



Titanium cation-exchanged montmorillonite as an active heterogeneous catalyst for the Beckmann rearrangement under mild reaction conditions

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ABSTRACT

Titanium cation-exchanged montmorillonite acts as an efficient heterogeneous catalyst for the Beckmann rearrangement of a wide range of ketoximes including aromatic, aliphatic, and alicyclic ketoximes under mild reaction conditions. After the rearrangement reaction, titanium cation-exchanged montmorillonite is easily separated by simple filtration, and can be reused with retention of high efficiency.

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Amides are vital synthetic intermediates and raw materials for medicines, agrichemicals, fragrances, and polymers. Various amides can be synthesized from ketoximes through the Beckmann rearrangement under liquid-phase conditions.^{1,2} The Beckmann rearrangement has often been conducted with the use of environmentally harmful acids, for example concentrated sulfuric acid, phosphorus pentachloride, and hydrogen chloride, resulting in the production of large amounts of waste. To overcome this problem, much effort has been devoted to the development of alternative and more environmentally-friendly catalysts in the liquid-phase Beckmann rearrangement.^{3,4} Heterogeneous catalysts have many advantages over homogeneous ones due to their ease of recovery and reuse. However, the heterogeneous catalysts reported to date for the Beckmann rearrangement have suffered from a limited substrate scope,^{4e} and the requirement of high temperatures (>130 °C),^{4f} pre-treatment before reuse of the catalyst^{4d} and microwave-heating.^{4a,c} Therefore, the development of highly efficient heterogeneous catalysts for the liquid-phase Beckmann rearrangements under mild reaction conditions is still a significant issue.

Montmorillonites of smectite clays are composed of negatively charged layers and an interlayer containing cationic species. The cationic species can be easily replaced by other metal polycations and these ion-exchanged montmorillonites have great potential as solid acid catalysts.⁵ In our continuing studies of metal-exchanged montmorillonite, we found that two-dimensional


titanium oxide species sandwiched in the montmorillonite layers were formed by treatment of sodium cation-montmorillonite with TiCl₄ aqueous solution. The titanium cation-exchanged montmorillonite (Ti⁴⁺-mont) was found to act as an efficient solid acid catalyst for many environmentally benign reactions such as the aromatic alkylation⁶ and acetalization of carbonyl compounds,⁷ the deprotection of acetals,⁸ the esterification of carboxylic acids,⁹ and the etherification of alcohols¹⁰ in which the titanium oxide species sandwiched in the layers exhibited high catalytic activities. Herein, we found that Ti⁴⁺-mont efficiently promoted the Beckmann rearrangement of a wide range of ketoximes under mild reaction conditions. The reaction proceeded more efficiently at lower temperatures (<100 °C) than previously reported heterogeneous catalyst systems without any additives or microwave-heating. Moreover, Ti⁴⁺-mont showed good reusability.

Ti⁴⁺-mont was prepared according to our previous report.⁶ We tested the catalytic activity of Ti⁴⁺-mont in the Beckmann rearrangement of cyclododecanone oxime (**1**) to ω-laurolactam (**2**), which is an important raw material of Nylon 12, as a model reaction at 90 °C in benzonitrile solvent.¹¹ Ti⁴⁺-mont showed high catalytic activity for the rearrangement; **2** was quantitatively obtained as the sole product after 3 h (Table 1, entry 2). The activities of various solid catalysts were compared with that of Ti⁴⁺-mont under similar reaction conditions (Table 1, entries 1 and 6–16). Other cation-exchanged montmorillonites such as Al³⁺-mont, Zr⁴⁺-mont, and Sc³⁺-mont afforded good yields of **2** (entries 6–8).¹² On the other hand, the parent Na⁺-mont did not give any products (entry 11), confirming that the active species are the exchanged cations in

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Table 1
Beckmann rearrangement of **1** to **2** using various solid acid catalysts^a

				
Entry	Catalyst	Time	Conv. ^b (%)	Yield ^b (%)
1	Ti ⁴⁺ -mont	1	81	81
2	Ti ⁴⁺ -mont	3	99	98
3 ^c	Ti ⁴⁺ -mont	3	99	98
4 ^d	Ti ⁴⁺ -mont	3	99	98
5 ^e	Ti ⁴⁺ -mont	3	99	97
6	Al ³⁺ -mont	1	75	74
7	Zr ⁴⁺ -mont	1	73	73
8	Sc ³⁺ -mont	1	62	60
9	V ³⁺ -mont	1	55	52
10	Hr ⁴⁺ -mont	1	35	34
11	Na ⁺ -mont	1	5	<1
12	Nafion-H NR50	1	35	32
13	Amberlyst-15	1	23	20
14	H-ZSM-5 (Si/Al=150)	1	15	15
15	H-USY (Si/Al=10)	1	13	12
16	H-mordenite (Si/Al=10)	1	3	3

^a Reaction conditions: catalyst (0.1 g), substrate (1.0 mmol), benzonitrile (5 mL), 90 °C, Ar.

^b Conversions and yields were determined by GC using an internal standard technique.

^c Reuse 1.

^d Reuse 2.

^e Reuse 3.

Table 2
Beckmann rearrangement of various ketoximes using Ti-mont^a

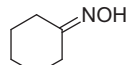
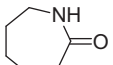
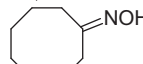
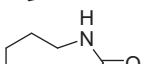
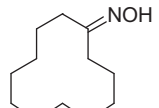
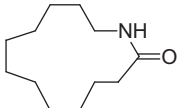
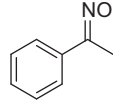
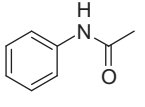
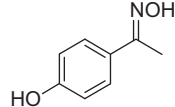
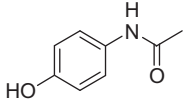
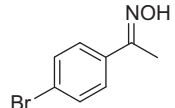
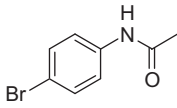
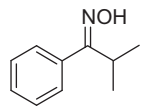
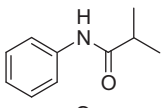
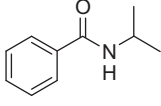
Entry	Substrate	Product	Time (h)	Conv. ^b (%)	Yield ^b (%)
1 ^{c,d}			20	96	74 (65) ^e
2 ^{c,d}			18	99	90
3			3	99	98 (97)
4			14	99	96
5			5	99	96 (89)
6 ^c			18	98	93 (88)
7			10	99	56
					44

Table 2 (continued)

Entry	Substrate	Product	Time (h)	Conv. ^b (%)	Yield ^b (%)
8			16	99	97 (92)
9 ^c			16	99	94 (86)
10 ^{c,d}			20	98	89 (77)
11			10	99	97 (91)
12			8	99	98

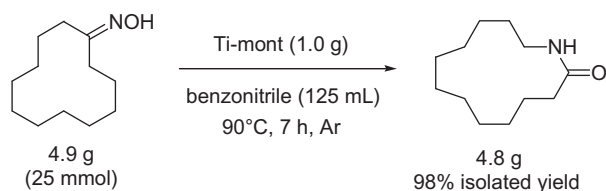
^a Reaction conditions: Ti⁴⁺-mont (0.1 g), substrate (1.0 mmol), benzonitrile (5 mL), 90 °C, Ar.

^b Conversions and yields were determined by GC using an internal standard technique. Isolated yields are shown in parentheses.

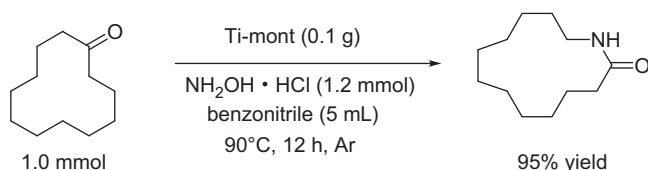
^c Substrate (0.5 mmol).

^d 110 °C.

^e Cyclohexanone was formed as a by-product.



Scheme 1. Beckmann rearrangement of **1** using Ti⁴⁺-mont under scale-up reaction conditions.



Scheme 2. One-pot synthesis of **2** from cyclododecanone with hydroxylamine using Ti⁴⁺-mont.

directly converted into **2** in excellent yield in the presence of Ti⁴⁺-mont and hydroxylamine (Scheme 2).

In conclusion, we demonstrated that Ti⁴⁺-mont acted as a highly active heterogeneous catalyst for the liquid-phase Beckmann rearrangement under mild reaction conditions. Various ketoximes including alicyclic, aromatic, and aliphatic ketoximes were sufficiently converted into the corresponding lactams and amides in high yields. The Ti⁴⁺-mont worked well under the scale-up reaction conditions and the recovered Ti⁴⁺-mont was reusable with retention of its efficiency. Furthermore, the catalytic system using Ti⁴⁺-mont was applicable to the one-pot synthesis of lactams from ketones through the Beckmann rearrangement.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2012.07.032>.

References and notes

- (a) Gawly, R. E. *Org. React.* **1988**, 35, 1; (b) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; John Wiley & Sons: New York, 2001. p 1415.
- For references of the gas-phase Beckmann rearrangements, see: (a) Yashima, T.; Oka, N.; Komatsu, T. *Catal. Today* **1997**, 38, 249; (b) Mao, D.; Chen, Q.; Lu, G. *Appl. Catal., A* **2003**, 244, 273; (c) Izumi, Y.; Ichihashi, H.; Shimazu, Y.; Kitamura, M.; Sato, H. *Bull. Chem. Soc. Jpn.* **2007**, 80, 1280; (d) Conesa, T. D.; Campelo, J. M.; Luna, D.; Marinas, J. M.; Romero, A. A. *Appl. Catal., B* **2007**, 70, 567; (e) Eickelberg, W.; Hoelderich, W. F. *J. Catal.* **2009**, 263, 42; (f) Cesana, A.; Palmery, S.; Buzzoni, R.; Spanò, G.; Rivetti, F.; Carnelli, L. *Catal. Today* **2010**, 154, 264; (g) Nagashima, S.; Kamiguchi, S.; Ohguchi, S.; Chihara, T. *Catal. Today* **2011**, 164, 135.
- For examples of homogeneous catalysts for the Beckmann rearrangements, see: (a) Furuya, Y.; Ishihara, K.; Yamamoto, H. *J. Am. Chem. Soc.* **2005**, 127, 11240; (b) Ramalingam, C.; Park, Y.-T. *J. Org. Chem.* **2007**, 72, 4536; (c) Hashimoto, M.; Obora, Y.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2008**, 73, 2894; (d) Liu, L.-F.; Liu, H.; Pi, H.-J.; Yang, S.; Yao, M.; Du, W.; Deng, W.-P. *Synth. Commun.* **2011**, 41, 553.
- For examples of heterogeneous catalysts for the liquid-phase Beckmann rearrangement, see: (a) Bosch, A. I.; De la Cruz, P.; Diez-Barra, E.; Loupy, A.; Langa, F. *Synlett* **1995**, 1259; (b) Ngamcharussrivichai, C.; Wu, P.; Tatsumi, T. *Chem. Lett.* **2004**, 33, 1288; (c) Li, Z.; Ding, R.; Lu, Z.; Xiao, S.; Ma, X. *J. Mol. Catal. A, Chem.* **2006**, 250, 100; (d) Botella, P.; Corma, A.; Iborra, S.; Montón, R.; Rodríguez, I.; Costa, V. *J. Catal.* **2007**, 250, 161; (e) Zhao, W.; Salame, P.; Launay, F.; Gédéon, A.; Hao, Z. *J. Porous Mater.* **2008**, 15, 139; (f) You, K.; Mao, L.; Yin, D.; Liu, P.; Luo, H. *Catal. Commun.* **2008**, 9, 1521; (g) Shiju, N. R.; Williams, H. M.; Brown, D. R. *Appl. Catal., B* **2009**, 90, 451.
- (a) Laszlo, P. *Acc. Chem. Res.* **1986**, 19, 121; (b) Adams, J. M. *Appl. Clay Sci.* **1987**, 2, 309; (c) Clark, J. H.; Kybett, A. P.; Macquarrie, D. J.; Barlow, S. J.; Landon, P. *J. Chem. Soc., Chem. Commun.* **1989**, 1353; (d) Cativiela, C.; Fraile, J. M.; García, J. I.; Mayoral, J. A.; Figueras, F.; De Menorval, L. C.; Alonso, P. *J. J. Catal.* **1992**, 137, 394; (e) Izumi, Y.; Urabe, K.; Onaka, M. *Catal. Today* **1997**, 35, 183; (f) Tateiwa, J.; Hayama, E.; Nishimura, T.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1923; (g) Guiu, G.; Gil, A.; Montes, M.; Grange, P. *J. Catal.* **1997**, 168, 450; (h) Sato, H.; Hirose, K.; Nagai, K.; Yoshioka, H.; Nagaoka, Y. *Appl. Catal., A* **1998**, 175, 201; (i) Ponde, D. E.; Deshpande, V. H.; Bulbule, V. J.; Sudalai, A.; Gajare, A. S. *J. Org. Chem.* **1998**, 63, 1058.
- Ebinitani, K.; Kawabata, T.; Nagashima, K.; Mizugaki, T.; Kaneda, K. *Green Chem.* **2000**, 2, 157.

7. Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2001**, 42, 8329.
8. Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Lett.* **2003**, 32, 648.
9. Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2003**, 44, 9205.
10. Mitsudome, T.; Matsuno, T.; Sueoka, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Green Chem.* **2012**, 14, 610.
11. Among the solvents tested, benzonitrile gave the best yield of ω -laurolactam. The yields of ω -laurolactam when using other solvents were as follows: toluene, 13%; N,N-dimethylacetamide, 3%; 1,4-dioxane, 0%; and DMSO, 0%.
12. The comparison of the catalytic activity of Ti-mont (0.1 g, Ti: 0.068 mmol) with those of other metal cation-exchanged mont such as Al-mont and Sc-mont based on the same amounts of active species was carried out in Beckmann rearrangement of cyclododecanone oxime at 90 °C for 1 h. Ti-mont showed the highest catalytic activity (81% yield) while Sc-mont and Al-mont provided ω -laurolactam in 67% and 49% yields, respectively.
13. Liu, X.; Xiao, L.; Wu, H.; Li, Z.; Chen, J.; Xia, C. *Catal. Commun.* **2009**, 10, 424.
14. Sardarian, A. R.; Shahsavari-Fard, Z. *Synlett* **2008**, 1391.