

## The Henry reaction catalyzed by zeolitic imidazolate framework ZIF-8

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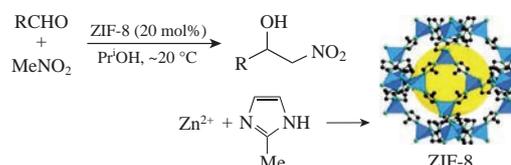
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**Heterogeneous catalyst ZIF-8, a representative of zeolitic imidazolate framework family, promotes the Henry reaction between aldehydes and nitromethane.**



Zeolitic imidazolate frameworks<sup>1</sup> (ZIFs) built of imidazolate linkers and transition metal ions (*e.g.*, Figure 1) are a subclass of a large family of the novel hybrid materials,<sup>2</sup> namely metal–organic frameworks (MOFs).

The interest to MOFs within two past decades is due to the prospects of their use as materials for separation and storage of gases, sensors, ion exchangers, means for targeted drug delivery and especially in heterogeneous catalysis.<sup>3</sup> Though examples of the use of MOFs as catalysts in some organic reactions are known, cases of using ZIFs are scarce. Successful implementations of the Knoevenagel reaction in the presence of zinc-containing ZIF-8 [Zn(mim)<sub>2</sub>, mim is 2-methylimidazolate]<sup>4–7</sup> and cobalt-containing ZIF-9<sup>8</sup> [Co(bim)<sub>2</sub>, bim is benzimidazoly] were reported. Catalysis with ZIF-8 is known for a one-pot process producing a C–P bond in the course of a sequence of the Knoevenagel and phospho-Michael reactions,<sup>9</sup> as well as for the Friedel–Crafts addition,<sup>10</sup> [3+3] cycloaddition<sup>11</sup> and formation of a cyclic carbonate from propylene oxide and CO<sub>2</sub>.<sup>12</sup>

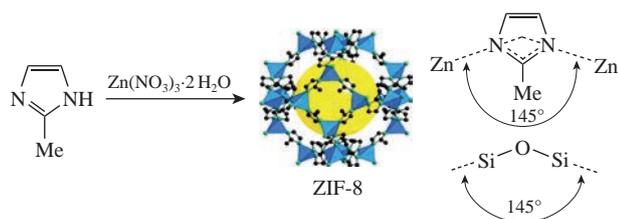
The Henry reaction (nitroaldol condensation) is one of the most efficient methods of C–C bond formation in organic chemistry. Among catalysts applied for this transformation,<sup>13</sup> only Zn-based MOFs containing Lewis acidic<sup>14</sup> or basic<sup>15,16</sup> groups have been reported as heterogeneous catalysts. In this study, we have tested ZIF-8, a readily available representative of zeolite-like frameworks, as a heterogeneous catalyst of nitroaldol condensation. Material ZIF-8 seems suitable for this transformation since its framework contains both Lewis acidic sites as Zn<sup>2+</sup> ions and 2-methyl-

imidazolate linkers of Lewis-basic nature. To our knowledge, the use of this and other ZIF materials for catalysis of the Henry reaction was not reported previously.

To date, a number of procedures for ZIF-8 preparation is known.<sup>1,6,17,18</sup> In this work, we obtained it by modified reported<sup>6,13</sup> methods (samples 1 and 2) as well as by our original procedure using liquid NH<sub>3</sub> as the reaction medium (sample 3). The samples synthesized by these procedures were found to be nearly identical in morphologies, textural (specific surface) and structural characteristics.<sup>†</sup> In fact, the crystal structure of the ZIF-8 samples obtained was identified by powder X-ray diffraction (XRD). The diffraction patterns of the samples were similar in intensity of the main reflexes and matched the published data<sup>19</sup> (Figure 2). According to XRD data, the samples crystallize in cubic syngony, space group  $\bar{I}43m$  (*cf.* ref. 19). Noteworthy, the crystal structure of ZIF-8 remained nearly the same after the catalytic experiments

<sup>†</sup> The X-ray diffraction (XRD) patterns of the ZIF-8 samples were obtained on a Panalytical Empyrean diffractometer using CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The textural properties of the samples were determined by nitrogen sorption measured on a Klyachko-Gurvich sorptometer<sup>22</sup> at liquid nitrogen temperature. Prior to the sorption measurements, ZIF-8 samples were activated *in vacuo* (2 Torr) at 403 K for 48 h. Specific surface areas were calculated using the Brunauer, Emmett and Teller (BET) method. The microstructure and morphology of the synthesized samples were studied by field emission scanning electron microscopy (FE SEM) with a Hitachi SU8000 field-emission electron microscope. The target-oriented approach was used for the optimization of the analytic measurements.<sup>23</sup> Elemental analyses were obtained on a Perkin Elmer 2400 CHN Analyzer. IR spectra were recorded on a Bruker Alpha-T spectrometer.

*Synthesis of ZIF-8 samples. Sample 1.* Aqueous NH<sub>3</sub> (64 ml, 25%) was added to freshly prepared Zn(OH)<sub>2</sub> (1.95 g, 19.7 mmol) and then a solution of 2-methylimidazole (0.82 g, 10 mmol) in MeOH (100 ml) was added dropwise with stirring at 20 °C. After 1 h, the precipitate formed. The supernatant was separated by centrifugation (3000 rpm), the precipitate was washed with water (3 × 10 ml), dried *in vacuo* (2 Torr) first at 20 °C and then at 130 °C for 48 h. Yield 0.7 g (61%), colourless crystals. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3423, 3135, 2930, 1590, 1422, 1308, 1175, 1145, 993, 749, 694, 419. Found (%): C, 42.27; H, 4.45; N, 24.60; Zn, 28.68. Calc. for C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>Zn (%): C, 42.22; H, 4.43; N, 24.62; Zn, 28.73.



**Figure 1** Synthesis and structure of ZIF-8. The Zn–Im–Zn angles in ZIF are equal to the Si–O–Si angles in zeolites (145°).



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