Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Electrocatalytic investigation on the water oxidation ability of a hangman complex based on the $[Ru(tpy)(bpy)(OH_2)]^{2+}$ motif

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ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form
29 September 2016
Accepted 16 October 2016
Available online xxx

Keywords:
Ruthenium
Catalysis
Water oxidation
Hydrogen bonds
Hangman

ABSTRACT

Many known single-site ruthenium complexes used in the catalytic water oxidation reaction react according to the WNA mechanism (WNA = water nucleophilic attack). During catalysis, a nucleophilic attack of a water molecule on a high-valent metal oxo species occurs and the efficiency is positively influenced by beneficial hydrogen-bonding interactions utilizing an external acid or base. Thus, installing a proton-donor/acceptor functionality in proximity to the catalytic site should have a dramatic influence on the catalytic activity. We recently prepared a "hangman" version of the known $[Ru(tpy)(bpy)(OH_2)]^{2+}$ complex (bpy = 2,2′-bipyridine, tpy = 2,2′;6′,2″-terpyridine) in which a carboxylic functional group is placed close to the ruthenium center. This catalyst was initially investigated in homogeneous catalysis using cerium (IV) ammonium nitrate as sacrificial electron acceptor. Unfortunately, due to the acidic conditions used, the positive effect on the catalytic performance according to the base-assisted WNA mechanism was in fact hampered. Further investigations on heterogenized systems are presented herein and reveal a clear dependence of the catalytic activity on the solution pH.

1. Introduction

The continuous burning of fossil fuels (gas, oil, coal) to secure world's energy supply leads to the accumulation of larger amounts of carbon dioxide in the atmosphere. A change towards renewable energy systems is necessary to avoid drastic climate changes and related unforeseen influences on the world economy. The splitting of water into hydrogen and dioxygen is one major pathway to clean and sustainable fuel technologies [1–3]. The oxidation of water into protons and dioxygen is the critical – high-energetic – half reaction of this process.

Several ways to overcome the high activation barrier have been investigated in homogeneous [4–7] as well as heterogeneous [8–14] systems. The major advantage of the homogeneous systems is the easier investigation of structure-activity relationships by modifying the ligand structure. However, heterogeneous catalysis has the advantage of better device development and integration in PEC (photo electrochemical cells) [15–18].

The use of earth abundant metals, like Mn [19,20], Fe [21–25], Cu [26–28], Co [29–34] or Ni [35,36], led to the development of a larger number of water oxidation catalysts (WOCs) [37–40]. Nevertheless, metal complexes of rare elements such as ruthenium and iridium still show higher activities [41–50]. Indeed, ruthenium catalysts proved to be the best homogeneous catalytic systems in terms of high turnover number (TON) and turn over frequency (TOF). Compounds based on the bda-type ligand (bda = 2,2′-bipyridine-6,6′-dicarboxylate) showed TONs up to 100,000 and TOFs up to 1000 s^{-1} [51,52].

One of the best characterized and investigated WOCs, despite its low catalytic activity, is $[Ru(tpy)(bpy)(OH_2)]^{2+}$ which functions as a single-site catalyst [53–58]. It is suggested that a base assisted water nucleophilic attack on a ruthenium-oxo species is the crucial step in the O—O bond formation [59]. In fact, the rate-limiting step is the attack of a water molecule on a $Ru(V) = O^{3+}$ species, with concomitant loss of a proton, to produce a hydroperoxo intermediate [60].

Based on the results of earlier work we wondered if this archetypical compound would show improved catalytic activity using the so-called hangman motif. A proton-donor/acceptor functionality, e.g. a carboxylic acid group, that is dangling in close proximity to the reaction center is the key characteristic of hangman compounds. Complexes incorporating the hangman motif have already been used in the H_2O_2 dismutation reaction as well as the oxygen reduction reaction (ORR) and showed improved catalytic performance compared to the non-functionalized systems [61–63]. As the oxygen-evolution reaction

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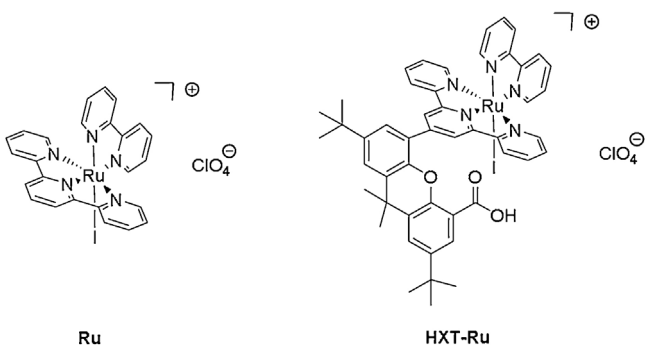
http://dx.doi.org/10.1016/j.cattod.2016.10.013
0920-5861/



Scheme 1. Ruthenium complexes investigated in this work; the hangman ruthenium complex **HXT-Ru** possesses a carboxylic acid function in its second coordination sphere that is able to function as a proton shuttle.

(OER) is just the reverse process of the ORR, we thought that the same motif could be used to enhance water oxidation activity. The working hypothesis is that the attacking water molecule is held in the secondary coordination sphere via hydrogen-bonding interaction to the functional group to allow for a more efficient O—O bond formation event to take place. Studies on the complex $[Ru(tda)(py)_2]^{2+}$ (with tda = [2,2′:6′,2″-terpyridine]-6,6″-dicarboxylate, py = pyridine) already showed that a carboxylic acid group in close proximity to the catalytically active site can lead to a drastic improvement of the catalytic performance [64]. It remains an open question how the functional group should be positioned best to have the most positive influence.

In order to understand in detail the elementary steps that occur at the reaction center, we recently synthesized the hangman version of the simple WOC $[Ru(tpy)(bpy)(OH_2)]^{2+}$ and investigated its activity in homogeneous systems [6]. First, a carboxylic acid group was connected via a xanthene backbone to a terpyridine unit to give the ligand **HXT**. In a second step, the ruthenium complex fragment was introduced and an anion exchange from chloride to iodide occurred. We were not able to isolate the hangman ruthenium compound with an aqua ligand on the ruthenium center but instead used the iodide-substituted version (**HXT-Ru**, Scheme 1) for the following experiments. Note, that in our as well as in earlier work of others it was shown that the exchange of an aqua ligand to an iodide ligand does not change the catalytic activity considerably [65]. To our delight, the mononuclear hangman complex indeed acted as catalyst for the chemically driven water oxidation using cerium(IV) ammonium nitrate (CAN) as oxidant. Surprisingly, the reference compound (**Ru**, Scheme 1) showed a much (almost 20-times) higher TOF_{max} of 1.41 min^{-1} as compared to **HXT-Ru** (TOF_{max} = 0.085 min^{-1} at pH = 1). Additionally, we discovered an unprecedented effect of the counter anion with perchlorate salts outperforming hexafluorophosphate salts [6]. The lower activity of the hangman complex was very likely related to a mismatch of pH because under the acidic conditions used the carboxylic acid group was protonated all the time and could not function as the wanted proton-donor/acceptor relay. The hydrogen-bonding interaction that was established with the protonated carboxylic acid very likely caused a deceleration of the catalytic activity. Unfortunately, we were not able to raise the pH and keep catalytic turnover under homogeneous reaction conditions. Other oxidizing reagents like $NaIO_4$ as well as a light driven water oxidation experiment with $Ru(bpy)_3^{2+}$ and $Na_2S_2O_8$ did not result in considerable catalytic activity [6].

Besides the photocatalytic activation of water, that would directly store solar energy in chemical bond energy (i.e. artificial photosynthesis) [37], electrochemical ways to activate water have been performed in order to replace the use of sacrificial agents. Thus, we also turned our interest to heterogeneous systems in which we immobilize our ruthenium hangman catalyst on an electrode and are now able to vary the pH of the solution over a wide range. The studies presented here reveal that at optimal pH and reaction conditions the hangman ruthenium complex indeed outperforms the non-functionalized reference compound.

2. Results

The synthesis of the ruthenium complexes **Ru** and **HXT-Ru** has been described earlier [6]. In various catalytic experiments we could demonstrate that the catalytic activity of **HXT-Ru** is significantly lower than **Ru** in highly acidic solutions [6]. The main reason was ascribed to the low pH of the aqueous solution, which was necessary when using CAN as sacrificial electron acceptor. In order to work at different pH values, we placed the catalysts on electrodes so that we do not require a sacrificial oxidizing reagent. Therefore, FTO (fluoride doped tin oxide) on glass was used as support and electrode material for the electrocatalytic experiments presented in this work. The plates were coated with a Nafion layer and then loaded with the homogeneous catalyst by dip coating. Afterwards the impregnated electrodes were investigated with different electrochemical methods for water oxidation activity. First, we will describe our results obtained with cyclic voltammetry (CV) on the compounds **Ru** and **HXT-Ru** in aqueous solution at different pH values in the region from 1 to 10. Second, chronoamperometric studies were done in solutions containing 0.1 M phosphate or citrate buffered electrolytes at pH 3.0, 4.6 and 7.0 in a gastight electrochemical cell under Ar atmosphere. All potentials reported in this publication are referenced to the Ag/AgCl/KCl(3.0 M) electrode unless otherwise noted.

Compounds **Ru** and **HXT-Ru** are immobilized via a self-developed method on FTO-coated glass slides. Other electrode materials like Steel, Nickel or Indium tin oxide on polyethylene terephthalate (ITO on PET) could be excluded because instable layers on the surface(s) were formed.

The FTO-coated glass slides were at first laminated by Scotchs® tape with a non-laminated area of 10 × 10 mm for the catalyst and an area of 5 × 5 mm for the electrode contact followed by a cleaning with ultrasound in methanol and water. Then, the electrodes were placed in a solution of 0.5 wt% of Nafion in methanol for 60 s and directly afterwards in a 0.1 M citrate or phosphate buffered solution for 24 h for swelling. Final coating for 30 min in 6 mL of a 0.7 mM solution (water:MeOH 1:2) of **Ru** or **HXT-Ru** leads to the desired immobilized catalyst systems. Note, that the electrodes need to be stored in a buffered water solution, as dried films tend to peel off the glass substrate.

In our earlier work, cyclic voltammetry was used to determine the electrochemical characteristics of the ruthenium compounds in acetonitrile solution. Complexes **Ru** and **HXT-Ru** show basically the same CVs with a reversible redox event assigned to the Ru^{II}/Ru^{III} couple at 0.45 V vs Fc^+/Fc and an irreversible event assigned to ligand reduction at around −2.0 V vs Fc^+/Fc. Thus, we could show that the hangman functionality does not influence the electronic properties of the $[Ru^{II}(tpy)(bpy)]$-unit [6].

Cyclic voltammetric experiments with the immobilized catalysts on the electrodes were done first to obtain an initial idea about the catalytic characteristics of the ruthenium compounds in aqueous solution. In Fig. 1 the pH dependency of the onset potential for OER for the reference complex **Ru** is presented. It becomes clear that the onset potential decreases with the increase of the pH and follows a monotonic behavior (see also Fig. 3 and Table 1). The onset potential was determined as the point of intersection of the rise of the oxidation curve with the baseline; it changes with ∼140 mV/pH for complex **Ru**.

Please cite this article in press as: P. Wrzolek, et al., Electrocatalytic investigation on the water oxidation ability of a hangman complex based on the $[Ru(tpy)(bpy)(OH_2)]^{2+}$ motif, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.10.013