Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.


# Catalytic distillation for ethyl acetate synthesis using microfibrous-structured Nafion-$SiO_2$/SS-fiber solid acid packings

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**Table S1.** Effects of coating composition on acidity and durability of the structured catalyst.

| Coating composition[a] | Total loading (wt%) | IEC (mmol $g^{-1}$)[b] | 1 h ultrasonic concussion (mmol $g^{-1}$) | 2 h ultrasonic concussion (mmol $g^{-1}$) | 3 h ultrasonic concussion (mmol $g^{-1}$) | 4 h ultrasonic concussion (mmol $g^{-1}$) | 5 h ultrasonic concussion (mmol $g^{-1}$) |
|---|---|---|---|---|---|---|---|
| Nafion | 10.7 | 0.09 | 0.01 | 0 | 0 | 0 | 0 |
| Nafion/$SiO_2$ | 17.5 | 0.07 | 0.03 | 0.01 | 0 | 0 | 0 |
| Nafion/TEOS | 25.3 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |

[a.] The coating solution were 5 wt% Nafion polymer dispersion, $SiO_2$ sol-gel in 5 wt% Nafion polymer dispersion and TEOS in Nafion polymer dispersion with the same Nafion:additives weight ratio of 2:1.

[b.] The ion-exchange capacity (IEC) was used to represent the catalyst acid capacity.

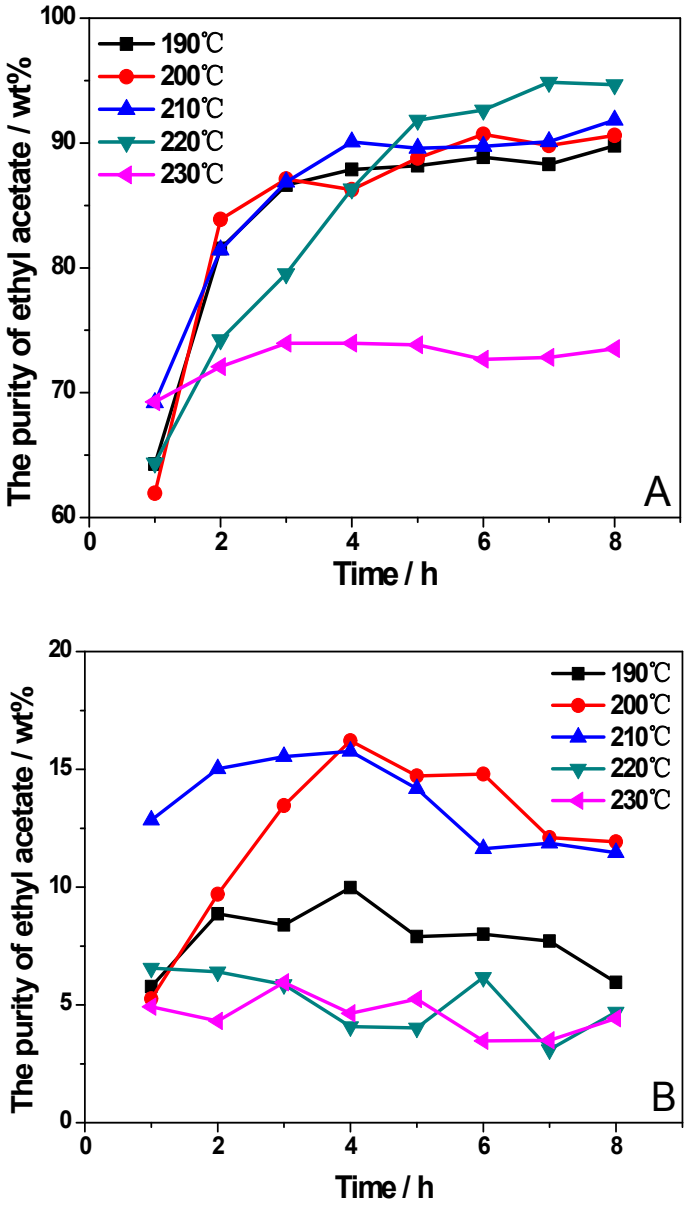


**Figure S1.** Effect of reboiler temperature (duty) on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: molar feed ratio of acetic acid to ethanol = 1:1, reflux ratio = 2.5, WHSV = 0.3 $h^{-1}$, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 8.5 mmol $H^{+}$.

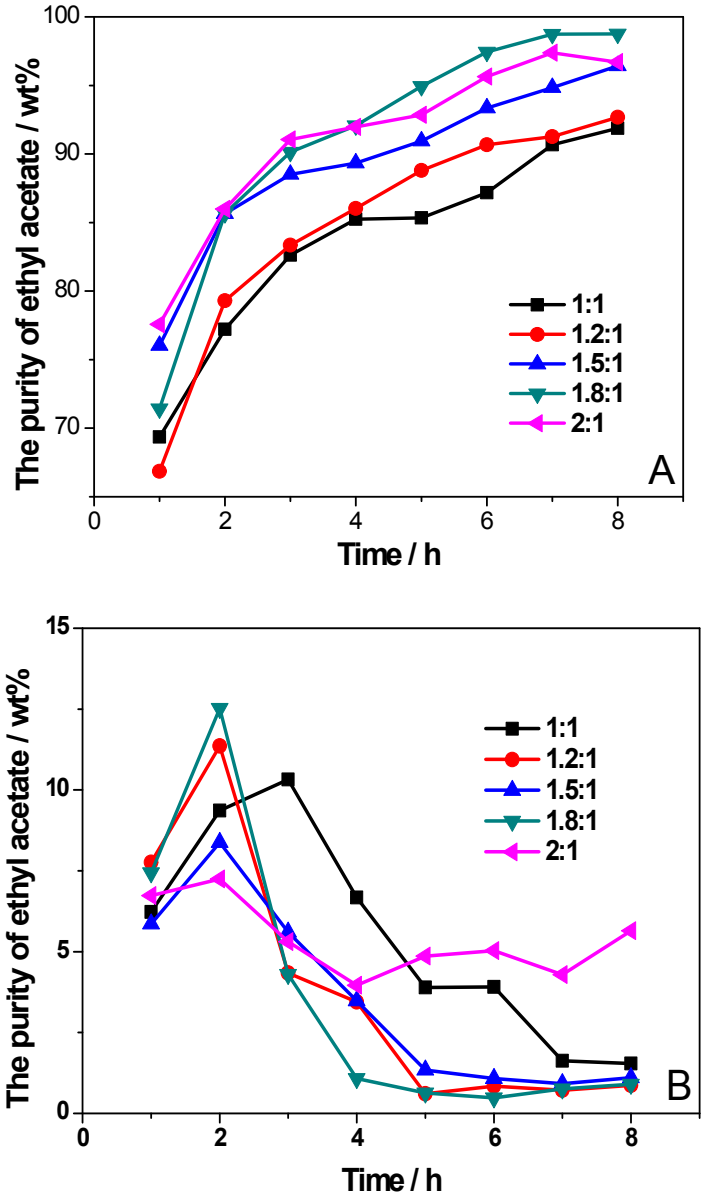


**Figure S2.** Effect of molar ratio of acetic acid to ethanol on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, reflux ratio = 2.5, WHSV = 0.3 $h^{-1}$, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 8.5 mmol $H^+$.

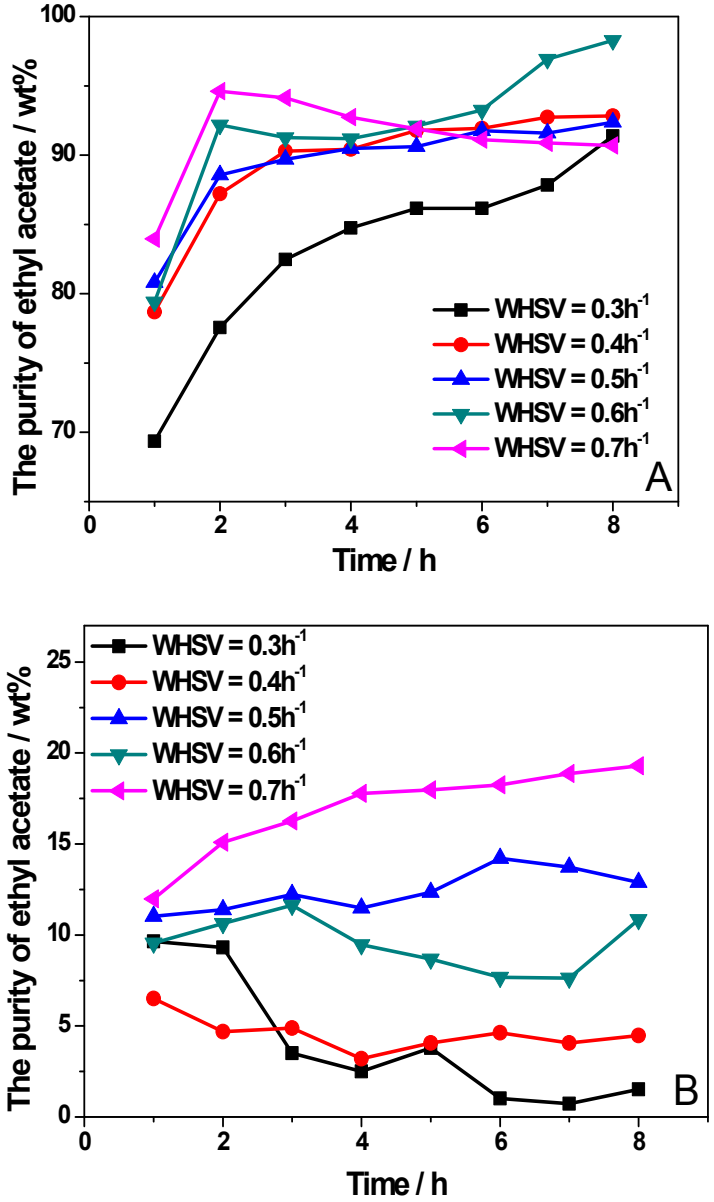


**Figure S3.** Effect of WHSV on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, reflux ratio = 2.5, molar feed ratio of acetic acid to ethanol = 1.2:1, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 8.5 mmol $H^+$.

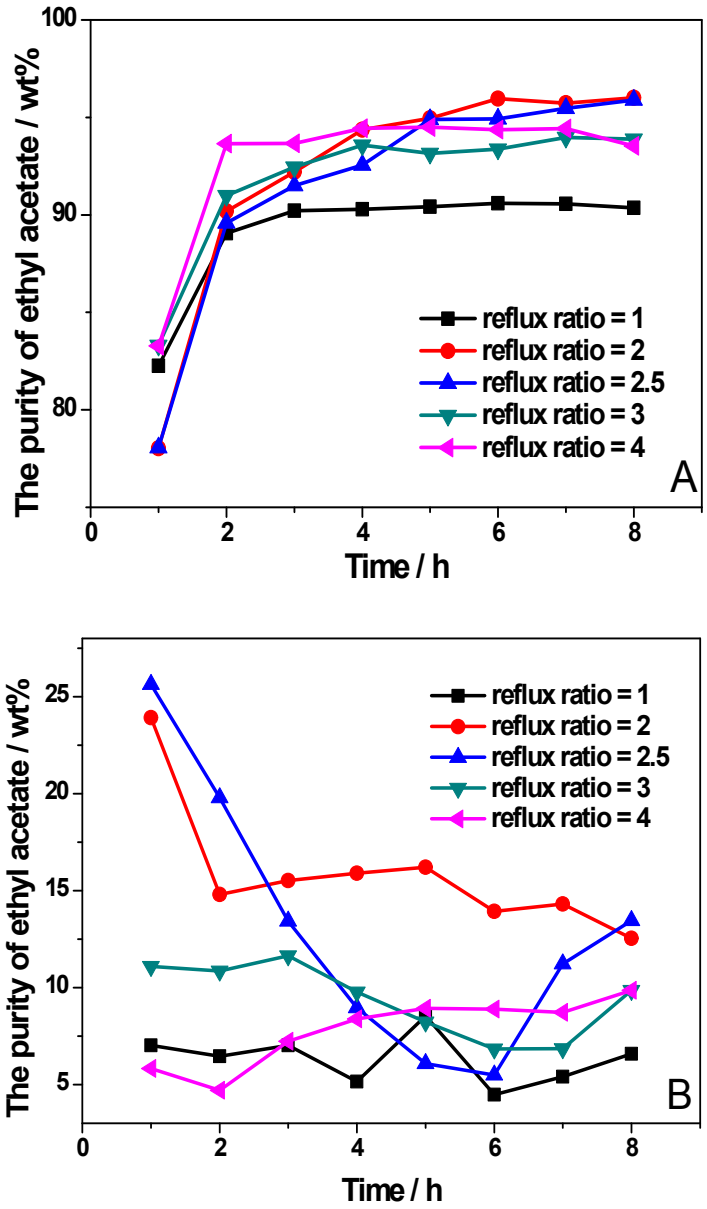


**Figure S4.** Effect of reflux ratio on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, molar feed ratio of acetic acid to ethanol = 1.2:1, WHSV = 0.5 $h^{-1}$, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 10.5 mmol $H^+$.

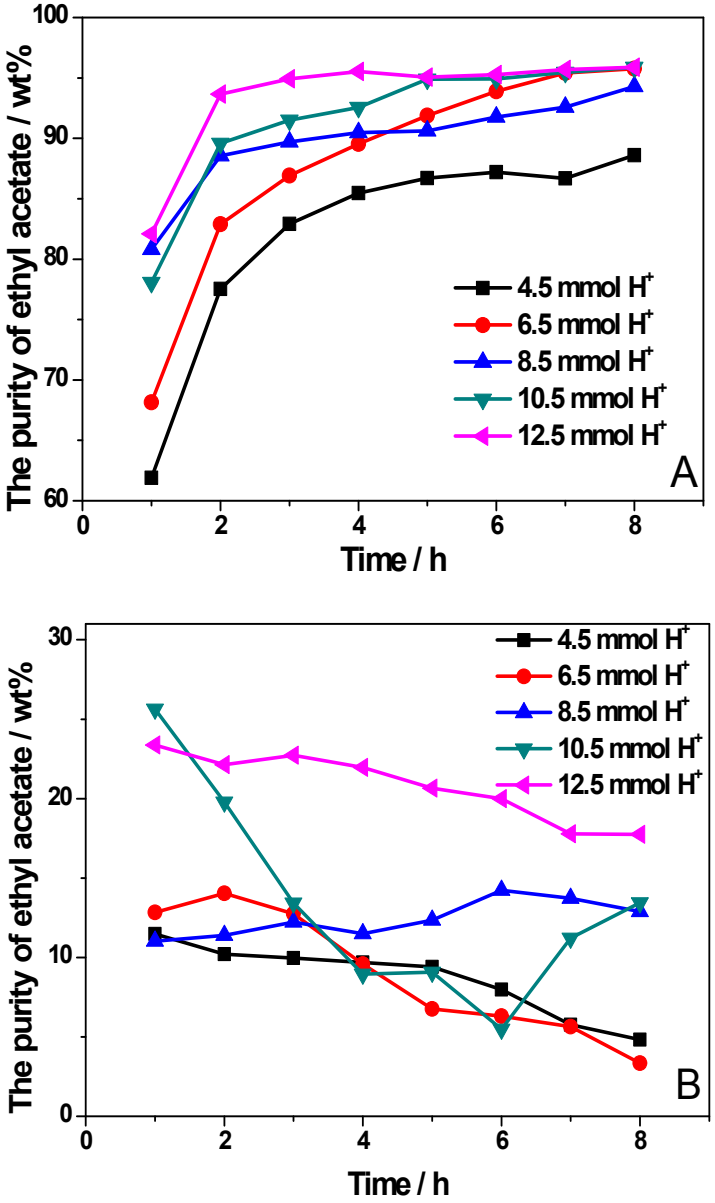


**Figure S5.** Effect of amount of the catalyst on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 $^{o}$C, reflux ratio = 2.5, WHSV = 0.5 $h^{-1}$, molar feed ratio of acetic acid to ethanol = 1.2:1, molar ratio of acetic acid to ethanol in the flask = 1.2:1.

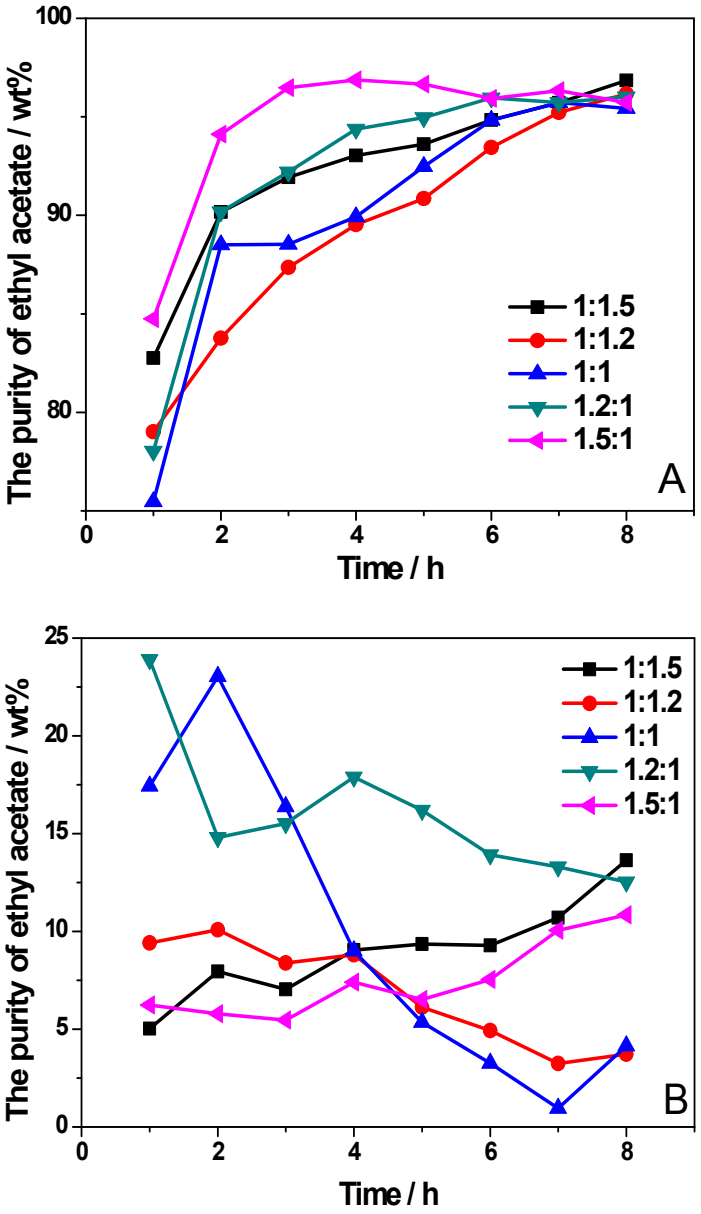


**Figure S6.** Effect of molar ratio of acetic acid to ethanol in the flask on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 $^{o}$C, molar feed ratio of acetic acid to ethanol = 1.2:1, reflux ratio = 2, WHSV = 0.5 $h^{-1}$, catalyst amount = 10.5 mmol $H^{+}$.

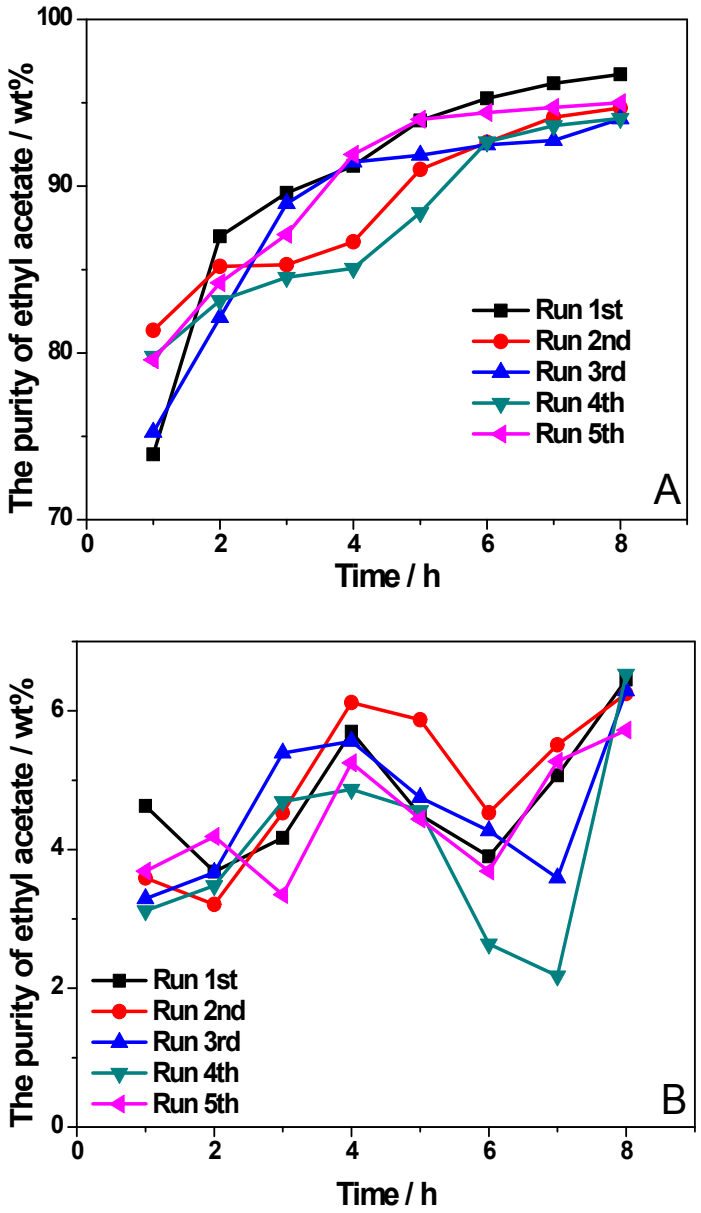


**Figure S7.** The stability test with structured catalyst on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour in five consecutive batch experiments. Reaction conditions: reboiler temperature = 220 $^{o}$C, molar feed ratio of acetic acid to ethanol = 1.2:1, reflux ratio = 2, WHSV = 0.5 $h^{-1}$, catalyst amount = 10.5 mmol $H^{+}$, molar ratio of acetic acid to ethanol in the flask = 1:1.2.