

# Supporting Information

## **Ion-Exchanging Fabrication of Hierarchical Al-MOF based Resin Catalysts for the Tandem Reaction**

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**Figure S1.** The optical microscope photographs of resins before and after OH<sup>-</sup> ions exchange. (a) Amberlite IRA900(Cl); (b) IRA900(0.05OH); (c) IRA900(0.1OH); (d) IRA900(0.2OH); (e) IRA900(0.3OH); (f) the particle-size distribution of IRA900(0.2OH) with the average particle size of 1 μm.

**Figure S2.** The XRD patterns of IRA-900(Cl/xOH)-MIL-101(Al)-NH<sub>2</sub>.

**Figure S3.** (a) The ATR-FTIR spectrums of resins before and after OH<sup>-</sup> ions exchange with different concentration of NaOH; (b) The ATR-FTIR spectrums of IRA-900(Cl/xOH) resins before and after NH<sub>2</sub>-BDC ligands ions exchange; (c) A partial enlargement of FTIR spectrum with a range from 4000-2500 cm<sup>-1</sup>; (d) The ATR-FTIR spectrums of a series of IRA-900(xOH)-MIL-101(Al)-NH<sub>2</sub> resins.

**Figure S4.** Photos of resin Amberlite IRA900(Cl) in different concentrations of sodium hydroxide solution, 1 : 0.05 mol/L, 2 : 0.1 mol/L, 3 : 0.2 mol/L and 4 : 0.3 mol/L, respectively.

**Figure S5.** Time dependence of reaction yields for the Knoevenagel condensation reaction by different catalysts.

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**Figure S7.** A photo (a) and SEM images (b - f) of IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub> after 5 times catalytic reactions.

**Figure S8.** The XRD patterns of IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub> and after 5 times catalytic reactions.

**Figure S9.** The leaching test of IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub>.

## **5. Reference**

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## 1. Materials and Reagents

Resin Amberlite IRA900(Cl) (IRA900(Cl) chloride-form anion exchange resin), 2-Aminoterephthalic acid ( $\text{H}_2\text{BDC-NH}_2$ ,  $\text{C}_8\text{H}_7\text{NO}_4$ , 99%) was purchased from Shanghai Titan Scientific Co. Ltd. (Shanghai, China). Aluminium chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 97%) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Sodium hydroxide (NaOH, 98%) was obtained from Energy Chemical Co. Ltd. (Shanghai, China). N, N'-dimethylformamide (DMF,  $\text{C}_3\text{H}_7\text{NO}$ , 99.5%) and malonitrile ( $\text{C}_3\text{H}_2\text{N}_2$ , 99%) were acquired from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). Ethanol (EtOH,  $\text{CH}_3\text{CH}_2\text{OH}$ , 99.7%) and toluene ( $\text{C}_7\text{H}_8$ , 99.5%) were obtained from Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjin, China). Benzaldehyde dimethyl acetal ( $\text{C}_8\text{H}_{12}\text{O}_2$ , 98%) was purchased from Energy Chemical Co. Ltd. (Shanghai, China). The internal standard substance ethylbenzene ( $\text{C}_8\text{H}_{10}$ , 99.5%) was acquired from Inno-chem (Beijing, China). Unless otherwise stated, all reagents were of analytical grade and were used as supplied without further purification. The solvents were dried with molecular sieve before use. In addition, the method of synthesis MIL-101(Al)- $\text{NH}_2$  was modified according to the literature.<sup>S2</sup>

## 2. Catalytic Reactions

The one-pot deacetalization-Knoevenagel condensation reaction was conducted in a round-bottom flask equipped with a temperature controller and magnetic drive. The reaction studied were performed at 110 °C under an autogenous pressure. In a typical process, 0.2 g catalyst together with a mixture of benzaldehyde dimethyl acetal (1.0 mmol), malononitrile (1.5 mmol), and internal standard ethylbenzene (100 µL) were firstly put into the reactor, then 3 mL methylbenzene solvent was added with continually stirring. The reaction was sampled for a period time with a pipette, and the liquid was centrifuged (12000 r/min, 5min). The supernatant was analyzed by gas chromatography (Agilent 7820A) equipped with FID and Agilent 6980 inert XL MSD (GC-MS). The conversion was calculated based on the consumption of benzaldehyde dimethyl acetal using the equation.<sup>1</sup>

Equation 1:

The conversion of reactant (%) =

$$\left[ \frac{\left( \frac{\text{area of reactant at 0 hour}}{\text{area of internal standard at 0 hour}} \right) - \left( \frac{\text{area of reactant at any time}}{\text{area of internal standard at any time}} \right)}{\frac{\text{area of reactant at 0 hour}}{\text{area of internal standard at 0 hour}}} \right] \times 100\%$$

### 3. Table

**Table S1.** The structure parameters of different samples.

Sample	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ ) <sup>a</sup>	$V_{\text{pore}}$ ( $\text{cm}^3\text{g}^{-1}$ ) <sup>b</sup>	$D_{\text{pore}}$ (nm) <sup>b</sup>
IRA900(Cl)	9.82	0.050	2.50
IRA900(0.2OH)-MIL-101(Al)-NH <sub>2</sub>	60.40	0.230	3.84

<sup>a</sup> Specific surface area measured by N<sub>2</sub> adsorption at 77 K and calculated by the Brunauer-Emmett-Teller plot. <sup>b</sup> Measured by the BJH desorption method.

**Table S2.** The concentration of all MOF supported resin catalysts obtained by ICP measurement.

Sample	Al/mg/L	MIL-101(Al)-NH <sub>2</sub> /wt%	The amount of MOFs in 200 mg/mg
IRA900(Cl)-MIL-101(Al)-NH <sub>2</sub>	6.100	1.075	2.15
IRA900(0.05OH)-MIL-101(Al)-NH <sub>2</sub>	25.107	4.425	8.85
IRA900(0.1OH)-MIL-101(Al)-NH <sub>2</sub>	29.177	5.179	10.36
IRA900(0.2OH)-MIL-101(Al)-NH <sub>2</sub>	38.201	6.776	13.55
IRA900(0.3OH)-MIL-101(Al)-NH <sub>2</sub>	19.559	3.449	6.90
IRA900(0.2OH)-MIL-101(Al)-NH <sub>2</sub> -cat	31.351	5.525	11.05

\* IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub>-cat stands for IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub> after 5 times catalysis reaction.

**Table S3.** Catalytic activities of one-pot tandem deacetalization-Knoevenagel condensation reaction over various catalysts. <sup>a</sup>

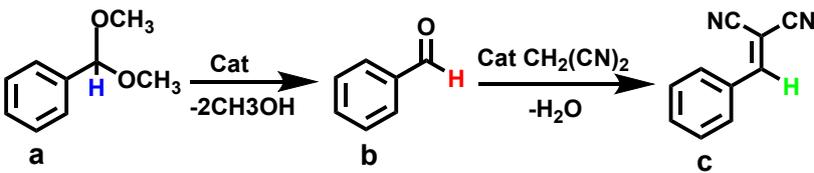
Sample	%Conversion of Benzaldehyde Dimethyl Acetal <sup>b</sup>	%Yield of Benzaldehyde <sup>c</sup>	%Yield of 2-benzylidene-nemalonitrile <sup>c</sup>
IRA900(Cl)	10.2	trace	10.2
IRA900(Cl)-MIL-101(Al)-NH <sub>2</sub>	47.4	trace	47.4
IRA900(0.05OH)-MIL-101(Al)-NH <sub>2</sub>	62.6	trace	62.6
IRA900(0.1OH)-MIL-101(Al)-NH <sub>2</sub>	73.9	trace	73.9
IRA900(0.2OH)-MIL-101(Al)-NH <sub>2</sub>	100	trace	100
IRA900(0.3OH)-MIL-101(Al)-NH <sub>2</sub>	50.6	trace	50.6
No catalyst	trace	trace	trace

<sup>a</sup> Reaction condition: 0.2 g catalysts, 1 mmol benzaldehyde dimethyl acetal and 100  $\mu\text{L}$  ethylbenzene as internal standard in a 3 mL of methylbenzene solvent. The reactions were conducted for 5 hours at 110°C.

<sup>b</sup> The calculation of % Conversion was calculated by using the equation 1.

<sup>c</sup> The calculation of Yield was [(area of the desired product)/(area of overall product)]  $\times$  100%

**Table S4.** Comparison of one-pot deacetalization-Knoevenagel condensation reaction catalyzed by various catalysts.



Entry	Catalyst	Conv. of <b>a</b> ( % )	Yield of <b>b</b> ( % )	Yield of <b>c</b> ( % )	Ref.
1	IRA900(0.2OH)-MIL-101(Al)-NH <sub>2</sub> <sup>a</sup>	100	Trace	100	This work
2	MIL-101(Al)-NH <sub>2</sub> <sup>b</sup>	100	6.0	94.0	S2
3	MIL-101(Cr)-NH <sub>2</sub> <sup>b</sup>	86	2	84	S2
4	AMSA- MIL-101-NH <sub>2</sub> <sup>c</sup>	100	Trace	100	S3
5	UiO-66@SNW-1 <sup>d</sup>	99.6	Trace	99.6	S4
6	PCN-124 <sup>e</sup>	100	Trace	100	S5
7	PCN-222-Co@TpPa-1 <sup>f</sup>	99.3	Trace	99.3	S6
8	Yb-BCD-NH <sub>2</sub> <sup>g</sup>	97.0	Trace	97.0	S7
9	Dy-BCD-NH <sub>2</sub> <sup>g</sup>	82.0	Trace	82.0	S7
10	Sm-BCD-NH <sub>2</sub> <sup>g</sup>	76.0	Trace	76.0	S7
11	ZIF8-A61-SO <sub>3</sub> H <sup>h</sup>	100	2.0	98.0	S8
12	MIL-53(Al) <sup>b</sup>	14	9	5	S2
13	Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	14.0	1.0	3.0	S2
14	HY-zeolite <sup>b</sup>	88.9	79.0	9	S2
15	SO <sub>3</sub> H-AA@MNP <sup>i</sup>	-	-	94.0	S9
16	BNP-2.1 <sup>j</sup>	100	1.5	98.5	S10

Reaction conditions:

<sup>a</sup> benzaldehyde dimethylacetal (1.0 mmol), malononitrile (1.5 mmol), toluene (3 mL), catalyst (200 mg), 110 °C and 5 h.

<sup>b</sup> benzaldehyde dimethylacetal (1.0 mmol), malononitrile (5.0 mmol), 1,4-dioxane (4 mL), catalyst (100 mg), 90 °C and 3 h.

<sup>c</sup> benzaldehyde dimethylacetal (5.0 mmol), malononitrile (6.0 mmol), toluene (10 mL), catalyst (80 mg), 90 °C and 10 h.

<sup>d</sup> benzaldehyde dimethylacetal (2.0 mmol), malononitrile (2.1 mmol), DMSO-d<sub>6</sub> (2 mL), catalyst (50 mg), 80 °C and 12 h.

<sup>e</sup> benzaldehyde dimethylacetal (2.0 mmol), malononitrile (2.1 mmol), DMSO-d<sub>6</sub> (3 mL), catalyst (6 mg), 50 °C and 12 h.

<sup>f</sup> benzaldehyde dimethylacetal (0.1 mmol), malononitrile (0.11 mmol), DMSO-d<sub>6</sub> (2 mL), catalyst (5 mg), 50 °C and 10 h.

<sup>g</sup> benzaldehyde dimethylacetal (2.0 mmol), malononitrile (2.1 mmol) and DMSO-d<sub>6</sub> (2 mL), catalyst (100 mg), 50 °C and 24 h.

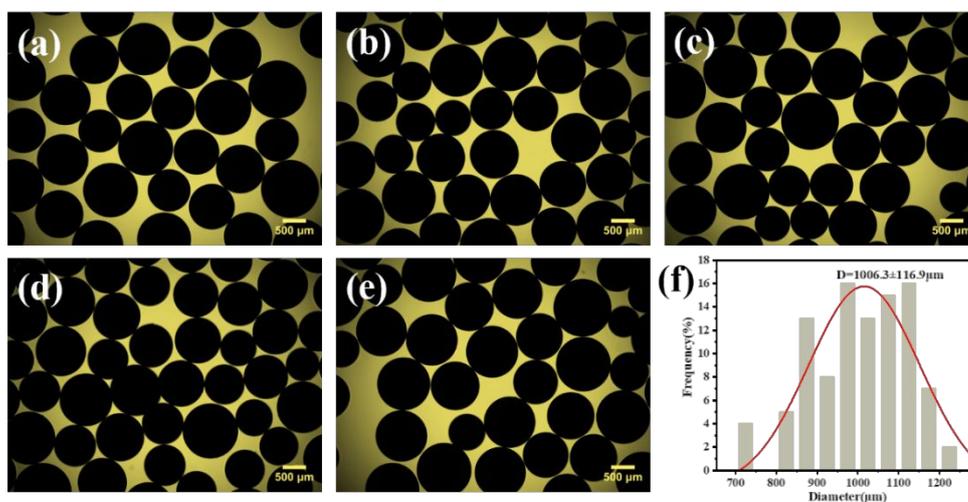
<sup>h</sup> benzaldehyde dimethylacetal (4.0 mmol), malononitrile (4.2 mmol), 1,4-dioxane (4 mL), H<sub>2</sub>O (0.5 mL), catalyst (100 mg), 90 °C and 4 h.

<sup>i</sup> benzaldehyde dimethylacetal (2.0 mmol), malononitrile (2.1 mmol), H<sub>2</sub>O (0.2 mmol), toluene (20 mL), catalyst (20

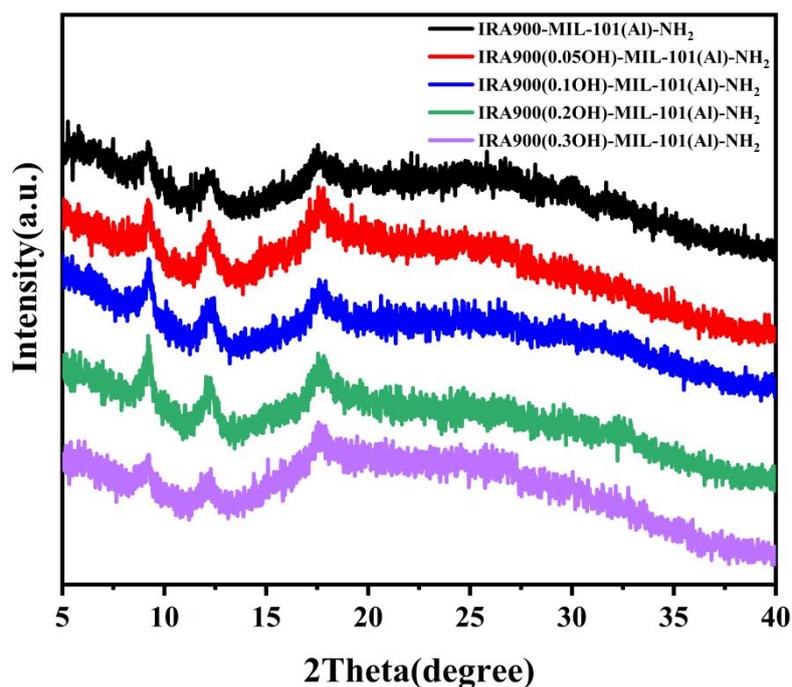
mg), 90 °C and 2 h.

*j* benzaldehyde dimethylacetal (2.5 mmol), malononitrile (3.0 mmol), toluene (20 mL), catalyst (100 mg), 80 °C and 24 h.

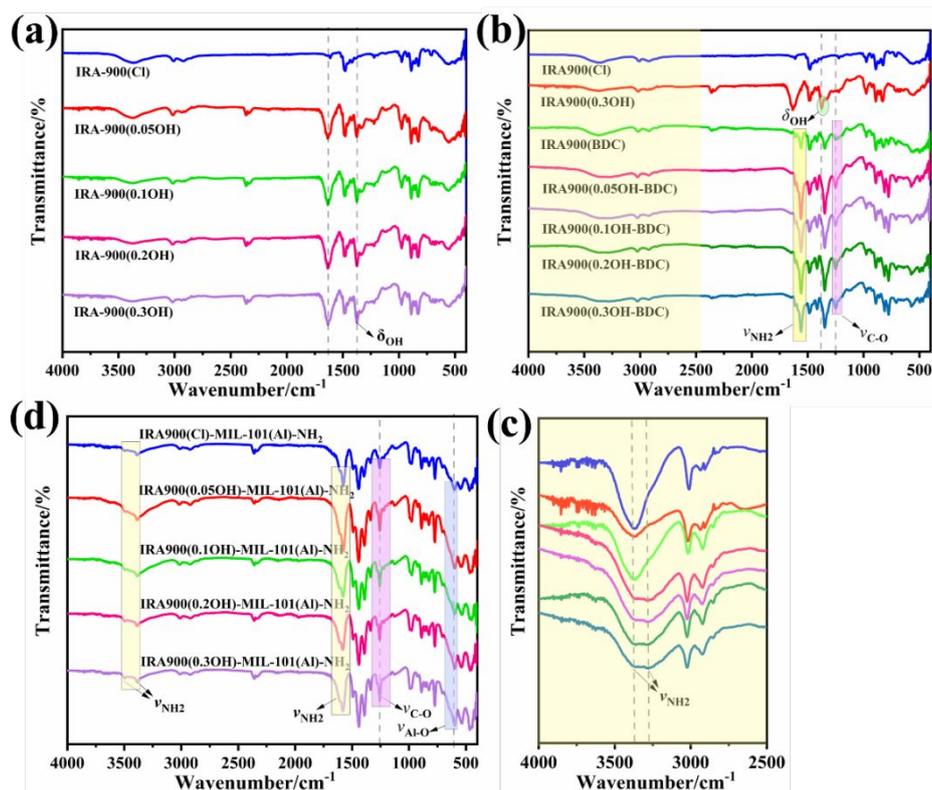
#### 4. Figure



**Figure S1.** The optical microscope photographs of resins before and after OH<sup>-</sup> ions exchange. (a) Amberlite IRA900(Cl); (b) IRA900(0.05OH); (c) IRA900(0.1OH); (d) IRA900(0.2OH); (e) IRA900(0.3OH); (f) the particle-size distribution of IRA900(0.2OH) with the average particle size of 1 mm.



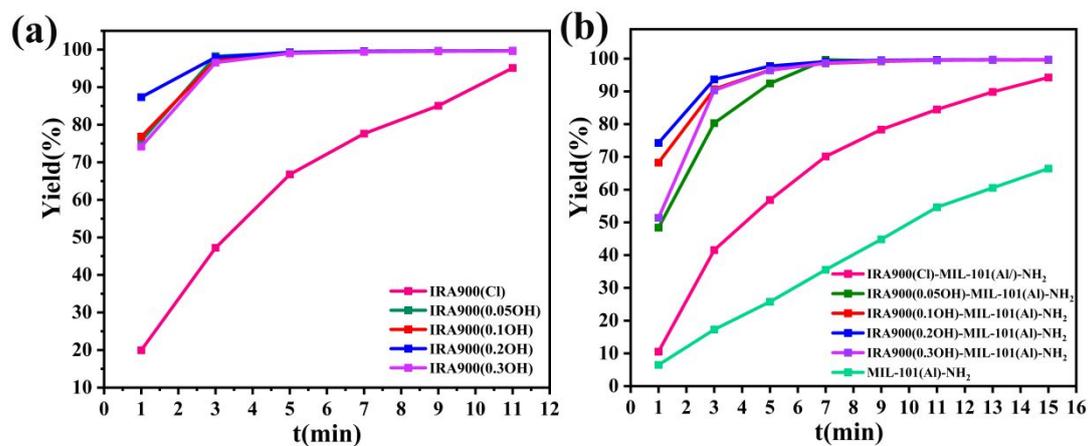
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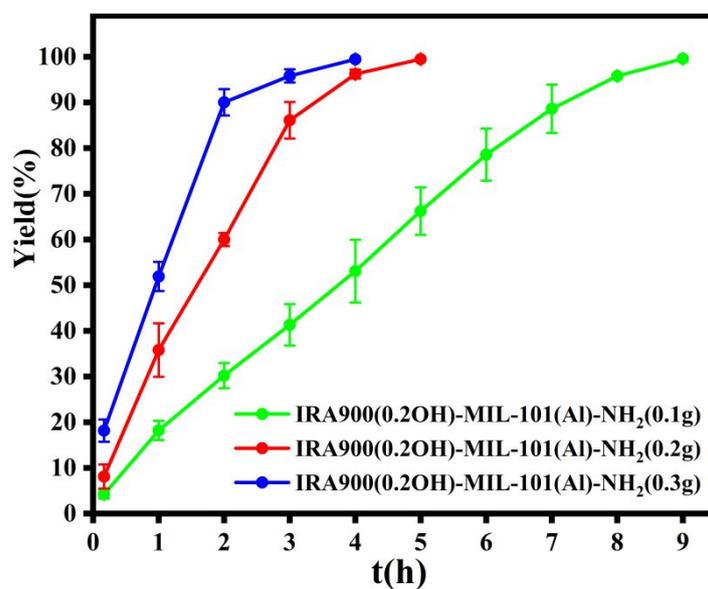
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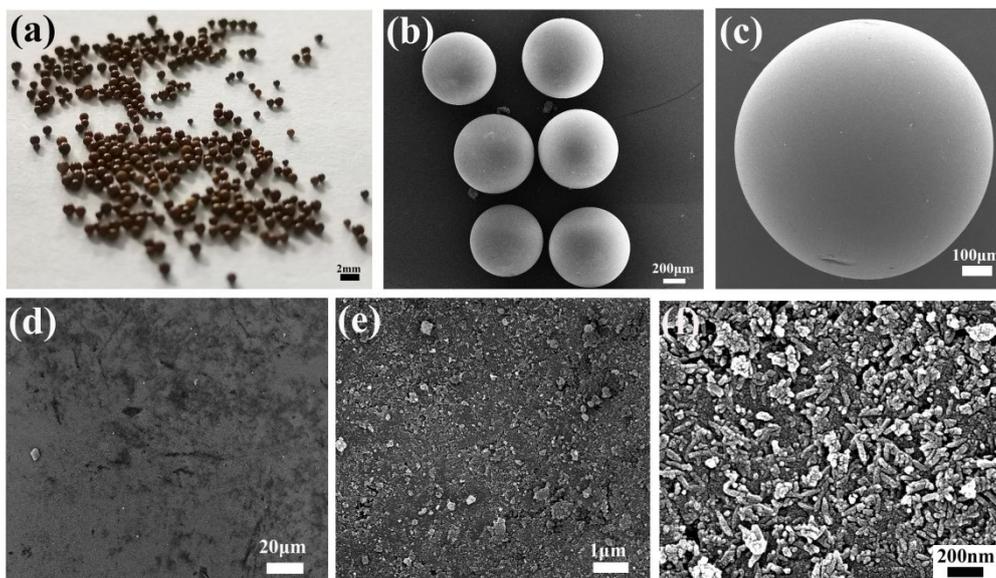
**Figure S4.** Photos of resin Amberlite IRA900(CI) in different concentrations of sodium hydroxide solution, 1 : 0.05 mol/L, 2 : 0.1 mol/L, 3 : 0.2 mol/L and 4 : 0.3 mol/L, respectively.



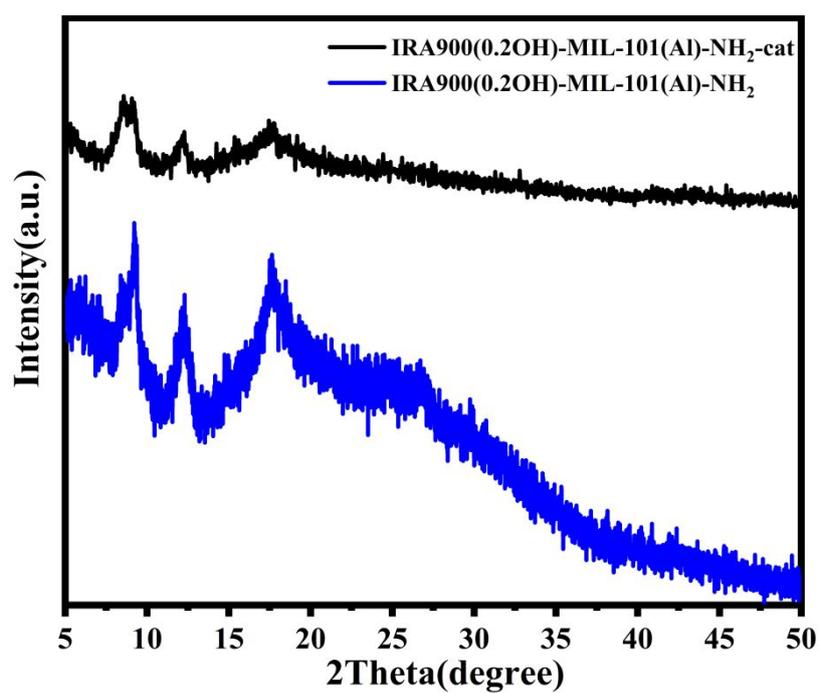
**Figure S5.** Time dependence of reaction yields for the Knoevenagel condensation reaction by different catalysts.



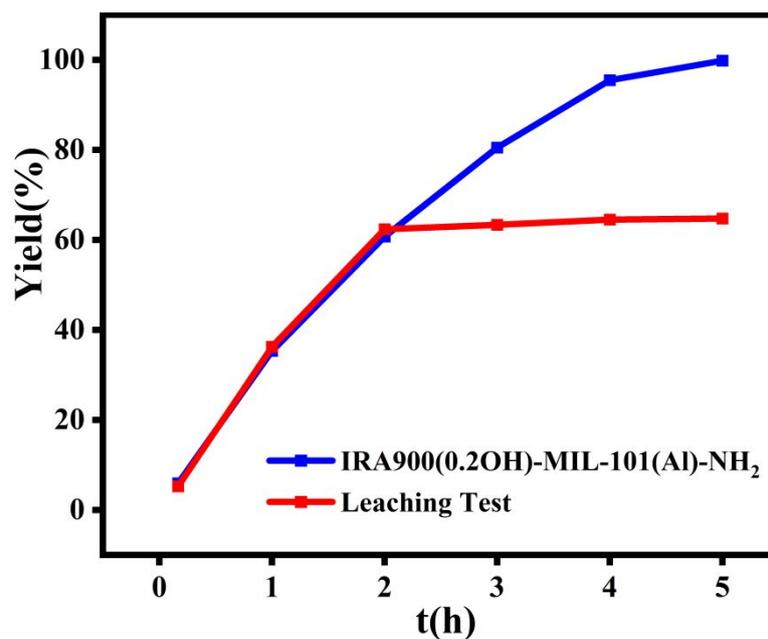
**Figure S6.** Time dependence of reaction yield for the cascade reaction of different amount of IRA900(0.2OH)-MIL-101(AI)-NH<sub>2</sub>.



**Figure S7.** A photo (a) and SEM images (b - f) of IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub> after 5 times catalytic reactions.



**Figure S8.** The XRD patterns of IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub> and after 5 times catalytic reactions.



**Figure S9.** The leaching test of IRA900(0.2OH)-MIL-101(Al)-NH<sub>2</sub>.

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