Journal of Catalysis 292 (2012) 26-31

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

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

Suppression of the water splitting back reaction on GaN:ZnO photocatalysts loaded with core/shell cocatalysts, investigated using a μ -reactor

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ARTICLE INFO

Article history: Received 31 January 2012 Revised 8 March 2012 Accepted 23 March 2012 Available online 3 May 2012

Keywords: Photocatalysis Hydrogen Core/shell Water splitting GaN:ZnO Hydrogen oxidation

1. Introduction

Photocatalytic water decomposition into hydrogen and oxygen using solar light is a clean and renewable way to store energy from the sun as chemical energy. Several approaches have been studied in order to find a catalytic system able to perform this highly desirable reaction in an efficient way [1,2]. One of the promising systems consists of a powder catalyst made of a semiconductor photocatalyst (i.e., a metal oxide or an oxynitride) with the surface decorated by smaller cocatalyst nanoparticles. Photocatalytic water splitting using this kind of catalyst is illustrated in Fig. 1a. This system has several advantages originating basically from its simplicity: there is only one photocatalyst material, there are no wire connections, and a powder catalyst has a high surface-areato-mass ratio. However, it also presents some technical challenges. Hydrogen and oxygen are produced in the same environment, and they can back react to form water. This is an unfortunate event because it implies a loss of products and thus a loss of energy/efficiency. In order to achieve high efficiency, this back reaction must be avoided. In this work, we show through direct experiments how the water formation reaction (water splitting back

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ABSTRACT

Using silicon-based μ -reactors, we have studied the photocatalytic water splitting reaction and the catalytic back reaction on the same catalysts. GaN:ZnO without cocatalyst and loaded with Rh, Pt, Cr₂O₃/Rh, Cr₂O₃/Pt, and Rh–Cr mixed oxide has been tested for gas-phase photocatalytic water splitting. The results confirm the high activity observed in liquid-phase experiments with Cr₂O₃/Rh and Rh–Cr mixed oxide as cocatalysts. To investigate the reason of this enhanced activity, the back reaction was studied by reacting stoichiometric H₂/O₂ and monitoring the water molecules produced. The comparison of the two experiments shows that the suppression of the back reaction with the core/shell cocatalysts and the Rh–Cr mixed oxide corresponds to an increase in the net photocatalytic water splitting activity. The fact that the back reaction is not completely suppressed with Cr₂O₃/Pt compared to Cr₂O₃/Rh may be the cause of the higher net activity of the Cr₂O₃/Rh.

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JOURNAL OF CATALYSIS

reaction) can be suppressed by cocatalyst modification. The photocatalyst that we have used for this purpose is GaN:ZnO loaded with five different cocatalysts: two noble metals, Pt and Rh, their corresponding core/shell modification (the noble metal particles covered by a Cr_2O_3 shell), and the mixed oxide $Rh_{2-\nu}Cr_{\nu}O_3$. They have previously been synthesized and tested in liquid phase by Maeda et al., and the same authors have shown that the chromia shell improves the activity for photocatalytic liquid-phase water splitting [3,4]. So far, the GaN:ZnO with a band gap of 2.6–2.7 eV is the photocatalyst with the highest reported activity in the visible region for overall water splitting (5.1% at λ = 410 nm when loaded with $Rh_{2-\nu}Cr_{\nu}O_{3}$ [4]. For this reason, we focus the study of the chromia core/shell cocatalyst on this photocatalyst. However, the positive effect of the chromia shell is not limited to GaN:ZnO. For example, it has been shown recently that overall water splitting can be observed when GaN nanowires are loaded with a Cr₂O₃/ Rh cocatalyst, while no measurable activity has been observed when only Rh was loaded [5]. Electrochemical experiments using electrodes to model the cocatalyst nanoparticles showed that the reason for the enhanced activity when a chromia shell is used to protect the noble metals is the suppression of the water splitting back reaction [6]. In this work, the water splitting back reaction rate is analyzed directly measuring the catalytic water formation from a stoichiometric 2:1 flow of H₂ and O₂ and on the same systems used for photocatalytic water splitting (cocatalyst deposited



^{0021-9517/\$ -} see front matter © 2012 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcat.2012.03.021

on photocatalyst powder). This experiment is similar to hydrogen oxidation experiments that have been extensively studied in heterogeneous catalysts on model system, that is, Pt single crystals and Pt nanoparticles on oxide support [7,8]. Thanks to those experiments, a lot of information is available on surface coverage and kinetics for this reaction. Differing from these experiments, our purpose is not to study the fundamental aspects of the H_2/O_2 reaction, but to perform the H_2/O_2 reaction on photocatalysts at conditions similar to photocatalytic water splitting conditions (presence of stoichiometric H_2/O_2 mixture, room temperature, 1 bar). Finally, we compare those results with the photocatalytic activities obtained for gas-phase water splitting using the same catalysts.

2. Experimental

2.1. Preparation of the GaN:ZnO photocatalyst

 $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution $(x \approx 0.12)$ was prepared by heating a mixture of β -Ga₂O₃ (1.08 g) and ZnO (0.94 g) powders under NH_3 flow (200 ml min⁻¹) at 1098 K for 13.5 h according to a similar method we have reported previously [9,10]. The as-synthesized $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ powder was then subjected to post-calcination in a static air atmosphere at 873 K for 5 h [11]. The effects of preparation parameters on the physicochemical properties of GaN:ZnO have been discussed in our previous papers [10,12] and are reported briefly in the present study as supporting information. XRD analysis confirms that the as-prepared sample exhibits a single hexagonal wurtzite phase (Fig. S1). The sample has a featureless morphology (Fig. S2) with a specific surface area of 7–8 $m^2 g^{-1}$ determined by nitrogen adsorption at 77 K. As shown in Fig. S3, the band gap of the material is estimated to be ca. 2.7 eV. In this manuscript, the as-prepared $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ is referred to as GaN:ZnO for simplicity.

2.2. Deposition of cocatalyst nanoparticles

The Rh- and Pt-loaded GaN:ZnO was first prepared by a photodeposition method from Na₃RhCl₆ and H₂PtCl₆ solution, respectively, in which 1 wt.% metal was dissolved in each case. Using the as-prepared metal-loaded samples, photodeposition of K₂CrO₄ was done. Considering the self-limiting nature of Cr₂O₃ photodeposition, it is expected that ~0.3 wt.% Cr is deposited [13].



Fig. 1. Photocatalytic water splitting and catalytic formation of water on a photocatalyst (yellow) loaded with a cocatalyst (green). (For the interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Nanoparticulate Rh–Cr mixed oxide ($Rh_{2-y}Cr_yO_3$), a cocatalyst assisting H_2 evolution, was loaded onto the as-prepared ($Ga_{1-x}Zn_x$) ($N_{1-x}O_x$) catalyst according to the method described previously [14,15]. Briefly, 0.1 g of ($Ga_{1-x}Zn_x$)($N_{1-x}O_x$) powder and 3–4 ml of distilled water containing an appropriate amount of Na₃RhCl₆·nH₂O (Rh 17.8 wt.%) and Cr(NO₃)₃·9H₂O were placed in an evaporating dish over a water bath. The suspension was stirred using a glass rod to complete the evaporation. The resulting powder was collected and heated in air at 623 K for 1 h to convert Rh and Cr species to $Rh_{2-y}Cr_yO_3$ [15]. Rh and Cr were loaded at rates of 1 and 1.5 wt.% (metallic content), respectively.

2.3. Gas-phase photocatalytic water splitting reaction and back reaction in μ -reactors

Both the photocatalytic water splitting reactions and the dark back reactions (water formation) were performed using siliconbased μ -reactor technology [16]. The μ -reactor used for this work is a flow reactor and consists in a 350-µm-thick silicon chip with an area of 16 mm by 20 mm. Channels that allow the gas to flow are etched in the silicon as well as a circular (diameter = 10 mm) 3-µm-deep reaction chamber (240 nl total volume). The catalyst is dispersed, sonicated in water solution, dropped in the chamber, and allowed to dry using a circular mask of 8 mm in diameter. The amount of material deposited is \sim 60 µg for each catalyst. After catalyst deposition, the wafer is bonded to a Pyrex lid by the cold bonding technique [17]. The Pyrex lid is basically transparent at wavelengths λ > 300 nm, and thus, it allows photocatalytic experiments with solar light [18]. The chip presents two inlets and two outlets. One of the outlets is connected to a quadrupole mass spectrometer (QMS) by a flow-limiting capillary (the magnitude of the flow conductance is $\sim 5 \times 10^{15}$ molecule/s at 1 bar reactor pressure) and defines the flow through the reaction chamber. The two inlet channels mix on the chip into a main channel. The major part of the flow of the main channel goes through the second outlet where a pressure controller sets the pressure (1 bar in the experiments presented here). The water vapor used in the photocatalytic experiments is obtained by bubbling helium carrier gas (AGA, scientific quality 6.0) through pure, liquid water (Millipore, 18.2 M Ω cm). This water-saturated helium flows in the first inlet channel, while pure, dry helium flows in the second inlet channel. Each flow is regulated by conventional flow controllers and the humidity adjusted via control of the ratio of dry to water-saturated helium. For the back reaction experiments, He is flowing in the first input channel, while H₂ (or O₂) is flowing in channel 2. Then, O₂ (or H_2) is introduced in channel 1. Both H_2 and O_2 are of scientific quality 6.0 (AGA). The temperature of the μ -reactor is monitored by a thermocouple and controlled by a heating band and a thermo-electric (Peltier) cooling element. Thermo-grease is used to assure good heat conductivity between the back side of the reactor and the cooling element. The calibration procedure to convert the raw ion currents measured by the QMS into molecule/s is described in a previous publication [19]. The light source used in the photocatalytic experiments is a high-power UV LED (Hamamatsu model LC-L2) assembled with a focusing lens (Hamamatsu L10561-220), able to produce an average irradiance on the sample area of \sim 460 mW/cm², as measured using a photodiode (Thorlabs model S120VC). The peak wavelength is $\lambda \sim 367$ nm, and the FWHM is \sim 9 nm. This light source has been used instead of visible light in order to have a better signal-to-noise ratio, even if all the cocatalyst-loaded samples were tested to be active with a 1-kW Xe-arc source with a longpass 420-nm cutoff filter. The LED was used at 20% (92 mW/cm²) of its full power for all the photocatalytic water splitting experiments.

H, (peak)

H_(stable)

O, (peak)

O_(stable)



H.C

b

splitting with GaN:ZnO loaded with different cocatalysts. Relative humidity 85%. UV LED at $\lambda \sim 367$ nm ($I \sim 92$ mW/cm²). The inset a is an enlargement of the results for Pt and Rh. In the histogram, the values of the initial rate (the peak that can be seen in the time evolution of the QMS currents in inset b appearing immediately after the light is switched on) are shown with full colored columns, while the values of the stable rate obtained after 5 min of illumination are shown with hatched colored columns. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results

3.1. Photocatalytic gas-phase water splitting

GaN:ZnO with no cocatalyst and GaN:ZnO with five different cocatalysts were tested for gas-phase overall water splitting using an UV LED (\sim 367 nm) as light source. In a previous publication, we have shown that if the relative humidity, and thus the adsorption of water on the catalyst, is increased, the activity also increases [20]. It has been proposed that the increase in adsorbed water can facilitate surface proton conduction, a necessary reaction step for the water splitting mechanism. As a consequence, relative humidity is an important parameter for gas-phase water splitting and its value has been kept constant at \sim 85% (constant water partial pressure \sim 27.3 mbar and temperature of the reactor \sim 25 °C, 298 K) in all the tests. No hydrogen and oxygen photocatalytic evolution could be detected with GaN:ZnO powder without a cocatalyst. All the other samples were active for gas-phase water splitting, and the comparison of their activities is shown in Fig. 2. Both the initial peak value and the stable value for both hydrogen and oxygen obtained after 5 min of irradiation are shown for every sample. The ratio between the evolved H_2 and O_2 is ~ 2.5 for the samples loaded with the Cr₂O₃/Rh, Cr₂O₃/Pt, and Rh_{2-v}Cr_vO₃ for both the initial and stable values. The noble metal-loaded samples show a stronger departure from the stoichiometric ratio for the initial activity rate, while the ratio decreases during illumination. The GaN:ZnO samples loaded with only noble metals have the lowest activity, while the samples where Cr is present have a higher activity. In particular, the Cr₂O₃ shell improves the activity of both the Pt sample and the Rh sample. Cr₂O₃/Rh has a higher activity than Cr_2O_3/Pt and comparable to $Rh_{2-y}Cr_yO_3$. Apart from $Rh_{2-y}Cr_yO_3/Pt$ GaN:ZnO, none of the materials have previously been reported in the literature to work in gas phase for photocatalytic overall water splitting. The activity of Rh_{2-v}Cr_vO₃/GaN:ZnO is similar to what has been reported in our previous study for the same catalyst obtained with slightly different preparation conditions [20]. The presented experiments have been repeated several times, and the reproducibility of the results with the optimized catalysts is usually within 10-15%. Possible sources of error can be attributed to small differences in the concentration of the catalysts in the solution from which the catalyst is drop-casted on the lid and errors in the estimation of the relative humidity.

3.2. Water splitting back reaction

Water formation from the catalytic reaction of H₂ and O₂ has been measured for all the samples. This experiment consists in measuring the amount of water evolved as detected by a QMS. Since this reaction evolves high amount of energy, it can be dangerous to perform in a macroscopic reactor. In our case, however, the reactor chamber is only 240 nl in volume, essentially eliminating the safety issues. We have performed the experiments at room temperature (25 °C, 298 K), diluting the H₂ (2 ml/min)/O₂ (1 ml/ min) flow mixture with 15 ml/min of He and at 1 bar of total pressure. Fig. 3a and b presents typical examples of a back reaction experiment. In Fig. 3a, the raw data of an experiment with the reactor loaded with Pt/GaN:ZnO are shown. At the beginning of the experiment, only O_2 and He are flowing through the reactor. A local minimum in the O₂ occurs instantly after the H₂ flow in the He channel is started (~90 min after we have mounted the reactor into the gas manifold). At the same time, a peak in the He is measured. These features are due to the sudden increase in the flow of channel 1 (passing from 15 ml/min of He to 17 ml/ min (15 of He and 2 of H_2)) and therefore not related to any catalytic activity (the same feature is observed in Fig. 3b). After the introduction of hydrogen, the water signal increases. At the same time, the oxygen is consumed, confirming the occurrence of the back reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1}$$

for the Pt-loaded sample (Fig. 1b). Notice that this spontaneous reaction ($\Delta G < 0$) occurs without the need of photoexcited carriers, but it is facilitated by the catalytic properties of the surface of the Pt nanoparticles. The dominant mechanism is a Langmuir-Hinshelwood type, involving the dissociative adsorption of hydrogen and oxygen. In Fig. 3b, the experiment has been repeated for $Rh_{2-\nu}Cr_{\nu}O_{3}/GaN:ZnO$. In this case, the introduction of hydrogen does not cause any noticeable evolution of water or consumption of oxygen, meaning that the back reaction is strongly suppressed with the Rh_{2-v}Cr_vO₃ cocatalyst. Notice that this second experiment shows also that if reaction 1 occurs on the hot filament in the QMS, the rate is negligible and below our detection limit. Thus, there is no need to repeat the experiment with an empty reactor.

This experiment was repeated for all the other samples including the GaN:ZnO without cocatalyst. In this latter case, no back reaction activity is observed. The highest back reaction activity is observed for Pt cocatalyst. Both core/shell cocatalyst exhibited less catalytic activity for the back reaction than their respective pure noble metal. A similar back reaction experiment was also performed for all the samples by changing the order of introduction of H_2 and O_2 . In this experiment, the initial flow is H_2 and O_2 is introduced later. So in this experiment, the sample is in a dry H₂ atmosphere when O₂ is injected, while in the experiments discussed before it was in a dry O₂ atmosphere when H₂ was injected. The results of the two kinds of back reaction experiments are summarized in Fig. 4 together with the photocatalytic water splitting results. For the latter, only the H₂ evolution is shown not to overload the plot with information, while for the back reactions experiment, the water formation rate measured after 30 min from the introduction of the second reactant gas $(H_2 \text{ or } O_2)$ is shown. All the raw data are available as Supplementary information. In the case when O₂ is introduced last, the water signal for the samples that have a finite back reaction rate presents an initial peak (with the maximum at \sim 4 min after the introduction of O₂). After that, the signal reaches a lower steady state. We noticed that neither the peak value nor the steady state is equal to the steady state of

1600



Fig. 3. QMS current for hydrogen molecules (m/z = 2), oxygen molecules (m/z = 32), water molecules (m/z = 18), and helium (m/z = 4) as a function of time for a water splitting back reaction experiment. The flow of H₂ is 2 ml/min, of O₂ 1 ml/min, and of He 15 ml/min. Water is evolved in the case of Pt/GaN:ZnO. No water could be detected with Rh_{2-v}Cr_vO₃/GaN:ZnO.



Fig. 4. Initial hydrogen evolution rate for overall photocatalytic water splitting (blue squares) and water evolution rate for the dark back reaction experiments starting with H_2 (green triangles) or O_2 (black circles) diluted in He. Notice that the 3 set of data are taken from three different kinds of experiments, as indicated in the labels. For the two back reaction experiments, H_2 and O_2 are mixed in the stoichiometric ratio. In the *x*-axis is indicated the cocatalyst loaded on the GaN:ZnO. The X indicates the bare GaN:ZnO powder without cocatalyst. (For the interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the other case, when O_2 is flowing as first reactant gas and H_2 is introduced later.

As previously mentioned, the reactions are carried out in the dark so the water formed in these experiments is not the result of light excitation of the catalyst. However, to study the effect of light, we have illuminated the sample with the UV LED light source used in the photocatalytic water splitting experiment with the maximum power (~460 mW/cm²) before the second reactant gas is introduced and after at least 30 min of this introduction (Figs. S4–S15). In the case of light exposure when only one of the reactant gases was present, we have performed that experiment first of all to clean eventually small amount of dirt accumulated on the surface from the air and second to have a reference to compare the light effect in the stoichiometric mixture. No effect of light can be seen for the GaN:ZnO without cocatalysts. The same holds for all the experiments with the Rh-based catalyst. If the light has an effect with these samples, it is negligible. It is noticeable that in the case of pure GaN:ZnO and GaN:ZnO loaded with Cr₂O₃/Rh and Rh_{2-v}Cr_vO₃, no back reaction rate can be detected even in the presence of light. A different situation occurs with Pt and Cr2O3/Pt cocatalysts. With these samples, an increase in the water evolution rate can be detected under illumination when the system is exposed to the stoichiometric H₂/O₂ mixture. This effect is particularly strong with Pt when we start flowing H₂. In that case, the water signal increases to a value approximately equal to the maximum of the initial peak and a new steady state is reached. To check whether this effect is due to a cleaning of the surface of Pt, from, that is, hydrocarbons contamination, we have repeated the back reaction experiment with Pt immediately after the first experiment, without dismounting the chip (Fig. S16). The sample showed exactly the same behavior, which rules out the hypothesis of photo-induced cleaning of the surface from contamination. We have noticed that in both the experiments just described, mass 28 is increased when the light is on under stoichiometric H_2/O_2 mixture together with a small CO_2 (m/z = 44) evolution. Since the time evolution of mass 28 is different than the one of mass 44, we assigned this signal mainly to N₂ (instead of CO) and thus to photocorrosion of the surface of the catalysts. This attribution is also supported by the ratio of the measured mass 14 and 28 (equal to 0.15). Notice, however, that these signals are two orders of magnitude smaller than the water signal. This small but detectable photocorrosion is also present with the Pt sample when the back reaction experiment starts with O2, but no evidence of photocorrosion has been seen during the photocatalytic water splitting experiments or with other samples.

4. Discussion

The trend of photocatalytic activities in Fig. 2 for the gas-phase water splitting reaction is in agreement with what has been reported for liquid phase [3,21]. In liquid-phase experiments, stoichiometric H₂ and O₂ production has been measured with GaN:ZnO loaded with Rh–Cr mixed oxide and core/shell cocatalysts, while in the reported gas-phase experiments, the ratio of H₂ and O₂ slightly exceeds the stoichiometric value. This behavior has been also reported and discussed in a previous publication about gas-phase water splitting with Rh_{2-y}Cr_yO₃/GaN:ZnO and could not be associated with any substantial amount of hydrocarbon contamination or H₂O₂ formation [20]. As shown in Fig. 2, overall photocatalytic water splitting was observed with all the samples loaded with cocatalysts but not with the GaN:ZnO alone. This fact shows

the importance of the cocatalyst in the photocatalytic production of H₂ and O₂ from pure water. The reason for this is that the cocatalyst improves catalytic kinetics at the surface and helps separating the photoelectrons from the photoholes, that otherwise would recombine. Following these considerations, one of the aims of this work is to obtain a better understanding of different cocatalysts and how their positive effect can be optimized. By comparing the different activities for photocatalytic overall water splitting, we can observe that there are marked differences between GaN:ZnO loaded with bare Pt and Rh and their modifications. Both Pt and Rh are known as good hydrogen evolution reaction (HER) catalysts, while the surface of GaN:ZnO acts as the oxygen evolution site (Fig. 1a). It is known by the experimental work of Trasatti for electrochemical hydrogen evolution [22] and by the theoretical study using DFT calculations of Nørskov et al. that Pt is a very good catalyst for HER [23]. The same holds for Rh. Even if the activity of Rh is lower than that of Pt. it is still one of the best catalysts for this reaction, as can be seen in the volcano plots obtained in the aforementioned works. On the other hand, Cr₂O₃ has not been reported to be a good HER catalyst. These considerations are not enough to explain the trend in Fig. 2, since the activity of both Pt and Rh is smaller than those of Cr_2O_3/Pt , Cr_2O_3/Rh , and $Rh_{2-\nu}Cr_{\nu}O_3$. However, we will show how the experimental results can be justified by the presence of O₂, formed by the splitting of water, close to the HER cocatalyst. This situation is different from the case of an electrochemical cell, where the HER and the oxygen evolution reaction (OER) occur in separated compartments. Instead in the system studied, H₂ and O₂ evolve in the same environment. If we consider the comparison between the noble metal and their core/shell modification shown in Fig. 5, we can see how the Cr₂O₃ shell has the simultaneous effect of suppressing the back reaction and enhancing the detected amount of $H_2 \mbox{ and } O_2.$ This is in agreement with what was found for the model electrodes, and explained by the fact that Cr₂O₃ can block O₂ from reaching the surface of the noble metal nanoparticle cocatalysts while H⁺ can still get through. The latter can penetrate the shell, react with the photoelectrons on the noble metal surface, and pass back through the shell again as H₂, due to its smaller molecular radius compared to O₂. In this way, the oxygen reduction reaction (ORR):

$$4H^+ + 4e^- + 0_2 \to 2H_20 \tag{2}$$



Fig. 5. Comparison between the two noble metals tested as cocatalysts and their core/shell modification. The cocatalysts were deposited on GaN:ZnO. In the figures, the initial hydrogen evolution rate for overall photocatalytic water splitting (blue) and the water evolution rate for the dark back reaction experiments starting with O_2 (black) are shown. The arrows further underline the opposite tendency between the H₂ detected in the water splitting experiments and the H₂O evolved in the back reaction. (For the interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Oxygen blocking by the proton- and hydrogen-permeable Cr_2O_3 shell. In the absence of Cr_2O_3 , the O_2 can react on the Rh cocatalyst and recombine with the hydrogen to form water (water splitting back reaction) (a). In the case of Cr_2O_3/Rh cocatalyst, the shell prevents the O_2 to reach the Rh, while protons can penetrate the shell and react with the photoelectrons on the Rh core forming hydrogen (b).

as well as the catalytic reaction between H_2 and O_2 (reaction Fig. 1b) is strongly suppressed. So the Cr_2O_3 acts as an oxygenblocking proton/hydrogen membrane (Fig. 6a and b). The fact that Pt and Rh show high activity for the back reaction is well known in fuel cell literature [24], where ORR is studied, and it is also illustrated in the volcano plot for ORR calculated using DFT by Nørskov et al. [25]. It can be seen from the comparison of the two volcano plots that even if the two noble metals, Pt especially, are very good for HER, they are also very good for ORR. So the trend shown in Fig. 2 is a trade-off between these two phenomena. If oxygen is able to reach the HER cocatalyst, this one needs to be a very bad ORR cocatalyst in order not to reduce it. It is very difficult to find a single material that has both these properties. It is probably a better approach to try and protect the HER catalyst with a membrane, like it has been done in the case with the Cr₂O₃ shell that separates it from the O_2 produced at the OER active sites.

The proposed explanation that the observed back reaction rates are the main cause of the deviation from the HER trend implies that the rate-determining step is the charge transfer at the cocatalyst molecules and not the one at the photocatalyst-cocatalyst (where possible different Schottky barriers can be thought to play a role). Indeed, Szklarczyk and Bockris have reported that the photocatalytic evolution of H₂ with a photocathode of p-InP coated with islets of different metals (Pb, Cd, Co, Au, Ni, Pt) correlates very well with the dark electrocatalytic evolution of H₂ from the bulk metal electrodes [26]. From this comparison, the authors conclude that the charge transfer at the photocatalyst-cocatalyst interface is not the step that determines the photoelectrochemical evolution of H₂ in the case of a semiconductor cover with metal islets. This conclusion is in agreement with the characteristic times for primary processes in TiO₂ photocatalysis reported by Fujishima et al. in a recent review [27]. From the comparison between the characteristic times, it is clear how in Pt-loaded TiO₂ the electron transfer from TiO₂ to the Pt clusters is much faster than the interfacial charge transfer to adsorbates.

The behavior of $Rh_{2-y}Cr_yO_3$ cocatalyst is more difficult to explain than the one of the core/shell cocatalysts. The experiments show that the chromia mixed with Rh is still preventing O_2 to be reduced. According to our previous study using XPS and XAFS, the valence state of Rh species in $Rh_{2-y}Cr_yO_3$ is trivalent, which remains unchanged even after water splitting reaction [28]. However, it is still not clear how the Rh species in the cocatalyst work during the working state of water splitting.

Comparing the results of the two kinds of back reaction experiments where the order of H_2 and O_2 introduction is changed, one can notice that they basically show the same trend: Pt has the

31

highest rate of back reaction, the back reaction rate from Cr₂O₃/Pt is reduced with respect to Pt, and the one from Cr₂O₃/Rh and $Rh_{2-\nu}Cr_{\nu}O_{3}$ is strongly suppressed with respect to the one of Rh. However, even if they present the same trend, there are some differences between the two kinds of back reaction experiments. In particular for Pt and Rh, the steady-state reaction rate reached when the sample is subject to an initial H₂ flow is lower in intensity than the one when O_2 is flown first. This difference could arise from different surface coverages of oxygen and hydrogen on the cocatalyst nanoparticles. Indeed, it is known that at low temperatures, as the one in our experiment, hydrogen has the effect of poisoning the surface due to the weak temperature dependence of its sticking coefficient with respect to the exponential temperature dependence of desorption. A hysteresis cycle with two different steady-state reaction rates has been reported for Pt, in agreement with our results [8,29]. The steady state reached after illumination in the case of Pt and Cr_2O_3/Pt can also be due to a different surface coverage, this time induced by the interaction of the adsorbates with the photoexcited carriers. Another difference that can be noticed comparing the two types of back reaction experiments is that the suppression of the back reaction due to the chromia shell seems to be stronger when the experiments start with O₂ instead of H₂. A possible explanation for this difference in behavior may be a partial reduction of the chromia under the initial hydrogen atmosphere. However, this case is less interesting than the one starting with oxygen since in typical water splitting experiments the catalyst is transferred from air to liquid water, so it is not subjected to a reducing hydrogen atmosphere. From Figs. 4 and 5, it is clear that the water formation rate is higher for the Cr₂O₃/Pt than for the Cr₂O₃/Rh, where it is basically negligible. This fact can likely be the cause for the higher net forward photocatalytic activity observed for the Cr₂O₃/Rh system compared to the Cr₂O₃/Pt system. Furthermore, this observation suggests that if Pt can somehow be protected more efficiently, then this system would have a higher activity, potentially even higher than protected Rh. This consideration agrees with the fact that the back reaction activity for the bare Pt is much higher than the one for the Rh, as expected from the ORR volcano plot, while their photocatalytic water splitting activity is comparable.

5. Conclusion

Gas-phase photocatalytic water splitting experiments show, in agreement with liquid-phase analogs, that Rh_{2-v}Cr_vO₃/GaN:ZnO and Cr₂O₃/Rh/GaN:ZnO have a superior activity for this reaction compared to Rh/GaN:ZnO, Pt/GaN:ZnO and Cr₂O₃/Pt/GaN:ZnO. The experiments also show that Cr₂O₃/Pt/GaN:ZnO has a higher activity than Pt/GaN:ZnO and Rh/GaN:ZnO. The results of the photocatalytic experiments find a correlation with the ones from the water splitting back reaction (stoichiometric H₂ oxidation). The sample with the Pt cocatalyst has the highest rate of back reaction and the Cr₂O₃ shell deposited on the Pt reduces this rate. In a similar way, the water formation rate for Cr_2O_3/Rh and $Rh_{2-\nu}Cr_{\nu}O_3$ is strongly suppressed and negligible compared to the one for Rh. The combination of the photocatalytic water splitting and its catalytic back reaction clearly shows the positive effect of the Cr₂O₃ shell in suppressing the water formation from H_2/O_2 back reaction, thereby enhancing the net production of H₂ and O₂ from water splitting.

Acknowledgments

Center for Individual Nanoparticle Functionality (CINF) is financed by the Danish National Research Foundation. This was also financed by the Research and Development in a New Interdisciplinary Field Based on Nanotechnology and Materials Science program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and The KAITEKI Institute, Inc. This project was further funded by the "Catalysis for Sustainable Energy" (CASE) research initiative, which is funded by the Danish Ministry of Science, Technology and Innovation.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.03.021.

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