Supplementary Information

Improved methane dehydrogaromatization reaction over Mo and Cr co-doped ZSM-5 catalyst

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1. Experimental Part

1.1 Catalyst preparation

Ammonium Molybdate Tetrahydrate (Wako FUJIFILM), Chromiium(III) Acetate (Wako FUJIFILM) and H^+ type ZSM-5 zeolite (822HOA, TOSOH Co.) were used without further purification. An incipient wetness impregnation was applied to load Mo or Cr on ZSM-5. First, ZSM-5 was mixed with an aqueous solution containing Mo or Cr. Afterward, the sample was dried at 363 K and calcined under air at 823 K for 5 h. The samples were donated as "Mo/ZSM-5" and "Cr(x)/ZSM-5", where x means the weight ratio of Cr [wt%]. Second, Mo was introduced to "Cr(x)/ZSM-5" by an incipient wetness impregnation similarly. Those samples were named "Mo/Cr(x)/ZSM-5". As a comparison, we loaded 1 wt % of Cr on Mo/ZSM-5. The sample was donated "Cr/Mo/ZSM-5"

1.2 Characterization

The crystal structures of all products were determined by X-ray diffraction (XRD) patterns recorded on a PANalytical X'Pert-MPD diffractometer using Cu-Kαradiation. The morphology of samples was observed by transmission electron microscopy (TEM) observation. The energy dispersive X-ray spectroscopy (EDX) for the determination of Cr contents was performed on JEOL JCM-7000. To obtain physical information of samples, N_2 adsorption measurements at 77 K were conducted using BELSORP-Max (MicrotracBel). Diffuse reflectance ultraviolet-visible (UV-vis) spectra of the samples were analyzed on a JASCO V-770 spectrophotometer. NH_3 temperature programmed deposition (NH_3-TPD) measurements were carried out to evaluate the acidity

1.3 Methane dehydroaromatization (MDA) reaction tests

MDA reactions over zeolite catalysts were carried out in a fixed bed reactor at atmospheric pressure referring to our previous work.The catalyst (0.05 g) was loaded into a quartz tube (i.d. 4 mm) and then the temperature was raised to 973 K under He flow. The feed gas of 66.5 vol% ethane and balanced He was fed at a total flow rate of 7.5 cm^3/min. The product stream was analyzed online with Shimadzu GC-2025 gas chromatographs equipped with a flame ionization detector. GS ALUMINA was used as a GC column. Methane conversion [%] and product yields [%] were calculated as follows:

$$(\text{Methane conversion [\%]}) = 100 \times \frac{(C-mol\ of\ methane\ at\ the\ inlet) - (C-mol\ of\ methane\ at\ the\ outlet)}{(C-mol\ of\ methane\ at\ the\ inlet)}$$

$$\text{(Product yields [\%])} = 100 \times \frac{(C - mol\ of\ product\ at\ the\ outlet)}{(C - mol\ of\ methane\ at\ the\ inlet)}$$

The amount of coke deposition on the spent catalysts was measured by Thermo Gravimetry Analyzer (TGA). The weight losses from 573 to 1073 K were assigned to the combustion of the deposited coke.

2. Supplementary tables and figures

Table S1 Si/Al, Si/Mo and Si/Cr ratios determined by EDX analysis

	Si/Al	**Si/Mo**	**Si/Cr**
ZSM-5	9.94	-	-
Cr0.5/ZSM-5	10.37	-	164.44
Cr1.0/ZSM-5	11.19	-	89.83
Cr3.0/ZSM-5	10.53	-	38.84
Mo/ZSM-5	9.94	5.34	-
Mo/Cr0.5/ZSM-5	10.18	6.54	199.62
Mo/Cr1.0/ZSM-5	9.87	7.17	127.34
Mo/Cr3.0/ZSM-5	9.43	6.53	47.20

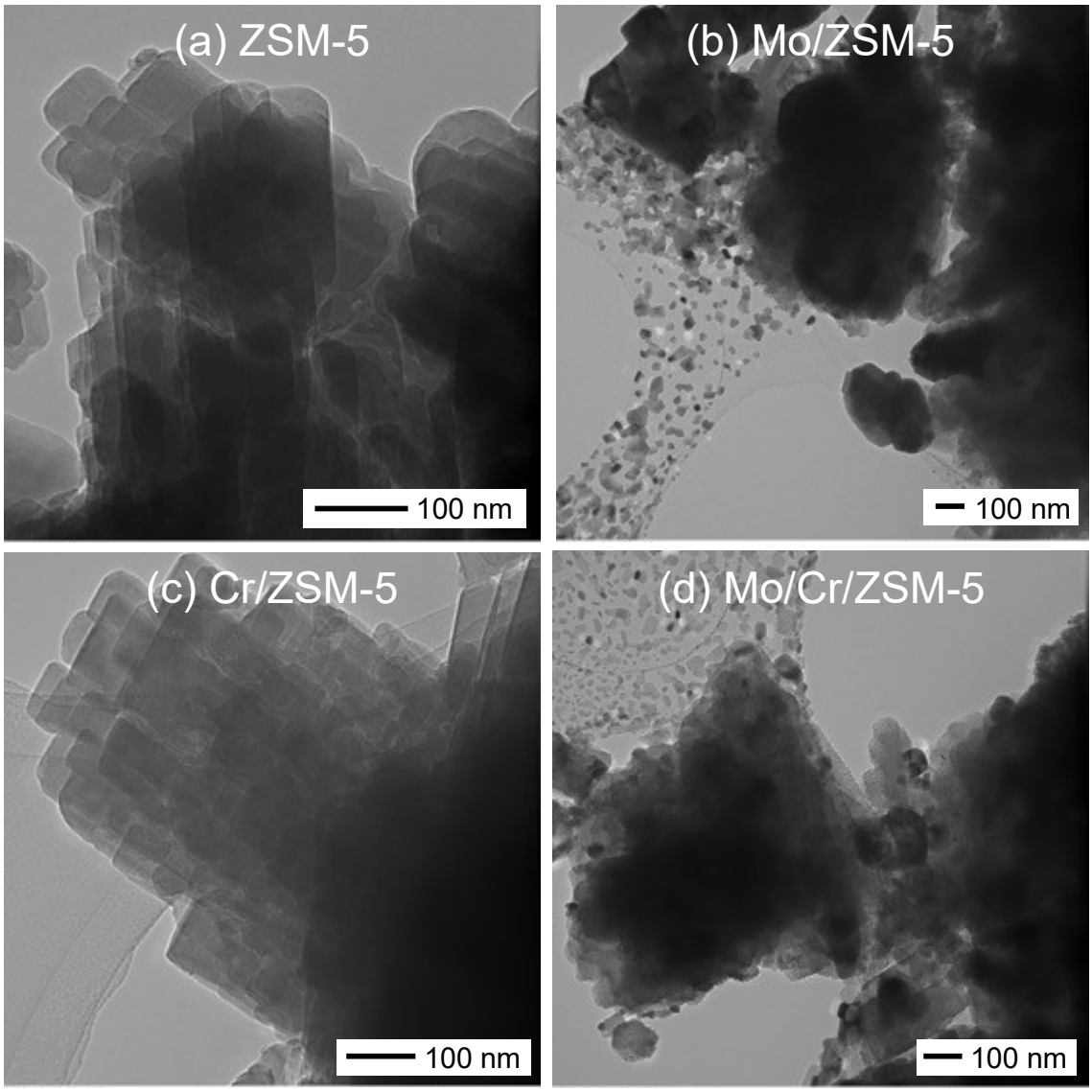

Fig. S1 (a) ZSM-5, (b) Mo/ZSM-5, (c) Cr/ZSM-5 and (d) Mo/Cr/ZSM-5.

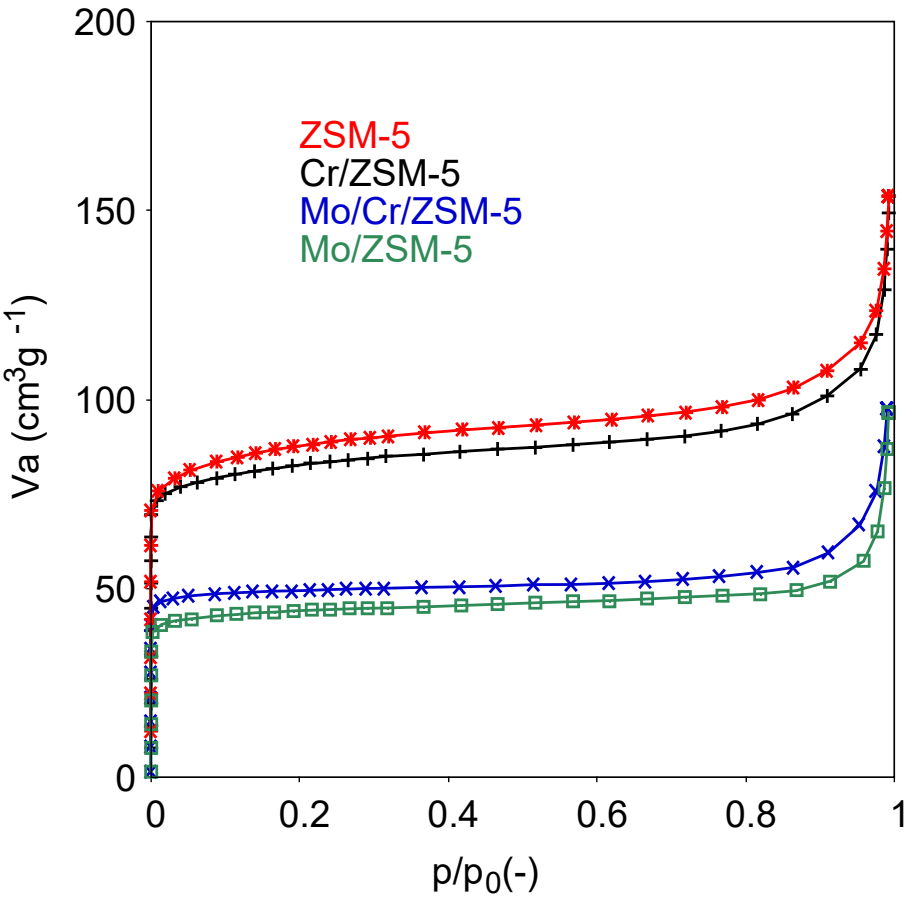

Fig. S2 N_2 adsorption isotherms of ZSM-5, Cr/ZSM-5, Mo/Cr/ZSM-5 and Mo/ZSM-5.

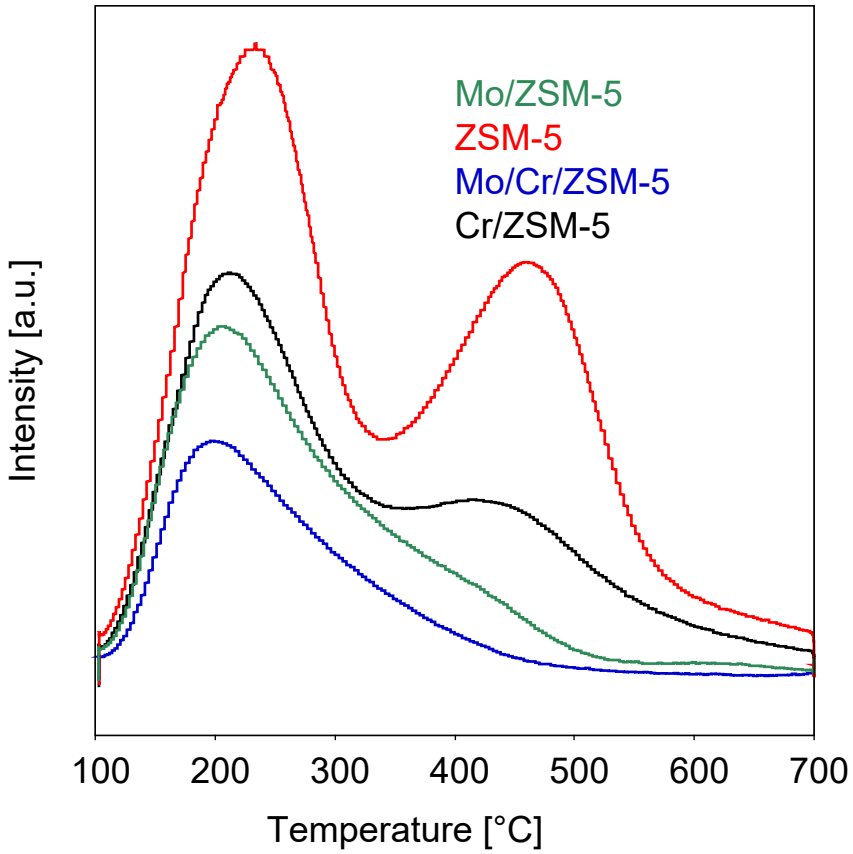

Fig. S3 NH_3-TPD profiles of ZSM-5, Cr/ZSM-5, Mo/Cr/ZSM-5 and Mo/ZSM-5.

Table S2 Conversion and yields during MDA reaction over Mo/ZSM-5.

Time on stream [min]	Methane Conversion [C-mol%]	Yield [C-mol%]			
		Ethane	Ethylene	Benzene	Toluene
60	1.19	0.02	0.38	0.81	0
120	1.51	0	0.34	0.52	0
180	1.40	0	0.32	0.37	0
240	1.01	0	0.27	0.27	0
300	0.71	0	0.25	0.25	0

Table S3 Conversion and yields during MDA over Mo/Cr1.0/ZSM-5.

Time on stream [min]	Methane Conversion [C-mol%]	Yield [C-mol%]			
		Ethane	Ethylene	Benzene	Toluene
60	2.43	0.20	0.35	2.66	0.15
120	1.80	0.12	0.46	1.81	0
180	3.47	0.07	0.49	1.31	0
240	2.35	0.06	0.53	1.17	0
300	2.46	0.05	0.54	1.01	0

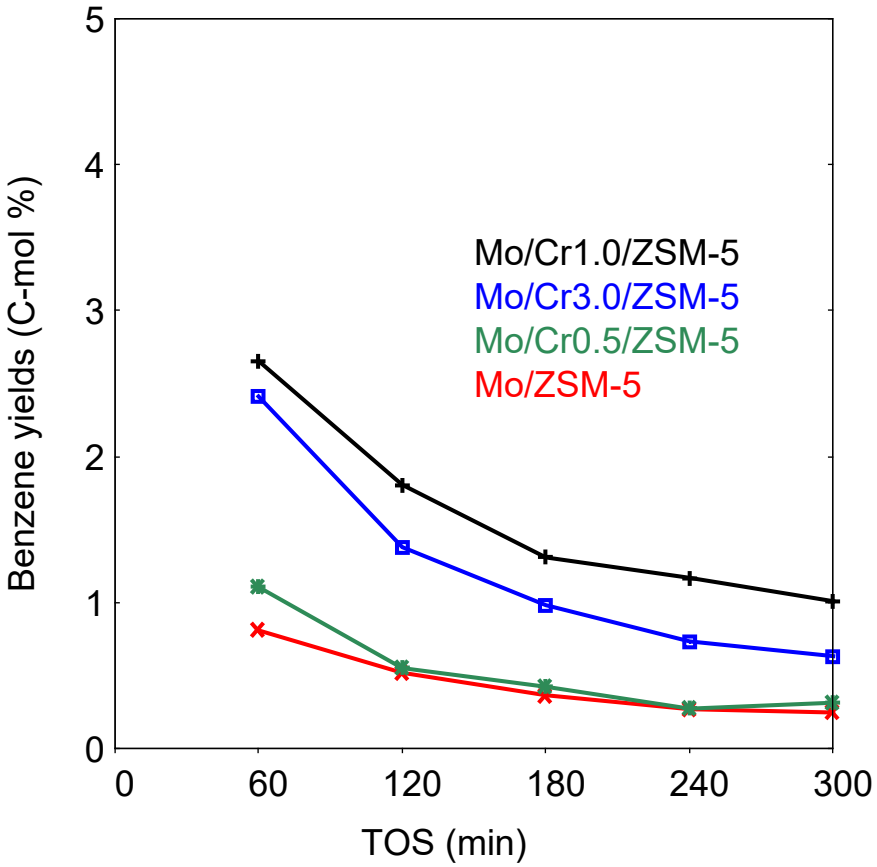

Fig. S4 Time courses of benzene yield over Mo/Cr(x)/ZSM-5 and Mo/ZSM-5.

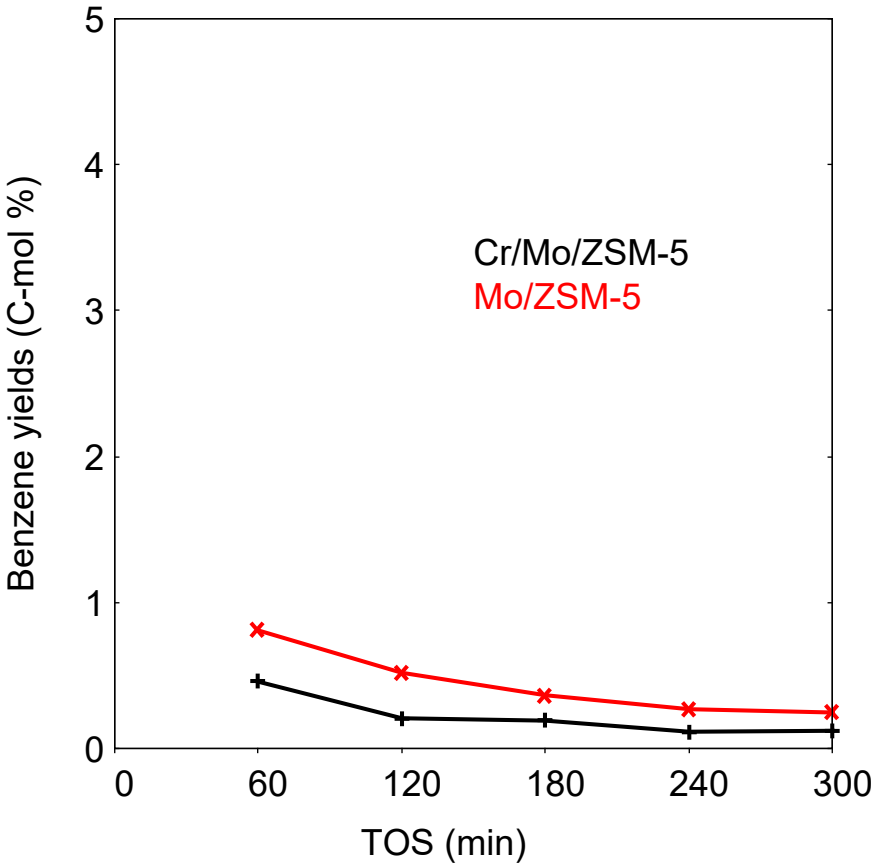

Fig. S5 Time courses of benzene yield over Cr/Mo/ZSM-5 and Mo/ZSM-5.