CO_2_ conversion in continuous photocatalytic membrane reactor

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Highlights

- CO_2_ photoconversion in a continuous membrane reactor
- C_3N_4 photocatalyst embedded in Nafion matrix
- MeOH and EtOH preferentially produced at a low residence time and high feed molar ratio

1. Introduction

Global warming is considered one of the principal environmental problems and CO_2_ being a greenhouse gas, largely contributes to the global climate change. Owing to this problem, an increasing concern has brought the scientific community to devote huge efforts towards CO_2_ reduction and/or valorization through a sustainable process. In this contest, photocatalytic membrane technologies can be a promising and innovative way to pursue CO_2_ transformation. It is, in fact, a green process and an attractive route from economic and environmental points of view. In presence of a photocatalyst having an appropriate energy band gap, CO_2_ can be converted in fuels by irradiating it with UV-Vis light at ambient pressure. To this purpose, a promising strategy is the use of catalytic polymeric membranes, taking advantages from the better exposition of catalyst to UV-Vis light to carry out the reaction, the tailoring of reactants and catalyst contact, the reduction of catalyst aggregates formation and its easier recovery.

In this work, a new photocatalytic membrane reactor (MR) was used for CO_2_ conversion. C_3N_4 catalyst was embedded within a polymeric Nafion matrix and then used for CO_2_ photoconversion in a continuous operation mode. The effects of the residence time and feed molar ratio on MR performance and species distribution were investigated. To the best of our knowledge, this is the first work where a photocatalytic membrane reactor is operated in a continuous mode using dense mixed matrix C_3N_4-based Nafion membranes for CO_2_ photoreduction.

2. Methods

Carbon nitride (C_3N_4) was prepared following the same procedure as reported in [1]. In particular, 10 g of melamine were directly heating at 2°C min^{-1} up to 520°C for 2 h, in a covered crucible exposed in a static air. The solid was pounded and then heated again, without coverage, at 3°C min^{-1} up to 500°C keeping this temperature for 4 h.

Nafion and catalytic Nafion membranes were prepared following the same procedure as reported in [2]. For catalytic membrane, catalyst (C_3N_4) in a due amount was added to polymeric solution before its casting; the resulting C_3N_4 was 1.23%. Comprehensive structural and morphological analyses by DRS, FT-IR, ATR-IR, SEM and N_2 and CO_2 permeability measurements were performed. The photocatalytic membranes were then used for the same reaction under UV-Vis irradiation in a membrane reactor operating in continuous mode.

3. Results and discussion
The photocatalytic measurements confirmed MeOH as major product when an excess of water and a short residence time were used (Figure 1-2). MeOH and EtOH flow rates increased with the H$_2$O/CO$_2$ feed molar ratio (Figure 1), reaching 17.9 and 14.9 µmol g$^{-1}$catalyst h$^{-1}$, respectively, at a feed molar ratio equal to 5 against 4 and 1.7 µmol g$^{-1}$catalyst h$^{-1}$ obtained at a feed molar ratio of 0.5.

MeOH and EtOH were preferentially produced at a low residence time (Figure 2). This was mainly attributed to the fast removal of reaction mixture from reaction volume which limits the secondary reactions such as partial oxidation of MeOH to HCHO. On the contrary, for the aforementioned reasons a longer residence time promoted HCHO production. The slow removal of the reaction mixture from reaction volume can induce MeOH and EtOH partial oxidation producing formaldehyde or full oxidation up to CO$_2$.

![Figure 1 - Species flow rate/catalyst weight as a function of feed H$_2$O/CO$_2$ molar ratio at feed flow rate 2.0 s](image1)

![Figure 2 - Species flow rate/catalyst weight as a function of C$_3$N$_4$ weight/CO$_2$ feed flow rate at feed molar ratio equal to 2.](image2)

4. Conclusions

The photocatalytic measurements carried out in the continuous membrane reactors confirmed MeOH and EtOH as major product when an excess of water and a short residence time were used. This was mainly attributed to the fast removal of reaction mixture from reaction volume, which limits the secondary reactions such as partial oxidation of MeOH to HCHO. On the contrary, a longer residence time promoted HCHO production. This work confirms the use of photocatalytic continuous membrane reactor as a promising way for an advanced rout of CO$_2$ conversion and underlines the importance of process parameters such as residence time and feed molar ratio in driving the performance of the reactor itself.

References


Keywords

Photocatalytic membrane reactor; CO$_2$ photoconversion; Carbon Nitride.