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PHOTOCATALYTIC GAS-SOLID PROPENE HYDRATION AND LIQUID-SOLID GLYCEROL DEHYDRATION BY USING KEGGIN HETEROPOLYACIDS SUPPORTED ON TiO_2

G. Marci[1], E. Garcia-Lopez[1], V. Vaiano[2], G. Sarno[2], D. Sannino[2], L. Palmisano[1]

[1] *"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[2] *Department of Industrial Engineering, University of Salerno*
Via Giovanni Paolo II, 84084, Fisciano (Salerno), Italia

Heteropolyacids (HPAs) are cheap and stable compounds that have been extensively used as acid and oxidation catalysts, due to their strong Bronsted acidity and ability to undergo multielectron transfer reactions without changing their structure. Keggin heteropolyacids (HPAs) are a wide class of discrete nanosized transition metal- oxygen clusters which are strongly acidic, oxidant and remarkably stable that combine acidic and redox reaction centers in one molecule. They absorb light producing a charge transfer-excited state HPA*, easily reduced to the relatively stable HPA⁻ which in turn can be oxidized to HPA [1]. Dispersing HPAs onto solid supports with high surface area is useful to increase their specific surface area and hence (photo) catalytic activity. The presence of the $H_3PW_{12}O_{40}$ (a type of HPA) supported on different semiconductor oxides has shown a beneficial role in photocatalytic reactions due to the ability of the activated HPA* species to be reduced by the photoproduced electrons of the conduction band of the UV-activated semiconductor [2].

In this work three HPA supported on TiO_2 have been investigated as (photo)catalysts in two reactions, i.e. propylene hydration and glycerol dehydration in gas-solid and in liquid solid regimes, respectively. These are reactions of great interest from the industrial point of view particularly when carried out at room conditions. The binary materials HPA/TiO_2 were prepared by impregnating the commercial support Evonik P25 with an aqueous solution containing the desired amount of the commercial $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ or $H_4SiW_{12}O_{40}$. The HPA amount deposited was 50 % in weight with respect to the support. The HPA:Ti molar ratio was held constant at 0.008:1. Moreover, $H_4SiW_{12}O_{40}$ was also deposited on TiO_2 by a solvothermal methodology. A solution was prepared by adding 7.5 ml of titanium isopropoxide (TTIP) to 50 ml of 2-propanol. Hereafter an appropriate amount of SiW_{12} was added under vigorous stirring to the Ti containing alcoholic solution. A gel was formed and successively introduced in an autoclave. The tightly closed system was heated for 48 hours at 200°C achieving a pressure equal to ca. 10 bar. The solid from the autoclave was washed four times with hot water, dried and annealed at 110°C for 12 h. The molar ratios of TTIP: 2-propanol : HNO_3 : H_2O : HPA were 0.5: 15: 40: 1.

Bulk and surface physico-chemical properties of the materials have been studied by FTIR, Raman and Diffuse reflectance spectroscopy, specific surface area measurements (BET), XRD analyses and SEM observations and the effect of light has been investigated by taking into account that the (photo)reactivity depends not only on the type of HPA but also on the preparation methods which influence the HPA features.

Propene hydration was carried out in a continuous photoreactor feeded with a flow rate of 20 $cm^3 \cdot min^{-1}$ of propene and water (40 mM and ca. 2 mM, respectively). The runs were carried out at atmospheric pressure and 85°C. The reactor was illuminated with a 365 nm UV LED (irradiance in the 315-400 nm range: 50 $mW \cdot cm^{-2}$). 2-propanol along with diisopropylether were obtained in both catalytic and photocatalytic reactions and the presence of UV light improved the activity of all of the solids. The presence of the HPA was essential for the conversion of propene both in catalytic and in photocatalytic reactions. The 2-propanol formation rate increased by irradiating the system in the presence of the HPA impregnated samples, although the reactivity dramatically decreased in the presence of the sample prepared solvothermally. This finding can be related to several factors, for instance the lower amount of HPA present in the composite and the different nature of the interaction HPA-support which influence the physic-chemical features of the HPA. The photocatalytic dehydration of glycerol to form acrolein was carried out in liquid phase. The experiments were realized using a Pyrex cylindrical photoreactor (ID = 2.5 cm) equipped with a helium distributor device (Q_{He}=200 cm^3/min (STP)) and a magnetic stirrer to maintain 0.1 g of photocatalyst suspended in 100 ml aqueous solution containing 0.4 mol of glycerol. The photoreactor was externally irradiated by four Philips Black Light UV tubes (32 W, emission 365 nm). The composition of the condensed reaction products and the unreacted glycerol in the reactor was analyzed by GC-MS analysis. In the presence of photocatalyst, the selectivity to acrolein ranged between 18 and 71%, and these figures resulted higher than that obtained in homogeneous medium (ca. 10%). The highest acrolein production has been obtained by using the $H_4SiW_{12}O_{40}$ based materials.

References:

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