Enhanced catalytic activity of H-β zeolite and MCM-41 in the cyclopentadiene Diels-Alder reactions

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The Diels-Alder cycloaddition reactions between cyclopentadiene and methacrolein are effectively catalyzed with the aluminum-modified mesoporous silica MCM-41 having a variety of metal cations in the pore such as Zn-, Co-, Ni- and La-MCM-41. The β zeolite (H-β) having protons in the pore shows a dramatically high catalytic activity in the same reaction to give a quantitative yield of cycloadducts at 0 °C in less than 1 h, and the dealuminated β zeolite is also a highly reactive catalyst. The Diels-Alder reactions of cyclopentadiene with 3-buten-2-one and 2-ethylacrolein are also activated with the H-β and Ni-MCM-41.

Key words: *zeolite, microporous catalyst, nanostructure, cation-exchange, Diels–Alder reaction*

1. Introduction

Carbon-carbon bond forming reactions by the aid of heterogeneous catalysts should be of great importance in the field of synthetic organic chemistry. Especially, catalysts immobilized in the size-defined pores of crystalline aluminosilicate zeolite can be effectively utilized for the discrimination of the size and/or shape of substrates so that not only the acceleration of reaction rate but also the improvement of selectivity and specificity is expected. zeolites, called Molecular Sieves (MS hereafter), capture only limited numbers of small molecules, such as water, ammonia, and methanol and so on, in the relatively small pores. However, mesoporous silicas (MCM-41, HMS, and SBA-15) and mesoporous aluminas having bigger pore size can also include substrates of ordinary molecular size in the pore.[1] If the transition structure of a certain reaction fits with the pore size and shape, high rate acceleration of the reaction would be expected. Examples have recently been reported for the cyclopentadiene Diels-Alder reactions[2-6] and carbonyl-ene reactions[7] in the pores of mesoporous silicas with the pore size of 1.5 to 10 nm.

We examined, in the cyclopentadiene Diels-Alder reactions, the catalytic activity of zeolites and mesoporous materials modified with a variety of internal cations through ion-exchange. In this communication, we present that some mesoporous materials such as metal-modified MCM-41 show significantly high catalytic activity in the Diels-Alder reactions of cyclopentadiene with methacrolein and related dienophiles, and that protonated β zeolite (H-β) having

protons as countercations induces dramatically high rate enhancement.

2. Experiment

Cation-exchange of zeolites and mesoporous materials: This can be performed by the repeated treatments with aqueous solution including excess amounts of an appropriate cation, followed by washing with distilled water, and the final drying at 300 °C in vacuo.

A typical experimental procedure: The Diels-Alder reactions were examined in the presence of solid mediators as mentioned below. To a mixture of cyclopentadiene (2.5 mmol), a dienophile (2.5 mmol), and triphenylmethane (0.125 mmol) as internal reference in deuteriochloroform (5 ml) was added zeolite or mesoporous material (100 or 200 mg/mmol). The resulting mixture was stirred at 0 °C for an appropriate period of time and a fixed volume (0.5 ml) of the reaction solvent was sampled. After the zeolite was filtered off, the filtrate was submitted to ^{1}H NMR analysis and the yield of cycloadduct was measured. All zeolite and mesoporous material were preactivated by heating at 300 °C in vacuo immediately prior to use.

3. Results and Discussion

We examined solid catalysts with a variety of pore sizes in the reactions of cyclopentadiene (**1**) and methacrolein (**2**). All the results are summarized in Table 1.

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Table 1. Cyclopentadiene Diels-Alder reactions to methacrolein over inorganic porous materials (part 1).
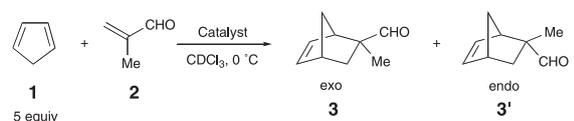
Entry	Catalyst[a]	Pore size	Si/Al ratio	Time/h	Yield/%[b,c]	exo/endo
1	none			21	nr	–
2	Na-MS4A	0.4 nm	1	21	nr	–
3	Ni-MS4A			21	nr	–
4	Na-13X	1	1	21	nr	–
5	Ni-13X			21	62	71/29
6	Mtl-13X[d]			21	nr	–
7	MCM-41	2.7	∞	19	53	86/14
8	Ni-MCM-41			16	88	81/19
9	Zn-MCM-41			16	77	82/18
10	Co-MCM-41			16	95	81/19
11	La-MCM-41			16	94	81/19
12	SBA-15	8.9	∞	7	6	71/29
13	Ni-SBA-15			19	nr	–

[a]200mg/mmol. [b]Determined by ^{1}H NMR using Ph$_3$CH as internal standard. [c]nr: no reaction. [d]Mtl: Na, Co(II), Cu(II), and La(III).

The Na$^+$ ion-exchanged MS 4A (Na-MS 4A, ϕ = 0.4 nm, Si/Al ratio = 1) and 13X zeolites (Na-13X, ϕ = 1 nm, Si/Al ratio = 1) were converted into the derivatives having other metal cations through the conventional ion-exchange procedures. Both Na- and Ni-MS 4A were totally inactive to give no trace of cycloaddition products (entries 2 and 3). On the other hand, Ni-13X, prepared by ion-exchange with nickel(II) ions, activated the reaction effectively to give a diastereomer mixture of cycloadducts (exo/endo = 79:21) in 62% yield after 21 h (entry 5).

Difference of the pore size seems to be critical for the effective catalysis, indicating that the reaction is more effectively catalyzed in the pore.[8] However, other metal derivatives such as Na-, Co-, Cu-, and La-13X were totally ineffective under the comparable reaction conditions (entry 6). Nickel(II) ion incorporated in the pore was special to work well as catalyst. It should be emphasized that simple ion-exchange of the original sodium cations of zeolites leads to a high catalytic activity.

Mesoporous silica MCM-41, having honeycomb-shaped channels with a relatively big diameter of ϕ = 2.7 nm,[1] can include compact-sized molecules such as cyclopentadiene and methacrolein in the channel.[9] Accordingly, enhancement of the reaction rate is expected in the limited reaction space of the channel. So, the aluminum-modified mesoporous silica Na-MCM-41 was prepared and it was further converted into Ni-MCM-41 by cation-exchange. Use of Ni-MCM-41 as catalyst in the above Diels-Alder reaction enhanced the reaction rate to give the exo/endo mixture of cycloadduct in 88% of the combined yield (entry 8). Not only Ni-MCM-41 but also the derivatives containing other metal cations such as Zn-, Co-, and La-MCM-41 were active as well (entries 9-11). Regardless of the low aluminum contents estimated for the metal-modified MCM-41,[10] such a high catalytic activity observed was surprising. This

was mainly based on the size effect of MCM-41 since MCM-41 itself also behaved as active catalyst (entry 7). SBA-15 is another mesoporous silica which has even bigger pore size with a diameter of 8.9 nm. However, the nickel(II) modified derivative Ni-SBA-15[10] showed no catalytic activity (entry 13), and SBA-15 itself does only a low reactivity (entry 12, 6%). The pore size of SBA-15 is probably too big for the maximum catalytic activation.

H-β zeolite has a much bigger Si/Al ratio of 21 and a smaller pore size of ϕ = 0.7 nm as compared with 13X zeolite. This zeolite was found to work as highly reactive catalyst for the Diels-Alder reaction between cyclopentadiene (**1**) with methacrolein (**2**) so that the reaction was complete in less than 1 h at 0 °C in deuteriochloroform (entry 2 of Table 2). Its catalytic activity is much higher than that of trifluoroacetic acid, as homogeneous protonic acid, which was used in a large excess of 25 equivalent (entry 1).[11] The detailed time course for the reaction between **1** and **2**, in the presence of H-β is shown in Fig. 1.

The reaction was actually so fast that the cycloadduct was produced in 70% yield after 2 min and almost quantitative in less than 30 min. To the best of our knowledge, this is one of the fastest Diels-Alder reactions promoted by inorganic porous material catalysts.
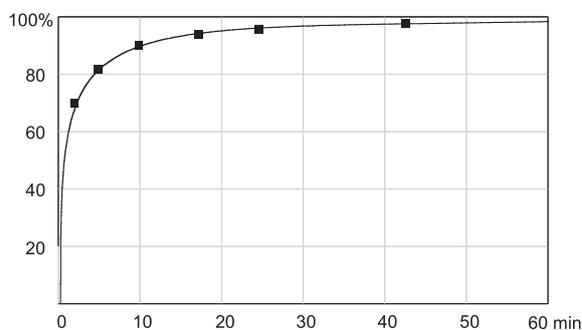
Fig.1 Time course for the cyclopentadiene Diels-Alder reaction to methacrolein in the presence of H-β zeolite (CDCl$_3$, 0 °C).

On the other hand, four kinds of H-type zeolites shown in Table 2 having different pore sizes and Si/Al ratios showed no catalytic activity at all (entries 4-7): Thus, ferrierite (ϕ = 0.42-0.54 nm) and ZSM-5 (ϕ = 0.51-0.58 nm) having smaller pores, mordenite (ϕ = 0.65-0.7 nm) containing more aluminate anions and hence more protons in the pore, and Y (ϕ = 0.74 nm) having a little bigger pore size and much more protons are absolutely inactive. These results indicate that cation content in the pore and the pore size close to 0.7 nm are not so essential factors for the high catalytic activity observed in the catalysis of H-β. The internal protons are not always necessary since the dealuminated H-β (Si/Al = 894) also showed a comparably high catalytic activity (entry 3).[12]

Table 2. Cyclopentadiene Diels-Alder reactions to methacrolein over a variety of zeolites (part 2).[a]

Entry	Catalyst[b]	Pore size	Si/Al Ratio	Time/h	Yield/%[c]	exo/endo
1	CF_3COOH[d]			20	67	83/17
2	H-β	0.7 nm	21	0.9	97	76/24
3	deAl-β[e]		894	3	93	71/29
4	Ferrierite	0.42-0.54	7	22	nr	–
5	ZMS-5	0.51-0.58	100	12	nr	–
6	Mordenite	0.65-0.7	10	12	nr	–
7	Y	0.74	2.5	12	nr	–

[a]Reaction condition is equivalent to those of the reactions shown in Table 1 except for the catalytic amounts. [b]100mg/mmol unless otherwise stated. [c]Determined by ^1H NMR using Ph_3CH as internal standard (nr: no reaction). [d]10 mol%. [e]deAl-β: dealuminated β-zeolite.

Such a dramatic rate enhancement by H-β in the cyclopentadiene/methacrolein Diels-Alder reaction was a big surprise to us. Accordingly, we further examined the catalysis of some other β zeolites prepared by different synthetic methods. The H-β zeolite we have employed in the reaction in Table 2 is coded HSZ-940HOA[13] (Table 3, entry 1). Other four samples such as HSZ-930HOA, BY-20, BY-40, and SB-8, were all assigned to be the H-type of β zeolites on the basis of the characteristic XRD patterns,[14] However, these showed quite different catalytic activities as shown in Table 3. HSZ-940HOA is the most active catalyst among them, and HSZ-930HOA and SB-8 are the next. Probably, not the shape of micro pore of these zeolites but any structural defects located in the micro pore would be a key portion where the Diels-Alder reaction is activated.

Table 3. Cyclopentadiene Diels-Alder reactions to methacrolein over other H-β zeolites

Entry	Catalyst[a]	Si/Al Ratio	Time/h	Yield/%[b]	exo/endo
1	HSZ-940HOA[c]	21	1	quant	78/22
2	HSZ-930HOA	13.5	22	quant	82/18
3	BY-20	11.6	22	35	77/23
4	BY-40	20	22	77	74/26
5	SB-8	21.6	22	95	73/27

[a]100mg/mmol. [b]Determined by ^1H NMR using Ph_3CH as internal standard. [c]H-β zeolite.

Diels-Alder reactions of cyclopentadiene with α,β-unsaturated carbonyl dienophiles other than **2** including 3-buten-2-one (**4**), 2-ethylacrolein (**5**), and t-butyl acrylate (**6**), were examined in the presence of either H-β or Ni-MCM-41 (Table 4). H-β acted again as reactive catalyst in the reactions with **4** and **5** to give quantitative yields the exo/endo mixtures of the corresponding cycloadducts although a prolonged reaction time of 24 h was needed (entries 2 and 5, reaction conditions were shown in the footnote of Table 4), while Ni-MCM-41 was a little less reactive in the reaction with **5** (entry 6). A bulky acrylate **6** (entries 8 and 9) and dienophiles bearing a β-substituent such as E-2-butenal, E-2-hexenal, cinnamaldehyde, and E-2-methyl-3-phenyl-2-propenal were not reactive at all.

Table 4. Cyclopentadiene Diels-Alder reactions to some dienophile over H-β zeolite and Ni-MCM-41.

Entry	Dienophiles	Catalyst	Yield/%
1		none	68
2	⟍⟍COMe **4**	H-β-zeolite	quant
3		Ni-MCM41	quant
4		none	–
5	⟍⟍CHO **5**	H-β-zeolite	quant
6	Et	Ni-MCM41	33
7		none	–
8	⟍⟍COOBu-t **6**	H-β-zeolite	8
9		Ni-MCM41	3

Catalyst (100 mg / mmol), Ph_3CH and a dienophile (0.5 mmol each), cyclopentadiene (2.5 mmol), at 0 °C in $CDCl_3$, 24 h.

The dramatic and specific rate enhancement observed in the reaction of **1** with **2**, unlike the reactions to other α,β-unsuturated carbonyl dienophiles **4-6**, would be due to the specifically high stabilization of the transition structure or structurally similar reacting species in the pore of H-β. If this is the case happened, small structure difference of substrate should sharply affect the reaction rate. Accordingly, we further examined the reaction of substituted cyclopentadiene with **2** (Scheme 1). A low rate enhancement appeared in the reaction of methylcyclopentadiene (**7**) with methacrolein (**2**) under the catalysis of H-β at 0 °C, giving a striking contrast to the case of cyclopentadiene reaction. On the other hand, Ni-MCM-41 having spacious pores and a protonic homogeneous catalyst were found to be effective in the acceleration of the reaction giving cycloadducts in 83 and 87% yields, respectively. Thus, the small change of substrate structure as seen in **7** caused only a negligible effect in the reactions in open space of Ni-MCM-41, but the serious inhibition of reaction happened in the size-fitting pores of H-β.

Scheme 1. Diels-Alder reactions of methylcyclopentadiene to methacrolein over various catalysts.

Catalyst (100 mg), Ph_3CH (0.125 mmol), **2** (0.5 mmol), **7** (2.5 mmol), at 0 °C in $CDCl_3$.

Catalyst	Time/h	Yield/%[a]
none	26	trace
CF_3COOH[b]	20	87
H-β	26	trace
Ni-MCM41	26	83

[a]Determined by ^1H NMR based on the internal standard Ph_3CH. [b]10 mol%.

Adsorption test for either cyclopentadiene (**1**) or methacrolein (**2**) in the pore of H-β was investigated at room temperature. Contrary to our expectation, the less polar diene **1** was captured readily and the more polar α,β-unsaturated aldehyde **2** was not adsorbed.[15] When 0.5 mmol of **1** was treated with 100 mg of H-β

in CDCl$_3$, the zeolite gradually colored orange and finally darkened in a period of 2 h with the weight loss of 12% of **1** in the chloroform solution (Scheme 2). Methylcyclopentadiene (**7**) was more readily captured under the equivalent conditions with rapid color change. Similar adsorption of diene **1** was also observed with MCM-41 (Scheme 3, entry 1)

Scheme 2. Weight percentage of dienes captured in the pore of H-β zeolite.

Contact time	Cyclopentadiene	Methylcyclopentadiene
15 min	2 %	22 %
60	6	40
120	12	

Conditions: H-β zeolite (100 mg), diene **1** (0.5 mmol), Ph$_3$CH (0.125 mmol each) in CDCl$_3$ (5 ml), rt.

The H-β and MCM-41, in which diene **1** had been captured, were used in the catalytic activity test with the reactions between **1** and **2** in CDCl$_3$ solutions, and the extremely decreased catalytic activity was observed for both catalysts (Scheme 3, entries 1 and 2). This observation is inconsistent with the previously reported case.[16] On the other hand, Ni-MCM-41 maintained the initial reactivity even after it was used for the adsorption test (entry 3). Reactivation of the zeolites used for the adsorption test was difficult only by heating at 200 °C in vacuo (23% in 18 h), indicating that diene **1** was tightly captured in the pore, probably through some chemical reactions.[17] With these results, we think that diene **1**, and **7** as well, was activated in the pore of H-β and reacts with **2**.

Scheme 3. Catalytic activity of H-β zeolite before and after the capture of cyclopentadiene in the pore.

$$\textbf{1}\ +\ \textbf{2}\ \xrightarrow[\text{0 °C, 22 h}]{\text{H-β zeolite (100 mg)}}\ \textbf{3}\ +\ \textbf{3'}$$

2.5 mmol 0.5 mmol
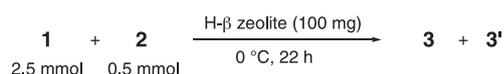
- H-β zeolite (100 mg), diene (0.5 mmol), CDCl$_3$ (5 ml), rt, 24 h.
- The H-β zeolite was separated, washed, and dried. This (100 mg/mmol) was used as catalyst for the reaction 1.
- New H-β zeolite preactivated (100 mg/mmol) was used in the reaction 2.

Entry	Zeolite	Captured/%	Reaction 1	Reaction 2	exo/endo[a]
1	H-β	65	17[b]	quant[b]	83/17
2	MCM-41	61	14	56	78/22
3	Ni-MCM-41	10	88	88	83/17

[a]For the reaction 2. [b]Reaction time: 2 h.

In summary, zeolites such as Mtl-MCM-41, Ni-13X, and β zeolites enhance the reaction rates of Diels-Alder reactions of cyclopentadiene and methylcyclopentadiene to α,β-unsaturated carbonyl compounds. Especially effective was H-β zeolites such as HSZ-940HOA, HSZ-930HOA, and SB-8. The reaction of cyclopentadiene to methacrolein in the presence of HSZ-940HOA at 0 °C is complete in less than 1 h giving a quantitative yield of the corresponding cycloadduct.

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8. Outer surface occupying ca 10% of the total surface of these zeolites shows a lower catalytic activity than that of inner surface of the pore.

9. The short distance diameter of cyclopentadiene is estimated to be 6.5 Å and that of methacrolein 6.3 Å based on the Chem3D-optimized structures.

10. Treatment of mesoporous silicas such as MCM-41 and SBA-15 with trimethylaluminum gives the aluminum-modified framework part of which is further converted to aluminate. Metal derivatives can be prepared by the conventional cation-exchange procedure. However, the cationic metal content of the metal modified mesoporous silica is usually very low.

11. Proton content of H-β zeolite is estimated to be 0.025 mmol / gram.

12. The dealuminated β zeolite can be prepared upon treatment of H-β zeolite with strong acid solution. The small Si/Al ratio (= 894) shows that most of the aluminum, and therefore counter protons, was eliminated by this conversion.

13. Both HSZ-940HOA and HSZ-930HOA were kindly supplied by Tosoh Corporation.

14. BY-20, BY-40, and SB-8 prepared by us were all assigned to β̃types on the basis of the XRD analysis.,

15. Change of the concentrations of substrate in CDCl$_3$ solution containing triphenylmethane as internal standard was measured by ^{1}H NMR analysis, before and after the treatment with H-β.

16. Similar tight adsorption of diene **1** in Na-Y zeolite has been reported: Imachi S.; Onaka, M. *Tetrahedron Lett.* **2004**, *45*,

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17. Weight loss of 65% and 61% was measured for diene **1** with H-β and MCM-41, respectively, under the conditions shown in Scheme 3. Solid NMR spectral analysis indicated that dienes **1** and **7** were probably captured through polymerization in the pore.