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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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