Supplementary Materials: Hydroconversion of Waste Cooking Oil into Green Biofuel over Hierarchical USY-Supported NiMo Catalyst: A Comparative Study of Desilication and Dealumination

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1 NH_3-TPD profiles of AHFS and alkaline treated USY

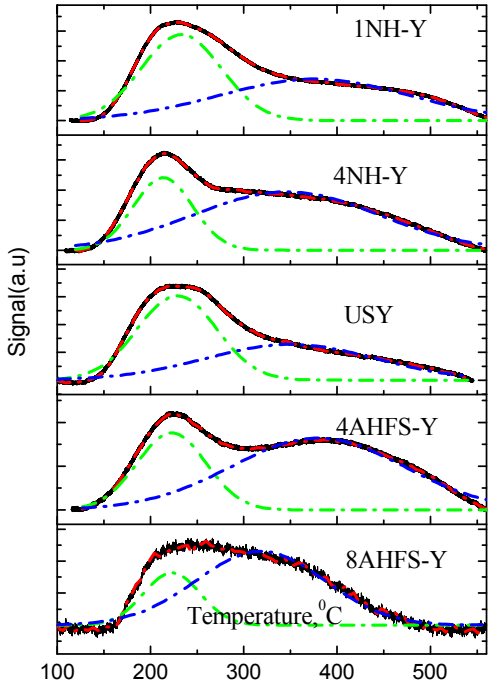

Figure S1 NH_3-TPD profiles of AHFS and alkaline treated USY

2 The adsorbed CO determined by TPD characterization

Table S1 The adsorbed CO determined by TPD characterization

Sample	Adsorbed CO (μmol/g)
NiMo/USY	1.33
NiMo/4AHFS-Y	1.40
NiMo/8AHFS-Y	2.28
NiMo/1NH-Y	1.47
NiMo/4NH-Y	1.71

3. NaOH and AHFS treatment

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The desilicated USY with NaOH solution was further dealuminated by AHFS solution. The obtained samples were labeled as xNHyAHFS-Y, where x and y represents the mass concentration of NaOH and AHFS, respectively.

3.1 Textural structures of desilicated and dealuminated USY composites

Table S2 Crystal structure parameters of modified USY

Sample	ao(A)	Si/Al (XRD)	Si/Al (XRF)	CRX , %
USY	24.515	4.1	8.8	100
1NH4AHFS-Y	24.455	5.3	9.5	50
4NH4AHFS-Y	24.515	4.1	8.7	37
4 NH8AHFS-Y	24.263	22.3	-	17

"-"no data were collected.

The $(Si/Al)_{XRD}$ ratios of NHAHFS-Y were higher than NH-Y because of the framework dealumination and lower than AHFS-Y because of the desilication at alkaline treatment. So Pre-desilication did influence the dealumination process.

3.2 Acidity distributionof desilicated and dealuminated USY

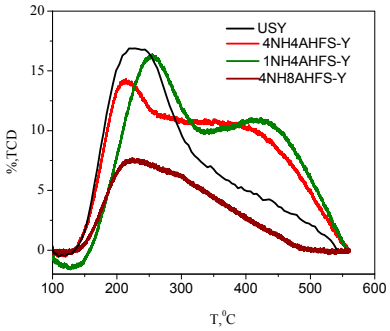


Figure S2 NH_3-TPD profiles of AHFS and alkaline treated USY

Table S3 Acidity properties of samples (μmol/g)

Sample	B	L	Weak acidity	Strong acidity
USY	1851	634	626	660
1NH4AHFS-Y	1980	697	671	1345
4NH4AHFS-Y	1710	962	517	1315
4NH8AHFS-Y	369	229	217	548

"-"no data were collected.

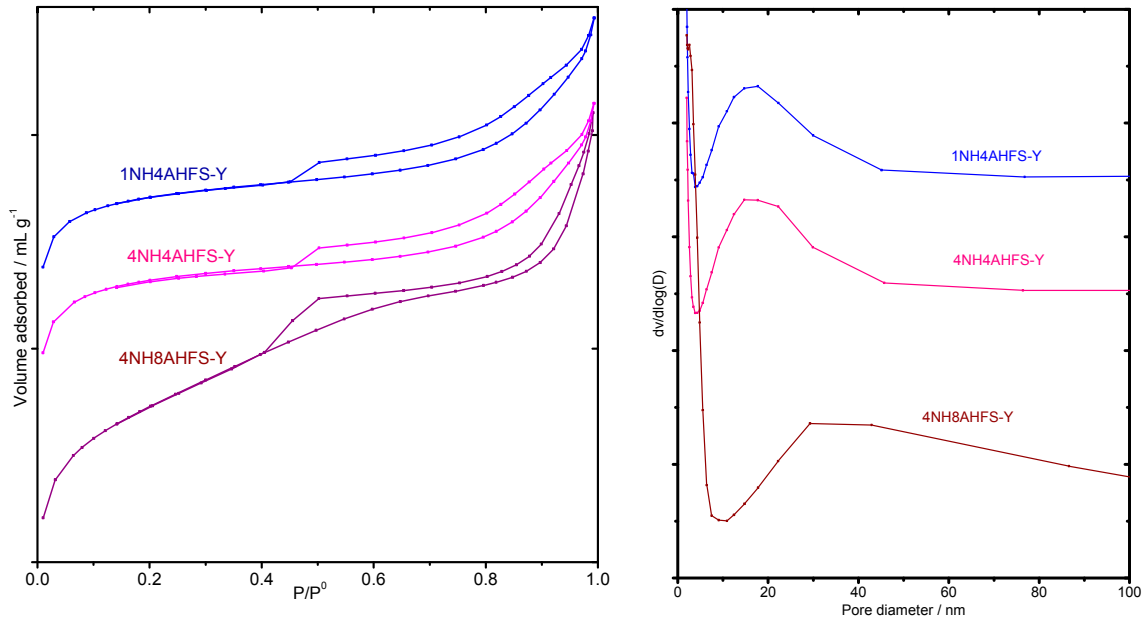
Treated USY zeolite with desilication before the AHFS treatment removed the non-framework aluminumim, which hided the Brønsted acid, so the amount of Brønsted acidity of the final product also increased.

3.3 Pore size of treated USY composites /N_2 sorption

Table S4 The surface area and pore volume data of all the Y type zeolites involved.

Samples	A_{micro}[a], m^2 /g	$A_{external}$ [b] m^2 /g	V_{micro}[c] cm^3 /g	$V_{mesopore}$[d] cm^3 /g	V_{BJH}[e] cm^3/ g	HF[f]
USY	609	49	0.28	0.07	0.07	0.0596
1NH4AHFS-Y	625	64	0.29	0.08	0.08	0.0728
4NH4AHFS-Y	622	65	0.29	0.08	0.08	0.0742
4NH8AHFS-Y	265	167	0.12	0.16	0.17	0.1657

[a] t-Plot Micropore Area.[b] t-Plot External Surface.[c] t-plot micropore volume.[d]Mesopore volume (V_{total}–V_{micro}), Vtotal is total pore volume test at p/p0 = 0.99.[e] BJH Adsorption cumulative volume of pores between 1.7 nm and 300 nm diameter. [f]The hierarchy factor (HF) = (V_{micro}/V_{pore}) × (A_{meso}/A_{BET}).



(a) (b)

Figure S3. (a) N_2 adsorption–desorption isotherms and (b) the mesopore size distribution for the AHFS treated and/ or alkaline- treated USY

Pre-desilication of the framework would increase the difficulty to keep the integrity of framework under dealumination. So the framework of 4NH8AHFS-Y collapsed and the crystallinity declined. Although the mesopore volume increased, the micropore volume decreased too much. The HF value of 4NH8AHFS-Y also proved it.

3.4 Hydrotreating of waste cooking oil

Table S5 Yield and selectivity of different hydrocabons in the hydrotreatmentwaste cookingwaste cooking oil

Sample	Y_{OLP} %	S_{C4-8} %	S_{C9-15} %	S_{C16-18} %	S_{ACHs} of jet fuel, %	C_{17}/C_{18}	CO/CO_2	Adsorbed CO(μmol/g)
NiMo/USY	78.5	76.6	9.3	14.1	29.8	1.6	5.8	1.33

NiMo/1NH4AHFS-Y	78.9	47.0	20.0	33.0	19.3	1.7	10.0	-
NiMo/4NH4AHFS-Y	77.3	37.3	24.0	38.7	26.8	0.6	5.4	-
NiMo/4NH8AHFS-Y	81.2	50.1	23.2	26.8	9.6	4.3	0	1.63

"-"no data were collected; S_{ACHs} is the selectivity of aromatic hydrocarbons.

From Table S5, the selectivity to jet fuel of NiMo/NH4AHFS-Y were higher than that of NiMo/4AHFS-Y and lower than that of NiMo/4NH-Y. The selectivity to jet fuel by NiMo/4NH8AHFS-Y was lower than that of 8AHFS-Y because that pre-desilication of the framework increased the difficulty of keeping the integrity of framework under dealumination and the crystallinity framework of 4NH8AHFS-Y declined. Although the mesopore volume of 4NH8AHFS-Y increased, the micropore volume decreased too much, which hindered the diffusion of products and improved the gasoline fraction.