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The effect of substrate size in the Beckmann rearrangement: MOFs vs. zeolites

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ABSTRACT

Catalytic activity of CuBTC and FeBTC was investigated in Beckmann rearrangement of a series of aromatic and non-aromatic oximes and compared with that of zeolites Beta and USY. The reactivity of substrates in Beckmann rearrangement increases in the order camphor oxime < cyclohexanone oxime < indanone oxime < acetophenone oxime. While zeolites show higher activity in the transformation of relatively small aromatic (acetophenone oxime, indanone oxime) and non-aromatic oximes (cyclohexanone oxime) providing 100% selectivity to the target lactams in all reactions, CuBTC was the most active in transformation of bulky oximes. It was deduced, that textural preferences of CuBTC may be the reason of its capability to facilitate the transformation of bulky camphor oxime in comparison with zeolites Beta and USY.

1. Introduction

Beckmann rearrangement of ketoximes (Scheme 1) is known as a fundamental tool in organic synthesis providing the connection among ketones possessing a remarkable synthetic flexibility and amides/lactams [1], which are widely used in drugs and pharmaceuticals, and also as detergents, lubricants, and raw materials for polyamides such as nylon-6 and nylon-12 [2].

Conventional methods for the activation of oximes are based on the use of strong Brønsted or Lewis acids. In a classical method, ε-caprolactam is industrially produced in the presence of sulfuric acid or oleum as catalysts [3]. A perceived disadvantage of this route is a large amount of ammonia sulfate formed as a side product. To overcome the by-product formation and reactor corrosion problems, more economic and environmentally friendly processes have been developed.

Liquid-phase Beckmann rearrangements have been attempted using chlorosulfonic acid [4], ethyl chloroformate and boron trifluoride diethyl etherate [5], anhydrous oxalic acid [6], chloral hydrate [7], or organocatalysts such as sulfamic acid [8], cyanuric chloride [9], diethyl chlorophosphate [10], triphosphazene [11] and poly(ethylene glycol)-sulfonic acid [12]. However, these catalysts could not be recovered or reused. Vapor-phase methods, with a particular focus on the sulfate-free industrial production of ε-caprolactam, have been performed using heterogeneous catalysts, such as high-silica zeolites [13,14], metal oxides [15,16], or clays [17] at temperatures as high as 300 °C. It was found that high-silica ZSM-5 zeolite (silicalite-1) [18–20] and boron-containing zeolite ZSM-5 [21,22] are highly active catalysts for the transformation of cyclohexanone oxime to ε-caprolactam. The rearrangement has been also explored in supercritical water [23,24]. However, the last 2 methods frequently suffer from low selectivity and a rapid decay of the activity of the catalyst as a result of the high temperatures used. Recently, Beckmann rearrangement was also reported in ionic liquids at room temperature [25,26]. Nevertheless, until now the occurrence of mild conditions was related to the use of rather toxic solvents and expensive reagents or solvents.

Beckmann rearrangement reaction is believed to be a typical acid-catalyzed reaction. Although the catalytic performance over solid acid catalysts under vapor phase conditions has been tested, the nature and position of the active sites in the solid catalysts remain controversial. Costa et al. reported on the Beckmann rearrangement of cyclohexanone oxime on alumina orthophosphate/γ-alumina catalysts [27]. They found that the reaction was catalyzed by Lewis and Brønsted acid centers and that the formation of caprolactam and 5-cyanopent-1-ene were competitive reactions. Yashima et al. [28] examined a range of different catalysts including H-ZSM-5, silicalite-1, silicagel, H-mordenite, H-ferrierite, Ca-A, Na-A, and clinoptinolite for Beckmann rearrangement. They concluded that weaker acid sites showed a higher selectivity to caprolactam. In the presence of stronger acid sites, multiple side reactions, namely ring opening, decomposition and polymerization were observed. In contrast to the above results, Corma and Kob with coworkers inferred that the

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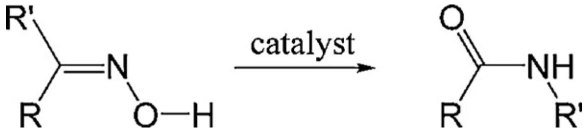


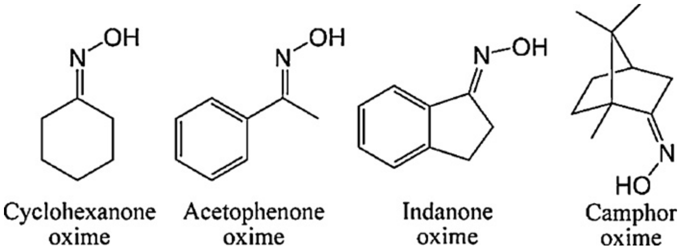
Scheme 1. Beckmann rearrangement of ketoximes.

strong acid sites on crystalline silica-alumina are favorable for gas phase Beckmann rearrangement [29–31]. However, the research group of Hölderich investigated the rearrangement of cyclohexanone oxime to caprolactam over high silica zeolites with MFI structure in fixed bed and fluidized bed reactors to determine the nature of the active centers on the catalysts [18,32–35]. According to Hölderich, extremely weak acidic silanol nests and vicinal silanol groups on the external surface of highly siliceous ZSM-5 zeolites were found to be the most suitable for the Beckmann rearrangement [18].

Thus, it can be concluded that there is no general agreement on the influence of the acidic properties of heterogeneous catalyst on the efficiency of Beckmann rearrangement. The understanding of this issue can be helpful in the development of efficient and mild catalytic method for the transformation of ketoximes into respective amides/lactams.

Metal-organic-framework (MOFs) represent crystalline hybrid organic–inorganic nanoporous materials with a reasonable stability [36,37], adjustable chemical functionality [38], extra-high porosity [39] and mild Lewis acidity [40–42]. In contrast, aluminosilicate zeolites are well-known solid acids, containing both Lewis and Brønsted acid sites [43–47]. A number of different reactions have been recently reported showing the interesting catalytic properties of MOFs. These include Friedländer condensation [40], Knoevenagel condensation [48], one-pot three-component coupling reaction between amines, aldehydes and alkynes [49], Huisgen cycloaddition [50], cyclopropanation of alkenes with diazoacetates [51], selective oxidation of cycloalkanes [52], or Friedel–Crafts benzylation [53]. Recently, we reported on the catalytic benefits of CuBTC and FeBTC (BTC = 1,3,5-benzenetricarboxylate) over large-pore aluminosilicate zeolites Beta and USY in Pechmann condensation of naphthol originating from the mild acidity, the regularity in the arrangement of active sites within the framework, and preferences in the pore size of corresponding MOFs [54].

Our contribution is aimed at the comparison of conventional large-pore zeolites Al-Beta (Si/Al = 12.5) and USY (Si/Al = 15) with MOFs (CuBTC, FeBTC) in the liquid-phase Beckmann rearrangement of cyclohexanone oxime, acetophenone oxime, 1-indanone oxime (subsequently – indanone oxime) and camphor oxime (Scheme 2) to establish the influence of the nature of substrate as well as the textural and acidic properties (e.g. nature and strength of active sites) of the catalyst on the efficiency of the Beckmann rearrangement.



Scheme 2. Substrates for Beckmann rearrangement.

2. Experimental

2.1. Materials

H-Beta (Si/Al = 12.5) and H-USY (Si/Al = 15) zeolites were purchased from Zeolyst. CuBTC (Basolite C300) and FeBTC (Basolite F300) were purchased from Sigma Aldrich. Cyclohexanone oxime (97%), acetophenone oxime (95%), indanone oxime (≥99%) and camphor oxime (≥97%) were used as substrates, mesitylene (≥99%) as internal standard and 1,4-dioxane (≥99%) as solvent in catalytic experiments. All reactants and solvents were obtained from Sigma Aldrich and used as received without any further treatment.

2.2. Characterization

The crystallinity of samples under study was determined by X-ray powder diffraction on a Bruker AXS D8 Advance diffractometer with a Vantec-1 detector in the Bragg-Brentano geometry using CuK_{α} radiation. To limit the effect of preferential orientation of individual crystals a gentle grinding of the samples was performed before measurements.

Adsorption isotherms of nitrogen at −196 °C were determined using an ASAP 2020 (Micromeritics) static volumetric apparatus. Before adsorption experiments the samples were degassed under turbomolecular pump vacuum at the temperature of 150 °C for MOFs and 250 °C for zeolites. This temperature was maintained for 8 h.

The concentrations of Brønsted and Lewis acid sites in zeolites were determined by pyridine adsorption at 150 °C followed by FTIR spectroscopy (Nicolet 6700) using self-supporting wafer technique, according to the methodology reported in Ref. [55]. Generally, a thin sample wafer of zeolite was activated prior to the experiment in a high vacuum (10^{-4} Torr) of 450 °C overnight. Adsorption of pyridine proceeded at room temperature for 30 min at a partial pressure of 5 Torr and was followed by 20 min evacuation at the temperature 150 °C. Determination of Lewis acid sites in CuBTC is discussed in detail elsewhere [42].

2.3. Beckmann rearrangement of oximes

The Beckmann rearrangement of oximes (cyclohexanone oxime, acetophenone oxime and indanone oxime) was performed in a liquid phase under atmospheric pressure and temperature of 60-100 °C in a multi-experiment work station StarFish (Radley's Discovery Technologies UK). Prior to use, 200 mg of the catalyst was activated at 150 (for MOFs) or 450 (for zeolites) °C for 90 min with a temperature rate 10 °C/min in a stream of air. Typically, 2.0 mmol of oxime, 0.4 g of mesitylene (internal standard) and 200 mg of catalyst were added to the 3-necked vessel, equipped with condenser and thermometer, stirred and heated. The amount of catalyst was varied between 0.025 and 0.1 g per 1 mmol of substrate.

To evaluate a potential influence of leaching of active species from the heterogeneous catalysts, a part of the reaction mixture was separated at the reaction temperature and the obtained liquid phase was further investigated in the Beckmann rearrangement under the same reaction conditions.

2.4. Reaction product analysis

Aliquots of the reaction mixture were sampled after 60, 120, 180, 240, 360, and 1260 min.

The reaction products were analyzed by gas chromatography (GC) using an Agilent 6850 with FID detector equipped with a non-polar HP1 column (diameter 0.25 mm, thickness 0.2 μm and length 30 m). Reaction products were identified using GC–MS analysis (ThermoFinnigan, FOCUS DSQ II Single Quadrupole GC/MS). The