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

Table S1 Physical properties of hierarchical catalysts.

Catalyst	Solid yields (%)	SiO_2 /Al_2O_3[a]	Al (10^{-4} mol/g)	Relative Crystal. /%[b]	Crystal Size /nm	Cation exchange ratio/%[c]	NH_3–TPD (10^{-4} mol/g)[d]
H-ZSM-5	66	111	3.0	56	40	100	4.1 (2.5)
GSR-10HS-H-ZSM-5	86	139	2.4	100	64	100	3.0 (1.6)
GSR-12HS-H-ZSM-5	92	163	2.0	84	51	100	2.6 (1.5)
GSR-13HS-H-ZSM-5	90	176	1.9	42	58	100	1.7 (1.1)
GSR-14HS-H-ZSM-5	90	173	1.9	0	-	100	1.2 (0.8)

a synthesized ZSM-5 zeolite determined by XRF analysis.
b Relative crystallinity was calculated by a maximum peak intensity as 100%.
c Na was not detected in H type by XRF although Na was detected before ion exchange.
d Total acid sites; Strong acid sites in parenthesis.

Table S2 Amounts of NH_3 adsorbed-desorbed and conversion of catalyst cracking

Catalyst	Amount of NH_3 adsorbed (10^{-4} mol/g)	Amount of NH_3 desorbed (10^{-4} mol/g)		
		Weak acid	Strong acid	Total acid
H-ZSM-5	6.0	1.6	2.5	4.1
GSR-10HS-H-ZSM-5	4.5	1.4	1.6	3.0
GSR-12HS-H-ZSM-5	4.2	1.0	1.5	2.6
GSR-13HS-H-ZSM-5	2.2	0.54	1.1	1.7
GSR-14HS-H-ZSM-5	1.6	0.38	0.83	1.2

Footnote of Table S2

40mg of the samples was packed into a 6mm stainless tube reactor with silica wool, was heated to 600^{o}C by 10^{o}C/min under He 10cc/min flow and was kept for 3h. After the reactor was cooled to 100^{o}C, 1.0 mL/pulse of NH_3 was introduced into the catalyst several times until no more adsorption occurred. In order to obtain the amount of NH_3 adsorbed, the reciprocal number of the peak area in GC-TCD per 1mL of NH_3 (25^{o}C, 1atm) was multiplied by the sum of peak areas corresponding to the amount of NH_3 adsorbed. NH_3 desorption was observed for the catalyst adsorbed by NH_3 when temperature was raised to 650^{o}C by 10^{o}C/min after adsorption measurement. Similarly the amount of NH_3 desorbed was calculated using the total peak area of NH_3 desorbed. Ammonia gas was detected in the outlet of the reactor by GC-TCD (GC-8A, Shimadzu Co. Ltd.). GC measurement conditions are as follows: INJ/DET 170^{o}C, COL 140^{o}C, ATTN 16, Current 100 mA, column flow rate 50mL/min, carrier gas He.

Table S3 Pore properties of each sample obtained by nitrogen adsorption-desorption measurement

Catalyst	BET Surface Area (m^2/g)	t-plot micropore surface area (m^2/g)	t-plot external surface area (m^2/g)	t-plot micropore volume (cm^3/g)	Total Pore volume (cm^3/g)	Average Pore diameter (nm)	BJH Surface area (m^2/g)	BJH Pore volume (cm^3/g)	BJH Pore diameter (nm)
H-ZSM-5	467	466	1.6	0.22	0.23	2.01	36	0.043	3.7
GSR-10HS-H-ZSM-5	429	421	2.8	0.19	0.21	1.94	11	0.029	3.7
GSR-12HS-H-ZSM-5	371	345	27	0.14	0.25	2.69	9.4	0.093	22
GSR-13HS-H-ZSM-5	277	180	98	0.048	0.87	12.6	72	0.77	16(42)
GSR-14HS-H-ZSM-5	175	57	115	0.019	1.68	38.3	170	1.70	39

Prior to the experiment, 0.040g of a sample was heated at 350^{o}C in vacuum for 3 h in Belprep II (BEL Japan, Inc.). Then, adsorption and desorption isotherms were obtained at 77K using Belsorp Mini II (BEL Japan, Inc.). Average pore diameter was calculated from values of BET surface area and total pore volume.

Table S4 Pore properties of each sample obtained by nitrogen adsorption-desorption measurement

Catalyst	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore diameter (nm)	BJH Surface area (m^2/g)	BJH Pore volume (cm^3/g)	BJH Pore diameter (nm)
C-ZSM-5	443	0.21	1.92	30.3	0.035	3.72
GSR-10HS-C-ZSM-5	407	0.19	1.91	9.46	0.028	3.72
GSR-12HS-C-ZSM-5	348	0.25	2.87	11.1	0.10	21.5
GSR-13HS-C-ZSM-5	279	0.88	12.6	71.9	0.80	21.5
GSR-14HS-C-ZSM-5	178	1.69	38.1	165	1.72	38.5

Prior to the experiment, 0.040g of a sample was heated at 350^{o}C in vacuum for 3 h in Belprep II (BEL Japan, Inc.). Then, adsorption and desorption isotherms were obtained at 77K using Belsorp Mini II (BEL Japan, Inc.). Average pore diameter was calculated from values of BET surface area and total pore volume.

Table S5 Coke yield of used catalysts by TG[a]

Catalyst	200-300℃	300-400℃	400-500℃	500-600℃	計 (mg)	Conv.[b] (%)
H-ZSM-5	0.02	0.02	0.04	0.07	0.15	90(91)
GSR-10HS-H-ZSM-5	0.01	0.02	0.05	0.14	0.22	85(87)
GSR-12HS-H-ZSM-5	0.02	0.01	0.02	0.04	0.09	98(99)
GSR-13HS-H-ZSM-5	0.02	0.01	0.02	0.03	0.08	97(97)
GSR-14HS-H-ZSM-5	0.02	0.02	0.02	0.02	0.08	93(94)

[a] Cat.: 10 mg, Temp.: 600^{o}C, Atmosphere: O_2, Programming rate: 10.0^{o}C/min.
[b] Value in parenthesis is total conversion including coke yield. The decrease in the range 400-600^{o}C was regarded as coke oxidation and was used to estimate the coke yield.

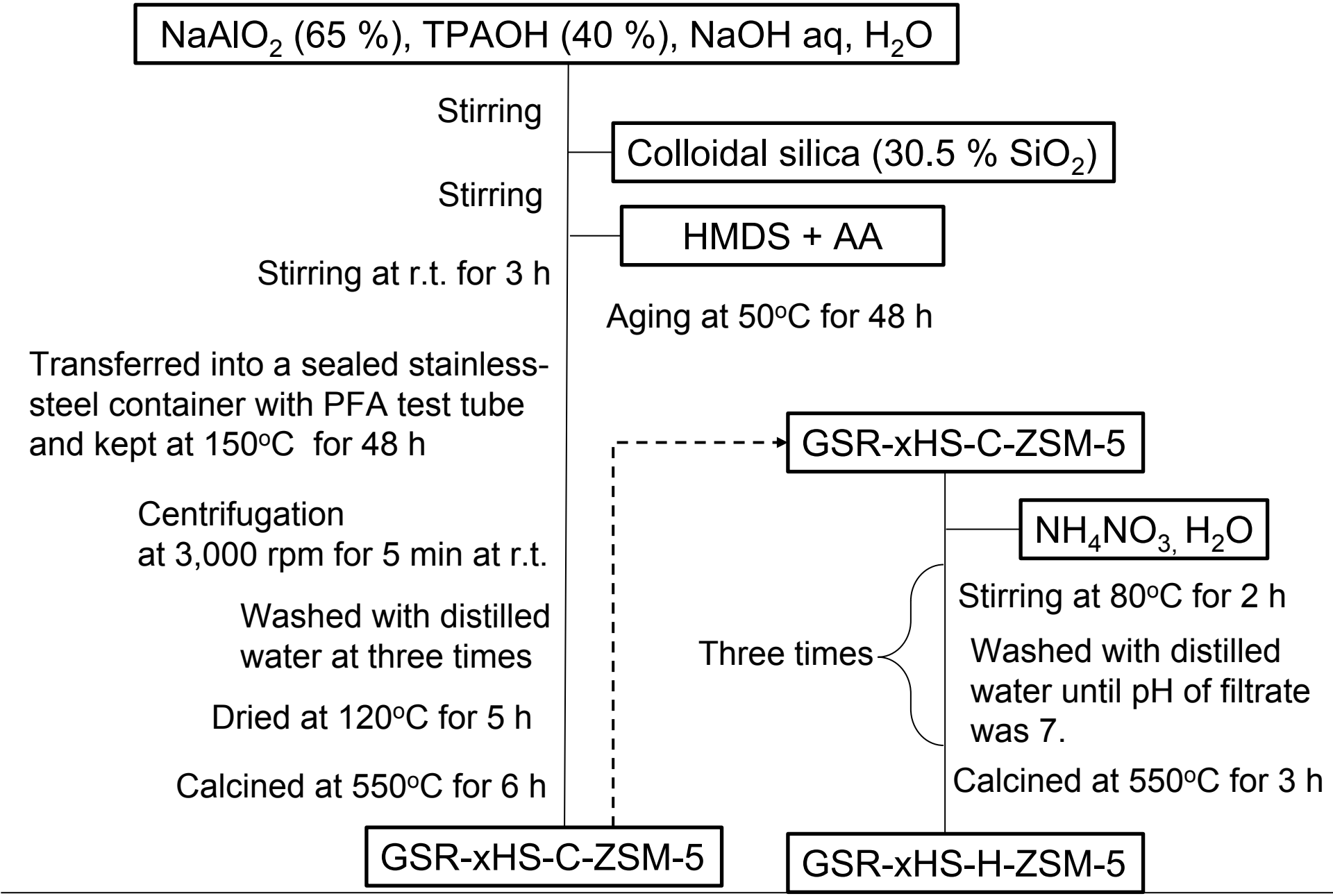


Fig. S1 Flowchart for preparation of GSR-xHS-H-ZSM-5.

In order to make H-ZSM-5, RSC Adv., 2016, 07, 1-8 was referred.

Footnote of Fig. S1

For an example in Fig. S1, the preparation method of GSR-10HS-C-ZSM-5 is introduced as follows: In to 200mL beaker are added $NaAlO_2$ 0.1352 g, TPAOH 2.306 g, NaOH 0.6532 g and H_2O 25.83 g and the mixture was stirred at 25^oC for 30 min. Colloidal silica SiO_2 17.90 g was added dropwise and the mixture was stirred at 25^oC for 3 h. Then after into the reinforcing agent HMDS (1.49g) and acetic anhydride (0.939g) solution was added the resulted solution, the mixture was stirred at 25^oC for 3 h and was aged at 50^oC for 48 h. The mixture was transferred into a sealed stainless-steel container with PFA test tube and was kept at 150^oC for 48 h. Products were centrifuged at 3000 rpm for 5 min and the resulted solid was washed three times by ion-exchanged water. After drying at 120^oC for 5 h, the solid was calcined under the condition, dried air 600ml/min, heating rate 2.29^oC/min, temperature 550^oC and time 6 h, to obtain GSR-10HS-C-ZSM-5 (C: Conventional).

In the notation of GSR-10HS-C-ZSM-5, GSR represents the gel skeletal reinforcement method, 10 a percent of the molar ratio of HMDS to SiO_2 in colloidal silica by 100, HS HMDS and H-ZSM-5 (H^+ exchanged).

Footnote of Fig. S1 (Continued)

Ion exchange of Na type in C-ZSM-5 to H type in H-ZSM-5

C-ZSM-5 includes Na+ as a cation. In order to obtain H^+ type, NH_4^+ type was prepared first and the calcination was performed. According to the flowchart in the right hand side of Fig. S1, 1.38g of ammonium nitrate was dissolved into 30.00g of water and 3.00g of C-ZSM-5 was added. After the mixture was stirred at 80^{o}C for 2 h, the solid was filtered with aspiration and was washed with ion-exchanged water until pH of the filtrate was 7. This process was repeated three times to obtain the complete exchange. The washed sample was dried at 100^{o}C for 1 h and was calcined under the condition, dried air 600ml/min, heating rate 2.5^{o}C/min, temperature 550^{o}C and time 3 h, to obtain H-ZSM-5. GSR-xHS-H-ZSM-5 (x=10, 12, 13 and 14) samples were prepared similarly. After ion exchange, Na was not detected in all the H type samples by the XRF analysis using Rigaku, ZSX Primus II. Yields, SiO_2/Al_2O_3 ratios, the crystallinity and other properties of prepared samples are given in Table 1.

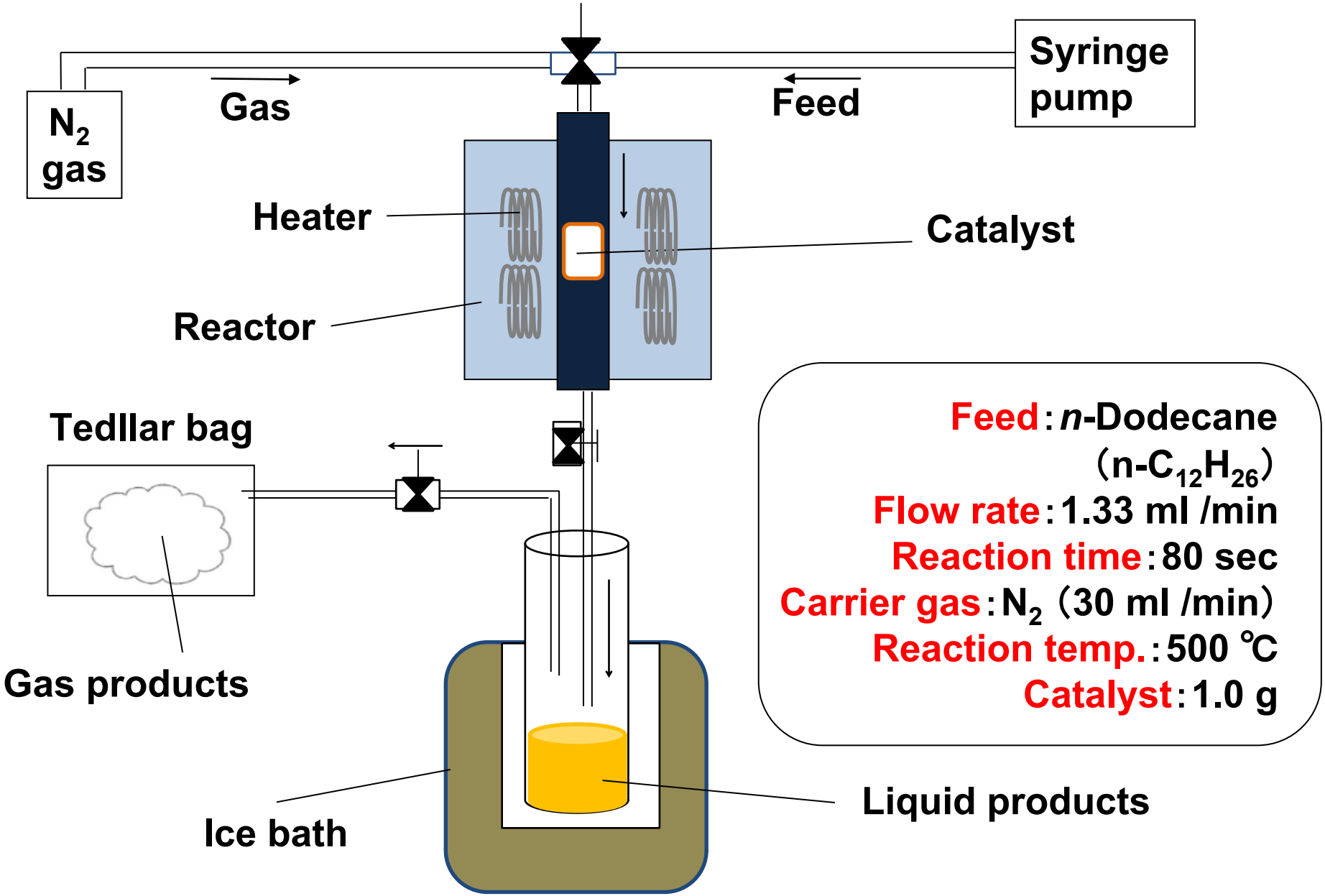


Fig. S2 Reaction apparatus of catalytic cracking.

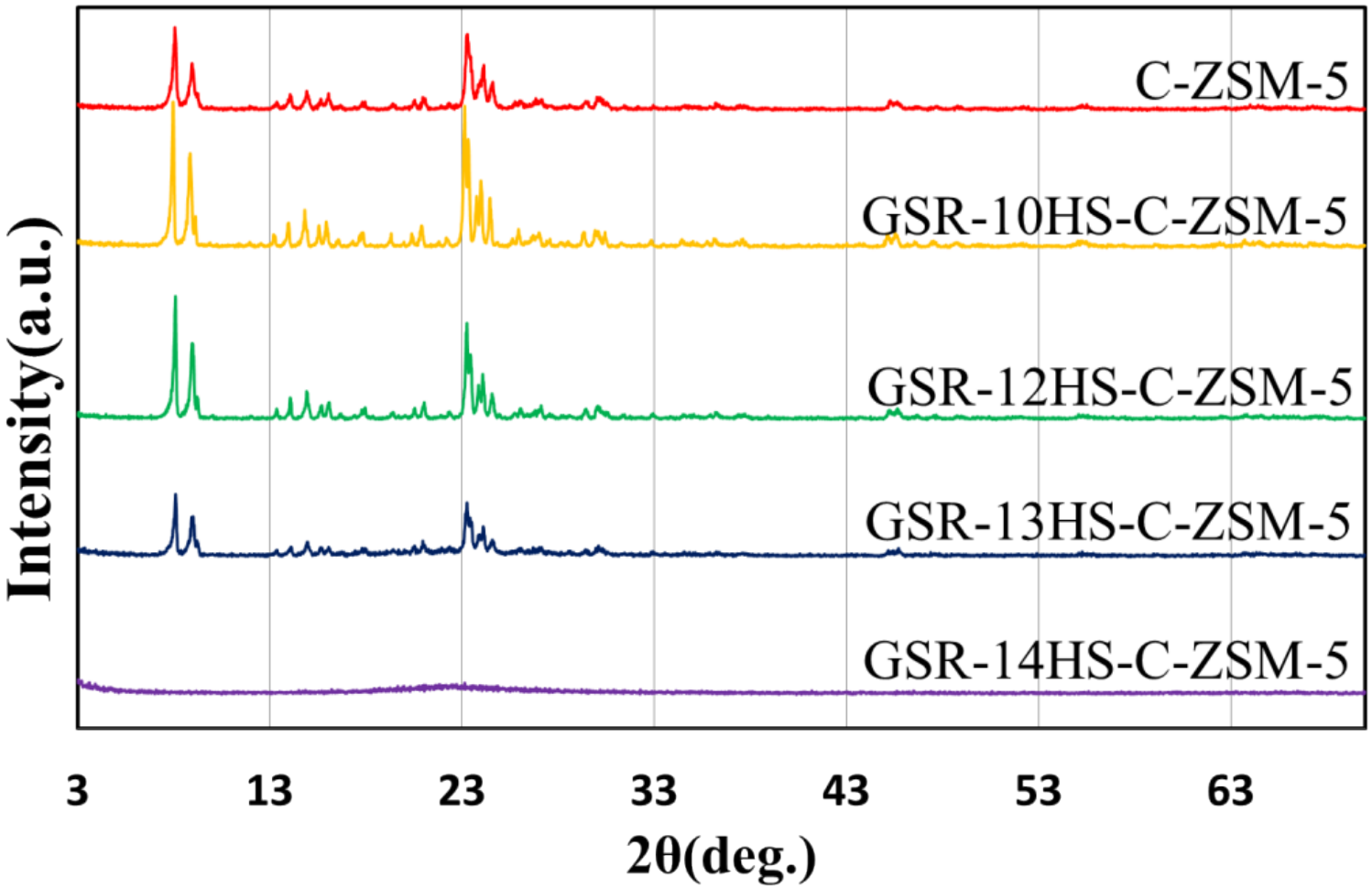


Fig. S3 XRD patterns of GSR-C-ZSM-5 zeolites

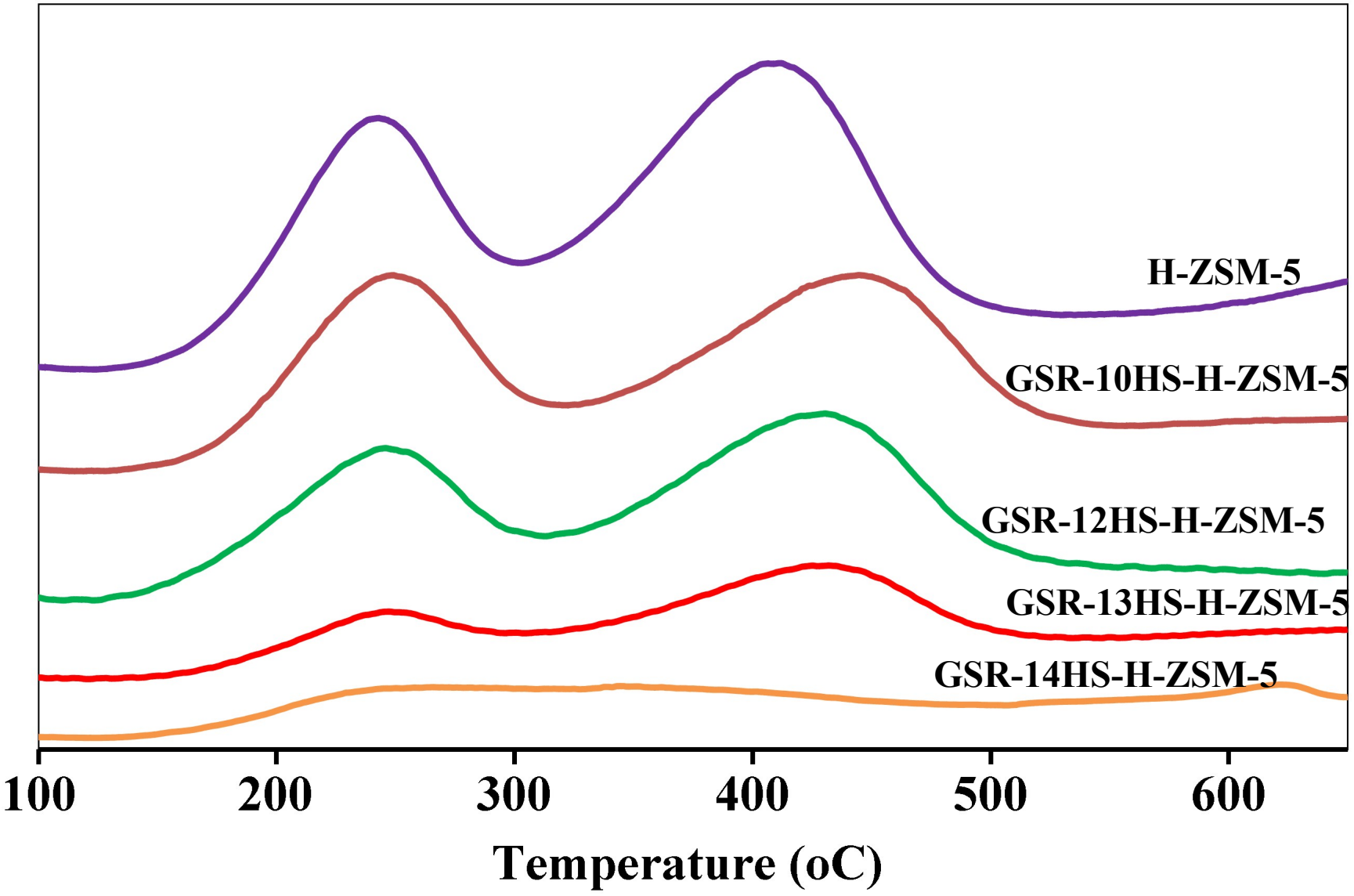


Fig. S4 NH_3-TPD patterns of hierarchical catalysts.

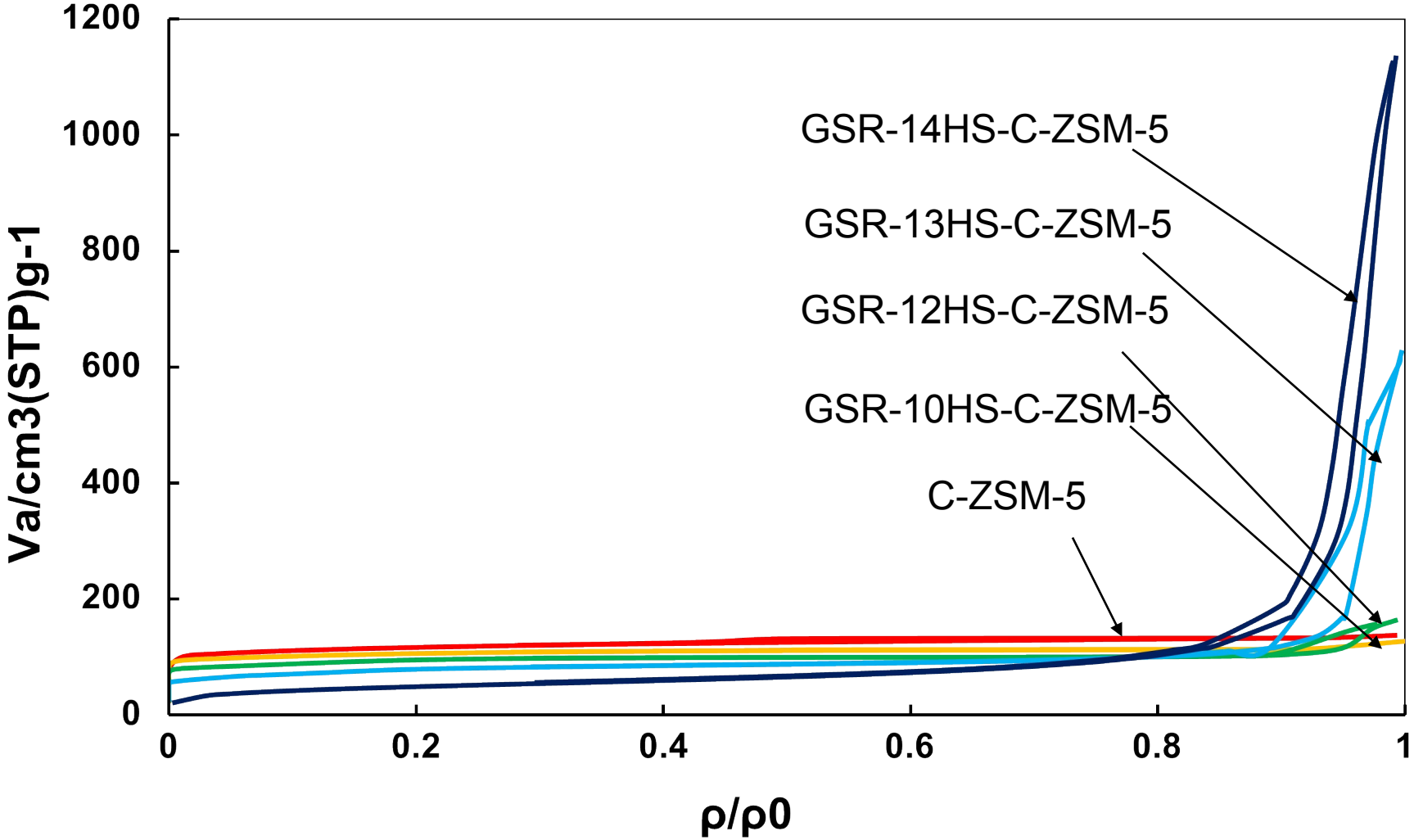


Fig. S5a Nitrogen adsorption and desorption isotherms of hierarchical GSR-xHS-C-ZSM-5 catalysts

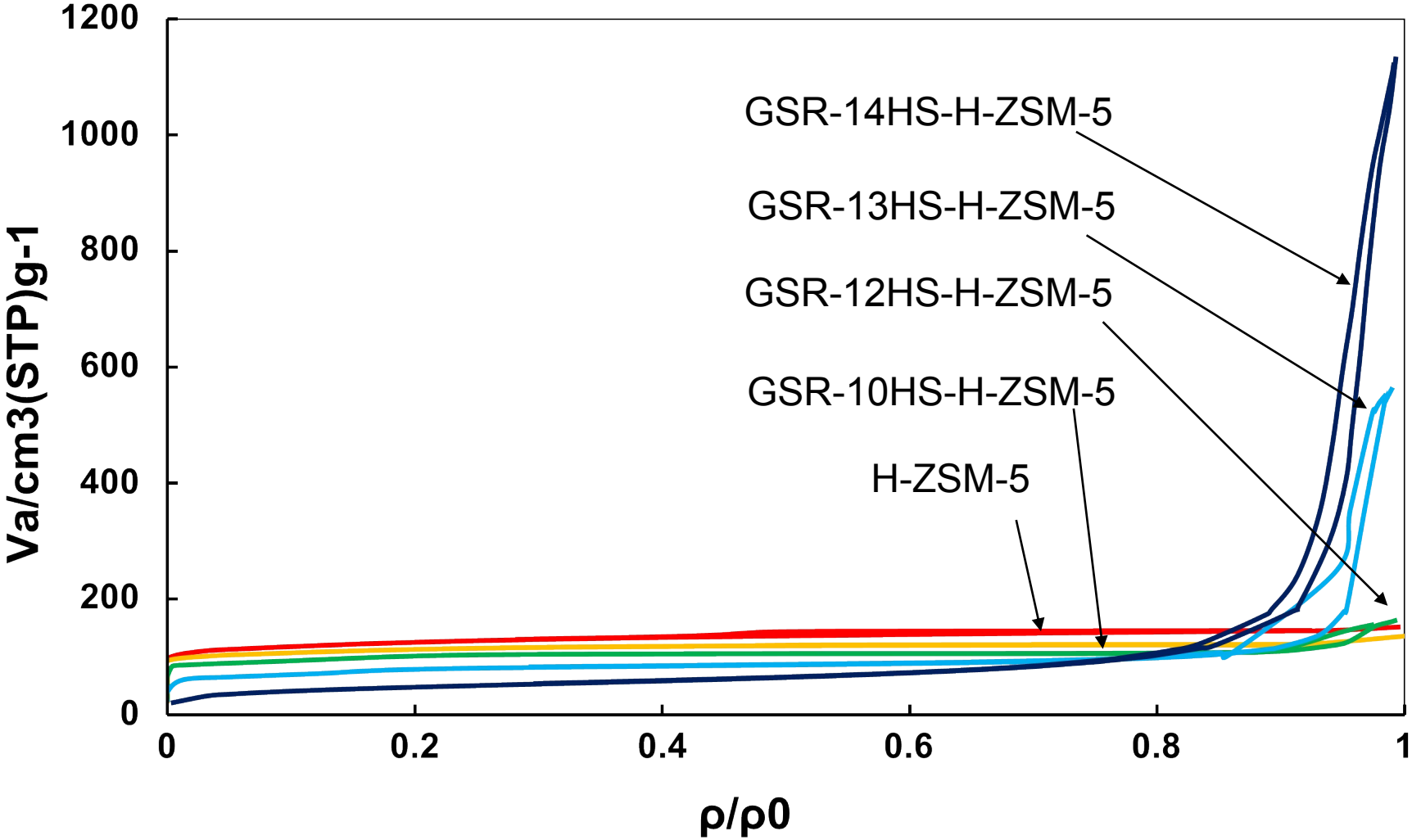


Fig. S5b Nitrogen adsorption and desorption isotherms of hierarchical GSR-xHS-H-ZSM-5 catalysts

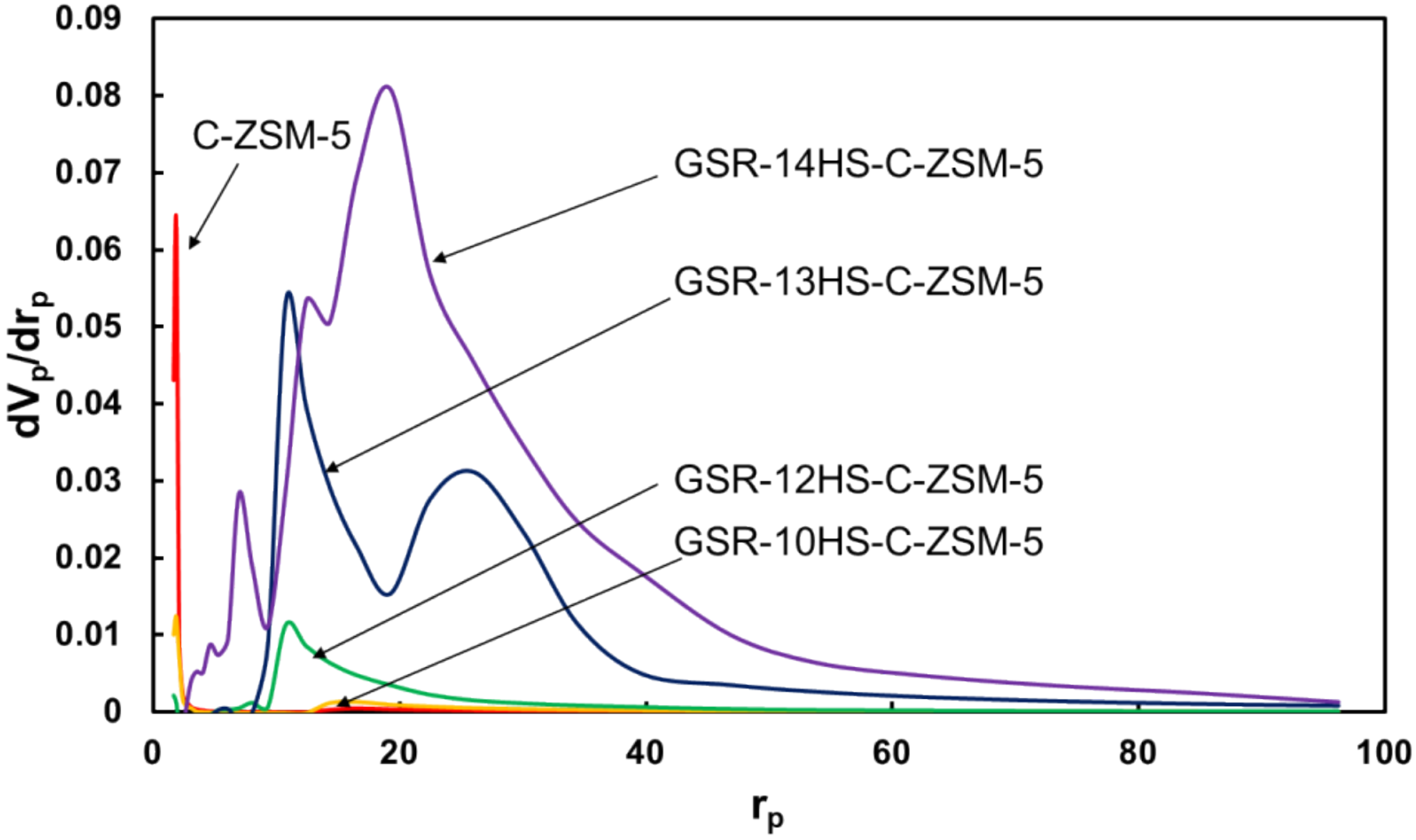
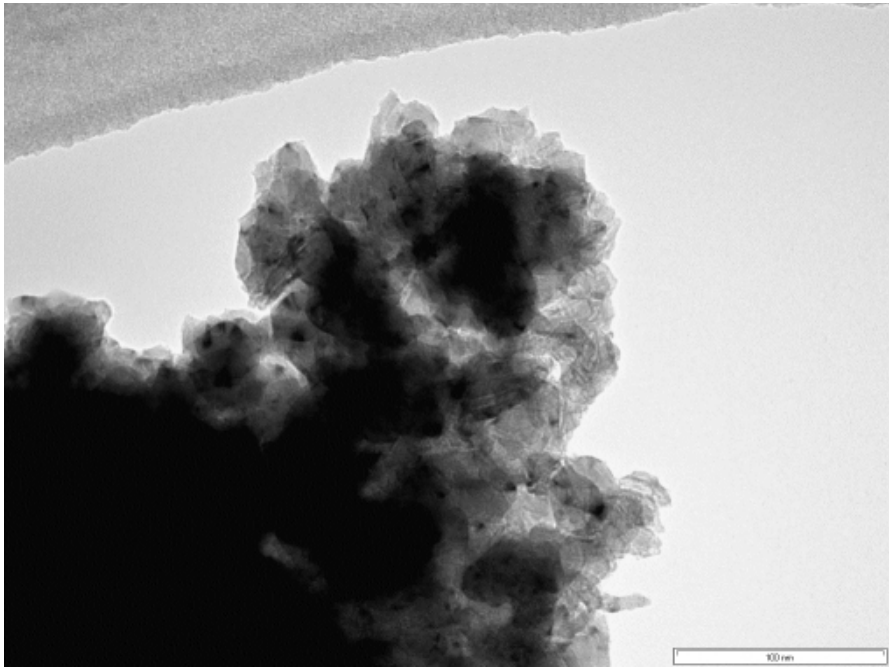


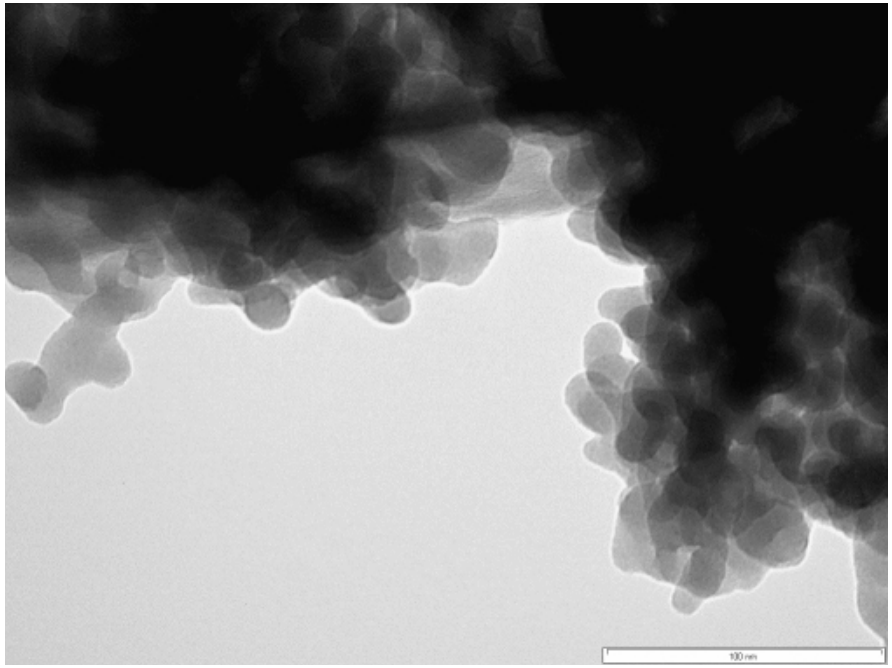
Fig. S6 BJH pore size distribution of original hierarchical catalysts

GSR-12HS-H-ZSM-5



100 nm

GSR-13HS-H-ZSM-5



100 nm

Fig. S7 TEM images of the GSR-12HS-H-ZSM-5 and GSR-13HS-H-ZSM-5.

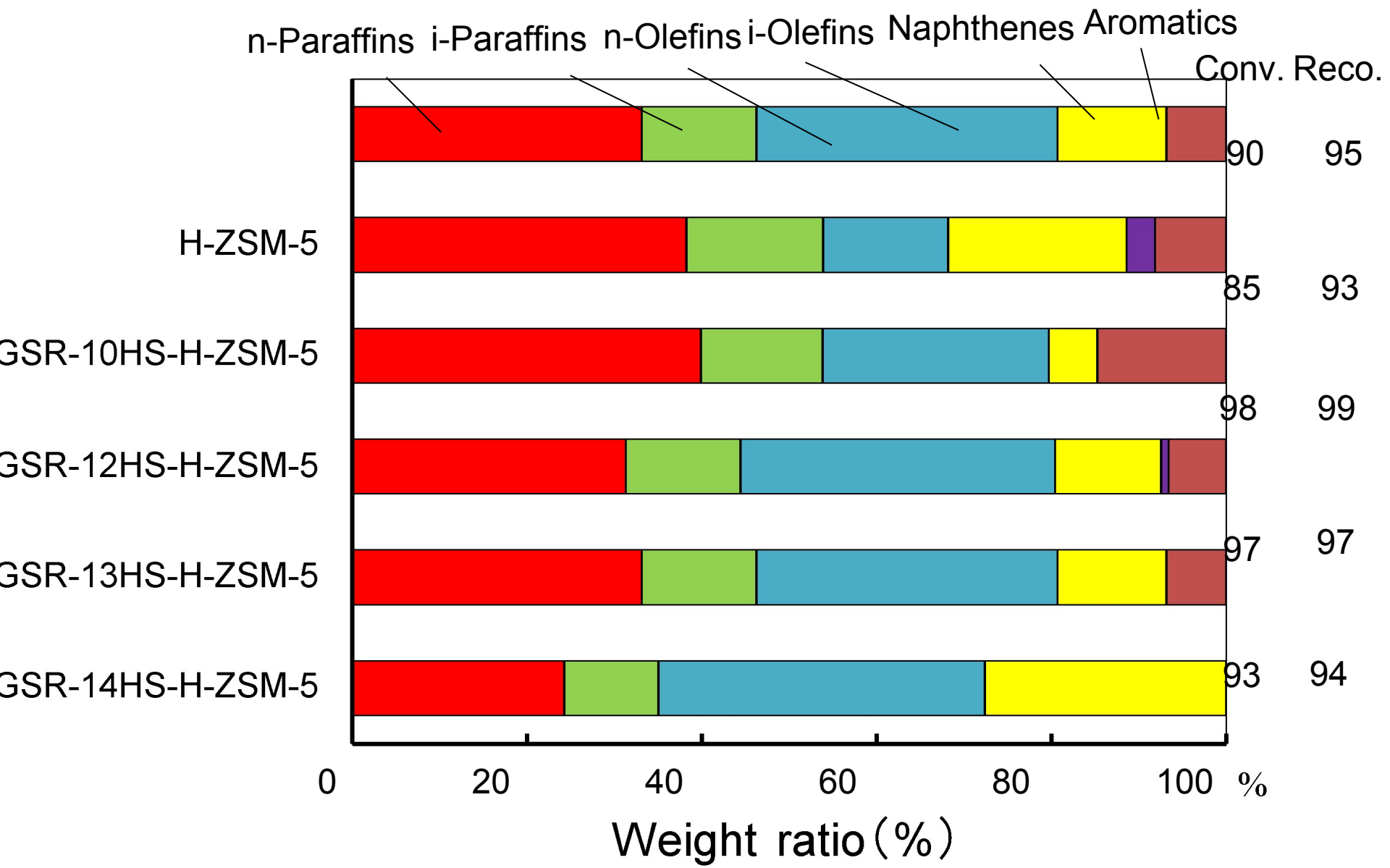


Fig. S8 Selectivity for Paraffins, Olefins, Naphthenes and Aromatics on catalytic cracking.

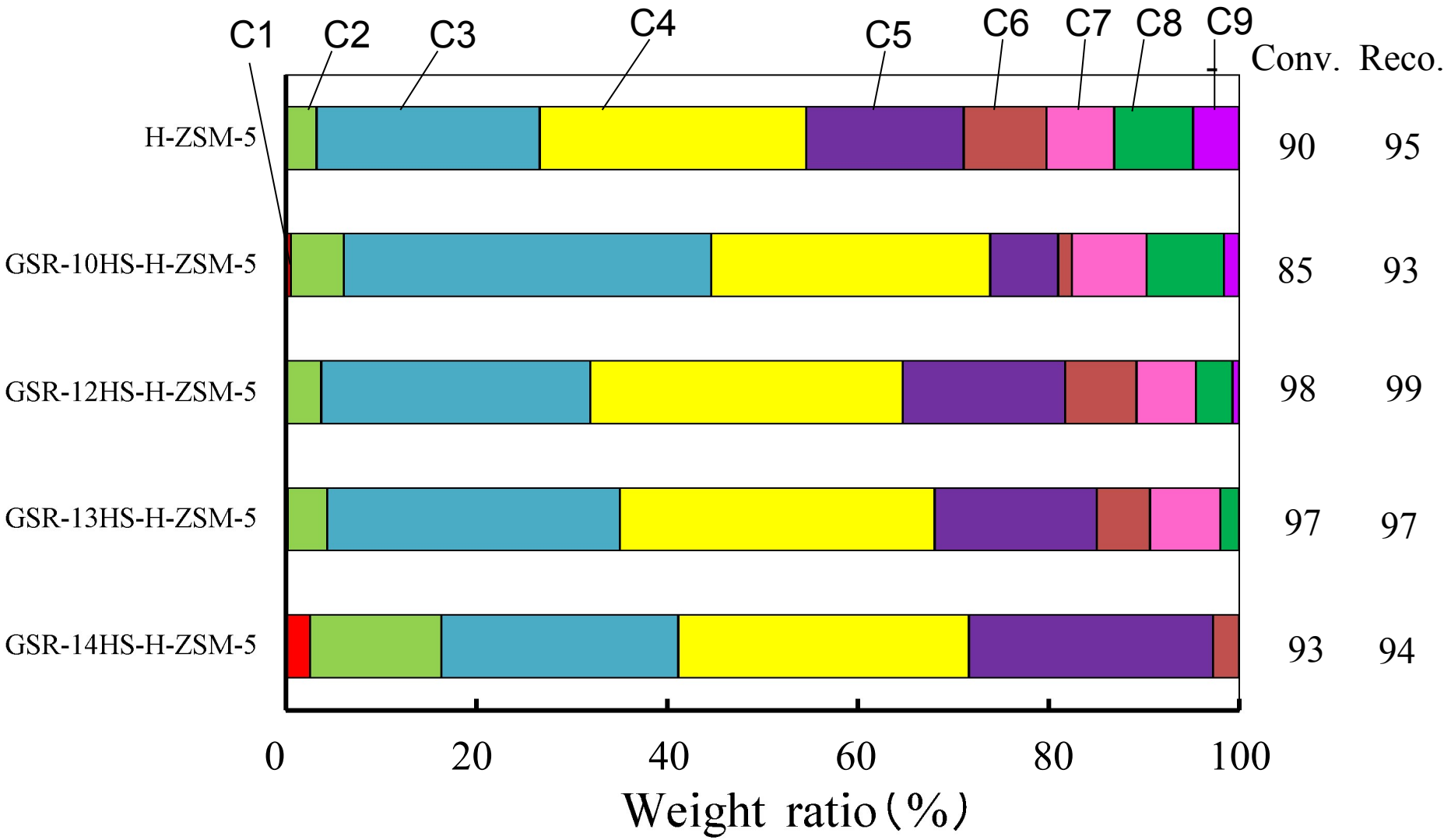


Fig. S9 Distribution of carbon numbers on catalytic cracking