



Catalytic behavior of metal-organic frameworks and zeolites: Rationalization and comparative analysis



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ABSTRACT

The catalytic performance of selected MOFs ($\text{Cu}_3(\text{BTC})_2$ and MIL-100(Fe)) and zeolites (BEA and USY) have been investigated in a set of acid-catalyzed reactions (Pechmann and Knoevenagel condensations, Friedel–Crafts acylation, Beckmann rearrangement, and Prins and annulation reactions). Characteristics determining the activity and selectivity of the catalysts (particularly their relation to the type and concentration of acid sites, the size of the channels, and structure of the active centers) were discussed in detail. The regular arrangement of active sites in MOFs was shown to provide their superior behavior in Pechmann and Knoevenagel condensation reaction, while higher porosity and concentration of mild Lewis acid centers allows the conversion of bulky substrates to desired products over MOFs in Beckmann rearrangement, Friedel–Crafts acylation, and annulation reactions. Advantages and drawbacks of MOFs as catalysts were fairly compared with zeolites based on results obtained under the same reaction conditions for all investigated materials.

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1. Introduction

To date, transition metal salts (in particular, metal carboxylates) have been used as effective catalysts for numerous reactions including industrially scaled ones [1–4]. However, the catalyst of such type can hardly be recovered or reused. This limitation can be overcome by using MOFs—porous crystalline hybrid solids consisting of nodes of metal ions or metal cluster ions, being held in the framework by multipodal organic linkers different in nature (geometry, charge, etc.) [5–7]. Such heterogeneous catalysts provide a number of significant advantages over homogeneous ones. They are easily recoverable, reusable, and minimize the undesired waste. In this respect, the investigation of the properties of MOFs and perspectives for their catalytic applications were attracting a particular attention during the last decade [8–12]. The possibility to fabricate MOF structure with a variety of transition metals as well as a large number of available and virtual organic linkers provides their innumerable combinations resulting in thousands of frameworks

different in structure and compositions [13–15]. This advantage of MOFs inability to be easily designed and synthesized sharply contrasts with common heterogeneous catalysts, in particular, zeolites, structure of which typically cannot be predicted by analyzing the geometry and self-assembly of the structure directing agent [16–18].

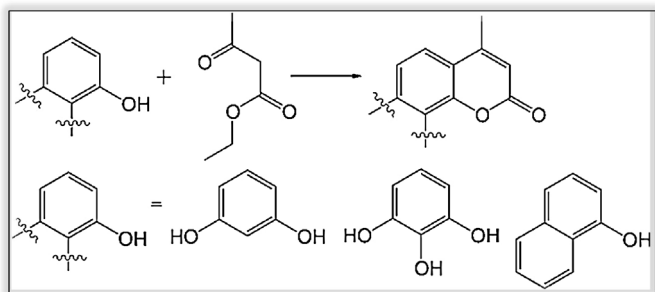
In contrast to zeolites, the strict orientation of metal–ligand coordination bonds in MOFs is responsible for the creation of a certain crystalline structure and porous system of these materials. At the same time, coordination bonds characterized by medium energy value between strong covalent linkages and weak intermolecular interactions can be relatively easily destroyed in the presence of aggressive reagents (e.g. solvents and reactants) or at elevated temperatures of catalytic process [19].

In addition, MOFs possessing pores with $d > 1$ nm are characterized by larger surface areas and pore volumes [20–22] and can overcome diffusional limitation being common for microporous heterogeneous catalysts (i.e. zeolites) [23–25].

Thus, tunable synthesis of MOFs with desired metals and linkers, high concentrations of potential active sites, and remarkable textural properties form a favorable background to make MOFs preferential heterogeneous catalysts in comparison with conventional zeolites or other catalysts for liquid-phase reactions proceeding under mild conditions [26].

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Scheme 1. Pechmann condensation of phenols with ethyl acetoacetate.

Table 1

Textural properties of the materials under study.

Catalyst	Crystal size (μm)	S_{BET} (m^2/g)	D_{micro} (\AA)	V_{micro} (cm^3/g)
BEA	0.2	670	6.6	0.20
USY	0.6	770	7.4	0.11
$\text{Cu}_3(\text{BTC})_2$	7	1500	9.0	0.64
MIL-100(Fe)	5	2250	8.6	0.90

To confirm this statement, a comparison of the catalytic activity of MOFs with respect to zeolites or related microporous solids is required. In other words, it is necessary to evaluate the “relative” activity and benefits/drawbacks of MOFs using conventional solids as the “standard”. Based on this, the present manuscript assesses the reported results devoted to comparative investigation of MOFs and zeolites as solid catalysts in transformations occurring in the liquid phase. For the sake of simplicity, only results related to MIL-100(Fe) and $\text{Cu}_3(\text{BTC})_2$ among MOFs as well as BEA and USY among zeolites are analyzed. Textural properties of these materials are summarized in Table 1. Selected reactions (Pechmann condensation, Friedel–Crafts acylation, Beckmann rearrangement, Knoevenagel condensation, Prins reaction, and annulation reaction of phenols with methylbutenol) lead to the products of interest as synthetic intermediates or compounds of commercial value.

1.1. Pechmann condensation

Pechmann reaction (Scheme 1) leads to the formation of coumarins, which are natural substances with wide applications in pharmaceutical and fragrance industries [27–29]. One of the main advantages of this route of the synthesis of coumarin derivatives is the utilization of simple and low-cost reactants (phenols and carboxylic acids or esters containing carbonyl group in β -position, e.g. ethyl acetoacetate) with high yields of target products [30,31].

Catalytic performance of MOFs and zeolites was compared in Pechmann condensation of resorcinol, pyrogallol and 1-pyrogallol

and 1-naphthol in [32,33]. Fig. 1 provides conversions of substrates (resorcinol, pyrogallol, 1-naphthol) and selectivities to target coumarins (at the same conversions) over compared catalysts. In general, more electron-rich aromatic compounds were more reactive in Pechmann condensation, due to the +M-effect of the additional hydroxyl groups [31]. For both zeolite catalysts, phenol conversions increased with increasing reactivity of substrates (1-naphthol < resorcinol < pyrogallol). While the maximal conversion of pyrogallol and resorcinol over zeolites was in the range 70–91 and 55–85%, respectively, the corresponding conversions of 1-naphthol did not exceed 25% [32]. At the same time, the selectivities to the target products were for all substrates in the range of 75–100%. The slightly higher activity of USY in condensation of most bulky 1-naphthol was explained by the presence of transport mesopores within USY resulting in a higher accessibility of active sites for the substrate molecules in comparison with zeolite BEA. In addition, the facilitation of transport of both reactants and product in the pore system of USY was assumed to prevent side transformations and to result in 98% selectivity to the target product of 1-naphthol condensation with ethyl acetoacetate (in contrast to 83% selectivity achieved over BEA) [32].

In contrast to zeolites, negligible transformation of resorcinol and pyrogallol to the target coumarins (selectivities $\leq 1\%$, Fig. 1) was achieved over MOFs. At the same time, conversion of 1-naphthol over $\text{Cu}_3(\text{BTC})_2$ and MIL-100(Fe) reached $\approx 90\%$ (with 95% selectivity to the target product) after 24 h (Fig. 1). The formation of the target product of 1-naphthol condensation over MOFs was confirmed using ^1H NMR spectroscopy and GC-MS [32] while the preservation of MOF structure after catalytic run was evidenced by XRD. In contrast, the crystal structure of $\text{Cu}_3(\text{BTC})_2$ collapsed in the presence of pyrogallol under the conditions of the reaction. Based on the presence of framework fragments of $\text{Cu}_3(\text{BTC})_2$ (trimesic acid) in a liquid phase after catalytic run, a replacement of organic linkers due to the dual interaction of Cu–Cu domains (two CUS sites) with two hydroxyl groups of pyrogallol with further substitution of trimesate by free OH-group of phenolic substrate was proposed. In a similar way, low catalytic activity of MOFs in Pechmann condensation of resorcinol was assumed to be caused by a strong adsorption of substrate on the active centers of MOF catalysts causing their blocking [32]. In the case of 1-naphthol, these interactions were not expected because of the presence of only one electron-donor OH-group in substrate molecule. To explain significant acceleration of 1-naphthol transformation over used MOFs compared with zeolites, the hypothesis of concerted effect of two neighboring CUS sites (Cu or Fe) was proposed [32]: since Pechmann condensation is bimolecular reaction [34], substrates (1-naphthol and ethyl acetoacetate) can simultaneously interact with the CUS sites of catalysts forming the adsorption complexes. Such interaction of a substrate molecule directly on the same catalytic site is possible only due to the high regularity and concentration of MOFs active

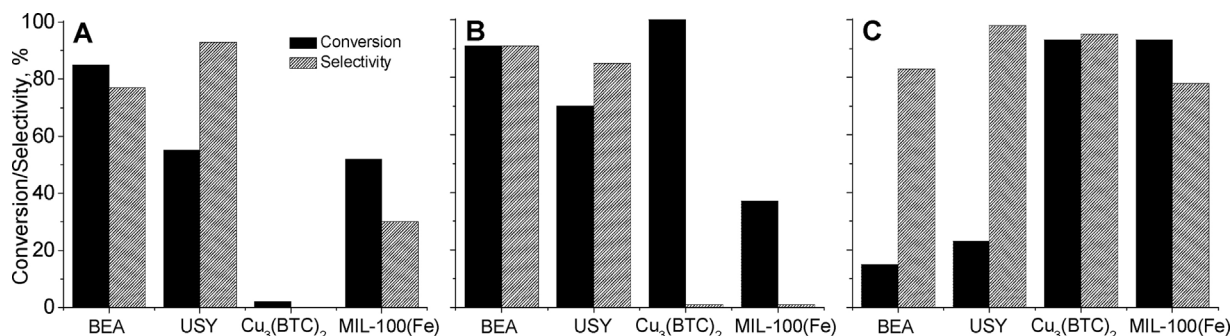


Fig. 1. Conversion of phenols and selectivity to the corresponding coumarin derivatives over MOFs and zeolites depending on the nature of the substrate: resorcinol (A), pyrogallol (B), 1-naphthol (C) (n (phenol) = 8.5 mmol, n (EAA) = 10 mmol, m (PhNO_2) = 10 g, m (catalyst) = 200 mg, T = 130 °C, t = 24 h, batch reactor) [32,33].

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