Dealumination of Zn/H-ZSM-5 by steam treatment for the suppression of coke formation in ethane dehydroaromatization

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Abstract: Steam-treated Zn/H-ZSM-5 exhibited a high activity and stability for ethane dehydroaromatization thanks to the suppression of coke formation. The results of XRD, UV-Vis spectroscopy and ICP-OES indicated that the steam treatment had little influence on the state and amount of Zn species. ^{29}Si MAS NMR spectra of H-ZSM-5 and Zn/H-ZSM-5 showed that dealumination of Al species in the framework (Al_F) was suppressed by Zn loading. This indicated that Al_F contributed to Brønsted acid sites in Zn/H-ZSM-5 were selectively dealuminated. Optimization of the amount of Brønsted acid sites is necessary to achieve the high stability to form aromatic hydrocarbons.

Keywords: Ethane dehydroaromatization, Zn/H-ZSM-5, dealumination.

1. Introduction

Ethane dehydroaromatization is one of the promising processes for converting natural gas to valuable aromatic hydrocarbons[1]. Compared with methane, using ethane is able to lower the reaction temperatures at less than 873 K, avoiding issues including the heat transfer and rapid deactivation of catalysts. In the ethane dehydroaromatization reaction, Zn/H-ZSM-5 is an effective catalyst to form aromatic hydrocarbons because Zn^{2+} cations promote the activation of ethane and **MFI**-type zeolite has micropores of about 0.55 nm, which is close to the kinetic diameter of benzene[2]. However, Zn/H-ZSM-5 is rapidly deactivated by coke formation. Thus, improvement in the stability is necessary. In this work, we found that steam treatment of Zn/H-ZSM-5 improved the stability to form aromatic hydrocarbons. Various characterizations were carried out to elucidate the influence of steam treatment on the catalyst.

2. Experimental

The H-ZSM-5 support was obtained by calcination of NH_4-ZSM-5 (HSZ-820NHA, Tosoh) at 773 K for 5 h. The loading of Zn was carried out by an ion-exchange method using the 0.02 M aqueous solution of $Zn(NO_3)_2\cdot6H_2O$ at 353 K for 24 h. The powder was separated by suction filtration, and dried in air at 393 K for 24 h. Then, the dried powder was calcined at 823 K for 5 h.

Steam treatment of H-ZSM-5 and Zn/H-ZSM-5 was conducted in a fixed bed reactor at 823 K for 1 h under H_2O/Ar flow. The steam-treated samples are denoted as H-ZSM-5 ST and Zn/H-ZSM-5 ST. Zn loading was also conducted by the ion-exchange method using the H-ZSM-5 ST support. The catalyst is denoted as Zn/H-ZSM-5 ST bef. IE.

Catalytic activity tests were carried out in a fixed bed reactor at 873 K and atmospheric pressure. The feed gas of 80vol% ethane and balanced nitrogen was supplied at a flow rate of 25 mL min^{-1} (SATP). Products were analyzed by a gas chromatography equipped with a thermal conductivity detector and an on-line gas chromatography equipped with a flame ionization detector.

Characterizations including TPO, XRD, UV-Vis spectroscopy, ICP-OES, ^{29}Si MAS NMR spectroscopy were conducted to elucidate the influence of steam treatment on the catalysts.

The details of experimental conditions are written in the literature[3].

3. Results and discussion

Catalytic activity tests were conducted to investigate the activity and aromatics selectivity. Results are shown in Figure 1. In comparison with H-ZSM-5, the initial activity greatly increased by Zn loading although it was rapidly deactivated. On the other hand, Zn/H-ZSM-5 ST showed the high activity and stability, indicating that steam treatment improved the stability. TPO measurements revealed that the amount of carbon deposition on the spent catalyst decreased by steam treatment, leading to the high stability. Zn/H-ZSM-5 ST bef. IE exhibited the low activity due to the low loading amount of Zn.

Then, various characterizations were carried out to elucidate the influence of steam treatment on the catalysts. XRD patterns indicated steam treatment had little influence on the **MFI** structure and Zn species were highly dispersed on the catalysts. In the UV-Vis spectra of Zn loaded catalysts, the absorption band attributed to ZnO was not observed. These results would indicate that Zn existed at ion-exchange sites of the support. ICP-OES measurements revealed that little changes in the loading amount of Zn occurred via steam treatment. Consequently, steam treatment did not greatly affect the state and amount of Zn species.

In addition, ^{29}Si MAS NMR spectra were measured to obtain information on the local structure of the supports. In the spectrum of H-ZSM-5, two peaks at -112 and -115 ppm were attributed to Q^4(0Al) and a peak at -106 ppm was attributed to Q^4(1Al). Q^4(0Al) and Q^4(1Al) mean $Si(OSi)_4$ and $(AlO)Si(SiO)_3$, respectively. The peak intensity of Q^4(1Al) markedly decreased after steam treatment. This clearly shows dealumination of Al species in the MFI framework (Al_F). On the other hand, a little decrease in the peak intensity of Q^4(1Al) was observed in the spectrum of Zn/H-ZSM-5. This would indicate that dealumination of Al_F was suppressed by Zn loading. On the basis of calculated Si/Al ratios[4], the parent H-ZSM-5 was easily dealuminated in comparison with Zn/H-ZSM-5. As a result, Al_F species contributed to Brønsted acid sites in Zn/H-ZSM-5 would be preferentially dealuminated. Therefore, the suppression of coke formation was achieved thanks to the optimal amount of Brønsted acid sites.

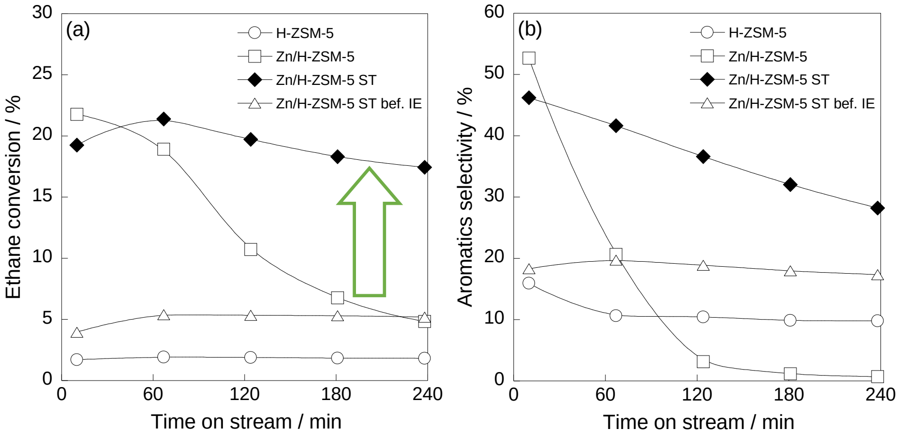

Figure 1. (a) Ethane conversion and (b) aromatics selectivity with time on stream over H-ZSM-5 and various Zn/H-ZSM-5 catalysts.[3]

4. Conclusions

We investigated the effects of steam treatment on the catalytic performance of Zn/H-ZSM-5 for ethane dehydroaromatization. The steam-treated Zn/H-ZSM-5 catalyst exhibited the high activity and stability because of the suppression of coke formation. XRD, UV-Vis spectroscopy and ICP-OES measurements revealed that steam treatment had little influence on the state and loading amount of Zn species. The ^{29}Si MAS NMR spectra indicated that dealumination of Al_F was suppressed by Zn loading and Al_F contributed to Brønsted acid sites were preferentially dealuminated. As a result, extra Brønsted acid sites which promote coke formation were removed. Therefore, Zn/H-ZSM-5 ST exhibited the high performance.

References

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