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Photo-reforming of glycerol over the microemulsion-mediated TiO₂ catalysts

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PURPOSE OF THE ABSTRACT

The use of biomass as renewable and abundant feedstock and its eco-friendly conversion into chemicals are becoming increasingly attractive to synthesize high-value-added products. In particular, glycerol, the multi-ton by-product of biodiesel production via triglyceride transesterification [1] is considered as suitable chemical platform for synthesis of valuable chemicals and hydrogen, which is not only the most promising sustainable alternative to the use of fossils as energy source, but also the way to increase the profit of biodiesel production. Overall reaction of glycerol reforming is endothermic process [2]. This infers that the high energy consumption leads to high operating costs. The presence of oxidizing agents and alkaline conditions are usually applied for oxidation of glycerol, which cause poisoning or over-oxidation of catalysts [3]. In contrast to the abovementioned, the photo-reforming of glycerol has gained a great interest in the field of hydrogen energy as well as selective transformation of glycerol into valuable chemicals. Among the catalysts studied for glycerol photo-reforming, TiO₂-based materials have drawn the greatest attention. Most of them consist of a noble metal co-catalyst which serves as cathode (Figure 1), thus, responsible for H₂ evolution. While the surface of semiconductor is considered as anodic site, where the photo-generated hole participates in oxidation of substrate (Figure 1) [1,4,5]. In the last ten years, the authors focused mainly on the anaerobic hydrogen production from glycerol using Pt [5-10], Au [6,10,9], Pd [6,10-11], Cu₂O [12-15] and NiO [16] nanoparticles introduced on commercial TiO₂ (Degussa P25; 80% anatase, 20% rutile) by different methods of preparation such as conventional impregnation, deposition-precipitation, photodeposition, and equilibrium deposition filtration. While the literature on selective photo-oxidation of glycerol under aerated and unaerated conditions is quite scarce. Glycerinaldehyde, dihydroxyacetone, acetol, acetaldehyde, methanol, and ethanol were reported as the main products of glycerol photo-oxidation in different conditions [1,17-19]. Besides, the challenge associated with the use of UV light, which refers only to 5% of the solar spectrum, directed the research towards the development of catalysts capable of absorbing the visible light. The surface plasmon resonance phenomenon, the collective oscillations of free electrons on the metal surface [20], inherent to the noble metal nanoparticles. Thus, introduction of such makes it possible to embrace the problem of visible light absorption as well as reduce electron-hole pair recombination in semiconductor [21-23]. Therefore, in this work the role of the support and the noble metal co-catalyst was studied on photo-reforming of glycerol under base-free, ambient anaerobic conditions. The first was evaluated in terms of the textural and structural parameters of synthesized TiO₂. The developed method of synthesis allows preparing semiconductor with desired phase composition, high surface area, and smaller size of nanoparticles with narrow distribution compared to commercially available TiO₂. The effect of co-catalyst (Au, AuCu and Pt NPs) on hydrogen production and selectivity of intermediate products of glycerol (Figure 2) photo-reforming was elucidated taking into account the method of co-catalyst preparation. It has been found that in the photo-catalytic hydrogen production by photo-reforming of glycerol with TiO₂-based catalysts, there is a combination of several factors influencing the performance such as: 1). absorption of the energetic UV radiation by the catalyst; 2). hydrodynamic diameter of the particles; and 3). size of Pt nanoparticles. The phase of TiO₂ was considered as affecting parameter on photo-reforming performance as well [9,24,25]. Higher H₂ rate and selectivity toward

pyruvaldehyde were observed for pure rutile compared to anatase phase, both synthesized by microemulsion method.

FIGURES

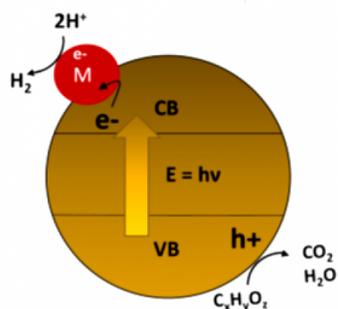


FIGURE 1

Scheme of oxygenates photo-reforming

VB: valence band, CB: conduction band, h+: photo-generated hole, e-: electron, M: noble metal nanoparticle

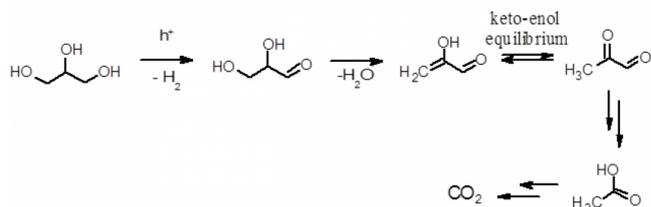


FIGURE 2

Scheme of glycerol photo-reforming under base-free anaerobic conditions.

The first step is the dehydrogenation of glycerol with glyceraldehyde formation, while the second step is the dehydration that results in pyruvaldehyde. Formation of CO₂ via formic acid indicates further oxidation of pyruvaldehyde.

KEYWORDS

Photocatalysis | hydrogen production | photo-reforming | glycerol

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