Catalyzing the Oxidation of Alcohols to Aldehydes with an Efficient Zr-based Metal-organic framwork

Saeed Farhadi, Faranak Manteghi*
Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

(e-mail: f_manteghi@iust.ac.ir)

Abstract

Metal-organic frameworks (MOFs) as Zeolite analogues with permanent porosity and absorption capacity are a class of hybrid functional materials that are self-assembled by the coordination of metal cations with organic linkers. The Zr-MOF synthesized in this study is a porous 3-D Framework. This compound has shown a very high thermal stability and is remarkably humidity-persistent. It is used as a recyclable and efficient heterogeneous catalyst for oxidation of primary and secondary alcohols to benzaldehydes. The selectivity of the catalyst is determined by gas chromatography (GC) and it has shown a 100% selectivity in the oxidation reaction. Scanning electron microscopy (SEM) shows a nanoporous network made by cubic crystals. The catalyst has been also characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR).

Keyword: Metal Organic Framework (MOF), Catalysis, Oxidation.

Introduction

MOFs have received considerable attention due to their high surface area, well-defined structure and chemical tunability. These unique properties enable myriad applications in various fields such as catalysis, gas storage, separation, drug delivery, and chemical sensing [1,2].

The title material is among the first examples of Zr(IV)-based UiO (University of Oslo) MOFs with coordinative unsaturated active metal centers [3].

From both synthetic and industrial points of view, Liquid-phase oxidation of alcohols is a very attractive reaction for the preparation of intermediates and fine chemicals. A case in point is the oxidation of primary alcohols to aldehydes which is a fundamentally important reaction in both laboratory and commercial scales [4].

The oxidation of alcohols has been traditionally achieved with stoichiometric amounts of inorganic oxidants. In this work, Zr-benzenedicarboxylate (UiO-66) is successfully synthesized via a facile solvothermal approach and applied to oxidation reactions as a catalyst [5].

Materials and Methods

Hydrogen peroxide (H_2O_2), acetonitrile (CH_3CN), benzyl alcohol (C_7H_8O), $ZrCl_4$, terephthalic acid ($BDCH_2$) and dimethylformaldehyde (DMF) used in this work, were highly pure and were bought from Merck company.

Experimental

Preparation of Zr-MOF

Zr-MOF was synthesized by scaling-up a previous procedure, with some changes. Typically, $ZrCl_4$ and $BDCH_2$ were mixed in DMF and dispersed on ultrasonication, then placed in an autoclave. The resulting white product was filtered off, washed with DMF and immersed in a chloroform solution [4].

After separation by filtration, the solid sample was dried. Crystallization was carried out under static conditions. The activation using chloroform is efficient to remove DMF and unreacted $BDCH_2$ from the pores enhancing porous structure and surface area [4,5].

Catalytic application of Zr-MOF in oxidation of Alcohols

To a 10 mL round-bottom flask containing 1.0 mmol of benzaldehyde, 2.0 mmol equivalent of 30% H_2O_2 was added. After that, 5mg of Zr-MOF and 2 mL of solvent was added and the mixture was stirred at 80 ˚C. The progress of reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the mixture was cooled to room temperature and the catalyst was removed by filtration. The products were identified by GC.

Results and Discussion

The FT-IR spectra of catalyst before and after activation are shown in Fig. 1. The activation of catalyst is achieved by using chloroform. Observed data from the FTIR of synthesized sample is similar to previous results.

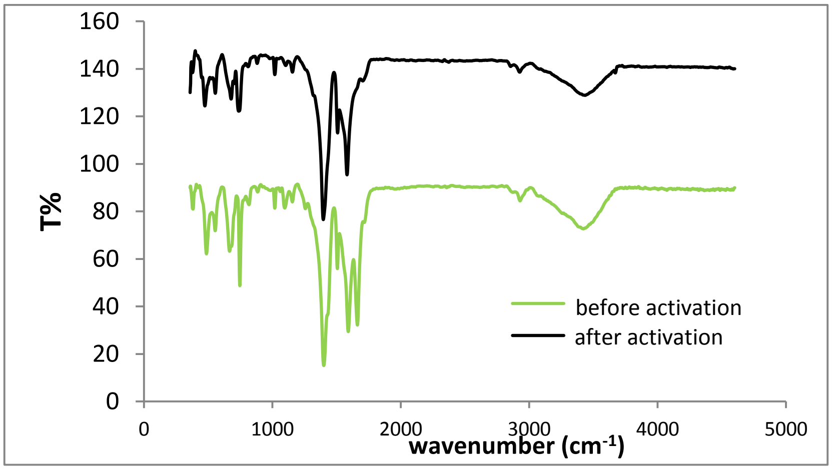

Fig. 1: FT-IR spectra of Zr-MOF, before (green) and after (black) activation.

The XRD pattern of the Zr-MOF reference sample and the sample prepared in this study by solvothermal method, respectively. The XRD pattern of the solovothermally synthesized sample was identical to the reference sample.

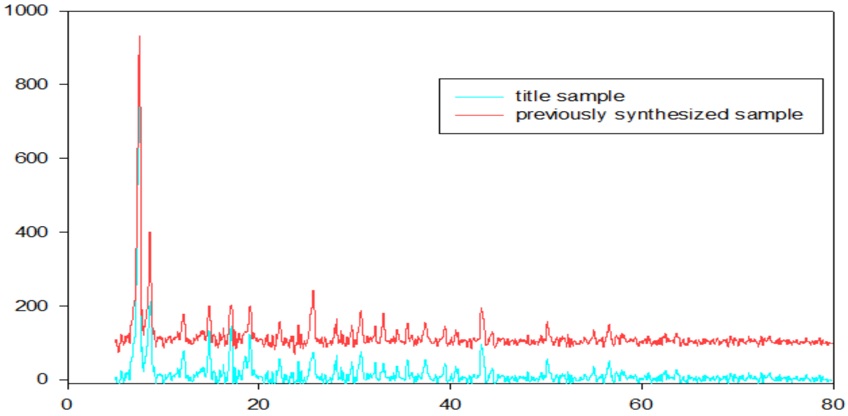

Fig. 2: XRD pattern of the previously synthesized sample (blue) and the title sample (red).

The formation of the title structure is confirmed by comparing with the synthesized sample (Fig. 1(a)) and also with theoretical powder pattern [3,5].

The Electron micrographs illustrate a morphology consisting of irregular intergrown microcrystalline polyhedral (Fig 3). Micrographs also indicate that the cubic crystals of Zr-MOF have a nanoscale diameter. It can be seen that the crystallite size of Zr-MOF was similar to cubic shape with about 100-150 nm size, while the previously synthesized sample size was 200 nm [5].

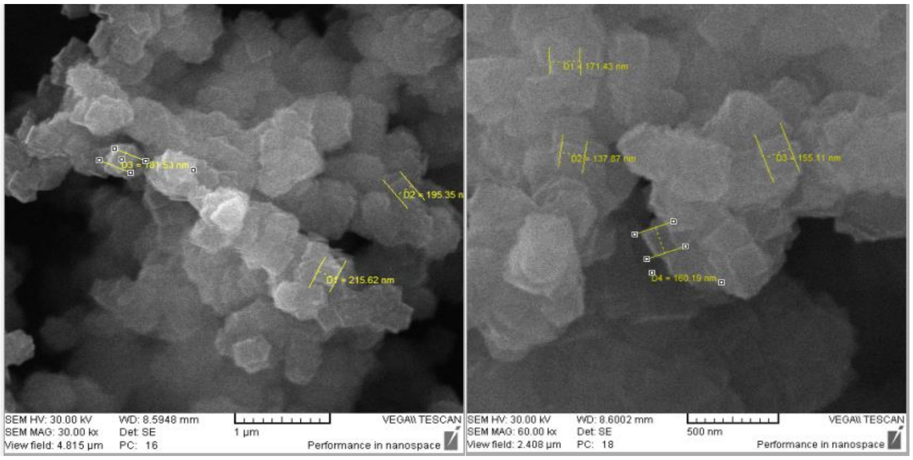

Fig. 3: The as-synthesized crystal morphology by SEM

Finally the title MOF was applied for oxidation of benzyl alcohol. Gas chromatograms show the peaks related to alcohol precursor and its resulting aldehyde. There are no peak other than that of two compounds which establishes the fact that no by-product is formed and the catalyst is highly selective. This is an evidence of a very high selectivity of the synthesized catalyst.

Catalyst	Solvent (ml)	H_2O_2 (µl)	Time (min)	Temp (°C)	Yield Zr- BDC	Selectivity Zr- BDC
Zr- BDC	CH_3CN	0.2	90	80	87%	99

Conclusion

A nano size Zr-MOF with high thermal stability and remarkable humidity-persistent was synthesized by a modified procedure after effective activation processes using solvent exchange method. The activation using chloroform is efficient to remove molecules of DMF and unreacted $BDCH_2$ from the pores enhancing porous structure and surface area and smaller grain size. According to the result, the synthesized MOF is a heterogeneous catalystwith a high surface area.

References

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Graphical Abstract