

Molecular Behaviors of Formaldehyde Encapsulated in Supercages of Zeolite NaY with Different Loadings and its Intrinsic Reactivity for the Carbonyl-ene Reaction with α -Methylstyrene[#]

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Abstract

The reactivity of formaldehyde (HCHO) adsorbed in the supercages of zeolite NaY toward α -methylstyrene for the carbonyl-ene reaction was very dependent on the loading amount of HCHO in the NaY pores. We first prepared a series of NaY samples with different amounts of HCHO, and applied them to the carbonyl-ene reaction with excess amounts of α -methylstyrene to evaluate their intrinsic reactivities. It was found that one formaldehyde molecule adsorbed in one supercage of NaY produced 3-phenylbut-3-en-1-ol in the highest yield (83%), while for higher loading amounts of HCHO on NaY, lower yields of the product were obtained because the supercages were narrowed by the HCHO molecules as well as the homoallylic alcohol product and its over-reaction products. We next investigated their states of HCHO adsorbed in the pores by ¹³CDD/CPMASNMR analysis. When three HCHO molecules were adsorbed in a supercage, it was clarified that all the HCHO was exclusively encapsulated in a monomeric form, while most of the adsorbed HCHO with much higher loading amounts was transformed into 1,3,5-trioxane inside the supercages of NaY as well as paraformaldehyde outside the supercages.

1. Introduction

Observation of labile molecules having a short lifetime, such as cyclobutadiene¹ and carbenes,² or reaction intermediates of hemiaminals³ and iminium ions⁴ by NMR even at ambient temperature for hours has been realized by generating and isolating them inside a specific nanospace provided by closed capsule carcerands,¹ open-ended cavitand receptors² or metaldirected self-assembled compounds.^{3,4} In these examples, the interior components of the host molecules interacted with the guest labile molecules and stabilized them. In contrast to these artificial organic host molecules, we have been interested in porous zeolites as inorganic host alternatives possessing cations located at specific sites on the extra-framework of the pores. The cations with coordination ability enable guest molecules to be fixed on specific sites in the subnano-sized confined pores of the zeolite. In some instances, the fixed guest molecules are activated so as to react with another externally provided reagent to afford the desired coupling products because the pores of the zeolite have intrinsic windows open to the external environment. Taking advantage of these zeolite characteristics, we have been engaged in incorporating unstable chemical species, such as acrolein⁵ and propynal,⁶ and allowing them to undergo novel organic reactions. One of our recent studies involved preserving unstable secondary benzylic carbocations in the zeolite pores and successfully observing them by ¹³C MAS NMR under ambient conditions, and elucidated why such labile carbocations could survive in the zeolite pores.⁷

Zeolites⁸ are microporous crystalline aluminosilicates and have been widely studied as catalysts, molecular sieves and adsorbents in both academic research and industrial applications.⁹ Zeolites are composed of a negatively charged porous aluminosilicate framework and compensating extra-framework cations, such as sodium, potassium and calcium.

Formaldehyde is an essential reagent not only for the homologation of organic compounds but also for the synthesis of



Figure 1. Quantum chemical calculation results for the trimerization equilibria of HCHO in the gas and adsorption phases. The interactions of the carbonyl or ether oxygens with the sodium ions in a supercage of NaY are indicated by the blue dotted lines.

valuable polymer materials,¹⁰ such as melamine resins, phenolic resins, polyoxymethylenes, etc. However, because of its low boiling point $(-19 \,^{\circ}\text{C})$ and high susceptibility to selfpolymerization into a cyclic trimer, 1,3,5-trioxane ((HCHO)₃) and chain-like polymers, paraformaldehyde,¹¹ and harmful properties to humans, we often encounter a lot of difficulties in utilizing the reagent in typical chemical laboratories.

In our first report,¹² we discovered that HCHO could remain monomeric without polymerization for months even at ambient temperature only when a small amount of gaseous HCHO was encapsulated into the pores of the sodium ion-exchanged Y-type zeolite (NaY), which is represented as HCHO@NaY. Maintaining the monomer form of HCHO was confirmed by ¹³C MAS NMR in which only carbonyl carbons were detected with an 8-ppm higher chemical shift at 204 ppm from 196 ppm for the free HCHO, definitely indicating that the carbonyl group was interacting with a sodium ion in the zeolite pores.

We also disclosed why HCHO was significantly stabilized in the NaY pores based on quantum chemical calculations.¹³ As shown in Figure 1, the calculation was targeted at a trimerization equilibrium between 3 molecules of HCHO and one molecule of (HCHO)₃, which was considered to be the most preferable oligomer to be accommodated inside the 1.3-nm-sized pores of NaY, which are referred to as supercages. It was found that (HCHO)₃ was much more stable than the three HCHO molecules in terms of the enthalpy term, having a negative ΔG value of -2.8 kcal/mol, in which ΔG indicates the difference in the Gibbs free energy for the equilibrium. On the contrary, in the adsorbed state, the difference in the adsorption energies of both substrates coordinating to the Na⁺ ions in the NaY considerably reduced the advantage of (HCHO)₃ in the enthalpy term over HCHO and hence produced a positive ΔG of 7.2 kcal/mol. Under these situations, it was deduced that the adsorption of the substrates into NaY affected the equilibrium in favor of HCHO over (HCHO)₃.

In addition to such efficient stabilization of HCHO in NaY, we also found that the encapsulated HCHO in NaY was concurrently activated sufficiently to react with subsequently-added olefins through the carbonyl-ene reaction to produce the corresponding homoallylic alcohols in excellent yields.¹² Considering that no carbonyl-ene reactions proceeded in the absence of NaY, it is worth noting that the sodium ions in NaY not only effectively work as strong coordination sites to carbonyl compounds, but also show efficient Lewis acid catalysis for the reactions. Such potentials of sodium ions have not been widely recognized in conventional synthetic organic chemistry.

The encapsulated HCHO is thus expected to have a significant potential as a safe and user-friendly alternative to gaseous HCHO itself for relatively small-scale organic synthesis. In this study, we focused on clarifying in detail how the loading amount of HCHO per supercage of NaY determines the behavior of the introduced HCHO and is responsible for the reactivity of the immobilized HCHO toward the carbonyl-ene reaction with α -methylstyrene to produce 3-phenylbut-3-en-1-ol.

In this paper, we describe each sample of formaldehyde adsorbed in the NaY zeolite as "HCHO(n)@NaY" in which n stands for the number of formaldehyde molecules per supercage.

2. Experimental

2.1 Materials and Analysis. Powdery NaY (Si/Al = 2.75, HSZ-320NAA) was obtained from the Tosoh Corporation (Japan), which has 0.63 mmol of supercages per g of NaY and 2.5 mmol of sodium ions at Site II per g of NaY. α -Methylstyrene was purchased and used after distillation.

The ¹³C DDMAS (Dipolar Decoupling/Magic Angle Spinning) and CP MAS (Cross Polarization/Magic Angle Spinning) NMR spectra were recorded with a Bruker Avance III 400 WB USPlus spectrometer operated at 100 MHz with a 4-mm zirconia rotor at a spinning rate of 10 kHz and 25 °C. Glycine was employed as an external standard to calibrate the chemical shifts.

The ¹H and ¹³C NMR spectra of the organic products were recorded in CDCl₃ with a Bruker Avance III 500 USPlus NMR spectrometer operated at 500 MHz for ¹H and 126 MHz for ¹³C. The chemical shift values (δ ppm) for ¹H and ¹³C were referenced to Me₄Si and the residual solvent resonances, respectively. The coupling constants (*J*) are given in Hz.

The GC-MS analysis was performed using a Shimadzu GCMS-QP2010 Plus with a capillary column (HP-1: 0.25 mm \times 30 m, 0.25 μ m; Agilent Technologies Inc.) at the injection/column temp. of 250 °C/elevated temperature to 250 °C.

2.2 Procedure for the Activation of NaY Zeolite. The NaY zeolite (1.26 g) was placed in a flask and heated at 400 °C for 4 h in a vacuum at less than 27 Pa. After the flask was cooled to ambient temperature, the flask was charged with nitrogen gas and capped. The amount of the activated NaY (\sim 1.0 g) was determined by the weight difference of the flask.

2.3 Preparation of of HCHO(1)@NaY. A specific amount of paraformaldehyde (for example, 25 mg, 0.83 mmol) was first placed in a flask which was connected with a plastic tube to a second flask containing the activated NaY (~1.0 g). The gaseous HCHO produced by heating the paraformaldehyde at $150 \,^{\circ}$ C for 10 min was introduced by flowing nitrogen at ~1 mL s⁻¹ into the gently stirred NaY at room temperature, and then the capped flask containing the HCHO-adsorbing NaY was weighed. The change in the weight of the flask determined the adsorbed amount of HCHO (~19 mg, 0.63 mmol),

which corresponded to one formaldehyde molecule adsorbed in a supercage of NaY (i.e., HCHO(1)@NaY).

2.4 Preparations of Different Amounts of Formaldehyde-Adsorbing NaY (HCHO(n = 2, 3, 4, 8, 14, 18, 20, or21)@NaY). In the first flask was placed the proper amount of paraformaldehyde. The adsorption procedure was almost the same as the 2.2 protocol, and repeated until the adsorbed weight of HCHO reached the desired amount for the number "n" in HCHO(n)@NaY.

2.5 Carbonyl-ene Reaction of HCHO(n = 1, 2, 3, or4)@NaY with α -Methylstyrene. α -Methylstyrene (60 equivalents to HCHO), which was distilled with CaH₂, was added to the flask containing a specific amount of HCHO(n)@NaY in a nitrogen atmosphere. The flask was sealed with a cap and heated at 50 °C for 1 h under neat conditions. Methanol (15 mL) was then added to stop the reaction as well as extract the organic products from the supercages of NaY. The mixture was filtered, and the residue on the filter paper was suspended in 15 mL of methanol and filtered again. This procedure was repeated twice. The filtrates were collected and evaporated in a vacuum. In order to remove the remaining fine NaY powder, dichloromethane (20 mL) and magnesium sulfate (10 mg) were added, followed by filtration. The filtrate was evaporated in a vacuum. 1,1,2,2-Tetrabromoethane was added as an internal standard to the crude products of the carbonyl-ene reaction, and the ¹HNMR vield was determined based on the signal of CH_2OH of the alcohol product at $\delta = 3.73$ ppm.

2.6 Carbonyl-ene Reaction between HCHO(3)@NaY and 3-Phenylbut-3-en-1-ol. To HCHO(3)@NaY (3.2 g, 5.8 mmol HCHO) in a flask were added dry cyclohexane (20 mL) followed by 3-phenylbut-3-en-1-ol (320 mg, 2.2 mmol). The flask was sealed and the mixture was heated with stirring at 50 °C for 1 h. The reaction was worked up using the same procedure as that described in Section 2.5. The filtrates were collected and evaporated in a vacuum. The products were separated by column chromatography on silica gel (Wakosil C-200) into the two fractions with different polarity.

3. Results and Discussion

3.1 Comparison between the Reactivities of HCHO-(n = 1-4)@NaY for the Carbonyl-ene Reactions with α -Methylstyrene. In case of the faujasite-type zeolite (FAU), it is well-known that cations can occupy five types of cation sites, i.e., I, I', II, III and III' in the framework as illustrated in Figure 2.¹⁴ Sites I and I' being located inside the framework do not act as adsorption sites because the inner space of the tetradecahedron sodalite cage and the hexagonal prism is too small for organic molecules to be accommodated. The sites II, III and III' facing the 1.3-nm diameter supercage are effective for adsorbing substances. Among the faujasite zeolites, ¹⁵ NaY with aluminum contents of Si/Al >2 holds its sodium ions only on sites I, I' and II. In our study, we used NaY with Si/Al =2.75. Therefore, we only have to focus on the cations on site II when organic molecules undergo adsorption in the supercages of NaY. There are four sites II in a supercage, and the corresponding sodium ions on sites II are tetrahedrally located near the surface of the supercage.

We were initially engaged in demonstrating the relation between the number of HCHO molecules adsorbed in a supercage



Figure 2. Location of cation sites in FAU. Sites I and I' are inside the narrow cages. Sites II are in front of the 6-rings facing the supercages. Site III is on the 4-rings and site III' is next to the 12-ring windows.



Scheme 1. The carbonyl-ene reaction of α -methylstyrene with HCHO(n)@NaY.

Table 1. The ¹HNMR-based yield of the carbonyl-ene reactions of HCHO(*n*)@NaY with α -methylstyrene^{a)}

Yield/%	n = 1	n = 2	<i>n</i> = 3	<i>n</i> = 4
2	83	70	57	37
5 ^{b)}	0	2	5	7
6 ^{b)}	0	0	0	2

a) Reaction conditions: HCHO/ α -methylstyrene = 1/60, neat, 50 °C for 1 h. b) Concerning the side-products, **5** and **6**, see Section **3.4**.

and their reactivity for the carbonyl-ene reaction with α methylstyrene: A series of HCHO(n = 1, 2, 3 and 4)@NaY samples using 1.0 g of the activated NaY were prepared and applied to the reaction with a large excess of α -methylstyrene (60 equivalents to the corresponding HCHO)¹⁶ without a solvent at 50 °C (Scheme 1). After heating at 50 °C for 1 h, methanol was added to completely extract the products from the supercages of NaY. After removing the NaY, the organic extracts with dichloromethane were condensed and analyzed by NMR.

For the reactions of HCHO(n = 1)@NaY encapsulating *one* HCHO molecule in *one* supercage as shown in Table 1, the only product was 3-phenylbut-3-en-1-ol (2). For n = 2, 3 and 4, however, small amounts of the side-products, such as 5 and 6, in Scheme 2 were formed besides the desired product (2), which were confirmed by ¹H NMR analysis. The formations of 5 and 6 will be discussed in detail in Section 3.4. It is clear that the yield of the product 2 was very dependent on the number (*n*) of adsorbed HCHO molecules in a supercage of NaY. In the case of n = 1 the yield was the highest at 83%, but that noticeably declined to 37% for n = 4.

3.2 ¹³C Solid NMR Observations of Chemical Species Included in HCHO(n = 1-4)@NaY. In order to understand the cause of the drastic reduction in the yield with the change in n = 1 to 4, the HCHO(n = 1-4)@NaY samples were analyzed



Scheme 2. The carbonyl-ene reaction of HCHO@NaY with α -methylstyrene 1, followed by another carbonyl-ene reaction as well as consecutive polyoxymethylenations with excess HCHO.



Figure 3. ¹³C solid NMR spectra of HCHO(n)@NaY samples (DD MAS spectra (DD) for (a) n = 1, (b) n = 2, (c) n = 3, (d) n = 4, (e) n = 8, (f) n = 14, (i) n = 21, and CP MAS spectra (CP) for (g) n = 18, (h) n = 20, (j) n = 21).

by ¹³C solid NMR in order to probe the adsorption forms of HCHO. The ¹³C DDMAS NMR spectra are shown in Figure 3. In the spectra of HCHO(n = 1-3)@NaY, only sharp signals of the carbonyl in HCHO were observed at $\delta = 204$ ppm, indicating only monomeric HCHO remained in such sparsely adsorbed samples (Figure 3a-3c). Conversely, in the spectrum of HCHO(n = 4)@NaY, a small, broad signal appeared at around 94 ppm in addition to the signal of the monomeric HCHO (Figure 3d). This broad signal was presumed to be paraformaldehyde, a polymer of HCHO, or 1,3,5-trioxane (HCHO)₃, a cyclic trimer of HCHO. Comparing the authentic samples of paraformaldehyde at 88 ppm and (HCHO)₃ at 94 ppm independently adsorbed in NaY by ¹³C DD MAS NMR, the broad signal was assigned to (HCHO)₃ in NaY.¹⁷ It can be said that for the sample of HCHO(n = 4)@NaY with the more densely loaded HCHO in NaY, HCHO was partially converted into (HCHO)₃ in the pores. Although the (HCHO)₃ peak was considerably small, the formation of (HCHO)₃ led to the decrease in the yield of the carbonyl-ene reaction product. In fact, it was confirmed in a separate experiment that the reaction of (HCHO)₃ with α -methylstyrene to 2 did not proceed at 50 °C.



Figure 4. The number (*n*) of loaded HCHO molecules per supercage in NaY as well as the HCHO weight (mg) per gram of NaY versus the amount (mg) of paraformaldehyde for pyrolysis to generate monomeric HCHO.

It has now been clarified that HCHO is preserved in its monomer form at ambient temperature when sparsely adsorbed (n = 1-3) in the NaY supercages, and forms (HCHO)₃ only when densely adsorbed $(n \ge 4)$. In addition to this, as the carbonyl-ene reaction proceeds, more polar alcohol products are formed, occupy and narrow the pore space, and consequently retard the reaction. These situations can account for why the yields of the carbonyl-ene reaction are reduced from n = 1 to 4.

It was revealed that it is vital to adsorb one HCHO molecule on a II-site sodium ion in the supercage of NaY in order to most effectively perform the carbonyl-ene reaction.

3.3 Molecular Behaviors of HCHO Molecules in NaY in the Case of Higher Loadings $(n \ge 8)$ of HCHO on NaY. Next, we focused on what would happen when more than four HCHO molecules were added to a supercage of NaY. As HCHO was introduced, the gain in weight of the NaY expectedly increased as shown in Figure 4. A linear rise in the number (n) of loaded HCHO molecules per supercage in NaY was observed up to the folding point at n = 20, and then the increment rate was suppressed to some extent.

In order to confirm the actual states of the adsorbed HCHO before and after the folding point, three kinds of HCHO(n = 8, 14, 21)@NaY samples were prepared and analyzed by ¹³C solid NMR. The ¹³C DD MAS NMR signal at 94 ppm of (HCHO)₃ of HCHO(8)@NaY was noticeable compared with that of HCHO(4)@NaY (Figure 3d and 3e). At the same time, the monomeric HCHO peak at 204 ppm declined. For the sample of HCHO(14)@NaY, the signal of HCHO almost disappeared (Figure 3f). It is not certain if all the introduced HCHO molecules are equally distributed into every supercage of NaY. Comparing the spectra between Figure 3e and 3f, it is presumed that once three HCHO molecules per sodium ion on site II are introduced in the supercage, i.e., in the case of n = around 12, most of the HCHO would be transformed into (HCHO)₃ coordinating to the sodium ions.

Interestingly, at n = 21, a small shoulder peak at around 88 ppm was detected on the main peak at 94 ppm in the ¹³C DD MAS NMR spectrum of the HCHO(21)@NaY. The ¹³C CP MAS NMR spectrum of the same sample was then measured, and the shoulder peak was assigned to chain-like para-

formaldehyde (Figure 3j). The CPMASNMR spectra of the chemical species adsorbed in the pores are generally different from the corresponding DD MAS NMR spectra because the cross-polarization efficiencies are sensitively influenced by the motions of the probe molecules encapsulated in the pores.¹⁸ In this study, the ¹³C signal of paraformaldehyde was more emphasized in the CPMAS spectrum than in the DDMAS spectrum. A very small peak of paraformaldehyde together with a major peak of (HCHO)₃ was also detected in the CPMAS spectrum of HCHO(20)@NaY (Figure 3h). Thus, it can be understood that paraformaldehyde began to be generated from HCHO outside the supercages of NaY once approximately 20 or more HCHO molecules were added to a supercage. The HCHO(n = 22)@NaY sample was also prepared and similarly analyzed, providing almost the same spectrum as HCHO(n =21)@NaY as shown in the Supporting Information 4b.

Figure 4 shows the relationship between the amount (mg) of paraformaldehyde employed to generate gaseous HCHO and the number (*n*) of adsorbed HCHO molecules per supercage in NaY. Based on this figure, it is clear that some introduced HCHO gas was not adsorbed into the zeolite when contacted with NaY. The curious adsorption profile of HCHO was found with an folding point at n = 20, which was explainable based on the micropore volume from the N₂ sorption data as follows: The micropore volume (V_{micro}) of the employed NaY was determined to be 0.34 cm³ g⁻¹ by a nitrogen adsorption analysis. The pore volume of a supercage of NaY ($V_{supercage}$) was calculated to be 0.89 nm³ from the following formula:¹⁹

$$V_{supercage} = rac{V_{micro} ullet M_{unit}}{8N_A}$$

where M_{unit} is the formula weight of the unit cell of the NaY crystals (12653.16 for Na₅₁Al₅₁Si₁₄₁O₃₈₄), V_{micro} is the micropore volume of NaY and N_A is Avogadro's number.

The molecular volume of a (HCHO)₃ was also calculated from the density and molecular weight of crystalline 1,3,5trioxane to be 0.13 nm³. Thus, one supercage can accommodate ca. 6.8 molecules of (HCHO)₃ based on our calculation.²⁰ The 6.8 molecules of (HCHO)₃ correspond to 20.4 molecules of HCHO, which exactly match the molecular number of HCHO contained in the HCHO(20)@NaY sample. Thus, it can be understood that the HCHO molecules thickly populated in the NaY pores start to trimerize at n = 4 to (HCHO)₃ until the pores are filled with the (HCHO)₃ molecules with up to n = 20. After the pores are fully occupied with (HCHO)₃ at n > 20, paraformaldehyde then begins to form outside the pores of NaY as more HCHO molecules are intentionally added to NaY (Figure 5).

3.4 Inspection of the Products for the Reactions of α -Methylstyrene with HCHO Densely or Highly Loaded on NaY. Since HCHO is a very reactive molecule, it was easily expected that HCHO densely loaded on NaY (n = 3 and 4) could further react with the carbonyl-ene product 2 except for the self-polymerization. As 2 has a vinylidene group, 2 could undergo the consecutive carbonyl-ene reactions with the excess HCHO on NaY to yield 3 as shown in Scheme 2. Terminal hydroxyl groups in the product 3 would be able to further react with HCHO to yield polyoxymethylene compounds 4 having different molecular weights. It would also be possible for 2



Figure 5. The conceptual drawings of the added HCHO and its polymers inside and outside the NaY pores depending on "n." (The four sodium ions at sites II are tetrahedrally arranged in a supercage, but in the figure, displayed in the plane.)

to react with excess HCHO to yield a hemiacetal product, 5, followed by polyoxymethylenation to 6 as well.

In order to confirm the structures of such prospective overreaction products, the isolated carbonyl-ene product **2** was allowed to further react with HCHO(3)@NaY including 2.6 equivalents of HCHO to **2** in cyclohexane²¹ at 50 °C for 1 h. After the routine work-up, the condensed crude reaction mixture was first analyzed by ¹HNMR, and then separated by column chromatography on silica gel to obtain two fractions with different polarities. The fraction with the lower polarity was determined by NMR to be a mixture (ca. 2.5:1) of **2** and **5** which was a hemiacetal product from the reaction of **2** with HCHO. In this case, a polyoxymethylenation product (**6**) from **5** was not observed.

The other fraction had higher polarity, which was dried in a vacuum and analyzed by GC-MS as well as ¹H, ¹³C, and ¹H-¹³C edited-HSQC (Hetero-nuclear Single Quantum Coherence).²²

The GC-MS of the fraction contained the species with m/z = 118 (1), 148 (2) and 178 (3), but other possible adducts with higher mass numbers of m/z > 178 were not detected (see the Supporting Information 5). It can be said that under the GC-MS conditions, even if the fraction included higher molecular weight adducts, they underwent pyrolysis to lower molecular weight compounds such as 1, 2 and 3.

The ¹H and ¹³C NMR spectra of the fraction are shown in Figure 6a and 6b. Both spectra were so complicated that the fraction was considered to be composed of a mixture of products. The mixture was then analyzed by the edited-HSQC NMR.

In the edited-HSQC spectrum ($\delta = 1/[2^1J(C,H)] = 3.45$ ms delay) of the fraction, it is generally known that the positive cross peaks displayed in black in Figure 6c indicate the CH or CH₃ unit, and that the negative cross peaks in red show the CH₂. In Figure 6c, five groups of the cross peaks were discriminated by five colored-circles: The two groups are assignable to phenyl CH and olefinic CH, and the other three groups are estimated to be O-CH₂-O, O-CH₂-C and C-CH₂-C. All the



Figure 6. NMR spectra of (a) ¹H, (b) ¹³C, and (c) ¹H-¹³Cedited HSOC of the mixture of 3 and 4.

olefinic CH cross peaks are shown as the peaks in black, indicating that there is no vinylidene group in the fraction products, while **2** has a vinylidene group. Therefore, the fraction with the higher polarity should include compounds having internal olefinic parts. Because the ¹³C signals of the O-CH₂-O group show lower chemical shifts up-field from normal vinylidene carbons and the ¹H signals have higher chemical shifts downfield from those of a normal alkane, these cross peaks were determined to be the acetal CH₂ unit.

Given these spectral features, it is deduced that the fraction with the higher polarity included not only **3**, which was derived from the carbonyl-ene reaction of **2** with HCHO@NaY, but also its polyoxymethylene derivatives which were produced by the reactions of the terminal hydroxyl groups in **3** with surplus HCHO. In the ¹HNMR of Figure 6a, a small aldehyde peak was observed. It is speculated that during the work-up and purification on silica, some retro-reactions took place to afford some formaldehyde in the mixture (see the Supporting Information 3f).

Summarizing the investigation by NMR of the over-reaction products from the reaction of 2 with HCHO(3)@NaY, the consecutive carbonyl-ene reactions and polymethylenation occurred to produce 3, 4 and 5. GC analysis of these over-reaction products, however, only detected the presence of 2 and 3 because the over-reaction products were easily decomposed by heat.

In cases of the reaction of α -methylstyrene with HCHO (n = 2-4) in Table 1, small amounts of the side-products were assigned by the ¹HNMR to be **5** and **6** based on the aforementioned analysis, but the formations of **3** and **4** were not observed. **6** was only observed by ¹HNMR analysis without any separation on silica gel or GC. It can be imagined that once the product **2** was formed and promptly adsorbed on a sodium ion, the entrapped **2** was not allowed to react with the adjacent HCHO activated on another sodium ion in the same supercage to produce **3**.

4. Conclusion

It was revealed that the number "n" of HCHO adsorbed in a supercage of NaY was directly responsible for the reactivity of the HCHO molecules toward α -methylstyrene. We can exclusively fix up to four monomeric HCHO molecules in a supercage of NaY because there are four sodium ions at sites II in a supercage. Only the adsorption state with one HCHO molecule per supercage demonstrated the highest yield, and as the number "n" increased from one to four, lower yields were obtained. This is because the remaining space in the supercage where the α -methylstyrene molecules can be accommodated narrows as the numbers of unreacted HCHO molecules as well as the formed homoallylic alcohol and its derivative products which have higher polarity than HCHO increase, resulting in the retardation of the corresponding addition reaction. The ¹³C DD/CP MAS NMR of the HCHO-adsorbing NaY clarified that HCHO monomers were exclusive or dominant with n from 1 to 4, and that with the n > 8 (HCHO)₃ was mainly formed together with paraformaldehyde outside the supercages of NaY especially for n > 20. We also confirmed by ¹³C and ¹H NMR as well as GC-MS analysis that in the reaction of HCHO(3)@ NaY with homoallylic alcohol 2, various over-reaction products, such as 3, 4 and 5, were formed.

Once the hazardous, gaseous HCHO is carefully and quantitatively adsorbed in NaY, the resultant NaY-loaded HCHO (HCHO@NaY) can work as an immobilized HCHO and provide many advantages especially when performing small scale organic synthesis.

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Supporting Information

The Supporting Information contains the experimental details and the characterization results by ${}^{1}\text{H}/{}^{13}\text{C}$ NMR and GC-MS. This material is available on http://dx.doi.org/10.1246/bcsj. 20170252.

References and Notes

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15 Faujasite zeolites are classified into two types according to their Si/Al ratios; i.e., 1–1.5 for the X-type zeolites and 1.5–3 for the Y-type ones.

16 In our early communication,¹² we prepared HCHO(n = 3.8)@NaY and analyzed it with ¹³C DD MAS NMR. We then applied it for the carbonyl-ene reactions under the conditions where α -methylstyrene reacted with three equivalents of HCHO. In contrast, in the present study, we used 60 excess equivalents of α -methylstyrene to HCHO included in HCHO(n)@NaY in order to compare the four reactions in Table 1 under as much the same reaction conditions as possible.

17 The formation of the (HCHO)₃ molecules would be possible during the pyrolysis of paraformaldehyde to HCHO. Therefore, the pyrolyzed HCHO gas was directly dissolved in CDCl₃ solvent at -60 °C, and then the solution was analyzed by ¹H NMR. It was found that (HCHO)₃ was hardly detected in less than 0.1% of HCHO.

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