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Desulfurization of Thiophene over HY Zeolite

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Abstract

HY zeolite was definitely active for the cracking of thiophene at 400°C under a helium stream. The cracking products of thiophene were mainly hydrogen sulfide and trace amounts of unidentified high boiling hydrocarbon. The activity of HY in the cracking of thiophene decreased with an increase of the pulse number but the decreased activity of HY was regenerated again by treatment at 500°C in an oxygen stream. The activity change of HY by calcination agreed with that of Brönsted acidity but was independent of that of Lewis acidity. The interaction between the surface acidic hydroxyl group, i. e. Brönsted acid site of HY and thiophene molecule was observed by the infrared spectra of adsorbed thiophene on HY.

It was concluded that the Brönsted acid site of HY surface acts as the active site for the cracking of thiophene. Models of adsorption state and cracking mechanism of thiophene on HY were also proposed.

1. Introduction

The hydrodesulfurization of thiophenes has been widely studied as a model reaction by many researchers to clarify the mechanism of the hydrodesulfurization of petroleum.[1~3] $CoO-MoO_3-Al_2O_3$ or $NiO-MoO_3-Al_2O_3$ catalysts are used in the industrial hydrodesulfurization of petroleum and these catalysts have been generally employed in the study of the hydrodesulfurization of thiophene[4]. However, there are many points which remain unclarified regarding the active sites of the catalysts and the mechanism in the hydrodesulfurization of thiophene due to the complexity of the surface structure of the catalysts after the reduction and sulfurization by the hydrogen/hydrogen sulfide mixture[5,6].

Recently, Nagai, *et al*[7,8]. studied the hydrodesulfurization of dibenzothiophene over HY and CoY zeolites, whose surface structure and acidic properties have been well defined, and they suggested that the acid sites of zeolite play an important role for the hydrodesulfurization of dibenzothiophene.

On the other hand, thiophene has a high thermal stability and the temperature of 871°C or above are necessary for the thermal cracking of thiophene.[9] Thus, it has been believed that the co-existance of gaseous hydrogen is indispensable for the catalytic cracking of thiophene. However, in the course of our systematic fundamental studies on the catalytic desulfurization of organic sulfur compounds in petroleum over solid acid catalysts,[10~14] it was found that HY zeolite shows a definite activity for the cracking of thiophene without gaseous hydrogen, i. e. under a helium stream. Thus, it will be worthwhile to investigate the cracking reaction of thiophene

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on HY without the presence of a hydrogen stream in order to obtain more fundamental knowledge with respect to the active sites and the mechanism in the hydrodesulfurization of thiophene.

In this paper, we have studied the active sites and the adsorption states of thiophene on HY zeolite, etc. by a pulse reactor and an infrared spectroscopic method to clarify the mechanism of the cracking of thiophene over HY zeolite.

2. Experiment

2.1 Experimental Apparatus

To examine the activity of HY for the cracking of thiophene, a conventional pulse reactor connected to a gaschromatograph was used with an 2.5 m analytical column packed with silicon DC-550. Helium, dried with a molecular sieve, was used as the carrier gas. The reactor was a U-type pyrex glass tube of 4 mm-ID, which was heated with an electric furnace. The temperature of the catalyst bed was controlled within ±1°C.

The infrared absorption spectra of adsorbed thiophene were recorded on a Hitachi spectrometer EPI-590 equipped with a conventional *in situ* cell connected to a vacuum line.

2.2 HY zeolite

HY was prepared by exchanging Na^+ in NaY zeolite (SK-40) with NH_4^+ in 0.2 mol/ℓ of NH_4Cl solution. The percentage of ion-exchange was determined by means of atomic absorption spectrometry and was found to be 78.6%. HY was calcined at 500°C for 4 hr in air and kept in a desiccator.

2.3 Material

Commercial guaranteed reagents of thiophene, pyridine and cumene were used without further purification, since no impurities were detected by the gaschromatographic analysis.

2.4 Procedure

The activities of HY for the cracking of thiophene and cumene were examined at 400°C by passing a carrier gas (He: Flow rate=30 mℓ/min) and by injecting 2 $\mu\ell$ of the reactant into the pulse reactor with a micro-syringe. The conversion, x, in the cracking of thiophene was determined from the peak area of thiophene before and after the cracking reaction.

For the infrared spectroscopic experiments, a finely powdered HY zeolite, after being calcined at 500°C for 4 hr in air, was formed into a thin disk of 20 mm in diameter under a pressure of about 300 kg/cm^2. The disk was placed in a cell and evacuated *in situ* at 10^{-4} torr at 500°C for 4 hr. And 5.5 torr of thiophene was introduced into the cell maintained at a given temperature for 0.5 hr and then thiophene in gas phase was evacuated at room temperature for 1 hr. The infrared spectra of thiophene adsorbed on HY were observed at room temperature.

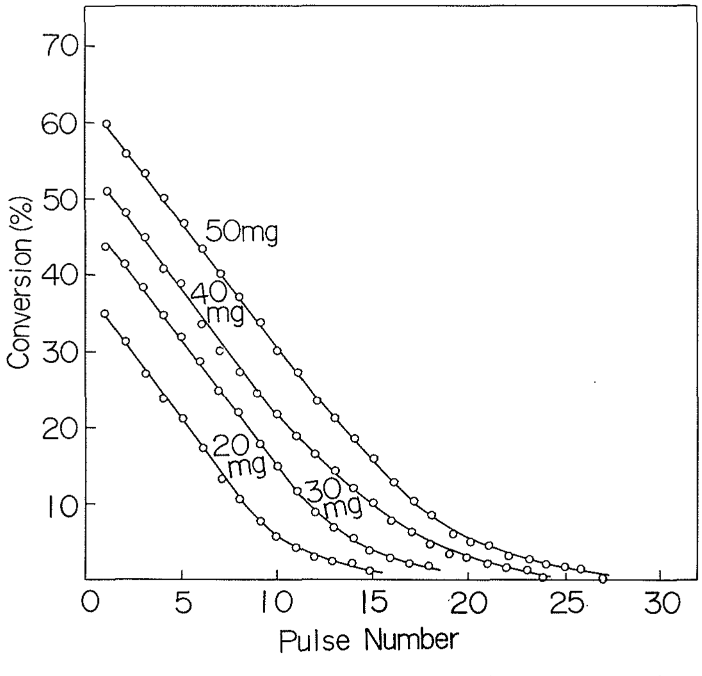
The existence of sulfur deposit on HY surface after the cracking of thiophene was examined by means of the Kitagawa sulfur dioxide detector tube as sulfur dioxide formed by heating of the used HY at 500°C in a oxygen stream.

3. Results and Discussion

3.1 Activity of HY for Cracking of Thiophene

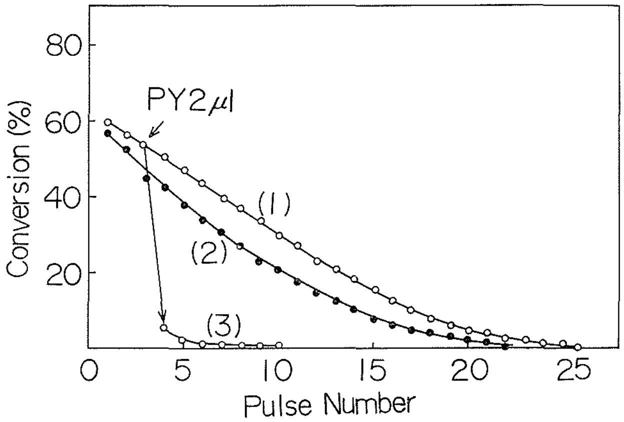
The activity of various solid catalysts, CaO, MgO, SiO_2, Al_2O_3, MoO_3, NiO, ZnO, $NiSO_4$, NiS, MoS_2, SiO_2-Al_2O_3, CoO-MoO_3-Al_2O_3, NaY, HY and solid phosphoric acid, for the cracking of thiophene were examined at 400°C in a helium stream. Only HY among these catalysts showed activity for the cracking of thiophene. The main cracking product was hydrogen sulfide and a trace amount of unidentified high boiling carbonaceous compound was also formed. Low molecular weight hydrocarbons such as methane, ethylene, propylene, and butenes, etc. were not detected. The sulfur deposit on HY surface after the cracking reaction was determined by means of sulfur dioxide detector tube and the amount of sulfur deposit on HY surface was about 10% of the total amount of hydrogen sulfide formed in the cracking of thiophene.

The conversion of thiophene on HY decreased with an increase of the pulse number and finally it became zero as shown in Fig. 1. The decreased activity of HY was, however, almost regenerated by the treatment with an oxygen stream at 500°C for 8 hr as shown in Fig. 2, indicating that the main cause of the deactivation of HY is the accumulation of carbonaceous polymer compounds on HY surface. No differences with respect to the activity of HY and products in the cracking of thiophene under hydrogen stream were observed. Furthermore, the activity of HY



Experimental Conditions: Carrier Gas (He) Flow Rate=30 mℓ/min, Injection of Thiophene=2 μℓ.
Numerical values in figure represent the weight of HY

Fig. 1. Cracking of Thiophene on Various Weight of HY at 400°C in Helium Stream.



(1) Fresh HY (2) HY regenerated by calcination at 500°C for 8 hr in oxygen stream (3) HY poisoned by pyridine. Weight of HY=50 mg, Reaction Temp.=400°C.

Fig. 2. Regeneration of Deactivated HY by Calcination with Oxygen and Effect of Poisoning by Pyridine.

in the cracking of thiophene was poisoned by the addition of 2 $\mu\ell$ of pyridine in the course of the cracking reaction as shown in Fig. 2. This result indicates that the acid sites of HY play an important role for the cracking of thiophene.

3.2 Irreversible First Order Kinetics

The linear relationship through the origin between the contact time, **W/F**, and $-\ln(1-x)$ were observed at each pulse number as shown in Fig. 3 and almost the same apparent activation energies of about 12~13 kcal/mole were obtained at each

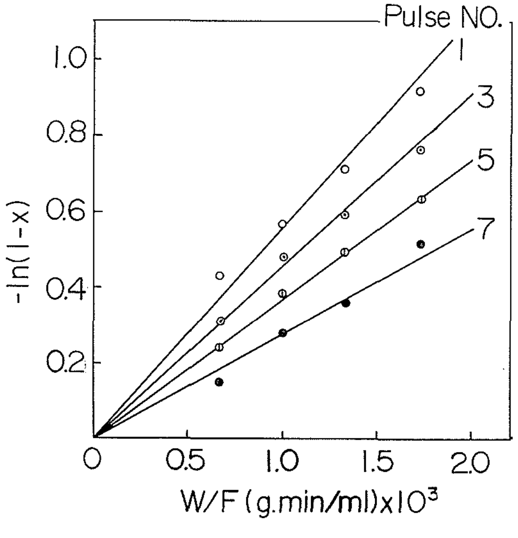


Fig. 3. Linearity Test for First Order Kinetics in Cracking of Thiophene at Various Stage of Pulse Number.

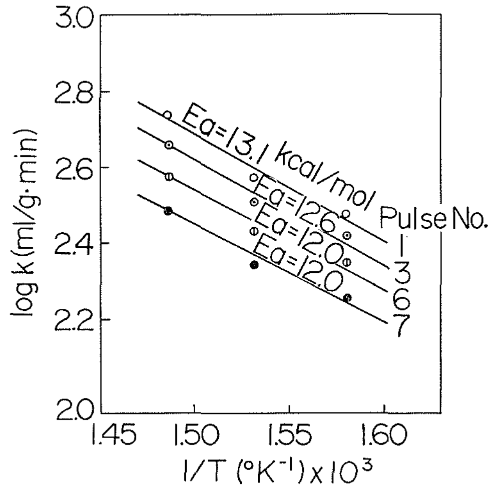


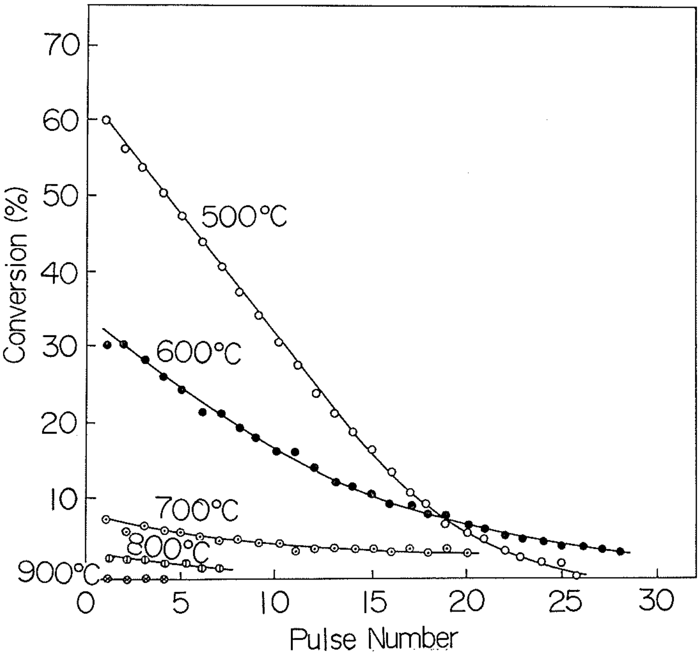
Fig. 4. Arrhenius Plot of Apparent First Order Rate Constant in Cracking of Thiophene on HY at Various Stage of Pulse Number.

pulse number from the Arrhenius plot of the apparent first order rate constant *k* in the cracking of thiophene as shown in Fig. 4. It is presumed that the cracking of thiophene on HY follows approximately irreversible first order kinetics as in the cracking of other sulfur compounds described in the previous paper[10,13] and the cracking mechanism of thiophene dose not change with the pulse number.

3.3 Active Sites of HY

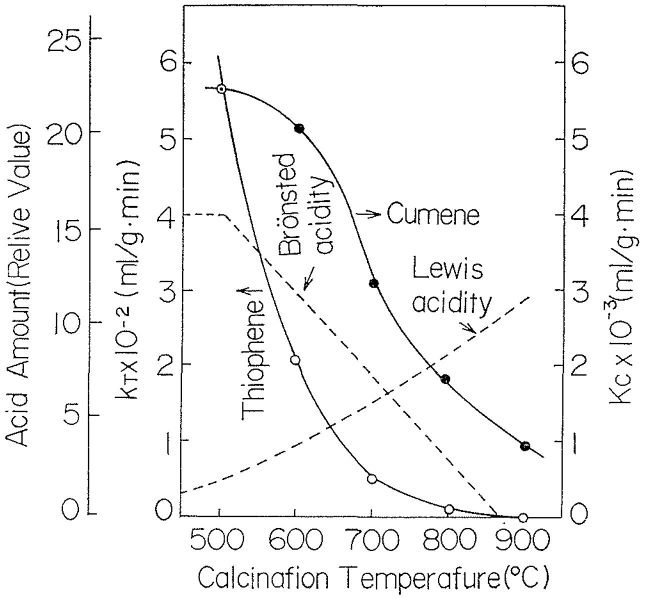
The effect of the calcination temperature on the activity of HY in the cracking of thiophene is shown in Fig. 5. The activity of HY at the first pulse decreased with an increase of the calcination temperature but the degree of deactivation of HY against the pulse number became smaller when heated at higher temperatures as shown in Fig. 5.

Furthermore, the initial activity of HY for the cracking of cumene, which is assumed to proceed on the Brönsted acid sites of the solid acid catalysts, also decreased with the increase of the calcination temperature as shown in Fig. 6. In Fig. 6, we also showed the results of Ward[15] by the dotted lines. By infrared spectroscopy of HY treated with pyridine, Ward determined the ratio of concentration of the Brönsted acid site to that of the Lewis acid sites of HY calcined at various temperature. The changes of the activities of HY in the cracking of thiophene and cumene by the calcination agreed with the decrease in the Brönsted acidity but was independent of that of Lewis acidity as shown in Fig. 6. These results indicate that the active sites of HY for the cracking of thiophene are the Brönsted acid sites of HY.



Numerical values in figure are the calcination temperature.
Wt. of HY = 50 mg, Reaction Temp. = 400°C.

Fig. 5. Effect of Calcination Temperature on Activity of HY in Cracking of Thiophene.



k_T and k_C are the apparent first order rate constants in the cracking of thiophene and cumene at 400°C. The dotted lines are the experimental results of Ward[15].

Fig. 6. Changes of Activities of HY for Cracking of Thiophene and Cumene by Calcination Temperature.

However, the other solid acid catalysts such as SiO_2-Al_2O_3 (SA) and solid phosphoric acid (SPA), which also have Brönsted acid sites, did not show activity for the cracking of thiophene. This may be attributed to the difference in the amount of the Brönsted acid sites of HY, SA and SPA. The amount of Brönsted acid sites of SA and SPA compared with that of HY is too small to show the appreciable activity for the cracking of thiophene. Topchieva, *et al.*[16] and Murakami, *et al.*[17] reported that the catalytic activity of solid acid catalysts for the cracking of cumene is proportional to the amount of the Brönsted acid sites of the catalysts and we found that the order of the catalytic activities of HY, SA and SPA in the cracking of cumene at 400°C was HY $(56.0 \times 10^2) > $SA $(5.81 \times 10^2) > $SPA (0.54×10^2). The numerical values in parentheses are the values of apparent first order rate constants (mℓ/g. min) in the cracking of cumene. Thus, it is concluded that the order of the amount of Brönsted acid sites of these solid acid catalysts would agree with the order of catalytic acitivity in the cracking of cumene and HY has a considerable number of the Brönsted acid sites for the cracking of thiophene as compared to SA and SPA.

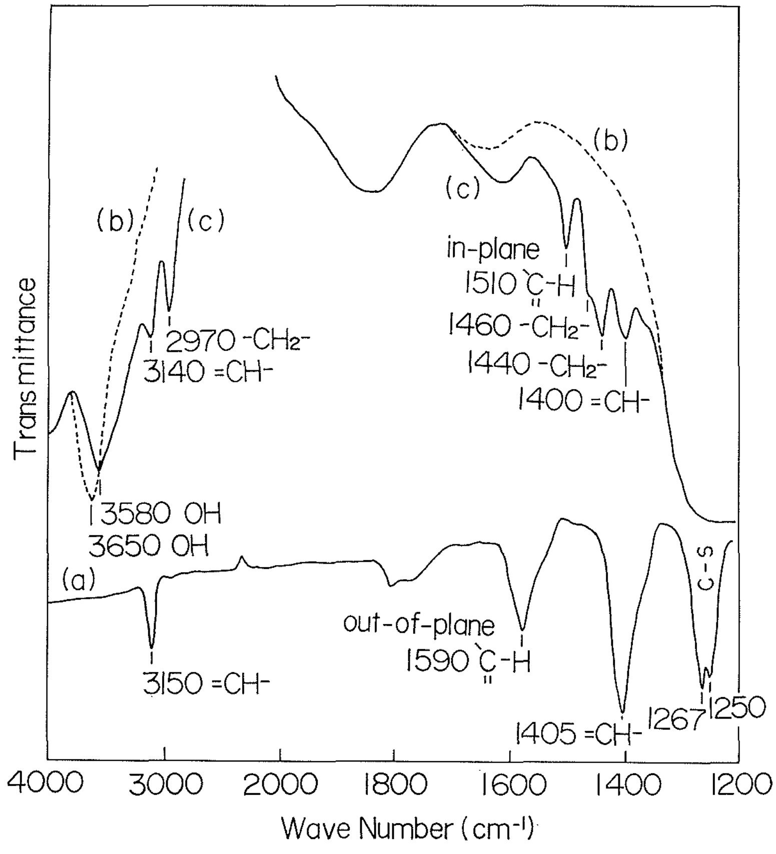
3.4 IR Spectra of Thiophene Adsorbed on HY

Fig. 7 shows the infrared spectra of thiophene adsorbed on HY. In Fig. 7, spectra a, b, and c indicate the spectra of thiophene in gas phase, background of HY and adsorbed thiophene on HY, respectively.

In the spectra of thiophene in gas phase (spectra a), stretching and bending mode[18] of the unsaturated CH group (=CH-) at 3150 and 1405 cm^{-1}, and the out-of-plane bending mode[18] of the CH group of thiophene ring at 1590 cm^{-1} were observed. In the spectra of adsorbed thiophene on HY (spectra c), absorption bands of the saturated CH_2 group ($-CH_2-$) at 2970, 1460 and 1440 cm^{-1}, and the in-plane bending mode of the unsaturated CH group at 1510 cm^{-1} were observed.

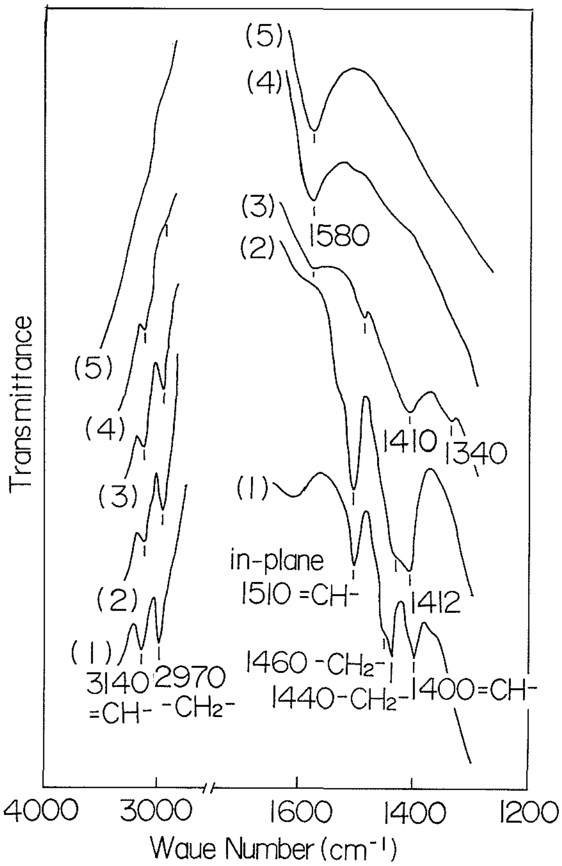
However, the out-of-plane bending mode of the unsaturated CH group at 1590 cm^{-1} of thiophene ring, which was observed in the gas phase thiophene, was not observed in the spectra of adsorbed thiophene on HY. This indicates that the thiophene molecule adsorbs HY maintaining a planar structure. The band of the acidic hydroxyl group on HY surface at 3650 cm^{-1} shifted to a lower frequency at 3580 cm^{-1}, implying an interaction between the acidic hydroxyl group, i. e, the Brönsted acid sites, on HY surface and thiophene molecule. The band of hydroxyl group region at about 3000–4000 cm^{-1} was broader after the adsorption of thiophene. This indicates the formation of hydrogen bonding between the adsorbed thiophene and HY surface.

The strength of absorption band of the saturated CH_2 group at 2970 cm^{-1} decreased simply with an increase of the evacuation temperature as shown in Fig. 8.



(a) Gas phase thiophene (b) Background of HY (c) Thiophene was adsorbed and evacuated at room temperature for 1 hr.

Fig. 7. Infrared Spectra of Thiophene Adsorbed on HY.

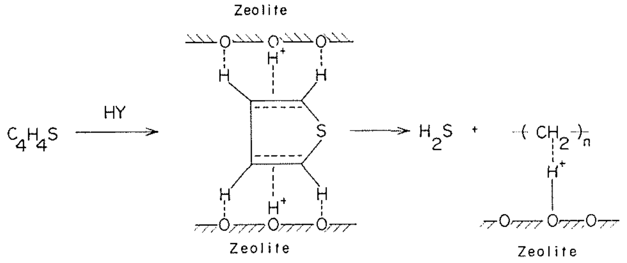


(1) Evacuation at room temperature for 1 hr
(2) 100°C (3) 200°C (4) 300°C (5) 400°C.

Fig. 8. Changes of IR Spectra of Adsorbed Thiophene on HY by Evacuation Temperature.

However, intricate changes in intensity and shape of the absorption bands at 1460 and 1440 cm^{-1} were observed with increase of the evacuation temperature as shown in Fig. 8. The formation of a large band around 1580 cm^{-1}, which was assigned as a carbonaceous deposit, was also observed after the disappearance of the band of CH_2 group by this treatment. The white color of HY changed to black by the evacuation treatment at high temperature but the black color of HY returned to the original white by the calcination with oxygen at 500°C for 1 hr in the i. r. cell, and the spectra of the background of HY returned to the original accompanying the disappearance of a large band around 1580 cm^{-1}. Thus, the bands of CH_2 group observed in the adsorption of thiophene on HY are assigned as those of a partially polymerized carbonaceous species[19] of cracking fragments of thiophene. This may be supported by the fact that tetrahydrothiophene adsorbed on HY shows different spectra from that of thiophene and it easily desorbed from HY surface by the evacuation at 50°C, and no CD band was observed in the adsorption of thiophene over HY surface treated with D_2O vapour[20].

From these results, we concluded that, in the adsorption of thiophene on HY, the proton of the acidic hydroxyl groups on the internal surface of HY strongly interact with π-electrons of the C=C double bound of thiophene molecule and the hydrogen atom of thiophene ring forms hydrogen bonding with the surface oxygen of zeolite skeletal structure, and thiophene molecules adsorbed on the HY surface maintain the adsorption state of planar structure.



It is expected that the thiophene molecule would be activated on HY surface by the formation of such an adsorption state and then the adsorbed thiophene molecule decomposes to form hydrogen sulfide and polymerized carbonaceous species like $(-CH_2-)_n$ on HY surface. Most of hydrogen sulfide formed in the cracking of thiophene will desorb to a gas phase but most of polymerized carbonaceous species remain on the HY surface and poison the Brönsted acid sites of HY. A small amount of the polymer compound would desorb to a gas phase as unidentified high boiling hydrocarbons.

4. Conclusion

HY zeolite showed the activity for the cracking of thiophene under a helium stream and the main product was hydrogen sulfide. The activity of HY for the cracking of thiophene was poisoned by the addition of pyridine. The change of the activity of HY in the cracking of thiophene and cumene by the calcination agreed with the decrease in the Brönsted acidity but was independent of that of Lewis acidity. The infrared spectra of adsorbed thiophene on HY indicated the existence of the interaction between thiophene molecule and surface acidic hydroxyl group, i. e. the Brönsted acid sites, of HY.

From these results, it was concluded that the active sites of HY for the cracking of thiophene are the Brönsted acid sites of HY surface. Models of adsorption state and the cracking mechanism of thiophene on HY were also proposed.

Furthermore, the importance of Brönsted acidity of catalysts in the hydrodesulfurization of petroleum was suggested from the information and knowledge obtained in this work.

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