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Amino-based metal-organic frameworks as stable, highly active basic catalysts

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ABSTRACT

Metal-organic frameworks (MOFs) with non-coordinated amino groups, i.e. IRMOF-3 and amino-functionalized MIL-53, are stable solid basic catalysts in the Knoevenagel condensation of ethyl cyanoacetate and ethyl acetoacetate with benzaldehyde. IRMOF-3_{DEF} exhibits activities that are at least as high as the most active solid basic catalysts reported, with a 100% selectivity to the condensation product. For IRMOF-3 samples the catalytic activity correlated with the accessibility of the basic sites. Diffusion limitations could be excluded for this most active catalyst. A new MOF based on the MIL-53 topology and non-coordinated amino groups has been synthesized and characterized. Although active its poor performance in the studied Knoevenagel condensations is attributed to strong adsorption and diffusion limitations in the 1-D pore structure of this framework. The performance of the IRMOF-3 catalysts demonstrates that the basicity of the aniline-like amino group is enhanced when incorporated inside the MOF structure, increasing the pK_a of the basic catalyst and more active than aniline as homogeneous catalyst. The IRMOF-3 catalysts are stable under the studied reaction conditions, and could be reused without significant loss in activity. The catalytic performance of IRMOF-3 in various solvents suggests that this open, accessible and well-defined structure behaves more like homogeneous basic catalysts, in contrast to other solid basic catalysts. By means of DRIFTS, the reaction mechanism has been elucidated, showing spectroscopic evidence of benzaldimine intermediates.

1. Introduction

The development of heterogeneous basic catalysts is a crucial requirement for sustainable chemistry [1]. Using solid catalysts, instead of stoichiometric amounts of soluble strong bases, the overall atom efficiency of reactions is improved, processes are simplified, the turn-over-number of the catalyst is increased, the volume of waste is significantly reduced, and product work-up becomes easier, if necessary at all. Compared to the broad application of solid acid catalysts, considerable less attention has been given to the development of solid basic catalysts [2]. Typically organic bases immobilized on different supports have been used as catalytic materials [3]. Progress has predominately been limited because of leaching of the active material from the various types of support used [3,4]. Other solid bases, such as layered double hydroxides or ion exchanged zeolites, are either very active when fresh but suffer from severe and rapid deactivation [5], or their initial activity is rather low [6].

Metal-organic frameworks (MOFs) constitute a new class of structured microporous materials, coordination polymers built up from organic linkers and inorganic connectors [7]. In principle, these MOFs can contain any functional group, especially connected to the organic linker, and the accessibility of these groups can be tailored to the application, from almost blocked to fully accessible. Although these properties make MOFs a promising class of new heterogeneous catalysts, it is generally acknowledged that the full potential of this new class of materials has not been identified [8]. Detailed studies on the catalytic performance of MOFs with catalysis taking place at the metal center have recently been published [9,10]. However, only a few proofs of concept of MOFs with catalytically-active functional organic sites (FOS, i.e. catalysis takes place at the organic linker [11]) have been reported [11–14]. Concerning base-catalyzed reactions, only Seo et al. [14] and Hasegawa et al. [11] have demonstrated the possibility to use as-synthesized MOFs as basic catalysts by introducing pyridyl and amide groups, respectively, in the organic linkers. However, the weak basicity of these functional groups implied only very low activities, while other important aspects such as recyclability and catalyst stability were not studied in further detail. Another approach to use MOFs as basic catalysts has been proposed very recently: the grafting of amino groups on coordinatively unsaturated metal centers of MOFs, yielding active catalysts for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate [15]. However, deactivation of the catalyst due to leaching of the active sites seems to be an issue using this approach.

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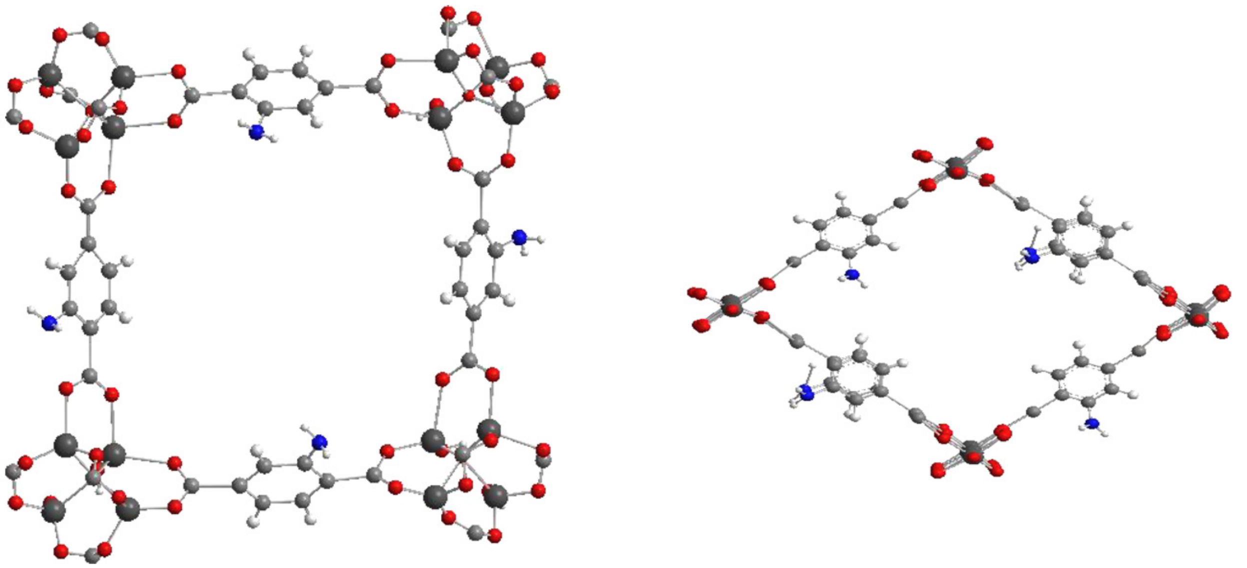

Fig. 1. Structure of the synthesized MOFs: (left) IRMOF-3, (right) amino-MIL-53(Al). (Oxygen atoms in red, carbon atoms in light gray, nitrogen atoms in blue, and Zn (left) and Al (right) in dark gray. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Although the synthesis and some applications of MOFs with amino groups have already been described [12,16], their use as basic catalysts has not yet been reported in the open literature. The best known amino-MOF is IRMOF-3, a member of the isoreticular MOF family first reported by Yaghi's group [16]. IRMOF-3 consists of Zn_4O clusters linked by 2-aminoterephthalic acid. Its crystalline structure is similar to the well known MOF-5 (or IRMOF-1); it consists of octahedral Zn_4O clusters linked by ditopic linear dicarboxylates [17] (Fig. 1a). However, all application work with this and similar MOF structures was either focused on gas adsorption [16], or on their use as intermediates for framework functionalization through the accessible non-coordinated amino groups [12,18]. Ingleson et al. [18] have demonstrated that the aromatic $-NH_2$ group interacts very easily with different solvents and its functionalization may trigger metal complex binding. Besides, the optimized geometry for IRMOF-3 shows that the benzene ring lies in-plane with the Zn_4O ring and this configuration is stabilized by an intramolecular hydrogen bond between the aromatic amino hydrogen atom and a carboxylate oxygen atom [19]. These findings suggest that IRMOF-3 and similar structures are interesting candidates for basic catalysis, since the reactivity of the amino group inside the MOF may be affected through these interactions.

In addition to IRMOF-3, other stable MOFs can be considered. Here we report the synthesis of a new structure based on MIL-53(Al) using 2-aminoterephthalic acid as linker. The MIL-53 series is built up from infinite chains of corner-sharing $MO_4(OH)_2$ ($M = Al^{3+}$ or Cr^{3+}) or $V^{4+}O_6$ octahedra interconnected by dicarboxylate groups resulting in a 3-D metal-organic framework containing 1-D diamond-shaped channels with pores of free diameter close to 7.5 Å (see Fig. 1b). The synthesis of a MOF with the MIL-53 structure and aminoterephthalic acid as linker has been very recently claimed by [20], named USO-1-Al. However, no proof (XRD, IR, elemental analysis) of the formation of such structure was provided so far.

The liquid-phase Knoevenagel condensation between a C=O functionality and an activated methylene group is an interesting classic route to C–C coupling for the preparation of important intermediates in the pharmaceutical industry and is often used as a test reaction for probing the activity of various solid base catalysts [21–26]. In fact, reacting benzaldehyde with compounds containing active methylene groups with different pK_a values, such as ethyl cyanoacetate ($pK_a \leqslant 9$) or ethyl acetoacetate ($pK_a \leqslant 10.7$) makes it possible to evaluate the basic strength of a catalyst.

The reaction may proceed according to two different mechanisms that depend essentially on the nature of the catalytic material used as solid base. For strong bases, direct deprotonation of the methylene group on the catalyst surface and reaction of the deprotonated intermediate with the slightly acidic benzaldehyde takes place, leading to the product.

When weaker bases, such as amino groups are involved in the catalytic process, formation of an imine intermediate occurs with the benzaldehyde (Schiff base, cycle 1 in Scheme 1). As consequence of the higher basicity of the formed benzaldimine compared to the free amine, the deprotonation of the methylene group takes places followed by reaction, regenerating the active site. The active methylene group can also react directly with the amino groups to form amides (Reaction 2 in Scheme 1), inhibiting then the interaction amine–benzaldehyde and causing the deactivation of the catalyst. Evidence for the formation of imine functionalities over modified silicas in the liquid phase using infrared spectroscopy have been recently reported [23].

In this paper, MOFs with basic groups similar to aniline ($pK_a = 4.6$) have been tested in the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate ($pK_a \leqslant 9$) and ethyl acetoacetate ($pK_a \leqslant 10.7$; Scheme 2), demonstrating an enhanced performance of the aromatic amine group, resulting in activities comparable to the best *state-of-the-art* solid bases, but without their deactivation due to leaching.

2. Experimental

2.1. General information

All chemicals were obtained from Sigma–Aldrich and were used without further purification. Inductively coupled plasma (ICP) emission spectrometry (Perkin–Elmer Optima 3000dv ICP-OES spectrometer) was used for the analysis of the bulk chemical composition of the synthesized MOFs. The crystalline materials were analyzed by X-ray diffraction (XRD) using a Bruker-AXS D5005 with Cu$K\alpha$ radiation. Scanning electron microscopy (SEM) on a Philips XL20 (15–30 kV) microscope was used to determine crystal morphology and size of the products. Thermogravimetric analysis of the MOFs was performed by means of a Mettler Toledo