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Entrapment of cyclopentadiene in zeolite NaY and its application for solvent-free Diels–Alder reactions in the nanosized confined environment

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Abstract—Nonpolar cyclopentadiene was stably entrapped as a monomer in the hydrophilic supercages of zeolite NaY. A monomer form of cyclopentadiene in the supercages was confirmed by ^{13}C MAS NMR spectroscopy. The adsorbed cyclopentadiene in the confined cavities performed the Diels–Alder reaction with typical dienophiles under solvent-free conditions more effectively than in organic and water media.

One of the major applications of crystalline microporous zeolites is for adsorbents: for example, adsorption separation of oxygen and nitrogen from air and linear and branched alkanes from the petrochemical cracking processes as well as desiccation of organic solvents and refrigerant gas.

The pore structure and its hydrophilic/hydrophobic character of zeolite are dependent on the crystalline type of zeolite and the ratios of Si and Al atoms in the zeolite framework. The more Al is involved, the more hydrophilic character the surface of zeolite has: for example, zeolites A with a Si/Al ratio of one are highly hydrophilic, whereas silicalites having few aluminum atoms show significant hydrophobicity and hence poor affinity for water.[1]

Concerning voluntary adsorption of organic molecules into zeolite cages, we have reported that polar, labile formaldehyde is stably stored in hydrophilic zeolite NaY as a monomer form without self-polymerization to paraformaldehyde at ambient temperature for a long period of time, and performs carbonyl-ene reactions in contact with various olefins effectively.[2]

Here we wish to report that *nonpolar* cyclopentadiene (CPD) is able to be spontaneously entrapped as a monomer inside the hydrophilic cages of zeolite NaY, and undergoes the Diels–Alder reactions with dienophiles such as acrylonitriles, acrylates, and methyl vinyl ketone inside the cavities *without solvent*.

The Diels–Alder reactions have frequently been employed for the formation of a six-membered carbon skeleton in synthesis of fine chemicals and pharmaceuticals. The rate enhancement of this reaction has been achieved by the use of Lewis acids,[3] in solvents such as supercritical CO_2[4] and ionic liquid,[5] and by the application of high pressure[6] or ultrasonic radiation.[7] In 1980, Rideout and Breslow demonstrated the Diels–Alder reactions were dramatically accelerated in water owing to 'hydrophobic effect':[8] Hydrophobic organic substrates tend to assemble in water so as to diminish the hydrocarbon–water interfacial area. Many organic chemists have paid much attention to the Diels–Alder reactions conducted in a hydrophilic, polar environment in terms of acceleration of organic reactions on exposure to 'hydrophobic effect' or 'internal pressure.'[9]

Olefinic compounds such as ethylene, furan, pyrrole, thiophene, and benzene are known to be adsorbed in hydrophilic zeolites.[10] Accordingly, CPD molecules possessing a 1,3-diene structure are expected to be similarly entrapped in the hydrophilic zeolite. As far as we know, however, the adsorption of CPD into zeolite and

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Keywords: Zeolite; Cyclopentadiene; Diels–Alder reaction; Internal pressure.

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the stability of a monomer CPD in the cavity have not been reported.

In this study, as an adsorbent we selected zeolite NaY (Si/Al = 2.4) composed of interconnected supercages of 1.3 nm in diameter with pore windows of 0.7 nm in diameter. The NaY has a specific surface area of 810 m^2/g, a pore volume of 0.34 mL/g, and hydrophilic supercages. CPD vapor in a N_2 flow was passed over NaY. When 3.4 mmol of CPD was adsorbed into 1 g of NaY, the adsorption was saturated.[11] In the saturated state, it was estimated that about 80% of the pore volume of NaY was occupied by the adsorbed CPD molecules, implying that every supercage on average contained five to six CPD molecules. As a control, CPD was also adsorbed on SiO_2 (MERCK, Silica gel 60; specific surface area: 500 m^2/g) adsorbing 2.0 mmol of CPD per gram of silica.

Firstly, the adsorbed cyclopentadiene in each support (symbolized as CPD@NaY and CPD@SiO_2, respectively), was investigated by the solid-state ^{13}C MAS NMR. All NMR experiments were carried out by means of single pulse direct excitation with proton decoupling (90° pulse = 5 μs, 5-s pulse delay, 1000 scans) and the probe temperature was maintained at 273 K. Chemical shifts were referenced to TMS as an internal standard, and sample spinning rates were adjusted to ca. 3 kHz.

In the ^{13}C MAS NMR spectra of CPD(2.0)@NaY, which indicates that 1 g of NaY contains 2.0 mmol of CPD (Fig. 1a), three sharp peaks were observed at δ 43, 134, and 137 ppm and a broad background signal near 110 ppm.[12] The three sharp peaks were assigned to a C-5 methylene carbon, C-1/C-4, and C-2/C-3 vinyl carbons, respectively. CPD in a $CDCl_3$ solution shows three peaks at δ 41.5, 132.2, and 133.0 ppm (Fig. 1c), while ^{13}C NMR of dicylopentadiene in $CDCl_3$ is shown in Figure 1d. By comparison of these spectra, it can be concluded that CPD molecules exist as a monomer form in NaY.

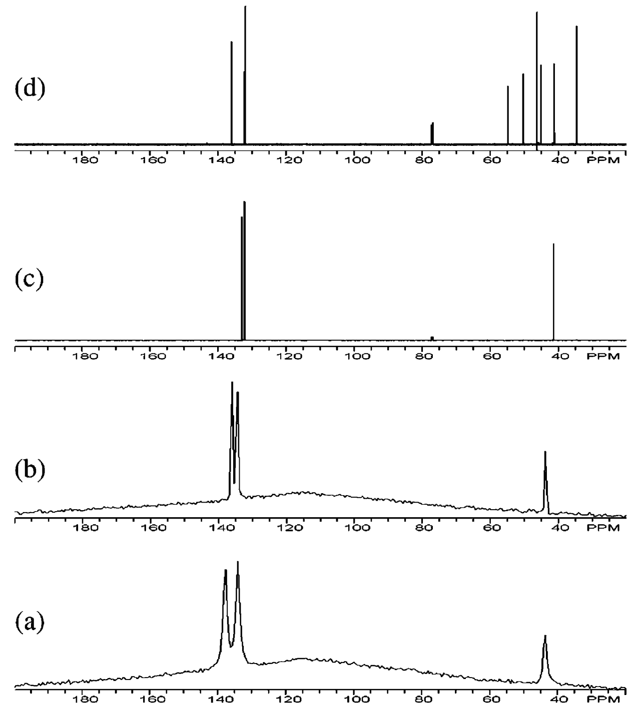


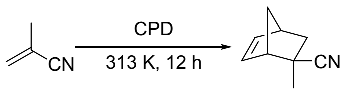
Figure 1. ^{13}C MAS NMR spectra of adsorbed cyclopentadiene, and ^{13}C NMR spectra of cyclopentadien and dicyclopentadiene in solution. (a) CPD(2.0)@NaY, (b) CPD(2.0)@SiO_2, (c) CPD in $CDCl_3$, and (d) dicyclopentadiene in $CDCl_3$.

The vinylic carbons in CPD(2.0)@NaY (134 and 137 ppm) have larger chemical shifts than those in CPD(2.0)@SiO_2 (133 and 135 ppm). We assume that the larger chemical shifts come from the π-interaction of CPD with Na^+ ions on NaY.[10]

Once nonpolar CPD molecules were involved in the hydrophilic cages of NaY, the entrapment was so tight that almost no desorption of CPD from CPD(2.0)@NaY was observed after the evacuation at 273 K under reduced pressure (133 Pa) for 1 h.

Secondly, the Diels–Alder reaction of CPD@NaY with methacrylonitrile, which has relatively poor reactivity toward cyclopentadiene was investigated *under solvent-free conditions* (Table 1). The adsorbed CPD content in NaY critically affected the reaction rate: The Diels–Alder reaction using CPD(3.0)@NaY smoothly proceeded to afford cycloadducts in a high yield (entry 1). By contrast, the reaction was retarded with a low content reagent, CPD(2.0)@NaY even though the total amount of CPD involved in the reaction was adjusted to be 3 mmol (entry 2). In the reaction with CPD adsorbed on SiO_2 possessing a random pore structure, the cycloaddition did not proceed smoothly (entry 3). The reason why the reaction using CPD(3.0)@NaY was well accelerated could be explained as follows: In the case of the low content reagent, two or three CPD molecules were estimated to bind to the hydrophilic polar surface of cages in NaY, resulting in low reactivity to methacrylonitrile. In contrast, with CPD(3.0)@NaY, loosely bound CPD molecules would reside in the center of the

Table 1. Diels–Alder reactions in various reaction media[a]



Entry	Reaction conditions	Yield (%)	*endo*:*exo*[b]
1	CPD(3.0)@NaY	92	12:88
2	CPD(2.0)@NaY	19	12:88
3	CPD(2.0)@SiO_2	25	13:87
4	CH_2Cl_2[c]	3	ND
5	CH_2Cl_2+NaY[d]	9	ND
6	Excess CPD[e]	14	12:88
7	H_2O[f]	3	17:83

[a] Methacrylonitrile (1.0 mmol) was reacted with CPD (3.0 mmol).
[b] Determined by ^1H NMR.
[c] CH_2Cl_2 (10 mL).
[d] NaY (1.0 g), CH_2Cl_2 (10 mL).
[e] Methacrylonitrile (1.0 mmol) was reacted with excess CPD (2.5 mL). The yield was determined by ^1H NMR using Ph_3CH as an internal standard.
[f] H_2O (10 mL).

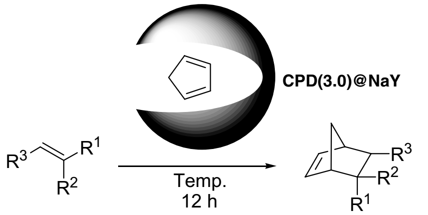
supercage, which are surrounded by the CPD interacting with the surface. The inner CPD molecules would be exposed to some ‘internal pressure’ from the hydrophilic zeolite surface, and hence would be activated to react with a dienophile which comes into the confined cavity.

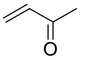
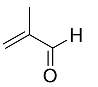
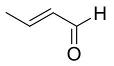
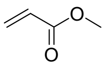
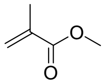
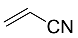
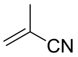
In order to confirm the advantages of the reaction performed in the zeolite cage, the reaction was also run in organic media such as CH_2Cl_2 and CPD (entries 4 and 6), giving only poor results. Interestingly, even in water we did not observe any obvious rate enhancement (entry 7). The comparison indicates that the Diels–Alder reaction is promoted more effectively in the NaY cavities where CPD and methacrylonitrile molecules are thickly packed than in organic solvents where organic substrates diffuse freely and occasionally bump into each other.

Only mixing CPD, methacrylonitrile, and powdery NaY in CH_2Cl_2 afforded the cycloaddition products in only 9% yield (entry 5).[13] This fact proves that the pre-adsorption of CPD molecules into NaY is essential to obtain high reactivity.

CPD(3.0)@NaY also reacted with other representative dienophiles to yield the corresponding cycloadducts in good yields (Table 2). Diastereoselection of the reactions was not specific to the reactions performed in zeolite, but rather governed by the inherent selectivity of each reaction.[14]

Table 2. Diels–Alder reactions using CPD(3.0)@NaY[a]



Entry	Dienophile	Temp (K)	Yield (%)	*endo*:*exo*
1		273	85[b]	84:16
2		293	79[c]	13:87
3		313	81[b]	78:22
4		293	90[b](14)[d]	75:25
5		313	73[b]	30:70
6		293	80[b]	54:46
7		313	92[b]	12:88

[a] A dienophile (1.0 mmol) was reacted with CPD (3 mmol) included in CPD(3.0)@NaY. *endo*/*exo* ratios were determined by ^1H NMR.

[b] Isolated yields.

[c] NMR yield using Ph_3CH as an internal standard.

[d] The figure in parentheses shows the yield of the reaction in CH_2Cl_2 (10 mL) without NaY.[13]

A typical procedure is described for the reaction of CPD@NaY and methacrylonitrile: Powdery NaY (1000 mg, JRC-Z-Y4.8 supplied from the Catalysis Society of Japan, activated at 673 K under below 133 Pa for 4 h) was placed in a flask. Vaporized cyclopentadiene (3.0 mmol, prepared by pyrolysis of dicyclopentadiene at 448 K) in dried N_2 flow was passed over NaY at 273 K for 1 h to afford CPD(3.0)@NaY (1198 mg). The amount of adsorbed cyclopentadiene was determined by an increment in the weight of NaY after adsorption. To CPD(3.0)@NaY containing 3.0 mmol of CPD was added neat methacrylonitrile (1.0 mmol) at 273 K using a syringe. After the powdery mixture was stirred for 12 h at 313 K, it was cooled down to 195 K. In order to extract the products, CH_2Cl_2 and CH_3CN were added at 195 K and the suspension was stirred for 5 min at 273 K. The mixture was filtrated and the solvents were removed. The crude products were purified by distillation using a Kugelrohr apparatus to afford 2-cyano-2-methylbicyclo[2.2.1]hept-5-ene in 92% yield (*endo*:*exo* = 12:88).

In summary, it was revealed that nonpolar cyclopentadiene was encapsulated in the hydrophilic supercages of ordinary zeolite NaY, and that remained intact as a monomer form. By simply putting together with dienophile reagents, the entrapped CPD showed the greater reactivity for the Diels–Alder reactions in the nanosized cages of NaY than in an organic or aqueous solution.

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11. The adsorption amount was determined by an increase in the weight of NaY after adsorption of CPD.

12. This broad background inevitably derived from the carbonaceous components around the sample probe in the NMR instrument.
13. The Diels–Alder reaction by mixing zeolite NaY with dienophiles and CPD in CH_2Cl_2 was also reported by Ghandi and co-workers. However, we were not able to reproduce their results: Najafi, H. M.; Ghandi, M.; Farzaneh, F. *Chem. Lett.* **2000**, 358–359.
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