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Additional Information

Annulation of phenols with methylbutenol over MOFs: the role of catalyst structure and acid strength in producing 2,2-dimethylbenzopyran derivatives

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Abstract

The catalytic behavior of metal–organic frameworks of different structures (Fe(BTC), MIL-100 (Fe), MIL-100(Cr) and Cu₃(BTC)₂) was investigated in annulation reaction between 2-methyl-3-buten-2-ol and phenols differing in size (phenol, 2-naphthol). The highest conversions of phenols (45 and 75 % after 1300 min of TOS for phenol and 2-naphthol, respectively) and selectivity (45 and 65 % at 16 % of phenol and 2-naphthol conversion, respectively) to target benzopyran were achieved over MIL-100 (Fe) possessing intermediate Lewis acidity, perfect crystalline structure, and the highest S_{BET} surface area. The increasing strength of Lewis acid centers for MIL-100(Cr) was found to result in the dramatically decreased activity of the catalyst, while negligible conversion of phenols (2 and 7 % after 1300 min of TOS for phenol and 2-naphthol, respectively) was found over Fe(BTC), characterized by a less ordered framework.

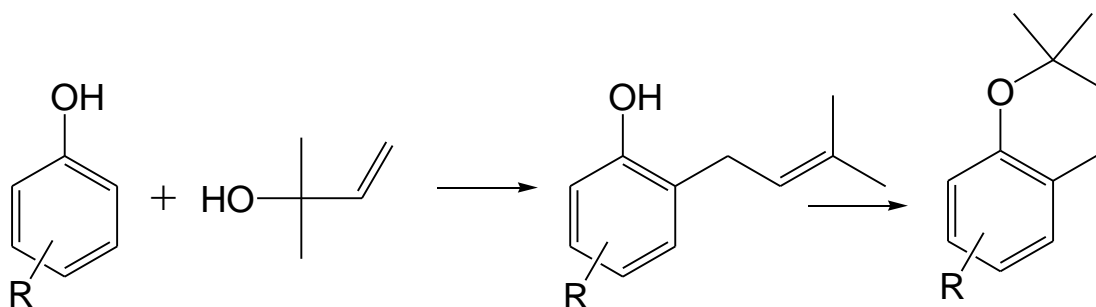
Keywords: metal-organic frameworks, acidity, annulation, prenylation

1. Introduction

The 2,2-dimethylbenzopyran unit is frequently present in many natural compounds exhibiting anti-HIV [1, 2], antihypertensive [3, 4] or antifeedant [5] activity. Antimycobacterial benzofurochroman [6], HIV inhibitory benzotripyrans [1] are typical examples. Several pharmaceuticals such as antioxidant vitamin E [7], antitumour clusifoliol [8] and anti-diabetic troglitazone [9] also possess the benzopyran moiety.

Both homogeneous and heterogeneous catalysts (H₃PO₄ [10], HCOOH [11], H₂SO₄ [12], HCl/AlCl₃ [13], BF₃·OEt [14], Montmorillonite KSF clay [15], Bi(OTf)₃ [16-18], Amberlyst 15

[19], zeolite HSZ-360 [20]) possessing Lewis and/or Brønsted acid centers were shown to produce 2,2-dimethylchromans through subsequent C-isoprenylation of phenols with isoprene or 2-methyl-3-buten-2-ol (MBO) resulting in formation of 2- and 4-isoprenylphenols followed by intramolecular cyclization of prenylated product (Scheme 1) with the formation of target derivatives of 3,4-dihydro-2H-1-benzopyran (chromane) [21]. Formation of the more stabilized carbocation of the 2-prenylphenol and attack by the oxygen of the phenolic OH group result in the formation of the six- and not the five-membered ring [21].



Scheme 1. Annulation of phenols with isoprene or 2-methyl-3-buten-2-ol.

MOFs represent crystalline hybrid organic–inorganic nanoporous materials with a quite high thermal stability [22, 23], adjustable chemical functionality [24], and extra-high porosity [25]. They are considered as one of the most fascinating classes of porous materials due to their potential in optoelectronic devices [26] and sensors [27], storage and separation of gases [28], medical imaging and drug delivery [29-34] and more recently emerging as highly interesting catalytic materials [35-37]. The presence of coordinatively unsaturated metalsites in some MOFs allows their application in catalysis as Lewis acids. MOFs can efficiently catalyze e.g. Friedländer condensation [38], Knoevenagel condensation [39-43], Huisgen cycloaddition [44], selective oxidation of cycloalkanes [45], and Friedel-Crafts benzylation [46].

Recently, we reported the catalytic benefits of $\text{Cu}_3(\text{BTC})_2$ and $\text{Fe}(\text{BTC})$ (BTC=1,3,5-benzenetricarboxylate) over large-pore aluminosilicate zeolites Beta and USY in Pechmann condensation of 1-naphthol [47], Beckmann rearrangement of bulky camphor oxime [48], Prins reaction of paraformaldehyde and β -pinene [49] originating from mild acidity, the regularity in the arrangement of active sites within the framework and preferences in pore size of corresponding MOFs.

Although MOFs appear to be promising solid catalysts for the liquid-phase annulation reaction, to the best of our knowledge, there are no reports on the catalytic performance of MOFs in this reaction. In this contribution, we investigate the catalytic behavior of Fe-containing MOFs of different structures, namely $\text{Fe}(\text{BTC})$, MIL-100 (Fe), and compare it with MIL-100(Cr), and

$\text{Cu}_3(\text{BTC})_2$ in annulation reaction between 2-methyl-3-buten-2-ol and phenols differing in size (phenol, 2-naphthol).

2. Experimental

Materials

$\text{Cu}_3(\text{BTC})_2$ (Basolite C300) and $\text{Fe}(\text{BTC})$ (Basolite F300) were purchased from Sigma Aldrich.

Iron(III) trimesate MIL-100(Fe) and chromium(III) trimesate MIL-100(Cr) were synthesized according to the literature [50, 51]. MIL-100(Fe) was prepared by mixing metallic iron (8.0 mmol, 0.45g), 1,3,5-benzenetricarboxylic acid (5.4 mmol, 1.13 g), 5 M HF (16 mmol, 3.2 ml), and 1 M HNO_3 (4.8 mmol, 4.8 ml) in deionized water (2.22 mol, 40ml). The mixture was heated at 160 °C for 24 h. The solid product was recovered by filtration and washed out with deionized water.

For the synthesis of MIL-100(Cr), metallic chromium (10 mmol, 0.52 g) was dispersed into an aqueous solution of 5 M HF (20 mmol, 4 ml). Then, trimesic acid (6.7 mmol, 1.41 mg) and H_2O (2.67 mol, 48 mL) were added and the mixture was heated at 220 °C for 48 h. The resulting green powder was washed out with deionized water and acetone and dried in air.

2-Methyl-3-buten-2-ol ($\geq 98\%$), phenol ($\geq 99\%$), 1- ($\geq 99\%$), and 2-naphthol (98 %) were used as substrates, mesitylene ($\geq 99\%$) as internal standard, 1,2-dichloroethane ($\geq 99\%$) as solvent in catalytic experiments. All reactants and solvents were obtained from Sigma Aldrich and used as received without any further treatment.

Characterization

The crystallinity of samples under study was determined by X-ray powder diffraction on a Bruker AXS D8 Advance diffractometer with a Vantec-1 detector in the Bragg-Brentano geometry using $\text{CuK}\alpha$ radiation. A gentle grinding of the samples was performed before measurements.

The shape and size of crystals were determined by scanning electron microscopy (SEM; Jeol, JSM-5500LV).

Adsorption isotherms of nitrogen at $-196\text{ }^\circ\text{C}$ were recorded using an ASAP 2020 (Micromeritics) static volumetric apparatus. Before adsorption experiments, the samples were degassed under turbomolecular pump vacuum at the temperature of $150\text{ }^\circ\text{C}$. This temperature was maintained for 8 h.

Determination of Lewis acid sites in MOFs is discussed in detail in our recent paper [52].

Catalysis

Annulation reaction between 2-methyl-3-buten-2-ol (MBO) and phenols (phenol, 2-naphthol) was performed in a liquid phase under atmospheric pressure and at reaction temperature 80 °C in a multi-experiment work station StarFish. Before catalytic experiments, 200 mg of the catalyst was activated at 150 °C for 90 min with a temperature heating rate 10 °C/min. Typically, 3 mmol of phenol, 0.4 g of mesitylene (internal standard), 200 mg of catalyst and 10 ml of 1,2-dichloroethane (solvent) were added to the three-necked vessel, equipped with condenser and thermometer, stirred and heated. When the desired reaction temperature was reached, 4.5 mmol of MBO was added into the reaction vessel through. 0.2 ml of the reaction mixture was sampled using syringe with needle after 20, 60, 120, 180, 300 and 1300 min.

To evaluate a potential influence of leaching of active species from the heterogeneous catalysts, a part of the reaction mixture was filtered at the reaction temperature and the obtained liquid phase was further investigated in condensation reaction under the same reaction conditions.

The reaction products were analyzed by gas chromatography (GC) using an Agilent 6850 with FID detector equipped with a nonpolar HP1 column (diameter 0.25 mm, thickness 0.2 µm and length 30 m). The reaction products were identified using GC-MS analysis (ThermoFinnigan, FOCUS DSQ II Single Quadrupole GC/MS).

3. Results and Discussion

Structure and textural properties of MOFs

The frameworks of MOFs under investigation are schematically depicted in Fig 1. In $\text{Cu}_3(\text{BTC})_2$ the Cu^2 -clusters are coordinated via carboxylate groups of benzene-1,3,5-tricarboxylate to form a paddlewheel unit in a three-dimensional porous cubic network (Fig. 1). $\text{Cu}_3(\text{BTC})_2$ is a rigid MOF with a zeolite-like structure and with free coordination sites on the Cu^{II} ion. It contains three types of pores, of which the larger two penetrate the structure in all three dimensions and are connected with pore windows of ca. 6 Å in diameter. The free coordination sites are oriented towards the center of one of the larger pore types [53]. MIL-100(Fe) and MIL-100(Cr) are built up from trimers of μ_3 -oxo bridged iron(III)/chromium(III) oxide octahedra and 1,3,5-benzenetricarboxylate linkers resulting in hybrid supertetrahedra that further assemble into zeotypic mesoporous material with mesoporous cages [51] (Fig. 1). The crystal structure of Fe(BTC) still remains unknown.

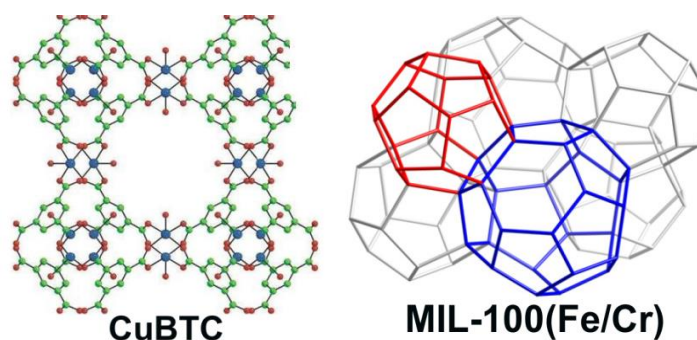


Figure 1. Frameworks of $\text{Cu}_3(\text{BTC})_2$, MIL-100(Fe/Cr).

XRD patterns of studied MOFs showed characteristic diffraction lines well-corresponding to the literature data (Fig. 2). No diffraction lines, attributable to additional phases, were observed. While $\text{Cu}_3(\text{BTC})_2$, MIL-100(Fe), and MIL-100(Cr) were found to be highly crystalline, Fe(BTC) represents less ordered material.

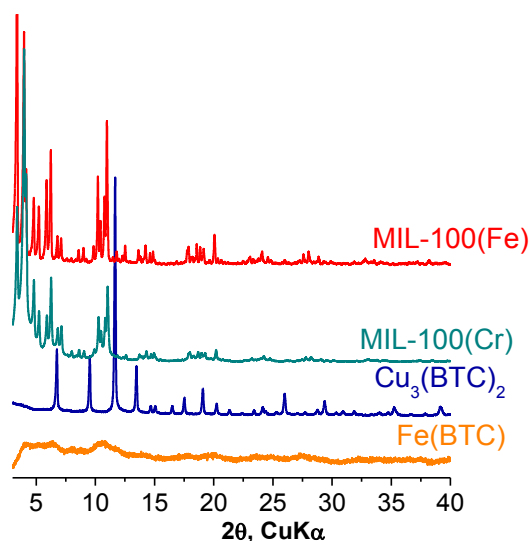
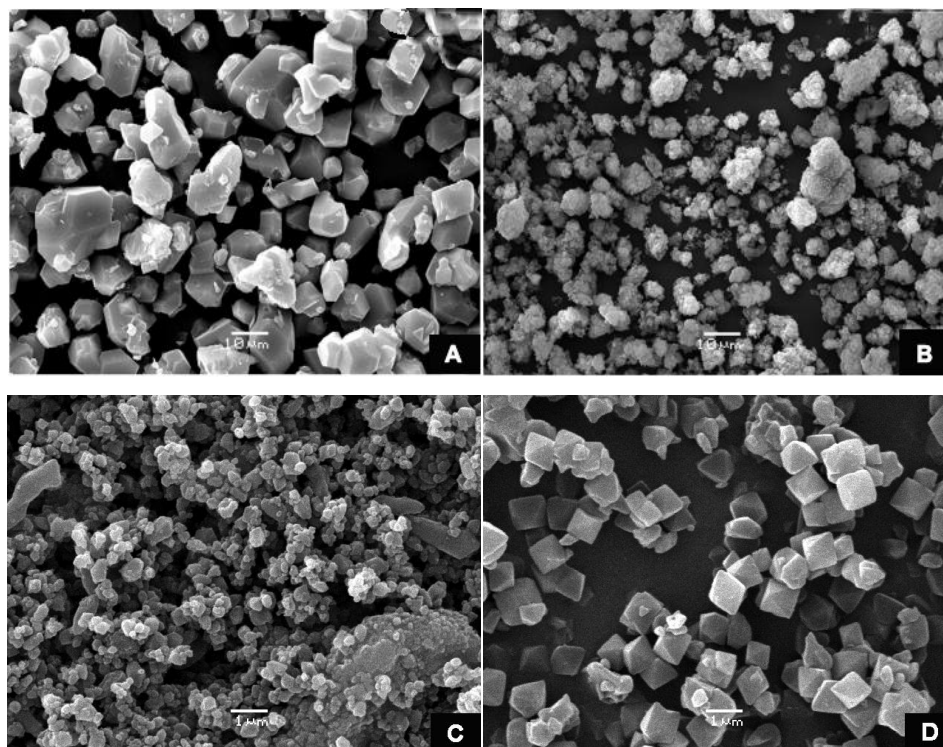


Figure 2. XRD patterns of MOFs.

The crystals of $\text{Cu}_3(\text{BTC})_2$ are rectangular prisms with the length of the edges of about $7\ \mu\text{m}$ while the size of the crystals of Fe(BTC) is about $3\ \mu\text{m}$ (Fig. S11, Table 1). MIL-100(Fe) and MIL-100(Cr) showed rectangular crystals of 0.5 and $1\ \mu\text{m}$ in size.



FigureS11. SEM images of MOFs: $\text{Cu}_3(\text{BTC})_2$ (A), $\text{Fe}(\text{BTC})$ (B), MIL-100(Fe) (C), MIL-100(Cr) (D).

All MOFs under investigation show a type I isotherm, which is typical for materials possessing micropores (Fig. 3). However, as the porosity of MIL-100 originates from both 25 Å and 29 Å mesopores, which are accessible via 5.5 Å and 8.6 Å windows [54], two secondary uptakes at ca. $P/P_0 = 0.06$ and 0.12 can be distinguished from the isotherms of MIL-100(Fe) and MIL-100(Cr). Textural properties of all catalysts are summarized in Table 1. While all MOFs under investigation possess micropores of close size, the micropore volume increases in the sequence $\text{Fe}(\text{BTC}) < \text{Cu}_3(\text{BTC})_2 < \text{MIL-100}(\text{Cr}) \approx \text{MIL-100}(\text{Fe})$. The textural properties of the MIL-100 (Fe) and MIL-100 (Cr) materials do not differ substantially while less ordered $\text{Fe}(\text{BTC})$ is characterized by lower micropore volume and S_{BET} surface area in comparison with $\text{Cu}_3(\text{BTC})_2$.

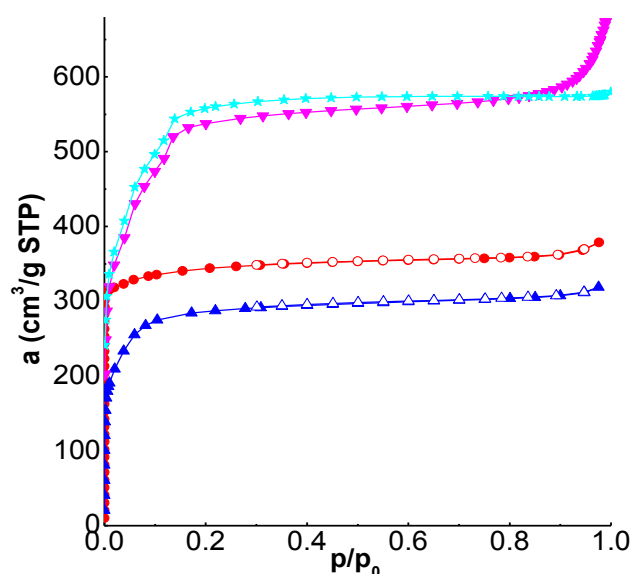


Figure 3. N₂ adsorption isotherms of the catalysts: Fe(BTC) (—▲—), Cu₃(BTC)₂ (—●—), MIL-100 (Cr) (—▼—), MIL-100 (Fe) (—★—). Open points represent adsorption, full points - desorption.

Table 1. Structural properties of used catalysts.

Catalyst	Crystal size ^[a] , μm	S _{BET} ^[b] , m ² /g	D _{micro} ^[b] , nm	V _{micro} ^[b] , cm ³ /g	Lewis acid centers ^[c] [mmol g ⁻¹]
Cu ₃ (BTC) ₂	7	1500	0.90	0.64	2.3
Fe(BTC)	3	1060	0.86	0.33	1.6
MIL-100(Fe)	0.5	2250	0.86	0.90	n.d. ^[d]
MIL-100(Cr)	1.05	2030	0.86	0.83	n.d.

[a] according to SEM images. [b] according to adsorption / desorption isotherms of N₂. [c] according to IR of adsorbed pyridine, [d] not determined

The investigations of Lewis acidity of MOFs [55, 56] and demonstration of correlations between amount of Lewis acid sites and catalytic activity of MOFs [57] are rather limited.

The absorption band at $\nu=1069\text{ cm}^{-1}$ assigned to C–C out-of-plane vibration in the pyridine molecule was chosen as the diagnostic band to evaluate the concentration of Lewis acid sites in Cu₃(BTC)₂ and Fe(BTC). The concentration of coordinatively bonded pyridine is equal to 2.30 and 1.90 mmol/g for Cu₃(BTC)₂ and Fe(BTC) activated at 473 K, respectively.

Rustad et al. [58] estimated the acid strength of Al(III), Cr(III), and Fe(III) μ₃-hydroxo functional groups from *ab initio* electronic structure calculations. It was found that =Fe₃OH and =Al₃OH groups have nearly the same strength, while =Cr₃OH groups appeared to be stronger ones. The ratio between metal charge and its ionic radius (e/r) can be used as an approximate

measure for evaluation of a hardness of metal cations as acid sites [59]. From this point of view the hardness of Lewis acid centers increases in the following sequence: Cu^{2+} ($e/r = 2.73$) < Fe^{3+} ($e/r = 4.65$) < Cr^{3+} ($e/r = 4.87$).

Catalytic behavior

The conversion of investigated phenols in annulation reaction with MBO over MOF catalysts was found to increase in the following: $\text{MIL-100}(\text{Cr}) < \text{Fe}(\text{BTC}) \ll \text{Cu}_3(\text{BTC})_2 < \text{MIL-100}(\text{Fe})$. It should be pointed out, that the highest conversions (45 and 75 % after 1300 min of TOS for phenol and 2-naphthol, respectively, Fig. 4) were achieved over MIL-100(Fe) possessing the highest V_{micro} and S_{BET} area (Table 1). At the same time, the increasing strength of Lewis acid centers for MIL-100(Cr) in comparison with MIL-100(Fe) [58, 60] results in the dramatic loss of the activity of the catalyst. This result is presumably caused by strong adsorption of phenol substrates on relatively strong Lewis acid centers of MIL-100(Cr). MIL-100(Fe) characterized by larger surface area and higher pore volume appeared to be more active in comparison with $\text{Cu}_3(\text{BTC})_2$ (45 vs 20 and 75 vs 60 % after 1300 min of TOS for phenol and 2-naphthol, respectively). The last result may also be caused by the relative weakness of the Cu^{2+} acid sites for the activation of substrates. If the metal cation is a weak Lewis acid, the intermediate catalyst–substrate complex is unstable. On the other hand, if the metal cation is very acidic, the formed complex is too stable to undergo further reaction. Therefore, MOFs having metal cations with intermediate Lewis acidity provide the highest catalytic activity.

Surprisingly, the negligible conversion of phenols (2 and 7 % after 1300 min of TOS for phenol and 2-naphthol, respectively) was found for Fe(BTC) possessing Fe Lewis acid centers.

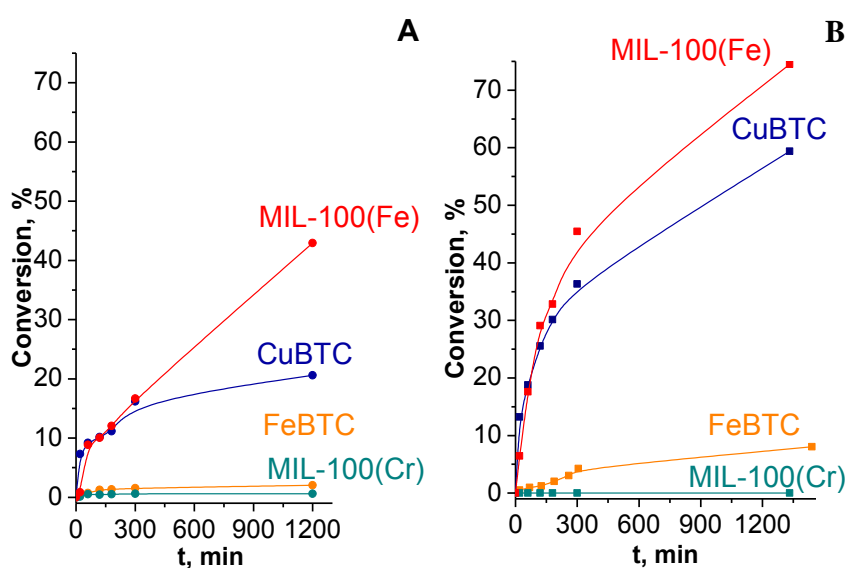


Figure 4. TOS dependence of phenol (A) and 2-naphthol (b) conversion in annulation with MBO over MOFs.

Limited confinement space for reactants in less ordered Fe(BTC) framework may be the reason of its poor catalytic behavior in annulation of phenols, involving bulky intermediate.

The reactivity of 2-naphthol in annulation with MBO over $\text{Cu}_3(\text{BTC})_2$ and MIL-100 (Fe) was found to be higher in comparison with phenol (Fig. 5), which is in agreement with Ref. [61]. Respective prenylphenols (PP, Fig. 5a,d) – the products of phenol and 2-naphthol prenylation with MBO, targeting 2,2-dimethylbenzopyranes (DMBP, Fig. 5b,e) and the products of their thermal rearrangement [62, 63] 2,2,3-trimethylbenzofuranes (TMBF, Fig. 5c,f) were detected in the reaction mixtures. The side-product of MBO oxidative dimerisation was found as well.

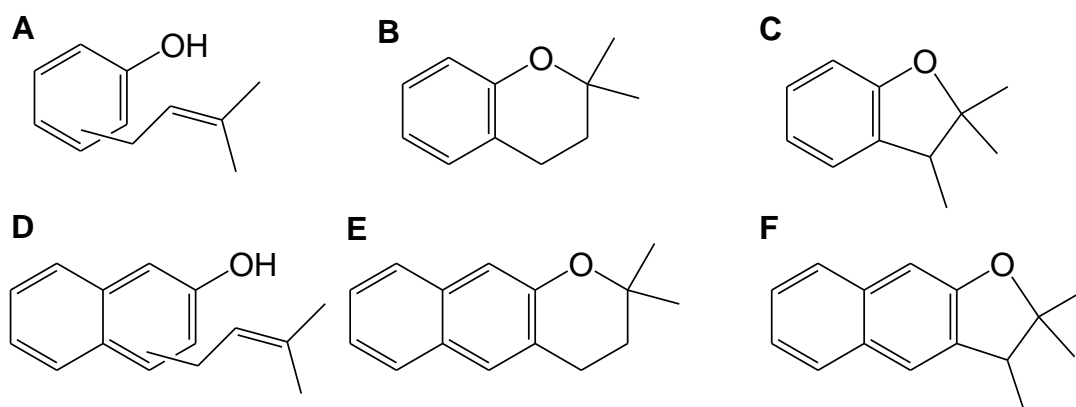


Figure 5. Isomeric products observed during annulation of phenol (a, b, c,) and 2-naphthol (d, e, f).

Figure 6 shows that the product distribution depends on the type of metal in MOF. The relative amount of intermediate PP (Fig. 5a,d) is higher for $\text{Cu}_3(\text{BTC})_2$ (22 vs 6 % in the case of phenol annulation over $\text{Cu}_3(\text{BTC})_2$ and MIL-100(Fe), respectively), while the products of consequent intramolecular cyclization DMBP (Fig. 5b,e) were mainly observed over MIL-100 (Fe). This result may indicate a higher rate of consecutive annulation over MIL-100 (Fe) in comparison with $\text{Cu}_3(\text{BTC})_2$ and may be connected with a higher acid strength of the former catalyst. Relatively higher amount of TMBF (Fig. 5c,f) produced over $\text{Cu}_3(\text{BTC})_2$ may also be caused by a lower rate of annulation producing substituted DMBP in comparison with the rate of thermally-induced rearrangement consuming it.

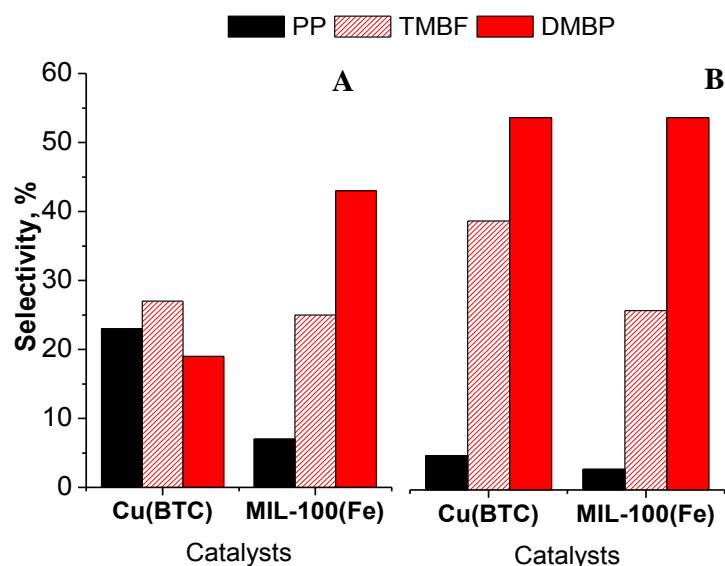


Figure 6. Selectivities to the products of annulation of phenol (A) and 2-naphthol (B) with MBO over MOFs at 16 % of substrate conversion.

The preservation of the frameworks of the most active MIL-100(Fe) and $\text{Cu}_3(\text{BTC})_2$ catalysts under the conditions of 2-naphthol annulation reaction was confirmed by means of XRD (Fig. 7). In particular, we observed neither the significant changes of the intensity of individual diffraction lines, attributed to the respective interplanar distances of MIL-100(Fe) and $\text{Cu}_3(\text{BTC})_2$, nor their positions.

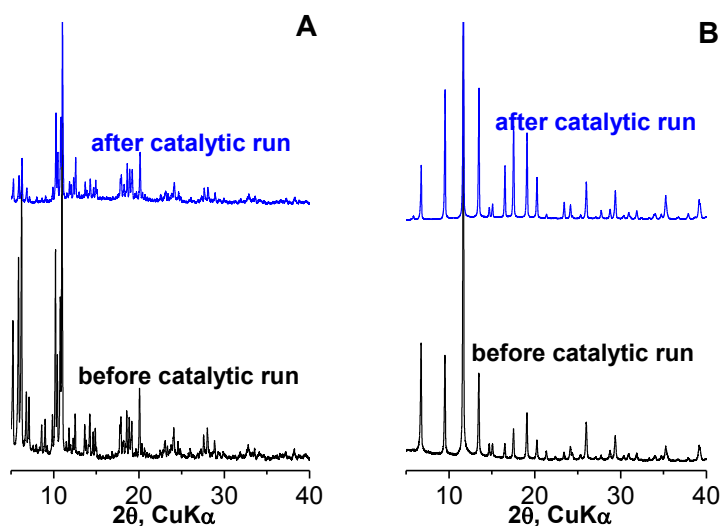


Figure 7. XRD patterns of MIL-100(Fe) (A) and $\text{Cu}_3(\text{BTC})_2$ (B) before and after annulation of 2-naphthol with MBO ($T = 80\text{ }^\circ\text{C}$, 1,2-dichloroethane as solvent).

The heterogeneous character of the reaction was evidenced in special experiments for the most active samples, MIL-100(Fe) and $\text{Cu}_3(\text{BTC})_2$. The respective catalysts were filtered off and

centrifugated after 120 min of reaction in 1,2-dichloroethane at 80 °C. At that time, MIL-100(Fe) and Cu₃(BTC)₂ achieved conversions of 2-naphthol about 30 and 25 %, respectively. Then, the filtrate without the catalyst was stirred at 80 °C for 1200 min. After removing the catalyst, further increase in the conversion of 2-naphthol (0.8 and 0.9 %, respectively) was negligible, providing evidence of heterogeneous catalysis (Fig. 8).

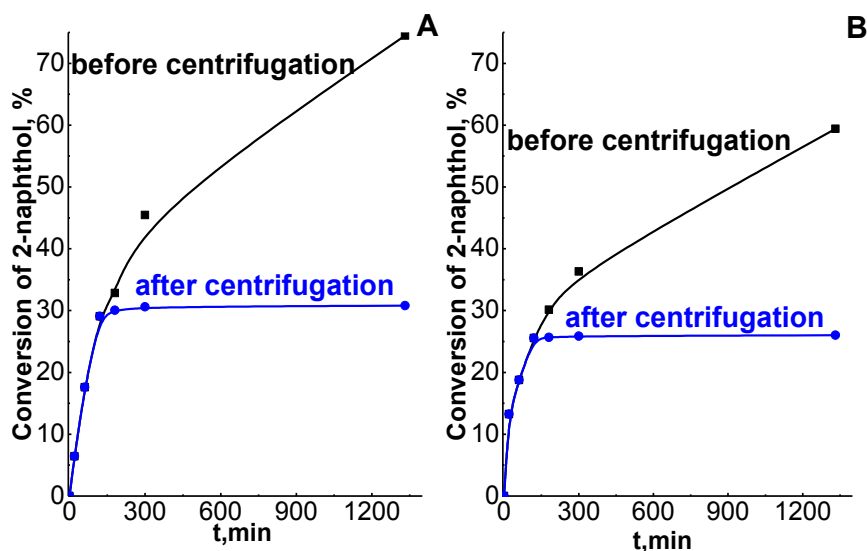


Figure 8. Leaching test of Fe³⁺ ions from MIL-100(Fe) (A) and Cu²⁺ ions from Cu₃(BTC)₂ catalysts (B) under conditions of 2-naphthol annulation with MBO (T = 80 °C, 1,2-dichloroethane as solvent, 3.0 mmol of 2-naphthol, 4.5 mmol of MBO, m (catalyst) = 0.2 g).

Conclusions

Catalytic behavior of Cu₃(BTC)₂, Fe(BTC), MIL-100(Fe), and MIL-100 (Cr) was investigated in annulation of phenol and 2-naphthol with 2-methyl-3-buten-2-ol and related with acidic and textural properties of the catalyst. The highest conversions of phenols (45 and 75 % after 1300 min of TOS for phenol and 2-naphthol, respectively) and selectivity to target chromane (42 and 56 % at 16 % conversion of phenol and 2-naphthol, respectively) were achieved over MIL-100 (Fe) possessing intermediate Lewis acidity, perfect crystalline structure and highest S_{BET} surface area. The highest acid strength of Lewis acid centers for MIL-100(Cr) was found to result in the dramatic decrease in the activity of the catalyst. While negligible conversion of phenols (2 and 7 % after 1300 min of TOS for phenol and 2-naphthol, respectively) was found over Fe(BTC) characterized by low ordered framework with a limited confinement space for the formation of quite bulky intermediate. The highest activity as well as the preservation of the structure and the active centers of MIL-100(Fe) make this MOF a promising catalyst for annulation reaction.

Acknowledgement

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