



Catalytic behavior of metal–organic frameworks in the Knoevenagel condensation reaction



Valentina N. Panchenko^a, Maria M. Matrosova^a, Jaewoo Jeon^b, Jong Won Jun^b,
Maria N. Timofeeva^{a,c,*}, Sung Hwa Jhung^{b,*}

^aBoreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090 Novosibirsk, Russian Federation

^bDepartment of Chemistry, Green-Nano Materials Research Center, Kyungpook National University, Sankyuck-Dong, Buk-Ku, Daegu 702-701, Republic of Korea

^cNovosibirsk State Technical University, Prospekt K. Marksa 20, 630092 Novosibirsk, Russian Federation

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ABSTRACT

Effect of basicity of porous metal-carboxylates, such as MIL-100(Al), Cu₃(BTC)₂·(H₂O)₃, UiO-66 and amino-modified UiO-66 materials (UiO-66-NH₂) on their catalytic performance, was studied in the Knoevenagel condensation of benzaldehyde with malononitrile to 2-benzylidenemalononitrile. According to physicochemical studies, the strength of the basic sites for MIL-100(Al), Cu₃(BTC)₂·(H₂O)₃, UiO-66 was in the range of 830–839 kJ/mol, while the amount of basic sites decreased in the order MIL-100(Al) > Cu₃(BTC)₂·(H₂O)₃ > UiO-66. The insertion of NH₂ groups into the UiO-66 framework led to an increase in the strength of basic sites from 839 to 867 kJ/mol. The catalytic activity of metal carboxylates correlated with the amount of basic sites and the strength of the interaction between metal and oxygen in the “Mⁿ⁺–O²⁻ Lewis acid–base” pair, which was estimated from ionic covalent parameters. The activity of the UiO-66-NH₂ materials was higher than that of UiO-66.

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1. Introduction

The development of new solid base catalysts is a challenging goal of catalysis because basic-type catalysts play a decisive role in a large number of chemical processes. Various solid base catalytic systems have been described in the literature. Among them are layered double hydroxides [1,2], zeolites [3,4], mixed oxides [5,6], and pillared clays [7]. Organic bases immobilized on different supports, for example, amino-grafting onto silica (NH₂–SiO₂) [8,9] have drawn a lot of attention as basic catalysts. Recently, new materials such as metal–organic frameworks (MOFs) and amino-grafting onto metal–organic frameworks (NH₂–MOF) [10–14] have been actively investigated due to their unique textural and physicochemical properties. Because the structure of MOFs is composed of organic linkers and inorganic connectors [15], the catalytic activity of MOFs can be related to either their coordinatively unsaturated metal centers or the functional groups incorporated in the linkers [13,16–18]. At present, the number of reaction in the presence of MOFs as a base catalyst is limited. These include

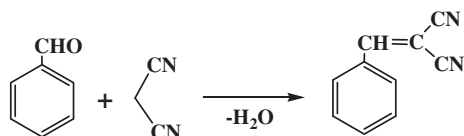
the Meinwald rearrangement [13], one-pot Meinwald rearrangement–Knoevenagel condensation [13], aza-Michael reaction [19], CO₂ cycloaddition of styrene oxide [20], and Knoevenagel condensation [11,12,21].

Knoevenagel condensation of benzaldehyde with malononitrile to 2-benzylidenemalononitrile (Scheme 1) is regarded not only as a weak base-catalyzed model reaction, but also as a reaction that generates a C–C bond for the synthesis of several fine chemicals [22]. It is well known that the Knoevenagel reaction can be catalyzed by alkali metal hydroxides, organic bases [23], and MOFs, such as IRMOF-3 [12,24], ZIF-8 [25], Cu₃(BTC)₂·(H₂O)₃ (Basolite C300) and Fe(BTC) (Basolite F300) [26]. Interestingly, Cu₃(BTC)₂·(H₂O)₃ is more active in comparison with Fe(BTC). It has been demonstrated that the catalytic activity of IRMOF-3 correlates with the specific surface area of the sample and is attributed to the variable accessibility of the active sites in the catalyst. Moreover, it was found that the behavior of IRMOF-3 catalysts was enhanced when amino groups were incorporated inside the IRMOF-3 structure.

Very recently, we demonstrated [27] that the UiO-66 (UiO = University of Oslo) family of microporous materials based on a 3D structure of zirconium-oxo clusters [28] has basic sites with a strength of 839 kJ/mol. The insertion of NH₂ groups into the UiO-66 framework led to an increase in the basicity of

* Corresponding authors. Address: Boreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 8056 (M.N. Timofeeva). Fax: +82 53 950 6330 (S.H. Jhung).

E-mail addresses: timofeeva@catalysis.ru (M.N. Timofeeva), sung@knu.ac.kr (S.H. Jhung).



Scheme 1. The Knoevenagel condensation of benzaldehyde with malononitrile.

UiO-66-NH₂ materials from 839 to 867 kJ/mol. Note that both UiO-66 and UiO-66-NH₂ materials also possess Lewis acid sites that allow the use of these materials as Lewis acids [29,30]. Interestingly, the basic NH₂ groups in UiO-66-NH₂ suppress byproduct formation and accelerate the cross-aldol reaction between benzaldehyde and heptanal [31].

In this investigation, we wished to estimate the effect of the acid–base properties on the catalytic behavior of MOFs, such as Cu₃(BTC)₂·(H₂O)₃, MIL-100(Al) and UiO-66 in the Knoevenagel condensation of benzaldehyde with malononitrile to 2-benzylidene-malononitrile. The basic properties were studied by IR spectroscopy using CDCl₃ as the probe molecule. Moreover, we estimated effect of NH₂ groups on basicity. For this aim, we synthesized amino-modified UiO-66-NH₂ with different amounts of NH₂ groups. This variation in the NH₂-group content in UiO-66-NH₂ was performed by changing the molar ratio of the mixtures of benzenedicarboxylic acid (H₂BDC) and 2-amino-benzenedicarboxylic acid (H₂N-H₂BDC) (H₂BDC/H₂N-BDC molar ratio = 1/0, 1/1 and 0/1). The catalytic properties of the UiO-66-NH₂ samples were also assessed in the Knoevenagel condensation of benzaldehyde with malononitrile. In this manner, we established relationships between basicity and catalytic activity.

2. Experimental

2.1. Materials

Zirconium(IV) chloride, terephthalic acid (TPA, H₂BDC), and malononitrile were purchased from Sigma–Aldrich. 2-Amino-terephthalic acid (amino-TPA, H₂N-H₂BDC) was procured from Alfa-Aeser. N,N-dimethylformamide (DMF), benzaldehyde, and 1,2-dichlorobenzene were obtained from Samchun Chemical. Diethylmalonate was obtained from Acros Organics. Propylene oxide and methanol were used without any further purification.

UiO-66 samples were synthesized following previously reported procedures [32]. Mixtures of ZrCl₄, TPA, DMF and HCl were reacted in an autoclave at 80 °C for 2 days for crystallization. After the reaction, the autoclave 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-NH₂ samples were synthesized following previously reported procedures [32]. Mixtures of ZrCl₄, amino-TPA, DMF, and H₂O were reacted and recovered similarly. The designation of the samples, the

reaction conditions of the synthesis, the textural properties, and the chemical composition of the samples are presented in Table 1. The data of X-ray diffraction (XRD) and thermogravimetric analysis (TGA) of the UiO-66 samples are shown in Figs. 1S and 2S (Supporting information).

2.2. Instrumental measurements

The porous structure of the materials was determined from the N₂ adsorption isotherm at –196 °C using a Micromeritics ASAP 2400 apparatus. The specific surface area (*S*_{BET}) was calculated from the adsorption data over the relative pressure range between 0.05 and 0.20. The total pore volume (*V*_Σ) 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 Cu K_α ($\lambda = 1.5418 \text{ \AA}$) radiation. The TGA patterns were measured under nitrogen flow with a thermal analyzer (SDT Q600 V20.9) up to 800 °C (the heating rate was 5 °C/min).

2.3. Infrared spectroscopy measurements (IR spectroscopy) of MOFs basicity

The samples were pressed into self-supporting wafers (7–20 mg/cm²) and pretreated within the IR cell by heating at 200 °C under vacuum for 3 h before the adsorption experiments. IR spectra were recorded on a Shimadzu FTIR-8300S spectrometer in the range between 400 and 6000 cm^{–1} with a resolution of 4 cm^{–1}.

For the analysis of the surface basicity, the samples were exposed to saturated CDCl₃ vapor for 3 min at room temperature. The spectra were obtained both before and after CDCl₃ adsorption, and the difference was calculated. The strength of the basic sites was estimated from the shift in ν_{C-D} using the following equation [33]:

$$\log \Delta \nu_{C-D} = 0.0066 PA - 4.36, \quad (1)$$

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

2.4. Spectroscopic measurements of malononitrile carbanion formation on MOFs

The samples were pretreated by heating at 200 °C under vacuum for 5 h before the experiments. Benzene solution of malononitrile was added to the MOFs at room temperature, and the mixture was heated at 40 °C for 24 h and then dried under vacuum at 30 °C for 5 h. The diffuse reflectance ultraviolet–visible spectra (DR-UV–vis) were recorded on a UV-2501 PC Shimadzu spectrophotometer with an IRS-250A accessory in the 190–900 nm range with a resolution of 2 nm. BaSO₄ was used as standard. IR spectra were recorded on a Shimadzu FTIR-8300S spectrometer in the range between 400 and 6000 cm^{–1} with a resolution of 4 cm^{–1}.

Table 1

Experimental conditions of the synthesis of MIL-100(Al), Cu-BTC, UiO-66 samples and textural properties and N contents of the synthesized UiO-66 samples.

	Reaction molar composition ZrCl ₄ /H ₂ BDC/H ₂ N-H ₂ BDC/DMF	N content (wt.%)	Textural properties		
			<i>S</i> _{BET} (m ² g ^{–1})	<i>V</i> _Σ (cm ³ g ^{–1})	<i>V</i> _μ (cm ³ g ^{–1})
UiO-66	1:2:0:76	0.0	670	0.30	0.29
UiO-66-NH ₂ (50)	1:1:1:76	2.0	705	0.33	0.29
UiO-66-NH ₂ (100)	1:0:2:76	3.7	650	0.32	0.27
MIL-100 (Al)	Al(NO ₃) ₃ ·9H ₂ O:Me ₃ -BTC:H ₂ O:HNO ₃ 1:0.67:255:1.26	–	1450	0.68	0.37
Cu-BTC	Cu(NO ₃) ₂ ·3H ₂ O:H ₃ BTC:H ₂ O:CH ₃ CH ₂ OH 1.82:1:333:102.5	–	1120	0.68	0.41

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