Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

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ARTICLE INFO

Article history: Received 15 May 2012 Received in revised form 10 September 2012 Accepted 18 September 2012 Available online 18 October 2012

Keywords: Beckmann rearrangement Oximes CuBTC Metal-organic-frameworks Zeolites

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.

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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,

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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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^{0920-5861/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cattod.2012.09.008



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 threecomponent 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=1,3,5benzenetricarboxylate) 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 (\geq 99%) and camphor oxime (\geq 97%) were used as substrates, mesitylene (\geq 99%) as internal standard and 1,4-dioxane (\geq 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 Xray 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 nonpolar HP1 column (diameter 0.25 mm, thickness 0.2 μ m and length 30 m). Reaction products were identified using GC–MS analysis (ThermoFinnigan, FOCUS DSQ II Single Quadrupole GC/MS). The



Fig. 1. XRD patterns of the catalysts: Beta and USY (a); CuBTC and FeBTC (b).

identity of reaction products was also confirmed using ¹H NMR spectroscopy (Varian Unity 300 spectrometer). The observed spectra corresponded to the previously published data [56].

3. Results and discussion

3.1. Structural and acid properties

The X-ray diffraction patterns of CuBTC and zeolites under investigation match well with those reported in the literature thus all catalysts are found to be highly crystalline and without the presence of any other phases (Fig. 1). At the same time it was confirmed that FeBTC is low-ordered material.

Nitrogen adsorption isotherms of individual catalysts are depicted in Fig. 2. While CuBTC, FeBTC, and Beta showed a type I isotherm, which is typical for microporous solids, adsorption isotherm for USY is a combination of types I and IV with hysteresis loop evidencing the presence of ink-bottle-type mesopores within USY pore system [57].

Acidic properties of zeolites, namely the type and concentrations of Brønsted and Lewis acid sites were analyzed using adsorption of pyridine followed by FTIR (Fig. 3). FTIR spectra of both Beta and USY exhibit characteristic absorption band at about 3739–3747 cm⁻¹, attributed to the silanol OH groups. The absorption bands of acidic bridging OH groups appear at 3609 cm⁻¹ for



Fig. 2. N₂ adsorption isotherms of the catalysts: CuBTC (\bigcirc); FeBTC (\triangle); Beta (\triangledown); USY (\Box), open points represent adsorption, full points – desorption.



Fig. 3. FTIR spectra of USY, Beta after activation at $450 \,^{\circ}$ C and 10^{-4} Torr and after pyridine adsorption after 20 min desorption at $150 \,^{\circ}$ C: region $3400-3800 \, \text{cm}^{-1}$ (a); region $1400-1600 \, \text{cm}^{-1}$ (b).

zeolite Beta and at 3564 and 3630 cm^{-1} for USY zeolites (Fig. 3a). Adsorption of pyridine removed these bands while new absorption bands appeared in the region $1400-1600 \text{ cm}^{-1}$. The absorption band around 1545 cm^{-1} is due to the interaction of pyridine with Brønsted acid sites while a new band around 1455 cm^{-1} is characteristic of the pyridine adsorbed on Lewis acid sites (Fig. 3b). Using the extinction coefficients [58], concentrations of Brønsted and Lewis acid sites were determined, see Table 1.

Catalyst	D _{pore} , nm	$S_{\text{BET}}, m^2/g$	IR		
			T des., °C	PyH⁺, mmol/g	PyL, mmol/g
CuBTC	0.90, 0.50, 0.35	1500	200	_	2.30
FeBTC	0.86	1060	200	-	2.56
USY	0.74	770	150	0.30	0.23
			250	0.22	0.18
			350	0.17	0.17
			450	0.08	0.13
Beta	0.66, 0.56	670	150	0.21	0.32
			250	0.18	0.24
			350	0.12	0.22
			450	0.05	0.19

Table 1	
Textural and acid properties of used catalysts	<i>.</i>

The distribution of Brønsted acid sites with regard to their strength was estimated by a stepwise desorption at increasing temperatures on zeolites having pre-adsorbed pyridine while recording the residual intensity of the remaining characteristic IR bands. With increasing of desorption temperature, the band of pyridinium ions (1545 cm^{-1}) gradually decreases. It can be concluded that both USY and Beta contain significant amount of strong acid sites, which are able to retain adsorbed base even after desorption at 450 °C.

Lewis acidity of CuBTC, arising from the presence of unsaturated Cu(II) centers [42], by analogy to zeolites, may be determined quantitatively by the adsorption of basic probe molecules. To estimate the acidity of the CuBTC band at 1069 cm^{-1} assigned to C–C out-of-plane vibrations was chosen. Characteristic bands in region $1400-1600 \text{ cm}^{-1}$ were not used for computation of the amount of acid sites within MOFs because of an undesirable overlap with the bands corresponding to MOF's framework. At the same time band at 1069 cm^{-1} cannot be used for evaluation of the concentration of acid centers in zeolites as it overlaps with the bands which corresponds to the vibration of Si–O bond. The concentration of coordinatively bonded pyridine was determined to be equal to 2.30 mmol/g for CuBTC activated at $200 \,^{\circ}\text{C}$ [42].

Textural and acidic properties of the catalysts under investigation are summarized in Table 1.

3.2. Beckmann rearrangement

To compare catalytic properties of conventional zeolites and MOFs in Beckmann rearrangement, cyclohexanone oxime was chosen as a model substrate. Fig. 4 provides conversion of cyclohexanone oxime after 360 min of TOS (Time-On-Stream) at 80 °C over zeolites and MOFs, as well as selectivity to caprolactam (at maximal conversion).

As it can be seen, the activity of the catalysts increases in the order FeBTC < CuBTC \approx Beta < USY. Conversions of cyclohexanone

oxime over zeolite Beta and CuBTC are very close (13% and 11%. respectively) while accessibility of active centers within CuBTC is obviously higher due to the presence of large micropores (Table 1). It may be explained by a higher concentration of strong acid sites within Beta in contrast to CuBTC, but at the moment there is not enough information about the strength of the Lewis acid sites of CuBTC for confirmation of this assumption. Despite the comparable activity of Beta and CuBTC in Beckmann rearrangement of cyclohexanone oxime the selectivity to caprolactam was much higher over Beta. Based on the earlier investigations of Beckmann rearrangement of cyclohexanone oxime [59], we can infer that the selective formation of caprolactam mostly occurred at the active sites on the external surface of zeolite Beta. In the case of cyclohexanone oxime rearrangement over CuBTC we can assume that the reaction proceeds inside the pore system of the catalyst. This may result in suffering of the target product from diffusion resistance in the pores, increasing the possibility of side reactions like decomposition or polymerization. The highest conversion of USY in comparison with zeolite Beta and both MOFs may be connected with the presence of transport mesopores within USY. It results in an accessibility of a higher amount of active sites for the substrate in comparison with zeolite Beta. High selectivity to ε -caprolactam over both Beta and USY, which are characterized by the strong acidity, should also be pointed out. This is in agreement with the results, obtained earlier by Corma's group [30,31,60], which proved that strong Brønsted acid sites are very active and selective for the formation of the amide in Beckmann rearrangement.

In contrast, when using acetophenone oxime having almost the same kinetic diameter as cyclohexanone oxime but containing aryl substituent near oxime group, we achieved much higher conversions of the initial substance over all used catalyst, except FeBTC (Fig. 5). The conversions of acetophenone oxime increased in the same order, as in the case of cyclohexanone oxime: FeBTC \ll Beta \approx CuBTC < USY. For comparison, after 360 min of TOS



Fig. 4. Conversion (a) of cyclohexanone oxime (at TOS = 360 min) and selectivity (at maximum conversion) of caprolactam (b) at 80 °C over Beta (Si/Al = 12.5), USY (Si/Al = 15), CuBTC, FeBTC.



Fig. 5. Conversion of acetophenone oxime over Beta (Si/Al = 12.5), USY (Si/Al = 15), CuBTC, FeBTC at 80 $^\circ$ C.

the conversion of cyclohexanone and acetophenone oxime over CuBTC was equal to 11% and 80% (approximately), respectively. Similarly to cyclohexanone oxime rearrangement, the less-ordered FeBTC appeared to be practically inactive in the transformation of acetophenone oxime.

The results imply that electron-rich aryl groups have better migrating aptitude than the alkyl group toward the oximino nitrogen. In this case, the reaction can proceed easily because aryl group stabilizes the reaction intermediate (Scheme 3) [61].

Indanone oxime also contains aryl group, that can facilitate the Beckmann rearrangement due to the stabilization of the reaction intermediate. But it is bulkier in comparison with acetophenone oxime. For indanone oxime we observed lower conversions in comparison with acetophenone oxime over USY (77% vs. 36% at 240 min TOS) and CuBTC (54 vs. 29% at 240 min TOS). In contrast, the conversions over zeolite Beta in the rearrangements of either acetophenone oxime or indanone oxime were nearly identical (Fig. 6). This result strongly confirms that the reactions of respective oximes proceed on the external surface of zeolite Beta.



Scheme 3. Rearrangement of aryl-containing substrate.



Fig. 6. Conversion of indanone oxime over Beta (Si/Al=12.5), USY (Si/Al=15), CuBTC, FeBTC at 80 $^\circ\text{C}.$



Fig. 7. Effect of catalyst loading (0.2, 0.1, 0.05 g) with respect to acetophenone oxime on yield of the corresponding amide in Beckmann rearrangement over CuBTC ($100 \degree$ C).

In contrast to cyclohexanone oxime, the selectivities to respective amides or lactams in acetophenone oxime and indanone oxime transformations, respectively, were 100% over all catalysts under investigation. The last result, obviously, is caused by the presence of aromatic ring in the two latter substrates hindering the side transformation of both substrates and products.

Conversion of acetophenone oxime in Beckmann rearrangement decreases with decreasing amount of MOF used (Fig. 7). 62% yield of the lactam after 400 min of the reaction was achieved in acetophenone oxime rearrangement over CuBTC using 0.2 g of the catalyst per 2 mmol of oxime. When 0.1 g of the catalyst was used, the yield of respective amide totaled only 52%. As expected, the selectivity was not dependent on the amount of the MOF used, it was found to be constantly 100%.

Unexpectedly, the increase in the reaction temperature resulted in decreasing conversion of acetophenone oxime over CuBTC. For comparison, when increasing the reaction temperature from 60 to $80 \,^{\circ}$ C and even to $100 \,^{\circ}$ C, the yield of the respective amide was reduced after 400 min of the reaction time over CuBTC from 100 to 95 and 62%, respectively (Fig. 8).

XRD patterns confirmed that the framework of MOFs remains unchanged during the liquid-phase Beckmann rearrangement of all substrates under investigation (Fig. 9). Thus, the unexpected influence of the reaction temperature on the conversion of acetophenone oxime over CuBTC may be explained in terms of the formation of a small amount of undesired products at higher temperatures leading to the fast deactivation of the catalyst.



Fig. 8. Effect of the temperature (60, 80, 100 $^{\circ}$ C) on the conversion of acetophenone oxime in Beckmann rearrangement over CuBTC.



Fig. 9. XRD patterns of CuBTC (a) and FeBTC (b) before and after catalysis.





Scheme 4. Transformations of camphor oxime under Beckmann rearrangement conditions.

Fig. 10. Leaching test of Cu^{2+} ions from the catalyst (CuBTC) under conditions of Beckmann rearrangement of acetophenone oxime (reaction temperature – 100 °C).

Also results of leaching test (obtained for acetophenone oxime rearrangement over CuBTC, Fig. 10) indicate that practically no leaching of the active species takes place.

It seems that the size effect dominates over acidic features of the catalysts studied in the case of the most bulky substrate – camphor oxime. While zeolite Beta appeared to be completely inactive in the process of Beckmann rearrangement of camphor oxime into 1,8,8-trimethyl-2-azabicyclo[3.2.1]octan-3-one, zeolite USY and CuBTC demonstrated quite high conversion of the substrate. As it can be seen (Fig. 11) the conversion value of camphor oxime increased together with increasing the pore size within the range of investigated catalysts Beta «USY < CuBTC. It should be



Fig. 11. Conversion of camphor oxime over Beta (Si/Al = 12.5), USY (Si/Al = 15), CuBTC, FeBTC at 80 $^{\circ}$ C.

noted the fragmentation of camphor oxime to nitriles [62] and also the formation of δ -lactams [63] under Beckmann reaction conditions (Scheme 4) were observed and the mixture was not analyzed further.

Most probably, the transformation of camphor oxime proceeds on the outer surface/in the pore mouths of the catalysts. Zeolite BEA and FeBTC were practically inactive in this reaction. It can be assumed that the molecule of camphor oxime cannot enter the pore entrances to reach the active sites of the catalyst. We assume that both CuBTC and zeolite USY are active in the transformation of camphor oxime as a result of appropriate size/curvature of their pore entrances, allowing the interaction of substrate and the active site. The mesopore entrances in USY zeolite, created by dealumination and steaming are obviously depleted in the concentration of active centers in comparison with CuBTC. It may be the reason of slightly higher conversion of camphor oxime over CuBTC (31% at 360 min of TOS) in comparison with USY (22.5 at 360 min of TOS).

4. Conclusions

In comparison with MOFs, zeolites show higher activity in transformations of relatively small aromatic (acetophenone oxime, indanone oxime) and non-aromatic oximes (cyclohexanone oxime) providing 100% selectivity to the target lactams or amides, respectively, in all reactions. While CuBTC is quite active in Beckmann rearrangement of indanone oxime and acetophenone oxime, it is the most active in transformation of bulky camphor oxime. It can be assumed, that due to the diffusional preferences, larger pore size of CuBTC may be the main reason of its capability to facilitate the transformation of bulky camphor oxime in comparison with zeolites Beta and USY.

Acknowledgements

The research of M.O. leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 228862. J.Č. thanks the Czech Grant Agency for the financial support (Centre of Excellence – P106/12/G015).

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