

KNOEVENAGEL REACTION CATALYZED BY IRON(III) 1,3,5-BENZENETRICARBOXYLATE IN FLOW

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C-C coupling reactions play important role in fine and industrial organic synthesis. Knoevenagel reaction – interaction of aldehydes or ketones with active methylene compounds – is one of the ways to form C-C bond. Development of the efficient heterogeneous catalysts for the Knoevenagel reaction is urgent task [1].

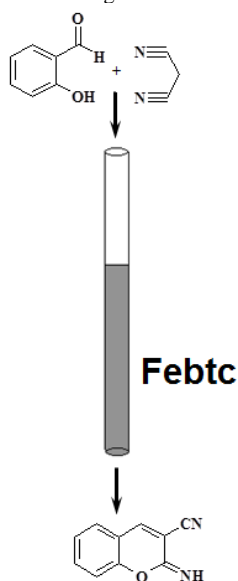


Fig. 1. Reaction of the salicylaldehyde and malononitrile at presence of the Febtc as catalyst in flow

Porous coordination polymers (PCP) with acidic or basic Lewis sites can catalyze Knoevenagel reaction activating carbonyl or active methylene compound, respectively. A new PCP of Fe^{3+} with 1,3,5-benzenetricarboxylate (btc^{3-}) $[\text{Fe}_2(\text{OH})_{0.3}(\text{H}_2\text{O})_{1.7} \times (\text{btc})_{4/3}]_n \text{Cl}_{1.7n} \cdot 2.8n \text{DMF} \cdot 1.9n \text{H}_2\text{O}$ (hereinafter referred to as Febtc) was tested as catalyst for such transformation. This PCP contains Fe^{3+} ions (Lewis acids) with coordinated H_2O molecules. Such H_2O molecules can be removed upon heating. It was previously shown that Febtc catalyzed reaction of salicylaldehyde and nitromethane at 100 °C and was stable in a batch reactor (catalyst suspension in toluene) [2]. Due to its activity and stability Febtc can be considered as promising heterogeneous catalyst for the Knoevenagel reaction in flow.

Passing the mixture of salicylaldehyde (0,1 M) and malononitrile (0,1 M) solutions in toluene at room temperature during 2 h through a column (40 mm length and 5 mm diameter) filled with Febtc resulted in 100 % conversion of salicylaldehyde. It was shown that only 2-imino-2H-chromen-3-carbonitrile was obtained as a product. Condensation of salicylaldehyde (0,7 M) and nitromethane (8,5 M) was carried out in the same flow reactor leading to 85 % yield of *trans*-nitrovinylphenol. High products yields at room temperature could be explained by a large ratio of the quantities of PCP active sites to reagents. Use of copper(II) 1,3,5-benzenetricarboxylate instead of Febtc in the same column for condensation of salicylaldehyde (0,7 M) and nitromethane (8,5 M) led only to 5 % yield of *trans*-nitrovinylphenol.

1. K. van Beurden, S. de Koning, D. Molendijk, J. van Schijndel, *Green Chem. Let. and Rev.*, 2020, 13:4, 349–364.

2. S. A. Sotnik, S. V. Kolotilov, M. A. Kiskin, Zh. V. Dobrokhotoва, K. S. Gavrilenko, V. M. Novotortsev, I. L. Eremenko, V. K. Imshennik, Yu. V. Maksimov, V. V. Pavlishchuk, *Russ. Chem. Bull.*, 2014, 63, 862–869.