Catalysis by Solid Acid: Selective Diels-Alder Reactions Are Promoted by Mesoporous Aluminosilicate with Zinc Ions and Nanometer Honeycomb Openings

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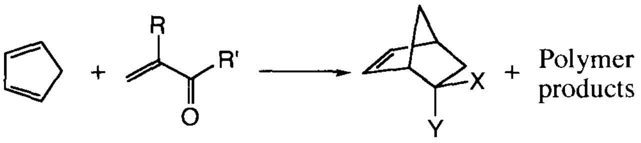
Zinc ion-exchanged mesoporous aluminosilicate has been designed specifically to accelerate the Diels-Alder reaction between cyclopentadiene and poor dienophiles such as methyl acrylate and methyl methacrylate. Catalysis on this aluminosilicate is more effective than on a K10-based solid acid catalyst.

Recently new mesoporous silicates such as MCM-41 with homogeneous as well as honeycomb-like pore openings of nanometer dimensions, and related porous materials, have been discovered.[1] Now the design of mesoporous materials is focused on applications as catalysts for organic reactions. The characteristics of the mesoporous silicates are as follows: 1) the size of mesopore opening is controllable at will, 2) it is easy to alter acid properties by introducing various metal ions into the SiO_2 framework, 3) the pore size is large enough to accommodate and diffuse a variety of organic substrates and reaction intermediates. Therefore, designing the composition of mesoporous silicates enables us to tailor solid acids to target reactions. In addition, a high electric field gradient is built inside the mesopores by lattice silanols, lattice oxygens of Si-O-Si, and metal ions included in the SiO_2 framework. If pericyclic reactions proceed in such polar and confined circumstances, we would expect results quite different from those of the reactions in a homogeneous solution where reaction substrates behave more freely.

The Diels-Alder [4+2] cycloaddition is one of the orbital-controlled pericyclic reactions available for the construction of six-membered carbon skeletons in organic synthesis.[2] In general, the reaction is performed in a combination of an electron-rich 1, 3-diene and an electron-deficient dienophile such as α, β-unsaturated carbonyl compounds. In order to accelerate the cycloaddition, the reaction has been performed by using a variety of catalysts or under specific reaction conditions: 1) by using homogeneous Lewis acids[3] or heterogeneous acids,[4] 2) under high pressure,[5] 3) in aqueous media,[6] 4) in confined spaces.[7] Among the heterogeneous promoters, zinc ion-exchanged K10 (Zn^{2+}-K10) is worthy of mention in terms of its high catalytic performance as a noncorrosive acid.[4] In this paper, we report a new mesoporous aluminosilicate-based solid acid which promotes selective Diels-Alder reactions between 1, 3-dienes and α, β-unsaturated carbonyl compounds.



1) R=H, R'=OMe; Endo: X=H,Y=CO_2Me; Exo: X=CO_2Me, Y=H.
2) R=Me, R'=OMe; Endo: X=Me, Y=CO_2Me;
Exo: X=CO_2Me, Y=Me.
3) R=Me, R'=H; Endo: X=Me, Y=CHO; Exo: X=CHO, Y=Me.
4) R=H, R'=Me; Endo: X=H, Y=COMe; Exo: X=COMe, Y=H.

An acidic mesoporous aluminosilicate (H^+-Al-MCM-41) was prepared from colloidal silica, sodium aluminate(Si/Al=23), and cetyltrimethylammonium chloride (Si/surfactant=6) according to the published method.[8] Zinc ion-exchanged aluminosilicate (Zn^{2+}-Al-MCM-41) was obtained by ion-exchange of the H^+-Al-MCM-41 in a 1 mol/l $ZnCl_2$ aqueous solution at pH 4.5.

The aluminosilicate catalyst (150 mg) was activated at 120 °C/ 0.5 mmHg (1 mmHg≈133.3 Pa). To the catalyst were added 1, 3-diene (3 mmol), dienophile (1 mmol), and CH_2Cl_2 (5 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h. Then the solid material was filtered off, and the Diels-Alder adducts were purified by distillation. The stereoselectivity of the products was determined by NMR. The residue after the distillation was weighed as polymeric by-products, and analyzed with NMR.

At first we analyzed the structures of H^+-Al-MCM-41 (Si/Al =15.2)[9] and Zn^{2+}-Al-MCM-41 (Si/Al=15.4, Zn/Al=0.54)[9] by powder X-ray diffraction and N_2 adsorption-desorption analysis, and confirmed that both catalysts have hexagonal pore openings (2.5 nm in diameter) and high specific surface areas (1017 and 1151 m^2/g, respectively).

The Diels-Alder cycloaddition of cyclopetadiene and methyl acrylate was conducted in the absence or presence of acid catalyst as shown in Table 1. Without catalyst, the reaction was too slow and exhibited poor stereoselectivity because of relatively poor reactivity of methyl acrylate as a dienophile. With the aid of acid catalyst, competing reactions are polymerization of the diene

Table 1. Diels-Alder reaction of cyclopentadiene with methyl acrylate[a]

Catalyst	Yield/%	Endo:Exo	Polymer products /mg
None	6[b]	79 : 21	1[c]
BF_3•OEt_2(10 mol%)	39	96 : 4	171[d]
Zn^{2+}-K10	46	94 : 6	20[c]
H^+-Al-MCM-41	84	96 : 4	1[c]
Zn^{2+}-Al-MCM-41	90	95 : 5	14[c]

[a] The reaction was performed in CH_2Cl_2 at 0 °C for 1.5 h.
[b] The reaction was performed in CH_2Cl_2 at 0 °C for 10.5 h.
[c] Only polycyclopentadiene.
[d] The content of polycyclopentadiene and polyacrylate is approximately 10:1 by NMR.

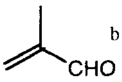
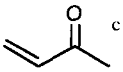
or dienophile, or both. A typical homogeneous Lewis acid, BF_3•OEt_2 (10 mol%), gave a high Endo/Exo ratio, but a low yield because strong acidity of BF_3•OEt_2 promoted the formation of polycyclopentadienes and polyacrylates in large amounts. In case of Zn^{2+}- K10,[10] a slight increase in the yield was observed. Apparently, Al-MCM-41[10] catalysts improved the synthetic yield maintaining high stereoselectivity. Especially, Zn^{2+}-Al-MCM-41 showed the highest yield.[11] In the presence of the solid acids, the polymeric by-products were derived only from cyclopentadiene. Irrespective of the use of homogeneous or heterogeneous catalyst, the high Endo/Exo ratios are intrinsic selectivity to the reaction between cyclopentadiene and methyl acrylate promoted by acid catalyst.

Higher catalytic efficiency of Zn^{2+}-Al-MCM-41 (51% yield, Endo/Exo=58:42) was also observed in the reaction of cyclopentadiene with methyl methacrylate (0 °C, 6 h), as compared with that of Zn^{2+}- K10 (5% yield, Endo/Exo=59:41).

K10 has an irregular pore structure and a broad mesopore distribution ranging from 2 to 10 nm.[12] By contrast, both H$^+$-Al-MCM-41 and Zn^{2+}-Al-MCM-41 have a straight-channel pore structure, and the size of the pore is 2.5 nm in diameter. We suppose that in the H$^+$-Al-MCM-41 and Zn^{2+}-Al-MCM-41, organic substrates can diffuse more smoothly and that the dienophile can be adsorbed tightly so as to be more activated at the acid sites on the internal surface of pores, leading to the higher catalytic performance, as compared with Zn^{2+}-K10.

Among a series of α, β-unsaturated carbonyl compounds, the reactivity as dienophile is generally recognized in the following order: acrolein > methacrolein > 3-buten-2-one (MVK) > methyl acrylate > methyl methacrylate. In the reactions of cyclopentadiene with methacrolein or MVK, Zn^{2+}-Al-MCM-41 has good catalytic activities. As shown in Table 2, however, there was little difference in the yield and stereoselection between Zn^{2+}-Al-MCM-41 and Zn^{2+}-K10 because methacrolein and MVK are reactive dienophiles toward cyclopentadiene in the Diels-Alder reaction.

Table 2. Diels-Alder reactions of cyclopentadiene with methacrolein or MVK [a]

	Zn^{2+}-K10 Yield/% (Endo:Exo)	Zn^{2+}-Al-MCM-41 Yield/% (Endo:Exo)
 [b]	68 (10 : 90)	70 (12 : 88)
 [c]	80 (96 : 4)	84 (96 : 4)

[a] Solid acid (50 mg).
[b] Cyclopentadiene (3 mmol), methacrolein (1 mmol), 0 °C, 1 h.
[c] Cyclopentadiene (5 mmol), MVK (1 mmol), 0 °C, 2 h.

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References and Notes

1 C. Kresge, M. E. Leonowicz, W. J. Roth., J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992); Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, and G. D. Stucky, *Nature*, **368**, 317 (1994).
2 J. March, "Advanced Organic Chemistry," 4th ed., John Wiley (1992), p. 839.
3 S. Yamabe, T. Dai, and T. Minato, *J. Am. Chem. Soc.*, **117**, 10994 (1995).
4 C. Cativiela, J. M. Fraile, J. I. Garcia, J. A. Mayoral, F. Figueras, L. C. de Menorval, and P. J. Alonso, *J. Catal.*, **137**, 394 (1992).
5 G. Isaacs, *Chem. Ber.*, **1987**, 47.
6 D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.*, **102**, 7816 (1980).
7 J. Kang and J. Rebek Jr, *Nature*, **385**, 50 (1997); E. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda, and Y. Aoyama, *J. Am. Chem. Soc.*, **119**, 4117 (1997).
8 R. Ryoo and J. M. Kim, *J. Chem. Soc., Chem. Commun.*, **1995**, 711; K. Ramesh Reddy, N. Araki, and M. Niwa, *Chem. Lett.*, **1997**, 637.
9 Analyzed by ICP.
10 K10 and H$^+$-Al-MCM-41 show almost the same acid strength of $-11.35 < H_0 \leq -8.2$ in CH_2Cl_2.
11 In a control experiment, no Diels-Alder reaction occurred by using 0.08 mmol of $ZnCl_2$ which corresponds to the amount of zinc ions included in 150 mg of Zn^{2+}-Al-MCM-41 (at 0 °C for 1.5 h). This result indicates that zinc ions in solution has no catalytic activity even if the zinc ions are leached out of Zn^{2+}-Al-MCM-41 during the reaction.
12 T. Shinoda, M. Onaka, and Y. Izumi, *Chem. Lett.*, **1995**, 493, 495.