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Adsorptive desulfurization of propylene derived from bio-ethanol

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Abstract We studied adsorption characteristics of a series of LTA zeolite as an adsorbent for desulfurization of propylene, that was produced from bioethanol by ethanol-to-olefin (ETO) conversion. A breakthrough curve (BTC) for adsorption of methanethiol, as one of the sulfur impurities of propylene produced from bioethanol, in the presence of propylene was measured using a fixed-bed column packed with the LTA zeolite. The BTC revealed that the effect of the competitive adsorption of propylene on the LTA zeolite strongly depended on a cation species exchanged in the micropores of the zeolite. Among the cation species examined in this study, bivalent cation of zinc (Zn^{2+}) was proved to be the most effective one to increase the amount of methanethiol adsorbed on the LTA zeolite under the presence of propylene. The specific interaction of methanethiol with the LTA zeolite exchanged with Zn^{2+} was confirmed by the measurement of a temperature-programmed desorption (TPD) spectrum of methanethiol.

Keywords Adsorptive desulfurization · Breakthrough curve · Fixed-bed column · LTA zeolite · Temperature-programmed desorption

1 Introduction

Due to the recent progress of global warming as well as exhaustion of fossil fuel, cellulose-derived bioethanol has been expected as an alternative chemical source to produce olefin by the ETO conversion (Rosillo-Calle and Walter 2006; Inoue et al. 2009). Depending on the fermentation route of a raw material of bioethanol, it contains dimethylsulfide and/or dimethylsulfoxide as sulfur impurities that are converted to methanethiol, ethanethiol or hydrogen sulfide during the ETO conversion. Due to the possibility of poisoning of a metal catalyst, that is used for the polymerization of olefin, even by a trace amount of sulfur impurities (Bartholomew 2001), desulfurization of olefin derived from bioethanol is necessary. Adsorption is one of the most effective and practical methods for this purpose.

A sulfur compound that possesses lone pair electrons strongly adsorbs on a metal oxide through Lewis acid/base interaction (Startsev 2009). Cui et al. (2009) examined adsorptive desulfurization of synthetic natural gas using an activated carbon loaded with metal oxides. Among various porous materials, a hydrophilic zeolite with a low Si/Al ratio is one of the most suitable adsorbents for desulfurization of olefin derived from bioethanol, since strong Lewis acid/base interaction between an acidic site (Al atom) and a sulfur compound is expected. In this study, adsorption characteristics of a series of LTA zeolite are examined by the measurement of a BTC for adsorption of methanethiol. Based on the measured BTC, the performance of the LTA zeolites for desulfurization of propylene is discussed. Furthermore, to study the specific interaction between methanethiol and the adsorbents, a TPD spectrum of methanethiol is measured.

2 Experimental

A LTA zeolite ($XK_2O{\cdot}(1-X)Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$, $X > 0.4$) in a pellet form is purchased from the Tosoh Corp.

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and is labeled as K-A in this study. An aqueous solution of a metal chloride ($CaCl_2$, $ZnCl_2$, $SrCl_2$) is used for cation-exchange of the purchased LTA zeolite, and the ion-exchanged samples are labeled as Zn-A, Ca-A and Sr-A, respectively. For comparison, an activated carbon (GS_{3X}) developed for gas-phase adsorption of methanethiol or hydrogen sulfide is purchased from the Japan EnviroChemicals, Ltd. The adsorbent is crushed and then sieved to obtain particles with a diameter of 250 to 500 μm.

Prior to the measurements, the adsorbents are degassed at 573 K. Adsorption isotherm of propylene is measured at 303 K using an automatic gas adsorption apparatus (Belsorp28SA, BEL Japan, Inc.). For the measurement of a BTC, 1 g of the adsorbent particles is packed in a glass column. Then, a nitrogen gas with the initial methanethiol concentration of 250 ppm is introduced to the glass tube that is kept at 303 K. During the measurement, the flow rate of the gas is adjusted to 10 cm^3(stp) min^{-1}. A BTC is also measured under the presence of 50 vol.% of propylene in the gas. The gas is sampled at the exit of the column and is analyzed using a GC-MS (Clarus500, PerkinElmer Co., Ltd.) A TPD spectrum of methanethiol is measured using a TPD apparatus (Belcat, BEL Japan, Inc.) equipped with a thermal conductivity detector (TCD). After outgassing 0.1 g of the adsorbent in a quartz cell at 773 K under a helium gas flow, a standard helium gas with the methanethiol concentration of 10,000 ppm is introduced to the cell at the flow rate of 30 cm^3(stp) min^{-1} for 10 min. Then, to measure the TPD spectrum, temperature of the cell was raised at a heating rate of 2.5 K min^{-1} from 313 to 773 K.

3 Results and discussion

Figure 1 shows the adsorption isotherms of nitrogen on a series of the LTA zeolite and GS_{3X}. One can see that nitrogen hardly adsorbs on K-A, indicating that the entrance width of the zeolite cage of K-A is smaller than the molecular dimension of nitrogen. On the other hand, nitrogen can adsorb on the LTA zeolites that are exchanged with a bivalent metal cation, and the amount of nitrogen adsorbed at relatively low pressure ($p/p_0 \approx 0$) depends on the cation species introduced to the zeolite cage. This reveals that the entrance of the cage of K-A is enlarged by the ion-exchange with bivalent metal cation. Based on the isotherms of nitrogen, the volume of the micropores that nitrogen molecules are accessible to is confirmed to decrease in the order of Ca-A > Zn-A > Sr-A > K-A. Porous properties of the adsorbents are summarized in Table 1. Adsorption isotherms of propylene on the tested adsorbents are shown in Fig. 2. It is clear that the amount of adsorbed propylene decreases with the decrease in the volume of micropores, that nitrogen molecules are accessible to. However, it seems that the volume of adsorbed propylene estimated from the isotherm is larger than the volume of the micropores of the zeolite. This is probably due to the larger accessibility of a propylene molecule to smaller micropores of the LTA zeolite at

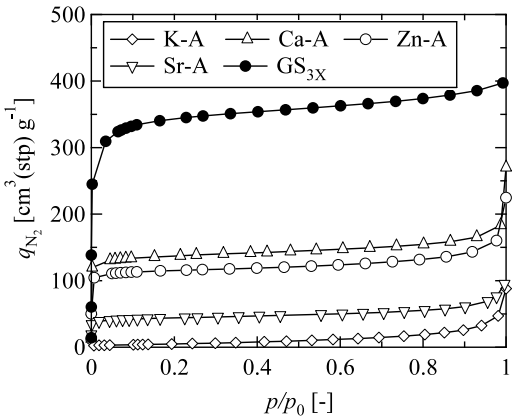

Fig. 1 Adsorption isotherm of nitrogen measured at 77 K. (Desorption branch of the isotherm is omitted, since it almost coincides with the adsorption branch)

Table 1 Porous properties of adsorbents and adsorbed amount of methanethiol

Adsorbent	S_{BET} [*1] ($m^2\ g^{-1}$)	V_{mic} [*2] ($cm^3\ g^{-1}$)	q_1 [*3] (mmol g^{-1})	q_2 [*4] (mmol g^{-1})	q_2/q_1 (–)
K-A	17	0.06	0	0	–
Ca-A	486	0.26	1.08	0.23	0.21
Zn-A	399	0.24	0.71	0.35	0.49
Sr-A	155	0.11	0	0	–
GS_{3X}	1196	0.61	0.32	0.13	0.40

[*1] S_{BET}: BET specific surface area estimated by applying the BET equation

[*2] V_{mic}: Micropore volume determined based on the α_s analysis

[*3] q_1: Adsorbed amount of methanethiol in the absence of propylene

[*4] q_2: Adsorbed amount of methanethiol in the presence of propylene

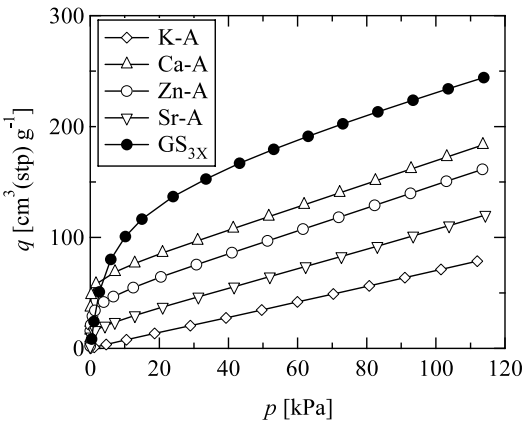

Fig. 2 Adsorption isotherm of propylene measured at 303 K

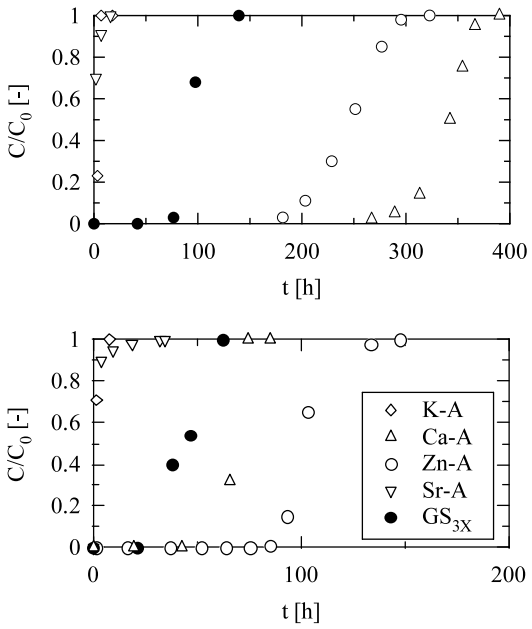

Fig. 3 Breakthrough curves for adsorption of methanethiol in the absence of propylene (*top*), and in the presence of propylene (*bottom*)

303 K than that of a nitrogen molecule at 77 K. One can also see that, irrespective of the cation species, the amount of propylene adsorbed on the LTA zeolites is less than that on GS_{3X} because of the smaller volume of the micropores in the LTA zeolites than that in GS_{3X}.

Figure 3 shows the measured BTC for adsorption of methanethiol over a series of LTA zeolites. The adsorption capacity of the adsorbent is determined from the breakthrough time, that equals to the time when C/C_0 reaches to 0.05. In the absence of propylene, the adsorption capacity decreases in the order of Ca-A > Zn-A > GS_{3X} ≫ Sr-A, K-A. This indicates that methanethiol molecule is not easily accessible to the zeolite cage of K-A or Sr-A. On the other hand, in the presence of propylene, the adsorbed amount of methanethiol decreases because of the effect of competitive adsorption of propylene. The adsorption capacity decreases in the order of Zn-A > Ca-A > GS_{3X} ≫ Sr-A, K-A. Table 1 summarizes the adsorption performance of the adsorbents. To compare the effect of propylene on the adsorption of methanethiol, the ratio (q_2/q_1) between the adsorption capacity of methanethiol in the presence of propylene (q_2) and that in the absence of propylene (q_1) is calculated. It is noteworthy that the result obtained by using Zn-A exhibits the largest q_2/q_1. This result suggests that the use of Zn-A is the most suitable for desulfurization of propylene among the examined adsorbents. Since the adsorption capacity of Ca-A or Zn-A is larger than that of GS_{3X} possessing larger volume of micropores, the performance of the adsorbents cannot be simply explained by the porous properties.

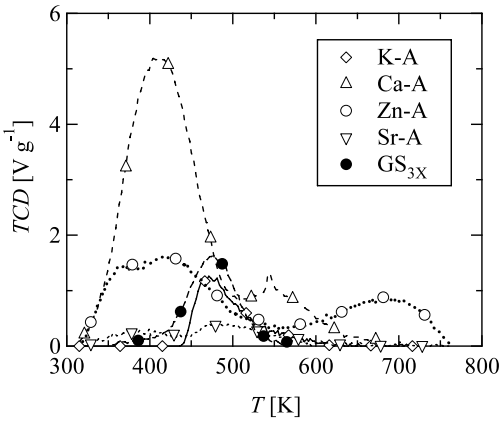

Fig. 4 TPD spectrum of methanethiol

To evaluate the specific interaction between methanethiol and the adsorbents, the TPD spectra of methanethiol are compared as shown in Fig. 4. The vertical axis indicates the intensity of the TCD signal that corresponds to the amount of desorbed methanethiol at the temperature. Higher desorption temperature indicates the stronger interaction between methanethiol and the adsorbent. The TPD spectrum measured by using Zn-A or Ca-A possesses double peaks. Considering the concentration (10,000 ppm) of methanethiol in the standard gas used in the TPD measurement, the peak detected in a relatively low temperature range (<500 K) suggests desorption of methanethiol that is physically adsorbed on the micropores of the zeolite. The peak detected in a relatively high temperature range (500–800 K) can be attributed to the strong interaction (Lewis acid/base interaction) between the active site (Al atom and exchanged metal cation) of the zeolite and methanethiol. The Lewis acid/base interaction is considered to be effective for adsorptive removal of trace amount of sulfur impurities from propylene. It should be noted that Zn-A requires the highest temperature for desorption of methanethiol. On the other hand, the area of the spectrum measured by using K-A and Sr-A is relatively small. It is also shown that the interaction of methanethiol with GS_{3X} is obviously weaker than that with Zn-A or Ca-A. This result confirms that, among the tested adsorbents, Zn-A is the most effective one for desulfurization of propylene. Further investigation is necessary to clarify the effect of cation species on the specific interaction between methanethiol and the LTA zeolite. The TPD spectrum also indicates the temperature for thermal regeneration of the spent adsorbent. For example, Zn-A can be regenerated by heat treatment at higher than 800 K. In a practical desulfurization system, the necessity for regeneration should be examined based on the cost of the adsorbent and its regeneration cost.

4 Conclusion

Adsorption characteristics of a series of LTA zeolite were studied for desulfurization of propylene produced from bioethanol. By the measurement of a breakthrough curve for adsorption of methanethiol in the presence of propylene, among the tested adsorbents, the LTA zeolite exchanged with Zn^{2+} (Zn-A) was found to be the most effective adsorbent for desulfurization. The strong interaction of methanethiol adsorbed on Zn-A was confirmed by the TPD measurement. Adsorption performance of the LTA zeolite for the other sulfur impurities, such as ethanethiol and hydrogen sulfide, will be examined in a subsequent study.

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