

Cs-, Mg-, Zn-CONTAINING HIERARCHICAL ZEOLITES AS EFFECTIVE CATALYSTS FOR 2-AMINOTIOPHENES PRODUCTION BY GEWALD REACTION

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Gewald reaction is widely used for 2-aminothiophenes production from cyclic ketones, sulfur and malonodinitrile. This process proceeds by 2 stages (fig.1): the first stage between ketone and malonodinitrile (also known as Knoevenagel reaction) takes place both at the acid and basic centers, while the reaction between **2** and sulfur needs basic centers in such catalysts [1]. Basic compounds (such as triethylamine, Zn- and Ti-containing zeolites [2,3]) are widely used as catalyst for this process. Hierarchical zeolites with developed external surface is effective catalysts for transformations including bulk molecules. It is expected that doped with basic oxides and titanium oxide hierarchical zeolites have high dispersion of metal particles and high availability for bulk molecules and thus will be effective catalysts for this process. Synthesis of the hierarchical zeolite matrices was proceeded by using Gemini-surfactants as structure-directing agents (SDA). Cesium forms of hierarchical zeolites obtained by ion exchange method, while Mg-, Ti-, Zn-containing zeolites were synthesized by impregnation of metal salts followed by their decomposition. The catalytic properties of the synthesized materials were investigated in the Gewald process of converting cyclohexanone (**1**) to 2-amino-4,5,6,7-tetrahydrobenzo [b]thiophene-3-carbonitrile (**3**) (Fig. 1). High yield of the target product is achieved for Cs- and Mg-containing hierarchical zeolites of structural type BEA, whereby in the case Cs-BEA (nanosponge), quantitative conversion of the ketone into the target product is achieved (Table 1).

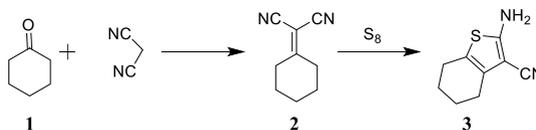


Fig 1. Scheme of Gewald process of 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**3**) production

Table 1. Catalytic properties of Cs-, Mg-, Ti- та Zn-containing hierarchical BEA zeolites in process of cyclohexanone (**1**) transformation into 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**3**)

Catalyst	Conversion 1 , %	Selectivity, %			Yield of 3 , %
		3	2	Other	
CsAl-BEA_nsheet	96,48	99,11	0,69	0,20	95,61
CsAl-BEA_nsponge	100,00	100,00	0,00	0,00	100
ZnO/Al-BEA_nsheet	93,35	42,93	55,11	1,97	40,07
MgO/Al-BEA_nsheet	95,59	97,91	2,02	0,07	93,58

1. Journal of heterocyclic chemistry, 1999, 36, 2, 333-345.
2. Microporous and Mesoporous Materials, 2016, 231, 100-109.
3. Applied Organometallic Chemistry, 2017, 31, 11, e3779.