance of the layered precursor. (3) Transformation of the layered precursor to the todorokite-type manganese oxide under hydrothermal conditions. The todorokite is referred to as M-todorokite, where M represents a foreign cation doped in the synthesis of birnessite samples and in the ion-exchange steps.

The typical synthesis of Ni-todorokite was as follows. These chemicals were purchased from Wako Pure Chemical Industries. Firstly, solution A ($Ni(NO_3)_2{\cdot}6H_2O$ (1.87 g, 6.43 mmol) and $MnCl_2{\cdot}4H_2O$ (6.37 g, 32.2 mmol) in 100 ml of distilled deionized water (DDW)) was added dropwise over a period of 10 min with vigorous stirring at room temperature (∼296 K) into solution B ($KMnO_4$ (2.02 g, 12.8 mmol) and NaOH (36 g, 0.90 mol) in 100 ml of DDW). After the solutions were mixed, they were stirred for a total of 30 min. The

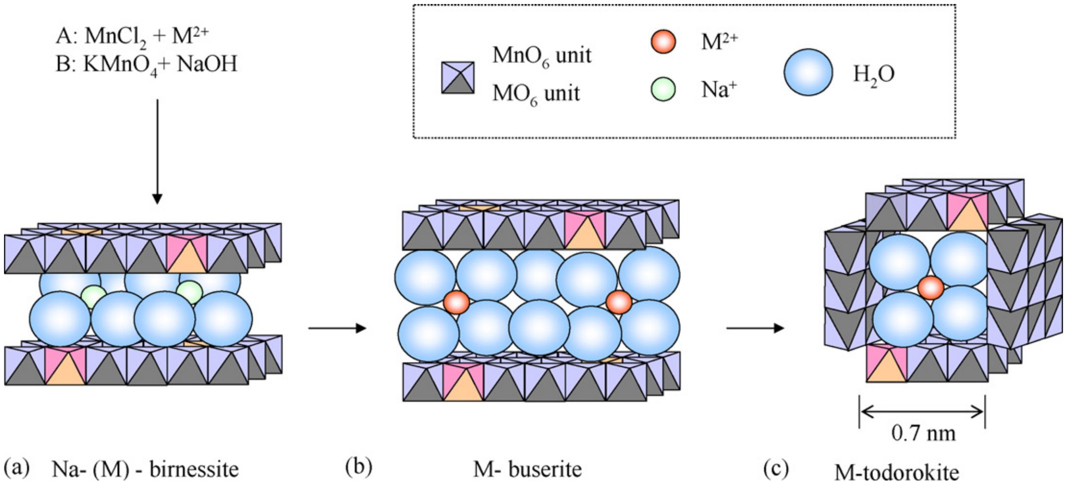

Fig. 1. Synthesis schematic images of Mg-todorokite. (a) A step of the preparation of birnessite materials by mixing the A and B solutions and by aging, (b) a step of the ion-exchange with $MgCl_2$ solutions, and (c) a step of the hydrothermal treatment.