

The influence of the source of carbon incorporated in MCM-48 molecular sieves applied to CO₂ photoconversion into methanol

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Abstract

In this work we applied MCM-48, (Carbon Ceramic Materials) CCM-MCM-48 decorated with Cu₂O/CuO nanoparticles in the photocatalytic reduction of CO₂ to CH₃OH.

Introduction

Many environmental problems are caused by the increase of CO₂ levels in the atmosphere. One useful way to tackle this problem is the photoconversion of CO₂ into solar fuels. This work describes the synthesis of cubic molecular sieve MCM-48 and Carbon Ceramic Materials CCM-MCM-48 which were impregnated with Cu₂O and CuO nanoparticles previously prepared. The materials were characterized by XDR, Uv-Vis and BET. The photocatalytic tests were carried out in a reactor using a solar simulator (AM 1.5). The results of the photocatalytic tests were monitored by gas chromatography technique (GC). We observed the formation of liquid CH₃OH.

Results and Discussion

MCM-48 and CCM-MCM-48 were synthesized following the references [1,2]. Copper oxide nanoparticles (Cu₂O and CuO) were prepared according to the literature. [3,4] The molecular sieves and the copper oxide nanoparticles were mixed in isopropyl alcohol 99%, using sonication at 5 wt.%. The materials were dried in oven at 150 °C for 24 h under inert atmosphere. The photocatalytic process occurs in a reactor containing 50 mg of catalysts, 300 µL of water and 2 bar of CO₂. The system was irradiated for 20 h. Next, the liquid phase was collected and analyzed by GC. The photocatalytic results were compared to those of TiO₂ P25 particles collected in the same conditions.

In Table 1 surface area analysis of graphite, MCM-48 and CCM-MCM-48 are shown.

Table 1- Surface area values of molecular sieves

Material	Surface Area (BET)(m ² .g ⁻¹)
Graphite	6
MCM-48	771
CCM-MCM-48	113

The decrease of surface area is due to the graphite incorporation (1/3 = SiO₂/C ratio) on the

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synthesis. In Table 2 photoconversion results of CO₂ to CH₃OH using solar simulation are shown.

Table 2- Photoconversion of CO₂ to CH₃OH

Material	µmol CH ₃ OH	Yield %
TiO ₂ P25	0	0
MCM-48/Cu ₂ O	131	2,43
CCM-MCM-48/Cu ₂ O	86	1,61
MCM-48/CuO	188	3,37
CCM-MCM-48/CuO	145	2,72

The results demonstrate the influence of surface area and nature of nanoparticles. MCM-48/CuO exhibit higher photoconversion for CH₃OH and, after graphite incorporation a decreased yield (-20%). The same phenomena were observed for CCM-MCM-48/Cu₂O and MCM-48/Cu₂O (-34,5%). This process can be associated to the blocking of the active sites caused by graphite. The higher photoconversion of CO₂ into CH₃OH using CuO/Cu₂O nanoparticles is attributed to the adequate energy levels and smaller value of band gap of semiconductors (CuO =1.7 eV and Cu₂O= 2.2 eV), who promote a more efficient electronic transfer for the CO₂ photoreduction into methanol, when compared with TiO₂ P25, (TiO₂=3,2 eV) material used as a reference.

Conclusion

The results showed that these materials are promising candidates for catalysts of CO₂ photoconversion to obtain higher value-added products. The incorporation of carbon on the material decreases the conversion, due to lower surface area, and possibility because of active sites blocking to the light.

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