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A new method for studying activity and reaction kinetics of photocatalytic water oxidation systems using a bubbling reactor

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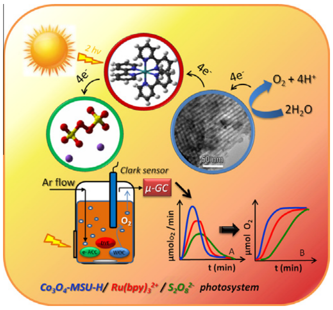
HIGHLIGHTS

- A new method is proposed for studying overall activity of water oxidation catalysts.
- Mass transfer phenomena in the bubbling reactor have been mathematically modelled.
- The actual rate of oxygen formation (R_{O_2}) as a function of time is calculated.
- Increase of sweeping gas flow enhances R_{O_2} by decreasing diffusional limitations.
- The method can be also applied for testing semiconductor photocatalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method is proposed for studying kinetics and overall activity of water oxidation (WO) catalysts using a bubbling reactor, where oxygen concentration is measured simultaneously in the liquid and in the gaseous phase. Total oxygen evolution is obtained from direct integration. The actual rate of oxygen formation as a function of time, $R_{O_2}(t)$ not accessible to direct measurement with batch reactors, is calculated from raw data through a simple but comprehensive mathematical model, taking into account mass transfer phenomena occurring in the system. Data concerning the activity of a nanostructured Co_3O_4 catalyst dispersed on a mesoporous silica (MSU-H), in the presence of tris(2,2′-bipyridyl)Ruthenium $[Ru(bpy)_3]^{2+}$ as sensitizer and $Na_2S_2O_8$ as sacrificial reactant, are used to illustrate data processing. Behaviour of the system is complicated by the occurrence, besides WO reaction, of the degradation of the sensitizer. Increase of sweeping gas flow increases $R_{O_2}(t)$, by decreasing diffusional limitations to the reactions in the system: conditions for minimizing those were established. Data reported show that the assumption generally made of equilibrium between gaseous and liquid phase through Henry's law is incorrect, the more so the smaller the apparent mass transfer coefficient, k_La. An additional reason for removing oxygen from the liquid phase through bubbling is the occurrence of a parasitic reaction of molecular oxygen with the sensitizer. The method seems to yield reliable values of both k_La and the set of $R_{O_2}(t)$ values: the former scales with the flow of sweeping gas, as expected; $R_{O_2}(t)$ curves are in qualitative agreement with accepted reaction mechanisms. Results concerning $R_{O_2}(t)$ lend support to our previous kinetic studies (M. Armandi et al., ACS Catal, 2013, 3, 1272) where the reaction rate was assumed as constant for the first ~15 min. Availability of $R_{O_2}(t)$ data not too biased by diffusional limitations opens the way to realistic studies of the kinetic features of WO heterogeneous reactions, in the present case as well as in many others.

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Nomenclature

Symbols

b_i	GC analyzer's sampling time (s)
C_{O_2}	oxygen concentration in the liquid (mol/m^3)
$C^*_{O_2}$	oxygen concentration in equilibrium with $p_{O_2,analyzer}$ calculated by Henry's law
$CumO_2$	cumulative oxygen in all the environments of the reactor (mol)
H	O_2 Henry's law constant (m^3 Pa mol^{-1})
k_La	gas–liquid mass transfer coefficient of the oxygen (s^{-1})
P	absolute pressure in the headspace of the reactor (Pa)
$p_{O_2,b}$	oxygen partial pressure in the gaseous bubbles (Pa)
p_{O_2}	oxygen partial pressure in the gas phase above the liquid (Pa)
$p_{O_2,analyzer}$	oxygen partial pressure in the GC analyzer (Pa)
Q	Argon sweeping gas flow rate ≈ gaseous bubble flow rate (m^3 s^{-1})
R	gas perfect constant (J mol^{-1} K^{-1})
R_{O_2}	reaction rate of O_2 generation (mol m^{-3} s^{-1})
R'_{O_2}	reaction rate of O_2 generation referred to V_R (mol s^{-1})
r_{is}	reaction rate of oxygen generation in the liquid phase, in the Laplace domain (mol m^{-3} s^{-1})
t	time (s)
T	absolute temperature (K)
V_l	liquid phase volume (m^3)
V_b	gaseous bubble phase volume (m^3)
V_R	reactor volume ($V_l + V_g$) (m^3)
V_g	gas phase in the headspace above the liquid (m^3)
X	oxygen concentration in the liquid, in the Laplace domain (mol/m^3)
Y	oxygen partial pressure in the gaseous bubbles, in the Laplace domain (Pa)
Z	oxygen partial pressure in the gas phase above the liquid, in the Laplace domain (Pa)

Greek characters

ε	gaseous bubbles hold up (−)
Δt	GC measurement delay (s)
Φ_{O2}	O_2 flow rate in the gas phase (m^3 s^{-1})

Subscripts and suffixes

exp	experimental value
sim	simulated value
_L	in the liquid phase
_out	flowed out to the GC analyzer
_gen	generated
_G	in the headspace above the liquid

Units are expressed as used in the equations; units in the figures are coherent with the captions.

1. Introduction

Researchers all over the world are investigating photochemical water splitting (WS) to H_2 and O_2, as a promising way to store solar energy [1], a challenging reaction thermodynamically uphill [2]. Hydrogen can then be used directly in combustion engines or fuel cells, or combined catalytically with CO_2 to make carbon containing fuels [2,3].

WS on semiconductors has been much studied since the pioneering work by Honda and Fujishima [4] with a TiO_2 photoelectrode under UV illumination. The wide band gap, however, of common semiconductors hampers their efficiency, since the absorption of the solar energy is limited to a tiny fraction of the total [5], basically in the UV. Thus, many new semiconductors are being studied [6].

A common approach consists in separating the functions of light harvesting from water oxidation (WO) and hydrogen formation [7]. As it concerns WO, different metal oxides (containing Ir, Co, Ru, Ni, Rh and Mn) and transition metal complexes (basically Co- and Ru-based) have been studied as heterogeneous [8] and homogeneous [9–11] catalysts to carry out the four electron oxidation of water to O_2 under photochemical conditions.

A possible way to measure the catalyst activity is by means of photoelectrochemical cells [12–14]. Alternatively, WO catalysts can be checked by the coupling with photosensitizers and sacrificial reagents [15–17]. This type of study is particularly suited to determine whether or not a given catalyst satisfies the kinetic and thermodynamic requirements for the water splitting reaction [16]. Very common is the use of a salt of tris(2,2′-bipyridyl)Ruthenium, $[Ru(bpy)_3]^{2+}$, in the presence of persulfate anions $S_2O_8^{2-}$) [8,18]. The photocatalytic cycle for such system is illustrated in Scheme 1 and consists of [19,20]: (a) visible light ($\lambda = 450$ nm) absorption by $[Ru(bpy)_3^{2+}]$ with formation of an excited state $[[Ru(bpy)_3^{2+,*}]]$; (b) oxidation of this latter species to $[Ru(bpy)_3^{3+}]$ by the persulfate, that is irreversible reduced (Eqs. (1) and (2)) and (c) in presence of the WO catalyst, the photosensitizer captures electrons from the catalyst surface, which in turn causes oxidation of water to O_2, while H^+ are produced (Eq. (3)). Without a WO catalyst, no O_2 is produced and the Ru^{3+} version of the photosensitizer rapidly decomposes due to OH^- attack on the bipyridile ring (Eq. (4)) [21], a reaction always competing with WO.

$$Ru(bpy)_3^{2+*} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{3+} + SO_4^{-2} + SO_4^{-\cdot} \quad (1)$$

$$Ru(bpy)_3^{2+} + SO_4^{-} \rightarrow Ru(bpy)_3^{3+} + SO_4^{-2} \quad (2)$$

$$4Ru(bpy)_3^{3+} + 2H_2O \xrightarrow{catalyst} 4Ru(pby)_3^{2+} + 4H^+ + O_2 \quad (3)$$

$$Ru(bpy)_3^{3+} + H_2O \rightarrow Ru(bpy)_3OH^{2+} + H^+ \\ \rightarrow \text{decomposition products} \quad (4)$$

Closed batch reactors are generally used for WO studies, where O_2 evolution is analysed either by measuring O_2 dissolved in liquid with a Clark-type electrode [8,11] or measuring O_2 partial pressure in the gas headspace by Gas Chromatography (GC), assuming equilibrium between the gas and the liquid phases [6,19,20]. The initial rate of reaction is considered as the slope of the linear portion of the O_2 concentration curves obtained by the first method, whereas the total O_2 produced is determined from the GC-based type of measurement. From these, the initial Quantum Yield (or Turn Over Frequency) and the Turn Over Number of the catalyst, respectively, are determined, the most important variables to compare the performance of different catalysts.

We have undertaken recently a systematic study of Co-containing catalysts for WO, including Co-APO-5 zeotype [12,22], Co_3O_4 (this work) and, more recently, Co-MOFs [23]. As it concerns Co-APO-5, a first set of photoelectrochemical measurements was carried out, showing the occurrence of WO process [12]. As a second step, a flow reactor was set up, where oxygen evolution was followed in the gas phase: based on such measurements, preliminary kinetic features of a WO system similar to the one under study