On the influence of Si:Al ratio and hierarchical porosity of FAU zeolites in solid acid catalysed esterification pretreatment of bio-oil

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Electronic Supporting Information

Table S1. Surface elemental analysis of FAU zeolite catalysts by XPS

Nominal Si:Al ratio	Concentration / wt%			Concentration / At%			Si:Al atomic ratio
	O	Si	Al	O	Si	Al	
2.6	46.3	32.1	21.5	59.9	23.7	16.5	1.4
6	48.5	42.4	9.2	62.1	30.9	7.0	4.4
30	47.8	50.4	1.9	61.6	37.0	1.4	25.9
HFAU30	48.8	49.2	2.1	62.5	35.9	1.6	23.0

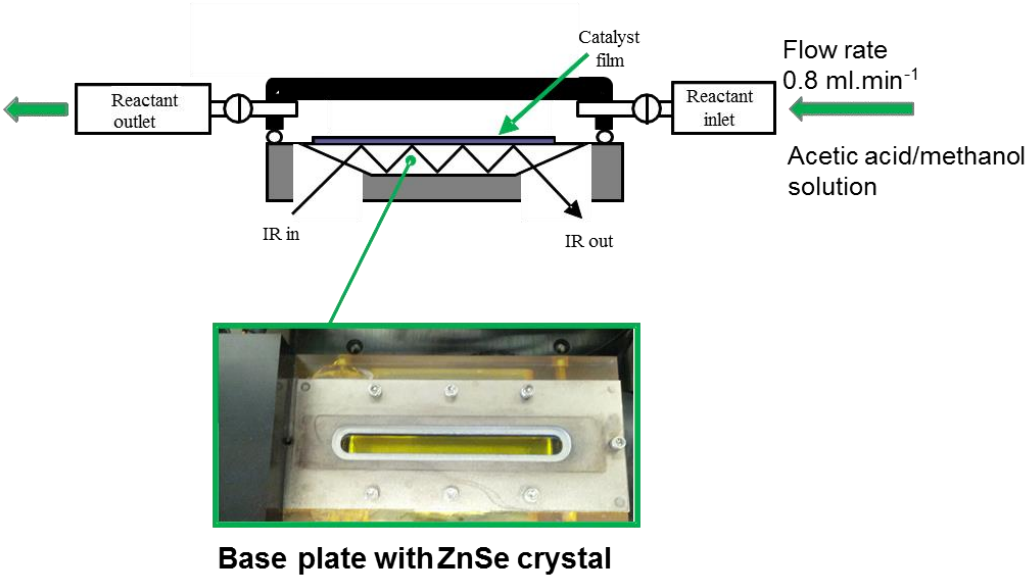

Figure S1. Schematic of *in-situ* ATR-IR flow cell.

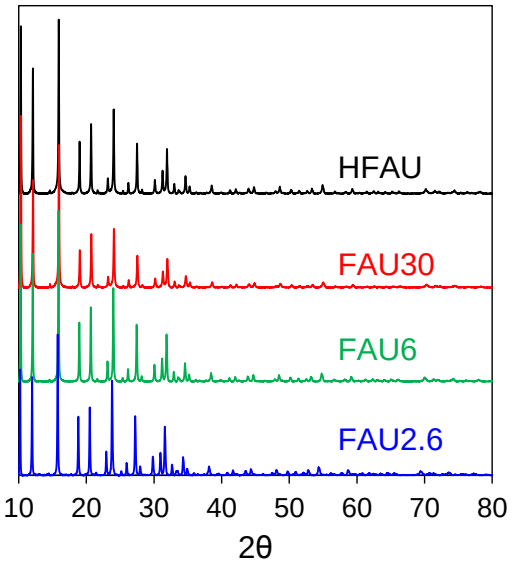

Figure S2. XRD patterns for FAU zeolites.

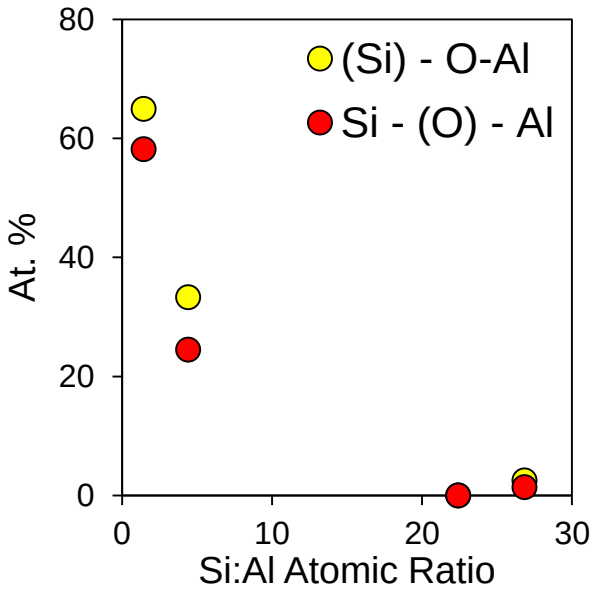

Figure S3. Surface atomic concentration of Si and O from quantification of Si 2p and O 1s XP spectra as a function of Si:Al ratio in FAU zeolites.

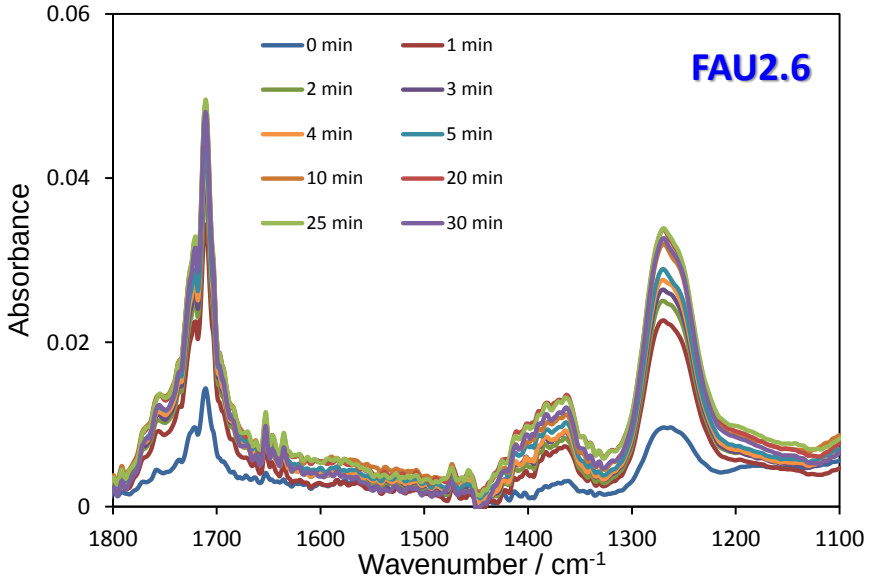

Figure S4. ATR-IR spectra of acetic acid adsorbed over FAU2.6 as a function of time.

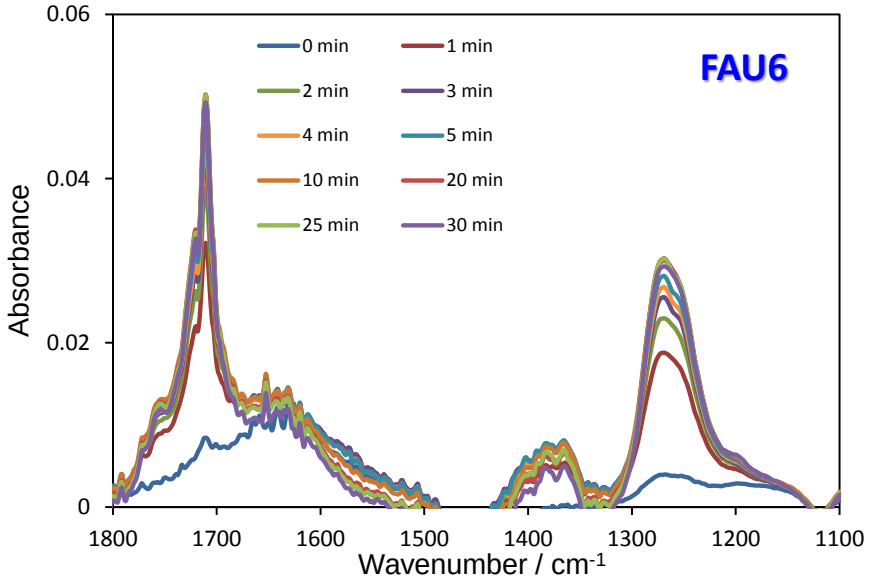

Figure S5. ATR-IR spectra of acetic acid adsorbed over FAU6 as a function of time.

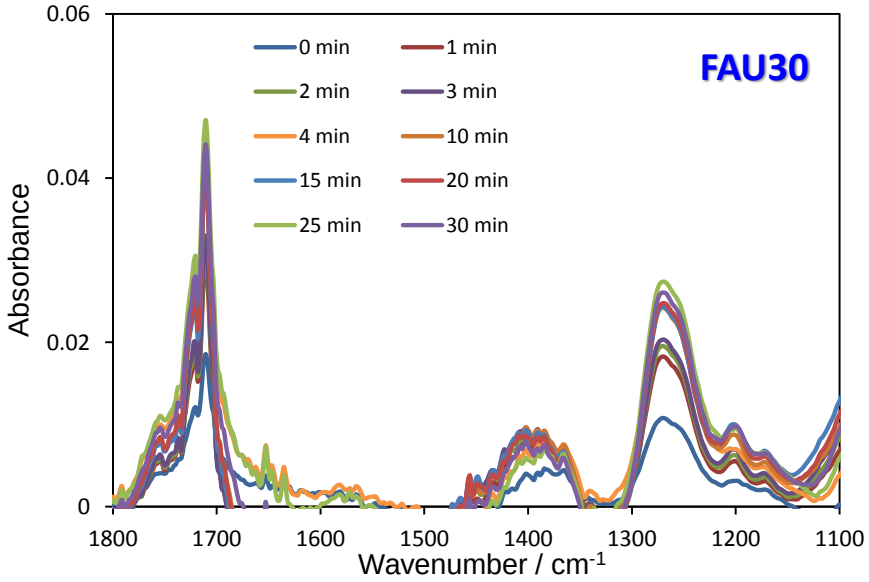

Figure S6. ATR-IR spectra of acetic acid adsorbed over FAU30 as a function of time.

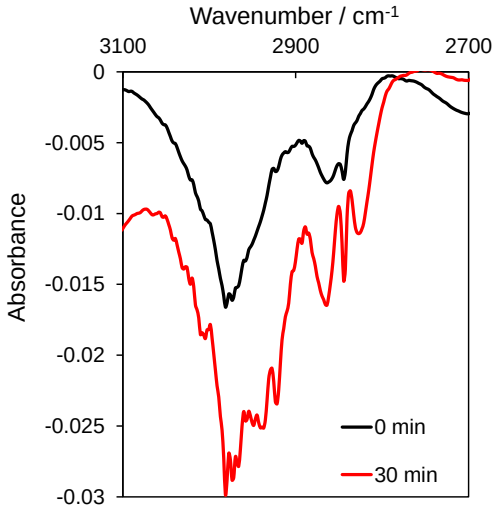

Figure S7. ATR-IR spectra of the Methoxy group region during the adsorption of acetic acid. At 0 min (black line) only methanol is adsorbed on the catalyst surface. After 30min of acetic acid flow (red line) the Methoxy peak is more broad and negative because of the competitive adsorption between the solvent and the probe molecule.

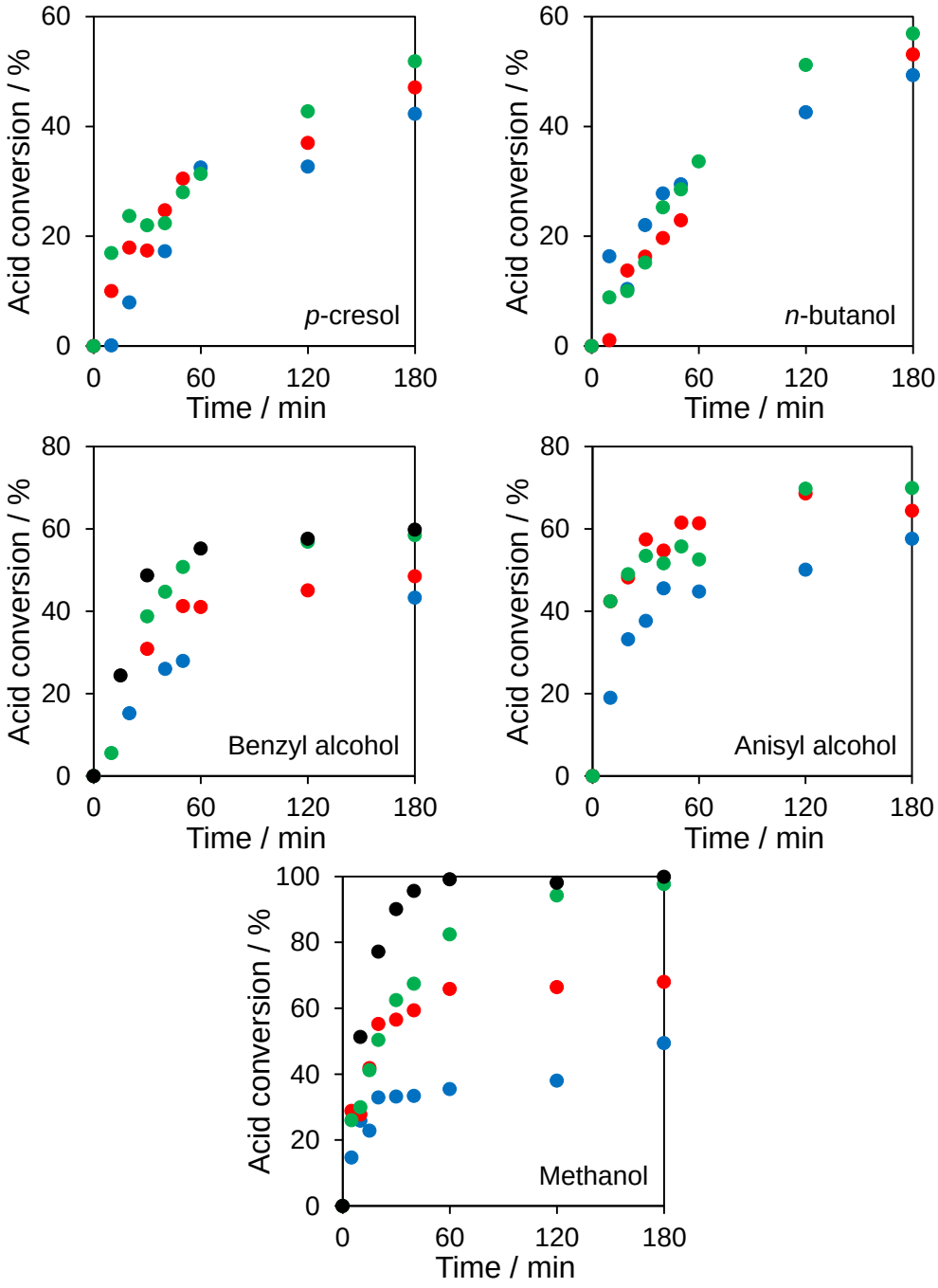

Figure S8. Esterification of acetic acid with various alcohols in an alcohol-rich media over FAU zeolites with 2.6 (●), 6 (●), 30 (●) Si:Al ratio and HFAU zeolite (●). (Reaction conditions: 5 mmol acetic acid, acid:alcohol = 1:5 mol:mol, 10 ml toluene, 100 mg catalyst, 100 °C)

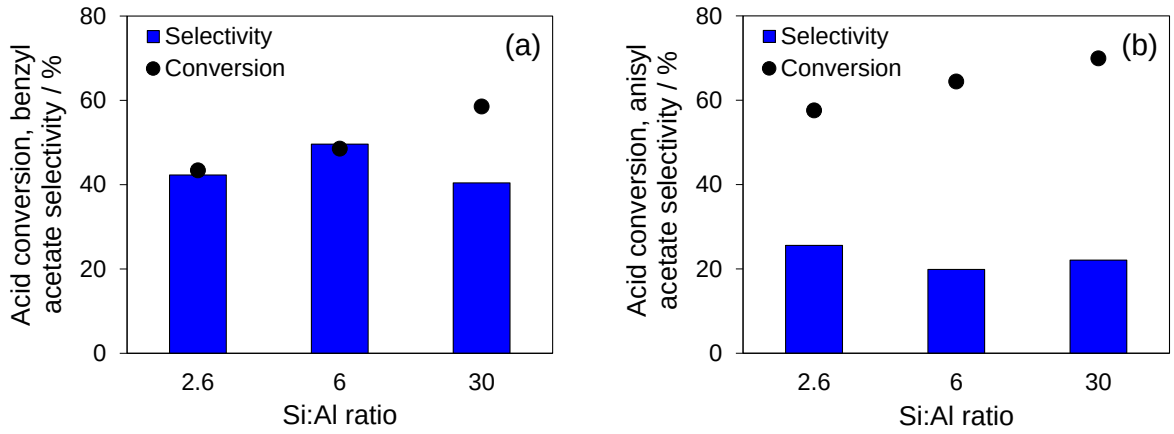

Figure S9. Acetic acid conversion and ester selectivity as a function of FAU zeolite Si:Al ratio for esterification with a) benzyl alcohol and b) anisyl alcohol. (Reaction conditions: 5 mmol acetic acid, acid:alcohol = 1:5 mol:mol, 10 ml toluene, 100 mg catalyst, 100 °C, 3h)

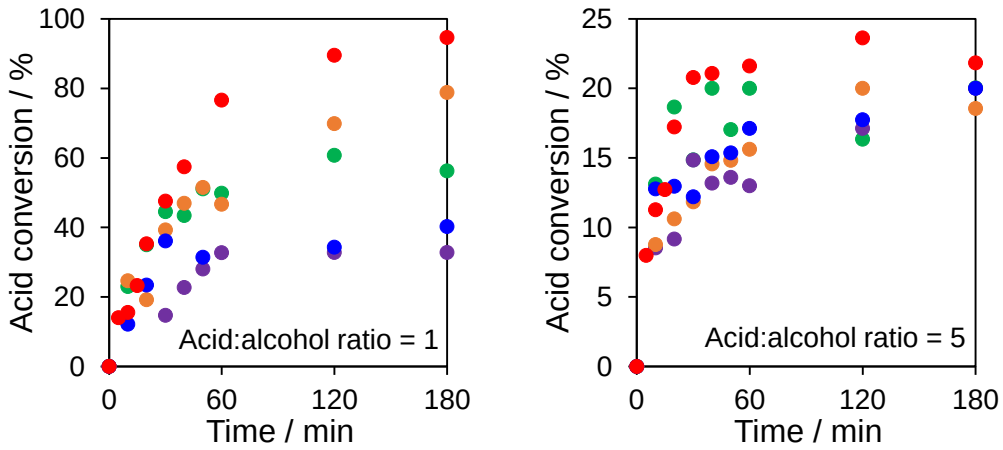

Figure S10. Esterification of acetic acid with methanol (●), anisyl alcohol (●), benzyl alcohol (●), *p*-cresol (●) and *n*-butanol (●) over FAU30. (Reaction conditions: acid:alcohol = 1 (left), 5 (right), 10 ml toluene, 100 mg catalyst, 100 °C)