Petroleum Research
Petroleum Research 2019 (June-July), Vol. 30, No. 111, 4-5
DOI: 10.22078/pr.2020.3827.2743

Immobilization of TiO_2 Nanoparticles Over Treated Natural Aluminasilicate for Hydrogen Production: Effect of Support Treatment and Operational Conditions of Process

Rojiar Akbari Sene*[1], Farhad Rahmani[1], Gholamreza Moradi[2], Shahram Sharifnia[2]
1. Department of Chemical Engineering, Faculty of Engineering, University of Kurdistan, Sanandaj
2. Catalyst Research Center, Department of Chemical Engineering, Razi University, Kermanshah, Iran
r.akbari@uok.ac.ir

DOI: 10.22078/pr.2020.3827.2743

Received: June/12/2019 Accepted: October/21/2019

Introduction

Hydrogen has been regarded as an ideal energy carrier for the future. One of the most promising renewable approaches for the production of hydrogen is photocatalytic water splitting over Titanium dioxide [1, 2]. However, the limited efficiency of TiO_2 for hydrogen production via water splitting restricts the practical application of tiania. One of the efficient approaches applied to overcome shortcomings is immobilization of TiO_2 particles on a highly porous zeolite. The abundance, high chemical stability, excellent absorption capacity, special ion-exchange ability and low extraction cost of clinoptilolite make this kind of zeolite a very attractive support [3]. The reproducibility of extracted samples and the difficulty in obtaining homogeneous material are the main drawbacks in the application of natural zeolites. To overcome these problems, chemical treatments such as ion exchange have been applied. The ion exchange treatment can affect the chemical and sorption characteristics of zeolite by replacement of the ion-exchangeable cations and removal of amorphous materials that initially present in the pores of natural zeolites [4]. In the present research, the photocatalytic water splitting has been carried out over titania nanoparticles immobilized on parent clinoptilolite and ion exchange-treated clinoptilolite with the aim of understanding the effects of chemical treatment method and also, assessing the effects of operational parameters.

Experimental Procedure

Photocatalyst preparation

In order to preparation of parent Clinoptilolite (CLT), the crushed and sieved Clinoptilolite tuff was washed to eliminate the undesirable water-soluble materials, and dried. The parent Clinoptilolite was then treated with NH_4NO_3 solution (1 M) at 80 °C for 8 h to obtain the ion exchange treated clinoptilolite sample. After filtration, the sample was washed with deionized water several times till pH of filtrated water becomes neutral. The treated Clinoptilolite sample was dried at 110 °C for 24 h, and then calcined at 500 °C for 4 h. TiO_2-based composites were synthesized by a facile and cost-effective approach known as solid state dispersion (SSD) method. Initially, TiO_2 (P-25 Degussa) was mixed thoroughly with Clinoptilolite samples using ethanol as a dispersing agent in agate pestle and mortar, the dispersing agent was then evaporated during blending. After drying at 110 °C overnight, the prepared samples were calcined in air at 500 °C for 6 h to obtain TiO_2-zeolite photocatalysts.

Photocatalytic Test

Photocatalytic hydrogen production was performed in an outer irradiation-type quartz photoreactor. To provide required temperature, the photoreactor was equipped with a condenser which was connected to the cooling water recirculation system, and the temperature of solution was kept constant at 25 °C. In our setup, the light source consists of three 125 W medium pressure Hg lamps. In a typical test, the photocatalyst load was 20 mg which dispersed in 200 mL aqueous solution that contained 10% of methanol (v/v) as a sacrificial agent by a magnetic stirrer during the 4 h irradiation. The photoreactor was then sealed and prior to the irradiation, the mixture was deaerated with He for about 30 min to completely remove air. Afterwards, the amount of H_2 evolution was analyzed using gas chromatography (GC), equipped with a thermal conductivity detector (TCD) and a Molecular Sieve 5 Å column. Finally, the amount of hydrogen evolution was reported in units of µmol/g $_{TiO_2}$ .h.

Results and Discussion Catalyst Characterization

The synthesized photocatalysts were characterized by XRD, FESEM, EDX, BET, PL and UV-vis techniques. The XRD analysis of the treated sample demonstrated that ion exchange did not disturb the crystallinity of resulting materials i.e. the crystal structure of Clinoptilolite was preserved. Furthermore, the FESEM results show the treated sample has highly open morphology with homogeneous distribution of crystal sizes and shapes. The calculated surface area for photocatalysts has indicated that the chemical treatment of Clinoptilolite support results in the expansion of the pore opening and volume and thereupon, the increase of the surface area. The fine dispersion of TiO_2 particles reflects higher surface density of active sites and lower recombination rate of electron-hole pairs, as evidenced by spectroscopy analyses.

Photocatalytic performances

The results presenting the amount of H_2 evaluated in versus irradiation time are illustrated in Figure 1. According to the obtained results, the treated sample exhibits better photocatalytic activity in comparison with that of TiO_2/CLT. This improvement in photocatalytic activity can be explained by the enhanced TiO_2 dispersion, stronger metal-support interaction and an increased accessibility of the micro-channels in the modified nanocatalyst.

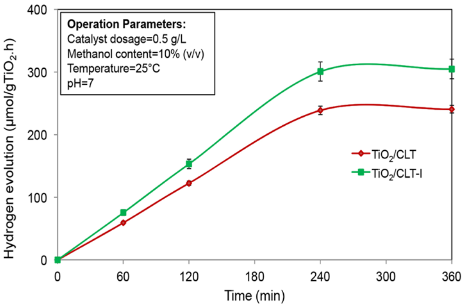

Fig. 1 Time-profiled Hydrogen evolution of synthesized photocatalyst.

By assessing the influence of the operational conditions, a maximum H2 evolution (859.74 µmol g^{-1} h-1) was obtained with optimum conditions set at irradiation time of 4 h, solution pH of 10 and photocatalyst dosage of 1 g L^{-1}. The enhancement of the rate of H_2 production at higher pH levels is probably due to increased concentration of physisorbed OH- groups, which participate in hole trapping processes and charge transfer reactions between the semiconductor and the electrolyte.

Conclusions

Based on the results, the chemical treatment method of support is concluded to be the useful solution to obtain more efficient Clinoptilolite supported TiO_2 photocatalyst for hydrogen production. The chemical treatment could improve the structural and textural properties of photocatalyst and consequently, increasing photocatalytic activity. Finally, by assessing the influence of the operational conditions, a maximum hydrogen evolution was obtained with optimum conditions set at irradiation time of 4 h, solution pH of 10 and photocatalyst dosage of 1 g L^{-1}.

References

1. Li H, Cui X (2014) A hydrothermal route for constructing reduced graphene oxide/TiO_2 nanocomposites: Enhanced photocatalytic activity for hydrogen evolution, Int J Hydrogen Energy, 39, 35: pp. 19877-19886.
2. Long L, Li J Wu L, Li X (2014) Enhanced photocatalytic performance of platinized CdS/TiO_2 by optimizing calcination temperature of TiO_2 nanotubes, Mat. Sci. Semicon. Proc., 26, 107-111.
3. Chica A (2013) Zeolites: Promised materials for the sustainable production of hydrogen, ISRN Chem Eng., 19.
4. Rahmani F, Haghighi M, Amini M (2015) The beneficial utilization of natural zeolite in preparation of Cr/clinoptilolite nanocatalyst used in CO_2-oxidative dehydrogenation of ethane to ethylene", J Ind Eng Chem., 31, 142-155.