Supplementary Information

Synthesis and Characterization of Fibrous Silica ZSM-5 for Cumene Hydrocracking

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Experimental

a. Catalysts Preparation.

In this study, a microemulsion system coupled with zeolite crystal seeds (CBV2314, Zeolyst International) were used to prepare fibrous silica ZSM-5 (FZSM-5). One mole of tetraethyl orthosilicate (TEOS) was dissolved in a mixture of 28 moles of toluene and 1.62 moles of 1-butanol. Then, the ZSM-5 seed was added to the solution and stirred for 30 minutes. A mixed solution of 0.9 moles of urea, 0.27 moles of cetyltrimethylammonium bromide (CTAB) and distilled water was then added. The resulting solution was exposed to intermittent microwave radiation (400W) for 6 h. The solid product was isolated by centrifugation at 20,000 rpm, followed by washing with acetone and distilled water, and was then dried overnight in air at 373 K. Finally, the product was calcined at 823 K for 6 h under an air atmosphere to obtain FZSM-5.

HFZSM-5 was obtained by two-fold protonation of FZSM-5 with NH_4NO_3 accompanied by drying at 383 K for overnight and calcination at 823 K for 3 h under an air atmosphere. HZSM-5 was obtained by calcination of an ammonium form of ZSM-5 (CBV 2314) under an air atmosphere at 823 K for 3 h. Pt/HFZSM-5 and Pt/HZSM-5 (0.5 wt% Pt) were prepared by incipient wetness impregnation of HFZSM-5 and HZSM-5 with an aqueous solution of $H_2PtCl_6.6H_2O$ followed by drying overnight at 383 K and calcination at 823 K for 3 h under an air atmosphere.

b. Catalytic measurement.

Cumene, 1,4-diisopropylbenzene (DIPB), and 1,3,5-triisopropylbenzene (TIPB) hydrocracking were conducted in a microcatalytic pulse reactor at atmospheric pressure in a temperature range of 373-623 K. Prior to the reaction, 0.1 g of catalyst was treated under an air

stream for 1 h, followed by a hydrogen stream for 3 h at 773 K, then cooled to the desired reaction temperature in a hydrogen stream. After the temperature became stable, a dose of reactant (17 µmole) was passed over the catalyst and the products were trapped at 77 K before being flash evaporated into an online 6090N Agilent gas chromatograph equipped with an HP-5 capillary column and an FID detector. The dose intervals were kept constant at 30 min. Product verification was carried out with an Agilent 5977E gas chromatograph/mass selective detector (GC/MSD) equipped with an HP-5 capillary column. For ethyl benzene (EB) dehydrogenation, 0.1 g of catalyst was treated under an air stream for 1 h followed with a hydrogen stream at 823 K for 3 h, and then the carrier gas was switched to nitrogen (100 ml/min) and cooled to the desired reaction temperature.

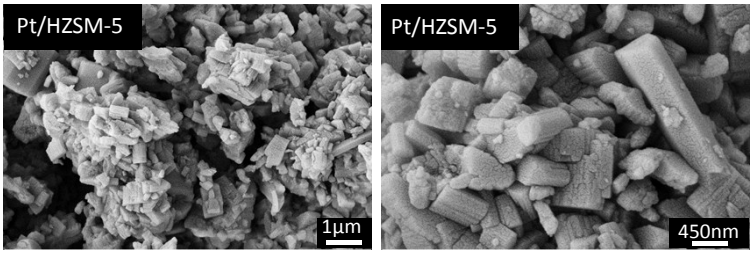

Figure S1. FESEM images of Pt/HZSM-5

Table S1. Physicochemical properties of catalysts

Catalysts	Si/Al Ratio[a]	Crystallinity (%)[b]	S_{BET}[c] (m^2/g-cat)	S_{mic}[d] (m^2/g-cat)	Total Pore Volume (cm^3/g-cat)	Mesopore Volume[e] (cm^3/g-cat)	Brönsted Acid Site[f] (µmole-B/g-cat)	Lewis Acid Site[f] (µmole-L/g-cat)	Metal Dispersion[g] (%)	Metal Particle Size[g] (Å)
FZSM-5	42	76	554	99	0.853	0.765	9.25	13.79	-	-
HFZSM-5	42	77	554	99	0.883	0.802	23.22	40.92	-	-
Pt/HFZSM-5	41	76	504	95	0.838	0.754	24.21	50.45	39.53	25.67
HZSM-5	25	100	294	141	0.266	0.133	62.11	20.22	-	-
Pt/HZSM-5	25	94	284	129	0.235	0.109	57.28	26.78	26.35	38.51

[a] Obtained by Microwave Plasma Atomic Emission Spectroscopy (MPAES)

[b] The calibration curve of crystallinity was used to determine the crystallinity of the catalyst. It was plotted against average peak intensity at $2\theta = 7.8^{o}$ and 8.9^{o} of mixture HZSM-5/SiO_2 with different ratio in which SiO_2 and HZSM-5 present 0% and 100% crystallinity, respectively. Crystallinity of fibrous silica ZSM-5 was calculated from linear equation acquires from the calibration curves.

[c] BET method

[d] Micropore surface area obtained from *t*-Plot Method

[e] Mesopore volume was obtained using total pore volume – micropore volume which was obtained from *t*-Plot method

[f] The amount of Brönsted and Lewis acid sites was calculated using the integrated molar extinction coefficients for which $\varepsilon_{1546} = 1.67$ cm µmole^{-1} for the Brönsted and $\varepsilon_{1442} = 2.22$ cm µmole^{-1} for the Lewis acid sites[17]. The catalysts were outgassed at 623 K.

[g] H_2 chemisorption method

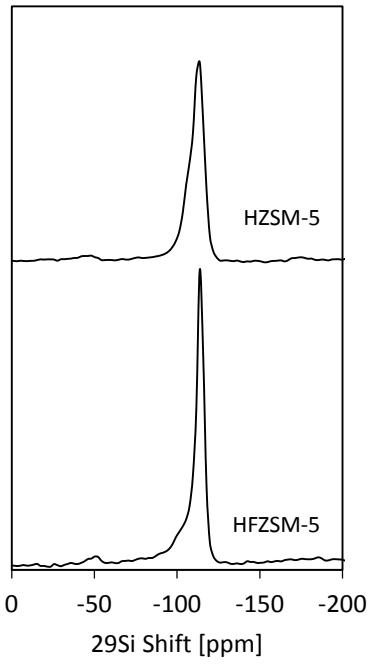

Figure S2 ^{29}Si MAS NMR spectra

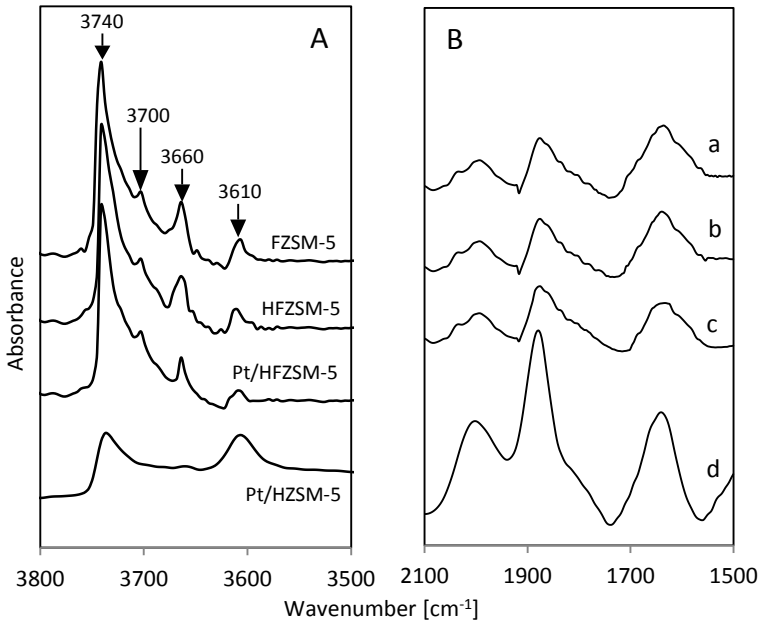

Figure S3. (A) IR spectra at hydroxyl stretching and (B) lattice stretching regions for (a) FZSM-5, (b) HFZSM-5, (c) Pt/HFZSM-5, and (d) Pt/HZSM-5

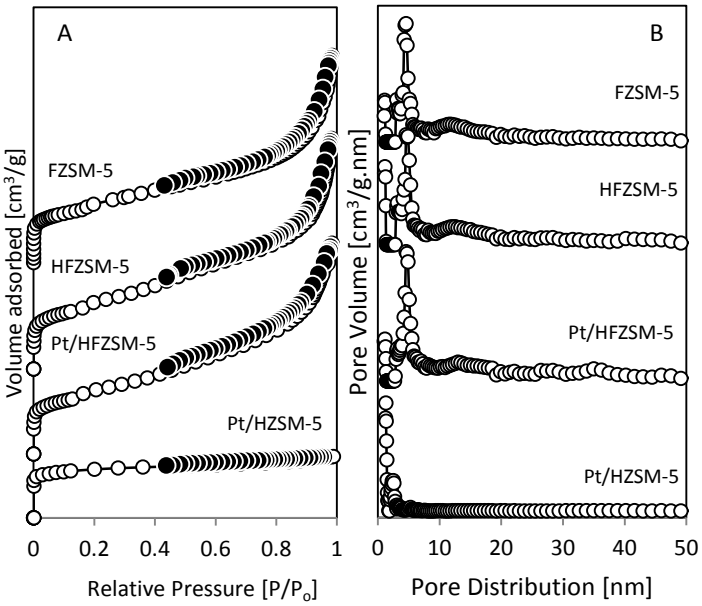

Figure S4. (A) Isotherm graph of all catalysts and (B) Pore size distribution of catalysts according to the NLDFT method.

Table S2. Acid Strength Distribution[a]

Catalyst	Acid Amount (mmole/g)				Total Acid Amount (mmole/g)
	$H_o \leq +2.8$	$H_o \leq +3.3$	$H_o \leq +4.8$	$H_o \leq +6.8$	
Pt/HFZSM-5	0.22	0.55	1.06	0.31	2.14
Pt/HZSM-5	0.09	0.21	0.46	0.72	1.68

[a]Data was obtained by using titration method with Hammett indicator. Neutral red (pKa: +6.8), methyl red (pKa: +4.8), methyl yellow (pKa: +3.3), and thymol blue (pKa: +2.8) were used as the indictors and *n*-Butylamine as the titrant. The titration was carried out by following the modified method from Wang *et al*[14].

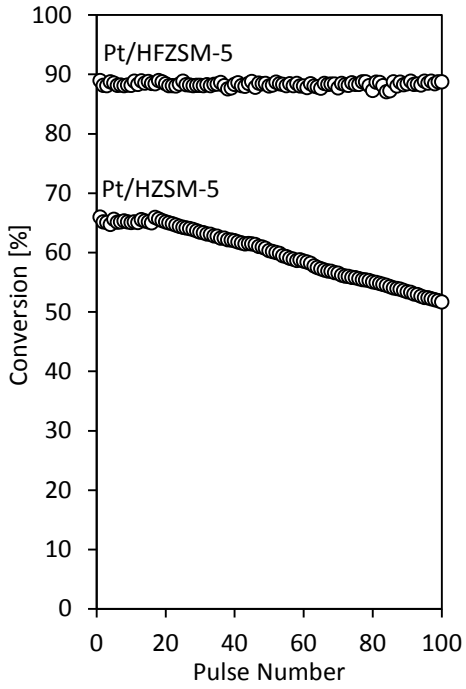

Figure S5. Cumene hydrocracking stability over Pt/HFZSM-5 and Pt/HZSM-5 at 573 K

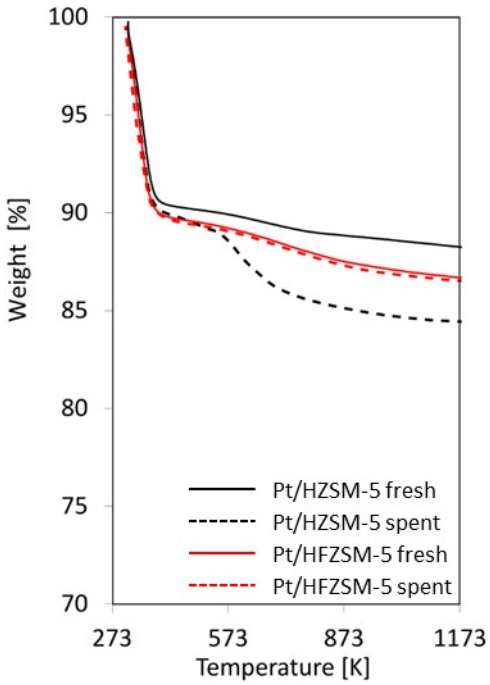

Figure S6. TGA profiles of fresh and spent catalysts during the cumene hydrocracking at 573 K after 100 doses of cumene

Table S3. The catalytic activity of fibrous silica ZSM-5 and other type of solid catalysts in the presence of hydrogen towards several acid-catalyzed reactions

Catalytic Reaction	Catalysts	Activation Temp (K)	Conversion (%)	Reaction Temp (K)	References
Cumene Hydrocracking	Pt/HFZSM-5	723	89.5	573	This study
	HFZSM-5	723	79.8	573	This study
	FZSM-5	723	12.1	573	This study
	Pt/HZSM-5	723	69.7	573	This study
	HZSM-5	723	65.8	573	This study
	HZSM-5(50)[a]	723	59.2	573	This study
	HZSM-5	723	70	523	[24a]
	Pt/WO_3-ZrO_2	723	50	573	[24b]
DIPB Hydrocracking	HFZSM-5	723	76.8	573	This study
	HZSM-5	723	58	573	This study
	HZSM-5(50)[a]	723	48.3	573	This study
	HZSM-5	893	32	723	[25]
	HY	893	35	723	[25]
TIPB Hydrocracking	HFZSM-5	723	75.3	573	This study
	HZSM-5	723	57.2	573	This study
	HZSM-5(50)[a]	723	47.8	573	This study
	HZSM-5	673	40.3	573	[26a]
	HZSM-5	673	61.9	573	[26b]
	HZSM-5/SBA-15	673	78.3	573	[26b]
Ethylbenzene Dehydrogenation[b]	Pt/HFZSM-5	773	56.3	773	This study
	Pt/HZSM-5	773	40.3	773	This study
	Pt/HZSM-5(50)[a]	773	38.1	773	This study
	1Pt/TSM	773	53	673	[27a]
	Pt/Activated Carbon	823	16	823	[27b]
	Fe-Ca/ZSM-5	823	40	823	[27b]

[a] Si/Al ratio : 50

[b] for ethylbenzene dehydrogenation, conversion [%] is switched into styrene yield [%]