catalysts

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Supplementary Materials

Investigation of the Hβ Molecular Sieve Deactivation Caused By Reactants and Products and Improvement of Continuous Thiophene Acylation

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Part 1 Molecular simulation.

The calculation results of sum of electronic and thermal enthalpies based on different basis set are given in Table S1. The experimental value [28] of $\Delta_f H^\theta$ for each materials (TH, AA, AC and 2-ATH) in the TH acylation reaction are given in Table S2.

Table S1. Calculation results.

Basis set	TH	AC	AA	2-ATH	$\Delta_r H^\theta$ (kJ/mol)
3-21	−550.1119	−379.5146	−227.7454	−701.8782	7.51
6-31	−552.8594	−381.4718	−228.9387	−705.4210	−74.74
6-31+(d,p)	−552.9463	−381.6288	−229.0240	−705.5641	−34.13

Take 6-31+ (d, p) as an example for calculation:

$$\Delta_{r(simulation)} H^\theta = \left((-705.5641 + -229.0240) - (-552.9463 + -381.6288)\right) \times 2622.99 = -34.13\ kJ/mol \quad \text{(S1)}$$

Note: 1 Hartree = 2622.99 kJ/mol.

Table S2. Experimental data.

	TH	AC	AA	2-ATH
$\Delta_f H^\theta$ (kJ/mol)	115.0	−572.5	−432.2	−59.2

$$\Delta_r H^\theta = \left(\Delta_f H^\theta_{2-ATH} + \Delta_f H^\theta_{AC}\right) - \left(\Delta_f H^\theta_{TH} + \Delta_f H^\theta_{AA}\right) = (-432.2 - 59.2) - (115 - 572.5) = -33.9\ kJ/mol \quad \text{(S2)}$$

$$\text{Error} = 1 - \frac{-33.9}{-34.13} = 0.67\% \quad \text{(S3)}$$

Part 2 Batch experiment.

Since the continuous reaction takes a long time, it is first necessary to verify its feasibility when the dosage of TH used is more than that of AC by batch reaction. This reaction is carried out in a three-necked flask. In each experiment, 1 g of Hβ and 20 mL of TH (0.252 mol) is used, and the dosage of AC is determined by different molar ratio (1:0.4, 1:0.5, 1:0.6, 1:0.7 and 1:0.8) to TH. Under different molar ratio conditions, different temperatures (50 °C, 60 °C, 70 °C and 80 °C,) are selected. During the reaction, samples are taken with a syringe every 50 min, and the conversion rate of AC is detected by chromatography.

Figure S1 gives the results of the batch experiment. In order to display all the experimental results in a figure, a 3D graph with color pellet is used. In this figure, the X, Y and Z axis are reaction temperature, molar ratio and reaction time, respectively. Besides, the color represents the conversion rate of AC. It can be found that the longer the reaction

time and the higher the reaction temperature, the higher the conversion rate of the reaction. It is worth noting that the smaller the dosage of AC, the higher the conversion rate of AC. This seems to be a very reasonable experimental result, but the subsequent continuous experiments did not show this trend. In general, it can be found that AC can obtain an ideal conversion rate (more than 80%) in intermittent experiments with excess thiophene, which verifies the feasibility of continuous experiments with excess thiophene.

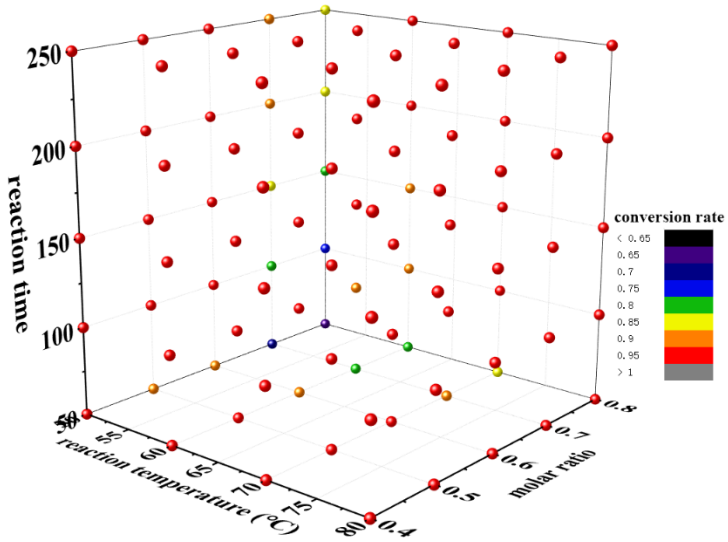

Figure S1. The results of the intermittent experiment.

Part 3 Calculation of void ratio.

First, it must be clear that the void ratio is that the proportion of the void volume of the bulk granular material in the bulk volume. Therefore, considering that the catalyst itself has a porous structure, during the actual measurement of the porosity, the catalyst needs to be saturated by adsorption. The specific operation is to use the reaction solution to soak the molecular sieve for 5 **h**, and then slightly dry until there is no visible liquid on the catalytic surface. Subsequently, a high-pressure constant-flow pump is used to pump the reaction liquid into the reaction tube with volume flowrate of 9 **mL**/min. The amount of catalyst used is 6 g, and it is piled up into a cylinder with a diameter of 18 mm with a height of 85 mm in the reactor.

$$\text{Catalyst volume } (V_1) = \pi \times 0.9^2 \times 8.5 = 21.63 \text{ cm}^3 \quad \text{(S4)}$$

$$\text{Void volume } (V_2) = 9 \times \frac{32}{60} = 4.80ml = 4.80 \text{ cm}^3 \quad \text{(S5)}$$

$$\text{Void ratio } (\varepsilon) = \frac{4.80}{21.63} = 22.19\% \quad \text{(S6)}$$

$$\text{Liquid flow velocity} = \frac{9}{\pi \times 0.9^2 \times 0.2219} = 15.94 \text{ cm/min} \quad \text{(S7)}$$

Part 4 Qualitative comparison of the difficulty of internal diffusion with different molar ratios.

This paper compares the difficulty of internal diffusion qualitatively by comparing the volume of reaction liquid that diffuses into the catalyst at the same residence time with different molar ratios. Table S3 provides the detailed calculation results.

$$\text{Permeated volume of raw materials } (V_3) = \text{Raw material volume } ((V_4)) - \text{Void volume } (V_2) \quad \text{(S8)}$$

$$V_3 = V_4 - V_2 = 0.05 \times 140 - 4.8 = 2.2 \text{ mL} \quad \text{(S9)}$$

$$\text{Permeation velocity} = 2.2 \div 140 = 0.0157 \text{ mL/min} \quad \text{(S10)}$$

Table S3. Comparison of penetration velocity.

Molar ratio	Volume rate (mL/min)	Residence time (min)	Permeation velocity (mL/min)
1:0.4	0.05	135	0.0144
1:0.5	0.05	140	0.0163
1:0.6	0.05	150	0.0180

Part 5 Calculation of apparent flow velocity.

$$\text{Apparent flow velocity } (V_A) = \frac{\text{Volume flowrate } (V_V)}{\text{Cross} - \text{sectional area } (V_C)} \quad \text{(S11)}$$

$$V_C = \pi r^2 \varepsilon = 3.1415 \times 0.9^2 \times 0.2219 = 0.5647 \text{ cm}^2 \quad \text{(S12)}$$

$$V_A = \frac{0.05}{0.5647} = 0.0885 \text{ cm/min} \quad \text{(S13)}$$

Part 6 The effect of different AA dosage on the reaction.

Based on the TH:AC =1:0.5, when the molar ratio of the TH:AA is 1:0, 1:0.1, 1:0.3 and 1:0.5, the production capacity of catalyst is about 21.56 g, 10.09 g, 9.38 g and 10.04 g, respectively. These results indicate that the effect of adding AA is not good. It has a significant inhibitory effect on the continuous reaction, and the inhibitory effect reaches the maximum at the TH:AC:AA=1:0.5:0.3. When the molar ratio of TH, AC and AA increases to 1:0.5:0.5, the production capacity of catalyst shows an increasing trend. At this time, the improvement of the flow situation in the pores of the molecular sieve by AA began to be prominent. Therefore, it is a feasible idea to find a suitable solvent to extend the life of molecular sieve. Figure S2 gives the results.

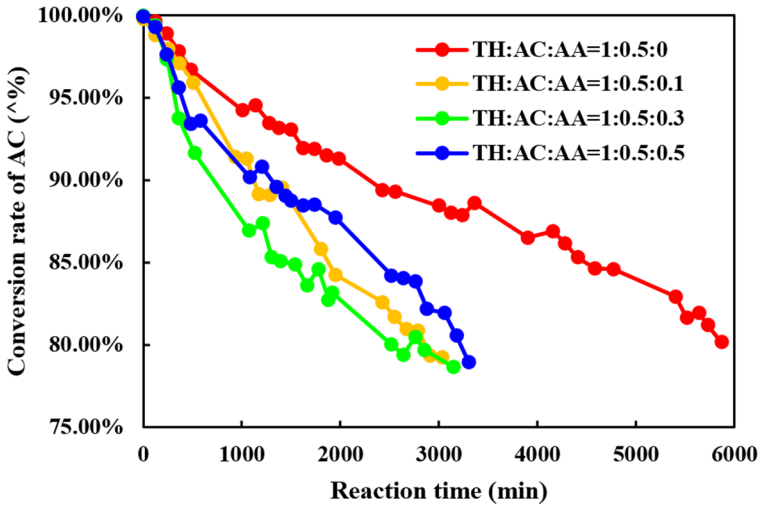

Figure S2. The influence of the AA in the continuous acylation of thiophene.