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Shape Selectivity in Toluene Disproportionation into para-Xylene Generated by Chemical Vapor Deposition of Tetramethoxysilane on MFI Zeolite Catalyst

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Abstract

Dependence of shape selectivity for para-xylene production by toluene disproportionation on conditions of chemical vapor deposition (CVD) of tetramethoxysilane on MFI (ZSM-5) zeolite were investigated in detail. The CVD after pelletization was necessary to obtain 0.7-1 mm particles with high selectivity. The influences of preparation conditions on the selectivity were investigated in detail to find the optimum conditions. The parent zeolite with small number of Brønsted acid sites on the external surface brought the high selectivity after the CVD. The catalyst prepared in the optimized conditions showed the selectivity 99.7% at ca. 10% of the toluene conversion.

Keywords Shape selectivity; Toluene disproportionation; para-Xylene; MFI zeolite; Chemical

vapor deposition of silica

Introduction

para-Xylene (1,4-dimethylbenzene) is one of the most valuable hydrocarbon compounds, because it is the raw material of polyethylene terephthalate (PET) [1]. para-Xylene is contained in crude oil and naphtha produced by the fluid catalytic cracking, but the purification from an isomer mixture consumes huge energy and resources [2], and therefore the selective production of para-xylene has been a subject of study. Zeolites, aluminosilicates with microporous structure, have shape selectivity in methylation of benzene or toluene (methylbenzene) and disproportionation of toluene, where para-xylene is preferentially formed compared to meta- and ortho-isomers (1,3- and 1,2-dimethylbenzene) with bulky molecular shapes [2,3]. The toluene disproportionation is the most efficient reaction for the production of xylenes [3], because toluene is relatively useless among benzene and its derivatives, and no other expensive reagent such as methanol is necessary. MFI type zeolite (ZSM-5) with 10-ring pores is known to have the para-xylene selectivity in the toluene disproportionation [2].

However, even the MFI zeolite shows the selectivity only at a very low conversion of toluene. In industrially operated conditions, namely at a certainly high conversion, the shape selectivity of unmodified MFI zeolite is negligible, although the shape selectivity has been introduced to be a good example of usage of microporous material. In a fact, many attempts have been made to improve the selectivity of MFI zeolite, and some of them have been industrially applied.

Modification of a zeolite with rare earth, boron, phosphorous and silicon compounds have been known to generate shape selectivity [4-25]. Formation of silicalite crystal (siliceous

MFI) on the external surface of MFI zeolite [26-28] should have similar effects. Coke, as a byproduct of the reaction or designed to have suitable nature, has also been known to improve the shape selectivity [29-32]. There has been a controversy about the origin of selectivity, because the discussed structure is always smaller than nanometric scale; the inactivation of active sites on the external surface [14,17,23,30,32], the control of pore-opening size [6,8,11,13,15,19,25] and both of them with each role [5,10,16,18,20,21,31] have been proposed, whereas increased tortuosity has also been a candidate [22].

Among them, the modification with silica has been investigated well as a practically important method to construct a stable structure. The first attempt of modification of the micropore size and pore-opening size of a zeolite with silane has been presented by Barrer et al. [4] Then, tetramethoxysilane, a safer silicon source, has been utilized to control the pore-opening size by Niwa et al. [8] These methods utilize a chemical vapor deposition (CVD) technique. Beck et al. have industrialized an impregnation method in an organic solvent [12], in other words, a method of chemical liquid deposition (CLD) [15,17,20,24,25] of silica using polyalkylsiloxane compounds. The industrial process according to this patent has been operated with 93% of the para-xylene selectivity (the rate of formation of para-xylene / the total rate of formation of xylene isomers and ethylbenzene) at 30% of the toluene conversion, and it has greatly improved the economic efficiency and saved the consumption of energy and resources for the production of PET. The CVD of tetraethoxysilane has also been developed in an industrial scale and applied to the production of para-diethylbenzene (1,4-diethylbenzene), a similar reaction [11,13,33]. We believe these studies approaching one of the most precise technologies which mankind has created and practically applied, because key of the works is the structure control in an atomic scale, the product is really useful, and the usefulness is related with

the molecular shape of product.

However, even at the selectivity 93%, a post treatment (currently pressure swing adsorption using a zeolite) for the separation of para-isomer from a mixture of xylene isomers (or C8 fraction) is necessary, because the para-xylene purity higher than 99.7% is required for the production of PET. We can count potential ways to reduce the cost and energy consumption of the separation process, improvement of the pressure swing adsorption [34,35] and development of molecular sieving membranes [36-40]. However, more efficient way is believed to be development of a catalyst with higher selectivity which can produce para-xylene with selectivity >99.7% at a sufficiently high conversion such as 10%. Efforts have been continued, but to the best of our knowledge, selectivity higher than that achieved by Beck et al. [12] has not been reported.

We have developed the CVD method of tetramethoxysilane on zeolites [41,42], including its application to the toluene disproportionation [10,18,43] and other materials [44-48]. Here detailed influences of the conditions of CVD on the shape selectivity of MFI zeolite in the toluene disproportionation were investigated. The selectivity was compared with the conventional techniques.

Experimental

An H-ZSM-5 (zeolite with the MFI structure) sample purchased from Mizusawa Chemical Industry with Si/Al₂ molar ratio 30 was utilized as the parent zeolite in most cases, while other zeolite species [H-ZSM-5 with Si/Al₂ = 24 ion exchanged from Tosoh Na-ZSM-5, H-ZSM-5 with Si/Al₂ = 48 from Mizusawa Chemical Industry and H-mordenite (zeolite with MOR structure) with Si/Al₂ = 20 from Reference Catalyst Division, Catalysis Society of Japan as

a reference catalyst JRC-HM-20] were employed in some cases, as mentioned in the following sections. The zeolite powder was ground, compressed under 20 MPa for 1-2 min, crashed and sieved. A fraction with 0.7 - 1 mm of the particle size was utilized. This procedure is termed pelletization hereafter.

Prior to the CVD of silica, tetramethoxysilane was pre-treated by passing a helium flow (atmospheric pressure, $30 \text{ cm}^3 \text{ min}^{-1}$ at atmospheric pressure = $20 \text{ } \mu\text{mol s}^{-1}$) at 273 K for >24 h to remove impurities. Then, 2 g of the zeolite sample was placed in a Pyrex tube (inner diameter 17 mm) as shown in Figure 1 and pretreated at 773 K for 3 h in a helium flow (atmospheric pressure, $20 \text{ } \mu\text{mol s}^{-1}$). Then a mixture of helium and $\text{Si}(\text{OCH}_3)_4$ (tetramethoxysilane, kept at a constant partial pressure) vapor was fed in the atmospheric pressure at a constant velocity and a controlled reaction temperature. After a desired reaction time passed, a mixture of water vapor (vapor pressure at the room temperature ca. 3 kPa) and helium (98 kPa, $20 \text{ } \mu\text{mol s}^{-1}$) was fed in atmospheric pressure at 773 K for 2 h. Finally, an oxygen flow (atmospheric pressure, $20 \text{ } \mu\text{mol s}^{-1}$) was fed at 773 K for 12 h to remove completely the organic residue.

As a comparison, modification of the MFI zeolite with the CLD method was carried out according to Beck et al. [12] The same pelletized H-ZSM-5 zeolite with $\text{Si}/\text{Al}_2 = 30$ (ca. 5 g) was put into a solution of dimethylphenylmethyl polysiloxane (Dow-550, the weight ratio of zeolite : Dow-550 was 10 : 1) in dodecane (the weight of zeolite : dodecane was 10 : 9). It was stirred for 2 h at the room temperature, and dodecane was removed by pumping. The sample was heated at 413 K for 2 h in a nitrogen flow (atmospheric pressure, $68 \text{ } \mu\text{mol s}^{-1}$), and then the temperature was elevated at 2 K min^{-1} up to 811 K and kept at 811 K for 2 h with keeping the flow rate of nitrogen. Subsequently the sample was cooled down to 573 K, the gas was switched into a mixture of nitrogen ($55 \text{ } \mu\text{mol s}^{-1}$) and oxygen ($14 \text{ } \mu\text{mol s}^{-1}$) in atmospheric pressure, and

the sample temperature was elevated at 2 K min^{-1} up to 811 K and kept at 811 k for 4 h. These procedures were repeated for 2-4 times.

As fundamental characterization, measurements of the X-ray diffraction, the nitrogen adsorption isotherm at 77 K and ammonia IRMS-TPD (infrared-mass spectroscopy / temperature-programmed desorption) [49 - 51] were carried out as shown in Supporting Information. Scanning electron micrographs were recorded by a Hitachi S-4800 microscope with 3 kV and 10 μA of the acceleration voltage and emission current, respectively.

Toluene disproportionation was carried out in fixed bed flow reactors. For experiments in the atmospheric pressure with P_{toluene} (partial pressure of toluene) = 65 kPa and P_{He} (partial pressure of helium as carrier gas) = 36 kPa, a Pyrex tube (8 mm inner diameter) was used. A stainless-steel tube (4 mm inner diameter) was used in experiments at an elevated pressure with $P_{\text{toluene}} = 75 \text{ kPa}$ and P_{H_2} (partial pressure of hydrogen as co-fed gas) = 500 kPa, and the total pressure in the reactor was controlled by a back-pressure valve installed at the outlet of reactor. After a pretreatment of catalyst at 773 K in helium or hydrogen flow, a mixture of toluene vapor and additional gas (helium or hydrogen) was fed to keep a constant W/F (weight of catalyst to flow rate of toluene) ratio at 773 K. The outlet gas was collected by a trap filled with hexane and chilled at 273 K; it has experimentally been confirmed that benzene, toluene, xylene and ethylbenzene were completely trapped. The collected products were separated by a gas chromatograph (GC) with a capillary column of Xylene Master (inner diameter 0.25 mm, length 50 m) and analyzed by a flame ionization detector (FID). In order to show a material balance, the aromatic ring balance was defined as follows.

Aromatic ring balance

$$= (\text{amount in mol s}^{-1} \text{ of recovered toluene} + \text{yielded benzene and alkylbenzenes})$$

$$/ \text{ amount in mol s}^{-1} \text{ of fed toluene)}$$

where the amount of material was determined by inner standard method.

To show the catalytic performance, the conversion and selectivity were expressed by the following indexes.

Toluene conversion

$$= 1 - (\text{amount in mol s}^{-1} \text{ of recovered toluene})$$

$$/ (\text{amount in mol s}^{-1} \text{ of recovered toluene} + \text{yielded benzene and alkylbenzenes})$$

Selectivity of para-xylene

$$= (\text{amount in mol s}^{-1} \text{ of yielded para-xylene})$$

$$/ (\text{amount in mol s}^{-1} \text{ of yielded xylene isomers and ethylbenzene})$$

In order to evaluate the extent of inactivation of Brønsted acid sites on the external surface, catalytic activity for dealkylation (cracking) of 1,3,5-tris(1-methylethyl)-benzene (1,3,5-triisopropylbenzene) was measured according to our previous paper in a pulse method [16]. The sample (5 mg) was packed in a Pyrex tube (4 mm inner diameter), pre-treated in a He flow (ca. 200 kPa, 20 $\mu\text{mol s}^{-1}$) at 773 K for 1 h, and then a pulse of 1,3,5-triisopropylbenzene (4.1 μmol) was fed at 473 K. The outlet of reactor was directly connected to a column of Silicone SE30, and the products were analyzed with an FID-GC. Most of the products were propene and benzene. The catalytic activity is shown by the conversion of 1,3,5-triisopropylbenzene in the

first pulse.

For the evaluation of pore-opening size, the rate of adsorption of ortho-xylene was measured according to our previous paper [16]. The sample (0.1 g) was placed in a glass basket hung by a quartz glass spring to monitor the weight change, and evacuated at 773 K until a constant weight was observed (usually 2 h). Then a vapor of ortho-xylene (0.53 kPa, vapor pressure at 273 K) was introduced into the vessel at 393 K. The rate constant k ($\text{mol kg}^{-1} \text{s}^{-1/2}$) is determined according to our previous paper based on the diffusion theory [52] by

$$k = \frac{M}{t^{1/2}}$$

where M (mol kg^{-1}) show the amount of ortho-xylene adsorbed at t (s) of the adsorption time.

Results and Discussion

Change in catalytic activity and selectivity by CVD

The amount of deposited silica was determined by weighing the sample in some experiments. Figure S1 shows that the deposition of silica proceeded quickly in the first several hours at 473 K on the powder sample up to ca. 1 wt% of SiO_2 , corresponding to ca. 8 Si atoms nm^{-2} on the external surface. Then, slow deposition continued in the following several days. The preparation of catalysts employed in the present study was mainly carried out in the region where the secondary slow deposition proceeded. Because the measurement of weight increase was not easy in the preparation system shown in Figure 1, the amount of silica was not quantified in most experiments. From Figure S1, the amount of silica in the following experiments is

supposed to roughly correspond to 8-10 Si atoms nm⁻².

Supporting Information (Figure S2) shows that the employed zeolites had crystal phase attributed to each type. The crystallinity was little changed by the CVD or CLD. Nitrogen adsorption isotherm was recorded as shown in Figure S3. Table S1 shows that the micropore volumes of MFI (Si/Al₂ = 30) and MOR (Si/Al₂ = 20) were not largely modified, whereas the micropore volumes of MFI samples (Si/Al₂ = 24 and 48) were slightly decreased by the CVD. The external surface area was calculated by a *t*-plot method [53] as shown in Table S1. The external surface area of MFI with Si/Al₂ = 48 was decreased, while it was not significantly modified in other cases.

The ammonia IRMS-TPD analysis was applied to selected samples in order to show the acidic property and its change by the modification with silica as shown in Supporting Information. Table S2 summarizes the number and strength (shown by the enthalpy of ammonia desorption) of acid sites. On MFI samples, the enthalpy of ammonia desorption from Brønsted acid sites was 137-144 kJ mol⁻¹, in agreement with the previously reported values on MFI [54], and that on MOR (158 kJ mol⁻¹) was also in agreement with our previous measurements [49]. In all the cases, modification with silica did not change the enthalpy of ammonia desorption. The numbers of Brønsted acid sites of MFI (Si/Al₂ = 30) and MOR (Si/Al₂ = 20) were not largely modified, whereas those of MFI samples (Si/Al₂ = 24 and 48) were decreased by the CVD. On the contrary, the number of Lewis acid sites was negligible in all the cases.

Supporting Information includes also the aromatic ring balance typically observed in the toluene disproportionation on the parent MFI zeolite and a silica-modified sample (Figure S6). The aromatic ring balance was sufficiently high, i.e., close to 100 %, under these conditions.

Figure S7 shows para-xylene selectivity (exactly, the molar ratio of para-xylene in the

isomers). As shown in literatures [5,6,10,31], the parent MFI showed the selectivity ca. 25%, close to the equilibrium composition, at the toluene conversion = ca. 10% as above. The CVD of silica greatly enhanced the shape selectivity, or, it can be said that the CVD created the shape selectivity for the production of para-xylene in the toluene disproportionation, as already published [10]. On the other hand, the activity was gradually decreased by the CVD of silica, as demonstrated by a typical case shown in Figure S8.

Influence of pelletization

As shown in Table 1 (B), the powder sample modified by the CVD at 503 K for 4 h performed ca. 7% of the toluene conversion and ca. 100% of the para-xylene selectivity, demonstrating the potential of practical application. Then, the influence of pelletization was investigated, because the industrialization requires the molding or pelletization of catalyst.

The parent powder sample was found to be aggregated fine particles with several tens to hundreds of nanometers in size, whereas the morphology of particles was modified by pelletization, as shown by SEM images (Figure 2). It was obvious that the pelletization after the CVD significantly decreased the selectivity [Table 1 (C)]. It is presumed that the external surface modification was the origin of high selectivity, and the grinding and crashing the powder destroyed each crystallite or external surface structure to expose the inner surface of zeolite which had poor selectivity. Therefore, the pelletization after the CVD is not suitable, and the CVD after pelletization should be necessary. Hereafter the influences of conditions of CVD after the pelletization will be discussed.

Variables of CVD

Fundamental influences of conditions of CVD on the shape selectivity were studied. Based on the influence of co-feed of hydrogen on the catalyst life as found in Supporting Information (Figure S9), the reaction tests are hereafter carried out at $P_{\text{toluene}} = 75$ kPa and $P_{\text{H}_2} = 500$ kPa. The conversion and selectivity will be shown by the average values for 4-50 h of the time on stream, because the stable conversion and selectivity were observed in all the cases (Figure S12).

On the other hand, the relationship between para-xylene selectivity and toluene conversion was studied with varying W/F (Figure 3). Based on this study, the selectivity will be shown by the conversion $X_{0.997}$ with which 99.7% of the selectivity can be obtained (see detail in Supporting Information).

$$X_{0.997} = X_1 \sqrt{\frac{0.003}{1 - S_1}}$$

The higher $X_{0.997}$ shows the higher selectivity (not showing activity). Considering the production of PET, the desired purity of para-xylene among isomers is 99.7%. The value $X_{0.997}$ indicates the conversion that makes it possible to omit the separation step after the reaction. Hereafter, the selectivity will be shown by $X_{0.997}$.

As shown in Figure 4 (●), $X_{0.997}$ was increased by the CVD of silica and showed the maximum at the optimized CVD time where detailed influence of CVD time was studied. Presumably, the control of pore-opening size proceeded with CVD resulting in the suppression of undesired reactions (formation of meta- and ortho-xylenes from toluene and isomerization of para-xylene into isomers), and excess silica prohibits also the desired reaction (formation of

para-xylene from toluene).

The difference in the selectivity by varying the reaction temperature is speculated to be due to the difference in uniformity of the surface silica layer. If one assumes that the extent of narrowing pore-opening size is dependent on the thickness of silica layer as suggested by our previous studies [9,10,16], it is believed that too thin layer of silica (or too small amount of silica) results in low selectivity, where not only para-xylene and benzene, but also meta- and ortho-xylene can go out from the pores as postulated in Figure 5 (A). Figure 5 (C) shows the case in which the thickness of silica layer is too large, and the diffusion of any aromatic compounds is limited. It is here assumed that affinity of aromatic compounds and micropore wall and / or acid site is strong, but the diffusion of molecules is slow, resulting in the high density of aromatic compounds in the micropores. Such a side reaction as disproportionation of alkyl chains to form long chain alkylbenzenes (e.g., ethylbenzene) proceeds, and then the dealkylation forming alkenes (e.g., ethene) and benzene occurs. Oligomerization of alkenes forms carbonaceous materials to suppress the activity. Thus, too thick layer should suppress the activity, resulting in the low $X_{0,997}$. Figure 5 (B) shows that the thickness of silica layer is ideal, where only para-xylene and benzene can go out from the pores, and diffusion rates of these molecules are sufficiently high. Figure 5 (D) explains the influence of heterogeneous thickness of silica layer, i.e., co-presence of too thin (non-selective) part and too thick (causing side reactions) part, resulting in the low activity and low selectivity.

It is therefore believed that, if a completely homogeneous layer with suitable thickness covers the external surface, the selectivity should be maximized with keeping the high activity, providing high $X_{0,997}$. The dependence of $X_{0,997}$ on the CVD time should reflect it.

On the other hand, Figure 4 suggests a trend that the high CVD temperature (483 K)

caused low $X_{0.997}$ even at the maximum compared to the low temperature (473 K). If a part of surface is covered by excess of silica while other part was covered incompletely, the rate of desired reaction should be suppressed before the selectivity was significantly increased (Figure 5, D). The balance of reaction and diffusion rates in the CVD process should affect the uniformity, and the high temperature CVD is therefore believed to cause the heterogeneous deposition. On the contrary, too low CVD temperature (463 K) seems to take a very long time for the formation of silica layer with the suitable thickness to generate the shape selectivity, and the optimum temperature for CVD is considered to be 473 K.

The influences of the flow rate of a mixture of helium and tetramethoxysilane (Table 2, Entries A-H) and the partial pressure of tetramethoxysilane (Table 2, Entries C-F and I-N) were investigated. It is concluded that the CVD at 473 K for ca. 20 h in $20 \mu\text{mol s}^{-1}$ of tetramethoxysilane 0.3 kPa / helium flow gave the highest selectivity.

Influence of support zeolite

As shown in Table 3, different zeolite samples were used as supports. Mordenite (zeolite with MOR structure) showed very low selectivity, as naturally imagined from its large pore size (12-ring). The ZSM-5 (MFI, 10-ring) with different sources showed low selectivities, while only the MFI sample with $\text{Si}/\text{Al}_2 = 30$ realized the high selectivity.

Table 3 also shows the catalytic activity for cracking (dealkylation) of 1,3,5-triisopropylbenzene, which is obviously larger than the pore size of 10-ring, demonstrating the number of Brønsted acid sites on the external surface. The CVD of silica diminished the activity in all the cases (not shown), presumably because the silica layer covered the external surface. It was found that the MFI sample with $\text{Si}/\text{Al}_2 = 30$ had little activity even before the CVD, whereas

the other zeolites showed high activity. The activity after the CVD were low in all the cases, and therefore it is not directly related with the difference in the selectivity. It was observed that the MFI zeolite with small number of external Brønsted acid sites provided high selectivity after the CVD of silica on the external surface. This is in agreement with Zheng et al., showing that dealumination of external surface enhanced the shape selectivity after the CLD of Si alkoxide [55]. It is speculated that the uniformity of deposition of silica layer was affected by the presence of acid sites on the external surface.

Comparison with preceding studies

Thus, the conditions for CVD of tetramethoxysilane to give the highly selective catalyst was studied. Some samples were prepared in the found conditions (CVD at 473 K for 18-24 h in 20 $\mu\text{mol s}^{-1}$ of tetramethoxysilane 0.3 kPa / helium on MFI with $\text{Si}/\text{Al}_2 = 30$), and the performance was evaluated with varying W/F ratio, as shown in Figure 3 (● and ○).

To the best of our knowledge, the method and conditions of CLD shown by Beck et al. [12] have given the catalyst with the highest para-xylene selectivity in toluene disproportionation in history. In addition, this method has been applied to the commercial process. The comparison of selectivity with the catalyst prepared according to the patent [12] is therefore believed to be very important. The catalytic performance of MFI modified with CLD method is also given in Figure 3. The symbol ▲ shows the results measured presently on the catalyst prepared according to the patent, whereas the symbol △ shows the results shown in the patent [12]. As already stated in the previous section, both results were approximately in agreement. More exactly, the selectivity on the same conversion level was higher in the present measurements (▲) than those reported by Beck et al (△). At least it can be said that the fair evaluation of the

conventional CLD method is possible based on the presently measured results ▲.

It is pointed out that the selectivity given by the CVD method was intrinsically higher than those by CLD. With the latter technique, 99.7% of the selectivity can be obtained at 7% of the conversion, able to be estimated from Figure 3 (▲) and also seen in $X_{0.997}$ value about 7% at 4 of the repetition time of CLD shown in Figure 6. Figure 3 (●) indicates that the conversion with which the selectivity reached 99.7% was 8-11% in the CVD method, as shown by $X_{0.997}$ level displayed in Figure 6. Thus, a potential of CVD-prepared catalyst exceeding the performance of conventional catalyst for the toluene disproportionation has been exhibited.

Many attempts have been presented for the generation of para-xylene selectivity in the toluene disproportionation. The selectivity-conversion relationships reported were compared in Figure 7. As stated in literature [5,6,10,31], the unmodified MFI (●) showed high selectivity only at very low conversion. The remarkable selectivity >90% at the conversion ca. 10% was obtained by the modification with Si compounds; ● [12], ○ (present study), ▲ [19] and ▼ [24]. Only a few studies showed the selectivity comparable to the conventional process using the CLD method (●) [12]. It is noteworthy that the conventional commercial process (●) [12] and a report by Halgeri and Das (▲) [19] are based on the catalysts which have been produced in a large scale. The present study (○) has been in the laboratory scale, but only one study which achieved the selectivity 99.7 % at more than 10 % of the conversion, where generally it becomes possible to consider the industrial applicability, to the best of our knowledge.

Here we emphasize that the difference in selectivity among CVD and CLD of silicate materials on MFI was small, and therefore origin of the difference among them should be small difference in the kinetics of deposition and mass transfer of Si compounds during the modification procedures. One feature of the precursor in the present study (tetramethoxysilane)

is the high reactivity in hydrolysis, and this is suspected to result in the selectivity, presumably due to the uniform structure of deposited silica layer.

Factor controlling selectivity

It has been proposed that (1) controlling the pore opening size and (2) inactivation of active sites on the external surface are the origin of generation of shape selectivity by the modification of external surface of zeolite [3,10,16]. In this study, the rate of ortho-xylene adsorption was measured. It has been clarified that the apparent rate of adsorption of this bulky molecule represents the diffusion of molecule in the micropore, and therefore it can be used as an index of micropore size [16]. On the other hand, the catalytic activity for cracking (dealkylation) of 1,3,5-triisopropylbenzene, which is believed to be larger than the micropore of MFI zeolite (10-ring), was measured as an index of activity of Brønsted acid site on the external surface. Here we discuss which parameter (ortho-xylene adsorption rate or 1,3,5-triisopropylbenzene conversion) shown in Table 4 can be correlated with the shape selectivity in toluene disproportionation.

Table 4 and, more clearly, Figure 8 shows that the selectivity was related with the rate of ortho-xylene adsorption. The lower diffusion rate, namely, the smaller pore-opening size, brought the high selectivity. On the other hand, Figure 9 indicates that the selectivity was not related well with the 1,3,5-triisopropylbenzene conversion, which shows the number of Brønsted acid sites on the external surface. These observations suggest that the selectivity was predominantly dependent on the extent of narrowing the pore-opening size. The inactivation of external surface is probably one of the necessary conditions, but it seems not only one factor at least in these cases.

Conclusions

Application of CVD of tetramethoxysilane on MFI to the toluene disproportionation was examined. The pelletization after the CVD significantly decreased the shape selectivity, presumably due to the destruction of crystallite or surface silica layer, and therefore the CVD after the pelletization was necessary. The investigation on influences of preparation variables clarified that the CVD at 473 K for suitable reaction time (in this scale, ca. 20 h) in $20 \mu\text{mol s}^{-1}$ of tetramethoxysilane 0.3 kPa / helium flow on the MFI zeolite with small number of Brønsted acid sites gave the high para-xylene selectivity. The selectivity was compared with preceding studies. It was found that the modification methods of MFI with Si compounds had a trend to show high selectivity, and among them, the present CVD method was only one method to have the selectivity 99.7 % at ca. 10 % of conversion.

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Table 1 Influence of pelletization on catalytic performance in toluene disproportionation at $W/F = 20 \text{ kg s mol}_{\text{toluene}}^{-1}$, $P_{\text{toluene}} = 65 \text{ kPa}$, $P_{\text{He}} = 36 \text{ kPa}$ and time on stream = 0.25 h.

Sample	Toluene conversion / %	para-Xylene selectivity / %
(A) Parent powder MFI (Si/Al ₂ = 30)	10.5	25.03
(B) (A) modified by CVD at 503 K for 4 h in 20 $\mu\text{mol s}^{-1}$ flow of tetramethoxysilane 0.3 kPa / helium mixture	6.6	99.80
(C) (B) followed by grinding, compressing, crashing and sieving	10.7	47.67

Table 2 Influences of flow rate of tetramethoxysilane / helium mixture and partial pressure of tetramethoxysilane on $X_{0.997}$ in toluene disproportionation at $P_{\text{toluene}} = 75$ kPa and $P_{\text{H}_2} = 500$ kPa.

The CVD was carried out at 473 K on MFI ($\text{Si}/\text{Al}_2 = 30$) after pelletization.

Entry	Flow rate of tetramethoxysilane / helium mixture / $\mu\text{mol s}^{-1}$	Partial pressure of tetramethoxysilane / kPa	Time of CVD / h	$X_{0.997}$ / %	
A	7	0.3	18	6.2	
B			30	3.2	
C	20		18	8.4-11.4	
D			24	11.2	
E			30	10.2	
F			40	9.1	
G			40	18	6.1
H				30	8.8
I	20		0.1	24	9.4
J				30	6.3
K				40	7.2
L			0.7	18	5.8
M		24		4.4	
N		40		1.8	

Table 3 Activity of acid sites on external surface (activity for 1,3,5-triisopropylbenzene dealkylation) and influence of support zeolite on $X_{0,997}$ in toluene disproportionation at $P_{\text{toluene}} = 75$ kPa and $P_{\text{H}_2} = 500$ kPa. The CVD was carried out at 473 K in 20 $\mu\text{mol s}^{-1}$ flow of tetramethoxysilane 0.3 kPa / helium mixture.

Support	1,3,5-Triisopropylbenzene conversion of unmodified support / %	Time of CVD / h	$X_{0,997}$ / %
MFI (Si/Al ₂ = 24)	46.9	12	1.3
		24	2.6
		30	2.1
MFI (Si/Al ₂ = 30)	2.6	6	3.5
		12	6.3
		24	11.2
		30	10.2
		40	9.1
MFI (Si/Al ₂ = 48)	41.0	30	0.1
MOR(Si/Al ₂ = 20)	40.8	6	0.01
		40	0.0007

Table 4 Influences of diffusion of bulky molecule (rate constant of adsorption of ortho-xylene) and activity of acid sites on external surface (activity for 1,3,5-triisopropylbenzene dealkylation) on shape selectivity. The modification was carried out by the CVD in 20 $\mu\text{mol s}^{-1}$ of tetramethoxysilane 0.3 kPa / helium mixture after pelletization on MFI (Si/Al₂ = 30), unless specific remark is shown.

Sample	Rate constant of adsorption of ortho-xylene / $\mu\text{mol g}^{-1} \text{s}^{-1/2}$	1,3,5-Triisopropylbenzene conversion / %	$X_{0.997}$
Parent MFI (Si/Al ₂ = 30)	26	3.3	0.10
Pelletization after CVD at 503 K for 4 h	2.2	0.56	0.12
CVD at 473 K for 18 h	1.3	0.27	0.14
CVD at 473 K for 30 h	0.61	0.33	4.5
CVD at 503 K for 6 h	0.47	0.21	9.1
CLD for four times	0.50	0.13	10.1

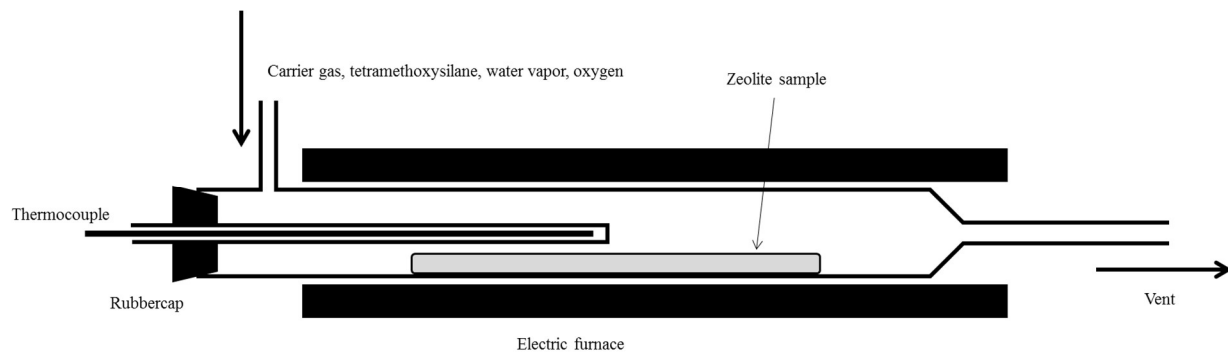


Figure 1 Location of zeolite sample in reaction tube for CVD.

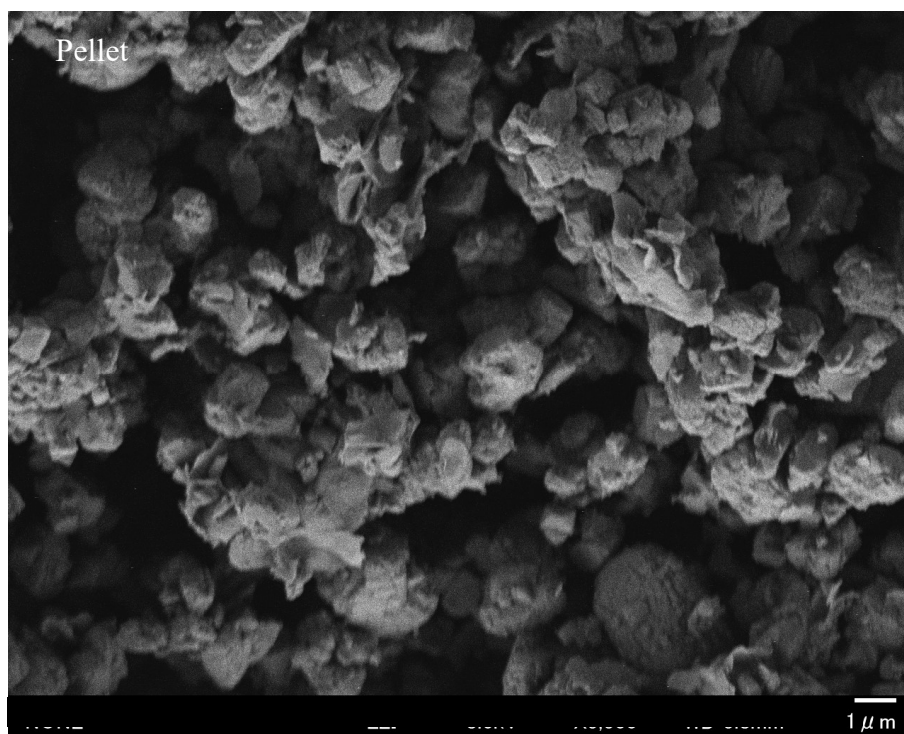
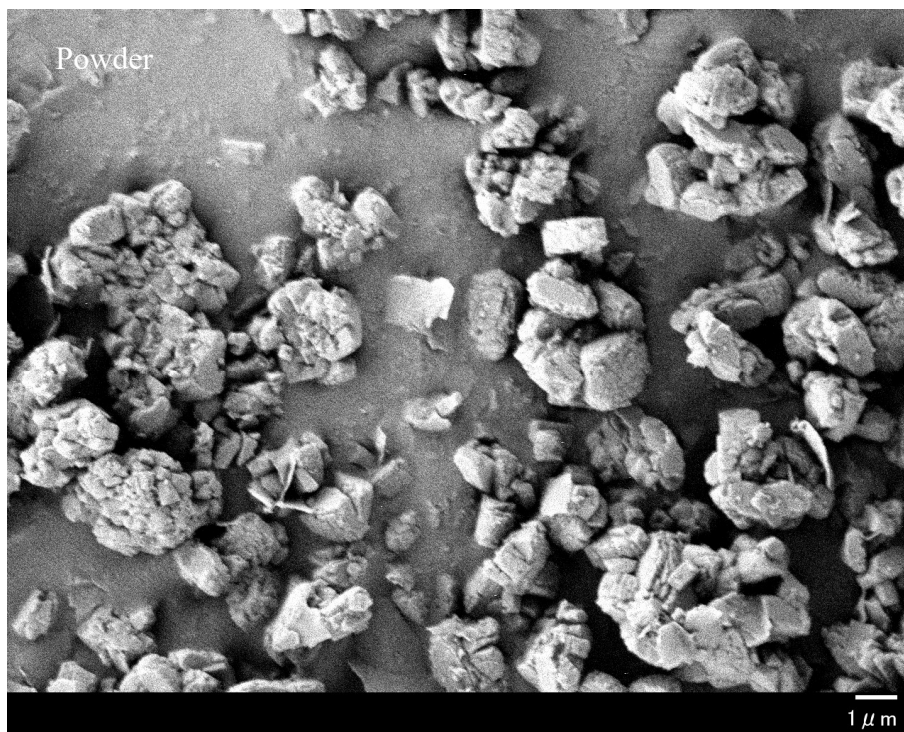


Figure 2 SEM images of powder (upper) and pellet (lower) samples of parent MFI ($\text{Si}/\text{Al}_2 = 30$).

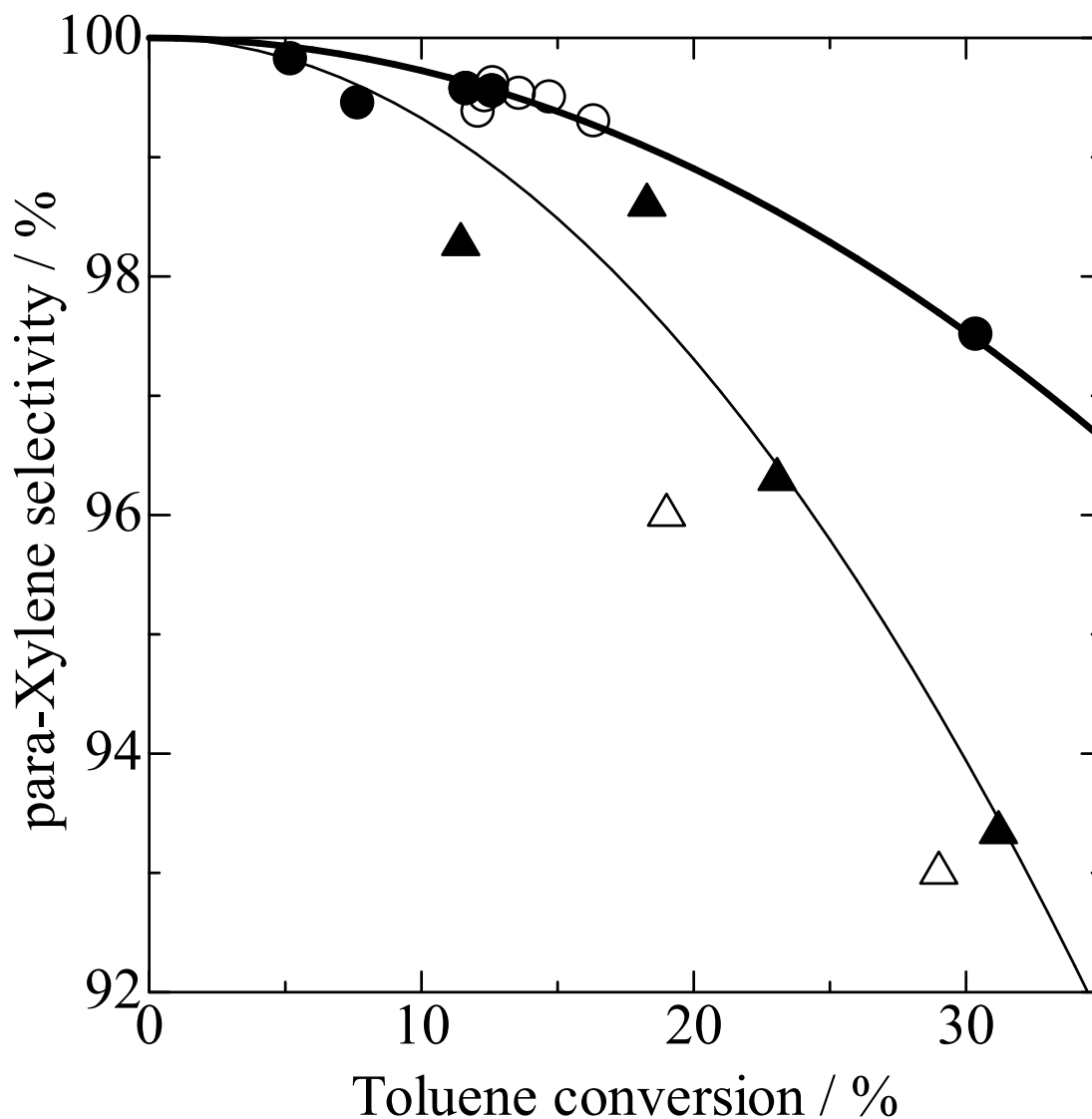


Figure 3 Plots of para-xylene selectivity against toluene conversion on MFI ($\text{Si}/\text{Al}_2 = 30$) modified by CVD at 473 K for 18-24 h in $20 \mu\text{mol s}^{-1}$ flow of tetramethoxysilane 0.3 kPa / helium mixture (● and ○) and modified by CLD (▲) after pelletization in toluene disproportionation at $P_{\text{toluene}} = 75 \text{ kPa}$ and $P_{\text{H}_2} = 500 \text{ kPa}$. The results ● were obtained on one sample (CVD for 18 h) with varying W/F , while ○ were on samples prepared in multiple experiments (CVD for 18-24 h) to show the reproducibility at $W/F = 20 \text{ kg s mol}_{\text{toluene}}^{-1}$. The

results ▲ were obtained on one sample (CLD for four times) with varying W/F . The thick line shows a relationship $S / \% = 100 - 0.00274(X / \%)^2$, fitting with ●, whereas the thin line shows $S / \% = 100 - 0.00673(X / \%)^2$, fitting with ▲, where S and X show the selectivity and conversion, respectively. The symbols Δ show the results on MFI modified by CLD for four times presented by Beck et al. [12]

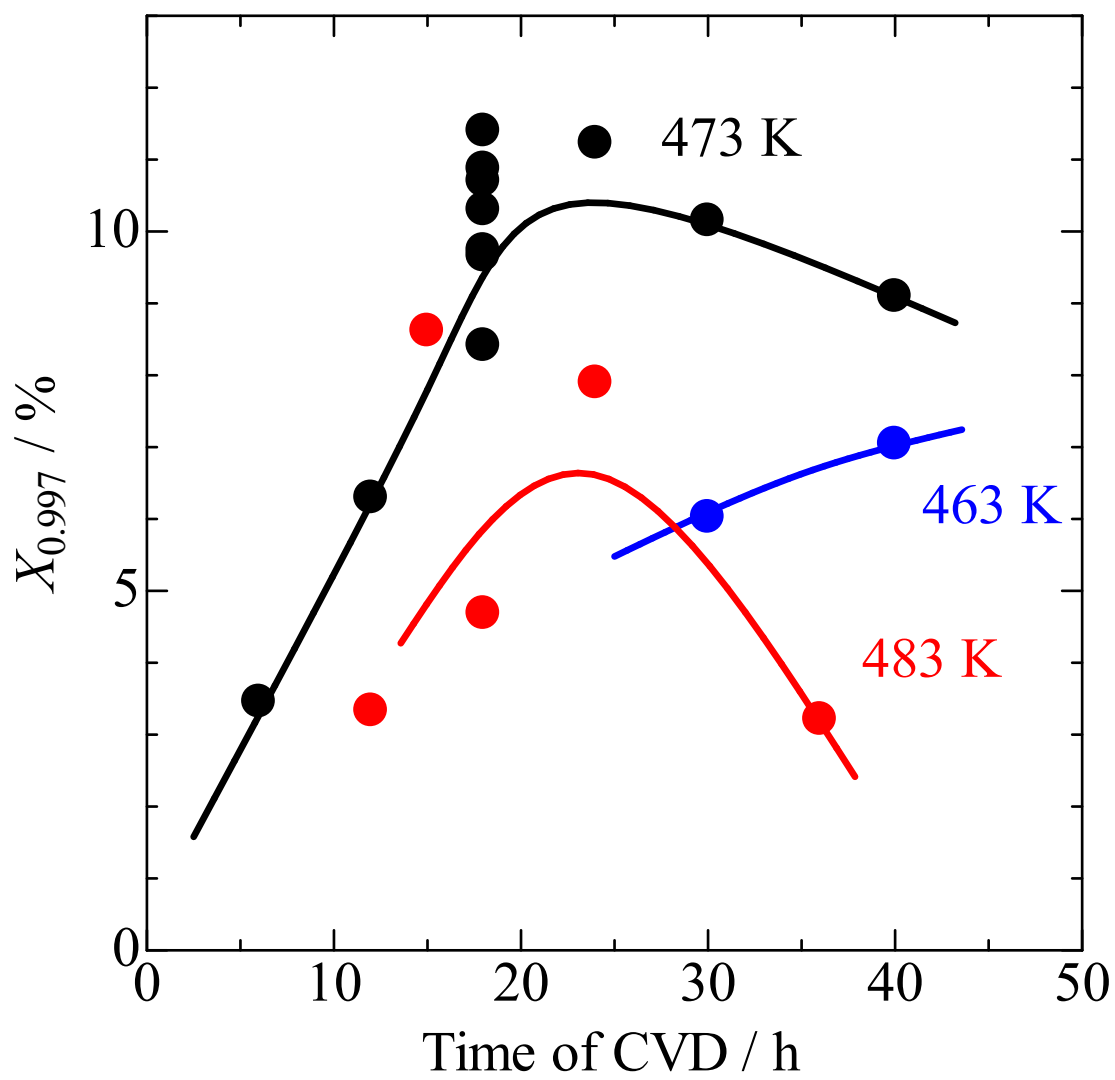


Figure 4 Change in $X_{0.997}$ by CVD at various temperatures in $20 \mu\text{mol s}^{-1}$ flow of tetramethoxysilane 0.3 kPa / helium mixture on MFI ($\text{Si}/\text{Al}_2 = 30$) after pelletization in toluene disproportionation at $P_{\text{toluene}} = 75 \text{ kPa}$ and $P_{\text{H}_2} = 500 \text{ kPa}$.

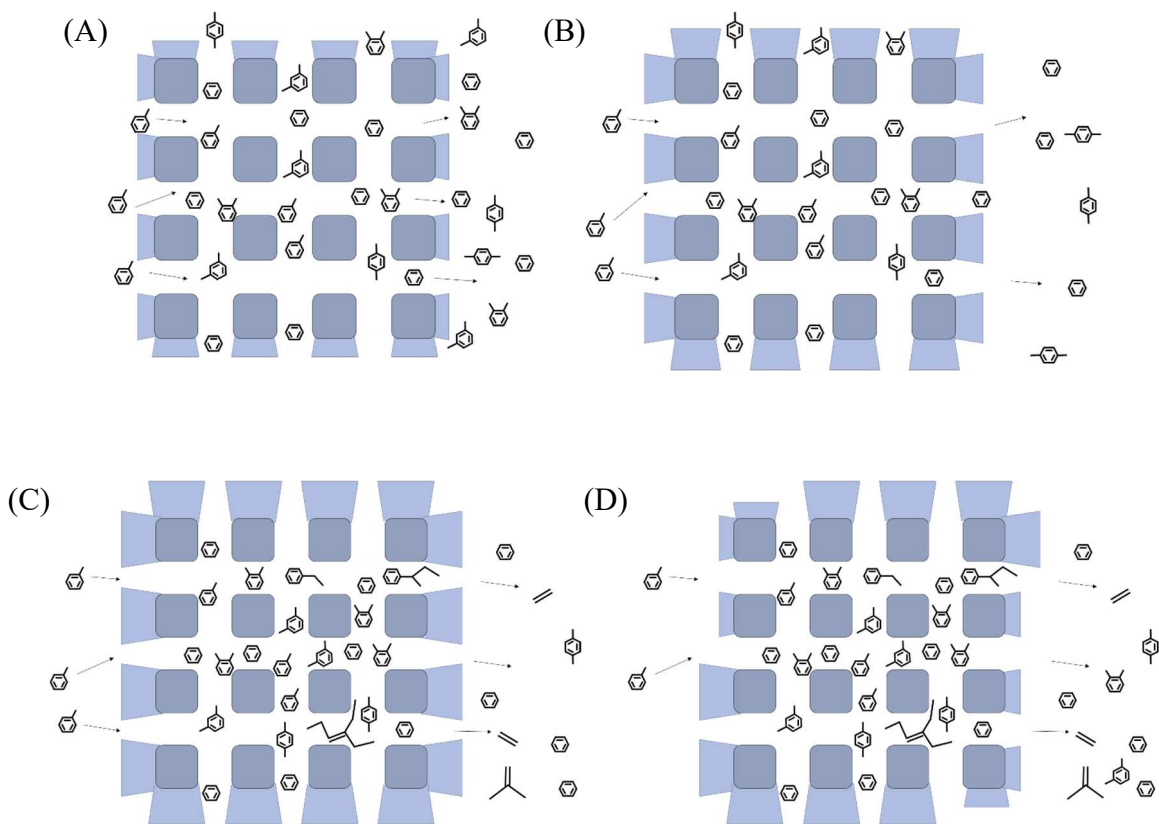


Figure 5 Schematic drawings of effect of structure of silica layer. (A) shows insufficient thickness. (B) shows ideal thickness. (C) shows too large thickness. (D) explains the influence of heterogeneous thickness.

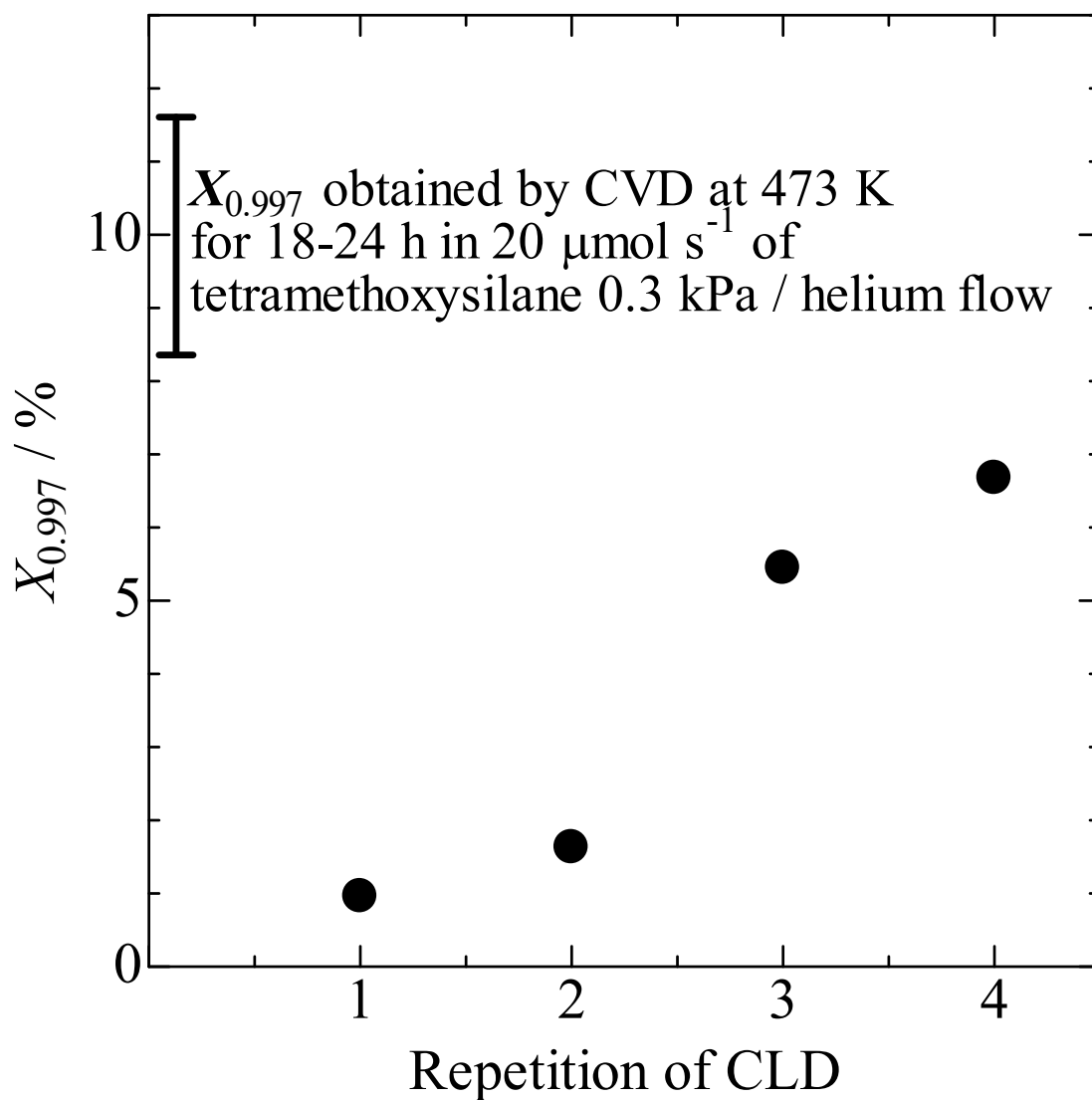


Figure 6 Plots of $X_{0.997}$ on MFI ($\text{Si}/\text{Al}_2 = 30$) modified by CLD [12] after pelletization in toluene disproportionation at $P_{\text{toluene}} = 75 \text{ kPa}$ and $P_{\text{H}_2} = 500 \text{ kPa}$.

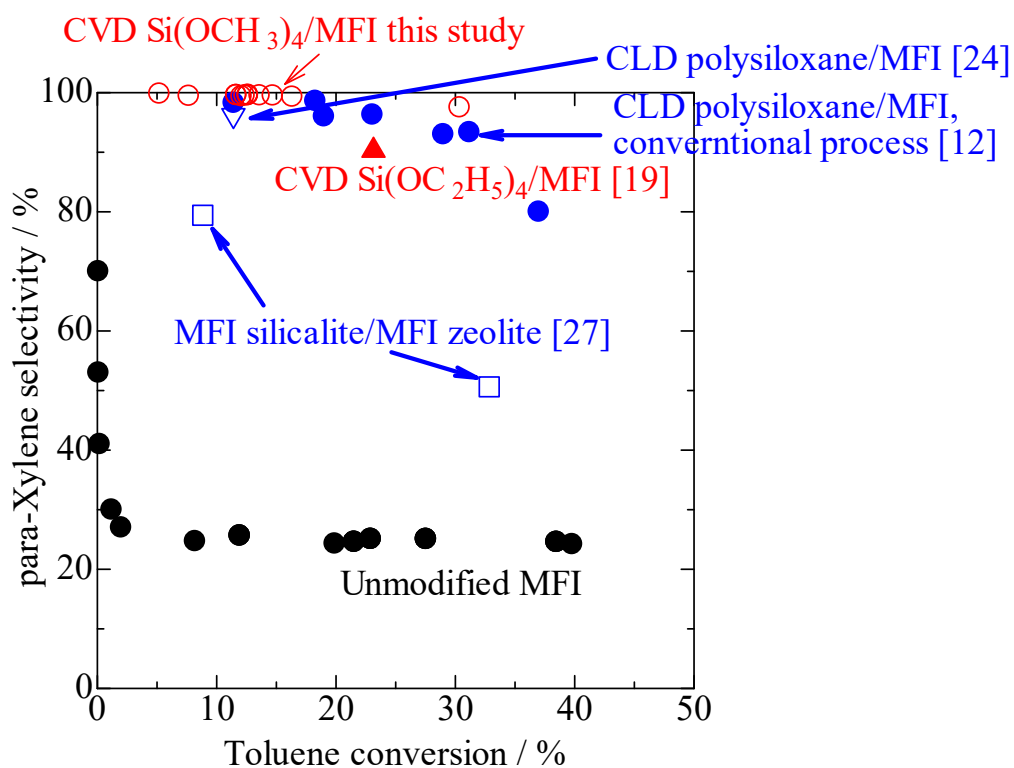


Figure 7 Plots of para-xylene selectivity against conversion on unmodified MFI (●, taken in this study and our previous paper [10]) and MFI modified with Si compounds by CVD (red) and liquid phase methods (blue) in laboratory scale (open) and industrial scale (filled) of catalyst preparation.

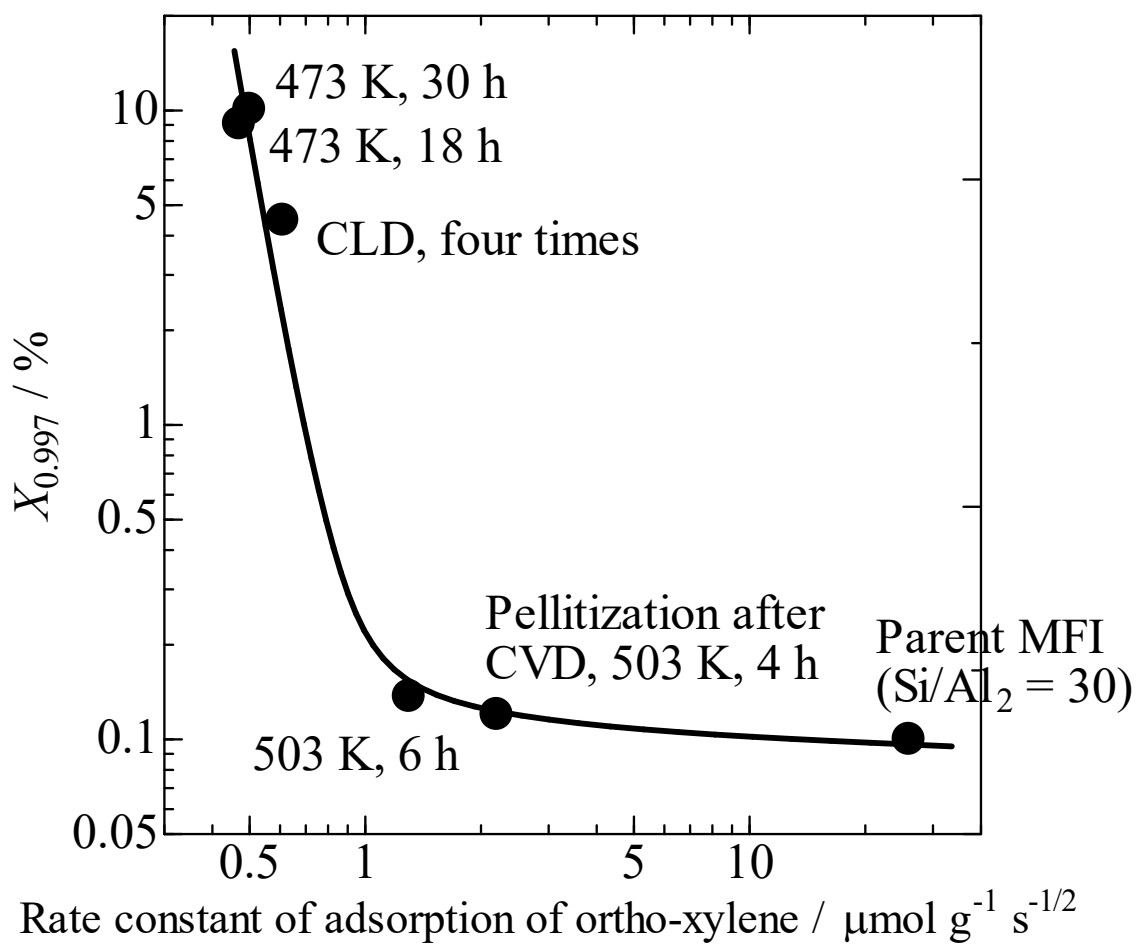


Figure 8 Plots of $X_{0.997}$ against rate constant of adsorption of ortho-xylene on selected catalysts. The modification was carried out by the CVD in $20 \mu\text{mol s}^{-1}$ of tetramethoxysilane 0.3 kPa / helium mixture after pelletization on MFI (Si/Al₂ = 30), unless specific remark is shown.

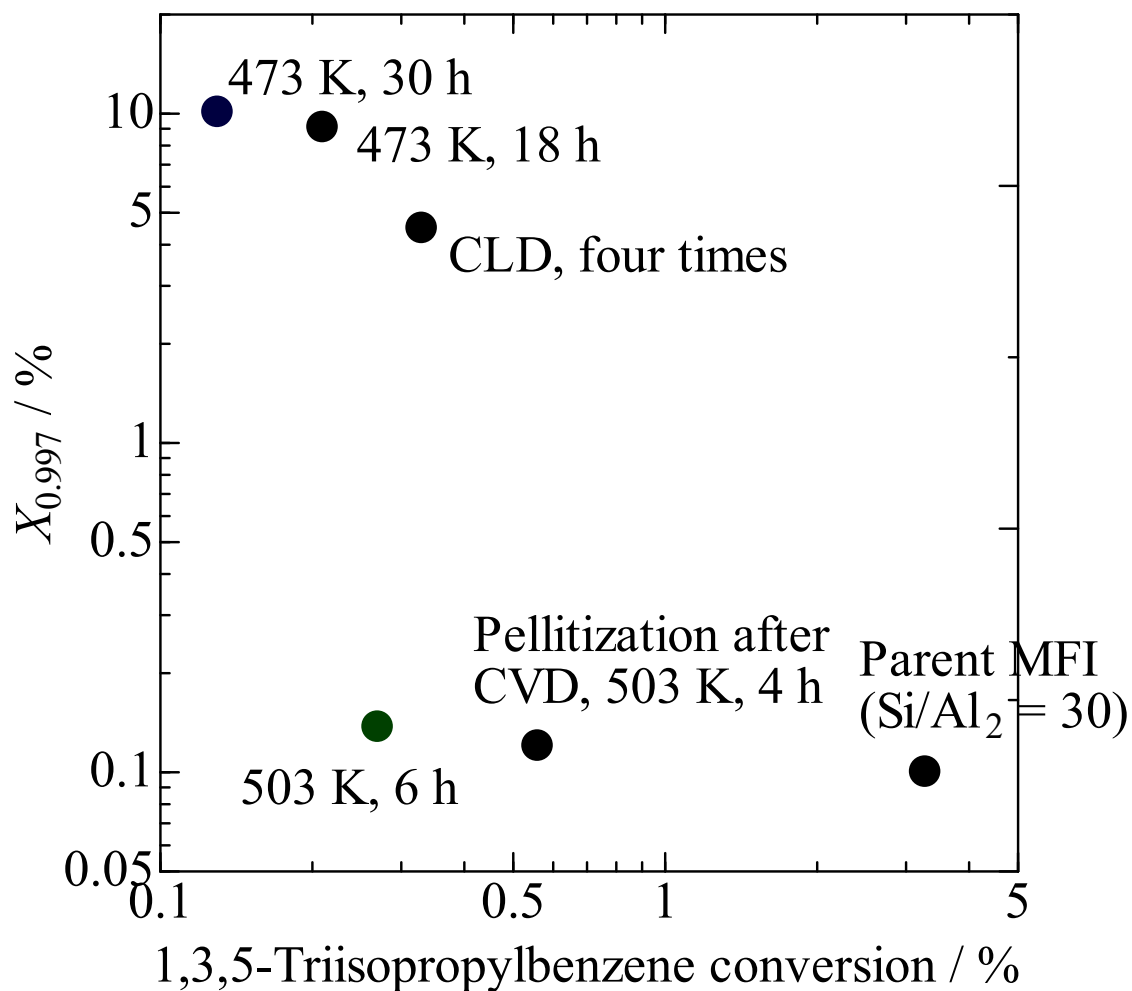


Figure 9 Plots of $X_{0.997}$ against conversion of 1,3,5-triisopropylbenzene on selected catalysts. The modification was carried out by the CVD in $20 \mu\text{mol s}^{-1}$ of tetramethoxysilane 0.3 kPa / helium mixture after pelletization on MFI (Si/Al₂ = 30), unless specific remark is shown.