[Regular Paper]

Adsorptive Removal of *t*-Butanethiol Using Metal Ion-exchange Y Type Zeolite under Ambient Conditions

Shigeo SATOKAWA*, Takuro OHNUKI, Tomoki TAKAHIRO, Kohei URASAKI, and Toshinori KOJIMA

Dept. of Materials and Life Science, Faculty of Science and Technology, Seikei University,
3-3-1 Kichijoji-kitamachi, Musashino, Tokyo 180-8633, JAPAN

Adsorptive removal of *t*-butanethiol (TBT), an odorant additive, from city gas was carried out using metal ion-exchange Y type zeolites at ambient temperature and pressure. The adsorption capacity of TBT on Na–Y under the wet gas condition was extremely low, although that under the dry gas condition was certainly higher. The adsorption capacity of TBT on silver ion-exchange Y type zeolites (Ag(Na)–Y) increased with higher silver ion-exchange ratio in Ag(Na)–Y under wet gas condition. In contrast, the adsorption capacity of TBT on Ag(Na)–Y under the dry gas condition decreased with higher silver ion-exchange ratio in Ag(Na)–Y. Formation of silver sulfide clusters in Ag(Na)–Y causes the decrease in sulfur adsorption capacity of it under the dry gas condition. The adsorption capacity of TBT on copper ion-exchange Y type zeolites (Cu(Na)–Y) increased with higher copper ion-exchange ratio in Cu(Na)–Y under the wet gas condition. In the case of Cu(Na)–Y, the decrease of TBT adsorption capacity under the dry gas condition did not occur with higher copper ion-exchange ratio in Cu(Na)–Y. The both spent samples of Ag(Na)–Y and Cu(Na)–Y were regenerated by heat treatment in air. The decrease in adsorption capacity of TBT on Cu(Na)–Y was slightly lower than that on Ag(Na)–Y.

1. Introduction

Development of the polymer electrolyte fuel cell (PEFC) as a primary generator for stationary and mobile source applications is one of the most promising ways to increase the efficiency of energy utilization. City gas is one of the most useful energy sources for the stationary applications because of the existing pipeline supply networks. The composition of city gas varies by region and locality[1]. A few ppm of sulfur-containing odorant, such as dimethylsulfide (DMS) and/or *t*-butanethiol (TBT), is generally added to city gas in order to give people warning of gas leakage in Japan. However, these sulfur compounds are extremely poisonous for steam reforming catalysts, so the city gas requires deep desulfurization before introduction to the reforming process for PEFC applications[2]. Current hydrodesulfurization (HDS) processes, involving catalytic hydrogen treatment to remove organosulfur compounds such as hydrogen sulfide (H_2S), combined with subsequent adsorption of H_2S on zinc oxide, operate at elevated temperatures ($>300℃$) and pressures (20 to 100 atm of hydrogen)[3]. Consequently, such HDS processes are difficult to apply to residential PEFC systems, which require quick and easy start-up, simple operation, and small reactor size. Therefore, a new desulfurization process for PEFC system has been developed based on the adsorption of sulfur compounds under ambient conditions.

Activated carbon and manganese dioxide were first proposed as materials for the desulfurization of pipeline natural gas at ambient temperatures[4], but the sulfur adsorption capacities were inadequate for practical use. DMS and TBT were removed from city gas by using Na^+ and H^+ exchange zeolites at ambient temperature[5]. However, the zeolites had significantly low sulfur capacity in the presence of 1000 ppm water[6]. Generally, little water vapor is contained in a city gas produced from liquefied natural gas (LNG). However, the city gas may be contaminated by a few hundred ppm of water vapor during the pipeline distribution from the gas production facility to the customer. Recently, silver ion exchange zeolites, especially Ag(Na)–Y zeolites, were reported as favorable adsorbents with high capacity and low leakage for desulfurization of city gas at ambient conditions even in the presence of water vapor[6,7]. Silver ion exchange

zeolites are also effective for removing sulfur compounds such as DMS[8)], tetrahydrothiophene[9)] and thiophenes[10)~14)].

The color change of Ag(Na)‒Y from white to yellow during TBT adsorption suggests the formation of silver sulfide clusters *via* C‒S bond cleavage of TBT adsorbed on silver ion and subsequent Ag‒S bond formation[7)]. The presence of silver sulfides (AgSH, Ag_2S monomer and Ag_4S_2 cluster) in TBT-saturated Ag(Na)‒Y samples was demonstrated by a combination of X-ray diffraction (XRD), Ag K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structures (EXAFS) methods[15)].

Recently, the concentration of sulfur compounds in city gas has been lowered because of the reduction in reactor volume for the reforming processes. Interestingly, the sulfur adsorption capacity of Ag(Na)‒Y zeolite for a gas stream containing a single component (only TBT) was lower than for a gas stream containing two sulfur components (TBT and DMS)[7)]. Therefore, TBT adsorption capacity of Ag(Na)‒Y zeolite was re-evaluated under wet and dry gas conditions. The adsorption capacity of TBT of other metal ion-exchange Y type zeolites was also investigated.

2. Experimental

2. 1. Preparation of Adsorbents

Na‒Y type zeolite (JRC-Z-Y 5.5, a reference catalyst of the Catalysis Society of Japan, $SiO_2/Al_2O_3 = 5.5$, surface area $= 870 \ m^2 \cdot g^{-1}$) was used to prepare silver, copper and zinc ion exchange zeolites by the conventional ion exchange method treating the Na‒Y zeolite with aqueous solutions of silver nitrate, copper acetate and zinc nitrate at 298 K for 6 h, respectively. After the ion exchange treatment, solid products were obtained by filtration, washing with water and subsequent air drying at 373 K for 12 h. Ion exchange ratios of metal ions were determined by elemental analysis using inductively coupled plasma atomic emission spectroscopy (Shimadzu, ICPS-7500). All samples were crushed, sieved to obtain particle sizes between 0.2 and 0.4 mm in diameter and heat-treated at 673 K in air. The ion exchange ratio was calculated from the molar ratio of Ag^+, Cu^{2+} or Zn^{2+} ion and the cation exchange capacity of Na‒Y. The sample name, *e.g.*, Ag(Na)‒Y(19), indicates that the silver ion exchange ratio of this sample is 19%.

2. 2. Adsorption Tests and Regeneration Methods

Adsorption experiments were carried out using a fixed-bed flow tubular reactor (3 mm inner diameter). 20 ppm of TBT in nitrogen was fed to 0.1 g of adsorbents at room temperature (298 K) without pretreatment. The gas flow rate was $500 \ cm^3 \cdot min^{-1}$ and the GHSV was about 180,000 h^{-1}. TBT concentration in the reactor effluent was measured by gas chromatography with a flame photometric detector (Shimadzu GC-14B with flame photometric detector). Water concentration of the reaction gas was less than 10 ppm (dry gas condition) and was also adjusted to 1000 ppm by passing part of the nitrogen flow through water (wet gas condition). The sulfur adsorption capacity was determined by the breakthrough capacity, *i.e.*, uptake amount of sulfur at the moment of first detection of TBT (about 0.1 ppm) in the outlet gas. The used adsorbents were regenerated by heat-treatment at 673 K for 2 h in air. The regenerated adsorbent was cooled to room temperature in nitrogen and used to re-evaluate the TBT adsorption capacity.

2. 3. Surface Analysis

In-situ Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Shimadzu FTIR 8300 equipped with the transmitting IR cell connected to a conventional flow reaction system. A sample was pressed into a 0.02 g self supporting wafer and mounted into a quartz IR cell with CaF_2 windows. The sample was heated at 473 K for 2 h and cooled to 298 K in the IR cell under a nitrogen flow. Spectra were measured with resolution of 4 cm^{-1} at 298 K and each spectrum consisted of 32 scans. A reference spectrum of the sample was recorded at 298 K in the IR cell purged by nitrogen flow for 30 min and used as the background spectrum. Reaction gas (100 ppm TBT diluted by nitrogen) was introduced onto the samples and the gas flow rate was controlled at $500 \ cm^3 \cdot min^{-1}$. The temperature was controlled by an electric heater with a thermocouple attached near the sample wafer. The spectrum of the sample was recorded at 298 K after the IR cell was purged with nitrogen for 30 min. *In-situ* FTIR spectra of adsorbed species were obtained by subtraction of the background spectrum from the sample spectra.

3. Results and Discussion

3. 1. Characterization of Samples

The XRD patterns of ion-exchange samples were almost the same as the XRD pattern of raw material (Na‒Y). No peaks due to metals and metal oxides except Y type zeolite were observed in the XRD patterns of all samples. Ag(Na)‒Y and Zn(Na)‒Y were white like Na‒Y and Cu(Na)‒Y was light blue, suggesting that the ionic states of silver, copper and zinc ions in Ag(Na)‒Y, Cu(Na)‒Y and Zn(Na)‒Y are Ag^+, Cu^{2+} and Zn^{2+}, respectively.

3. 2. TBT Adsorption on Ag(Na)‒Y

Figure 1 shows the effects of the silver ion-exchange ratio of Ag(Na)‒Y on the removal of TBT under dry and wet conditions. The adsorption capacity of TBT on Na‒Y was certainly high under the dry gas condition. However, the adsorption capacity on Na‒Y under the wet gas condition was extremely low. Strong
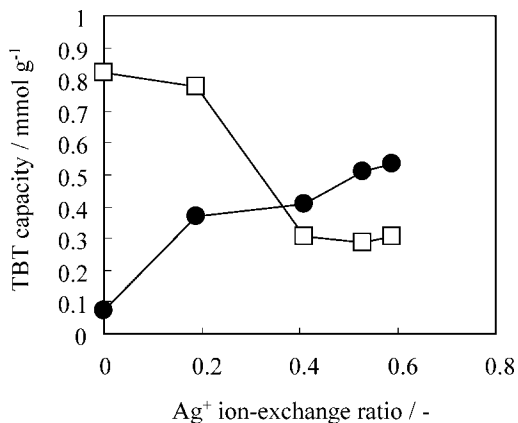
Feed: 20 ppm TBT in nitrogen with (●) or without (□) 1000 ppm of water vapor.

Fig. 1 Effect of Silver Ion-exchange Ratio in Ag(Na)–Y Zeolite on TBT Adsorption Capacity
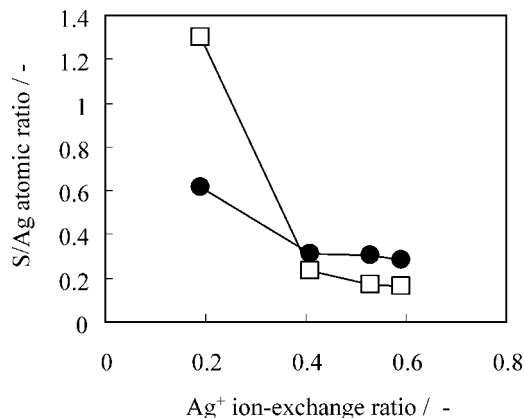

Fig. 2 Effect of Silver Ion-exchange Ratio in Ag(Na)–Y Zeolite for S/Ag Atomic Ratio Defined by Sulfur Adsorption Capacity and Silver Content
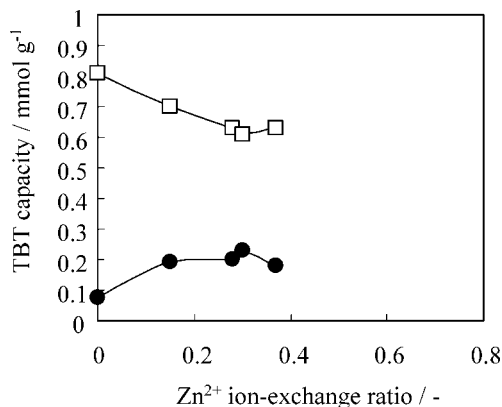

Feed: 20 ppm TBT in nitrogen with (●) or without (□) 1000 ppm of water vapor.

Fig. 3 Effect of Copper Ion-exchange Ratio in Cu(Na)–Y Zeolite on TBT Adsorption Capacity

interactions between water molecules and sodium ions in Na–Y probably caused the inhibition of TBT adsorption on Na–Y under the wet gas condition.

The TBT adsorption capacities on Ag(Na)–Y increased with higher silver ion-exchange ratio of Ag(Na)–Y under the wet gas condition. The increase of TBT adsorption capacities on Ag(Na)–Y under the wet gas condition results from the interaction between silver ions in Ag(Na)–Y and TBT molecules. In contrast, the adsorption capacity of TBT on Ag(Na)–Y under the dry gas condition decreased with higher silver ion-exchange ratio of Ag(Na)–Y.

Color change of Ag(Na)–Y was observed after adsorption experiments under the dry gas condition. The color of Ag(Na)–Y changed from white to yellow in the case of low silver ion content in Ag(Na)–Y and changed from white to brown in the case of relatively high silver ion content in Ag(Na)–Y. On the other hand, no color change was observed for Ag(Na)–Y after adsorption experiments under the wet gas condition. Therefore, some reactions except for adsorption between silver ions and TBT molecules occurred in Ag(Na)–Y during adsorption experiments under the dry gas condition.

Figure 2 shows the change in S/Ag atomic ratio as defined by sulfur adsorption capacity at the TBT breakthrough time and silver content in Ag(Na)–Y. Significant decrease of the S/Ag atomic ratio occurred with higher silver ion-exchange ratio of Ag(Na)–Y under both dry and wet gas conditions. AgSH molecule, Ag_2S monomer and Ag_4S_2 cluster are the dominant silver species in TBT saturated Ag(Na)–Y according to the previous mechanistic study on adsorptive removal of TBT on Ag(Na)–Y[15]. Therefore, the amount of Ag_4S_2 clusters probably increased with increased number of silver ions in Ag(Na)–Y and the formation of Ag_4S_2
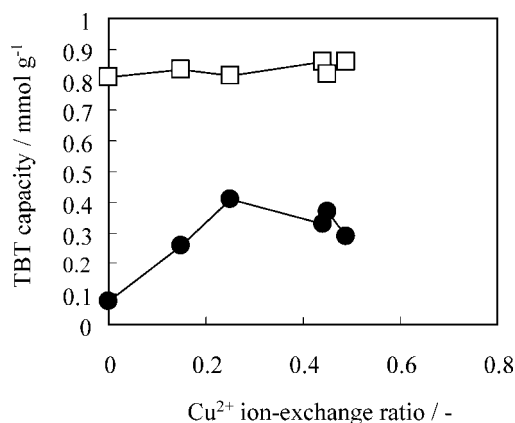
clusters caused a decrease in S/Ag value to 0.5 under both dry and wet gas conditions. The decrease in pore volume caused by the formation of large Ag_4S_2 clusters occurred at around the breakthrough point[15]. Further growth of Ag_4S_2 cluster size under the dry gas condition causes further decrease of TBT adsorption capacity by hindrance of gas diffusion in the zeolite micropores resulting in the observed color changes[16].

3. 3. TBT Adsorption on Cu(Na)–Y and Zn(Na)–Y

Cu(Na)–Y changed from light blue to light green after the adsorption experiment. Color change was not observed for Zn(Na)–Y. **Figure 3** shows the effects of the copper ion-exchange ratio of Cu(Na)–Y for removal of TBT under dry and wet gas conditions. The adsorption capacity of TBT on Cu(Na)–Y under the wet gas condition was larger than that on Na–Y. The adsorption capacity of TBT on Cu(Na)–Y(25) was 0.41 mmol·g^{-1}, and was the highest adsorption capacity

Feed: 20 ppm TBT in nitrogen with (●) or without (□) 1000 ppm of water vapor.

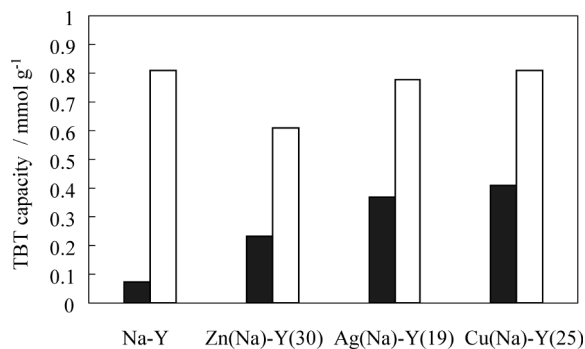Fig. 4 Effect of Zinc Ion-exchange Ratio in Zn(Na)‒Y Zeolite on TBT Adsorption Capacity

Fig. 5 Comparison of TBT Adsorption Capacities on Various Metal Exchanged Zeolites under Wet (solid line) and Dry (open line) Gas Conditions
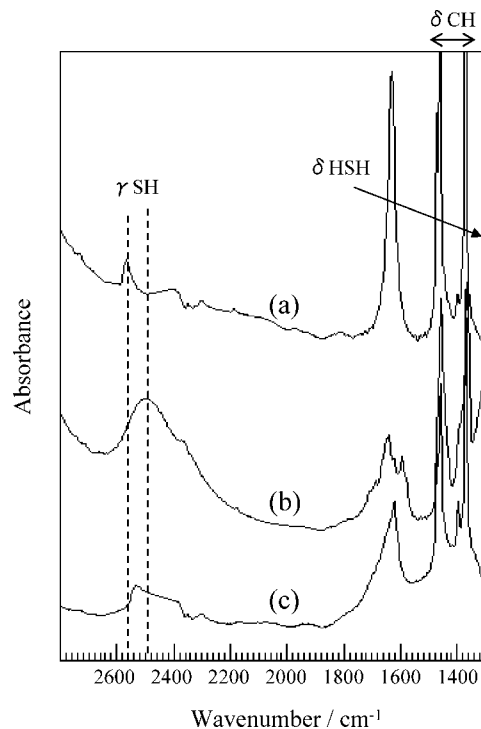

Fig. 6 *In-situ* IR Spectra of Adsorbed Species on (a) Na‒Y, (b) Ag(Na)‒Y(19) and (c) Cu(Na)‒Y(25) after Contact with 100 ppm TBT in Nitrogen Flow for 30 min, Followed by Purging with Nitrogen for 30 min

of TBT under the wet gas condition for Cu(Na)‒Y. The adsorption capacity of TBT on Cu(Na)‒Y under the dry gas condition was almost the same as that on Na‒Y. Decrease of adsorption capacity of TBT on Cu(Na)‒Y under the dry gas condition did not occur with higher copper ion-exchange ratio in Cu(Na)‒Y.

Figure 4 shows the effects of the zinc ion-exchange ratio of Zn(Na)‒Y for removal of TBT under dry and wet gas conditions. The adsorption capacities of Zn(Na)‒Y were slightly lower than those of Cu(Na)‒Y under both dry and wet gas conditions. Efficiencies of TBT removal by Na‒Y, Ag(Na)‒Y(19), Cu(Na)‒Y(25), and Zn(Na)‒Y(30) under dry and wet gas conditions are compared in **Fig. 5**. The highest sulfur adsorption capacities under both dry and wet gas conditions were achieved with Cu(Na)‒Y(25).

3. 4. Surface Analysis by *In-situ* FTIR

In-situ FTIR spectrum of Na‒Y after adsorption of TBT is shown in **Fig. 6(a)**. The γ(SH) band at 2560 cm^{-1} observed in the spectrum of Na‒Y was assigned to physically adsorbed TBT. Bands at 1465,

1454, 1370 and 1360 cm^{-1} due to the δ(CH) band of the *t*-butyl group of adsorbed TBT were observed in the CH deformation region for Na‒Y. Therefore, the TBT molecule is probably physically adsorbed onto Na‒Y[5),17)].

The spectrum of Ag(Na)‒Y(19) after adsorption of TBT is shown in **Fig. 6(b)**. In contrast to the spectrum of Na‒Y, the γ(SH) band shifted to lower wavenumber was observed in the spectrum of Ag(Na)‒Y(19). A broad absorption peak not seen in the spectrum of Na‒Y was observed at 1310 cm^{-1} which was assigned to the δ(HSH) band. On the basis of previous studies, a relatively sharp band centered around 1640-1650 cm^{-1} was assigned to adsorbed molecular *i*-butene[18)~20)]. Broad bands at 2500 and 1310 cm^{-1} were assigned to the γ(SH) and δ(HSH) bands of the H$_2$S molecule on Ag‒Y. The adsorbed TBT molecules react with silver ions in Ag(Na)‒Y(19) and decompose to hydrogen sulfide and *i*-butene[15)].

The spectrum of Cu(Na)‒Y(25) is shown in **Fig. 6(c)**. The γ(SH) peak observed at 2540 cm^{-1} and bands at 1465, 1454, 1370, and 1360 cm^{-1} due to the δ(CH) of the *t*-butyl group of absorbed TBT were observed in the CH deformation region. These peaks are similar to the spectrum of TBT physically adsorbed on Na‒Y. Neither the absorption bands of γ(SH) and δ(HSH) derived from H$_2$S nor the relatively sharp adsorption bands derived from *i*-butene which were observed in
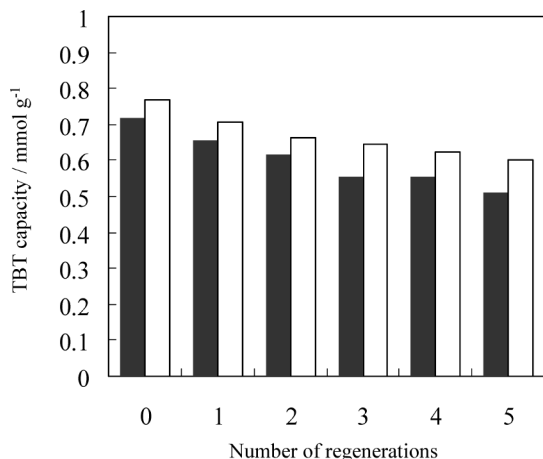
Fig. 7 Change in Adsorption Capacity of TBT on Fresh and the Regenerated Adsorbents; Ag(Na)−Y(19) (solid line) and Cu(Na)−Y(25) (open line)

Fig. 6(b) were observed in **Fig. 6(c)**. Therefore, TBT is probably physically adsorbed on Cu(Na)−Y(25) and decomposition of TBT molecules did not occur in the adsorption experiments on Cu(Na)−Y(25).

3. 5. Regeneration

All used Ag(Na)−Y and Cu(Na)−Y with color changes after the adsorption experiments were returned to the original color by regeneration treatment. The adsorption capacity of TBT on the regenerated Ag(Na)−Y(19) or Cu(Na)−Y(25) decreased slightly. **Figure 7** compares the TBT adsorption capacities of fresh and regenerated Ag(Na)−Y(19) and Cu(Na)−Y(25) under the dry gas condition. The adsorption capacity of TBT decreased gradually with the number of regeneration cycles. The adsorption capacities of TBT on Ag(Na)−Y(19) and Cu(Na)−Y(25) regenerated five times were reduced to 28% and 21% compared with the fresh capacities, respectively. The decrease rate of TBT adsorption capacity on Cu(Na)−Y(25) was lower than that on Ag(Na)−Y(19).

3. 6. Affinities of Transition Metal Ions with TBT

The HSAB (hard soft acid base) theory is widely used in chemistry for explaining the stability of compounds, reaction mechanisms and pathways. The terms (hard) or (soft), and (acid) or (base) are assigned to chemical species. Hard applies to species which are small with high charge states and are weakly polarized. Soft applies to species which are large with low charge states and are strongly polarized. According to the HSAB theory, silver ions and TBT molecules are classified as soft acid and soft base, respectively. Sodium ions and water molecules are classified as hard Lewis acid and hard Lewis base, respectively. Copper and zinc ions are classified as middle acids. The adsorption capacities of all adsorbents under the wet gas condition were increased by exchanging to transition metal ions instead of sodium ions in raw Na−Y zeolite because of the low interaction between metal ions and water molecules.

4. Conclusions

Sulfur adsorption capacities on silver, copper and zinc ions exchange Y type zeolites under the wet gas condition increased with higher ion-exchange ratio. However, in the case of silver ion, adsorption capacity under the dry gas condition decreased with higher ion-exchange ratio. The decrease of sulfur adsorption capacity would be caused by the formation of Ag_4S_2 clusters in Ag(Na)−Y in the TBT adsorption experiment under the dry gas condition because of the strong interaction between TBT molecules and silver ions. Therefore, the highest sulfur adsorption capacity under both dry and wet gas conditions was achieved with Cu(Na)−Y(25).

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要　　旨

金属イオン交換 Y 型ゼオライトを用いたターシャリーブタンチオールの常温吸着除去

里川　重夫，大貫　琢郎，高廣　智基，浦崎　浩平，小島　紀徳

成蹊大学理工学部物質生命理工学科，180-8633 東京都武蔵野市吉祥寺北町3-3-1

　金属イオン交換 Y 型ゼオライトを用いて都市ガスに含まれる付臭剤成分であるターシャリーブタンチオール（TBT）の常温吸着除去を行った。乾燥ガス条件では市販の Na–Y 型ゼオライトでも適度な TBT 吸着容量を示すが，含水ガス条件では低下した。銀イオン交換 Y 型ゼオライトは含水ガス条件で銀の導入量に従い TBT 吸着容量は増加するが，乾燥ガス条件では銀の導入量に従い低下した。硫化銀クラスタの生成が性能低下を引き起こしていると思われた。銅イオン交換 Y 型ゼオライトは含水ガス条件では銅の導入量に従い TBT 吸着容量は増加し，乾燥ガス条件では Na–Y 型ゼオライトと同等の TBT 吸着容量を示した。銅イオン交換 Y 型ゼオライトがいずれの条件でも適度な性能を示すことが分かった。使用後のサンプルを空気中で加熱処理すると再生できるが，銀イオン交換 Y 型ゼオライトより銅イオン交換 Y 型ゼオライトの方が性能低下割合は小さかった。

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