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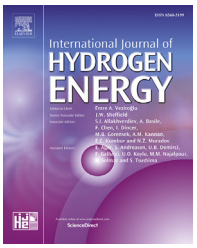

Evaluation of Pd-TiO_2/ZSM-5 catalysts composition effects on hydrogen production by photocatalytic water splitting

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ABSTRACT

The photocatalyst composition can significantly affect their physicochemical properties that are directly related to their photocatalytic activity. In this work, the influence of the Pd-TiO_2/ZSM-5 catalyst composition on hydrogen production by photocatalytic water splitting was studied. The ZSM-5 zeolite was use as support for the active phase of titanium dioxide; palladium was also incorporated as a metallic co-catalyst. The concentrations of TiO_2 and Pd were varied during catalyst synthesis according to a factorial rotational experimental design. The catalysts were characterized and employed in hydrogen production under ultraviolet radiation. Empirical models were obtained for relating physicochemical properties and hydrogen production as functions of palladium and titanium dioxide content. Relative crystallinity of the support and specific surface area were affected only by the titanium dioxide contend while band gap energy and hydrogen production were affected by nominal percentage of metallic co-catalyst and active phase. The most active catalyst was the 1.5%Pd-28%TiO_2/ZSM-5, which promoted hydrogen production rate of 1148 μmol g_{cat}^{-1} h^{-1} under low power irradiation font.

Introduction

The production of hydrogen by water splitting using energy from a light source in the presence of a heterogeneous catalyst, known as photocatalytic water splitting, is indeed environmentally attractive because it combines two abundant and renewable sources: water and sunlight [1–4]. Although undeniably promising, the hydrogen production by photocatalytic water splitting is still considered to be a low

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efficiency process and which requires further development [5–7]. Therefore, the study of the factors involved in this process is fundamental, such as the synthesis of more active catalysts for hydrogen production.

The photocatalytic water splitting was firstly reported in 1972, with a photoelectrochemical system, combining a titanium dioxide electrode and a platinum counter electrode [8]. Titanium dioxide remains as one of the most used catalysts, in this reaction as in several other photocatalytic processes [9–11]. Some properties like high photocatalytic activity, chemical and thermal stability, non-toxicity and high availability of titanium dioxide contributed to its wide use [12–14].

Generally, photocatalytic processes can be analyzed in more details observing individually their major steps. Briefly the photocatalytic water splitting can be divided in four steps: generation of charge carriers, separation of the electron/hole pair, water oxidation and hydrogen ion reduction [15]. In each of these steps, there are specific requirements to be achieved in order to the photocatalysis global process presents a suitable efficiency. The electron/hole pair recombination reaction is usually very fast and should be retarded, so that oxidation and reduction reactions could occur [16]. In this sense, several techniques have been applied for the synthesis of more active materials, like using microporous supports and metal doping.

Among microporous materials, zeolites are employed as photocatalysts supports with good prospects [17]. The high dispersion of the active phase obtained onto materials like zeolites enables significant increase in its catalytic activity [18]. The zeolites electron donor or receptor property is also an important advantage in its application as a support for water splitting catalyst since its matrix acts as charge carrier separation, helping in the lagging of electron/hole pair recombination [19]. Another interesting advantage of zeolites is its ion exchange capability that enables the incorporation of transition metals, which have important photocatalytic properties due to their vacant d-orbitals [20]. ZSM-5 zeolite is an aluminosilicate widely used in heterogeneous catalysis due to its strong acidity, high surface area and chemical stability, among other interesting properties [21]. This zeolite matrix has been used as support for titanium dioxide in many different photocatalytic processes, like carbon dioxide photoreduction [22], degradation of volatile organic compounds [23] and degradation of dyes in liquid phase [24], besides photocatalytic water splitting [21].

Metal particles on photocatalytic surface act as electrons capture sites, preventing their recombination with holes [25]. These metallic sites are also important due to their hydrogen affinity that favors its adsorption on the photocatalyst surface [26]. Among the noble metals used as co-catalysts for hydrogen production by photocatalytic water splitting, platinum is often employed. However, palladium could be considered as an excellent platinum substitute since it has similar chemical properties and its costs are approximately 20% of the platinum while being 50 times more abundant [14]. Moreover, the great hydrogen-palladium affinity cannot be ignored [27] as this metal is a good hydrogen adsorbent [28], which contributes in the reduction reaction step of the photocatalytic process. It has been reported that palladium when incorporated as co-catalyst to titanium dioxide promotes a significant increase in photocatalytic hydrogen production [27,29]. Barrios et al. [29] compared palladium with nickel and cobalt and observed that Pd has promoted better photocatalytic activity under ultraviolet irradiation. Furthermore, the combination of palladium and a mesoporous support in photocatalytic water splitting enables a high hydrogen yield, which can be attributed to the synergic effects of great specific surface area, pore structure, good co-catalyst dispersion and contact between Pd and TiO_2 particles [30]. The interaction between active phase and palladium particles was also considered of essential importance in Pd/TiO_2 catalysts under UVB radiation by Wu and coworkers [14].

The photocatalytic activity in water splitting presents a strong dependence on the physicochemical properties of the catalytic materials. At the charge carriers generation step, the minimum energy that must be absorbed by the photocatalyst for promoting one electron/hole pair is equivalent to the band gap energy of the material [31,32]. Thus, the catalysts that show lower band gap energies tend to be more active under less energetic light sources. On the other hand, the structural and surface properties directly affect the charge carriers separation step and the reagents adsorption on oxidation and reduction sites, respectively [33]. Among the structural properties the crystallinity is associated to the defects in the crystalline structure, which can act as charge carriers recombination sites [15]. Regarding photocatalysts surface properties, a great specific surface area is considered to be essential in obtaining high efficient materials for water splitting [34].

The materials synthesis composition could be related also to the hydrogen yield obtained by photocatalytic water splitting. Thus, evaluating how the catalyst composition affects catalysts properties and hydrogen yield should make it possible to relate how catalyst properties influence its activity in water splitting. The objective of this work is to evaluate qualitatively and quantitatively the effect of catalyst composition in physicochemical properties and in hydrogen yield by photocatalytic water splitting, using palladium and titanium dioxide supported on ZSM-5 zeolite catalysts. This analysis was performed with the help of a statistical based experimental design and simple empirical models, what showed to be very helpful in the evaluation of the effects of catalyst composition, particularly in the hydrogen production rate.

Materials and methods

Catalysts synthesis

The ZSM-5 zeolite used as support was synthesized according to the procedure described by Calsavara et al. [35]. Aluminum sulfate (Synth, 98%), Aerosil silica (Degussa, 380) and ethanol (Synth, 99.5%) were used as aluminum and silicon sources and template, respectively. The crystallization of the zeolite was carried out under autogenous pressure at 165 °C during 96 h in stainless steel autoclaves equipped with Teflon cups. The obtained material was recovered by filtration, washed with deionized water and then calcined in a muffle type oven at 500 °C for 4 h. The synthesis was repeated until enough zeolite mass for all the catalysts preparation was obtained.

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