Study on the Catalytic Performance of Different Crystal Morphologies of HZSM-5 Zeolites for Biodiesel Production: Strategy to Increase Catalyst Effectiveness.

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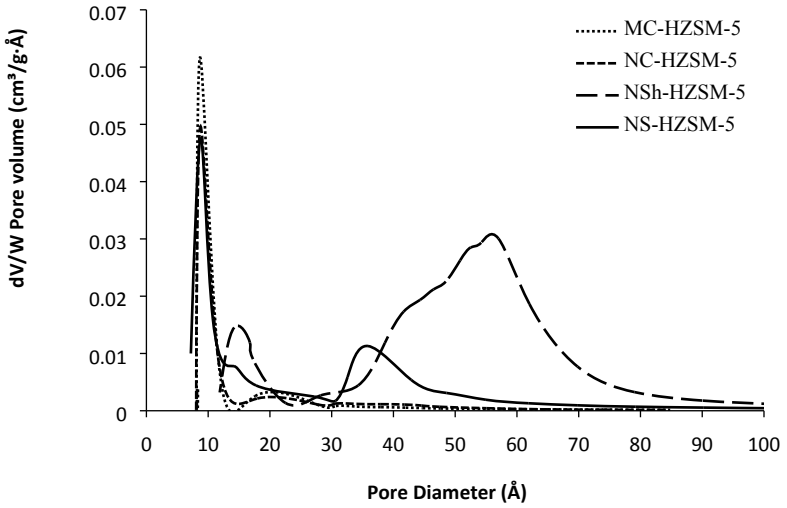
Supplementary Information

Section S1: Structure directing agents' synthesis

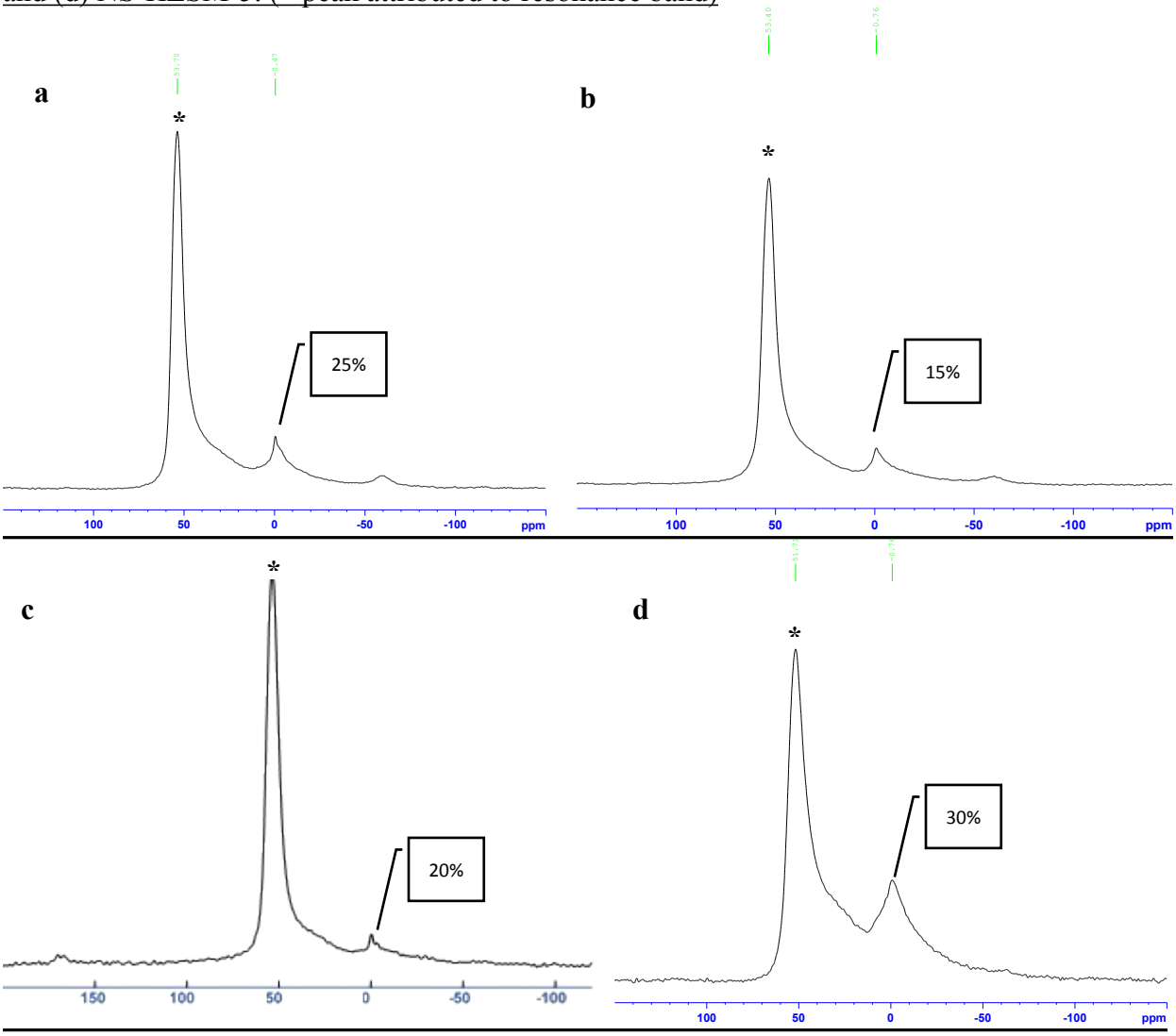
The di-quaternary ammonium-type surfactant $C_{22}H_{45}$-$N^+(CH_3)_2$-C_6H_{12}-$N^+(CH_3)_2$-$C_6H_{13}Br_2$ (abbreviated as C22-6-6), used for the ZSM-5 nanosheet synthesis were synthesized following a modified procedure reported by Na et al. (Na et al. 2010). First, 0.01 mol of 1-bromodocosane and 0.1 mol of N,N,N',N'–tetramethyl–1,6–diaminohexane were dissolved in 100 mL of acetonitrile/toluene mixture (1:1 v/v) and reacted under magnetic stirring at 60 °C for 10 h. After cooling to room temperature, the solvent was evaporated and the product [$C_{22}H_{45}$-$N^+(CH_3)_2$-C_6H_{12}-$N(CH_3)_2$]Br (denoted C22-6-0) was washed with diethyl ether and dried in a vacuum oven for 2 h at 50 °C. Second, 0.01 mol of C22-6-0 and 0.02 mol of 1-bromohexane were dissolved in 40 mL of acetonitrile and refluxed for 10 h under stirring.

For the production of ZSM-5 nanosponges, the zeolite- SDA -functional surfactant $C_{18}H_{37}$–$N^+(CH_3)_2$–C_6H_{12}–$N^+(CH_3)_2$–C_6H_{12}– $N^+(CH_3)_2$–$C_{18}H_{37}(Br^-)_3$ (abbreviated as 18–N_3–18) was prepared by separately synthesizing $C_{18}H_{37}$–$N^+(CH_3)_2$–C_6H_{12}–$Br(Br^-)$ and $C_{18}H_{37}$– $N^+(CH_3)_2$–C_6H_{12}–$N(CH_3)_2$ through organic reactions as described by (Na et al. 2011). First, $C_{18}H_{37}$–$N^+(CH_3)_2$–C_6H_{12}–$Br(Br^-)$ was prepared by dissolving 0.034 mol of N,N'–dimethyloctadecylamine and 0.34 mol of 1,6–dibromohexane in 1000 mL acetonitrile/toluene mixture (1:1 v/v). The mixture was heated under stirring at 60 °C for 12 h with reflux. Second, 0.030 mol of 1–bromooctadecane and 0.300 mol of N,N,N',N'–tetramethyl–1,6–diaminohexane were dissolved in 600 mL acetonitrile/toluene mixture (1:1 v/v) and heated at 60 °C for 12 h to obtain a solid product with the formula of $C_{18}H_{37}$–$N^+(CH_3)_2$–C_6H_{12}–$N(CH_3)_2(Br^-)$. Finally, equimolar amounts of $C_{18}H_{37}$–$N^+(CH_3)_2$–C_6H_{12}–$Br(Br^-)$ and $C_{18}H_{37}$–$N^+(CH_3)_2$–C_6H_{12}–$N(CH_3)_2(Br^-)$ were dissolved in acetonitrile (60 mL) and refluxed for 12 h under agitation to produce the 18–N_3–18 surfactant.

Section S2: Micropore and mesopore size distribution of the calcined exchanged samples MC-HZSM-5, NC-HZSM-5, NSh-HZSM-5 and NS-HZSM-5



Section S3: ^{27}Al MAS NMR spectra of (a) MC-HZSM-5, (b) NC-HZSM-5, (c) NSh-HZSM-5, and (d) NS-HZSM-5. (* peak attributed to resonance band)



Section S4: Yields of produced methyl esters and residual linoleic acid using MC-HZSM-5, NC-HZSM-5, NSh-HZSM-5 and NS-HZSM-5 zeolite catalysts

		MC-HZSM-5		NC-HZSM-5		NSh-HZSM-5		NS-HZSM-5	
Temperature variation (^{0}C) at 12:1 Methanol to LA ratio, 6 h reaction time and 10% catalyst		Average (%)	SD	Average (%)	SD	Average (%)	SD	Average (%)	SD
60	Methyl esters	34.40	1.45	32.25	3.02	36.12	2.83	15.60	3.60
	Linoleic acid	64.48	1.83	61.56	4.62	63.51	9.46	68.38	5.83
140	Methyl esters	30.93	5.34	31.25	0.66	50.48	0.78	31.16	4.10
	Linoleic acid	60.33	4.58	61.97	2.55	55.97	13.69	41.72	1.52
180	Methyl esters	45.76	4.85	51.31	5.33	76.58	3.47	68.60	4.24
	Linoleic acid	47.74	4.55	57.50	10.87	52.23	23.75	23.67	1.42
Methanol to LA ratio variation at 180 ^{0}C, 6 h reaction time and 10% catalyst									
6 to 1	Methyl esters	76.62	1.37	46.68	6.58	90.76	1.17	86.40	2.16
	Linoleic acid	14.98	8.17	46.22	8.88	10.44	0.23	5.00	4.16
12 to 1	Methyl esters	45.76	4.85	51.31	5.33	76.58	3.47	68.60	4.24
	Linoleic acid	47.74	4.55	62.39	6.83	23.67	1.42	12.95	5.61
25 to 1	Methyl esters	27.85	7.83	34.50	7.01	72.01	5.77	53.62	10.51
	Linoleic acid	68.70	10.98	59.95	4.66	19.16	7.17	56.18	6.71
Reaction time variation (h) at 6:1 Methanol to LA ratio, 180 ^{0}C and 10% catalyst									
0.5	Methyl esters	8.93	0.21	13.01	0.18	14.89	0.26	16.25	2.58
	Linoleic acid	83.73	2.58	88.80	1.23	73.56	2.34	82.15	0.52
1	Methyl esters	11.42	0.45	24.53	0.27	18.38	0.85	19.98	1.23
	Linoleic acid	74.02	3.75	81.74	2.14	74.02	3.75	75.39	4.82
2	Methyl esters	20.36	0.79	31.60	0.06	36.26	1.95	41.04	0.69
	Linoleic acid	52.84	4.55	78.26	0.58	52.84	4.55	63.75	1.64
3	Methyl esters	69.27	0.65	49.82	0.99	65.82	0.12	70.59	4.42
	Linoleic acid	39.1	0.14	54.94	2.47	39.12	0.14	48.12	2.76
4	Methyl esters	78.72	1.06	70.66	0.85	93.87	1.25	82.91	0.56
	Linoleic acid	6.83	2.85	42.24	1.89	6.83	2.85	11.29	3.41
6	Methyl esters					90.76	1.17		
	Linoleic acid					5.34	1.77		
8	Methyl esters					81.01	1.21		
	Linoleic acid					18.54	3.26		
16	Methyl esters					23.53	0.02		
	Linoleic acid					73.62	3.73		
24	Methyl esters					23.78	0.78		
	Linoleic acid					67.02	1.32		

Section S5: Wilke-Chang method used to calculate the molecular diffusion coefficient (D_{AB})

The effect of external mass transfer limitation by calculating the Mears criterion (Ju et al., 2011).

$$C_M = \frac{r_0 \ \rho \ d \ n}{2 \ k_c \ C_0} \qquad \text{S1}$$

where, r_0 is the initial reaction rate that is equal to the linoleic acid esterification rate at 60 min (= $\frac{moles\ of methyl\ esters\ produced\ in\ the\ reaction\ time\ (mol)}{catalyst\ loading\ (g)\ \times reaction\ time\ (min)}$) (Sert et al., 2013), ρ is the density of the HZSM-5 matrix, d is the mean diameter of the catalyst, n is the reaction order (the esterification reaction obeyed the pseudo first-order reaction kinetics, C_0 is the linoleic acid initial concentration, and k_c is the mass transfer coefficient, calculated using the equation developed by Dwivedi and Upadhyay (Dwivedi & Upadhyay, 1977) :

In the kinetic study, the external mass transfer diffusion resistance is insignificant when the Mears criterion value is lower than 0.15. C_M were 3.93×10^{-7}, 1.08×10^{-9}, 1.79×10^{-11}, and 7.00×10^{-10} for MC-HZSM-5, NC-HZSM-5, NSh-HZSM-5 and NS-HZSM-5, respectively. This indicates that the solid-liquid interface-external mass transfer limitations were surmounted when the stirring speed was 550 rpm.

Section S6: Wilke-Chang method used to calculate the molecular diffusion coefficient (D_{AB})

$$D_{AB} = \frac{7.4 \,.\, 10^{-8} (\partial \, M_B)^{1/2} \, T}{\varphi_B \, V_A^{0.6}}$$

Where,
M_B is the molecular weight of solvent B (methanol) (g/mol)
T is the temperature of the reaction (Kelvin)
$\varphi_B$is the viscosity of solvent B at *T (cP)*
$V_A$molar volume of solute A at *T* (m^2/mol)
∂ association factor of solvent B (dimentioneless; 1.9 for methanol)

Section S7: -ln(1-$Yield_{ME}$) versus reaction time at catalyst loading of 10 wt%, methanol to linoleic molar ratio of 6:1, reaction temperature of 180 °C, and stirring rate of 550 rpm