Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
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Supplementary Information

High coke deposition resistance by Cr loading on zeolite defects: reduced regeneration in cracking reactions

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Contents

1. Experimental Part

1.1 Catalyst preparation

Chromium(III) acetate (Wako FUJIFILM) and H^+ type Beta zeolite (TOSOH) were used as received. The Cr/Beta(x) was prepared by incipient wetness impregnation of commercial Beta with an aqueous solution of Chromium(III) acetate at mass ratio of Cr/Beta = x/100 (x = 0.1, 0.5, 1, 5, and 10). Afterward, the sample was dried at 363 K and calcined under air at 823 K for 2 h. Cr/ZSM-5(1) was prepared through a similar procedure using commercial ZSM-5 (TOSOH, Si/Al = 12).

Two types of physical mixtures were prepared: (1) a mixture of Cr(VI) oxide (Wako FUJIFILM) and H^+ type Beta zeolite (TOSOH) and (2) a mixture of CrOx, synthesized by the calcination of Cr acetate, and H^+ type Beta zeolite (TOSOH)

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-Kα radiation. The morphology of the samples was observed by transmission electron microscopy (TEM). The energy dispersive X-ray spectroscopy for the determination of the Cr contents was performed on a JEOL JCM-7000. To obtain physical information of the samples, N_2 adsorption measurements at 77 K were conducted using BELSORP-Max (MicrotracBel). Before N_2 adsorption measurements, the samples were heated at 523 K under vacuum. The diffuse reflectance ultraviolet-visible (UV-vis) spectra of the samples were recorded on a JASCO V-770 spectrophotometer. X-ray photoelectron (XP) spectroscopy was performed on a KRATOS ULTRA2 (SHIMADZU). Fourier transform infrared (FT-IR) spectra of the samples were acquired using an TGS detector using an average of 128 scans at 4 cm^{-1} resolutions in the 4000–400 cm^{-1} range to investigate the detailed chemical states of Cr species and silanol groups. The ^{29}Si CP MAS NMR spectrum was recorded at ambient temperature using 4.0 mm diameter zirconia rotors spinning at 14 kHz on an ECA-500 NMR (JEOL Ltd.). FT-IR spectra of the pyridine-adsorbed samples were acquired using an MCT detector using an average of 128 scans at 4 cm^{-1} resolutions in the 4000–400 cm^{-1} range. Before IR spectroscopy, pyridine was adsorbed and purged by He at 373 K for 15 min to remove excess pyridine.

1.3 Polyethylene catalytic cracking

The catalytic effect of the obtained samples on LDPE decomposition was evaluated using thermogravimetry (TG). The LDPE/catalyst mixtures or pure LDPE were placed in an alumina pan for thermogravimetric analysis. The mass ratio of the catalyst/LDPE mixtures was fixed at 20/80. The mixtures were heated to 873 K with a heating rate of 5 K min^{-1} under an N_2 atmosphere. The amount of deposited coke of each catalyst after LDPE cracking was measured by using TG with a heating rate of 5 K min^{-1} under air. The weight losses from 623 to 873 K were assigned to

the combustion of the deposited coke. The percentage of the deposited coke was the ratio of the mass of coke to the mass of zeolite. The products were investigated using a BEL CAT II and BEL mass analyzer (MicrotracBEL).

2. Supplementary tables and figures

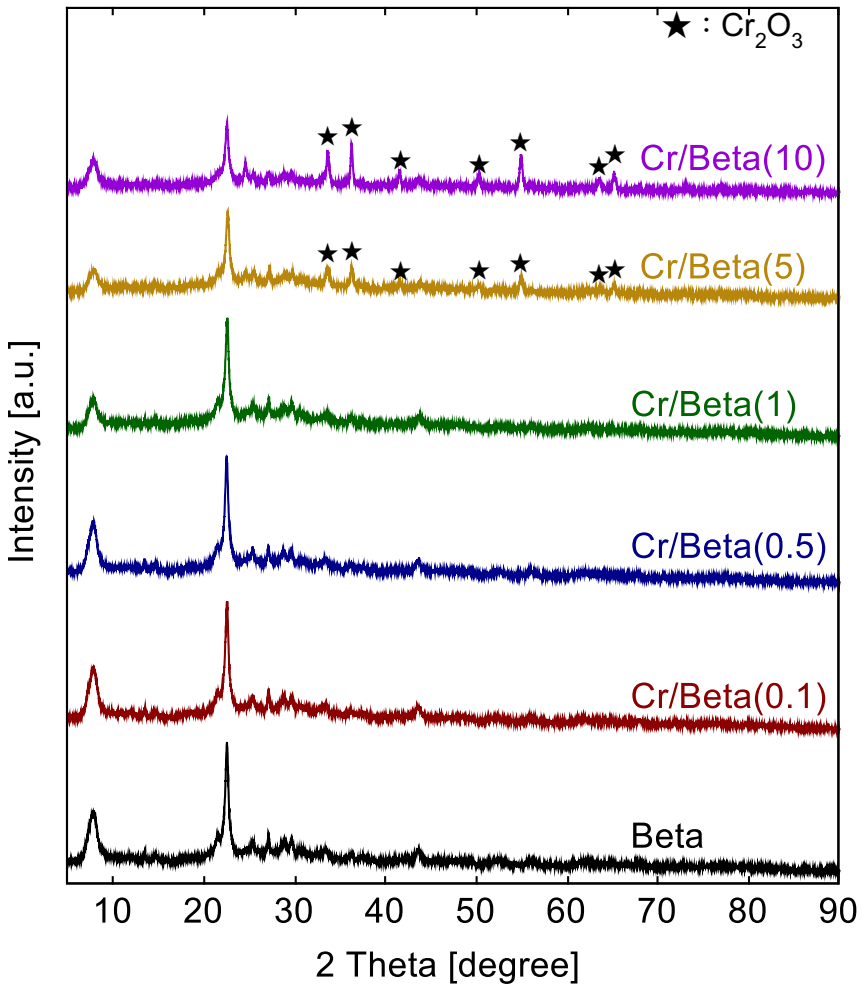

Fig. S1 XRD patterns of Beta and Cr/Beta.

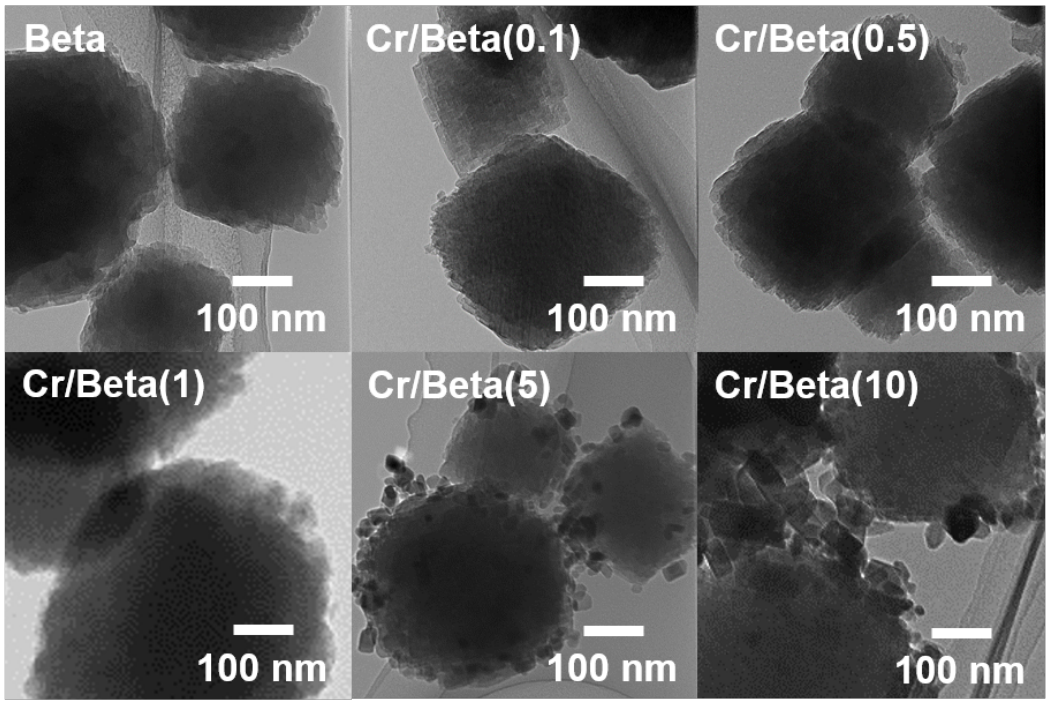

Fig. S2 TEM images of Beta and Cr/Beta.

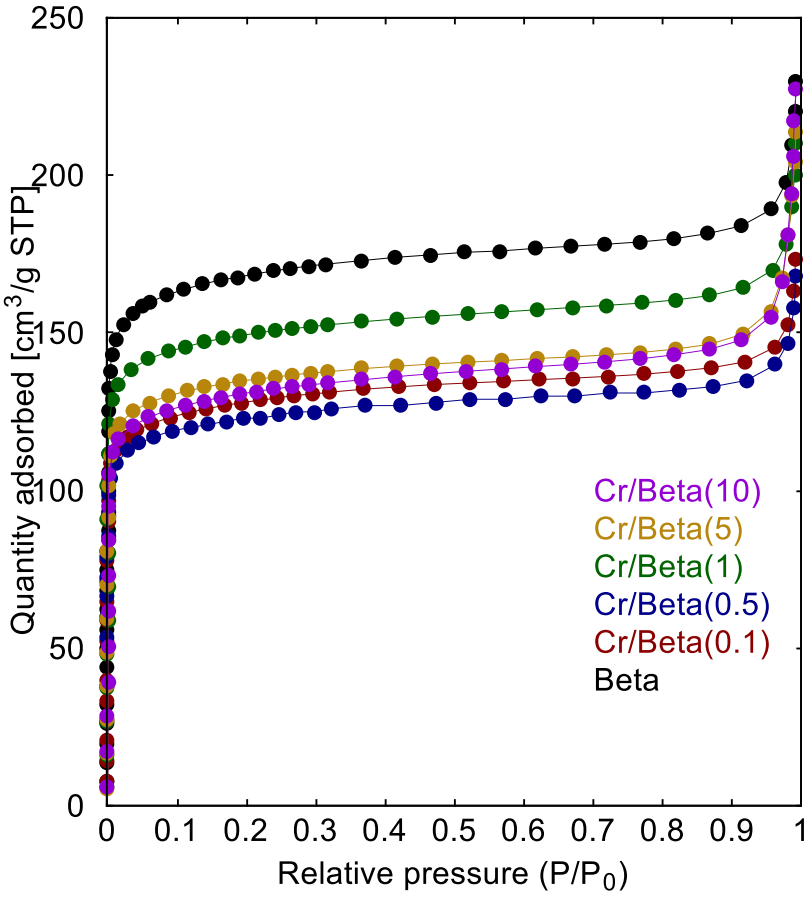

Fig. S3 Nitrogen adsorption isotherms of Beta and Cr/Beta.

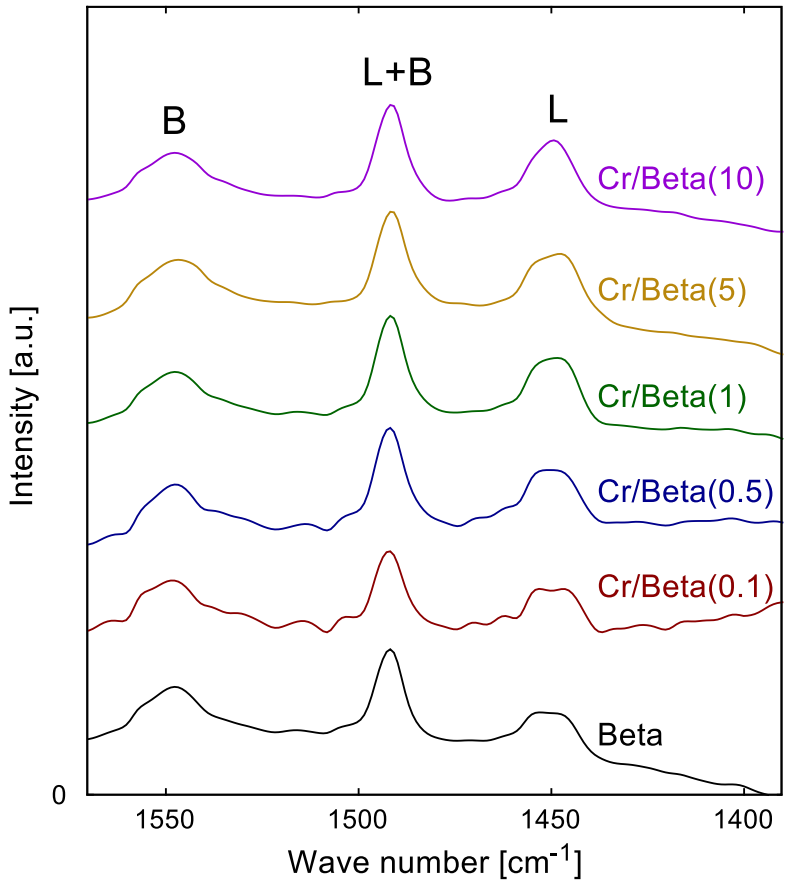

Fig. S4 FT-IR spectra of pyridine adsorbed on Beta and Cr/Beta.

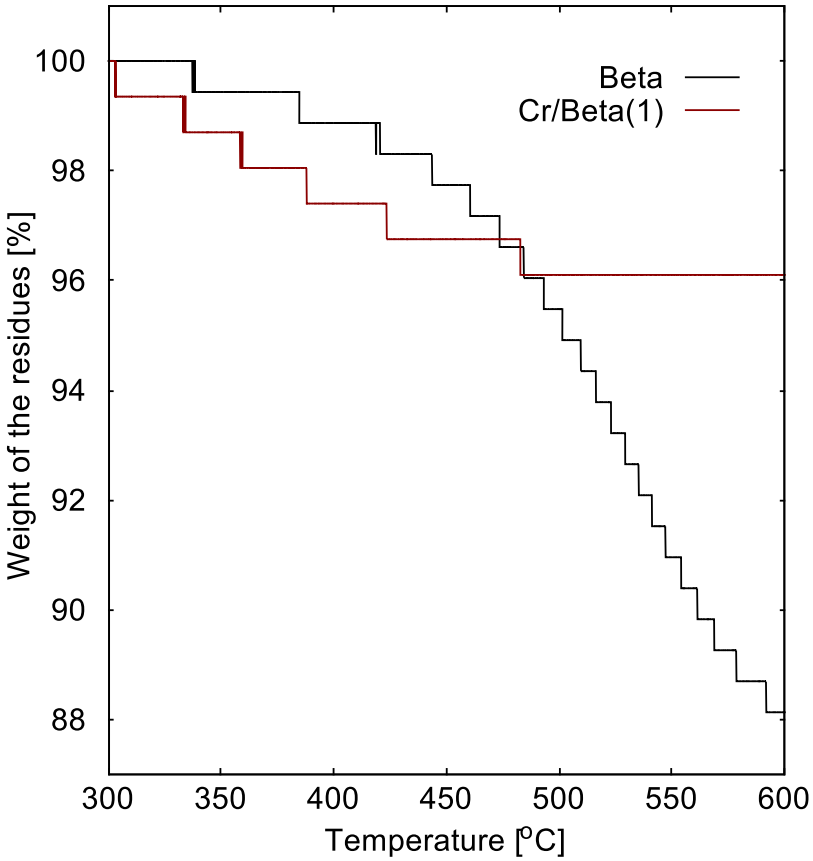

Fig. S5 TG analysis during the coke combustion with air.

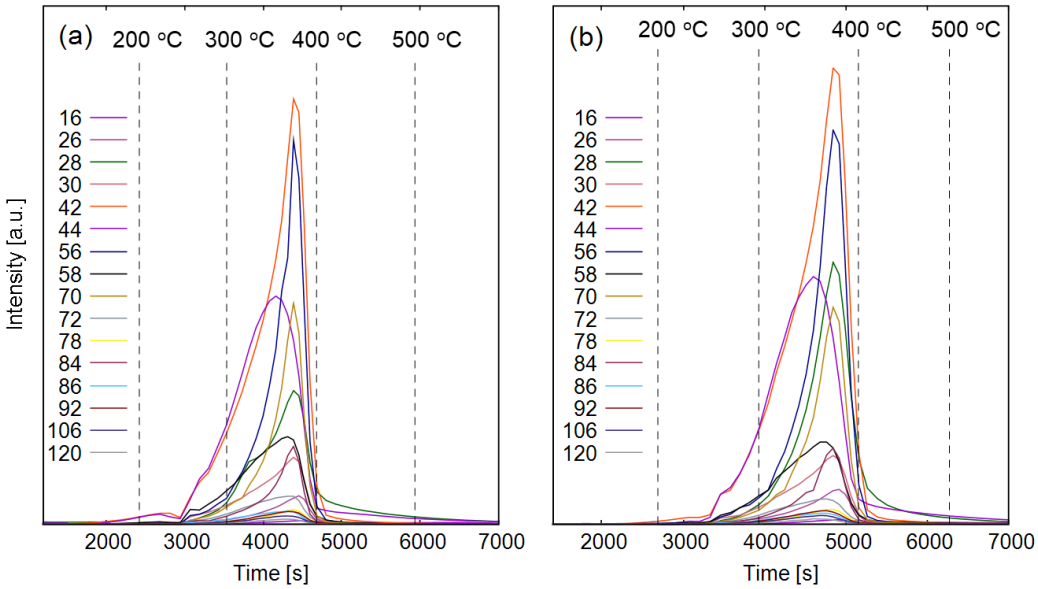

Fig. S6 Mass spectra obtained for (a) Beta and (b) Cr/Beta(1) after catalytic cracking.

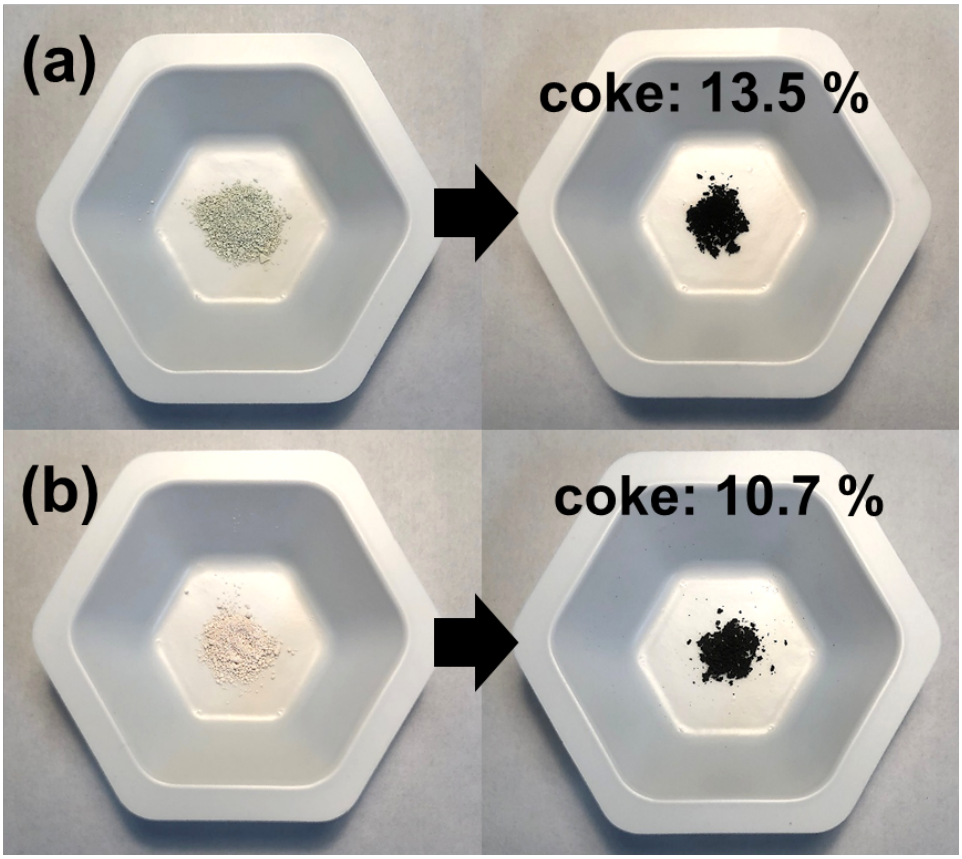

Fig. S7 Changes in the colors of a (a) physical mixture of CrOx, synthesized by the calcination of Cr acetate, and commercial Beta and (b) physical mixture of commercial Cr^{6+} oxide and commercial Beta.

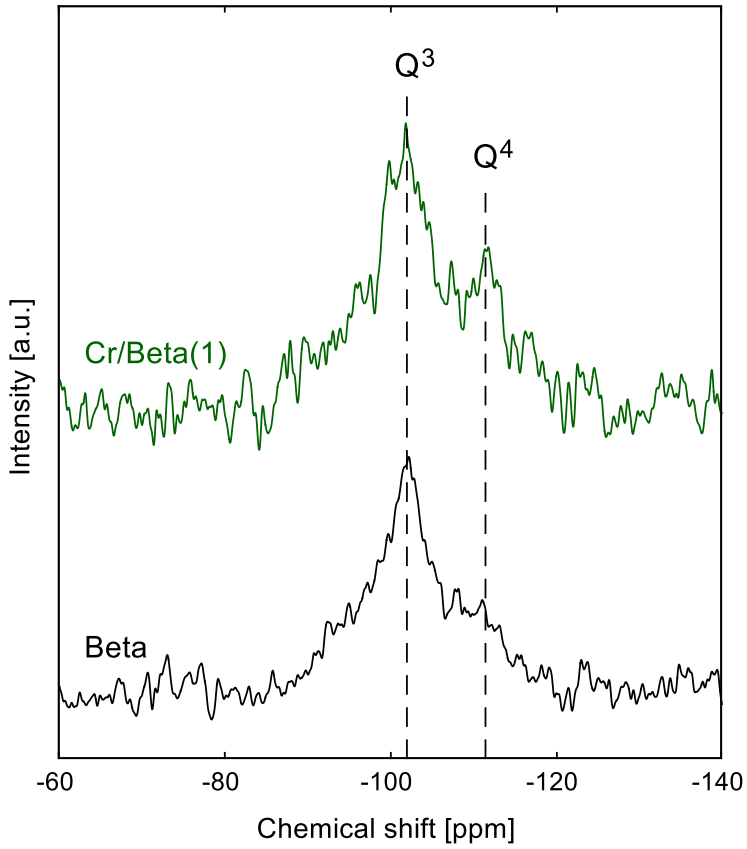

Fig. S8 ^{29}Si CP MAS spectra of Beta and Cr/Beta(1).

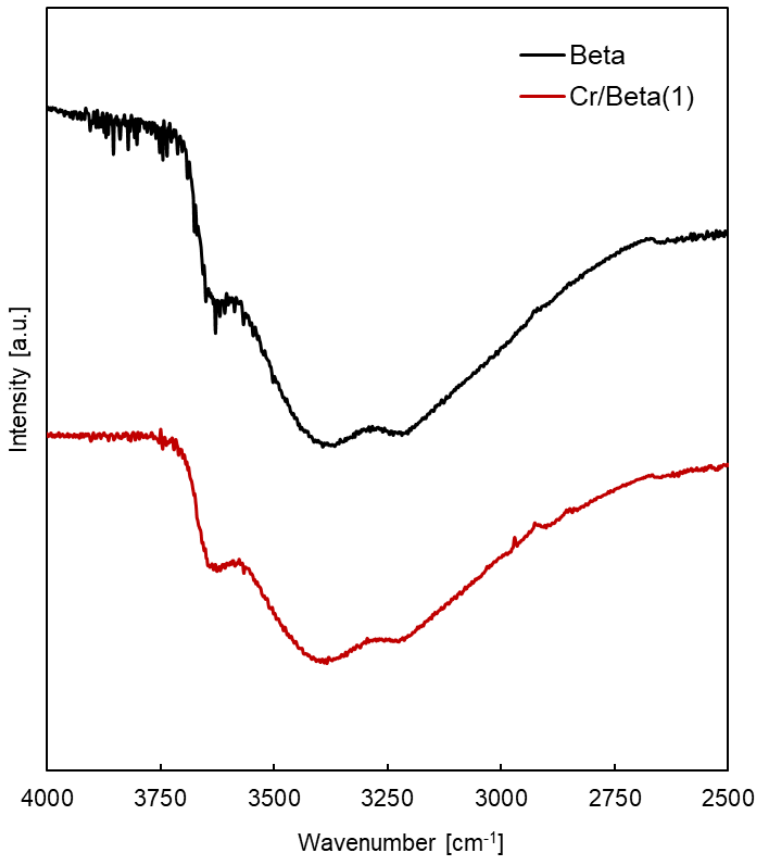

Fig. S9 FT-IR spectra in the hydroxyl region of Cr Beta and Cr/Beta.

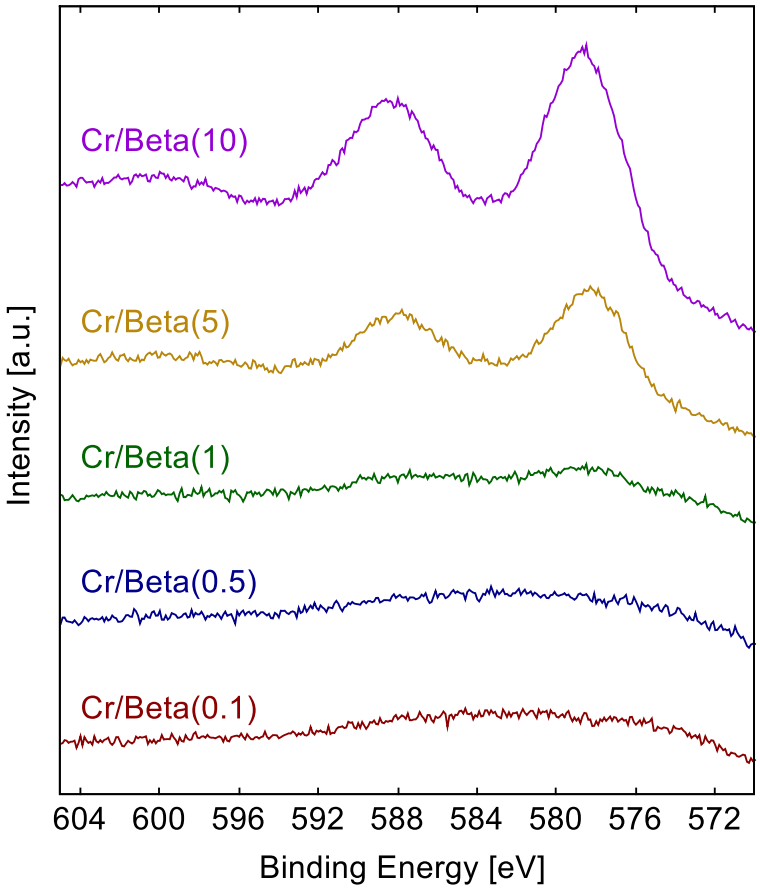

Fig. S10 Cr 2p XP spectra of Cr/Beta.

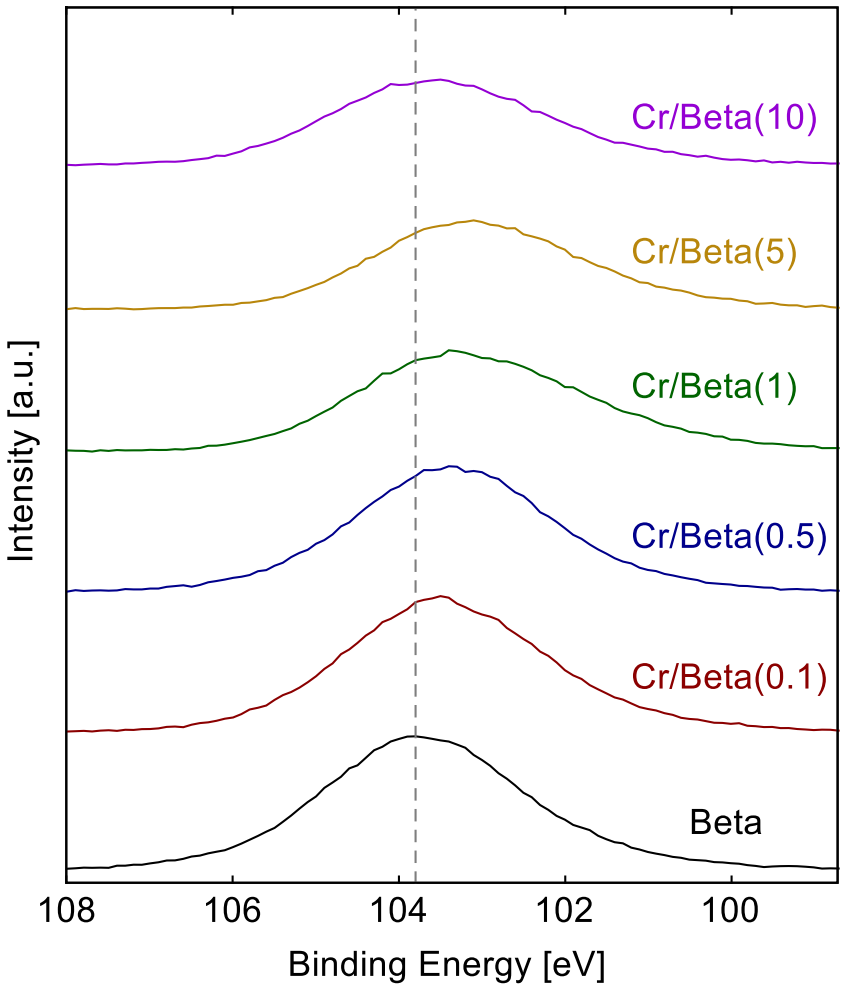

Fig. S11 Si 2p XP spectra of Beta and Cr/Beta.

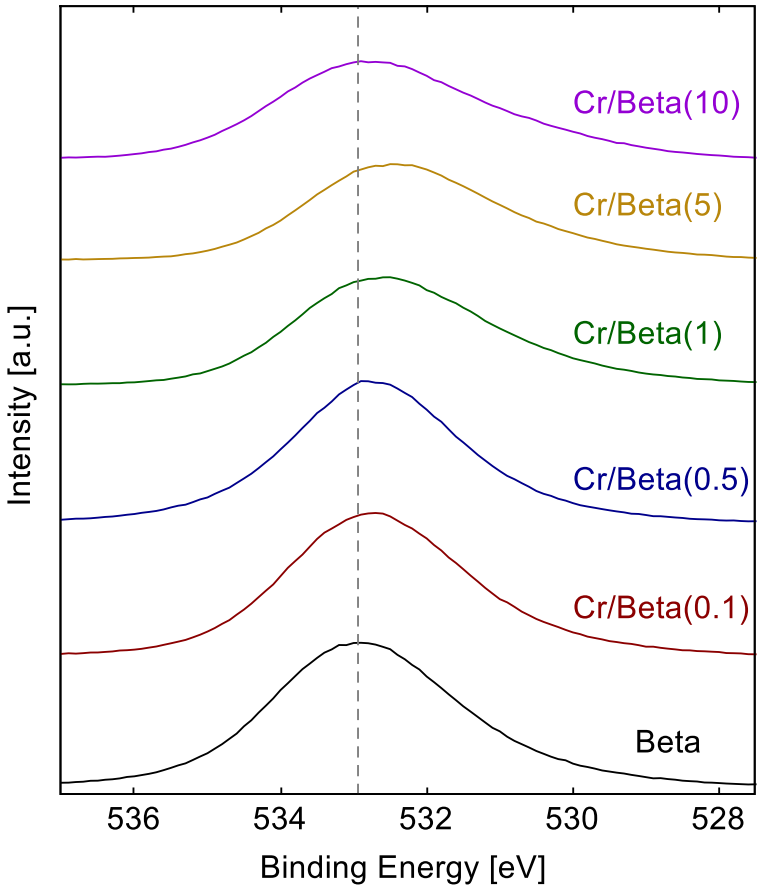

Fig. S12 O1s XP spectra of Beta and Cr/Beta.

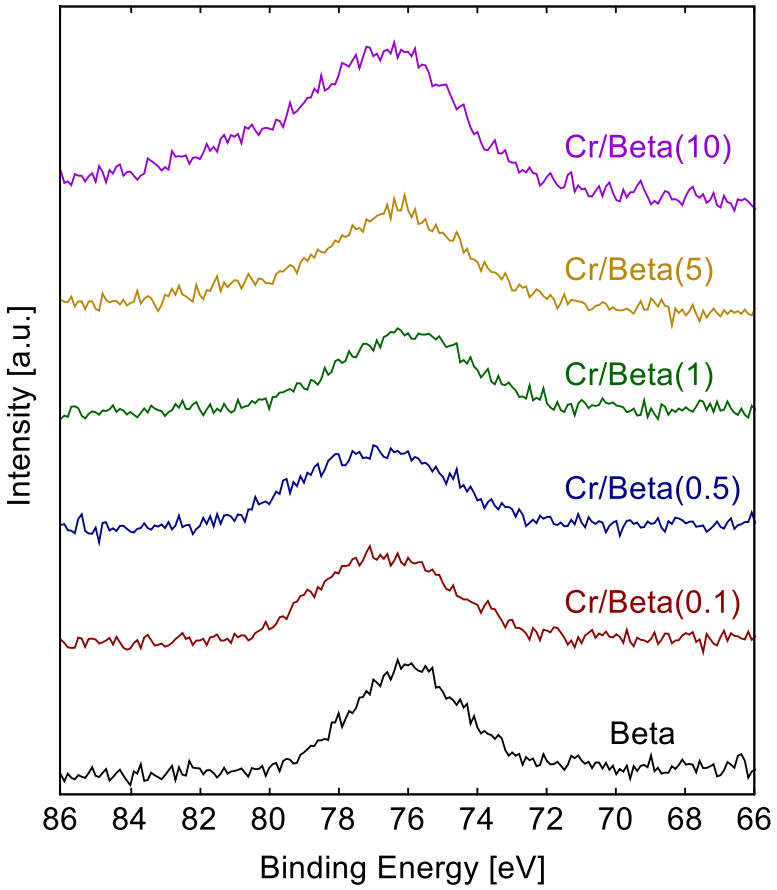

Fig. S13 Al 2p XP spectra of Beta and Cr/Beta.

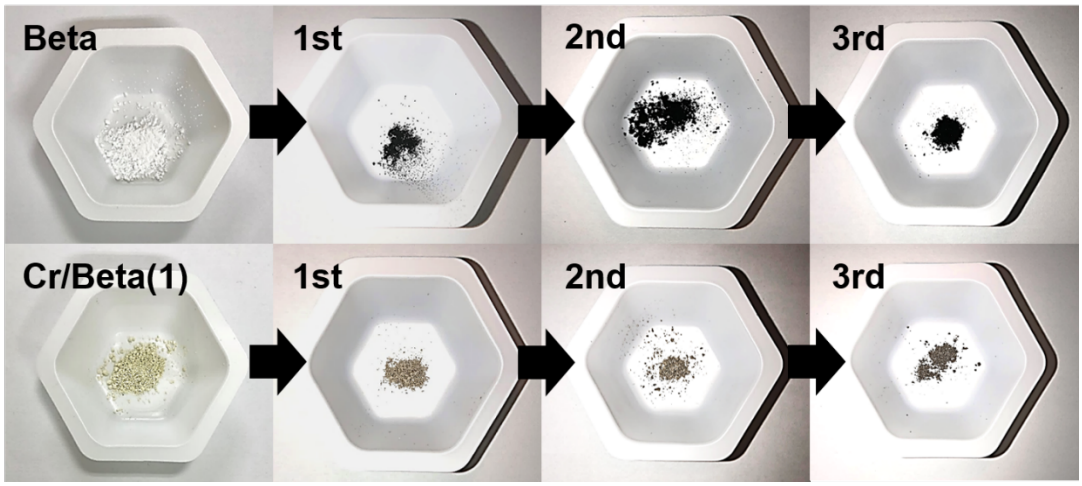

Fig. S14 Changes in the colors of Beta and Cr/Beta(1) after repeated cycles of LDPE cracking.

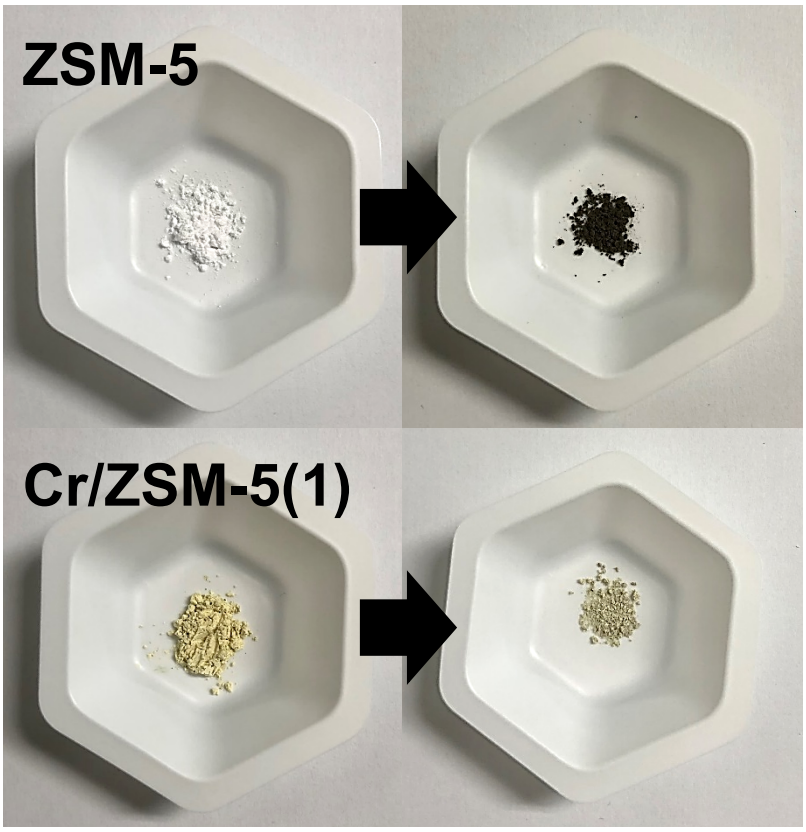

Fig. S15 Changes in the colors of ZSM-5 and Cr/ZSM-5(1) before and after LDPE cracking.

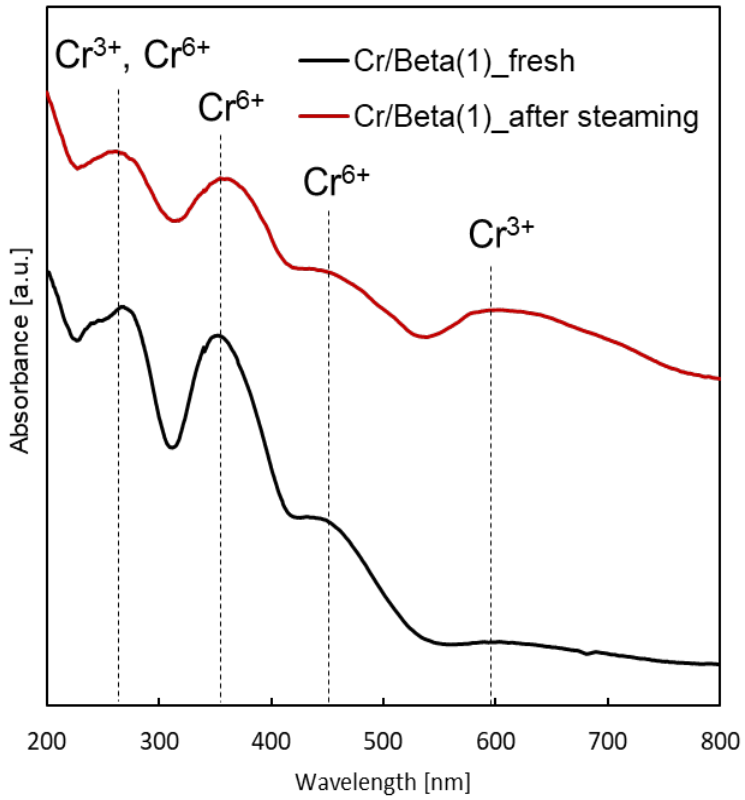

Fig. S16 UV-vis spectra of Cr/Beta(1) before and after steaming.

Table S1 Physicochemical properties of Beta and Cr/Beta samples

	Cr [wt%]	Si/Al	S_{BET} [m^2/g]	S_{ext} [m^2/g]	S_{micro} [m^2/g]	V_{micro} [cm^3/g]
Beta	-	12.24	849.7	18.82	830.85	0.259
Cr/Beta(0.1)	0.07	12.34	645.1	13.70	631.38	0.199
Cr/Beta(0.5)	0.47	12.22	621.4	13.28	608.1	0.190
Cr/Beta(1)	0.97	12.14	758.4	17.42	740.96	0.230
Cr/Beta(5)	4.71	12.13	682.4	17.94	664.49	0.206
Cr/Beta(10)	8.61	12.18	656.4	18.74	637.64	0.201