Manganese oxides as water-oxidizing catalysts for artificial photosynthetic systems: The effect of support

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ABSTRACT

Herein the effect of support on water-oxidizing activity of amorphous Mn oxides was investigated. We used nanoparticles of CuO, NiO, MgO, SiO_2 or ZrO_2 as support and placed Mn oxides on these oxides. The compounds were synthesized by a simple procedure and characterized by high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray diffraction spectrometry. In the next step, the water-oxidizing activities of these compounds were considered in the presence of cerium(IV) ammonium nitrate. We found that the efficiency of Mn oxide toward water oxidation depends upon the nature of the support. A turnover frequency ~5 based on Mn was observed for Mn oxides on NiO.

Introduction

Water splitting at huge-scale is a promising route to store sustainable energies that are usually intermittent [1–6]. For water splitting into H_2 and O_2, water oxidation is a bottleneck, and thus the finding of an efficient, inexpensive, environmentally friendly and stable water-oxidizing compound is highly desirable [1–6]. Among different compounds, Ir and Ru are efficient catalysts toward water oxidation [4,7,8] but they are not promising to use in industrial scale because they are expensive and toxic. Among cheap, environmentally friendly, efficient and stable compounds [4,7,8], Mn oxides are promising to use as water-oxidizing catalysts in artificial photosynthetic systems [9].

Interestingly, the biological water-oxidizing complex of Photosystem II in plants, algae and cyanobacteria is a nano-sized Mn–Ca oxido cluster considered a nano-sized Mn oxide in a protein matrix with high proton and electron conductivity [10].

Since 1968, Glikman, Shcheglova [11], Morita [12], Shilov [13], and Harriman [14] groups introduced and extended Mn

oxides as catalysts for water oxidation in the presence of different oxidants. After these pioneering studies, other groups reported different Mn oxides as catalysts for the reaction [9]. The effects of support on water-oxidizing activity of Mn oxides, and of even other metal oxides are rarely considered. Harriman's group loaded iridium oxide onto a variety of supporting materials such as ZnO, MgO, TiO₂, Al₂O₃, SiO₂, TiO₂, ZrO₂, SnO₂ and V₂O₅ [14]. They reported that the most effective supports are ZnO and MgO [14]. The group proposed a direct reaction between IrO₂ and some supports such as BaO, CaO and SrO to form iridate, and then production of small aggregates of catalytically active material. The group also found that neutral oxides, such as Al₂O₃ and SiO₂, make inferior supports compared with ZnO and MgO [14]. The group suggested that the clusters of IrO₂ will agglomerate on the surface of Al₂O₃ and SiO₂, forming bigger nanoparticles. On the other hand, acidic oxides, such as SiO₂, ZrO₂, SnO₂ and V₂O₅, are not good supports for IrO₂ toward water oxidation [14]. In this case, the acidic surface stabilizes lower oxidation states of Ir, and most probably, formation of IrO₂ is not easy under these conditions [14]. In 2010, Jiao and Frei reported nanostructured Mn oxide clusters supported on mesoporous silica in the presence of $Ru(bpy)_3^{3+}$ [15]. They proposed that the high-surface area silica support, protecting the active Mn centres of the catalyst from deactivation through surface restructuring and assisting in deprotonation during photocatalysis are important for the efficiency of these systems [15]. The use of zeolites by Najafpour's group showed that small particles of Mn oxides are formed in the presence of zeolite [16,17]. However, these very small particles are decomposed in the presence of cerium(IV) ammonium nitrate (Ce(IV)) [16,17]. The group also showed that leaking of catalysts is important for Mn oxides on montmorillonite in the presence of Ce(IV) [18,19]. Carbon nanostructures are found to be not very stable when used as support for Mn oxides in the water-oxidation reaction [20–22]. Herein we report the effect of nanoparticles of CuO, NiO, MgO, SiO₂ or ZrO₂ as support on water-oxidizing activity of Mn oxides in the presence of Ce(IV).

Experimental

Material and methods

All reagents and solvents were purchased from the commercial sources and were used without a further purification. Nano metal oxides were purchased from Neunano Company (see specification for the nanopowders in ESI). For HRTEM and TEM, samples were placed on copper grids covered with carbon film and examined with a 300 keV Transmission electron microscope JEM-3010 UHR (Jeol Ltd., Japan), equipped with a retractable high-resolution slow scan CCD-Camera (Gatan Inc., USA) with GOS phosphorous scintillator and lanthanum hexaboride cathode as the electron source. The X-ray powder patterns were recorded with a Bruker D8 ADVANCE diffractometer (CuK$_\alpha$ radiation). Mn atomic absorption spectroscopy (AAS) was performed on an atomic absorption spectrometer Varian Spectr AA 110. Prior to the analysis, the compounds were added to 1 mL of concentrated nitric acid and H₂O₂, left at room temperature for at least 1 h to ensure that the oxides

were completely dissolved. The solutions were then diluted to 25.0 mL and analysed by AAS.

Synthesis

A simple method was used to synthesize Mn oxides on support: $Mn(OAc)_2 \cdot 4H_2O$ (1.0 g) was added to 15 mL water. To the solution, CuO, NiO, MgO, SiO₂ or ZrO₂ (2.0 g) was added, and the mixture was stirred for 24 h under Ar. The solid was centrifuged, and washed by water. Then, the solid was added to a basic KMnO₄ solution (KMnO₄: 50.0 mg; KOH: 250 mg; water: 5.0 mL) and stirred for 20 min. The solid was centrifuged, washed with water to remove KMnO₄, and dried at 60 °C in air.

Results and discussion

Supports are used to control size, morphology, phase and crystallinity, electronic properties, diffusion of reagents and products in the catalysts structure, and capillary condensation of the reaction products [23]. They are also important for modifying the mechanical strength of the catalysts [23]. We used nanoparticles of CuO, NiO, MgO, SiO₂ or ZrO₂ with diameter <50 nm. These supports have different acidic, basic, redox active, and redox inert characters.

Mn oxides on supports were synthesized by a simple method. In the first step, Mn(II) was attached to the support, most probably by coordinating to OH groups on the surface:

$$M-OH \ (M: Cu, Ni, Mg, Si \ and \ Zr) + Mn(II) \rightarrow M-O-Mn(II) \quad (1)$$
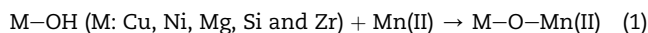
In the next step, we oxidized the Mn^{2+} ions on the surface of the supports with MnO_4^-.

$$M-O-Mn(II) + MnO_4^- \rightarrow M-O-MnO_2 \quad (2)$$
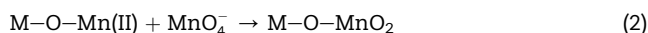
In the IR spectra of the compounds, a broad band at $\sim 3200-3500 \ cm^{-1}$ is observed that is related to antisymmetric and symmetric O–H stretchings. The peak at $\sim 1630 \ cm^{-1}$ is related to the H–O–H bending (Figs. S2–S4). The absorption bands characteristic for an MO_6 core are observed in the region $\sim 450-600 \ cm^{-1}$, stemming from stretching vibrations of M–O bonds.

HRTEM images for CuO, NiO, MgO and ZrO₂ indicate the presence of Mn oxide with birnessite structure covered with a thin layer of Mn oxide (Fig. 1). However, the long-range order is not observed in this structure. In accordance with these images, Mn oxides form a well-dispersed phase on these supports (Fig. 1).

On the other hand, amounts of Mn oxides on the surface of metal oxides are low. Thus, Mn oxides were not detected by XRD and FTIR.

SEM and EDX results for Mn oxides on SiO₂ are shown in Fig. 2. A good dispersion of Mn oxides on SiO₂ is observed under these conditions.

It is important to note that X-ray diffraction shows no special phase for Mn oxides on the structure of these catalysts (Figs. S5–S14). It shows that in accordance with HRTEM, the Mn oxides on the support are amorphous. AAS results show that amounts of Mn in CuO, NiO, MgO, SiO₂, and ZrO₂ are