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 $Cu_3(BTC)_2$) was investigated in annulation reaction between 2-methyl-3-buten-2-ol and phenols differing in size (phenol, 2-naphthol). MIL-100(Fe) possessing intermediate Lewis acidity, perfect crystalline structure, and the highest S_{BET} surface area showed the highest activity (TOF = 0.7 and 1.4 h^{-1} for phenol and 2-naphthol, respectively) and selectivities to target benzopyran (45% and 65% at 16% of phenol and 2-naphthol conversion, respectively). 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 was found over Fe(BTC), characterized by a less ordered framework.

It is a great pleasure to provide a contribution honoring the 60th birthday of Professor Thomas Bein on a subject where he has made inspiring contributions.

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 (H_3PO_4 [10], HCOOH [11], H_2SO_4 [12], HCl/AlCl$_3$ [13], BF$_3$·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].

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 metal sites 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 benzoylation [46].

Recently, we reported the catalytic benefits of $Cu_3(BTC)_2$ and Fe(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 adequate pore size of the most active MOFs.

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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 Fe(BTC), MIL-100(Fe), and compare it with MIL-100(Cr), and $Cu_3(BTC)_2$ in annulation reaction between 2-methyl-3-buten-2-ol and phenols differing in size (phenol, 2-naphthol).

2. Experimental

2.1. Materials

$Cu_3(BTC)_2$ (Basolite C300) and Fe(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, 0.45 g), 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, 40 ml). 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.

2.2. 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 CuKα 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 °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 °C. This temperature was maintained for 8 h.

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

2.3. 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

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

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 of 10 °C/min. The chosen temperature of activation provides not only the releasing of the most part of chromium [53], iron [54] and copper [55] unsaturated sites, but also the preservation of original structure ordering of the MOFs. 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. 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 non-polar 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).
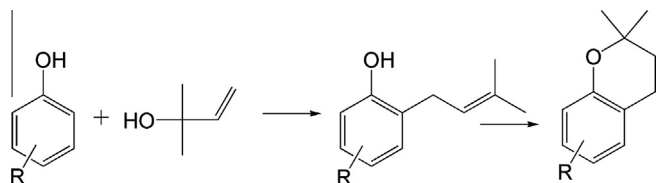
3. Results and discussion

3.1. Structure and textural properties of MOFs

The frameworks of MOFs under investigation are schematically depicted in Fig 1. In $Cu_3(BTC)_2$ 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). $Cu_3(BTC)_2$ 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 [56]. 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.

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 $Cu_3(BTC)_2$, MIL-100(Fe), and MIL-100(Cr) were found to be highly crystalline, Fe(BTC) corresponds to a less ordered material.

The crystals of $Cu_3(BTC)_2$ are rectangular prisms with the length of the edges of about 7 μm while the size of the crystals of Fe(BTC) is about 3 μm (Fig. SI1, Table 1). MIL-100(Fe) and MIL-100(Cr) showed rectangular crystals of 0.5 and 1 μm in size.

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 [57], two secondary uptakes at ca. $P/P0 = 0.06$ 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 Fe(BTC) < $Cu_3(BTC)_2$ < MIL-100(Cr) $\approx$ MIL-100(Fe). The textural properties of the MIL-100(Fe) and MIL-100(Cr) materials do not differ substantially, while less ordered Fe(BTC) is characterized by lower micropore volume and lower S_{BET} surface area in comparison with $Cu_3(BTC)_2$.