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Gas-phase Beckmann rearrangement of cyclododecanone oxime on Al,B-MCM-41 mesoporous materials

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Abstract Gas-phase Beckmann rearrangement of cyclododecanone oxime (Cdox) to ω-laurolactam is reported for the first time on Al,B-MCM-41 catalysts. The Cdox conversion was studied by using a temperature programmed reaction experiment in the 325–450 °C temperature range employing 0.15 M Cdox in toluene/acetone solution. The oxime conversion increased gradually with reaction temperature from ca. 90% at 325 °C to ca. 95% at 450 °C, whereas the yield of the desired product ω-laurolactam decreased. The optimal reaction temperature was 375 °C, which balanced the conversion of Cdox, selectivity to ω-laurolactam and catalyst lifetime. In parallel, liquid-phase experiments were carried out under conventional heating. Weak and medium strength acid sites, higher strong acid B/L ratios and adequate pore diameter of untreated Al,B-MCM-41 materials favored an optimal performance for the gas-phase Beckmann rearrangement of Cdox, clearly improving the conversion, selectivity to ω-laurolactam and catalyst lifetime in gas-phase with respect to the conventional liquid-phase reactions.

Introduction

ω-Laurolactam (ω-l) is used exclusively as a monomer for the polymerization of polyamide (especially Nylon 12). Polyamide 12 exhibits a high performance especially for polymer applications (e.g., automotive industry, medicine, sport, manufacture of food packaging articles). The production of ω-1 is estimated to be in the order of 50,000 tons per year worldwide, with production sites located in Europe (e.g., Germany, France) and Japan [1]. As for ε-caprolactam, its commercial production in liquid phase is energy consuming and co-produces a substantial amount of ammonium sulphate.

The gas-phase Beckmann rearrangement of cyclic ketoximes (e.g., cyclohexanone oxime) to lactams has been performed using a range of solid acids [2–5]. While several reports can be found on the preparation of ε-caprolactam [6–9], only a few reports deal with the gas-phase Beckmann rearrangement of cyclododecanone oxime (Cdox), mostly patent literature [10, 11]. Its synthesis has mainly been reported under liquid-phase conditions using mineral acids including H_2SO_4 [12–15], HCl [16, 17], anhydrides of organic sulfonic acids [18], or solid acid catalysts [10, 19–21].

Since their discovery in the early 90s, the unique properties of MCM-41 based materials made them attractive candidates for a wide range of applications including semiconductors, biosensors, novel materials, and catalysis [22–25]. We have previously reported the preparation of highly ordered aluminum and/or boron incorporated MCM-41 catalysts [5, 26, 27]. B-MCM-41, Al-MCM-41 and Al,B-MCM-41 were proved to be very effective catalysts in the gas-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, providing selectivities up to 90% to the desired product over Al,B-MCM-41 [5, 26].

Inspired by the excellent results obtained for Al,B-MCM-41 materials, we report here the gas-phase Beckmann rearrangement of Cdox using Al,B-MCM-41 and fluorinated Al,B-MCM-41 catalysts. Results were compared to those

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obtained in the liquid-phase reaction in toluene and chlorobenzene, respectively. The temperature effect was correlated with oxime transformation, ω-1 selectivity and the catalyst lifetime in order to achieve optimal reaction conditions. Deactivated catalysts were also studied and characterized by thermal analysis (TG-DTA) and Diffuse Reflectance Fourier-Transform (DRIFT) experiments.

Experimental

Catalysts

Three Al,B-MCM-41 [Si/(Al + B) molar ratio 20] with Al/B ratio in the range 2–0.5, along with their counterparts treated with NH_4F aqueous solution, were employed. The detailed preparation procedure has been previously reported [5]. Furthermore, for comparison, Si-MCM-41 (Si41 and Si41-F), B-MCM-41 (Si/B = 20), and Al-MCM-41 (Si/Al = 20) mesoporous materials and commercial microporous Beta75 zeolite (Si/Al = 37.5, Zeolyst Inc.) were also screened. Samples were denoted AlB-*X* or AlB-*X*F (NH_4F treated), where $X = 2$, 1, and 0.5 are the Al/B ratios in the synthesis gel.

Catalytic experiments

Gas-phase Beckmann rearrangement of Cdox

The gas-phase reaction was conducted in a similar way as previously reported [11]. Product characterization was performed by GC and GC-MS using a Varian CP-3800 Gas Chromatograph coupled with a Varian 1200 Quadrupolar MS. Reaction products were ω-l, Cdone, dodecanenitrile and 11-dodecenenitrile (CN). Blank runs in the absence of catalyst gave virtually no conversion of starting material.

Liquid-phase Beckmann rearrangement of Cdox

Liquid-phase experiments were performed following a methodology previously reported by Corma et al. [19]. Thus, a solution of cyclododecanone oxime (Cdox, 100 mg) in chlorobenzene or toluene (20 mL, both from Aldrich) was prepared in the presence of 100 mg of catalyst in a 50 mL two-necked round-bottom flask fitted with a reflux condenser and a septum. The reaction mixture was heated for 24 h at a constant temperature of 130 °C for chlorobenzene and 110 °C for toluene, respectively, under stirring. Aliquots (ca. 0.5 mL) were withdrawn from the reaction mixture, filtered and subsequently analyzed using a HP-5890 series II gas chromatograph with FID fitted with a capillary column (HP-101, 25 m × 0.2 mm × 0.2 μm thickness). Reaction products were ω-l, Cdone and CN. No conversion was detected in the filtrate for Beckmann rearrangement of Cdox. Blank runs in the absence of catalyst gave virtually no conversion of starting material.

Characterization of deactivated samples

Thermal analysis was performed by simultaneous TG-DTA measurement using a Setsys 12 Setaram thermobalance. Samples were heated in air or argon in the 30–1000 °C temperature range at a heating rate of 10 °C min^{-1}.

Diffuse reflectance FTIR (DRIFT) spectra were recorded on a Bomem MB series instrument equipped with an "environmental chamber" (Spectra Tech, P/N 0030-100) placed in the diffuse reflectance attachment (Spectra Tech, Collector). The resolution was 8 cm^{-1}, and 256 scans were averaged to obtain spectra in the 4000–500 cm^{-1} range. Fresh samples were dried at 150 °C for 24 h, mixed with KBr to 15 wt%, heated to 100 °C, and held at this temperature for 1 h prior to spectrum measurement. The deactivated catalyst was thermally treated for 1 h 550 °C in air. Then, it was cooled at 100 °C and its DRIFT spectrum acquired (see procedure above).

Results and discussion

Characterization

Al,B-MCM-41 materials properties have been previously reported [5, 26] and acidity values and trends were described [5]. Table 1 summarizes the acid properties of the Al,B-MCM-41 that we would refer to when discussing the materials catalytic activity.

Gas-phase Beckmann rearrangement of Cdox

Al,B-MCM-41 were extremely active catalysts for the Beckmann rearrangement of cyclohexanone oxime at high temperatures [5, 26], so we assumed an analogous performance in the gas-phase transformation of Cdox. For this reason, we conducted a TPR-Cdox experiment to obtain additional information about optimum reaction conditions (maximum conversion of Cdox and selectivity to ω-l). The TPR-Cdox experiment was conducted with AlB-2 under continuous flow of vaporized 0.15 M Cdox in toluene/acetone (60/40 v/v) solution between 325 and 450 °C (1 °C/min heating rate). Results are shown in Fig. 1. The relatively flat temperature-insensitive shape of the conversion curve reflected bulk mass transfer control. Oxime conversion was found to increase gradually with the reaction temperature from 90.1% (325 °C) to 95.2% (450 °C). However, the yield of the desired ω-l product remarkably

Table 1 Surface acid properties, B/L ratios (calculated as DMPy/Py-DMPy) and contributions to the total area for Py-TPD profiles of AlB-*X* and AlB-*X*F materials

Catalyst	Titration at 300 °C			Py-TPD (Area %)			
	Py (μmol g^{-1})	DMPy (μmol g^{-1})	B/L	~175° C	~300 °C	~475 °C	~600 °C
Beta75	216	190	7.31	60	6	14	19
Al-20	170	93	1.21	25	32	27	16
AlB-2	196	85	0.77	51	15	24	10
AlB-1	175	68	0.63	44	29	19	8
AlB-0.5	139	53	0.61	46	26	21	6
AlB-2F	215	75	0.53	32	39	22	7
AlB-1F	158	50	0.46	48	23	18	11
AlB-0.5F	100	35	0.54	52	21	20	7

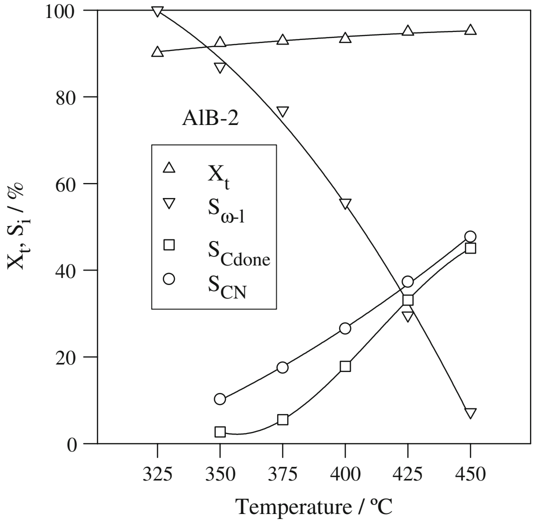

Fig. 1 Cdox conversion and product distribution temperature programmed reaction profiles for AlB-2 material at 1 °C/min heating rate

Table 2 Total conversion (X_T, %) and product distribution (S_i, %), at different temperatures, of AlB-2 catalyst in the gas-phase Beckmann rearrangement of Cdox[a] (0.15 M Cdox in toluene/acetone)

T/°C	Time on stream/6 h				Time on stream/18 h			
	X_T	$S_{\omega\text{-}l}$	S_{Cdone}	S_{CN}	X_T	$S_{\omega\text{-}l}$	S_{Cdone}	S_{CN}
350	94.6	90.1	6.8	3.1	61.9	81.9	16.1	2.0
365	95.9	84.6	3.4	12.0	70.3	81.6	6.6	11.8
375	97.7	83.6	0.0	16.4	91.6	81.9	0.0	18.1

[a] W/F = 113 g h/mol

Table 3 Total conversion (X_T, %), product distribution (S_i, %), and durability (*D*, lifetime at X_T = 100%) in the gas-phase Beckmann rearrangement of Cdox[a] (0.1 M Cdox in toluene, 375 °C) over AlB-*X* and AlB-*X*F materials

Catalysts	Time on stream/6 h				Time on stream/18 h				D/h
	X_T	$S_{\omega\text{-}l}$	S_{Cdone}	S_{CN}	X_T	$S_{\omega\text{-}l}$	S_{Cdone}	S_{CN}	
Beta75	73.5	83.0	6.5	10.5	44.1	80.5	8.1	11.4	–
Si41	77.9	65.7	16.7	17.9	–[b]	–	–	–	2
Si41-F	78.5	73.9	14.9	11.2	–[b]	–	–	–	–
B-20	98.1	76.3	4.5	19.2	63.8	65.1	17.9	17.0	5
Al-20	>99	79.2	1.1	19.7	94.8	79.9	8.1	12.0	16
AlB-2	>99	80.6	0.0	19.4	>99	82.4	1.7	15.9	32
AlB-1	>99	81.7	0.0	18.3	>99	81.3	1.4	17.3	27
AlB-0.5	>99	81.7	0.0	18.3	84.6	76.7	5.5	17.8	13
AlB-2F	>99	82.8	2.6	14.6	91.1	84.2	5.3	14.5	9
AlB-1F	87.4	81.1	5.5	13.4	60.1	77.6	4.7	17.7	2
AlB-0.5F	82.0	84.3	6.6	9.1	52.4	77.9	4.8	17.3	2

[a] W/F = 169 g h/mol; [b] Not measured

decreased with the temperature (especially at temperatures >375 °C), while the yield of Cdone and CN increased.

Consequently, the catalytic deactivation of the AlB-2 catalyst was investigated in the 350–375 °C temperature range (Table 2). Selectivity and deactivation rate of the AlB-2 catalyst were strongly influenced by the reaction temperature while the initial catalytic activities were ca. 95 %. The activity decreased up to 36.6%, 26.7%, and 4.6% at 350, 365, and 375 °C, respectively, from 6 to 18 h reaction time. Henceforth, the reaction temperature was set at 375 °C as standard optimized value.

The catalytic performance of Al,B-MCM-41, Si-MCM-41, Al-MCM-41, B-MCM-41, and Beta75 in the transformation of Cdox were compared at 375 °C and results are summarized in Table 3 and Fig. 2. Quantitative Cdox conversion was obtained for all samples during the initial hours of reaction. All solid acids exhibited a high *ω*-l selectivity (~80%) but the deactivation rates were found to be substantially different between materials. Al,B-MCM-41 treated with NH_4F aqueous solution deactivated rapidly, as demonstrated by the durability (*D*, defined as lifetime at $X_T = 100\%$) and this conversion drop was more pronounced with increasing boron contents. AlB-*X* materials exhibited a similar trend (Table 3). Nevertheless, AlB materials exhibited the highest durability values (e.g., up to 32 h for AlB-2).

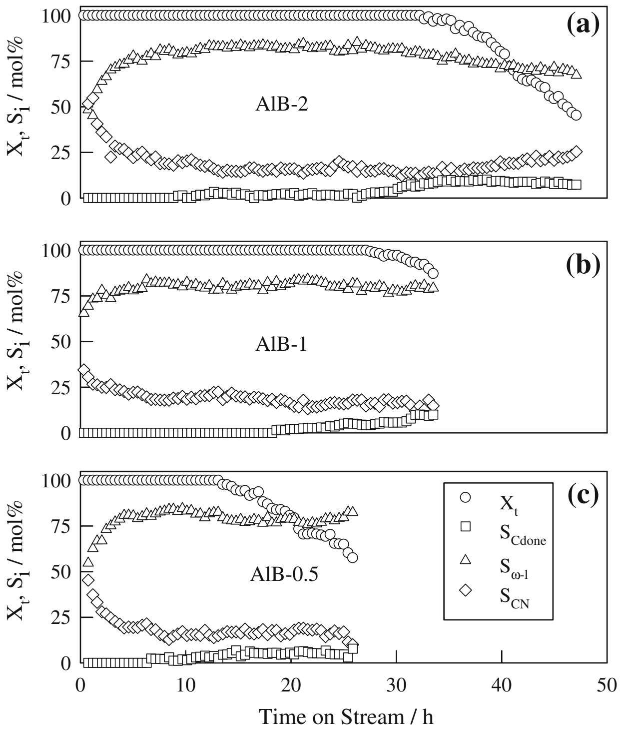

Fig. 2 Variation of Cdox conversion (X_T, %) and product selectivity (S_i, %) with time on stream in the gas-phase Beckmann rearrangement of Cdox over AlB-*X* materials: **a** AlB-2, **b** AlB-1, **c** AlB-0.5. Reaction conditions: $T = 375$ °C; 0.1 M Cdox in toluene; $W/F = 169$ g h/mol

The most appropriate durability achieved in AlB-*X* catalysts was associated to their higher ratios of strong Brönsted/Lewis acid sites. In any case, catalytic activity, selectivity to ω-l and durability of Si41, Si41F, Al-20, and B-20 materials were inferior to those of AlB-2 and AlB-1. Nonetheless, Cdone selectivity increased with time on stream on all screened catalysts due to the hydrolysis of the oxime to the corresponding ketone catalysed by the external silanol groups on the catalyst surface [19]. The deactivation process can be related to Cdone formation (Fig. 2), subsequent formation of polycondensation products with restricted diffusional capability (via aldol reaction) and finally products adsorption and coking, leading to the materials deactivation.

Comparatively, Si41, Si41-F and B-20 catalysts possessed only weak acid sites (no adsorption of Py or DMPy at 300 °C) [27] exhibiting lower activities and poor catalyst durabilities with respect to AlB-*X* materials (Table 3).

Liquid-phase Beckmann rearrangement of Cdox

Liquid-phase experiments were conducted to be compared with results obtained in the gas-phase. This will let us to determine the most efficient methodology for this process.

The liquid-phase Beckmann rearrangement of Cdox using Al,B-MCM-41 materials as catalysts was investigated in chlorobenzene and toluene at 130 and 110 °C, respectively. AlB-1 and AlB-1F activities were also investigated at 110 °C in chlorobenzene, allowing us to compare the effect of the solvent. The conversion and selectivity values (obtained at reaction times $t = 5$ h and $t = 24$ h, respectively) are summarized in Table 4.

Beta zeolite has proven to be very effective in the Cdox to ω-l transformation under liquid-phase conditions [19]. Our results for Beta75 zeolite were in good agreement with these observations as it exhibited the highest activity and selectivity to ω-l at 130 °C using chlorobenzene as solvent. Under these reaction conditions, Al,B-MCM-41 provided lower conversions and selectivities to ω-l. Boron loading deeply affected the activity of AlB-*X* and AlB-*X*F, reflected in a decrease in oxime conversion with an increase in boron loading. Selectivities remained almost unchanged for both AlB-*X* (ca. 65%, $t = 5$ h) and AlB-*X*F (ca. 80%, $t = 5$ h). AlB-*X* gave higher Cdox conversions than those of AlB-*X*F, in good correlation with results obtained in the gas-phase experiments.

Of note was also the decrease in Cdox conversion when toluene was employed as solvent. This phenomenon could

Table 4 Total conversion (X_T, %) and product distribution (S_i, %) in the liquid-phase Beckmann rearrangement of Cdox (using chlorobenzene or toluene as solvents) over AlB-*X* and AlB-*X*F materials

Catalyst	5 h				24 h			
	X_T	$S_{\omega\text{-l}}$	S_{Cdone}	S_{CN}	X_T	$S_{\omega\text{-l}}$	S_{Cdone}	S_{CN}
Chlorobenzene at 130 °C								
Beta75	78.6	97.0	2.5	0.5	80.2	95.8	3.0	1.2
Al20	44.7	83.9	0.0	16.1	51.9	84.0	1.2	14.8
AlB-2	39.3	65.0	9.0	26.0	43.3	64.4	8.3	27.3
AlB-1	26.8	63.8	9.3	26.8	30.8	66.0	8.6	25.3
AlB-0.5	25.3	67.2	9.5	23.3	29.9	60.9	11.0	28.1
AlB-2F	20.2	81.2	0.0	18.8	24.8	73.8	5.3	20.9
AlB-1F	18.9	79.9	4.8	15.3	19.3	78.2	4.7	17.0
AlB-0.5F	17.2	77.9	2.3	19.8	19.7	70.0	6.1	23.9
Toluene at 110 °C								
Beta75	18.8	71.8	25.0	3.2	19.4	68.0	25.3	6.7
Al20	34.0	90.6	0.0	9.4	36.8	87.7	1.5	10.8
AlB-2	12.1	82.6	0.0	17.4	15.6	77.3	2.5	20.2
AlB-1	7.6	80.2	0.0	19.8	9.8	65.3	9.2	25.5
AlB-0.5	4.8	70.8	0.0	29.5	8.6	46.2	5.8	48.8
AlB-2F	12.8	78.9	0.0	21.1	19.7	74.1	6.1	19.8
AlB-1F	8.2	76.9	0.0	23.1	13.0	62.3	10.8	26.9
AlB-0.5F	3.3	69.7	0.0	30.3	6.6	45.5	24.2	30.3
Chlorobenzene at 110 °C								
AlB-1	8.0	56.2	11.2	32.6	15.0	49.3	7.3	43.4
AlB-1F	8.9	45.2	13.8	41.0	14.1	52.8	9.7	37.5

be attributed to the temperature of reaction. Except for Beta75 zeolite, the product distribution in chlorobenzene (130 °C) and toluene (110 °C) did not appreciably change after 5-h reaction. However, the selectivity to ω-l drastically decreased in chlorobenzene at 110 °C. Longer times of reaction (e.g., 24 h) did not favor the formation of ω-l due to an increase in Cdone and CN selectivity coming from the hydrolysis of Cdox as well as to the ring opening reaction of ω-l. This effect was also influenced by the boron content in samples (the more boron the lower selectivity to ω-l). Relatively short times of reaction (e.g., <5 h) were optimum for the highly selective synthesis of ω-l. Similarly, to the results obtained in gas-phase, ω-l can be strongly adsorbed on the catalysts acid sites and further converted to undesired CN products before desorbing from the surface.

Gas-phase versus liquid-phase

Al,B-MCM-41 were proved to be less active but similarly selective with respect to Beta75 zeolite in the liquid-phase Beckmann rearrangement of Cdox at 110 °C in toluene (Table 4). In addition to this, gas-phase results demonstrated that Beta75 zeolite displayed the lowest Cdox conversion and durability for the gas-phase Beckmann rearrangement at 375 °C (Table 3). The faster deactivation rate in the gas-phase reaction may be attributed to the smaller pore diameter of the Beta75 zeolite, which may promote the formation of by-products and may restrict the diffusion of reactant and products under the reaction conditions.

In summary, the weak and medium strength acid sites, higher strong acid B/L ratios (Table 1) combined with adequate pore diameters (ca. 24 Å) of AlB-*X*(F) favored an optimum performance in the gas-phase Beckmann rearrangement of Cdox. The effectiveness of Al,B-MCM-41 in the gas-phase protocol was clearly improved (in terms of Cdox conversion, ω-l selectivity, and catalyst lifetime) in comparison with the liquid-phase reaction.

Catalyst deactivation

DRIFT and TG-DTA experiments were performed in order to characterize the deactivated samples. Results obtained for Al,B-MCM-41 catalysts deactivated at 375 °C in the gas-phase Beckmann rearrangement of Cdox are depicted in Fig. 3.

DRIFT spectrum of the AlB-0.5F catalyst deactivated at 375 °C disclosed several new absorption bands in the 3700–2800 cm^{-1} range (Fig. 3A—c), indicating the presence of organic compounds on the catalyst [28] that could be removed after thermal treatment at 550 °C in air for 1 h (Fig. 3A—b). The regenerated material gave a very similar DRIFT spectrum to that of the fresh catalyst. The band at ca. 1595 cm^{-1} was assigned to highly unsaturated carbonaceous matter (coke formation) on the catalyst surface [28, 29]. TG-DTA results were in good agreement with DRIFT observations, showing two main mass loss steps accompanied by exothermic peaks in the DTA curve, centered at ca. 345 and 513 °C (Fig. 3B). These steps could be attributed to the desorption, decomposition, and oxidation of the organic compounds, and to the oxidation of coke, respectively.

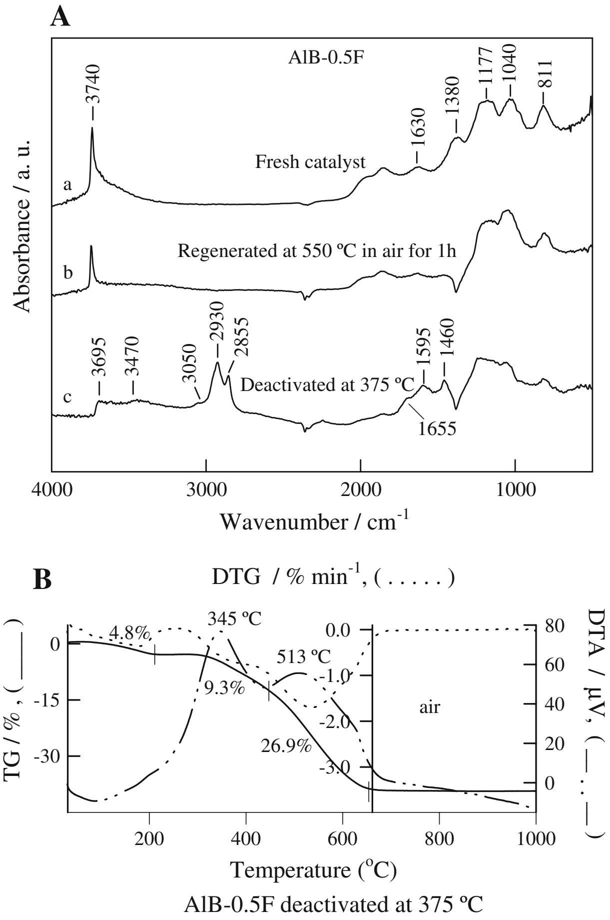

Fig. 3 **A** DRIFT spectra of AlB-0.5F (100° C): (a) Fresh, (b) deactivated at 375 °C (time on stream: 23 h; conversion level: 46 %), and (c) deactivated at 375 °C: treated at 550 °C in air for 1, employing KBr as reference. **B** TG-DTA profiles (oxidant atmosphere) of AlB-0.5F material deactivated at 375 °C

A further insight into these results show that in order to completely remove all carbonaceous/organic species from the catalyst surface (to ensure a fully recycled catalyst), we will need to regenerate the catalyst at a temperature superior to 600 °C in air.

Conclusions

Aluminum-boron-silicate mesoporous MCM-41 materials and their counterparts treated with NH_4F aqueous solution were active and selective in the Beckmann rearrangement of Cdox. The weak and medium strength acid sites, higher strong acid B/L ratios and adequate pore diameter of AlB-*X* catalysts favored the materials optimum performance in the gas-phase Beckmann rearrangement of Cdox, clearly improving the conversion of Cdox, selectivity to ω-laurolactam and catalyst lifetime with respect to the liquid-phase reaction. The catalysts deactivation may be related to cyclododecanone formation, which can generate self-condensation products via aldol reaction. These high molecular weight by-products can be adsorbed and coked on the catalyst surface causing the catalytic deactivation of the sample. Owing to the desirable properties of untreated Al,B-MCM-41, we believe the above materials could be further optimized and employed as heterogeneous solid acids for the environmentally benign production of ω-laurolactam.

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References

1. United Nations Environment Programme Publications. http://www.chem.unep.ch/irptc/sids/OECDSIDS/947046.pdf
2. Forni L, Fornasari G, Giordano G, Lucarelli C, Katovic A, Trifiro F, Perri C, Nagy JB (2004) Phys Chem Chem Phys 6:1842
3. Mao D, Chen Q, Lu G (2003) Appl Catal A 244:273
4. Maheswari R, Shanthi K, Sivakumar T, Narayanan S (2003) Appl Catal A 248:291
5. Conesa TD, Campelo JM, Luna D, Marinas JM, Romero AA (2007) Appl Catal B 70:567
6. Misono M, Inui T (1999) Catal Today 51:369
7. Tsuji H, Setoyama T (2005) Chem Lett 34:1232
8. Ushikubo T (2000) Catal Today 57:331
9. Forni L, Fornasari G, Tosi C, Trifiro F, Vaccari A, Dumeignil F, Grimblot J (2003) Appl Catal A 248:47
10. Corma A, Iborra S, Rodríguez MI (2004) WO Patent 2004037785 A1
11. Conesa TD, Mokaya R, Yang Z, Luque R, Campelo JM, Romero AA (2007) J Catal 252:1 and references therein
12. Michel JC, Potin P (1980) US Patent 4 211 700
13. Kuroda N, Kawai J, Shimomura H (2003) EP Patent 1 329 448 A1
14. García L, Del Pino M (1994) ES Patent 2 048 098
15. Ollivier J (1998) US Patent 5 719 316
16. Ollivier J, Drutel D (1999) WO Patent 9 901 424
17. Ollivier J (1997) EP Patent 0 798 290 A1
18. Hans M, Heinz-Werner V (1987) US Patent 4 689 412
19. Camblor MA, Corma A, García H, Semmer-Herléndan V, Valencia S (1998) J Catal 177:267
20. Yamamoto S, Haruta A, Fukuda Y (2005) JP Patent 2005022977
21. Yamamoto S, Haruta A, Fukuda Y (2005) JP Patent 2005023014
22. Corma A (1997) Chem Rev 97:2373
23. Gonzalez-Arellano C, Corma A, Iglesias M, Sanchez F (2004) Adv Synth Catal 346:1316
24. Bhattacharyya S, Lelong G, Saboungi ML (2006) J Exp Nanosci 1:375
25. Gonzalez-Arellano C, Corma A, Iglesias M, Sanchez F (2008) Eur J Org Chem 1107
26. Campelo JM, Conesa TD, Luna D, Marinas JM, Romero AA (2005) Stud Surf Sci Catal 158:1421
27. Conesa TD, Hidalgo JM, Luque R, Campelo JM, Romero AA (2006) Appl Catal A 299:224
28. Rozwadowski M, Lezanska M, Wloch J, Erdmann K, Golembiewski R, Kornatowski J (2001) Chem Mater 13:1609
29. Praserthdam P, Isarangura na Ayutthaya S (2004) Catal Today 97:137