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Removal and complete combustion of 1,4-dioxane in water by a two-step reaction combining adsorption and catalytic combustion

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Abstract

Catalytic wet air oxidation is not so effective to decompose 1,4-dioxane in water, while there have been several studies on this reaction. As an alternative, we propose a two-step purification system for removal and complete combustion of 1,4-dioxane, where the first step is removing 1,4-dioxane from water by adsorption, and in the second step, the adsorbent is heated to release 1,4-dioxane, and the released 1,4-dioxane is completely combusted by gas-phase catalytic reaction. We had searched for adsorbents and combustion catalysts suitable for the system and found a high-silica MFI zeolite and Pt/SiO_2, respectively. The high-silica MFI zeolite adsorbed up to 121 mg g^{-1} of 1,4-dioxane, and 1.1 mmol L^{-1} of 1,4-dioxane in water was almost completely removed by 10 g L^{-1} dose. The zeolite was reusable for adsorption-desorption cycles at least five times without any loss of the performance. Pt/SiO_2 was highly active for the complete combustion of 1,4-dioxane even at 200 °C. By using the high-silica MFI zeolite and Pt/SiO_2, we conducted the release of 1,4-dioxane from the zeolite by heating and the gas-phase catalytic combustion of 1,4-dioxane using two reactors connected in series, which were filled with the zeolite and Pt/SiO_2, respectively, and demonstrated that all 1,4-dioxane was released by 300 °C and was completely combusted in the upstream and downstream reactors, respectively.

Keywords: 1,4-dioxane; adsorption; zeolite; catalytic combustion; platinum catalyst

1. Introduction

In the past, 1,4-dioxane was used as a stabilizer for chlorinated solvent, and currently is used as an aprotic solvent in organic synthesis and for manufacturing various products including electronic devices, synthetic leather, paint, and so on [1, 2]. A report shows that the current annual world production of 1,4-dioxane is at least 10000 tons [2]. In addition to intended production, 1,4-dioxane is formed as a by-product in the production of some chemicals including ethylene glycol, ethylene oxide and some daily necessities like surfactant and detergent [1, 3].

1,4-Dioxane has hydrophilic nature and is water-miscible in any proportion [1, 4, 5]. In addition, 1,4-dioxane has low affinity to natural rock, soil, and sand [1, 4, 5]. Because of such characteristics, 1,4-dioxane is highly mobile in natural environment once it is released to the environment. Furthermore, 1,4-dioxane is persistent and hardly decomposed in nature due to stable ether bonds. Unfortunately, such properties cause the environmental pollution in surface water and groundwater [1, 6-8]. In fact, environmental pollution with 1,4-dioxane has currently occurred in many countries and regions [1, 6].

Some literatures report that 1,4-dioxane shows acute and chronic toxicity to human [1, 6, 9, 10]. Based on the result of toxicity test, US Environmental Protection Agency (US EPA) has classified 1,4-dioxane as a probable human carcinogen [6, 9, 11]. Considering the risk of 1,4-dioxane to human health, the Ministry of the Environment in Japan has set allowable concentration of 1,4-dioxane in groundwater at 50 μg L^{-1} [12]. Meanwhile, the Ministry of the Environment in Japan has also set the emission standard for 1,4-dioxane in industrial wastewater to be less than 500 μg L^{-1} [13]. Thus, 1,4-dioxane must be removed from contaminated drinking water and wastewater to avoid our health problem and the environmental pollution.

Catalytic wet air oxidation (CWAO) is a method in which organic contaminants in water are combusted in the presence of caalysts [14-20]. CWAO is particularly effective against non-biodegradable contaminants. In fact, so far, wide variety of catalysts including noble metals (Ru, Rh, Pd, Ir, and Pt) and metal oxides (Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ce, and their mixed

metal oxides) have been intensively investigated for decompositions of phenolic and nitrogen-containing compounds and carboxylic acids in water [14-20]. However, there are only few papers on CWAO of 1,4-dioxane.

Choi et al. reported that 1,4-dioxane in water was oxidatively decomposed with O_2 over Pt/CeO_2-ZrO_2-Bi_2O_3/SBA-16 [21] and Pt/CeO_2-ZrO_2-SnO_2/SBA-16 [22], which showed 34 and 44 % conversion of 1,4-dioxane, respectively, for the reactions with 100 ppm of 1,4-dioxane at 80 °C for 4 h. Indeed, those catalysts promoted CWAO of 1,4-dioxane, but the reaction rate is still not fast enough for practical applications. In addition, CWAO of 1,4-dioxane has serious problem that certain amount of 1,4-dioxane transfers from water to gas phase without being decomposed at the reaction temperature, as is mentioned in the papers [21, 22]. To confirm this, we performed CWAO of 1,4-dioxane in water in the presence of Pt/SiO_2 as a preliminary experiment and observed that most of 1,4-dioxane was transferred from water to gas phase at the reaction temperature of 80 °C (Fig. S1), which rendered this methodology ineffective. This issue can be solved by developing much active catalysts so that the reaction will be performed at low temperature to suppress the transfer of 1,4-dioxane to gas phase, but it is unlikely to be realized easily.

Adsorptive removal of pollutants in water using adsorbents has great advantages of simple operation, mild reaction conditions, and rapid treatment [23-25]. Activated carbon is a common adsorbent and in fact, has been applied for the removal of 1,4-dioxiane in water. While activated carbons often show decent adsorption performances for organic pollutants [26], generally 1,4-dioxane is hard to be adsorbed on them due to the high-water solubility, giving small adsorption capacity and thus adsorptive removal using activated carbons is ineffective especially for low concentration 1,4-dioxane. To address this issue, Woodard et al. applied a synthetic resin named AmberSorb™ 560, which is produced by partial pyrolysis of sulfonated styrene-divinylbenzene copolymer, as an adsorbent for 1,4-dioxane in water [27]. They demonstrated the high adsorption capacity of this resin for 1,4-dioxane owing to its hydrophobic nature and unique pore structure.

Chen et al. investigated adsorption of 1,4-dioxane in water over Ti-containing MFI zeolite named TS-1 and found that it showed a large adsorption capacity (85.17 mg g^{-1} = 0.9663 mmol g^{-1}) for 1,4-dioxane at 25 °C [28]. They further investigated adsorption mechanism by thermodynamic analysis and molecular dynamics simulation, and demonstrated that the adsorption of 1,4-dioxane was both enthalpy and entropy driven ($\Delta H < 0$ and $\Delta S > 0$) and that 1,4-dioxane was strongly adsorbed in the micropores since the molecular size matched well with the micropore size of the zeolite. According to this mechanism, Ti in the framework of TS-1 does not seem to be necessary for the adsorption of 1,4-dioxane. Unfortunately, however, adsorption performances of common aluminosilicate zeolites for 1,4-dioxane in water have not been evaluated and thus the necessity of Ti for the adsorption is still unknown.

As described above, adsorptive removal of 1,4-dioxane is effective for rapid treatment of wastewater and polluted water, but post-treatment, namely decomposition of adsorbed 1,4-dioxane, is still necessary. In some papers, removal and biological decomposition of 1,4-dioxane in water were achieved by using bioaugmented adsorbents [29] and by the treatment of spent adsorbent in bacterial culture [28], but the efficiency of the process was still unsatisfactory because the biological decomposition was slow.

Despite vigorous research to date mentioned above, only a few effective methods have been developed to purify water contaminated with 1,4-dioxane. To overcome this situation, in the present study, we wish to propose a two-step purification system combining adsorptive removal and gas-phase catalytic combustion for removal and complete decomposition of 1,4-dioxane in water. In this system, 1,4-dioxane in water is removed by adsorption and then 1,4-dioxane is desorbed from the adsorbent by heating, followed by gas-phase catalytic combustion in air over a catalyst. This reaction system could be an innovative way to solve the problems of the adsorption method and CWAO at once. For this to be realized, we first investigated adsorption properties of various aluminosilicate zeolites for 1,4-dioxane in water to find high-performance adsorbents. Then, we searched for supported metal catalysts effective for gas-phase combustion of 1,4-

dioxane. As a result, we found that high-silica MFI zeolite and Pt/SiO_2 for an adsorbent and a combustion catalyst, respectively, were suitable for the two-step purification system. Finally, we demonstrated removal of 1,4-dioxane in water and complete decomposition of 1,4-dioxane by the two-step purification system with the zeolite and catalyst that we found in this study.

2. Experiments

2.1. Adsorbents and catalysts

Aluminosilicate zeolites with different framework structures (BEA, MFI, FER, FAU, and MOR) used in this study are listed in Table 1. Proton-form zeolites were used as received. Ammonium-form zeolites were calcined in air at 550 ℃ for 3 h to transform into corresponding proton-form one. FER zeolite, which was potassium-form zeolite, was treated in an aqueous solution of NH_4NO_3 (Wako Pure Chemical Co.) at room temperature for 4 h to exchange K^+ with NH_4^+, and then calcined in air at 550 ℃ for 3 h. These zeolite samples are denoted as "three alphabets representing framework and Si/Al_2 ratio", e.g. MFI(200). For comparison, SiO_2 (Japan Aerosil Co., Aerosil® 300, 289 $m^2\ g^{-1}$), Al_2O_3 (Japan Aerosil Co., AEROXIDE® Alu C, 80 $m^2\ g^{-1}$), and SiO_2-Al_2O_3 (Reference catalyst of Catalysis Society of Japan, JRC-SAH-1, 498 $m^2\ g^{-1}$) were also tested for adsorption of 1,4-dioxane in water. SEM images and IR spectra of some adsorbents are given in Fig. S2 for reference.

Silica-supported Pt catalyst (Pt/SiO_2) was prepared by an impregnation method. An aqueous solution of H_2PtCl_6 (Wako Pure Chemical Co.) was added dropwise to SiO_2 (Japan Aerosil Co., Aerosil® 300). After dried at 100 ℃ overnight, the obtained solid was calcined in air at 400 ℃ for 4 h, followed by reduction with H_2 at 450 ℃ for 2 h. The loading amount of Pt was 3 wt. %. Other supported Pt catalysts were prepared with the same procedure as that for Pt/SiO_2, but CeO_2 (Reference catalyst of Catalysis Society of Japan, JRC-CEO-2), MgO (Ube Material Ind. Ltd.), TiO_2 (Japan Aerosil Co., AEROXIDE® P25), Al_2O_3 (Japan Aerosil Co., AEROXIDE® Alu C), and ZrO_2 (Reference catalyst of Catalysis Society of Japan, JRC-ZRO-2) were used instead of SiO_2.

148 Silica-supported Pd, Ru, Rh, and Ir catalysts were also prepared by the same procedure as
149 that for Pt/SiO_2, but $PdCl_2$ (Wako Pure Chemical Co.), $RuCl_3 \cdot nH_2O$ (Wako Pure Chemical Co.),
150 Na_3RhCl_6 (Wako Pure Chemical Co.), and $IrCl_4$ (Wako Pure Chemical Co.) were used instead of
151 $H_2PtCl_6 \cdot 6H_2O$.
152
153 *2.2. Characterization*
154 Nitrogen adsorption isotherms were taken at –196 ℃ using an automatic apparatus
155 (BELSORP mini, Bel Japan). Thermogravimetric (TG) profile for the adsorbent after adsorption
156 of 1,4-dioxane was measured in air on a thermogravimetric analyzer (TG8120, Rigaku Co.).
157 Scanning electron microscopy images were taken on a scanning electron microscope (S-4800,
158 HITACHI). Infrared spectra were obtained by a KBr method on an infrared spectrometer (FT/IR-
159 6100, JASCO Co.).
160 For supported Pt catalysts, the surface area of Pt particles was estimated from chemisorbed
161 amount of CO at 50 ℃, which was taken on an automatic instrument (BEL-CAT, Bel Japan). The
162 catalysts were pretreated in H_2 at 450 ℃ for 2 h just before CO adsorption. The stoichiometry of
163 the adsorbed CO to surface Pt and surface density of Pt were assumed to be 1 and 1.25×10^{19} m^{-2},
164 respectively.
165
166 *2.3. Adsorption of 1,4-dioxane*
167 Adsorption of 1,4-dioxane in water on adsorbents was performed in a test tube with a screw
168 cap. An aqueous solution of 1,4-dioxnae (10 mL, 1.1 mmol L^{-1}) and 0.1 g of an adsorbent were
169 added to a test tube, and it was capped. Then, the test tube was set in an aluminum block heater
170 with a magnetic stirrer, and the mixture was stirred while keeping temperature at 25 °C. After 1
171 h, the adsorbent was separated by centrifugation and the supernatant was analyzed by a high-
172 performance liquid chromatograph (Prominence, Shimadzu) equipped with an ion-exclusion
173 column (Rezex ROA-Organic Acid LC, Phenomenex) to determine the concentration of 1,4-

dioxane, where an aqueous solution of $HClO_4$ (10 mmol L^{-1}) was used as eluting solution.

Adsorption isotherms were measured using aqueous solution of 1,4-dioxane with different concentrations ranging from 0.1 to 34 mmol L^{-1}.

2.4. Catalytic gas-phase combustion of 1,4-dioxane

Gas-phase combustion of 1,4-dioxane over a supported metal catalyst was performed in a fixed-bed continuous flow reactor. The outlet of the reactor was connected to a flame ionization detector (FID). The catalyst was put in a glass reactor and the temperature was increased from room temperature in He flow. When the temperature reached 200 ℃, a mixed gas containing 0.1% 1,4-dioxane, 20% O_2 and He (balance) was fed to the reactor at a rate of 50 mL min^{-1}. To avoid condensation of 1,4-dioxane, the gas line of the reaction system was heated at 120 ℃. The concentration of organic compounds including 1,4-dioxane and partial oxidation products at the outlet of the reactor was continuously monitored by FID.

Temperature-programmed combustion of 1,4-dioxane was performed with a similar manner to the reaction experiment at constant temperature mentioned above, but the temperature was increased from 200 to 500 ℃ at 10 ℃ min^{-1}.

2.5. A two-step reaction for adsorptive removal of 1,4-dioxane and catalytic combustion of 1,4-dioxane

While details will be presented in Results and Discussion section, the optimal adsorbent and combustion catalysts were MFI(200) and Pt/SiO_2, respectively. Therefore, these were applied for removal of 1,4-dioxane in water and catalytic combustion of 1,4-dioxane by a two-step reaction.

Removal of 1,4-dioxane in water was performed in a batch-type reactor. An aqueous solution of 1,4-dioxane (100 mL, 34 mmol L^{-1}) and 1 g of MFI(200) were put in an Erlenmeyer flask and the suspension was stirred at 25 ℃. After 3 h, MFI(200) with 1,4-dioxane was collected by filtration and 0.1 g of it was put in the first (upstream) reactor shown in Fig. 1, while 0.5 g of

200 Pt/SiO_2 was put in the second (downstream) reactor. The gas line from the outlet of the first reactor
201 to FID through the second reactor was heated at 120 ℃. Then, the temperature of the first reactor
202 was increased from 25 to 300 ℃ at 10 ℃ min^{-1} to desorb 1,4-dioxane from MFI(200), while O_2-
203 He mixture (20 % O_2 in He and total flow rate of 50 mL min^{-1}) was fed and the temperature of
204 the second reactor was kept at 300 ℃. After the first reactor reached 300 ℃, the temperature was
205 held for 15 min.
206
207 **3. Results and discussion**
208 *3.1. Adsorption of 1,4-dioxane*
209 First, screening of adsorbents suitable for adsorptive removal of 1,4-dioxane in water was
210 performed under the conditions with 1.1 mmol L^{-1} of 1,4-dioxane at 25 ℃ for 1 h. As will be
211 shown later, 1 h was enough to reach adsorption equilibrium. Fig. 2 shows the adsorbed amount
212 of 1,4-dioxane on various adsorbents under the conditions. The adsorbed amount was greatly
213 different depending on the zeolites. It was found that BEA(25) and MFI(36) exhibited large
214 adsorbed amount, while only little 1,4-dioxane was adsorbed on FER(18), FAU(5.2), and
215 MOR(20). SiO_2 and Al_2O_3 were not effective as an adsorbent for the removal of 1,4-dioxane,
216 while a moderate amount of 1,4-dioxane was adsorbed on SiO_2-Al_2O_3. There was no clear
217 relationship between the adsorbed amount and Si/Al_2 ratio of the tested zeolites. Therefore, good
218 matching of the micropore size and micropore shape of BEA and MFI with 1,4-dioxane would
219 bring about the large adsorption amount of 1,4-dioxane.
220 To further investigate the adsorption properties of BEA and MFI zeolites, adsorption
221 isotherms for 1,4-dioxane in water were taken at 25 ℃. Influence of Si/Al_2 ratio on the adsorption
222 property was also investigated using BEA and MFI zeolites with low and high Si/Al_2 ratios (Fig.
223 3). Regardless of the Si/Al_2 ratio and framework structure, adsorbed amount of 1,4-dioxane
224 steeply increased at low concentrations and then became almost constant at the equilibrium
225 concentrations above 20 mmol L^{-1}, namely Langmuir-type adsorption. In fact, those adsorption

isotherms were well fitted to a Langmuir's adsorption equation (eq. 1),

$$Q_{eq} = \frac{Q_{max}[\text{1,4-dioxane}]_{eq}K_{eq}}{1+[\text{1,4-dioxane}]_{eq}K_{eq}} \quad (1)$$

where Q_{eq}, Q_{max}, $[\text{1,4-dioxane}]_{eq}$, and K_{eq} are adsorbed amount, maximum adsorption capacity, concentration of 1,4-dioxane at adsorption equilibrium, and adsorption equilibrium constant, respectively. The Langmuir's parameters (Q_{max} and K_{eq}) obtained by the curve fitting are summarized in Table 2. The micropore volumes estimated from the adsorption isotherms of N_2 at –196°C are also included in that table. For both BEA and MFI, the zeolites with high Si/Al_2 having less amount of Brønsted acid site had larger Q_{max} than those with low Si/Al_2. In addition, Q_{max} was greater for MFI than BEA, and MFI(200) had the largest Q_{max}, which was 112 mg g^{-1}. From the density of 1,4-dioxane at 25 °C (d = 1.03 g mL^{-1}) and Q_{max}, the volume of adsorbed 1,4-dioxane at the state of Q_{max}, which is named V_{max}, was calculated, and the ratio of V_{max} to the micropore volume, which is called filling factor here, was estimated (Table 2). While the filling factor for BEA(25) was only 35%, it was increased to 52% for BEA(300) but this value indicates that about 50% of the micropore was empty even at the state of Q_{max}. Comparing MFI and BEA with similar Si/Al_2, it is noted that the filling factor for MFI was about 1.5 times larger than that for BEA. In particular, the filling factor for MFI(200) reached 80%.

Since the molecular size of 1,4-dioxane (0.52×0.59×0.67 nm) [28] is almost equal to the aperture size of the micropores in MFI zeolite (0.51×0.55 nm and 0.53×0.56 nm), while is smaller than that in BEA zeolite (0.66 × 0.67 nm and 0.56×0.56 nm), it is considered that 1,4-dioxane was packed neatly almost without gaps in the micropores of MFI(200). In addition, the good matching between the molecular size of 1,4-dioxane and the micropore size of the MFI zeolite can bring strong van der Waals forces from the pore walls of the zeolite to 1,4-dioxane, which may also be the reason for large Q_{max} of MFI. In fact, the adsorption equilibrium constant (K_{eq}) of MFI(200)

for 1,4-dioxane was 0.86 which was larger than that of BEA(300) (K_{eq}=0.60).

The adsorption of 1,4-dioxane on the zeolites in this study occurred in water, and thus the adsorption of water on the zeolites did competitively with that of 1,4-dioxane. Since water strongly adsorbs on Brønsted acid sites, the effective pore volume available for the adsorption of 1,4-dioxane in water, which is the pore volume not occupied by adsorbed water, is expected to be smaller for the zeolites with low Si/Al_2 than those with high Si/Al_2. To avoid the influence of water on the adsorption of 1,4-dioxane, we measured adsorption isotherms of 1,4-dioxane in gas-phase for MFI(36) and MFI(200) at 25 °C after pretreatment of the zeolites in vacuo at 200 °C to desorb water from them, and compared the adsorption isotherm for MFI(200) with that for MFI(36) (Fig. S3). As the two isotherms clearly showed, MFI(36) and MFI(200) gave almost the same saturated adsorption amounts, supporting our hypothesis. In general, it is known that BEA zeolites have many defects in the framework structure [30], which makes it relatively hydrophilic. This also explains why the adsorbed amount of 1,4-dioxane in water for BEA was smaller than that for MFI. Adsorption of organic contaminants in water using zeolites has been widely investigated, and in many cases, high-silica zeolites exhibited high adsorption capacity mainly due to their hydrophobic nature inside the micropores as MFI(200) for 1,4-dioxane [31-33].

Based on these results, we concluded that MFI(200) was the best adsorbent for the two-step purification system in the adsorptive removal of 1,4-dioxane from water. The subsequent studies were performed with MFI(200).

Next, the adsorption rate of 1,4-dioxane on MFI(200) and the amount of MFI(200) required to completely remove 1,4-dioxane from water were investigated. Both experiments were performed at 25 °C. As shown in Fig. 4(A), the concentration of 1,4-dioxane in the solution remained constant after 0.5 h, suggesting that the adsorption of 1,4-dioxane on MFI(200) was fast and reached equilibrium within 0.5 h. Fig. 4(B) shows the relationship between the amount of MFI(200) added to 1 L of 1,4-dioxane solution (1.1 mmol L^{-1}) and the concentration of 1,4-dioxane in the solution at equilibrium. The concentration of 1,4-dioxane in the solution at

277 equilibrium was decreased as the dose of MFI(200) was increased, and almost all 1,4-dioxane in
278 the solution was removed at 10 g L^{-1} dose. The adsorbed amount of 1,4-dioxane on MFI(200)
279 with 10 g L^{-1} dose was 0.11 mmol g^{-1}, which was about 10% of Q_{max} of this zeolite.
280
281 *3.2. Catalytic gas-phase combustion of 1,4-dioxane*
282 We then searched for a catalyst to promote catalytic gas-phase combustion of 1,4-dioxane.
283 Fig. 5 compares the catalytic activities of various SiO_2-supported catalysts for gas-phase
284 combustion of 1,4-dioxane at 200 °C. Ru/SiO_2 and Rh/SiO_2 were inactive for the reaction under
285 the reaction conditions, while the combustion of 1,4-dioxane proceeded over Ir/SiO_2 somewhat,
286 but the catalytic activity of this catalyst was not so high. In contrast to them, Pt/SiO_2 and Pd/SiO_2
287 greatly promoted the combustion of 1,4-dioxane. Among them, Pt/SiO_2 was the best catalyst
288 showing the highest catalytic activity. Supported platinum catalysts are known to be good
289 catalysts for gas-phase combustion of a variety of organic pollutants such as volatile organic
290 compounds [34, 35], and saturated and unsaturated hydrocarbons [36], and those are consistent
291 with that Pt/SiO_2 can serve as a catalyst for combustion of 1,4-dioxane.
292 The support materials for the supported Pt catalyst were then screened. The results are
293 shown in Fig. 6. While Pt/MgO showed no activity, the activities of Pt/ZrO_2 and Pt/Al_2O_3 were
294 only little. Pt/CeO_2 and Pt/TiO_2 promoted combustion of 1,4-dioxane, but their catalytic activities
295 were still lower than that of Pt/SiO_2. From these results, we concluded that Pt/SiO_2 was the best
296 combustion catalyst suitable for the two-step purification system.
297 Fig. 7 shows the relationship between the surface area of Pt particles for the supported Pt
298 catalysts, which was estimated from the amount of chemisorbed CO, and catalytic activity for
299 combustion of 1,4-dioxane at 200 °C. In general, the larger the surface area of Pt particles was,
300 the higher the catalytic activity became, but the results of Fig. 7 showed that the highly active
301 Pt/SiO_2, Pt/CeO_2, and Pt/TiO_2 had rather small surface area of Pt particles.
302 It is known that the acidity and basicity of support materials for supported precious metal

303 catalysts strongly affect their catalytic activities for the reactions occurring in oxidative
304 atmosphere, namely combustion reactions. Yazawa et al. systematically investigated the effect of
305 acidity and basicity of support materials for supported Pt catalysts on propane combustion activity
306 [37, 38]. They demonstrated that the metal oxides with high acidity prevented Pt from oxidation
307 in the oxidative atmosphere and thus Pt on such metal oxides showed excellent catalytic activities.
308 The acidity of the metal oxides that we used in this study was increased in the order of MgO <
309 ZrO_2 < Al_2O_3 < TiO_2 < SiO_2, according to the acid strength estimated by Hammett indicator
310 method [37] and from isoelectric points [39, 40]. It is noted that this order was in good agreement
311 with that of the catalytic activity for combustion of 1,4-dioxane shown in Fig. 6. Therefore, it can
312 be considered that the acidic support material like SiO_2 suppressed the oxidation of Pt in the
313 reaction conditions, resulting in the high catalytic activity for combustion of 1,4-dioxane. Pt/CeO_2
314 exhibited moderate catalytic activity for combustion of 1,4-dioxane, despite CeO_2 is generally
315 classified as a solid base [41]. It is known that Pt is strongly interacted with CeO_2 surface, causing
316 redispersion of Pt on CeO_2 in oxidative atmosphere [42]. Since the CO adsorption measurement
317 to determine the surface area of Pt particles was performed after the pretreatment in H_2 at 450 ℃
318 in this study, the dispersion of Pt for Pt/CeO_2 might be underestimated, and under the reaction
319 conditions for combustion of 1,4-dioxane, Pt was highly dispersed, which may explain the
320 relatively high activity of Pt/CeO_2 for the reaction.

321 The catalytic gas-phase combustion of 1,4-dioxane over Pt/SiO_2 was compared to that of
322 non-catalytic one, where the latter reaction was performed without a catalyst. The combustion of
323 1,4-dioxane was performed by increasing the temperature from 200 to 500 °C at 10 °C min^{-1},
324 namely temperature-programmed combustion, and the results are given in Fig. 8. Without a
325 catalyst, no reaction occurred at 200 °C, and the combustion of 1,4-dioxane started above 300 °C.
326 At 500 °C, about 90% of 1,4-dioxane was combusted. However, the conversion was not likely to
327 reach 100% even if the temperature was further increased, suggesting that complete combustion
328 of 1,4-dioxane into CO_2 and H_2O was hard to occur without a catalyst. On the other hand, as

mentioned earlier, combustion of 1,4-dioxane occurred even at 200 °C in the presence of Pt/SiO_2, and the conversion reached 100 % at higher temperatures, indicating that 1,4-dioxane was completely combusted into CO_2 and H_2O. Thus, catalytic combustion using Pt/SiO_2 was demonstrated to be more efficient especially at lower temperature than non-catalytic one.

3.3. Desorption of 1,4-dioxane from MFI(200) and combustion of desorbed 1,4-dioxane over Pt/SiO_2 in the two reactors connected in series

The desorption of 1,4-dioxane from MFI(200) was then investigated by measuring the thermogravimetric (TG) and temperature-programmed desorption (TPD) profiles in air. Fig. 9(A) shows a TG profile of MFI(200) to which 1,4-dioxane was taken in advance. On the TG profile, a large weight loss began at around 100 °C, and the weight loss was almost completed by 300 °C, meaning that all 1,4-dioxane was desorbed from MFI(200) by this temperature, and the final weight loss was –10.8%. If this weight loss was entirely only due to the desorption of 1,4-dioxane, the desorbed amount of 1,4-dioxane was estimated to be 121 mg g^{-1}. This value was almost the same as the saturated adsorption amount (Q_{max}=112 mg g^{-1}) estimated from the adsorption isotherm of 1,4-dioxane.

It was demonstrated that MFI(200) was reusable as an adsorbent at least five times as follows. After saturated amount of 1,4-dioxane was adsorbed on MFI(200) under the conditions mentioned above, it was heated in air at 300 °C for 30 min to desorb 1,4-dioxane. Then, 1,4-dioxane was adsorbed on that MFI(200) again. This operation was repeated five times in total. The adsorbed amount of 1,4-dioxane on MFI(200) at the fifth time was 108 mg g^{-1}, which was almost the same as that in the first adsorption (112 mg g^{-1}), demonstrating that MFI(200) was reusable without any loss of the performance as an adsorbent.

Finally, the desorption of 1,4-dioxane from MFI(200) and combustion of desorbed 1,4-dioxane over Pt/SiO_2 were performed using two reactors connected in series (Fig. 1), in which the first and second reactors were filled with MFI(200) with 1,4-dioxane and Pt/SiO_2, respectively.

The temperature of the second reactor was kept constant at 300 °C. The temperature of the first reactor was increased from room temperature to 300 °C at 10 °C min^{-1}, while 20 % O_2 in He was flown into the reactor. For comparison, the same experiment was also conducted without a catalyst in the second reactor. The results are shown in Fig. 9(B). In case of the experiment without a catalyst in the second reactor, 1,4-dioxane desorbed from MFI(200) flowed out of the second reactor without combustion (dashed line in Fig. 9(B)). In contrast, when Pt/SiO_2 was put in the second reactor (solid line in Fig. 9(B)), the gas at the outlet of the second reactor contained no organic matter (no signal on the FID), meaning that 1,4-dioxane was completely combusted into CO_2 and H_2O. From the above, we concluded that the two-step purification system using MFI(200) and Pt/SiO_2 as an adsorbent and combustion catalyst, respectively, can rapidly and effectively remove 1,4-dioxane from water and completely combust it in the series-type reactor.

4. Conclusions

In this study, we propose a two-step purification system, where the first step is removal of 1,4-dioxane from water by adsorption, and in the second step, the adsorbent is heated to release 1,4-dioxane, and the released 1,4-dioxane is completely combusted by catalytic reaction, as a method to purify water contaminated with 1,4-dioxane. We had found MFI zeolite with a high Si/Al_2 ratio (=200), namely high-silica MFI zeolite, and Pt/SiO_2 as a good adsorbent and combustion catalyst, respectively, suitable for the system. The high-silica MFI zeolite adsorbed up to 121 mg g^{-1} of 1,4-dioxane, and was reusable at least five times without any loss of the performance, while Pt/SiO_2 showed high catalytic activity for the combustion of 1,4-dioxane even at 200 °C. Finally, release of 1,4-dioxane from the zeolite and the gas-phase catalytic combustion of released 1,4-dioxane by Pt/SiO_2 were performed using two reactors connected in series, and all 1,4-dioxane desorbed from the zeolite by 300 °C was completely combusted to CO_2 and H_2O over Pt/SiO_2.

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CRediT authorship contribution statement

Jieqiong Zhang: Conceptualization, Data curation, Investigation, Writing-original draft. **Yuan Huang:** Methodology, Investigation. **Miyu Sato:** Data curation. **Xin Zheng:** Methodology, Investigation. **Shin-ichiro Noro:** Methodology, Writing-review & editing. **Ryoichi Otomo:** Supervision, Writing-review & editing. **Yuichi Kamiya:** Conceptualization, Methodology, Supervision, Writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data used in this study are available from the corresponding author upon reasonable request.

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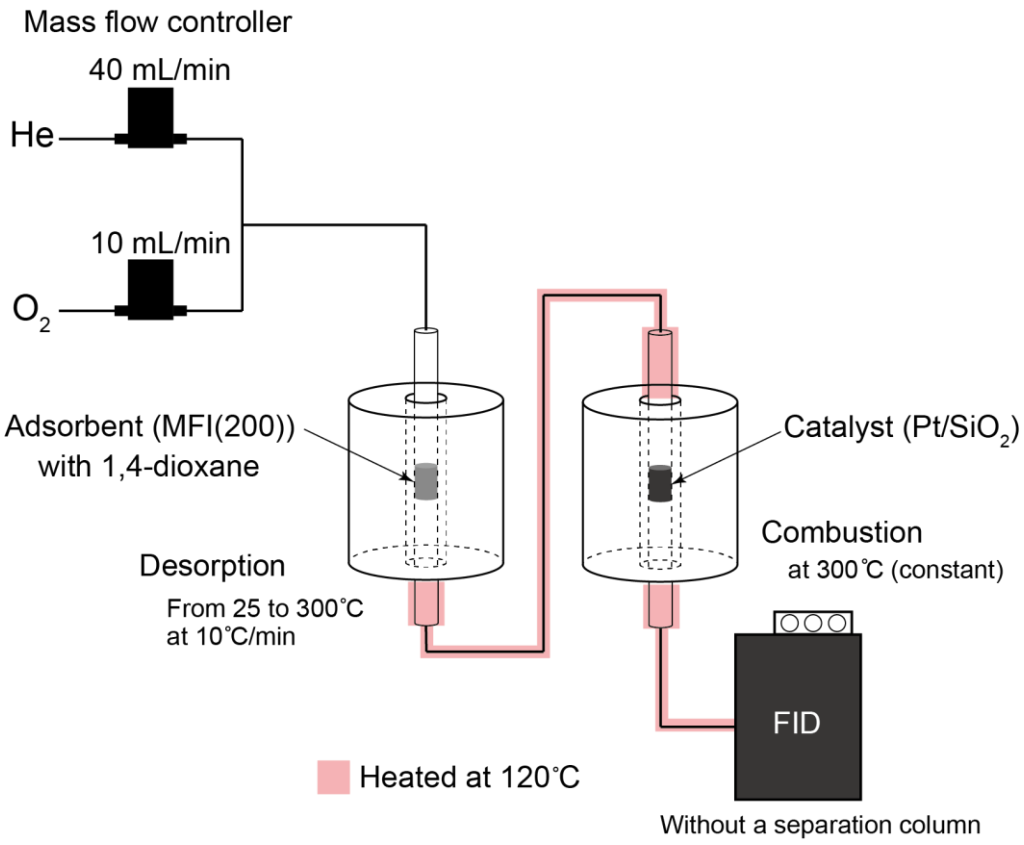

Fig. 1. A reaction apparatus for desorption of 1,4-dioxane from an adsorbent and combustion of desorbed 1,4-dioxane over a combustion catalyst. MFI(200) and Pt/SiO_2 were used as an adsorbent and combustion catalyst, respectively, in this study.

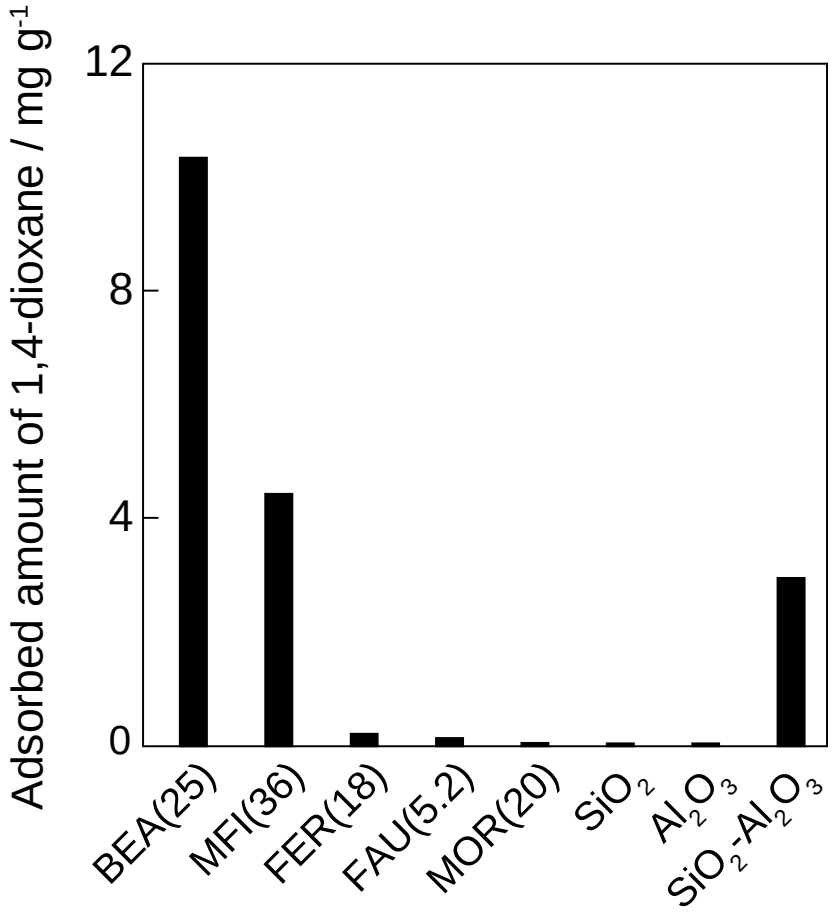

Fig. 2. Comparison of adsorbents for adsorption of 1,4-dioxane in water. Conditions: adsorbent, 0.1 g; $[1,4\text{-dioxane}]_0$ = 1.1 mmol L^{-1}; volume of the solution, 10 mL; temperature, 25 ℃; and time 1 h.

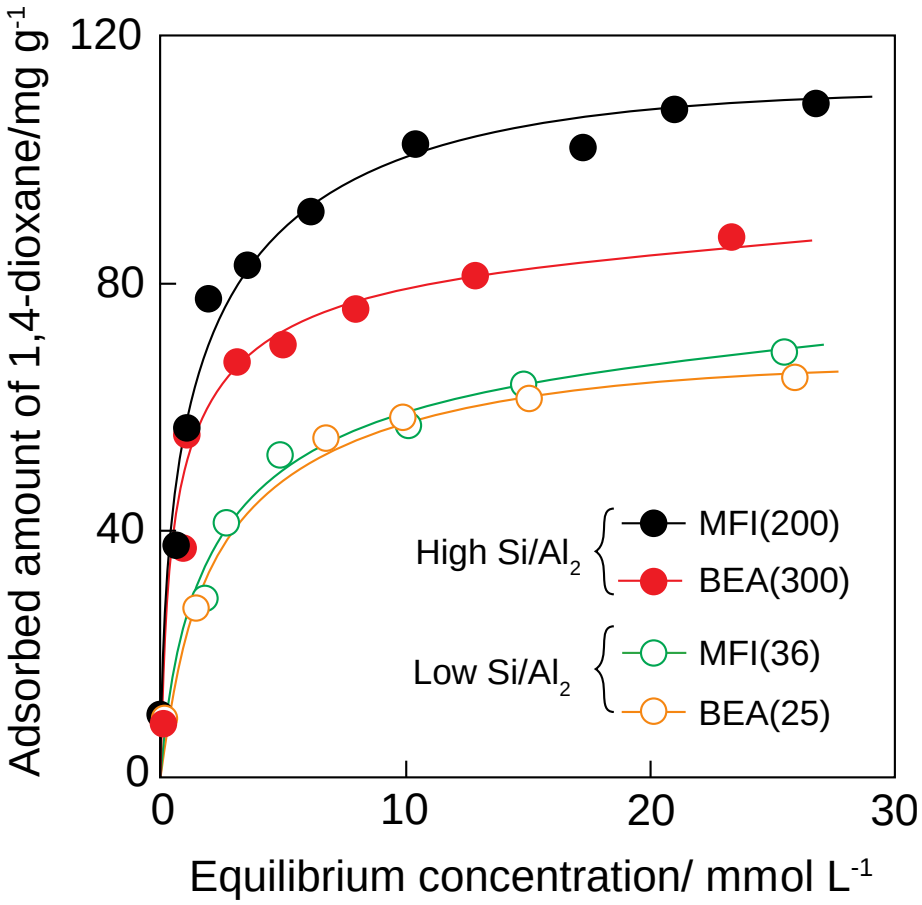

Fig. 3. Adsorption isotherms for 1,4-dioxane in water over MFI(200), BEA(300), MFI(36), and BEA(25). Conditions: adsorbent, 0.1 g; $[1,4\text{-dioxane}]_0$ = 0.1 ~ 34 mmol L^{-1}; volume of the solution, 10 mL; temperature, 25 °C; and time 1 h.

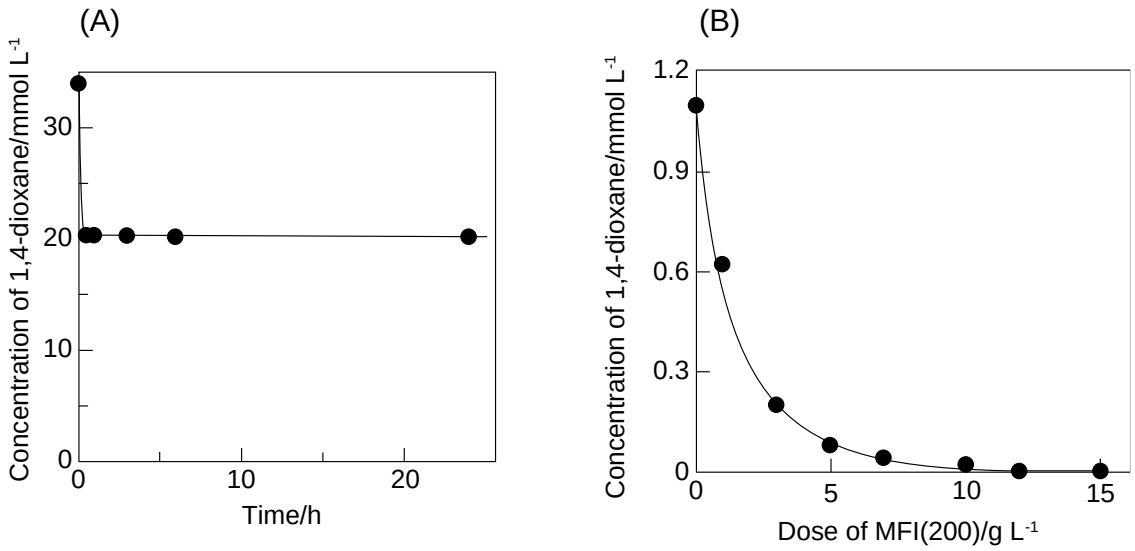

Fig. 4. (A) Kinetics for adsorption of 1,4-dioxane over MFI(200) and (B) effect of the dose of MFI(200) on adsorptive removal of 1,4-dioxane (right). Conditions for kinetics: adsorbent (MFI(200)), 1 g; $[1,4\text{-dioxane}]_0 = 34$ mmol L^{-1}; volume of 1,4-dioxane solution, 100 mL; and temperature, 25 ℃. Conditions for effect of the dose: adsorbent (MFI(200)), 0.01 ~ 0.15 g; $[1,4\text{-dioxane}]_0 = 1.1$ mmol L^{-1}; volume of the solution, 10 mL; temperature, 25 ℃; and time, 1 h.

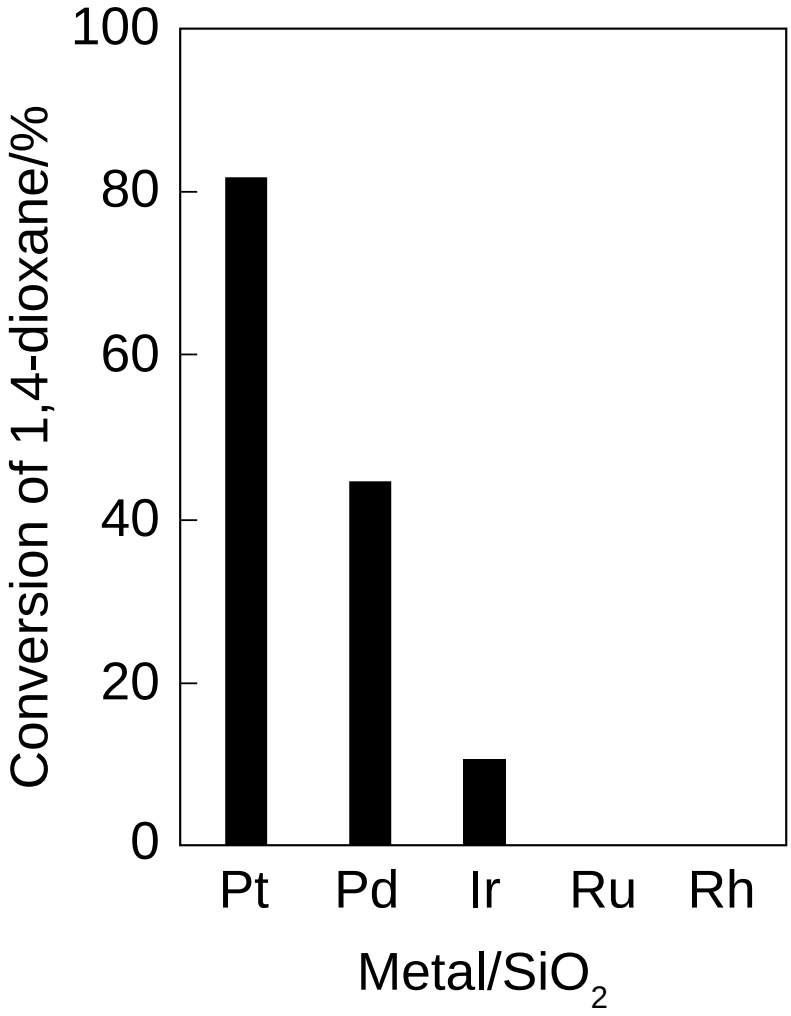

Fig. 5. Comparison of silica-supported catalysts for gas-phase combustion of 1,4-dioxane. Reaction conditions: catalyst, 0.1 g; gas mixture, 1,4-dioxane/O_2/He=0.1/20/79.9; total flow rate, 50 mL min^{-1}; and reaction temperature, 200 ℃.

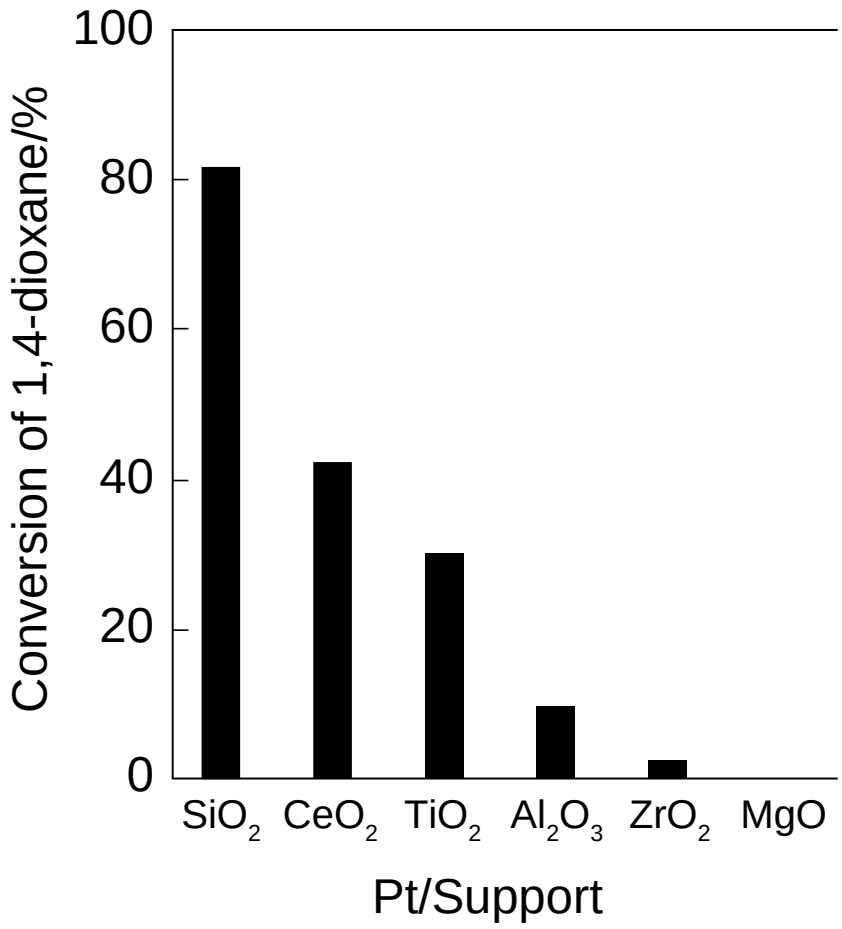

Fig. 6. Influence of support on the catalytic performance of supported Pt catalysts for gas-phase combustion of 1,4-dioxane. Reaction conditions were the same as those shown in Fig. 5.

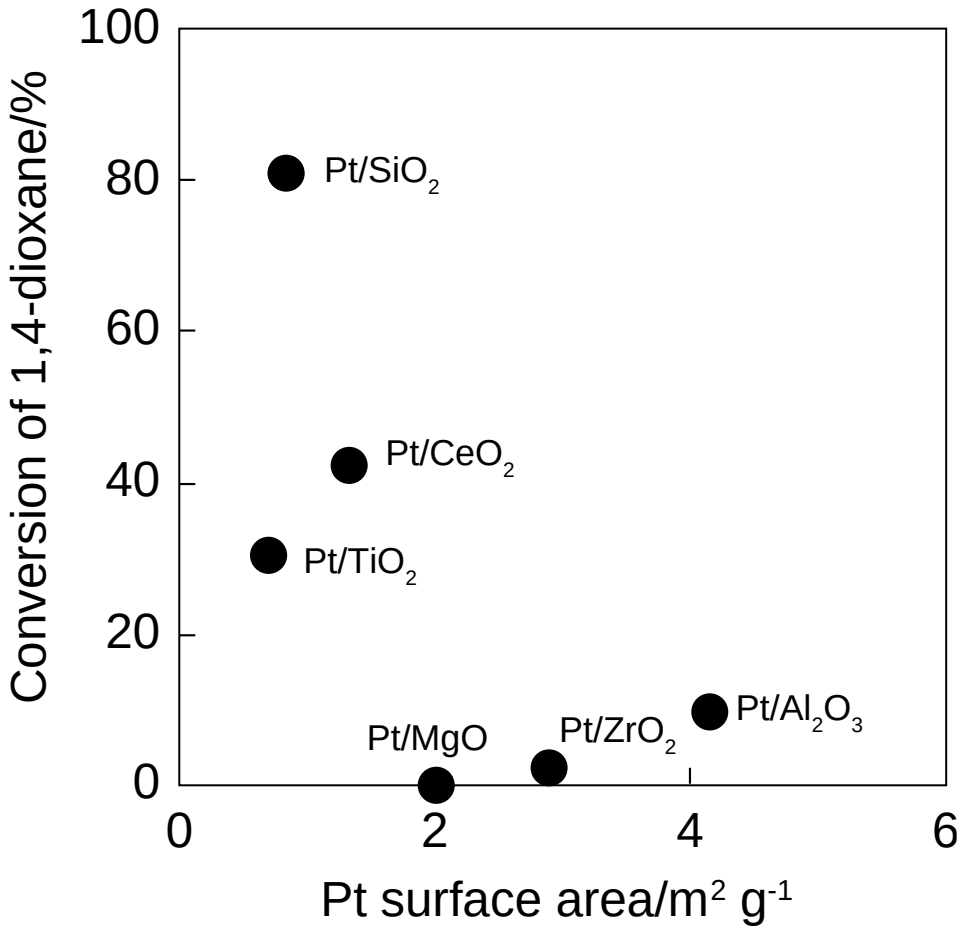

Fig. 7. Relationship between Pt surface area and catalytic activity for gas-phase combustion of 1,4-dioxane. Pt surface areas of supported Pt catalysts were determined from chemisorbed amount of CO at 50 ℃ by assuming that the ratio of adsorbed CO to a surface metal atom was unity.

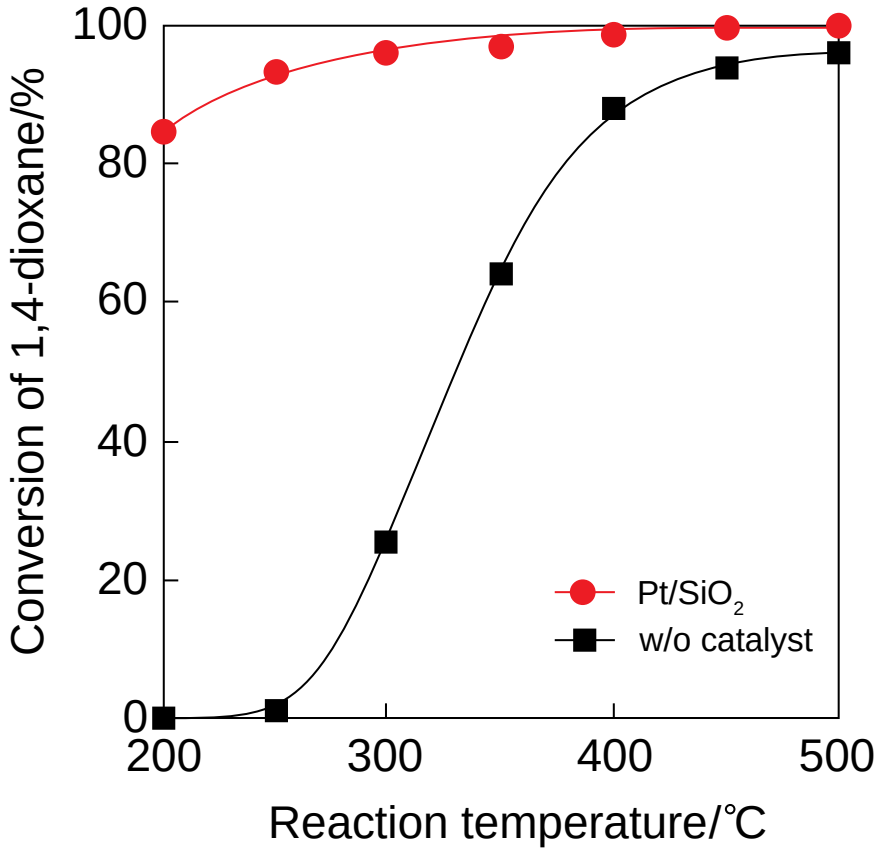

Fig. 8. Temperature-programmed profiles for gas-phase combustion of 1,4-dioxane over Pt/SiO_2 and without a catalyst. Reaction conditions: catalyst, 0.1 g or without a catalyst; gas mixture, 1,4-dioxane/O_2/He=0.1/20/79.9; and total flow rate, 50 mL min^{-1}. Reaction temperature was increased from 200 to 500 °C at a rate of 10 °C min^{-1}.

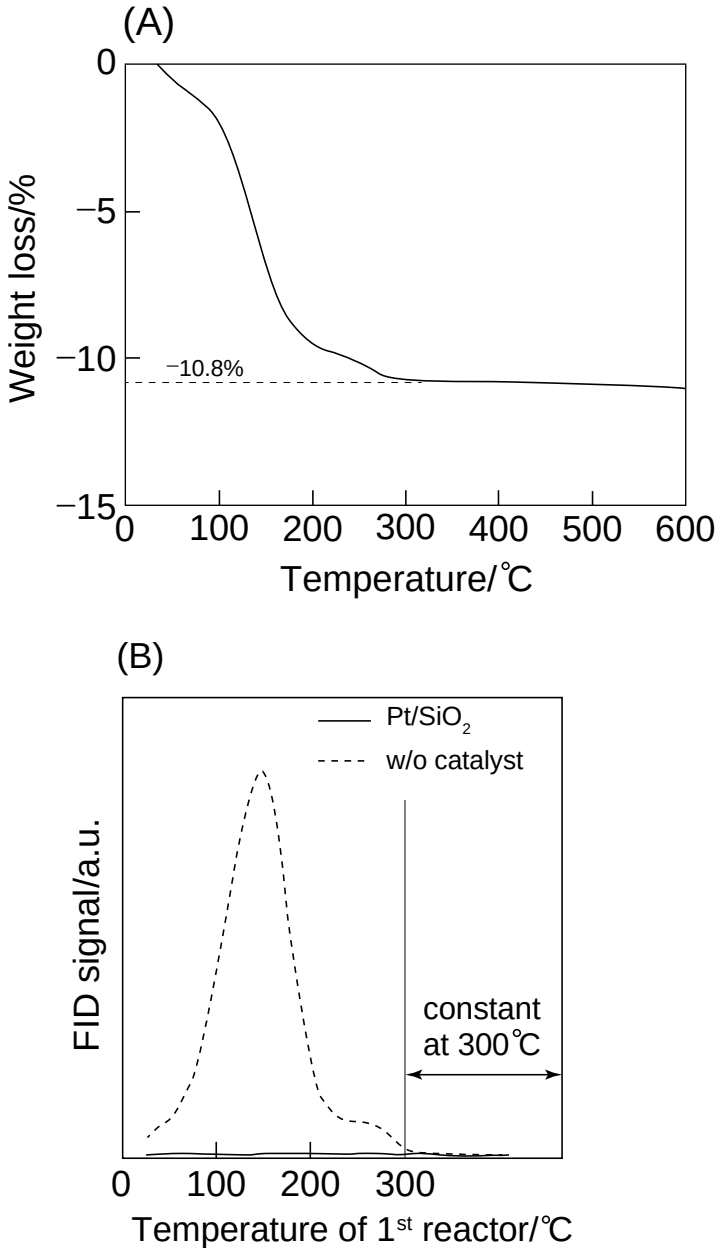

Fig. 9. (A) TG profile for MFI(200) on which 1,4-dioxane was pre-adsorbed and (B) combustion of 1,4-dioxane over Pt/SiO_2 desorbed from MFI(200) performed in a reaction system shown in Fig. 1. TG profile was measured in air and the heating rate was 10 ℃ min^{-1}. The combustion of 1,4-dioxane over Pt/SiO_2 in the downstream reactor was performed at 300 ℃, while the temperature of the upstream reactor was increased at a rate of 10 ℃ min^{-1}.

Table 1

List of aluminosilicate zeolites used as adsorbents.

Framework	Si/Al_2	Surface area ($m^2\ g^{-1}$)[1)]	Manufacture or provider	Product code
BEA	25	555	Zeolyst	CP 814E
	300	520	Zeolyst	CP-811C-300
MFI	36	385	Tosoh	HSZ-860HOA
	200	388	Tosoh	HSZ-870NHA
FER	18	290	Tosoh	HSZ-720KOA
FAU	5.2	367	Catalysis Society of Japan	JRC-Z-HY-5.2
MOR	20	246	Catalysis Society of Japan	JRC-Z-HM-20

[1)]BET surface areas were estimated from N_2 adsorption isotherm taken at –196 ℃.

Table 2

Parameters for Langmuir-type adsorption of 1,4-dioxane and micropore volumes of BEA and MFI zeolites with different Si/Al_2 ratios.

Adsorbent	Maximum adsorption capacity[1)] (Q_{max}) /mg g^{-1}	Adsorption equilibrium constant (K_{eq})	Micropore volume[2)] /mL g^{-1}	Filling factor[3)] /%
BEA(25)	68 (0.066)	0.58	0.186	35
BEA(300)	93 (0.090)	0.60	0.173	52
MFI(36)	74 (0.072)	0.59	0.136	53
MFI(200)	112 (0.110)	0.86	0.138	80

[1)]Figures in parenthesis are the volumes of adsorbed 1,4-dioxane (mL g^{-1}) as if it was present as liquid. Density of 1,4-dioxiane is assumed to be 1.03 g mL^{-1} at 25 ℃.

[2)]Micropore volumes were estimated by applying *t*-plot method to the adsorption isotherms of N_2 at –196 ℃

[3)]Filling factor is defined as the ratio of the volume of adsorbed 1,4-dioxane at the maximum adsorption to the micropore volume.