Microporous coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ as a heterogeneous catalyst for the Knoevenagel reaction*

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The catalytic properties of the microporous metal—organic coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ (dmf is N,N'-dimethylformamide, ur is urotropine, and ndc^{2-} is 2,6-naphthalenedicarboxylate) for the Knoevenagel reaction were studied. The reaction between aromatic aldehydes (benzaldehyde, α -naphthaldehyde, 4-biphenylaldehyde, and 1-pyrenaldehyde) and malononitrile was studied. The coordination polymer was shown to be a heterogeneous catalyst that makes it possible to achieve 95% yield in the reaction between benzaldehyde and malononitrile. The selectivity of the catalyst depends on the size of aldehydes used in the reaction.

Key words: metal—organic coordination polymers, zinc, urotropine, heterogeneous catalysis.

The chemistry of porous coordination polymers has been the subject of active investigation in recent two decades as evidenced by an increasing number of articles, reviews, and special issues of scientific journals. In addition to the sorption of gases and selective separation of various mixtures, heterogeneous catalysis is one of the promising areas for application of these materials.^{1,2} A high selectivity of sorption or catalytic process reported for coordination polymers is determined in the first instance by the presence of various active sites on the internal surface with affinity to molecules of a certain type. As a rule, these sites represent coordinatively unsaturated metal cations with the Lewis type acidity.³ A considerable number of works deals with the targeted preparation of coordinatively unsaturated sites inside the porous structure and the study of the catalytic activity of the considered coordination polymers.⁴⁻⁹ At the same time, many chemical reactions and syntheses of important compounds occur in the presence of alkalis or catalytic sites of the basic type; however, examples for the syntheses of porous coordination polymers containing active basic Lewis sites (lone electron pairs) are rather few. Thus, the preparation of new porous coordination polymers containing atoms with lone electron pairs on the channel walls and the study of their properties are important tasks.

We have recently synthesized the biporous framework $[Zn_4(dmf)(ur)_2(ndc)_4]$ (dmf is N,N'-dimethylformamide, ur is urotropine, and ndc^{2-} is 2,6-naphthalenedicarboxylate) with channels ~1 nm in diameter. Internal surface of these frameworks contains tertiary nitrogen atoms with the accessible lone electron pair (Fig. 1). The compound exhibits interesting sorption and luminescence properties and unique step-by-step substitution of guest molecules.^{10,11} In this work, the catalytic activity of the coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ is described.

Results and Discussion

The existence of lone electron pairs on the nitrogen atoms of urotropine on the channel walls in the porous compound $[Zn_4(dmf)(ur)_2(ndc)_4]$ suggests catalytic activity of this compound. The condensation of malononitrile and aldehydes (Knoevenagel reaction) was chosen as a test reaction. It is known that the Knoevenagel reaction is catalyzed by bases (Scheme 1).

The reaction was carried out in 1,4-dioxane under argon using the Schlenk technique to avoid contact with air moisture. Preliminary experiments showed that the presence of even insignificant amounts of water in the reaction mixture destroys the catalyst and, therefore, anhydrous calcium chloride was added to the reaction mixture. We elucidated preliminarily that calcium chloride itself does

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Fig. 1. Structure of the $[Zn_4(dmf)(ur)_2(ndc)_4]$ framework based on the X-ray diffraction data. The unit cell is shown by lines. Designations of atoms: Zn is blue-, O is red-, N is dark blue-, and C is gray-colored. *Note.* Figure 1 is available in full color in the on-line version of the journal (http://www.springerlink.com).



<u>H</u> is the vinyl proton, the signal intensity of <u>H</u> in the ¹H NMR spectrum was used to determine the yield of the product.

not catalyze the reaction. In all experiments, the reaction course was monitored by NMR spectroscopy taking aliquots from the reaction mixture. The concentration of the reaction products was determined by comparing integrals of the singlet of the solvent and the singlet at δ 8.4 corresponding to the vinyl proton of the condensation product.

Entry	Reaction conditions ^a				Yield (%)
	Aldehyde	Aldehyde : malononitrile (mol.)	Catalyst amount (mol.%)	τ/h	
1	PhCHO	1:2	5	24	17
<i>2</i> -1	PhCHO	1:2	5	7	8
2-2 ^b	PhCHO	1:2	5	38	8
3	PhCHO	1:2	10	24	29
4 ^c	PhCHO	1:10	10	9	95
5	1-NaphCHO	1:2	10	25	13
6	4-BpCHO	1:2	10	25	11
7	1-PyrCHO	1:2	10	24	11

Table 1. Conditions and the product yield of the reaction $CH_2(CN)_2 + R$ —CHO in the presence of $[Zn_4(dmf)(ur)_2(ndc)_4]$

^{*a*} All reactions, except that in entry 3, were carried out in argon in the presence of 50-100 mg of CaCl₂ at 25 °C. The structures of aldehydes are given in Fig. 2.

^b Filtration in 7 h.

^c Reaction temperature 40 °C.



Fig. 2. Kinetic curves for catalytic entries 1, 2 and 3, 4; Y is yield.

The results of the catalytic experiments are presented in Table 1 and Fig. 2.

When using the catalyst in an amount of 5 mol.% of the reaction mixture at the reactant ratio 1 : 2 in the presence of calcium chloride at 25 °C in argon, the yield of the product is ~17% (see Table 1, entry 1). The choice of the molar ratio of the reagents was based on the experimental data which indicated too low reaction rate in the case of equimolar amounts of the reactants. According to the X-ray diffraction data, the coordination polymer retained crystallinity during the process. The heterogeneous character of catalytic transformations was confirmed by the test to filtration (see Table 1, entry 2). The reaction was carried out under the conditions similar to conditions shown in entry I; however, in 7 h the catalyst was removed from the reaction mixture. The reaction stopped completely. The yield of the product remained unchanged within 38 h after the beginning of the reaction.

A twofold increase in the amount of the used catalyst significantly accelerates the reaction: in the presence of 10 mol.% catalyst, the conversion attains 29% (see Table 1, entry 3). A more considerable increase in the reaction rate is induced by heating the reaction mixture to 40 °C: conversion attains 95% within 9 h (see Table 1, entry 4).

In compound $[Zn_4(dmf)(ur)_2(ndc)_4]$ two nitrogen atoms of each urotropine molecule participate in the formation of the coordination polymer, and the remaining two nitrogen atoms are not coordinated. Based on the assumption that all non-coordinated nitrogen atoms of urotropine act as catalytically active sites, we determined that the turnover frequency of the catalyst (*N*) for entries *1*, *3*, and *4* is 0.9, 0.6, and 2.4, respectively.

In entry 4, N > 1, indicating that the catalytic reaction occurs between malononitrile and benzaldehyde. In entries 1 and 3, N is somewhat lower than unity, which does not allow one to conclude that the catalytic reaction occurs. It appears that the coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ participates as a stoichiometric reagent or the catalytic sites are rapidly blocked by the reaction products.

It is important to know whether the reaction occurs on the external surface of crystals of the coordination polymer or inside the channels of $[Zn_4(dmf)(ur)_2(ndc)_4]$. If the reaction proceeds *via* the second mechanism, the coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ should be sizeselective, *i.e.*, the reaction rate depends on the size of substrate molecules. To check this assumption, we studied the Knoevenagel reaction for aromatic aldehydes of various sizes (Fig. 3).

To be prove that all aldehydes exhibit comparable activity in the Knoevenagel reaction, we carried out tests



Fig. 3. (*a*) Conversion of aldehydes PhCHO (*1*), 4-BpCHO (*2*), 1-NaphCHO (*3*), and 1-PyrCHO (*4*) *vs* reaction time; (*b*) molecular models of aldehydes and their characteristic van der Waals dimensions.

with PhCHO, 1-NaphCHO, 4-BpCHO, and 1-PyrCHO under homogeneous conditions using urotropine as a catalyst. In all cases, the reaction rates were equally high, the yield was close to the quantitative one, and no dependence on the molecular size of aldehyde involved in the reaction was observed.

Completely different results were obtained for these aldehydes under heterogeneous conditions using $[Zn_4(dmf)(ur)_2(ndc)_4]$ as a catalyst (Table 2).

All reactions were carried out under the same conditions: 10 mol.% $[Zn_4(dmf)(ur)_2(ndc)_4]$ were used, the corresponding aldehydes and malononitrile were taken in the molar ratio 1:2, and the reaction occurred in dioxane in the presence of CaCl₂ in argon at 25 °C. As can be seen from Table 2, the formation of the product with the highest yield is observed in the reaction with benzaldehyde. At the same time, the yields in the reactions with other three larger aldehydes are comparable and significantly lower than that in the case of PhCHO. It is most likely that the dimensions of benzaldehyde molecule allow the compound to diffuse easily to the channel of the coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ and to interact with the basic sites of nitrogen, whereas the diffusion of 1-NaphCHO, 4-BpCHO, and 1-PyrCHO is more difficult and the catalytic reaction occurs on the external surface of $[Zn_4(dmf)(ur)_2(ndc)_4]$ crystals.

Table 2. Yield of the product of the catalytic reaction vs size of the aldehyde

Aldehyde	τ/h	Yield (%)
PhCHO	24	24
1-NaphCHO	25	13
4-BpCHO	25	11
1-PyrCHO	24	11

Note that the crystals of $[Zn_4(dmf)(ur)_2(ndc)_4]$ isolated from the reaction mixtures with 1-NaphCHO and 1-PyrCHO are slightly colored, most likely, due to the partial adsorption of the aldehydes on the crystal surface of the coordination polymer. The color does not disappear upon washing the crystals with dioxane, which indicates fairly strong interaction of the aldehydes with the surface. After the reaction mixture is kept in air for 30 min only, the color of the crystals significantly changes (from light vellow to bright orange), and the color corresponds to the color of the product of the Knoevenagel reaction. Since the formation of the product was confirmed by NMR spectroscopy, it is evident that the reaction continues to occur involving the solid phase. This interaction can involve aldehydes adsorbed on the crystal surface and malononitrile molecules, some of which exist in the polymer channels and some molecules are located as the adsorbed species on the polymer surface. Thus, the coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ can catalyze the reaction not only in solutions but in the solid state as well. At present the reactions in the solid state evoke considerable interest of researchers, because this reactions can be important for the development of new ecologically pure processes.

Thus, the catalytic activity of the porous coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ was demonstrated. The catalytic activity is due to the presence of nitrogen atoms in the nanosized channels which play the role of basis sites. The coordination polymer is a heterogeneous catalyst that makes it possible to attain 95% yield in the Knoevenagel reaction between malononitrile and benzaldehyde. The catalyst also demonstrates selectivity to the substrate size. Unfortunately, the contribution of the catalytic sites localized on the crystal surface significantly decreases the selectivity, but it can be hoped that a further study of the catalytic properties of the $[Zn_4(dmf)(ur)_2(ndc)_4]$ framework provides examples for reactions with a more pronounced selectivity.

Experimental

Synthesis of $[Zn_4(dmf)(ur)_2(ndc)_4]$. Colorless crystals of the coordination polymer $[Zn_4(dmf)(ur)_2(ndc)_4]$ were obtained by the earlier published procedure.¹¹

Catalytic experiments. Catalytic experiments were carried out in a temperature-controlled pre-evacuated two-necked glass flask in argon. Prior to use in catalytic experiments, compound $[Zn_4(dmf)(ur)_2(ndc)_4]$ was heated for 2 h in a dynamic vacuum at 45 °C to remove sorbed water. An aliquot of the reaction mixture (50 μ L) was dissolved in DMSO-d₆ (200 μ L). The identification and quantitative analysis of the products were performed using NMR spectroscopy (Fig. 4).

Reaction between benzaldehyde and malononitrile. *Test.* Malononitrile (0.132 g, 2.00 mmol) and benzaldehyde (0.106 g, 1.00 mmol) were dissolved in dioxane (2.5 mL). Anhydrous $CaCl_2$ (101 mg) was added to the reaction mixture to remove water traces, after which 10 mol.% urotropine (0.014 g, 0.1 mmol) was added. The reaction was carried out at 25 °C. Samples were taken every 30 min. To show the absence of catalytic activity of $CaCl_2$ in this reaction, an ex-



Fig. 4. NMR spectra of the reaction mixture without the catalyst (a, b) and 24 h after the addition of the catalyst (c) in entry 1.

periment without urotropine was carried out under similar conditions.

Study of the catalytic activity of $[Zn_4(dmf)(ur)_2(ndc)_4]$. (1) Malononitrile (0.132 g, 2.00 mmol) and benzaldehyde (0.106 g, 1.00 mmol) were dissolved in dioxane (2.5 mL). Anhydrous CaCl₂ (0.110 g) was added to the reaction mixture to remove water traces, and 5 mol.% $[Zn_4(dmf)(ur)_2(ndc)_4]$ (74 mg, 0.05 mmol) was then added. The reaction was carried out at 25 °C. Samples were taken 9, 19, and 42 h after the reaction onset. (2) Test to filtration. The reaction was carried out under similar conditions. Seven hours after the reaction onset, the catalyst was separated from the reaction mixture by centrifugation. Samples were taken 7, 17, and 38 h after the reaction onset. (3) Optimization of the vield. The experiment was carried out under similar conditions, but CaCl₂ (0.040 g) and 10 mol.% [Zn₄(dmf)(ur)₂(ndc)₄] (148 mg, 0.1 mmol) were used. Samples were taken 0.5, 6.25, 19, and 24 h after the reaction onset. (4) Malononitrile (0.660 g)10.00 mmol) and benzaldehyde (0.106 g, 1.00 mmol) were dissolved in dioxane (2.5 mL). Anhydrous CaCl₂ (0.062 g) was added to the reaction mixture to remove water traces, and 10 mol.% $[Zn_4(dmf)(ur)_2(ndc)_4]$ (148 mg, 0.1 mmol) was then added. The reaction was carried out at 40 °C.

Reaction between α **-naphthaldehyde and malononitrile.** *Test.* α -Naphthaldehyde (0.156 g, 1.00 mmol) and malononitrile (0.132 g, 2 mmol) were dissolved in dioxane (2.5 mL). Anhydrous CaCl₂ (101 mg) was added to the reaction mixture to remove water traces, and 10 mol.% urotropine (0.014 g, 0.1 mmol) was then added. Samples were taken at an interval of 30 min.

Study of the catalytic activity of $[Zn_4(dmf)(ur)_2(ndc)_4]$. α -Naphthaldehyde and benzaldehyde were dissolved in dioxane (2.5 mL). Anhydrous CaCl₂ (101 mg) was added to the reaction mixture to remove water traces, and 10 mol.% $[Zn_4(dmf)(ur)_2(ndc)_4]$ (148 mg, 0.1 mmol) was then added. Samples were taken 8 and 25 h after the reaction onset.

Reaction between 4-biphenylaldehyde and malononitrile. *Test.* 4-Biphenylaldehyde (0.182 g, 1.00 mmol) and malononitrile (0.132 g, 2.00 mmol) were dissolved in dioxane (2.5 mL). An-hydrous CaCl₂ (101 mg) was added to the reaction mixture to remove water traces, and 10 mol.% urotropine (0.014 g, 0.1 mmol) was then added. Samples were taken every 30 min.

Study of the catalytic activity of $[Zn_4(dmf)(ur)_2(ndc)_4]$. 4-Biphenylaldehyde (0.182 g, 1.00 mmol) and malononitrile (0.132 g, 2.00 mmol) were dissolved in dioxane (2.5 mL). Anhydrous CaCl₂ (101 mg) was added to the reaction mixture to remove water traces, and 10 mol.% $[Zn_4(dmf)(ur)_2(ndc)_4]$ (148 mg, 0.1 mmol) was then added. Samples were taken 8, 21, and 25 h after the reaction onset.

Reaction between 1-pyrenaldehyde and malononitrile. *Test.* 1-Pyrenaldehyde (0.230 g, 1.00 mmol) and malononitrile (0.132 g,

2.00 mmol) were dissolved in dioxane (2.5 mL). Anhydrous $CaCl_2$ (101 mg) was added to the reaction mixture to remove water traces, and 10 mol.% urotropine (0.014 g, 0.1 mmol) was then added. Samples were taken every 30 min.

Study of the catalytic activity of $[Zn_4(dmf)(ur)_2(ndc)_4]$. 1-Pyrenaldehyde (0.230 g, 1.00 mmol) and malononitrile (0.132 g, 2.00 mmol) were dissolved in dioxane (2.5 mL). Anhydrous CaCl₂ (101 mg) was added to the reaction mixture to remove water traces, and 10 mol.% $[Zn_4(dmf)(ur)_2(ndc)_4]$ (148 mg, 0.1 mmol) was then added. Samples were taken 9.5 and 25 h after the reaction onset.

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