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PHOTOCATALYTIC MEMBRANES BASED ON TiO_2 CATALYSTS AND FLUORINATED POLYMERS FOR CO_2 CONVERSION

Introduction

The use of catalytic membranes is a promising strategy to perform efficient and eco-friendly catalytic chemical processes. One of these latters is the CO_2 reduction to methane and/or methanol, which are short-chain fuels representing a sustainable alternative to conventional fossil fuels.
When a catalyst is embedded within or on the surface of a membrane, the characteristics of the material used and the membrane structure can enhance the catalytic performance and the same catalyst can be reused several times favouring a lower environmental impact [1].

Results and discussion

In this work, two home prepared bare (Catalyst 1) and Cu 1% loaded (Catalyst 2) TiO_2 photocatalysts were immobilized into different polymeric membranes, constituted by Hyflon (a perfluoro amorphous polymer) and Nafion (a perfluorosulfonic acid polymer). These materials were chosen because of their excellent UV-resistance properties and their good film forming characteristics, as the prepared membranes were intended to be used as catalytic membranes for CO_2 photo reduction with H_2O as a reducing agent, under UV irradiation.
The Catalysts 1 and 2, obtained starting from $TiCl_4$ and $CuCl_2 \cdot 2H_2O$ as precursors, were constituted by badly crystallized crystalline anatase and rutile phases along with a big fraction of amorphous phase. The specific surface areas were 54 $m^2 \cdot g^{-1}$ and 76 $m^2 \cdot g^{-1}$ for Catalyst 1 and for Catalyst 2, respectively, and the band-gap values were 3.0 eV and 2.8 eV.
The preparation conditions were investigated and the obtained catalytic polymeric membranes were subjected to SEM imaging, diffuse reflectance UV-Vis spectroscopy and gas permeation tests.
BSE-SEM images showed a good catalyst distribution within the polymeric matrixes and the UV-Vis analysis demonstrated the spectroscopic integrity of the embedded catalysts (**Figure 1**), as absorption peaks at the typical TiO_2 absorption frequency [2] were observed.

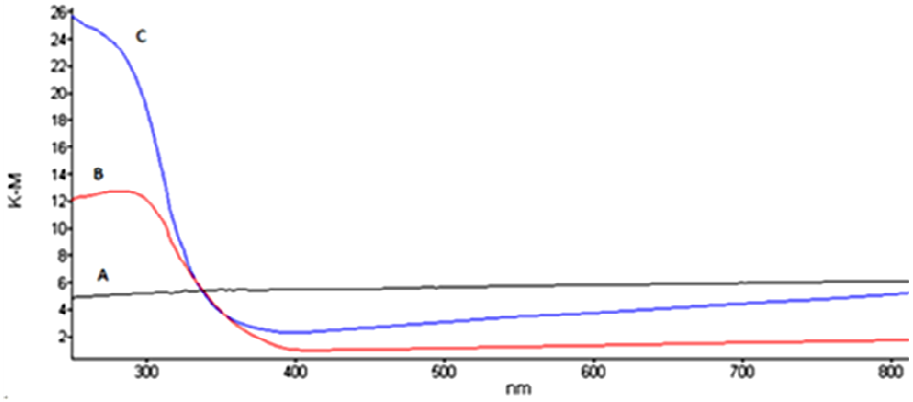

Figure 1. Spectra of absorbance (Kubelka-Munk units) versus wavelength (nm), obtained from UV-Vis reflectance analysis, of: (A) Nafion membrane; (B) Nafion+Catalyst 1 membrane; (C) Nafion+Catalyst 2 membrane.

Subsequently, the membranes were used to perform catalytic tests under UVA irradiation for the reaction of CO_2 photo reduction in gas-solid phase. The experiments were carried out in a continuous mode, feeding pure CO_2 into a membrane reactor module by means of a mass flow controller. To the feed line was also sent a stream of water vapour by using a pump, the CO_2:H_2O molar ratio being 1:5. The module was equipped with a quartz window in order to allow the UV irradiation. Chromatographic analysis showed that methanol was obtained as a product.

Conclusions

The morphological and chemical-physical analysis carried out on the polymeric catalytic membranes prepared demonstrated the good catalysts distribution within the polymeric matrix, as well as their structural stability.
The catalytic tests showed that Nafion membranes with embedded catalysts could be suitable to perform the reaction of CO_2 photo reduction with H_2O as a reducing agent under UV irradiation. Methanol was obtained as a reaction product as indicated by the chromatographic analysis. This results obtained are interesting, the methanol being the most promising reduction product, as it can be easily transported, stored and used as gasoline-additive.

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