An advanced gas-solid UV LEDs photocatalytic reactor for organic syntheses and environmental applications

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Introduction

Photocatalysis is a "green" technology with potential applications in various disciplines, such as chemical synthesis and environmental technologies. For the industrial applications, photocatalytic reactors design mainly requires to overcome actual mass and photons transfer limitations. Fluidized bed reactors are well known in enhancing mass transfer. With respect to photon transfer, microscale illumination systems seem to be a promising solution [1]. Recently, we have developed a gas-solid photocatalytic fluidized bed reactor at high performances [2]. The device couples positive aspects such as wide exposition of catalyst to the radiation to the effective use of UV Leds which are long-lasting, robust, small in size and high in light efficiency. Illumination efficiency, defined in [1], appeared as key paramenter to compare different reactors configurations, and resulted higher than reported for slurry systems, spinning disc reactors, monolithic reactors and microreactors.

In this work different photocatalytic applications in the high efficiency gas-solid photocatalytic reactor are reported.

Materials and Methods

Several catalysts were prepared by wet impregnation of titania and or alumina based supports with an aqueous solution of ammonium heptamolybdate or ammonium metavanadate, followed by calcination in air at 400°C. Sulphated photocatalysts were obtained according to [3].

The bidimensional fluidized bed reactor has 40 mm x 10 mm cross section, 2 mm thick, and 230 mm height pyrex-glass walls (2mm in thickness), supplied with an internal electrical heater to control the reaction temperature. A bronze filter (5 μm size) was used for gas feeding to provide uniform gas distribution. The reactor was illuminated by two or four UV-LEDs modules of 20 pieces each positioned in front of the pyrex windows. An electrical control system connected to the modules allows to control the light intensity incident to the external walls of the photoreactor The light intensity was regulated at 100 mW/cm^2. Each UV-LED module consists of up to 20 pieces of UV-LEDs (Nichia Corporation) emitting at 365 nm. Moreover the fluidized bed reactor is equipped with Catalytic tests were carried out in the fluidized bed photoreactor feeding 830 $(stp)cm^3/min$. The gas composition was continuously measured by an on-line quadrupole mass detector (TraceMS, ThermoElectron) and a continuous CO-CO_2 NDIR analyser (Uras 10, Hartmann & Braun).

Photocatalytic tests started feeding the reaction gaseous mixture to the photoreactor at reaction temperature in dark. After the complete adsorption of hydrocarbon on the catalyst, UV-LEDs were switched on. In the absence of light, no reaction products were observed, either during hydrocarbon dark adsorption or after that hydrocarbon adsorption equilibrium on catalyst were completed.

Results and Discussion

This system allows to realize the photocatalytic deep oxidation of volatile organic compounds such as toluene, benzene and acetone on V_2O_5/TiO_2 catalysts, with a contact time of 300 ms in a small reaction volume (0.1L). Selective photocatalytic oxidation of hydrocarbons can be achieved by selection and optimization of catalyst formulation, finely tuning of active species loading, polymolybate, and/ or polyvanadate and sulphate, on different supports like TiO_2, Al_2O_3, TiO_2/Al_2O_3, TiO_2/SiO_2. The photocatalytic oxidative dehydrogenation of cyclohexane to cyclohexene or benzene has been obtained with 100% selectivity and with a higher activity in comparison to previous photoreactor configurations [2, 4-5]. Photocatalytic tests feeding ethylbenzene showed the effectiveness in styrene production on sulphated MoO_x/Al_2O_3 catalysts with 100% selectivity. In all the applications, no deactivation phenomena were detected. Finally, the designed photocatalytic reactor was tested in the selective oxidation of alcohols to the corresponding aldehydes in gas phase. Photooxidative dehydrogenation of ethanol was carried out on V_2O_5/TiO_2 catalysts with high photoactivity and acetaldehyde selectivity (97%). The main results are reported in Table 1.

Table 1 List of the main reaction studied and their results

Reaction	Catalyst	Hydrocarbon conversion %	Selectivity %	Reaction temperature,°C
Benzene to CO_2	V_2O_5/TiO_2	27	100	80
Cyclohexane to benzene	MoO_3/TiO_2	33	99	120
Cyclohexane to cyclohexene	MoO_3/γ-Al_2O_3	28	100	120
Ethylbenzene to styrene	MoO_3/γ-Al_2O_3	27	100	120
Ethanol to acetaldehyde	V_2O_5/TiO_2	100	97	100

Significance

The UV-LEDs photocatalytic fluidized bed reactor was useful both for removing volatile organic compound and partial oxidation reactions under mild conditions with high selectivity, avoiding catalyst deactivation phenomena, resulting of high productivity and versatility.

References

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