Characteristics of H-beta Zeolite Catalyst for Catalytic Decomposition of t-Butyl Mercaptan

Shigeo SATOKAWA*, Takehiro MISU, Nao KOIDE, and Naohiro SHIMODA

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

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Catalytic direct decomposition of t-butyl mercaptan (TBM), which is a sulfur compound added to city gas as an odorant, was investigated over H-beta zeolite catalyst without hydrogen addition. High TBM conversion was achieved at the initial stage of the reaction at 60 °C, and hydrogen sulfide was only detected in the outlet gas. Subsequently, TBM conversion decreased and concentration of isobutene increased. TBM was stably decomposed to hydrogen sulfide and isobutene after 490 min, indicating that the activity of H-beta zeolite was sufficiently durable. Temperature programmed oxidation (TPO) analysis of the spent catalyst suggested that hydrocarbon species were desorbed below 300 °C and carbon species were oxidized to carbon dioxide above 300 °C. Spent catalyst heated under a flow of air at 300 °C completely recovered the catalytic activity. Therefore, hydrocarbon species formed at the initial stage of the reaction were oligomerized within the zeolite pores and caused the decrease in catalytic activity for TBM decomposition.

Keywords
Catalytic decomposition, Desulfurization, Durability, Regeneration, t-Butyl mercaptan, Zeolite catalyst

1. Introduction

Use of natural gas as a fuel is clearly effective for reducing carbon dioxide emissions. Natural gas consists of lower hydrocarbons, mainly methane, and also small amounts of nitrogen, carbon dioxide, and sulfur compounds as impurities. The liquefaction process required for transporting natural gas removes the sulfur compounds due to the difference in boiling points. However, a sulfur compound is sometimes added as an odorant for leak detection before distribution to retail customers. t-Butyl mercaptan (TBM, (CH₃)₃CSH) is a sulfur compound contained in crude natural gas and is also commonly used as an odorant for city gas. However, the reform of city gas into hydrogen depends on a catalytic transformation. Sulfur compounds are poisons for reforming catalysts and so must be removed by a desulfurization process prior to feeding the catalyst converters⁴⁻⁶. Hydrodesulfurization and adsorptive desulfurization methods are commonly used for removing sulfur compounds in city gas. The hydrodesulfurization method requires addition of hydrogen to remove sulfur compounds⁷⁻⁹. The adsorptive desulfurization method requires periodic replacement of adsorbent⁸⁻¹⁰. We have developed a catalytic direct decomposition desulfurization method to decompose organic sulfur compounds into hydrogen sulfide and hydrocarbons over acidic zeolites without requiring addition of hydrogen. However, catalyst deterioration may occur due to carbon deposition on the catalyst surface¹¹⁻¹⁴. Our previous study showed that H-Y and H-beta zeolites cause stable decomposition of TBM into hydrogen sulfide at 60 °C and 150 °C; activity is decreased due to carbon species deposition at the beginning of the reaction; and TBM conversion reaches a constant value after a few hours¹⁵. However, the carbon species formation behavior during the reaction remains unclear. Additionally, the properties of the carbon species formed on the zeolite catalyst are unknown. The present study investigated the reaction behavior of TBM decomposition over H-beta zeolite, the characteristics of the formed carbon species, and the regeneration behavior of the deteriorated catalyst.

2. Experimental

2.1. Catalyst Preparation
Commercially available H-beta zeolite (Si/Al = 92.5)

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* To whom correspondence should be addressed.
* E-mail: satokawa@st.seikei.ac.jp
supplied by Clariant Catalyst K. K. (H-BEA-150) was used as a catalyst. Catalyst powder was molded, crushed, and sieved to 150-250 μm size, then heated at 400 °C for 2 h as a pretreatment prior to the reaction test.

2. 2. Catalytic Activity Test

Reaction tests to assess activity for TBM decomposition were carried out using a fixed-bed continuous flow reactor at atmospheric pressure. Catalyst 0.1 g was placed in a quartz tube with 6-mm inner diameter using quartz wool. The reaction gas mixture (100 ppm TBM/N2 balance) was fed into the catalyst bed at a total flow rate of 500 mL min⁻¹. The reaction test was conducted at 60 °C or 150 °C for 490 min. The outlet gas was analyzed using a gas chromatograph equipped with a flame photometric detector (GC-FPD) for sulfur-containing compounds and a gas chromatograph with a flame ionization detector (GC-FID) for hydrocarbon compounds. The lower detection limit of hydrocarbons was around 10 ppm. Since light hydrocarbons including unknown hydrocarbons were formed quantitative analysis of hydrocarbons was not conducted, but the peak area of each component was taken to show the formation of each hydrocarbon component. First gas analysis was conducted at 10 min after the beginning of the reaction, and subsequently at 30 min intervals.

Regeneration of the spent catalyst was conducted at 300 °C for 1 h under 20 % O2/N2 (500 mL min⁻¹) after the reaction test, and the reaction test was carried out again.

2. 3. Catalyst Characterization

The spent catalyst was analyzed by a temperature programmed oxidation (TPO) method to investigate the regeneration temperature of the deteriorated catalyst using a BELCAT-ADVANCE instrument (MicrotracBEL Corp.) equipped with a mass spectrometer. The spent catalyst was placed in a quartz cell and heated up from room temperature to 900 °C at a heating rate of 10 °C min⁻¹ in 20 % O2/N2. Total carbon amount of the spent catalyst was not calculated because some adsorbed species would desorb during the exposure to air after the reaction test.

The N2 adsorption isotherms of catalyst samples were measured using a BELSORP-mini II instrument (MicrotracBEL Corp.) at −196 °C. Prior to N2 adsorption measurement, the samples were degassed at 60 °C for 2 h to remove any moisture adsorbed on the surface and inside pores.

3. Results and Discussion

3. 1. TBM Decomposition over H-beta Zeolite

The changes in the concentrations of TBM and hydrogen sulfide contained in the outlet gas detected by GC-FPD during TBM decomposition over H-beta zeolite at 60 °C are shown in Fig. 1(a). The total sulfur amount in the outlet gas did not reach 100 ppm during the entire reaction. Therefore, some unreacted TBM and/or decomposition products of TBM should be adsorbed on the catalyst. The changes in the concentration of TBM and hydrocarbon components detected by GC-FID are shown in Fig. 1(b). No TBM and ca. 80 ppm of hydrogen sulfide was detected in the outlet gas at 40 min after starting the reaction test, which suggests that most of the TBM was decomposed into hydrogen sulfide. Since no hydrocarbon component was detected in the outlet gas at this stage, the hydrocarbon components presumably remained on the catalyst surface. TBM is decomposed to hydrogen sulfide and isobutene on acid zeolite catalyst, and produced isobutene is sequentially oligomerized on the catalyst.
and remains as carbon species on the catalyst\(^{15}\). We considered that our findings were similar. The concentration of hydrogen sulfide gradually decreased, and the concentration of unreacted TBM increased in the outlet gas after reaction for 70 min (Fig. 1(a)) suggesting reduced TBM decomposition activity of the catalyst. The increase in the concentration of unreacted TBM reached to an almost constant value after ca. 190 min, and unreacted TBM slightly increased continuously after 190 min. The concentration of hydrogen sulfide also continued to slowly decrease from 70 to 490 min.

The concentration of isobutene increased from 70 to 130 min, reached the maximum value, then decreased from 160 to 490 min as shown in Fig. 1(b). Formation behaviors of hydrogen sulfide and isobutene were very similar after 160 min. Therefore, stoichiometric decomposition of TBM occurred according to Scheme 1 after 160 min. If stoichiometric TBM decomposition occurs from the beginning of the reaction, isobutene should be produced according to the dotted line in Fig. 1(b). However, isobutene was not detected in the outlet gas before 70 min. Isobutene is unstable on zeolite acid sites and dimerization and oligomerization of isobutene may also occur according to Scheme 2\(^{16}\). Therefore, the difference between the amount of hydrogen sulfide and the amount of isobutene produced in the outlet gas from 10 to 160 min indicates the amount of oligomerized hydrocarbon species accumulated on the catalyst. Consequently the gray-colored portion in Fig. 1(b) shows the amount of solid hydrocarbon species formed by sequential oligomerization of isobutene during decomposition of TBM on the catalyst\(^{15}\). Trace amounts of hydrocarbon components considered to be lower hydrocarbons rather than isobutene (\(i.e.\) ethylene) were observed in the outlet gas after 160 min. These hydrocarbons were produced by the decomposition of TBM and/or oligomerized hydrocarbon species formed on the catalyst.

The changes in the concentrations of the sulfur components contained in the outlet gas of TBM decomposition at 150 °C as detected by GC-FPD are shown in Fig. 2(a). The changes in the concentrations of TBM and hydrocarbon components detected by GC-FID are shown in Fig. 2(b). Approximately 100 ppm of hydrogen sulfide was detected from the start of the reaction test, which indicates that stable decomposition of TBM occurred at 150 °C. Since the reaction rate at 150 °C was faster than that at 60 °C, no change in hydrogen sulfide concentration was detected in Fig. 2(a). On the other hand, the concentration of isobutene in the outlet gas gradually increased from the beginning of the

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**Scheme 1** Reaction Scheme of TBM Decomposition on the Acid Sites of Zeolite

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\begin{align*}
\text{CH}_3\text{C}-\text{SH} & \rightarrow \text{H}_2\text{S} + \text{CH}_3\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3 & \rightarrow \text{H}_2\text{S} + \text{CH}_3\text{CH}_2\text{CH}_3
\end{align*}
\]

**Scheme 2** Reaction Scheme of Isobutene Oligomerization on the Acid Sites of Zeolite

\[
\begin{align*}
2\text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3 \\
\text{2,4,4-trimethyl-2-pentony} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3
\end{align*}
\]
reaction to 140 min as shown in Fig. 2(b). The gray area indicates the amount of oligomerized and accumulated hydrocarbon species produced by TBM decomposition. Formation of solid hydrocarbon species occurs on the catalyst during the initial reaction stage and the amount of hydrocarbon species decreases gradually in TBM decomposition over H-beta zeolite. The findings of outlet gas analysis also support the results of the previous study15).

3.2. TPO Measurement

The TPO profiles of the spent catalysts reacted at 60 °C and 150 °C for 490 min are shown in Figs. 3(a) and 3(b), respectively. The peaks of mass signals of m/z = 43 and 56 detected at ca. 220 °C in both spent catalysts were assigned to desorption of C3H7 and C4H8 species, respectively. These species were presumably formed by decomposition of the adsorbed TBM and/or oligomerized hydrocarbon species on the spent catalyst.

Two peaks were observed at around 220 °C and 500 °C in the TPO profile of the m/z = 44 signal. No peak derived from the formation of water occurred at around 500 °C, so the peak of m/z = 44 at around 500 °C was assigned to CO2 generated by oxidation of carbon species in the spent catalyst. On the other hand, the peak of m/z = 44 appearing at 300 °C or less was assigned to hydrocarbon species (C3H6) and/or CO2 generated by the oxidation and/or decomposition of oligomerized hydrocarbon species in the spent catalyst. The peak at m/z = 18 around 300 °C did not coincide with the peak at m/z = 44, so was assigned to desorption of adsorbed water on the spent catalyst.

The peak at m/z = 34 derived from hydrogen sulfide was slightly observed below 300 °C from the catalyst tested at 60 °C, suggesting that a small amount of hydrogen sulfide was adsorbed on the catalyst. On the other hand, no peak at m/z = 34 signal was detected in the TPO profile of the spent catalyst tested at 150 °C, so the amount of adsorbed hydrogen sulfide was negligible.

3.3. Catalyst Regeneration

The results of TPO analysis suggested that two different carbon based residues were present on the spent catalysts after TBM decomposition tests at 60 °C and 150 °C for 490 min, a hydrocarbon species that can be desorbed at below 300 °C and a carbon species that cannot be desorbed and can be oxidized at above 300 °C during TPO measurement. To identify the substances affecting degradation of the catalyst for TBM decomposition, heat treatment at 300 °C in oxidizing atmosphere was conducted as for catalyst regeneration. Figure 4 shows the result of the TBM decomposition test over regenerated catalyst at 60 °C. The reaction behavior of the regenerated catalyst was similar to that of the fresh catalyst. Therefore, degraded catalyst was regenerated completely by heat treatment at 300 °C. Consequently, the cause of the decrease in catalytic activity is the accumulation of hydrocarbon species desorbed at below 300 °C, and the carbon species causing the CO2 production peak at around 500 °C during the TPO test is irrelevant to the degradation of activity for TBM decomposition.

3.4. Degradation Mechanism

TBM conversion decreased to about half of the initial value with reaction time at 60 °C, as shown in Fig. 1(a). After catalyst regeneration at 300 °C, the hydrocarbon component present on the catalyst was removed, and the catalyst recovered to the initial performance (Fig. 4(a)). Therefore, regeneration of the deteriorated catalyst by heat treatment is easy, and the hydrocarbon species desorbed on the catalyst occupy the active sites for TBM decomposition. TBM conversion was almost 100% at 150 °C as shown in Fig. 2(a). Degradation of catalyst under the present reaction conditions was impossible to detect.

The acid sites of zeolite are located on the particle surface and inside the micropores. The activity of the surface acid sites is little affected by the physical size
of the reactants and the products. On the other hand, the activity of the micropore acid sites is limited by the physical size of the reactants and the products. Since solid products obtained by the side reaction tend to accumulate in the active sites located in the pores, the pores of the catalyst are likely to be blocked after TBM decomposition.

The N_2 adsorption isotherms of the fresh and the spent catalysts (at 60 °C and 150 °C for 490 min) are shown in Fig. 5. The micropore volumes of the spent catalysts were drastically decreased compared to the fresh catalyst as shown in Fig. 5. Therefore, accumulation of oligomerized hydrocarbon species and deposited carbon species in the zeolite pores probably causes the deterioration of catalytic activity. Reduced catalyst performance is caused by the coverage of the active sites in the pores by the hydrocarbon and carbon species formed on the active sites of the catalyst during TBM decomposition.

4. Conclusions

Catalytic direct decomposition of TBM over H-beta zeolite was examined. TBM was decomposed into hydrogen sulfide and isobutene on the acid sites, and the produced isobutene was sequentially oligomerized on the same sites. Since the oligomerized products remained at the acid sites in the micropores, initial deterioration of TBM decomposition would occur. On the other hand, TBM decomposition into hydrogen sulfide and isobutene proceeded stably for a long time over the acid sites located at the catalyst surface. Spent catalyst was easily regenerated by heating under a flow of air at 300 °C.

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要 旨

1-ブチルメタノール分解反応でのH-ベータ型ゼオライト触媒の特性

里川 重夫，三須 健裕，小出 奈央，霜田 直宏

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

都市ガスに付着剤として含まれる硫黄化合物である1-ブチルメタノール（TBM）の直接分解をH-ベータ型ゼオライト触媒を用いて行った。60℃でTBMを分解したところ、反応初期はTBM転化率が高く、出口ガス中には硫化水素のみが検出された。その後、TBM転化率が減少し触媒が劣化した。劣化とともにイソプタンの生成が認められ、490分後にはTBMは硫化水素とイソプタンに安定的に分解し、H-ベータ型ゼオライト触媒には十分な耐久性のあることが分かった。反応後触媒の昇温酸化法（TPO）分析から、触媒中には300℃以下で脱離する炭化水素種と300℃以上で燃焼する炭素種が存在することと推定された。劣化触媒は300℃空気流通下で焼成処理を通じて初期性能に戻った。したがって、反応初期に生成した炭化水素種がゼオライト細孔内でオリゴマー化し、初期活性の低下をもたらしたのではないかと考えた。

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