EFFECT OF COPPER AND SILVER MODIFICATION OF MOF ON THE PHOTOREDUCTION OF CO_2

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Metal-organic frameworks (MOFs) are porous materials made of secondary building units linked together by organic linkers. Their unique structure makes them excellent sorbents for gases, organic pollutants, and even salt ions. Most this type materials containing a transition metal in structure can act as visible-light photocatalysts. One of these material is NH_2-MIL-125 (Ti), which is composed of Ti^{4+} ($Ti_8O_8(OH)_4$) clusters and 2-amino terephthalic acid as linker [1]. To increase its activity under visible light, it can be modified with metals (such as Ag, Cu, Pt, Au, Pd). So far, NH_2-MIL-125 (Ti) has been studied in photocatalysis mainly in the process of pollutant degradation and hydrogen generation. There is still lack of information about the application of NH_2-MIL-125 (Ti) in carbon dioxide photoreduction to produce useful fuels. Attempts have been made to enhance the visible-light activity of NH_2-MIL-125 (Ti) by synthesizing materials modified with cobalt - 38.4 $\mu mol/hg_{cat}$ HCOOH [2] or nickel – main 5 $\mu mol/hg_{cat}$ CH_4 [3]. In the presented study, a new copper- or silver-metallized NH_2-MIL-125 (Ti) photocatalyst was prepared. The type of metalation method and amount of Cu was investigated. The studies included extensive physicochemical characterization of the obtained samples (UV-Vis spectroscopy, FTIR, photoluminescence, XRD structural analysis, surface morphology, BET surface area, CO_2 sorption) and investigation of photocatalytic activity in the formic acid generation process. In addition, the stability of the best sample over several photoconversion cycles was performed. The obtained pristine MOFs and modified MOFs were characterized by a typical octahedral morphology. Based on ^1H and ^{13}C NMR analysis, it was confirmed that formic acid was generated from CO_2 photoreduction. Copper and silver modification improved photoconversion performance under visible light. A significant correlation can be seen between the determined energy gaps and the photocatalytic efficiency and carbon dioxide sorption of the material. In addition, modified MOFs show high thermal and photocatalytic stability.

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