



Metal-organic frameworks as efficient catalytic systems for the synthesis of 1,5-benzodiazepines from 1,2-phenylenediamine and ketones



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ABSTRACT

Benzodiazepines and their derivatives are a very important class of nitrogen-containing heterocyclic compounds with biological activity that are widely used in medicine. In this study, we demonstrated synthesis of 1,5-benzodiazepines from 1,2-phenylenediamine and ketones (acetone, cyclohexanone, acetophenone, methyl ethyl ketone) in the presence of isostructural porous metal-benzenetricarboxylates of the families MIL-100(M) (M: V³⁺, Al³⁺, Fe³⁺ and Cr³⁺) and three porous aluminium trimesates Al-BTCs (MIL-96(Al), MIL-100(Al) and MIL-110(Al)). A combination of catalytic, theoretical and physicochemical methods showed that reaction rates and yields of 1,5-benzodiazepines were adjusted by the type of metal ions and accessibility of active sites. The yield of 1,5-benzodiazepines in the presence of MIL-100(M) was comparable with zeolites, such as HY, H-ZSM-5, β -zeolite and heulandite.

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1. Introduction

1,5-Benzodiazepine derivatives have received significant attention as compounds with biological activity [1]. 1,5-Benzodiazepine derivatives possess antifungal, antibacterial, antifeedant, anti-inflammatory, analgesic and anticonvulsant activities. Moreover, 1,5-benzodiazepines are widely used as synthons for the synthesis of triazole [2,3] and oxadiazole derivatives [4,5]. The traditional approach for synthesis of 1,5-benzodiazepines is based on the acid-catalysed reaction of 1,2-phenylenediamine (I) with ketones. Various catalytic systems for this reaction have been reported in the literature, a great number of which have appeared only very recently [6–12]. Thus, synthesis of 1,5-benzodiazepines has been achieved using different homogeneous catalysts, such as ZnCl₂ [10], YbCl₃ [11], BF₃-etherate [13], and 1-butyl-3-methylimidazolium bromide (ionic liquid) [14]. As solid acid catalysts, polyphosphoric acid on SiO₂ [15], sulfated zirconia [7], polymer-supported FeCl₃ [12], H₂SO₄/SiO₂ [8], Amberlyst-15 [9], and zeolites [16,17] were used. Le et al. [18] suggested the use of

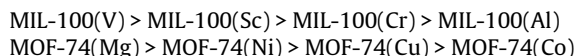
metal-organic frameworks (MOFs), such as MOF-235(Fe), MOF-5 (Zn), Mn(BDC), MOF-199(Cu), and Ni₂(BDC)₂(DABCO), as heterogeneous catalysts for the cyclocondensation of acetone with different 1,2-diamines, including 1,2-phenylenediamine, 4-chloro-1,2-phenylenediamine, 4-bromo-1,2-phenylenediamine, and 4-methyl-1,2-phenylenediamine, to the corresponding 1,5-benzodiazepines. It was found that MOF-235(Fe) was highly active compared with other studied MOFs. Unfortunately, the effects of the structure of MOFs and the nature of active sites in the frameworks of MOFs on the reaction rate and product distribution were not investigated.

During last few years, metal-organic frameworks have attracted significant interest as materials for catalytic applications due to their unique structure and physicochemical properties [19–21]. Of material importance is that a large variety of structural types and chemical compositions can be obtained by changing either the organic linker or the metal. A large specific surface area, homogeneous distribution and high accessibility of active sites for reactants also govern the catalytic properties of MOFs. The latest investigations note that the type of metal ions in the framework of MOFs affects their catalytic properties [22–24]. Thus, the effect of the metal ion on catalytic properties of the isostructural MOFs of the families MOF-74(Co, Cu, Mg, Ni) and MIL-100(Al, Cr, Sc, V) was investigated in reactions of 3,4-dihydro-2 H-pyran with

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alcohols [24]. It was found that the yield of tetrahydropyranlyl ether decreased in the following orders:



The main reasons for these trends are related to the accessibility and strength of open metal sites. The dependence of catalytic properties on the type of metal ions was also demonstrated for the isostructural MOFs of the families MIL-100(M) and MIL-53(M) (M = V, Al, Fe and Cr) and mixed MIL-53(Al,V) (Al/V – 100/0, 75/25, 50/50, 25/75 and 0/100 atom/atom) in the synthesis of solketal from acetone and glycerol (I) [23]. According to this investigation, glycerol conversion decreased in the following order $\text{V}^{3+} > \text{Al}^{3+} > \text{Fe}^{3+} > \text{Cr}^{3+}$, which was in agreement with the value of the zero point of charge of the surface (pH_{PZC}). Reasonably, the type of metal ions in the framework of MOFs should also be important for the reaction between (I) and ketones.

As a part of a systematic study on the catalytic behaviour of MOFs and with a view to increase knowledge about the dependence of their catalytic properties on the type of metal ions, we report for the first time on variable catalytic activity of isostructural MOFs of the families MIL-100(M) (M: V^{3+} , Al^{3+} , Fe^{3+} and Cr^{3+}) and three porous aluminium trimesates Al-BTCs (MIL-96(Al), MIL-100(Al) and MIL-110(Al)) in the cyclocondensation of (I) with acetone to 2,3-dihydro-2,2,4-trimethyl-1H-1,5-benzodiazepine (1,5-benzodiazepine, (III)) (Scheme 1). We suggested that the type of metal ions in the MOFs should allow to adjust the catalytic activity of MIL-100(M). Moreover, three porous aluminium trimesates Al-BTCs are good candidates for our investigation because their textural properties are different, important for analysis of the effect of the amount of active sites and their accessibility to the reactants. Thus, the structure of MIL-96(Al) ($[\text{Al}_{12}\text{O}(\text{OH})_{18}(\text{H}_2\text{O})_3(\text{Al}_2(\text{OH})_4)]\text{BTC}]_6 \cdot 24\text{H}_2\text{O}$) has three types of cages. The pore-opening diameters of these cavities are in the range of 2.5–3.5 Å [25]. MIL-110(Al) ($[\text{Al}_8(\text{OH})_{12}\{(\text{OH})_3(\text{H}_2\text{O})_3\}]\text{BTC}]_3 \cdot 42\text{H}_2\text{O}$) also has a honeycomb topology. MIL-110(Al)'s structure is built up from the connection of an octahedrally coordinated aluminium octameric unit through trimesate ligands delimiting one-dimensional, large hexagonal channels (16 Å) [26]. At the same time, mesoporous MIL-100(Al) ($[\text{Al}_3\text{O}(\text{OH})(\text{H}_2\text{O})_2]\text{BTC}] \cdot 24\text{H}_2\text{O}$) possesses a three-dimensional framework structure with two types of cavities [27,28]. The first type of cavity is delimited by 12 pentagonal windows with a size of 5.5 Å (dodecahedral cage); the second cavity is delimited by 12 pentagonal windows and 4 hexagonal windows with a size of 8.6 Å (hexadodecahedral

cage). The amount of Lewis acid sites (LAS) in MIL-100(M) and Al-BTCs was measured by EPR spectroscopy using the 2,2',6,6'-tetramethyl-1-piperidinyloxy radical (TEMPO) as the probe molecule. Earlier, we successfully used this technique in the analysis of coordinatively unsaturated sites ($\text{Al}_{\text{CUS}}^{3+}$) in Al-BTCs, such as MIL-100(Al), MIL-96(Al) and MIL-110(Al) [22]. This method is based on the reaction of TEMPO with only one acid site [29–31]. According to this property, the maximum amount of radicals adsorbed (until the EPR spectrum of the TEMPO radical appears in the solution) corresponds to the concentration of acid sites. Analysis of the main factors that affect the reaction rate and the isomer selectivity was based on a combination of catalytic, theoretical and physicochemical methods. Another purpose of our investigation was to demonstrate the catalytic potential of the studied MOFs as heterogeneous catalysts for this reaction. To this end, we investigated cyclocondensation of (I) with other ketones, such as cyclohexanone, acetophenone and methyl ethyl ketone, to obtain the corresponding 1,5-benzodiazepines.

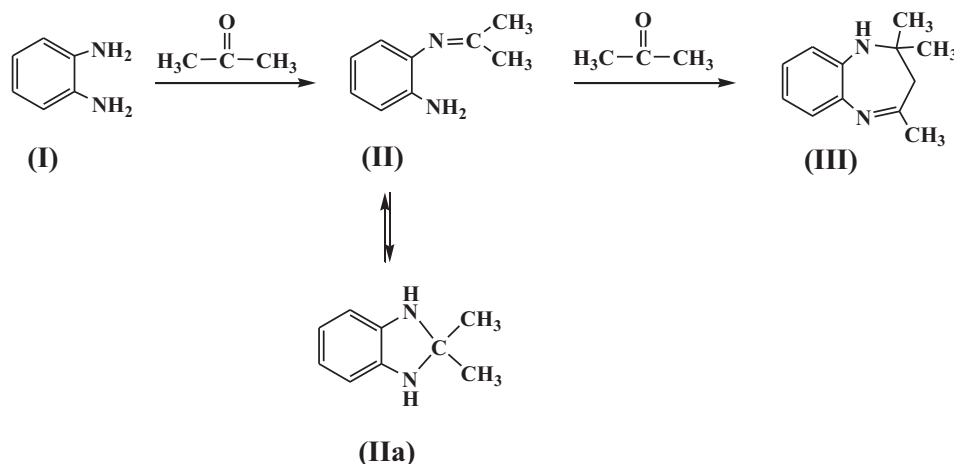
2. Experimental

2.1. Materials

Commercial methanol, acetone (Acros Organics), 1,2-phenylenediamine (Acros Organics), cyclohexanone (99+%, Acros Organics), acetophenone (98%, Acros Organics), 2-butanone (99+%, Acros Organics), 2,2',6,6'-tetramethyl-1-piperidinyloxy radical (TEMPO) (Aldrich), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98 wt%, Junsei), 1,3,5-benzenetricarboxylic acid (H_3BTC) and 1,3,5-trimethyl-benzenetricarboxylate ($\text{Me}_3\text{-BTC}$, 98%, Aldrich), ortho-phosphoric acid (H_3PO_4 , 85 wt%, Merck), sodium hydroxide (NaOH , 4 M), nitric acid (HNO_3 , 60 wt%), iron powder (Fe^0 , 99%, DC Chemical Co.), CrO_3 (98%, Junsei) and hydrofluoric acid (HF, 48%, OCI Company Ltd.) were used without any further purification. Beta zeolite (Si/Al 30, framework type BEA) and H-ZSM-5 (Si/Al 28, framework type MFI) were synthesized in a way similar to reported methods [16,32].

2.2. Synthesis of metal-benzenetricarboxylates

Al-BTCs were synthesized from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1,3,5-benzenetricarboxylic acid (H_3BTC) or trimethyl 1,3,5-benzenetricarboxylate ($\text{Me}_3\text{-BTC}$), sodium hydroxide (NaOH , 4 M), nitric acid (HNO_3 , 60%) and deionized water similar to the reported methods for MIL-100(Al) [27,28], MIL-110(Al) [27] and MIL-96(Al) [25] under autogenous pressure at 210 °C. The reactant compositions for the desired phases are shown in Table S1 (Sup-



Scheme 1. The cyclocondensation of 1,2-phenylenediamine with acetone.

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