Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Kinetic modeling of hydrogen generation over nano-$Cu_{(s)}/TiO_2$ catalyst through photoreforming of alcohols

Laura Clarizia [a], Ilaria Di Somma [b], Luca Onotri [c], Roberto Andreozzi [a], Raffaele Marotta [a,*]

[a] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, p.le V. Tecchio 80, 80125 Napoli, Italy
[b] Istituto di Ricerche sulla Combustione, Centro Nazionale delle Ricerche IRC-CNR, p.le V. Tecchio 80, 80125 Napoli, Italy
[c] Centro Interdipartimentale di Ricerca Ambiente, Università di Napoli Federico II, via Mezzocannone 16, 80136 Napoli, Italy

ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form 20 May 2016
Accepted 21 May 2016
Available online xxx

Keywords:
Nano-photocatalytic materials
Catalytic photoreforming
Sacrificial photocatalysis
Hydrogen production
Kinetic modeling
Copper modified-TiO_2

ABSTRACT

The production of hydrogen by photocatalytic reforming of methanol and glycerol was investigated using metal copper-modified TiO_2 nanoparticles, prepared "in situ" by reduction of cupric ions. A modeling investigation was performed through the development of a simplified kinetic model taking into account the mass balance equations for the main reactive species involved in the photocatalytic system. The kinetic model was tested to predict hydrogen generation rates for experimental runs carried out at different initial concentrations of sacrificial agent (methanol and glycerol) and at varying photocatalyst load.

The modeling investigation allowed to estimate for the first time the equilibrium adsorption constants and the kinetic constant for the hole-capture by sacrificial agents, as well as the quantum yield and the rate constant of electron-hole recombination for the copper modified-TiO_2 nano-photocatalyst. This study provide a reliable approach to model photocatalytic reforming of alcohols over metal modified-TiO_2 catalyst for hydrogen generation.

1. Introduction

A great attention has been devoted by researchers in recent years to hydrogen as a clean energy carrier, along with the identification of new processes for its production from non-fossil fuels [1–4]. Water photosplitting [5], photoelectrolysis [6] and photoreforming [7] are some of new sustainable technologies expected to allow in the near future an efficient conversion of solar energy into chemical one. However at present photosplitting and photoreforming efficiencies are still too low for industrial applications and new studies are still necessary. Although an efficient water photosplitting represents the final goal of all the investigations carried out in this field, photoreforming is of direct interest to the research community due to its ability of integrating hydrogen generation and wastewater treatment [8–10].

Indeed, wastewater organic pollutants or biomass-derived feedstocks can be used as hole scavengers able of reducing the occurrence of electron–hole recombination reaction, thus enabling photogenerated electrons to react with protons [7].

However, the scavenging effect exerted by organic species does not provide interesting hydrogen generation efficiencies. Literature reviews report different strategies to enhance hydrogen generation efficiency. One of these approaches is to modify TiO_2, the most used semiconductor in photocatalytic studies, with noble metal nanoparticles, such as Au, Ag, Pd, and Pt deposited on the oxide photocatalyst surface [11–14]. An increase in hydrogen generation rate is generally recorded on metal modified-TiO_2 catalysts as a result of photogenerated electrons transfer from TiO_2 surface to superficial metal spots. This photogenerated electrons transfer helps prevent electron-hole recombination [29]. The use of copper species, such as Cu_2O, CuO, and Cu, instead of noble metals deposited on the semiconductor surface for hydrogen production has been investigated in the last years and recently reviewed [15].

In previous studies some of the Authors investigated hydrogen generation from different oxygenated compounds by adopting a nanocopper modified-TiO_2-P25 catalyst prepared by a "in situ" deposition process [16,17]. Investigations on the nature of copper deposited on TiO_2, supported by different diagnostic techniques, confirmed the formation of zero-valent copper nanoparticles with particle diameter of about 30 nm. Moreover, the results obtained during these investigations indicated that hydrogen may be produced for the most part of the organic species tested at significantly higher rates than bare TiO_2-P25. In particular, the best results were

* Corresponding author:
E-mail address: rmarotta@unina.it (R. Marotta).

http://dx.doi.org/10.1016/j.cattod.2016.05.053
0920-5861/

observed for organic species strongly adsorbed on the catalyst surface such as methanol, glycerol, and formic acid.

In the present work, investigations were extended to the development of a suitable mathematical model capable of simulating hydrogen production over the same catalyst (nano-$Cu_{(s)}/TiO_2$), developed in the previous study, when glycerol or methanol were adopted as sacrificial agents [17].

2. Material and methods

2.1. Materials

All organic compounds used as sacrificial agents, TiO_2 nanopowder (commercial grade, Aeroxide TiO_2-P25, average particle size 21 nm, specific surface area $50 \pm 15\ m^2\ g^{-1}$, 80/20 anatase/rutile), cupric sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$,>98%) and chromotropic acid disodium salt dihydrate ($C_{10}H_6Na_2O_8S_2{\cdot}2H_2O$, 78.5%) were purchased from Sigma Aldrich. Glycerol (≥99.5%) was purchase from Sigma Aldrich, whereas methanol (99.9%) was purchased from Carlo Erba Reagents. Doubly glass–distilled water was used throughout this study.

2.2. Photocatalytic procedure

Photocatalytic runs were carried out in an annular glass batch reactor (0.300 L) thermostated at 25n°C and equipped with a magnetic stirrer. On the top of the reactor, an inlet allowed to feed reactants and nitrogen gas, and an outlet was used to collect liquid and gaseous samples at varying reaction times [30].

The reactor was endowed with a high-pressure mercury vapor lamp by Helios Italquartz (power input: 125 W), principally emitting at 305, 313, and 366 nm (manufacturer's data). The effective irradiances ($I^0_{\lambda_i}$) at 305, 313 and 366 nm are 2.56×10^{-6}, 2.70×10^{-6} and 3.30×10^{-6} Einstein s^{-1}, respectively. The lamp was located inside a glass cooling jacket in the center of the reactor and surrounded by the reacting solution.

For each run a fixed amount of TiO_2-P25 nanopowder was initially suspended in an unbuffered doubly distilled aqueous solution containing the sacrificial species.

In order to avoid the undesired reaction between dissolved oxygen and photogenerated electrons, before starting the photocatalytic experiment, a nitrogen stream was bubbled into the solution for 30 min. After this period, cupric sulfate pentahydrate was quickly added to the mixture.

Moreover, throughout the photocatalytic runs, nitrogen was continuously fed at a flow rate of 0.3 L min^{-1} in order to prevent the air inlet into the reactor.

2.3. Analytical procedures

At different reaction times (≥5 min), gaseous samples were collected by means of Tedlar gas sampling bags (1 L) and injected into the gas-chromatograph to record the rate of hydrogen generation. For this purpose, a gas chromatograph (Agilent 7820A) was used equipped with a HP-PLOT Molesieve 5A column (Agilent) and a TCD detector using argon as carried gas. Liquid samples, collected at different reaction times, were filtered on regenerated cellulose filters (pore diameter 0.20 μm, Scharlau). The filtrate was used to measure concentrations of total dissolved copper and formaldehyde produced through the oxidation of methanol.

In order to evaluate the concentration of total dissolved copper (cupric and cuprous species), a colorimetric method using an analytical kit (Macherey-Nagel) based on oxalic acid bis-cyclohexylidenehydrazide (cuprizone) was adopted. An UV/vis spectrophotometer (Cary 100 UV–vis Agilent) was used for the measurements at a wavelength of 585 nm. The concentration of formaldehyde was determined by the colorimetric method by Bricker and Vail [28], based on the use of chromotropic acid. The pH of the solution was monitored by means of an Orion 420 p pH-meter (Thermo).

Irradiance measurements were carried out on the external wall of the reactor at different heights through a digital radiometer (Delta Ohm HD 2102.1). Two sets of measurements were done, the first on an empty reactor and the second with the catalyst slurry inside it. From each set of data it was possible to estimate the total power emerging from the reactor, in both the absence and the presence of absorption by the slurry. The difference between these two values was assumed as the power absorbed by the catalyst.

2.4. Kinetic model

A simplified network of reactions was singled out by considering that, upon irradiation of $Cu_{(s)}/TiO_2$ catalyst nanoparticles, a couple of charge carriers is generated (r_1):

$$Cu_{(s)}/TiO_2 \xrightarrow{h\nu} e^- + h^+ \quad \text{(r1)}$$

$$\text{reaction rate}: \quad G = \frac{\Phi_{UV}}{V} \cdot \mathbf{Q}_{a,UV} + \frac{\Phi_{VIS}}{V} \mathbf{Q}_{a,VIS}$$

The rate of reaction r_1, which is a photochemical step, was accounted for by the products between quantum yields, in both the UVA (Φ_{UV}) and the visible range (Φ_{VIS}), and the respective average volumetric rates of photon absorption[34] by the catalyst suspension ($\mathbf{Q_{a,UV}/V}$, $\mathbf{Q_{a,VIS}/V}$), where V is the volume of irradiated solution (V = 0.280 L).

Charge carriers may recombine through radiative or non-radiative processes (r_2):

$$e^- + h^+ \xrightarrow{k_r} heat\ and\ light \quad \text{(r2)}$$

$$\text{reaction rate}: \ k_r \cdot \left[h^+\right] \cdot \left[e^-\right]$$

As reported by others [18], reaction r_2 is regulated by a second-order kinetic law in which k_r is the electron/hole recombination reaction constant.

Otherwise, charge carriers can be scavenged. In particular, photogenerated holes can also react with the adsorbed sacrificial organic compound (S^*), which successively oxidizes on the catalyst surface (r_4–r_5), where reaction r_4 is the rate-determining step for substrate oxidation:

$$S + \therefore^* \rightleftarrows S^* \quad \text{(r3)}$$

$$[S^*] = \frac{C_T \cdot K_{ads} \cdot [S]}{(1 + K_{ads} \cdot [S])}$$

$$S^* + h^+ \xrightarrow{k_{h^+}} S^{\bullet *} + H^+ \quad \text{(r4)}$$

$$\text{reactionrate}: \ k_{h^+} \left[h^+\right] [S^*]$$

$$S^{\bullet *} + H^+ \xrightarrow{H^\bullet/\text{fast}} \therefore^* + S_{ox} + 2H^+ \quad \text{(r5)}$$

As previously proposed [19], the direct reaction between positive holes and organic substrates is only possible if organics are strongly adsorbed on the catalyst surface. The adsorbed species concentration [S^*] may be obtained by a Langmuir-type model for adsorption, as reported for the equilibrium r_3 in which K_{ads} (M^{-1}) is the adsorption equilibrium constant, and C_T (M) is the total concentration of active sites on the catalyst surface for a fixed catalyst load q (g L^{-1}). The term C_T was calculated through the formula $C_T = q \cdot N$,

Please cite this article in press as: L. Clarizia, et al., Kinetic modeling of hydrogen generation over nano-$Cu_{(s)}/TiO_2$ catalyst through photoreforming of alcohols, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.05.053