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Manganese oxides supported on nano-sized metal oxides as water-oxidizing catalysts for water splitting systems: 2-Water-oxidizing activities

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ARTICLE INFO

Article history:

Received 5 July 2016

Received in revised form

5 August 2016

Accepted 14 August 2016

Available online xxx

Keywords:

Artificial photosynthesis

Catalyst

Effect of support

Manganese oxide

Nanoparticle

Water oxidation

ABSTRACT

Synthesis and characterization of Mn oxides on the surface of nanoparticles such as $KAl_3(SO_4)_2(OH)_6$, Co_3O_4 , CuO , Fe_3O_4 , MgO , NiO , SiO_2 , SnO_2 , TiO_2 , WO_3 , zeolite, ZnO , and ZrO_2 have been reported previously. Herein, we reported the effect of support on the water-oxidizing activity of amorphous Mn oxides in the presence of cerium(IV) ammonium nitrate. We found that the efficiency of systems toward water oxidation depends on the nature of the support, and a significant effect was observed in the case of redox-active supports.

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Introduction

Splitting of water for large-scale hydrogen production is a very promising way to store sustainable energies [1–8]. However, water oxidation is a bottleneck for water splitting. Among many compounds [9–15], Mn oxides are promising to be used as water-oxidizing catalysts in water splitting systems [11,16]. In the same way, Nature uses a Mn oxide cluster as the water-oxidizing complex in plants, algae, and cyanobacteria [17].

In 1968, Glikman and Shcheglova reported water oxidation of metal oxides such MnO_2 in the presence of ceric perchlorate [18]. In 1979, Morita reported electrochemical water oxidation of Mn oxide and found Mn(III) ions as active sites for water oxidation [19]. In 1981, Shilov extensively used Mn oxides for water oxidation in the presence of different chemical oxidants [20]. In 1988, Harriman's group introduced and extended metal oxides as catalysts for water oxidation in the presence of different oxidants [21]. Interestingly, the research group loaded iridium oxide onto a variety of supporting materials such as ZnO , MgO , TiO_2 , Al_2O_3 , SiO_2 , ZrO_2 , SnO_2 , and V_2O_5 [15]

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<http://dx.doi.org/10.1016/j.ijhydene.2016.08.087>

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and reported that the most effective supports are ZnO and MgO [21]. The group proposed a direct reaction between IrO₂ and some supports such as BaO, CaO, and SrO to form iridate, followed by production of small aggregates of catalytically active materials. They also found that neutral oxides, such as Al₂O₃ and SiO₂ can make inferior supports compared with ZnO and MgO [21]. The clusters of IrO₂ were agglomerated on the surface of Al₂O₃ and SiO₂, forming larger nanoparticles. However, acidic oxides, such as SiO₂, ZrO₂, SnO₂ and V₂O₅, are not good supports for IrO₂ toward water oxidation [21]. The research group suggested the acidic surface stabilizes lower oxidation states of Ir, and most probably, the formation of IrO₂ was not easy under these conditions [21].

The effects of support on the water-oxidizing activity of other metal oxides have rarely been considered.

Synthesis of nanostructured Mn oxide clusters supported on mesoporous silica for water oxidation in the presence of Ru(bpy)₃³⁺ was reported [22]. Protection of active Mn centers of the catalyst from deactivation through surface restructuring and assisting the deprotonation of the catalyst during photocatalysis are important factors for the efficiency of these systems [22]. The water-oxidizing activity of small Mn oxide particles into zeolite was reported by Najafpour's group [23,24]. However, the transformation of such tiny Mn oxide to MnO₄⁻ was observed in the presence of cerium(IV) ammonium nitrate (Ce(IV)) [23,24]. For Mn oxides on the montmorillonite in the presence of Ce(IV), the leaking of catalysts is important [25,26].

In contrast to SiO₂ based supports, carbon nanostructures were found to be not very stable when used as a support for Mn oxides in the water oxidation reaction [27–31].

The synthesis of nano-sized Mn oxides on different supports is an appropriate strategy to design of promising water-oxidizing catalysts. Recently, the effect of nanoparticles of CuO, NiO, MgO, SiO₂ or ZrO₂ as support on the water-oxidizing activity of Mn oxides in the presence of Ce(IV) were reported [32]. The order of increasing the water oxidation activity of Mn oxides on different oxides is as follows:

NiO > ZrO₂, SiO₂ > MgO, CuO

Most likely, redox reactions play an important role in increasing the efficiency of the redox active supports toward water oxidation. We also found that the instability of MgO in an acidic condition of the experiment caused the decomposition of fragile Mn oxides deposited on it. On the other hand, SiO₂ or ZrO₂ showed no particular effect on the water-oxidizing activity of Mn oxides.

Herein, to study and improve the water-oxidizing activity of Mn oxides, we reported our new results on the effect of KAl₃(SO₄)₂(OH)₆, Co₃O₄, CuO, Fe₃O₄, MgO, NiO, SiO₂, SnO₂, TiO₂, WO₃, zeolite, ZnO or ZrO₂ as supports on the water-oxidizing activity of amorphous Mn oxides.

Experimental

Material and methods

All reagents and solvents were purchased from the commercial sources and used without a further purification. Cyclic

voltammetry studies were performed using an EmStat³⁺ device from the PalmSens Company (Netherlands) with a conventional three-electrode setup, in which a Nafion/catalyst/FTO, an Ag|AgCl|KCl(sat) and a platinum rod served as the working, reference, and auxiliary electrodes in LiClO₄ (0.25 M) at room temperature, respectively.

Synthesis

Please, see ref. [33].

Water oxidation in the presence of Ce(IV)

Oxygen evolution from aqueous solutions in the presence of Ce(IV) (0.11 M) was investigated using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 °C in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continuously with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with Ce(IV) solution. Without the catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, the catalyst was added as several small particles and oxygen evolution was recorded with the oxygen meter under stirring. The formation of oxygen was followed, and the oxygen formation rates per Mn sites were obtained from linear fits of the data by the initial rate. Water oxidation was performed with a setup shown in Fig. S1.

Results and discussion

Three usual methods to test the water-oxidizing activity of a catalyst are photochemical, electrochemical and chemical methods. [Ru(bpy)₃]²⁺ is an interesting photosensitizer in photochemical methods [34]. [Ru(bpy)₃]²⁺ plays a role similar to the reaction center Chlorophyll (Chl) in Photosystem II [34].

The illumination excites one electron from a t_{2g} orbital to a ligand-centered orbital in [Ru(bpy)₃]²⁺. The excited molecule is converted to a long-lived triplet state, ³[Ru(bpy)₃]^{2+*}, that has the potential to be engaged in a single-electron transfer [34]. This excited state has a long enough lifetime for reacting with an electron acceptor. The photochemical reaction is very complicated and depends on the reactor, intensity, wave-number of light, buffer, concentrations of buffer, [Ru(bpy)₃]²⁺ and S₂O₈²⁻. Interestingly, ³[Ru(bpy)₃]^{2+*} is a powerful oxidant and reductant. Thus, it can be used as a reductant and forms [Ru(bpy)₃]³⁺ [34]. In the next step, [Ru(bpy)₃]³⁺ oxidizes the water-oxidizing catalyst. In the presence of S₂O₈²⁻, it is proposed that SO₄⁻ is formed [34]. SO₄⁻ is a powerful oxidant and may change water oxidation to oxygen evolution [34]. In other words, in this condition one or both oxygen atoms for dioxygen formation may originate from oxidant than water [34]. Electrochemical water oxidation is also complicated, and the conductivity of catalyst is very important in this condition. To find the effect of supports on water oxidation, we selected Ce(IV) as a frequently used chemical oxidant. Ce(IV) is a commercially available non-oxo transfer agent that is a one-

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