

# Ethane dehydroaromatization over Co/H-ZSM-5 catalyst

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**Abstract:** Non-oxidative ethane dehydroaromatization to form aromatic hydrocarbons was investigated over Co supported on H-ZSM-5 catalysts prepared by two methods. Co/H-ZSM-5 prepared by an ion-exchange (IE) method exhibited high catalytic performance than Co/H-ZSM-5 prepared by an impregnation method thanks to low carbon deposition. Temperature programmed reduction measurements and X-ray absorption near edge structure analysis (XANES) indicate that only Co<sup>2+</sup> cations exist at ion-exchange sites in Co/H-ZSM-5 prepared by the IE method. Therefore, Co<sup>2+</sup> cations would activate ethane with less carbon deposition.

**Keywords:** Ethane dehydroaromatization, Co/H-ZSM-5 catalyst, coke formation.

## 1. Introduction

Benzene, toluene, xylene, so called BTX, are important and valuable chemicals. Producing BTX directly from ethane, one of the components of natural gas, is an attractive process because natural gas is a cheap feedstock. In ethane dehydroaromatization, Zn/H-ZSM-5 exhibits high catalytic activity.<sup>1</sup> However, zinc oxides are easily reduced and vaporized under reductive conditions. Therefore, a novel metal catalyst that is stable under the reaction conditions is necessary. Thus, we investigate an optimal active metal belonging to the fourth period in the periodic table. As a result, Co/H-ZSM-5 exhibits a high catalytic performance. In addition, Co/H-ZSM-5 prepared by an ion-exchange method exhibited a high stability for ethane dehydroaromatization. Various characterizations were conducted to elucidate the nature of Co species on the catalysts.

## 2. Experimental

The H-ZSM-5 support was obtained by calcining NH<sub>4</sub>-ZSM-5 (CBV 5524G, Zeolyst) at 823 K. H-ZSM-5 catalysts containing 5wt% active metal were prepared using an impregnation (IM) method. V, Mn, Fe, Co, Ni, Cu, or Ga was used as an active metal. First, H-ZSM-5 was soaked in distilled water and was stirred for 2 h *in vacuo*. Next, a solution of the metal precursor was added to the suspension and it was stirred at atmospheric pressure for 2 h. The vanadium precursor was its ammonium salt, and others were their nitrates. After evaporating the suspension to dryness and drying in air, the catalyst was calcined at 773 K for 5 h. Co was also loaded by an ion-exchange (IE) method. H-ZSM-5 was added to the 0.02 M solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and the suspension was stirred at 353 K at 24 h. After suction filtration and drying in air, the catalyst was calcined at 773 K for 5 h. Co/H-ZSM-5 prepared by the IM method and IE method are denoted as Co/H-ZSM-5 IM and Co/H-ZSM-5 IE, respectively.

Ethane dehydroaromatization was conducted in a fixed bed reactor at 873 K for 4 h, using 0.2 g of the catalyst. The gas containing 80vol% of ethane and balanced nitrogen was fed at a total flow rate of 25 mL min<sup>-1</sup>(SATP). Online GC-FID was used for the analyses of hydrocarbons and GC-TCD was used for the analyses of H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. Temperature programmed oxidation (TPO) measurements, X-ray diffraction (XRD) analysis, temperature programmed reduction (TPR) measurements, and Co K-edge X-ray absorption near edge structure (XANES) analyses were conducted for the characterizations of catalysts. Further details of the experiment procedure are explained in the literature.<sup>2</sup>

## 3. Results and discussion

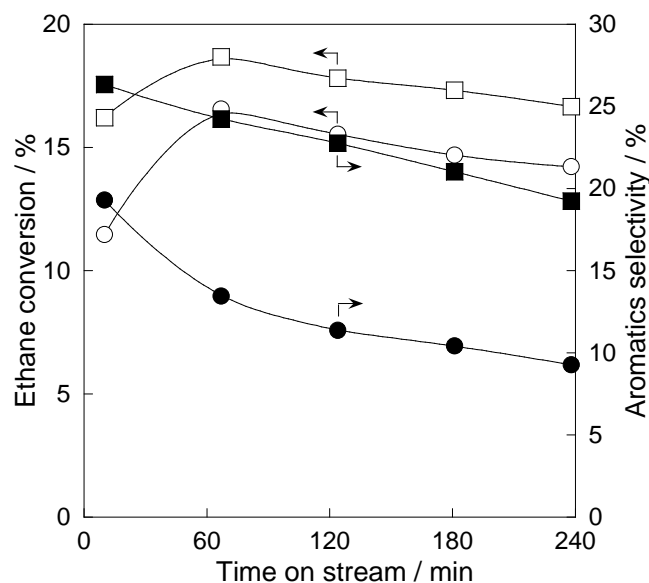
Among various metal-loaded catalysts, we found that Co/H-ZSM-5 IM exhibits relatively high catalytic performance and aromatics selectivity.<sup>2</sup> However, its activity still decreased with time on stream because of carbon deposition. Therefore, Co/H-ZSM-5 IE was prepared, and its performance was tested.

Figure 1 presents the ethane conversion and aromatics selectivity with time on stream over Co/H-ZSM-5 IM and Co/H-ZSM-5 IE. Co/H-ZSM-5 IE exhibited high catalytic activity and aromatics selectivity. Moreover, Co/H-ZSM-5 IE exhibited higher stability for the reaction than Co/H-ZSM-5 IM. TPO measurements revealed that the amount of carbon deposition on Co/H-ZSM-5 IE was smaller than that on Co/H-ZSM-5 IM. Therefore, the high stability of Co/H-ZSM-5 IE is attributable to the suppression of carbon deposition.

Then, characterizations of Co species were conducted to elucidate why coke formation was suppressed. First, XRD analysis was conducted to investigate the Co species on the catalysts. In the XRD pattern of Co/H-ZSM-5 IM, a peak attributed to  $\text{Co}_3\text{O}_4$  was observed. This indicates that  $\text{Co}_3\text{O}_4$  exists on the external surface on Co/H-ZSM-5 IM. On the other hand, peaks attributed to Co species were not observed in the XRD pattern for Co/H-ZSM-5 IE. This indicates that Co species on Co/H-ZSM-5 IE are highly dispersed.

Next, TPR measurements were conducted to investigate the reducibility of Co species on the catalysts. In the TPR profile of Co/H-ZSM-5 IM, reduction peaks were observed at 641 K and 718 K, which indicates that Co species were readily reduced from  $\text{Co}_3\text{O}_4$  to CoO and from CoO to  $\text{Co}^0$ . In addition, a peak at 935 K was observed, which is attributed to the reduction of  $\text{CoO}_x$  ( $1 \leq x \leq 1.5$ ) clusters existing in the micropore.<sup>3</sup> On the other hand, no reduction peaks were observed in the TPR profile for Co/H-ZSM-5 IE. This indicates that Co species existing at ion-exchange sites were not reduced easily.

Finally, Co *K*-edge XANES analyses were conducted to elucidate the electronic state of Co species on Co/H-ZSM-5 IM and Co/H-ZSM-5 IE. The spectra indicate that fresh Co/H-ZSM-5 IM contains  $\text{Co}_3\text{O}_4$  and the spent Co/H-ZSM-5 IM contains  $\text{Co}^0$ . On the other hand, the fresh and spent Co/H-ZSM-5 IE catalysts contain only  $\text{Co}^{2+}$  species. Therefore,  $\text{Co}^{2+}$  species would exist at ion-exchanged sites in Co/H-ZSM-5 IE stably even during the reaction. These  $\text{Co}^{2+}$  species are non-reducible and are highly dispersed on the catalyst. The active sites would contribute to the formation of BTX with less carbon deposition, leading to the high catalytic performance of Co/H-ZSM-5 IE.



**Figure 1.** Ethane conversion (open symbols) and aromatics selectivity (closed symbols) with time on stream over Co/H-ZSM-5 IM ( $\circ$ ,  $\bullet$ ) and Co/H-ZSM-5 IE ( $\square$ ,  $\blacksquare$ ).<sup>3</sup>

#### 4. Conclusions

Non-oxidative ethane dehydroaromatization over Co/H-ZSM-5 catalysts was investigated. Co/H-ZSM-5 prepared by the IE method exhibited high catalytic performance. TPO measurements revealed that the amount of carbon deposition on Co/H-ZSM-5 IE was very small. XRD analyses indicate that Co species are highly dispersed on Co/H-ZSM-5 IE. TPR measurements and XANES analyses indicate that only  $\text{Co}^{2+}$  cations exist at ion-exchange sites in Co/H-ZSM-5 IE. These active sites contributed to the activation of ethane with less carbon deposition.

#### References

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