1. Introduction

Fuel cell systems can generate clean primary power for stationary and mobile source applications. In addition, fuel cell co-generation systems can generate electric power and heat resulting in highly efficient energy source utilization. The advantages of the stationary fuel cell co-generation system are reduced transmission loss and waste heat recovery as steam and warm water. Therefore, the fuel cell co-generation system has many benefits for residential use.1

Power generation by the fuel cell consumes oxygen in air and hydrogen. Hydrogen is obtained by steam reforming of natural gas. Pipeline distribution of natural gas, and was easily decomposed into hydrogen sulfide and isobutene over H-Y and H-beta at low temperatures of 25-150 °C. However, catalyst deactivation of H-beta was observed at 60 °C and oligomerized products of isobutene were observed on the catalyst surface after long reaction times. The deactivation rate of TBT decomposition over H-beta increased with higher acid amounts of H-beta. The amount of oligomerized products deposited on the catalyst increased with lower TBT conversion in the initial stage of reaction. The deposition of oligomerized products and catalyst deactivation decreased after several hours. The amount of the oligomerized products deposited on the catalyst reached approximately 6 wt% after 8 h and remained constant after 125 h over H-beta (Si/Al = 92.5) at 150 °C. The initial TBT conversion was constant during 125 h.

Keywords
Desulfurization, t-Butanethiol, Direct decomposition, Hydrogen sulfide, Zeolite catalyst

1. Decomposition of t-Butanethiol into Hydrogen Sulfide without Hydrogen Addition over H-Y and H-beta Zeolites

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Catalytic direct decomposition of t-butanol (TBT) into hydrogen sulfide over zeolites without hydrogen addition was examined as a new desulfurization process for fuel cell systems. TBT is a widely used odorant in pipeline natural gas, and was easily decomposed into hydrogen sulfide and isobutene over H-Y and H-beta at low temperatures of 25-150 °C. However, catalyst deactivation of H-beta was observed at 60 °C and oligomerized products of isobutene were observed on the catalyst surface after long reaction times. The deactivation rate of TBT decomposition over H-beta increased with higher acid amounts of H-beta. The amount of oligomerized products deposited on the catalyst increased with lower TBT conversion in the initial stage of reaction. The deposition of oligomerized products and catalyst deactivation decreased after several hours. The amount of the oligomerized products deposited on the catalyst reached approximately 6 wt% after 8 h and remained constant after 125 h over H-beta (Si/Al = 92.5) at 150 °C. The initial TBT conversion was constant during 125 h.

Keywords
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pounds over long-term use for many years without any replacement.

We previously proposed a catalytic decomposition desulfurization (CDS) process as a new desulfurization process that requires no hydrogen addition. In the CDS process, sulfur compounds are decomposed to hydrogen sulfide over suitable catalysts without hydrogen addition. Since hydrogen sulfide can be captured by reaction with some metal oxides (e.g. ZnO), decomposition of organic-sulfur compounds to hydrogen sulfide without hydrogen addition is a valuable new reaction for the reforming process of stationary fuel cell systems. Zeolites are reported to catalyze direct decomposition of sulfur compounds. Ethanethiol (C₂H₅SH), dimethyl sulfide, and thiophene (C₅H₇S) are decomposed into hydrocarbons and light sulfur compounds by catalytic decomposition over modified zeolites, and the acid strength of Brønsted acid site may control the decomposition activity and selectivity of zeolites²⁴,²⁵. Additionally, methanethiol is decomposed into hydrogen sulfide and several hydrocarbons over H-Y, H-ferrierite, and H-ZSM-5 type zeolites without hydrogen addition²⁶,²⁷. However, no study has investigated the catalyst for TBT decomposition, although TBT is widely used as an odorant for the pipeline distribution of natural gas.

In the present study, TBT decomposition into hydrogen sulfide and hydrocarbons (C₄H₉SH→H₂S + Hydrocarbons) over acid-form zeolites was examined at low temperatures without hydrogen addition.

2. Experimental

2.1. Materials
Na-Y (JRC-Z-Y5.5: Si/Al = 2.8) and H-Y (JRC-Z-Y5.3: Si/Al = 2.8) zeolites were supplied by the Catalyst Society of Japan. H-beta (H-BEA-25, -35, and -150: Si/Al = 12, 18.5, and 92.5, respectively) and H-ZSM-5 (SM27: Si/Al = 12.5) were supplied by Clariant Catalysts. H-mordenite (HSZ-640HOA: Si/Al = 9.2) was supplied by Tosoh. Samples are named as follows: “exchangeable cation-flame work type-Si/Al ratio,” e.g., H-FAU-2.8. Al₂O₃ (JRC-SAH-1) and SiO₂-Al₂O₃ (JRC-ALO-8) reference samples were obtained from the Catalyst Society of Japan. All catalyst powders were pelletized, crushed, and sieved to obtain particle sizes between 150-250 μm and calcined in air at 400 °C for 2 h before the catalytic activity tests.

2.2. Catalytic Activity Tests
Catalytic activity tests were carried out in a fixed-bed flow tubular reactor under atmospheric pressure. The catalysts 20-100 mg were placed in the quartz reaction tube with 4 mm inner diameter. Reaction temperature was controlled at 25-150 °C, and TBT 20 ppm in nitrogen was continuously passed through the reaction tube. Total gas flow rate was adjusted to 500 cm³ min⁻¹. The concentrations of TBT and hydrogen sulfide in the effluent gas were measured by a gas chromatograph (GC-14B, Shimadzu) equipped with a flame photometric detector (FPD). The products of TBT decomposition at 150 °C over H-FAU-2.8 were identified by analysis of the reacted gas with a quadrupole mass spectrometer (Q-mass, OmniStar, Pfeiffer). The obtained mass signals were compared with those under the conditions of the feed (TBT 100 ppm in N₂) and inert (N₂) gases.

2.3. Characterization
The acid amount of zeolites was analyzed by the ammonia temperature programmed desorption (NH₃-TPD) method with a mass spectrometer (BELCAT-A, Bel Japan). Zeolites were placed in a quartz cell and heated in helium at 400 °C for 2 h as pretreatment. The sample was cooled to 25 °C, then ammonia was fed into the quartz cell for 30 min until saturation adsorption occurred. After the adsorption stage, steam treatment was carried out to clear the low temperature desorbed peak which was attributed to hydrogen-bonded ammonia. The NH₃-TPD measurement was carried out at a heating rate of 10 °C min⁻¹ from room temperature to 650 °C in helium. The mass signal of 16 m/z attributed to the desorbed ammonia was detected with a quadrupole mass spectrometer.

The amount of carbon species on the spent zeolites was measured with an elemental analyzer (EA3000, EuroVector). The spent sample (1 mg) was placed in a tin cell and heated in 50 % oxygen in helium up to 1020 °C. Acetanilide was used as a reference substance for the carbon components.

Adsorbed species on the zeolite surface under the reaction conditions were analyzed with an in-situ Fourier transform infrared spectrometer (FT/IR-4100, JASCO) using the transmission method equipped with a glass reaction cell (Makuhari Rikagaku Garasu Inc.). The sample thin disk was made with only the zeolite powder and was placed in the glass reaction cell. The background spectrum was recorded at 25 °C under nitrogen flow, and the FTIR spectrum of zeolite was measured after heat treatment in nitrogen at 400 °C for 2 h. TBT 100 ppm in nitrogen was then fed into the glass reaction cell for 30 min. After the adsorption stage, the remaining TBT gas in the glass cell was replaced with nitrogen gas and the FTIR spectra were recorded at 25 °C in the nitrogen atmosphere. Adsorption species on the zeolite were identified from the differential spectra obtained before and after the adsorption of TBT.

3. Results and Discussion

3.1. Decomposition of TBT at 25-150 °C
Figure 1 shows the reaction behaviors of TBT decomposition over H-FAU-2.8 and Na-FAU-2.8 at 25 °C. Hydrogen sulfide was detected in the effluent gas from the early stage of the reaction over H-FAU-2.8, and its
concentration increased gradually with longer reaction time as shown in Fig. 1(a). No TBT was detected in the effluent gas for 350 min. These findings suggest that all TBT molecules are adsorbed on H-FAU-2.8 firstly, and some adsorbed TBT molecules decompose into hydrogen sulfide over H-FAU-2.8 without hydrogen addition. In contrast, no TBT was observed in the effluent gas over Na-FAU-2.8 during reaction for 210 min as shown in Fig. (1b). The TBT concentration increased rapidly after 210 min and reached approximately the initial TBT concentration at 350 min. Therefore, TBT is adsorbed physically on Na-FAU-2.8 at 25°C.

The temperature dependences of TBT decomposition reactions over H-FAU-2.8 at 40-150°C are shown in Fig. 2. The concentration of hydrogen sulfide gradually increased with longer reaction time and reached 13 ppm after 120 min at 40°C, whereas no TBT was observed in the effluent gas during 240 min. The hydrogen sulfide concentrations reached 17 ppm and 20 ppm immediately after the reactions started at 60°C and 100°C, respectively. Simultaneously, some TBT and/or intermediates should be accumulated on the catalyst surface at low temperature (less than 100°C). On the other hand, TBT was converted into hydrogen sulfide completely from the beginning of the reaction and the catalytic activity was maintained for 240 min at 150°C. No sulfur species should be accumulated on the catalyst surface at more than 150°C.

3.2. Reaction Scheme of TBT Decomposition over H-Y Zeolite

The products of catalytic TBT decomposition over H-FAU-2.8 at 150°C were analyzed by a Q-mass spectrometer. Concentration of TBT in the feed was adjusted to 100 ppm in nitrogen. Figure 3 shows the fluctuation of ionic currents of $m/z = 34$, 56, and 90 under the reacted gas, feed gas, and inert gas conditions. The mass signals of $m/z = 34$, 56, and 90 are assigned to H$_2$S, C$_4$H$_8$, and C$_4$H$_9$SH, respectively. The ionic currents of $m/z = 34$, 56, and 90 in the inert gas condition indicate the baseline of no detection for all signals. Hydrogen sulfide ($m/z = 34$) and butene ($m/z = 56$) were observed in the reacted gas. The mass signal of $m/z = 56$ was detected in both the feed gas and the reacted gas conditions, but increased with $m/z = 90$ in the feed gas.
Therefore, \( m/z = 56 \) in the feed gas condition must be the fragment of TBT. The strength of \( m/z = 90 \) in the reacted gas was the same as in the inert gas, which indicates that \( m/z = 56 \) in the reacted gas is not derived from fragmentation of TBT but from the decomposition of TBT. Presumably the slight amount of butene, most probably isobutene, was formed through the dissociative adsorption of TBT with the cleavage of the C-S bond over H-FAU-2.8 at 150°C. The formation of hydrogen sulfide and isobutene from TBT above 60°C has also been detected in the TPD of TBT adsorbed on H-beta zeolite28).

Figure 4 shows the in-situ FTIR spectra of H-FAU-2.8 before (a) and after (b) the adsorption of TBT at 25°C, and the subtraction spectrum (c) of (b)-(a). As shown in Fig. 4(a), the bands of 3540 cm\(^{-1}\) and 3637 cm\(^{-1}\) were detected corresponding to the OH groups of the Brønsted acid sites29). After TBT adsorption at 150°C, the 3540 cm\(^{-1}\) and 3667 cm\(^{-1}\) bands decreased, and new bands were observed at 2968 cm\(^{-1}\) and 1632 cm\(^{-1}\), as shown in Fig. 4(b). In addition, the subtracted spectra showed the absorption bands of 2870-2968 cm\(^{-1}\) and 1632 cm\(^{-1}\) as assigned to the t-butyl group as shown in Fig. 4(c)30). The decreases of the absorption bands of 3540 cm\(^{-1}\) and 3637 cm\(^{-1}\) indicate new bond formation between the adsorbed TBT molecule and the Brønsted acid sites of H-FAU-2.8. The appearance of the S-H stretching band at 2390 cm\(^{-1}\) is ascribed to the newly formed S-H bond in the intermediate species31). Furthermore, the S-H stretching band at 2567 cm\(^{-1}\) is due to the S-H bond of the thiol group contained in adsorbed TBT on H-FAU-2.832). These findings suggest that TBT decomposition over H-FAU-2.8 occurs via the surface reaction as shown in Scheme 1. The unshared electron pair (lone pair) in the sulfur atom of TBT forms a coordinate bond with the proton of the zeolite and the alkylsulfonium ion is
formed on the zeolite surface (Step 1). After cleavage of the S–C bond in the alkylsulfonium ion, hydrogen sulfide and a carbocation are formed. In addition, the H–S–H bending band of hydrogen sulfide at 1310 cm⁻¹ was not observed in the FTIR spectrum as shown in Fig. 4, suggesting that hydrogen sulfide desorbs immediately from the zeolite surface (Step 2). Finally, the Brønsted acid sites are regenerated to form isobutene from the carbocation intermediate, and the surface of H-FAU-2.8 reverts to the original state. Since the C=C stretching band was observed in Fig. 4, some isobutene remains on the Brønsted acid sites of zeolite (Step 3). A similar reaction scheme was proposed for the reaction of TBT over Ag-Y zeolite in our previous study30). Therefore, the Brønsted acid sites of H-Y zeolite are considered to have an important function.

The TBT decomposition activities of Al₂O₃, and SiO₂−Al₂O₃ catalysts at 150 °C were also evaluated to identify the effective active site for the TBT decomposition reaction. TBT was also decomposed over SiO₂−Al₂O₃ catalyst with Brønsted acid sites but was not decomposed over Al₂O₃ catalyst with Lewis acid sites (results not shown). Therefore, the Brønsted acid site is clearly important in TBT decomposition.

3.3 Effect of Zeolite Structures

The effects of the zeolite structures on TBT decomposition were studied. Hydrogen sulfide and unreacted TBT concentrations in the effluent gas during TBT decomposition at 60 °C over H-FAU-2.8, H-BEA-12, H-MFI-12.5, and H-MOR-9.2 are shown in Fig. 5. H-FAU-2.8 and H-BEA-12 decomposed TBT to hydrogen sulfide continuously, resulting in no detection of TBT in the effluent gas during 250 min as shown in Figs. 5(a) and 5(b). H-FAU-2.8 and H-BEA-12 have three-dimensional pore structures, with large pore diameters (0.74 nm × 0.74 nm for H-FAU-2.8 and 0.76 nm × 0.64 nm for H-BEA-12) compared with the molecular size of TBT (0.52 nm × 0.52 nm)₃₃. These large pores allow the TBT molecules to penetrate into the zeolite structure. Therefore, the high TBT decomposition activities of H-FAU-2.8 and H-BEA-12 were due to the decomposition reaction occurring within the inner pores and on the outer surface of the zeolite. In addition, H-FAU-2.8 and H-BEA-12 have high proton exchange ratios (92 % for H-FAU-2.8 and 99 % for H-BEA-12). Therefore, the characteristics of H-FAU-2.8 and H-BEA-12 can adsorb and activate the TBT molecules at 60 °C. In contrast, TBT molecules also decomposed to hydrogen sulfide over H-MFI-12.5 and H-MOR-9.2 initially, but TBT molecules were observed in the effluent gas after 100 min and 40 min, respectively, as shown in Figs. 5(c) and 5(d). The small pore diameter (0.56 nm × 0.53 nm) of H-MFI-12.5 and the one-dimensional pore structure of H-MOR-9.2 are presumably insufficient to catalyze the TBT molecules at 60 °C. Concentrations of both hydrogen sulfide and TBT suddenly increased after 110 min in the TBT decomposition over H-MFI-12.5. These changes are considered to be due to desorption of the produced hydrogen sulfide and the unreacted TBT adsorbed on the zeolite surface. Therefore, hydrogen sulfide increased at the same time as the detection of unreacted TBT after reaching adsorption saturation, and no further sulfur compounds were adsorbed on the surface.

3.4 Stability of H-beta Zeolites with Various Si/Al Ratios

The stability of TBT decomposition over H-beta zeolites with various Si/Al ratios was evaluated under severe reaction condition. The catalyst weight was adjusted to 20 mg. Figure 6 shows the changes in TBT and hydrogen sulfide concentrations in the effluent gas over the H-beta zeolites H-BEA-12, -18.5, and -92.5. More than 15 ppm of hydrogen sulfide was formed over the H-beta zeolites during the initial reaction stage, and no unreacted TBT was detected in the effluent gas. This result suggests that unreacted TBT is adsorbed on the zeolite. The initial catalytic activity of the H-beta zeolites was very high. However, unreacted TBT was detected in the effluent gas immediately. The TBT concentration gradually increased with longer reaction time. The increase rate of the TBT concentration was affected by the Si/Al ratio of the H-beta zeolite. The TBT concentration in the effluent gas increased above 10 ppm after 190 min for H-BEA-12 (Fig. 6(a)), 230 min for H-BEA-18.5 (Fig. 6(b)), and 325 min for
deactivation rate of the H-beta zeolite decreased with higher Si/Al ratio. Generally, the acid amounts of H-type zeolite decrease with higher Si/Al ratio. According to the NH₃-TPD measurements, the acid amounts of H-BEA-12, -18.5, and -92.5 used in the present study were 0.55, 0.50, and 0.12 mmol g⁻¹, respectively. Therefore, the deactivation rate may be evaluated from the slope of the increase in TBT concentration. To avoid the effect of adsorption, the maximum slope values of the dotted lines shown in Fig. 6 were estimated as the catalyst degradation rates. The degradation rates of H-BEA-12, -18.5, and -92.5 were 2.47, 2.31, and 1.32 nmol min⁻¹, respectively. The degradation rate of H-BEA-92.5 was considerably less than those of H-BEA-12 and -18.5, because H-BEA-92.5 had fewer acid amounts. Figure 7 shows the relationship between the acid amounts of the H-beta zeolite and the degradation rate for TBT decomposition. The degradation rate increased with higher number of acid amounts of the H-beta zeolite. These findings suggest that catalytic deactivation may be caused by undesirable reactions over the Brønsted acid sites.

3.5. Formation of Carbonaceous Species on H-beta Zeolites

The formation of solid oligomers on the catalyst surface was observed over H-BEA-12 and -92.5. Figure 8 shows the changes in carbon amounts contained in the spent H-BEA-12 and H-BEA-92.5 after TBT decomposition at 60 °C for 60-360 min. The catalyst weight was adjusted to 20 mg. The carbon amounts on the spent zeolites were increased with longer reaction time. Therefore, the degradation of H-BEA catalysts is probably caused by the formation of solid carbonaceous species. The carbon amounts on the spent H-BEA-12 and H-BEA-92.5 were almost the same.
same values after reaction at 60 °C for 60 min, but were different after 60 min. The carbon amount in the spent H-BEA-12 was 3.4 wt% at 180 min and became constant. Similarly, the carbon amount in the spent H-BEA-92.5 was 5.9 wt% at 300 min and became constant. Therefore, the amounts of carbon on H-BEA-12 and H-BEA-92.5 are saturated after 180 min and 300 min, respectively. The degradation rates of H-BEA-12 and H-BEA-92.5 were slower after 180 min and 300 min, respectively, as shown in Fig. 6. Therefore, catalyst degradation may be suppressed after the formation of carbonaceous species becomes saturated.

Isobutene formed on zeolite acid sites is unstable, suggesting that the π-bonded isobutene on the acid sites of zeolite is dimerized, resulting in 2,4,4-trimethyl-2-pentoxy formed via 2,2,4-trimethyl-1-pentene and 2,2,4-trimethyl-2-pentene\(^3\)). Therefore, dimerization and oligomerization of isobutene tend to proceed over zeolites with higher acidity. The degradation of TBT decomposition over H-BEA zeolites may be caused by the formation of solid carbonaceous species through dimerization and oligomerization of adsorbed isobutene on the Brønsted acid sites of zeolites. Figures 6 and 8 suggest that after the micropores were blocked by the deposition of oligomerized carbonaceous species by diffusion, carbon deposition was reduced, and the carbon amount on the catalyst did not increase. As the carbon amount reached saturation as shown in Fig. 8, catalyst degradation for TBT decomposition slowed as shown in Fig. 6. Therefore, active sites not covered with oligomerized carbon species may be present on the zeolite. In addition, the carbon amount deposited on H-BEA-92 was higher than on H-BEA-12 as shown in Fig. 8. These results indicate that deposition of oligomerized carbon species occurs at the entrance of the micropores in H-BEA-12 because the acid amount is larger than in H-BEA-92. In con-
contrast, the carbon amount deposited on H-BEA-92.5 was higher because blocking of the micropores was slow compared with H-BEA-12.

Catalyst degradation was caused by deposition of oligomerized products from isobutene on the catalyst. Since the degradation rate depended on the acid amount of zeolite, the oligomerized product deposited on the active site causes serious problems with the catalytic activity for TBT decomposition. The TBT decomposition activity of H-BEA-92.5 clearly decreased in the reaction test at 60°C as shown in Fig. 6. However, TBT conversion tended to stabilize at a constant value. Therefore, if the rate of TBT decomposition is adequate at high temperature, the apparent TBT conversion will stabilize at constant value from the initial stage. Figure 9 shows the changes in the hydrogen sulfide concentration over H-BEA-92.5 and the carbon amounts formed on the spent catalysts at 150°C for 125 h. Hydrogen sulfide was produced continuously for 125 h, and the amount of the oligomerized product had stabilized after 8 h.

We consider that the oligomerization of isobutene occurs on the Brønsted acid sites located both in the micropores and on the outer surface of zeolites. The oligomerization of isobutene in the micropores of zeolites causes the serious problem of reduced molecular diffusion in the zeolite pores, resulting in degradation of the TBT decomposition reaction. However, the effect of oligomerization of isobutene on the outer surface of the zeolite is small. Therefore, TBT continues to decompose over the active sites located on the outer surface of the zeolite during the long-term reaction.

4. Conclusions

TBT was decomposed into hydrogen sulfide and isobutene over H-Y and H-beta zeolite catalysts at the temperature (25-150°C), and the Brønsted acid sites were very important in TBT decomposition. However, the catalytic activity decreased in the long-term reaction, and oligomerized products were identified on the spent zeolite. The amount of deposited solid carbonaceous species increased with longer reaction time. The degradation of catalyst activity for TBT decomposition increased with higher acidity of the zeolites. In contrast, no degradation of H-beta zeolite for TBT decomposition was observed at high temperature of 150°C, and the decomposition activity was maintained for 125 h.

References

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要 旨

H-Y および H-ベータ型ゼオライトによる水素非共存下での t-ブタンチオールの硫化水素への分解

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燃料電池発電システムの水素製造プロセス用の脱硫法としては、水素を添加しない t-ブタンチオール (TBT) の直接分解にについてゼオライト触媒を用いて検討した。TBT は H-Y 型および H-ベータ型ゼオライト上で、25 〜 150 ℃の反応温度で硫化水素に分解した。60 ℃で長時間試験を行うと、徐々に TBT 転化率が低下して、使用後の触媒上に重合物が検出した。劣化速度はゼオライトの酸量が大きいほど増加し、触媒上に重合物が検出した。重合物の析出量は TBT 転化率の低下とともに増加したが、一定量まで析出し後の転化率もほぼ一定となった。反応温度 150 ℃で耐久試験を行ったところ、触媒上への重合物の析出は 6 wt%で一定となり、TBT 転化率も 125 時間低下しなかった。

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