Supporting information for "Catalytic effect of SUS316 reactor surface on hydrolysis of benzamide in sub- and supercritical water"

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Details of experimental procedure.

Materials of experimental set-up. As the reactors, coil tubes made of SUS316 were used. Details of the reactor coils are summarized in following Table S1. For the mixing of distilled water and benzamide aqueous solution, low dead volume tee made of SUS 316 having 0.3 mm inner diameter (SS-1F0-3GC, Swagelok Co., USA) was used to obtain rapid mixing.

Table S1. Details of the reactor coils.

Inner diameter [mm]	S/V ratio [mm^{-1}]	Thickness [mm]	Length [m]
0.25	16	0.67	20
0.50	8.0	0.54	6.0, 10
1.00	4.0	0.29 or 0.50	4.0, 10
2.17	1.8	0.50	3.0, 6.0

Pressure control. The pressure was controlled using a back pressure regulator (26-1761; TESCOM Co., USA or SCF-Bpg; JASCO Co., Japan) so that the pressure at right before the back pressure regulator (P1 in Figure 1) became desired value (25.0, 35.0, 45.0, and 65.0 MPa).

Temperature control. The temperature at the entrance of the reactor (T1 in Figure 1) was kept 400 °C by changing the oven temperature which heats the preheat line. The oven temperature which heats the reactor was set to 400 °C in order to keep the reaction temperature. In addition, it can be considered that temperature changes caused by the heat of hydrolysis reaction are neglected because the concentration of amide is small and the heat capacity of supercritical water is large.

Reaction conditions. Reaction conditions are summarized in following Table S2. The volume ratio of the aqueous solution of benzamide (4.13×10^{-2} mol/dm^3 in the ambient condition) to the distilled water was 1:9. Residence times were controlled both by changing the reactor length and by changing the flow rate. The Reynolds numbers (*Re*) of some reaction conditions are below 2.1×10^3 (laminar flow) and that of some other reaction conditions are above 4.0×10^3 (turbulent flow), which indicates that our experiments were conducted both in the laminar and turbulent flow conditions. The difference in the flow condition did not likely to affect the reaction rates in our experiments because the reaction conducted in different flow rates showed same benzamide conversion at the same residence time (Figure S1). The Peclet numbers (*Pe*), which indicates the ratio of transport rate by

flow to transport rate by diffusion, were large for all reaction conditions, and it suggests that the reactors can be regarded as plug-flow reactors.

Table S2. Reaction conditions.

Pressure [MPa]	*S*/*V* ratio [mm^{-1}]	Concentration [mol/m^3]	Residence time [s]	*Re* [10^3]	*Pe* [-]
25	1.8	0.687	37.1-446	0.17-2.0	4.2×10^5-5.0×10^6
	4.0		10.5-130	0.44-2.2	2.6×10^6-2.0×10^7
	8.0		3.27-39.2	0.73-8.8	7.9×10^6-1.6×10^8
	16		9.81-49.0	0.58-2.9	4.2×10^7-2.1×10^8
35	1.8	1.96	31.8-211	0.52-1.7	1.3×10^6-7.1×10^6
	4.0		8.95-89.5	0.38-3.8	2.6×10^6-2.6×10^7
	8.0		5.60-67.1	0.38-7.6	7.9×10^6-2.6×10^8
	16		9.33-56.0	0.76-4.6	1.1×10^8-6.3×10^8
45	4.0	2.29	43.5-261	0.33-2.0	6.6×10^6-3.9×10^7
	8.0		6.53-78.4	0.33-3.9	7.9×10^6-1.6×10^8
	16		10.9-65.3	0.65-3.9	1.1×10^8-6.3×10^8
65	4.0	2.58	49.2-295	0.28-1.7	6.6×10^6-3.9×10^7
	8.0		7.38-88.5	0.28-3.4	7.9×10^6-1.6×10^8
	16		12.3-73.8	0.57-3.4	1.1×10^8-6.3×10^8

Details of HPLC and IC analysis

Organics in the effluents were analyzed using high-performance liquid chromatography-ultraviolet (HPLC-UV) analysis (LC-980; JASCO Co., Japan) with a packed column (Finepak SIL C18S; JASCO Co., Japan). As the mobile phase solvent, mixture of acetonitrile and a buffer solution of phosphoric acid (4:1 in volume) were used. The buffer solution contains 9.4 mmol/dm^3 of phosphoric acid and 50 mmol/dm^3 of potassium dihydrogenphosphate. The flow rate was 0.90 ml/min and the detector wavelength was 225 nm. A chromatogram is shown in the following Figure S1 (a) as an example.

Ammonia in the effluents was quantified using ion chromatography (IC). The same HPLC system with a packed column (Y-521; Showa Denko K. K., Japan) was used for separation, and ammonium ion was detected using ion conductivity detector (CDD-6A; Shimadzu Corp., Japan). The mobile phase solvent was 4 mmol/dm^3 of nitric acid aqueous solution, and the flow rate was 1.2 ml/min. A chromatogram is shown in the following Figure S1 (b) as an example.

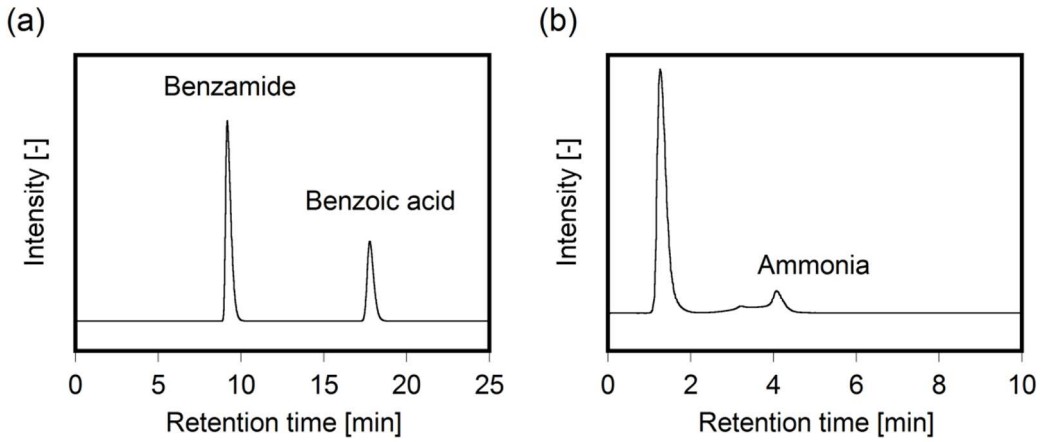

Figure S1. HPLC and IC chromatogram (400 °C, 35 MPa, S/V=8.0 mm^{-1}, t=67.1 s).

(a) HPLC, (b) IC.

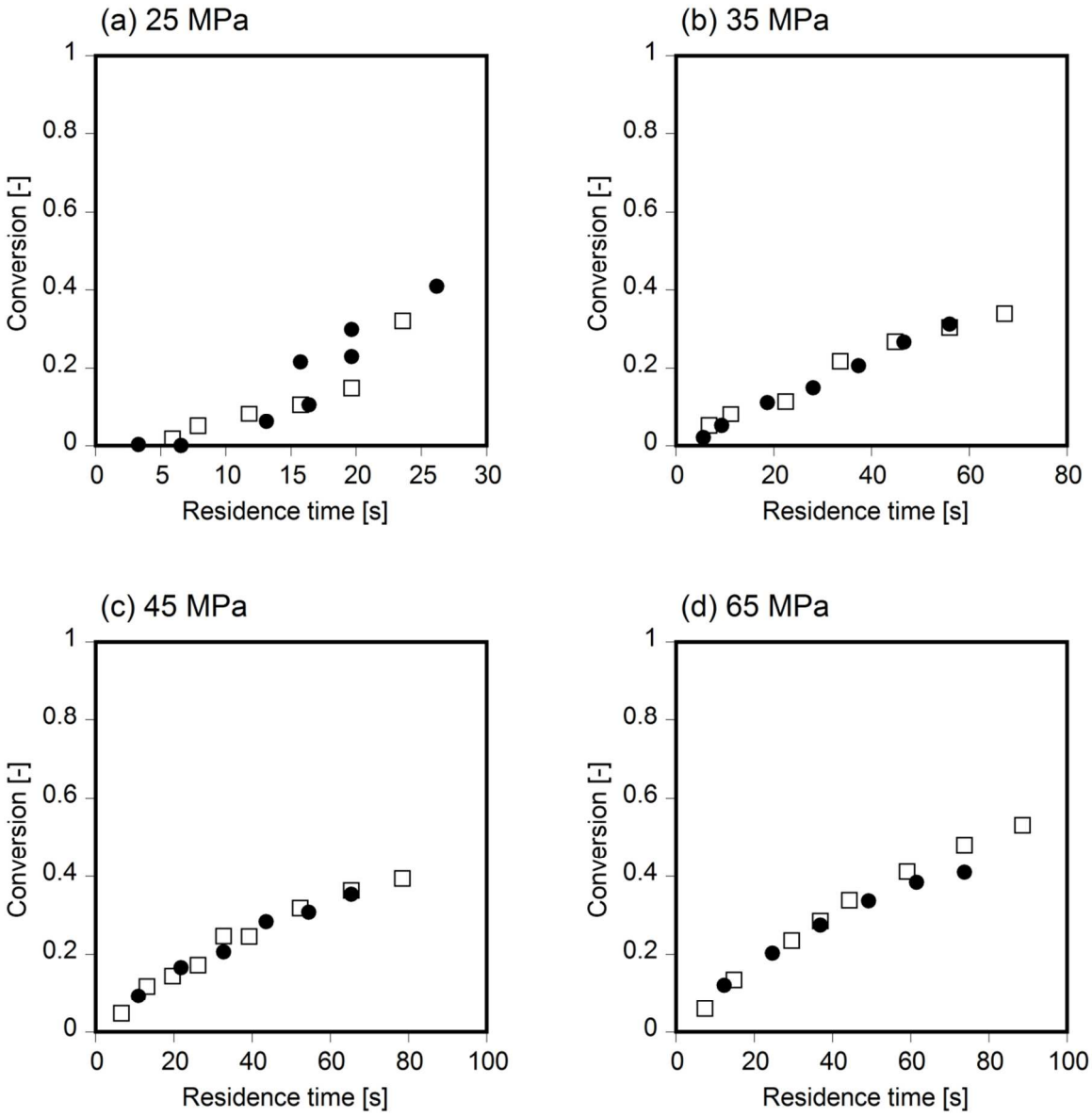

Figure S2. Effect of flow rate on benzamide conversion at 400°C and *S*/*V* ratio = 8.0.

(a) 25 MPa, (b) 35 MPa, (c) 45 MPa, (d) 65 MPa.

Reactor length: (□) 6 m, (●) 10 m.

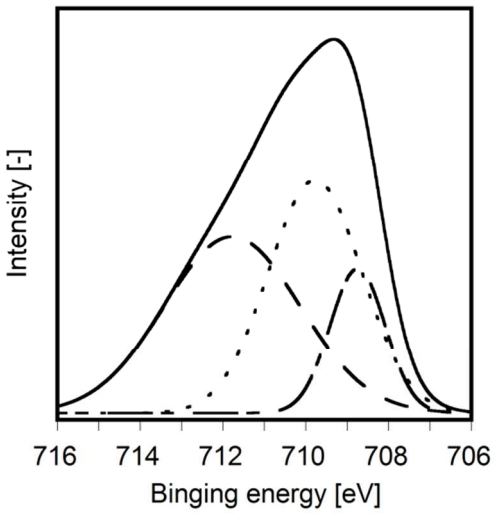

Figure S3. Peak division of XPS spectrum (Fe 2p) after supercritical water treatment. The calculation was conducted using Origin 2016, and the back ground spectrum was determined by Tougard method. (– – –) peak A corresponding to Fe_2O_3, (·····) peak B corresponding to Fe_3O_4 Fe^{3+}, (·–·–) peak C corresponding to Fe_3O_4 Fe^{2+}, (—) total peak. The peak areas for peak A, B, and C are 6.4, 5.8, and 2.1, respectively.

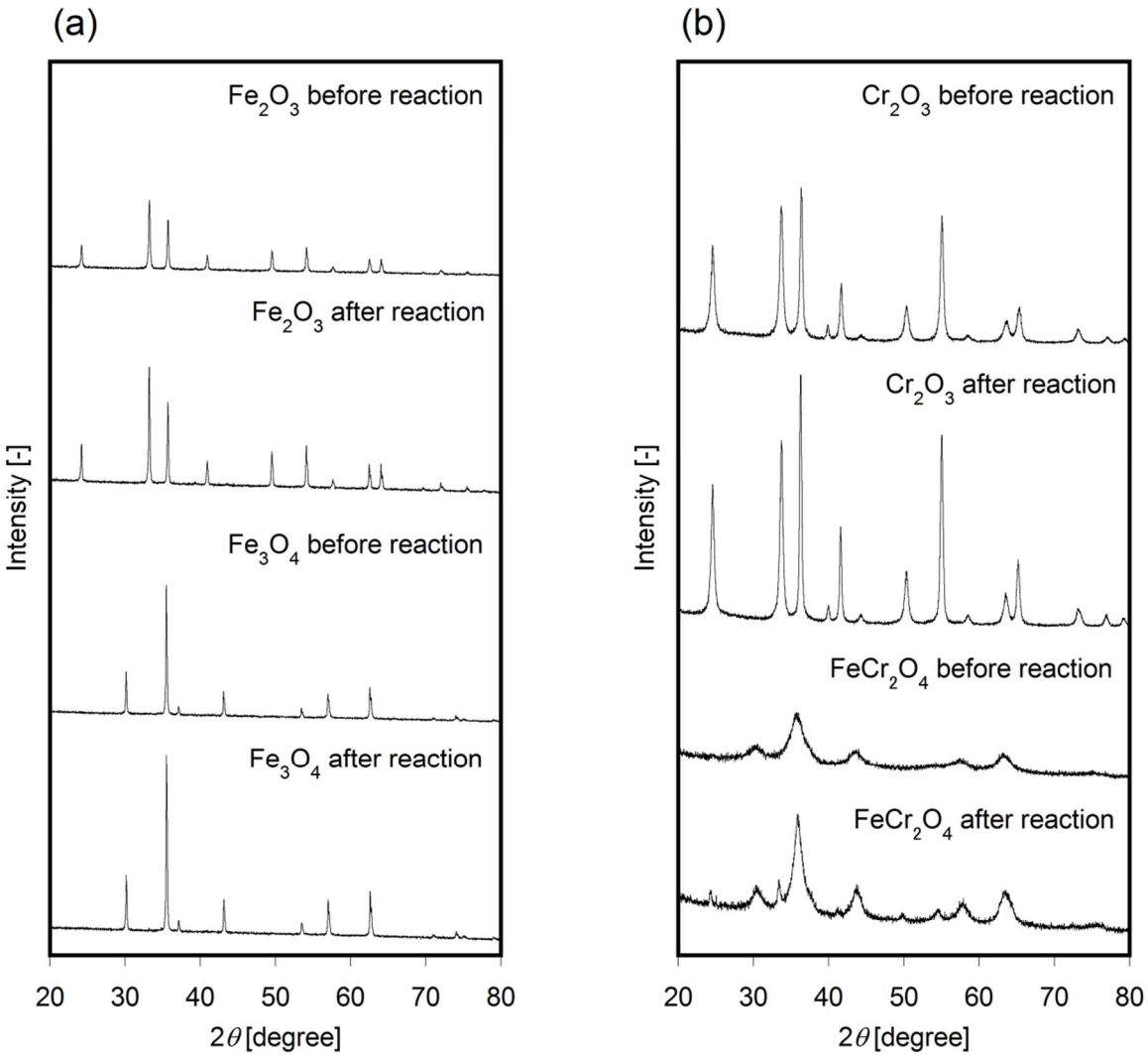

Figure S4. XRD patterns of metal oxide catalysts before and after the reaction.

(a) Fe_2O_3 and Fe_3O_4, (b) Cr_2O_3 and $FeCr_2O_4$.