

Nanoporous Solid Acid Catalyst for the Diels-Alder Reaction of 1,3-Dienes with Acrylates

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Nanoporous aluminosilicate, Al-HMS with a high aluminum content, strong acidity, and nanoporosity was found to catalyze the Diels-Alder reaction of 1,3-dienes with methacrylate and acrylate, and turned out to be a green alternative to homogeneous acid catalysts.

The Diels-Alder reaction is an important and widely used reaction in organic synthesis and in the chemical industry. Rate enhancement of this reaction has been achieved by the use of Lewis acids such as $\text{La}(\text{OTf})_3$,¹ 5 M LiClO_4 in Et_2O ,² solvents such as water,³ supercritical CO_2 ,⁴ and ionic solvent,⁵ and under high pressure,⁶ or radiation of microwave⁷ and ultrasound.⁸ Solid acids such as zeolite,⁹ clay,¹⁰ and alumina¹¹ also accelerate the reaction.

From a standpoint of Green Chemistry concerning safe handling and disposal, solid acids are expected to be alternatives to mineral acids and Lewis acids which have been conventionally employed in fine chemicals synthesis in chemical industry. We previously found that acidic mesoporous aluminosilicate, H^+ -Al-MCM-41 and Zn^{2+} -Al-MCM-41 with mesopores of 2.5 nm in diameter and high specific surface area of over 1000 m^2/g were efficient catalysts for the Diels-Alder reaction of methyl acrylate with cyclopentadiene.¹² However, when the catalysts were applied to the reaction of less reactive, bulkier dienophile like methyl methacrylate with acyclic 1,3-diene, poor results (chemical yield = < 50%) were obtained.

Then, we focused on another type of mesoporous aluminosilicate, HMS developed by Pinnavaia¹³ in order to find more active solid acid catalyst for the reaction. HMS has several advantages: 1) HMS can be easily formed in the sol-gel reaction of $\text{Si}(\text{OR})_4$ and $\text{Al}(\text{OR}')_3$ in the presence of primary alkylamine as template at room temperature (RT). 2) The acidic properties of HMS are dependent on the density and distribution of aluminum sites in the silicate structure. HMS with a high Al content and high dispersion of Al sites can be prepared via the sol-gel process. 3) The pore structure of HMS is rather wormhole-like than straight channel-like, but the pore-size distribution is narrow. 4) HMS consists of small primary particles forming textural mesoporosity. Pinnavaia urged that as compared with MCM-41, HMS should be more favorable for a catalyst in liquid-phase reactions owing to its textural mesoporosity which enables more reaction substrates to diffuse into the mesopores from a solution.¹⁴

To a vigorously stirred solution of $n\text{-C}_{16}\text{H}_{33}\text{NH}_2$ (3.31 mmol) in EtOH (153 mmol) and deionized water (257 mmol) was added at a time a homogeneous mixture of $\text{Si}(\text{OEt})_4$ (10 mmol) and $\text{Al}(\text{O}^i\text{Pr})_3$ (1.43 mmol) at RT. The mixture was vigorously stirred for 48 h at RT. The white gels formed were collected, dried at RT under a N_2 flow, and finally calcined in dry air in an electric furnace at 500 °C for 5 h. The prepared aluminum-containing HMS (abbreviated as Al-HMS) was analyzed with ICP and N_2 gas adsorption methods: a Si/Al ratio of 6.8, specific surface area of

1055 m^2/g , and pore diameter of 1.9 nm.

To Al-HMS (0.15 or 0.3 g) predried at 400 °C/0.5 mmHg (1 mmHg \approx 133.3 Pa) for 2 h was added a mixture of acrylate (1 mmol) and 1,3-diene (3 mmol) in solvent (6 ml) at -1 °C, and the mixture was stirred at -1 °C for a specified time. After filtration of Al-HMS, the Diels-Alder adducts were purified by distillation, or analyzed by GC. The stereoselectivity of the products was determined by NMR.

The acid catalysis of Al-HMS on the Diels-Alder reaction was influenced by the reaction media: nonpolar hydrocarbons such as hexane and cyclohexane are a more desirable solvent than benzene and dichloromethane.¹⁵

Table 1 shows the comparison of the acid catalysis between representative aluminosilicate solid acids such as Al-HMS, amorphous silica-alumina ($\text{SiO}_2\text{-Al}_2\text{O}_3$), commercially available solid acid K10, dealuminated Y-type zeolite (H-Y), and β -type zeolite (H- β) in the reaction of methacrylate or acrylate with isoprene or cyclopentadiene. Aluminum sites in the aluminosilicates are responsible for acid catalysis, and hence the weight of solid acid catalyst was adjusted so as to have the same or more amount of aluminum atoms than that of Al atoms contained in Al-HMS. In this comparison, Al-HMS (Si/Al = 6.8) was the best solid acid for the Diels-Alder reaction of methacrylate and acrylate with 1,3-dienes. It is likely that the aluminum atoms are homogeneously dispersed in the silicate framework and hence effectively function as acid sites though Al-HMS (6.8) contains a high content of aluminum.

Al-HMS (6.8) was confirmed to be recyclable as acid catalyst in the reaction of methyl acrylate with isoprene: 1st run, 94%; 2nd run, 90%; 3rd run, 87%. A gradual decrease in the catalytic activity is mainly due to irreversible adsorption of polymeric by-products from isoprene on Al-HMS which are unable to be removed with a rinse of organic solvent.

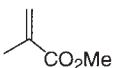

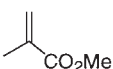



Table 2 summarizes the comparison between Al-HMS and AlCl_3 -catalyzed Diels-Alder reactions. The molar quantity of AlCl_3 used is the same as that of aluminum atoms in Al-HMS used. The acid catalysis of Al-HMS was found to be comparable to that of homogeneous Lewis acid AlCl_3 in the Diels-Alder reaction of acrylate derivatives. Considering that it is often a troublesome work to separate AlCl_3 from products, Al-HMS becomes an alternative to homogeneous acid catalysts in fine chemicals synthesis in terms of safe handling and easy work-up procedures of the solid acid.

In summary, we developed a green solid acid with strong acidity and nanoporosity which catalyze the Diels-Alder reaction of 1,3-dienes with relatively poor dienophiles like methacrylate.

We gratefully acknowledge Prof. Masakazu Iwamoto of Tokyo Institute of Technology for the analysis of Al-HMS with ICP.


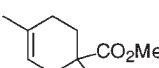

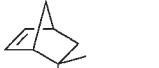

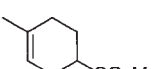

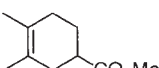

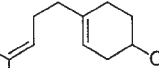

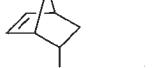
We dedicate this article to Professor Teruaki Mukaiyama on

Table 1. Comparison of solid acid catalysts in the Diels-Alder reactions^a

Dienophile	1,3-Diene	Acid catalyst (Si/Al ratio)	Weight of acid /g	Al content ^b /mmol	Time /h	Yield /%	Isomer ratio ^c
		Al-HMS (6.8)	0.3	0.64	32	87	95 : 5
		SiO ₂ -Al ₂ O ₃ (2.6) ^d	0.3	0.81	32	48	97 : 3
		K10 (4.3)	0.3	0.95	32	4	98 : 2
		dealuminated H-Y (7.5) ^e	0.3	0.59	32	17	98 : 2
		H-β (12.5) ^f	0.52	0.64	32	11	98 : 2
		Al-HMS (6.8)	0.15	0.32	8	95	54 : 46
		SiO ₂ -Al ₂ O ₃ (2.6) ^d	0.15	0.40	8	94	55 : 45
		K10 (4.3)	0.15	0.47	8	8	54 : 46
		dealuminated H-Y (7.5) ^e	0.15	0.30	8	48	55 : 45
		H-β (12.5) ^f	0.26	0.32	8	37	58 : 42
		Al-HMS (6.8)	0.15	0.32	18	94	97 : 3
		SiO ₂ -Al ₂ O ₃ (2.6) ^d	0.15	0.40	18	74	96 : 4
		K10 (4.3)	0.15	0.47	18	4	95 : 5
		dealuminated H-Y (7.5) ^e	0.15	0.30	18	32	98 : 2
		H-β (12.5) ^f	0.26	0.32	18	62	98 : 2

^aThe reactions were run at -1 °C in a hexane suspension of solid acid. ^bThe amount of aluminum atoms contained in the solid acid catalyst. ^cThe ratios of 1,4-/1,3-substituted isomers or end/exo isomers. ^dReference catalyst JRC-SAL-2 supplied from the Catalysis Society of Japan. ^eProton-exchanged dealuminated Y-type zeolite (HSZ-360HUA) supplied from Tosoh Corp. ^fReference catalyst JRC-Z-HB25 supplied from the Catalysis Society of Japan.

Table 2. Al-HMS- and AlCl₃-Catalyzed Diels-Alder reactions

1,3-Diene	Main adduct	Yield/% (Time/h)	Isomer ratio ^c
(a) The reactions of methyl methacrylate with 1,3-dienes.			
		87 (32) ^a	95 : 5
		63 (32) ^b	97 : 3
		95 (8) ^a	54 : 46
		66 (8) ^b	62 : 38
(b) The reactions of methyl acrylate with 1,3-dienes.			
		94 (18) ^a	97 : 3
		73 (18) ^b	97 : 3
		96 (8) ^a	---
		89 (RT, 1) ^b	---
		84 (18) ^a	96 : 4
		quant (8) ^b	95 : 5
		91 (2) ^a	96 : 4
		95 (2) ^b	97 : 3

^aThe reactions were run at -1 °C in a hexane suspension of Al-HMS (6.8). ^bThe reactions were run at -1 °C in a toluene solution of AlCl₃. ^cThe ratios of 1,4-/1,3-substituted isomers or end/exo isomers.

the occasion of his 75th birthday.

References and Notes

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- The reaction of isoprene with methyl acrylate in the presence of Al-HMS (6.8) was run at RT for 3 h in four solvents: hexane (the yield of the Diels-Alder adducts = 95%), cyclohexane (98%), benzene (85%), and dichloromethane (65%). The isomeric ratios of the adducts in the four solvents were 97 : 3–98 : 2.