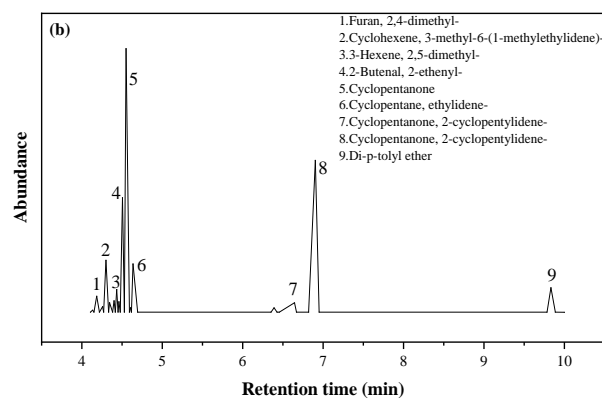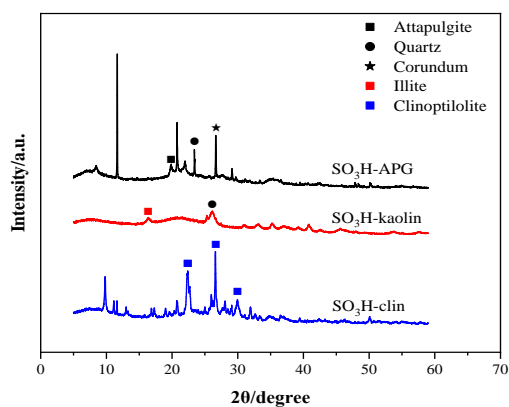# 1 Products Analysis

Figure S1. Main products and TIC diagram of cyclopentanone condensation reaction on SO$_3$H-APG catalyst.

Figure S2. XRD patterns of clay-based catalysts.

2. Response Surface Methodology (RSM) Analysis

From the results of the path of steepest ascent experiment, the values of each factor were determined as 0 mL, 0.8 mL, 1.6 mL, 2.4 mL and 3.2 mL of -SH group loading; the reaction temperatures were 110 °C, 130 °C, 150 °C, 170 °C and 190 °C, and the reaction times were 2 h, 3 h, 4 h, 5 h and 6 h.

Table S1. Optimization of Box-Behnken test factors and levels for C10 yield conditions.

Factors	-1	0	1
X_1 -SH loading/ml	0	1.6	3.2
X_2 reaction temperature/℃	110	150	190
X_3 reaction time/h	2	4	6

Table S2 Optimization of Box-Behnken test results and analysis for C10 yield conditions.

	X1	X2	X3	C10 yield/%
1	0	110	4	26.35
2	3.2	110	4	26.48
3	0	190	4	32.76
4	3.2	190	4	35.68
5	0	150	2	30.03
6	3.2	150	2	31.98
7	0	150	6	34.61
8	3.2	150	6	37.06
9	1.6	110	2	38.36
10	1.6	190	2	30.03
11	1.6	110	6	35.78
12	1.6	190	6	32.41
13	1.6	150	4	59.05
14	1.6	150	4	58.98
15	1.6	150	4	59.03
16	1.6	150	4	59.05
17	1.6	150	4	58.74

Using Design expert V8.0.6 software to fit the data in Table S2, the regression equation S1 was obtained.

$$Y = 58.97 + 0.93X_1 + 0.49X_2 + 1.18X_3 + 0.7X_1X_2 + 0.13X_1X_3 + 1.24X_2X_3 - 14.69X_1^2 - 13.96X_2^2 - 10.86X_3^2$$

(Eq. S1)

Analysis of variance was performed on the above regression equation and the results are tabulated in Table S3.

Table S3 Variance analysis of response surface experiments results.

Variance Source	Square Sum	Degrees of Freedom	Mean Square	F-value	P-value	Salience
Model	2510.42	9	278.9	18.48	0.0004	**
X_1	6.94	1	6.94	0.46	0.0396	*
X_2	1.91	1	1.91	0.13	0.0225	*
X_3	11.19	1	11.19	0.74	0.0479	*
X_1X_2	1.95	1	1.95	0.13	0.7302	
X_1X_3	0.063	1	0.063	0.0041	0.9505	
X_2X_3	6.15	1	6.15	0.41	0.5436	
X_1^2	908.46	1	908.46	60.17	0.0001	**
X_2^2	821.00	1	821.00	54.38	0.0002	**
X_3^2	496.70	1	496.70	32.90	0.0007	**
Residual	105.68	7	15.10			
Proposed item loss	105.61	3	35.20	2029.01	0.0591	
Error term	0.069	4	0.017			
Sum	2616.10	16				

Note: "*" indicates a significant effect on the results (P < 0.05); "**" indicates a highly significant effect on the results (P < 0.01).

**Table S4** Ammonia and carbon dioxide desorption activation energy (DAE).

	CO$_2$ E_d (kJ/mol)				NH$_3$ E_d (kJ/mol)	
	Yang		Hu		Yang	Hu
	0-150°C	150-450°C	0-150°C	150-450°C		
APG	9.88	36.38	12.37	36.29	25.52	18.34
SO$_3$H-APG	10.48	25.73	22.61	44.11	23.72	20.99
SO$_3$H-kaolin	-	-	-	-	17.89	24.65
SO$_3$H-clin	-	-	-	-	13.72	14.09

Table S5 Physiochemical properties of catalysts.

|	CO_2 E_d (kJ/mol)				NH_3 E_d (kJ/mol)	
	Yang		Hu		Yang	Hu
	0-150°C	150-450°C	0-150°C	150-450°C		
APG	9.88	36.38	12.37	36.29	25.52	18.34
SO₃H-APG	10.48	25.73	22.61	44.11	23.72	20.99
SO₃H-kaolin	-	-	-	-	17.89	24.65
SO₃H-clin	-	-	-	-	13.72	14.09

3. Reaction Kinetic Analysis
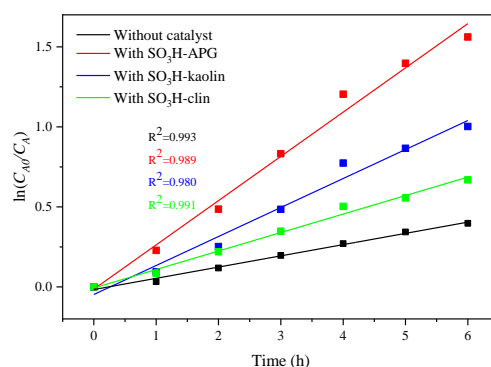
Figure S3. The kinetic plots for the cyclopentanone aldol condensation.

According to the Arrhenius equation: $k = k_0 \cdot e^{\left(-\frac{E}{RT}\right)}$, take the logarithm to get $\ln k = \ln k_0 - \frac{E}{RT}$, make the graph of $\ln k - \frac{1}{T}$, the slope is $-\frac{E}{R}$, and the intercept is $\ln k_0$.

Table S6 The reaction rate constants k at different temperatures.

| T/°C	130	150	170
k	0.5470	0.4949	0.4677
$\frac{1}{T}$/K⁻¹	0.00248	0.00236	0.00226
$\ln k$	-0.6033	-0.7034	-0.7599
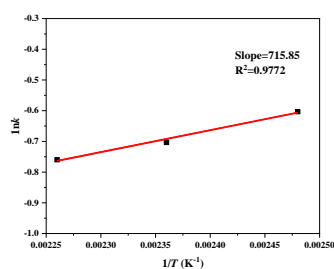
Figure S4. The Arrhenius equation curve.

From the calculation, we could get $E = -(715.85) * 8.314 = 5952$ J/mol;

k_0=0.093.

The reaction rate constant was $k=0.093e^{(-\frac{5952}{RT})}$, and the reaction rate equation was $r_A=0.093e^{(-\frac{5952}{RT})}c_A$.

4. Modelling of cyclopentanone adsorption

Cyclopentanone adsorption on SO₃H-APG catalyst was simulated by VASP. Sulfur atom got electron from cyclopentanone to build a stable chemisorption that would be conformed via DFT calculation. Adsorption energy $E_{ad} = E_{tot} - (E_{sub} + E_{mol})$ was computed to determine the strength of reactant molecule adsorbed on the SO₃H-APG catalyst, where E_{tot}, E_{sub}, and E_{mol}, referred to the total energy of the combined system, the substrate alone and the adsorbate in the gas phase, respectively. And the E_{ad} was got as -0.511948 eV which was indicated a exothermal adsorption of cyclopentanone. Electron density increasing of the adsorbate will facilitate its activation and further condensation.
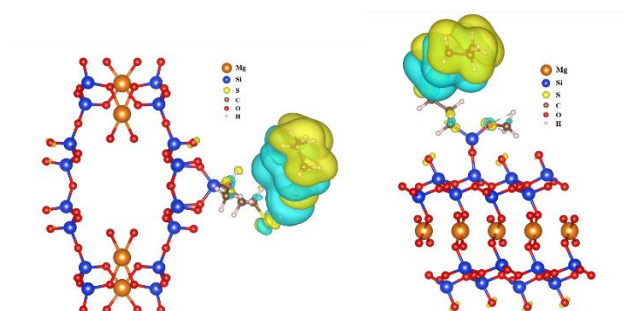
Figure S5. Charge density differences of cyclopentanone adsorption on SO₃H-APG catalyst.

Blue and yellow areas represent electron accumulation and depletion, respectively. Atom

color: S-yellow, C-brown, O-red, and H-white.