



# Effects of linker substitution on catalytic properties of porous zirconium terephthalate UiO-66 in acetalization of benzaldehyde with methanol

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## ABSTRACT

A family of isorecticular metal–organic frameworks (MOFs), based on the UiO-66 structure, were synthesized from the two linker ligands containing electron-donating NH<sub>2</sub>-groups (2-amino-benzenedicarboxylic acid (H<sub>2</sub>N-H<sub>2</sub>BDC)) and electron-withdrawing NO<sub>2</sub>-groups (2-nitro-benzenedicarboxylic acid (O<sub>2</sub>N-H<sub>2</sub>BDC)). The catalytic performance of these materials was investigated with a combination of physicochemical and catalytic approaches in acetalization of benzaldehyde with methanol. The investigation of basicity and Lewis acidity was done by IR spectroscopy using CDCl<sub>3</sub> and 5-nonanone as probe molecules, respectively. The combination of physicochemical and catalytic investigations demonstrates that acid–base and catalytic properties of these materials depend on amount and type of functional groups presented in the linker units. Insertion of electron-donating NH<sub>2</sub>-groups into linker ligand leads to increase in the strength of basic sites in contrast to electron-withdrawing NO<sub>2</sub>-groups. The strength of Lewis acid sites decreases in order of UiO-66-NO<sub>2</sub> > UiO-66 > UiO-66-NH<sub>2</sub>, that leads to the decrease in their catalytic activity in acetalization of benzaldehyde with methanol in the same order.

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## 1. Introduction

Nowadays, numerous studies of metal–organic frameworks (MOFs) have attracted wide scientific attention, as can be seen from the increasing number of publications devoted to their applications in gas adsorption, molecular storage, drug delivery and heterogeneous catalysis due to their unique structural, textural and physicochemical properties [1–4]. Noteworthy, a wide-ranging perspectives of MOFs application in catalysis are opened by a high specific surface area, the ability to adjust their porosity by variation of organic ligands and acid–base or/and redox properties by variation both nature of metals and organic ligands.

The UiO-66 (UiO = University of Oslo) family of microporous MOF materials is based on a 3D structure of hexamers of eight

coordinated ZrO<sub>6</sub>(OH)<sub>2</sub> polyhedra and 1,4-benzene-dicarboxylate (BDC) linkers [5,6]. UiO-66 with cubic and rigid 3D structure consists of octahedral and tetrahedral cavities having diameters of 11 Å and 8 Å, respectively. Accessibility to the cavities is ensured through microporous triangular windows of 5–7 Å diameter. UiO-66 material possesses high thermal stability, a good chemical resistance toward water, acetone, benzene and dimethylformamide that may be useful for applications in catalysis. Note that application of functionalized 1,4-benzene-dicarboxylate linkers allows to obtain a family of isorecticular MOFs, based on the UiO-66 structure, such as UiO-66-NH<sub>2</sub>, UiO-66-NO<sub>2</sub>, UiO-66-Br [7–9]. Such modification does not strongly change thermal and chemical stability [8], but can remarkably change the nature of acid–base sites.

Ahn et al. [10] demonstrated that catalytic activities of UiO-66 and UiO-66-NH<sub>2</sub> correlate with their Lewis acid–base properties in cycloaddition of CO<sub>2</sub> to styrene oxide. De Vos et al. [11] reported that of UiO-66 and UiO-66-NH<sub>2</sub> also differed in activities of jasminaldehyde synthesis via cross-aldol condensation of benzaldehyde and heptanal. UiO-66 was less active in comparison with UiO-66-NH<sub>2</sub>. It was proposed that UiO-66-NH<sub>2</sub> acts as a bi-functional catalyst, which suppresses byproduct formation and accelerates

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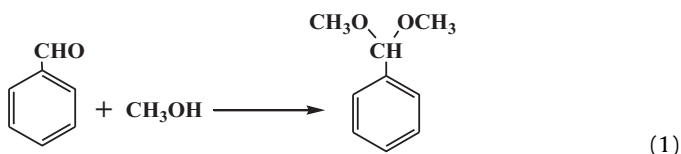
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the cross-aldol reaction due to the close occupation of Zr-formed Lewis acid sites and basic  $\text{NH}_2$ -groups inside the cages.

Effect of functionalized 1,4-benzene-dicarboxylate linkers on catalytic properties of UiO-66 was also demonstrated in the citronellal cyclization [13]. Combination of catalytic and computational molecular modeling indicates that type of functional groups presented in the linker units can alter the Lewis acidic properties and also induce additional stabilizing/destabilizing effects on the reactants depending on their electronic properties. Thus, in the citronellal cyclization, the initial reaction rate in the presence of UiO-66- $\text{NO}_2$  was at least 56 times higher in comparison with UiO-66 due to the low free energies of the adsorbed state and of the transition state. To the best of our knowledge, the applications of UiO-66 materials in catalysis are limited to the above mentioned three reports.

In this work, we investigated the effect of two linker ligands containing electron-donating  $\text{NH}_2$ -groups and electron-withdrawing  $\text{NO}_2$ -groups ( $\text{O}_2\text{N-H}_2\text{BDC}$  and  $\text{H}_2\text{N-H}_2\text{BDC}$ ) on acid–base properties, and therefore, catalytic properties of a family of isorecticular MOFs, based on the UiO-66 structure in the reaction of acetalization of benzaldehyde (BA) with methanol (Eq. (1)) which is often used by organic chemists to protect the aldehyde group:



Garcia et al. [13] demonstrated that  $\text{Fe}(\text{BTC})$ ,  $\text{Al}_2(\text{BDC})_3$  and  $\text{Cu}_3(\text{BTC})_2$  can be applied as Lewis acid catalysts for acetalization of aldehydes by methanol at room temperature due to their mild acid strength and large hydrophobicity.  $\text{Cu}_3(\text{BTC})_2$  possessed the higher activity in comparison with  $\text{Fe}(\text{BTC})$  and  $\text{Al}_2(\text{BDC})_3$ . Thus, conversions of BA in acetalization of BA with methanol to the corresponding dimethyl acetal in the presence of  $\text{Fe}(\text{BTC})$ ,  $\text{Al}_2(\text{BDC})_3$  and  $\text{Cu}_3(\text{BTC})_2$  for 24 h were 71%, 66% and 88%, respectively. It was suggested that this difference can reflect the relative Lewis acidity of the materials. Garcia et al. [14] also compared catalytic performance of  $\text{Fe}(\text{BTC})$  and MIL-100(Fe) in this reaction. It was found that the catalytic properties of  $\text{Fe}(\text{BTC})$  and MIL-100(Fe) are very similar to each other in spite of the fact that amounts of Lewis acid sites were 1.1 mmol/g and 2.0 mmol/g, respectively. Therefore, effect of Lewis acidity on activity of metal-benzenetricarboxylates (M-BTCs) is opened and needs further investigation. In our investigation we are going to reveal effect of Lewis acidity on activity of MOFs. In this manner, we have established relationships between preparation conditions, acid–base properties and catalytic activities of a family of isorecticular MOFs based on the UiO-66 structure with two linker ligands containing electron-donating  $\text{NH}_2$ -groups and electron-withdrawing  $\text{NO}_2$ -groups, such as  $\text{H}_2\text{N-H}_2\text{BDC}$  and  $\text{O}_2\text{N-H}_2\text{BDC}$ .

## 2. Experimental

### 2.1. Materials

Zirconium(IV) chloride, terephthalic acid (TPA,  $\text{H}_2\text{BDC}$ ), were purchased from Sigma–Aldrich. 2-Nitro-terephthalic acid (nitro-TPA,  $\text{O}_2\text{N-H}_2\text{BDC}$ ) and 2-amino-terephthalic acid (amino-TPA,  $\text{H}_2\text{N-H}_2\text{BDC}$ ) were procured from Alfa-Aesar. N,N-dimethylformamide (DMF) and benzaldehyde, 1,2-dichlorobenzene were obtained from Samchun Chemical. 5-Nonanone (Aldrich–Sigma) was dried under molecular sieves NaX.

UiO-66 sample was synthesized following a procedure previously reported in Ref. [7]. Mixtures of  $\text{ZrCl}_4$ , TPA, DMF and HCl were crystallized at  $80^\circ\text{C}$  for 2 days. After reaction, the autoclave used for the synthesis was cooled to room temperature in air. The resulting white product was filtered off, washed with DMF to remove the excess un-reacted TPA, then repeatedly washed with methanol and dried at room temperature. UiO-66- $\text{NH}_2$  samples were synthesized following procedures previously reported in Ref. [7]. Mixtures of  $\text{ZrCl}_4$ , amino-TPA, DMF and  $\text{H}_2\text{O}$  were crystallized at  $80^\circ\text{C}$  for 2 days. UiO-66- $\text{NO}_2$  sample was synthesized analogously by replacing  $\text{H}_2\text{N-H}_2\text{BDC}$  with the equivalent molar amount of  $\text{O}_2\text{N-H}_2\text{BDC}$  [8]. The designation of the samples, the reaction conditions of this synthesis, textural properties and chemical composition of samples are presented in Table 1 and Figs. S1–S4 (Supplementary Information).

### 2.2. Instrumental measurements

The porous structure of the materials was determined from the adsorption isotherm of  $\text{N}_2$  at  $-196^\circ\text{C}$  on a Micromeritics ASAP 2400 equipment. The specific surface area ( $S_{\text{BET}}$ ) was calculated from adsorption data over the relative pressure range between 0.05 and 0.20. The total pore volume ( $V_{\Sigma}$ ) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The X-ray diffraction patterns were measured on a X-ray diffractometer (ThermoARL) with  $\text{Cu-K}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The TGA patterns were measured under nitrogen flow with a thermal analyzer (SDT Q600 V20.9) up to  $800^\circ\text{C}$  (the heating rate was  $5^\circ\text{C}/\text{min}$ ).

### 2.3. IR spectroscopic measurements

The samples were pressed into self-supporting wafers ( $7\text{--}20 \text{ mg}/\text{cm}^2$ ) and pre-treated within an IR cell by heating at  $200^\circ\text{C}$  under vacuum for 3 h before the adsorption experiments. FT-IR spectra were recorded on a Shimadzu FTIR-8300S spectrometer with a resolution of  $4 \text{ cm}^{-1}$ .

For the analysis of the surface basicity the samples were exposed to saturated  $\text{CDCl}_3$  vapors for 3 min at room temperature. The spectra were obtained both before and after  $\text{CDCl}_3$  adsorption, and the difference was calculated. The strength of the base sites was estimated from the shift of  $\nu_{\text{C-D}}$  using the following Eq. (2) [15]:

$$\log(\Delta\nu_{\text{C-D}}) = 0.0066\text{PA} - 4.36 \quad (2)$$

where  $\Delta\nu_{\text{C-D}}$  is the shift, in  $\text{cm}^{-1}$ , of C–D vibration and PA is the proton affinity.

For studies of Lewis acidity, the samples were exposed to saturated 5-nonanone vapors for 2 h at room temperature. The spectra were obtained both before and after 5-nonanone adsorption, and the difference was calculated.

### 2.4. Catalytic test

The reaction of acetalization of BA with methanol was carried out at  $30^\circ\text{C}$  in a glass reactor equipped with magnetic stirrer. Before the reaction, all samples were evacuated at  $200^\circ\text{C}$  for 4 h to remove residual water in the samples. Then 0.94 mmol of BA and 3 ml methanol, 0.01 mmol nitrobenzene (as internal standard) and 50 mg of catalyst were added into the reactor and the reaction mixture was vigorously stirred (1000 revolutions per minute). At different time intervals aliquots were taken from reaction mixture and analyzed. A gas chromatograph (Agilent 7820) equipped with a flame ionization detector and HP-5 capillary column HP-5 was used to analyze products quantitatively.

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