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SYNTHESIS OF Cu-Zn-MCM-41 NANOCATALYST

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Introduction

The relatively low energy requirements compared to other catalysts are one of the many reasons that have led to the successful use of copper in the formulation of bi-metallic catalysts for a variety of hydrogen generation reactions. In general, copper-based catalysts are characterized by high catalytic activity and good selectivity. Thus, various types of catalysts were explored for methanol steam reforming reactions, compared to a commercial CuZnO or $CuZnO/Al_2O_3$ catalyst. Promoters such as Zn have been successfully used to improve the stability of Cu-based catalysts. The interaction between Cu and Zn plays an important role in lowering the reaction temperature. The method of synthesis can affect the level and nature of the interaction between the two metals which in turn affects possible reaction pathways that could change the selectivity to the undesired product. MCM-41 is a versatile nanomaterial that has been used for numerous applications, such as drug delivery, membranes or catalyst support. In this study, one direct synthesis method starting from an inorganic silicate is presented.

Materials and methods

CTAB was dispersed in ultrapure water, the mixture being stirred for 2h at ambient temperature. Then, sodium silicate solution was added dropwise with stirring. After 2h, the metal salts ($Cu(NO_3)2.2.5H_2O$ and $Zn(NO_3)_2.6H_2O$ both dissolved in ultrapure water) were added, shaking the mixture for 2-3 h. After this, TMAOH was added and the mixture was stirred for another 30 minutes, after which the mixture was placed in a Teflon autoclave at 100 °C for 5 days. The mixture was then filtered, washed with ultrapure water and the sample dried for calcination. The grey powder was calcined at 550 °C for 6 h to remove excess surfactant, resulting in a dark grey final product.

Results and conclusions

The content of Cu and Zn was determined by atomic absorption spectrometry (AAS). The Cu-Zn-MCM-41 had a content of 4.60 wt.% Cu and 1.17 wt.% Zn.
Once the metals were introduced, the specific surface area of the support decreased, to 496 m^2/g, and the average pore diameter was 3.14 nm (Figure 1).

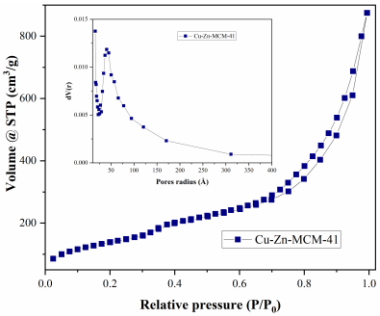

Fig.1. Adsorption-desorption isotherm and pore diameter distribution

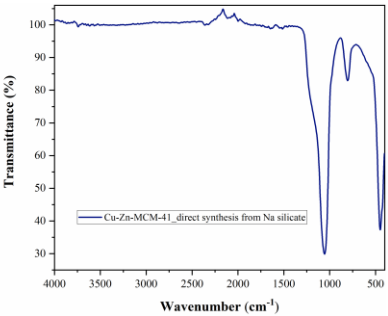

Fig.2. FTIR spectra

It was observed that the mesopore volume increased spectacularly to 1.228 cm^3/g for the system obtained from sodium silicate. A possible explanation would be that metals have entered the mesoporous silica matrix. The change in the shape of the Cu-Zn-MCM-41 isotherm can be explained by the introduction of metals directly into the silicate sol-gel solution, but also by the inorganic nature of the silicate, leading to a decrease in the specific surface (Figure 1).

The bimetallic systems presented morphology with spherical and partially elongated particles with dimensions below 100 nm. After the introduction of metals, the ordered morphology typical of MCM-41 mesoporous silica was maintained.

Metallic interactions led to increased distortions and vibrations of the silicon-oxygen tetrahedron resulting in a more pronounced asymmetry. When the metals were introduced, the FTIR spectrum (Figure 2) underwent changes: a shoulder appeared at 577 cm^{-1}, which was attributed to Si-O-metal vibrations, concluding that Cu species successfully impregnated on MCM-41. The introduction of metals was also confirmed by the disappearance of the peak at 615 cm^{-1} specific to stretching vibrations for the Si-O- groups on the silica surface, confirming the positioning of the metal on the silica surface.

The introduction of an adequate amount of metallic copper effectively affects the physicochemical properties of MCM-41 and will ensure an increased efficiency of the catalytic pyrolysis process. The addition of Zn leads to the promotion of specific reaction pathways, including dehydration, decarboxylation, decarbonylation, aromatization, and Diels – Alder reactions, which can also lead to the formation of olefins and aromatics.

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