

Supporting Information

Sulfonic acid-modified MOFs as heterogeneous bifunctional catalysts for ethylene oligomerization at room temperature without cocatalysts

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2. Figures and Tables

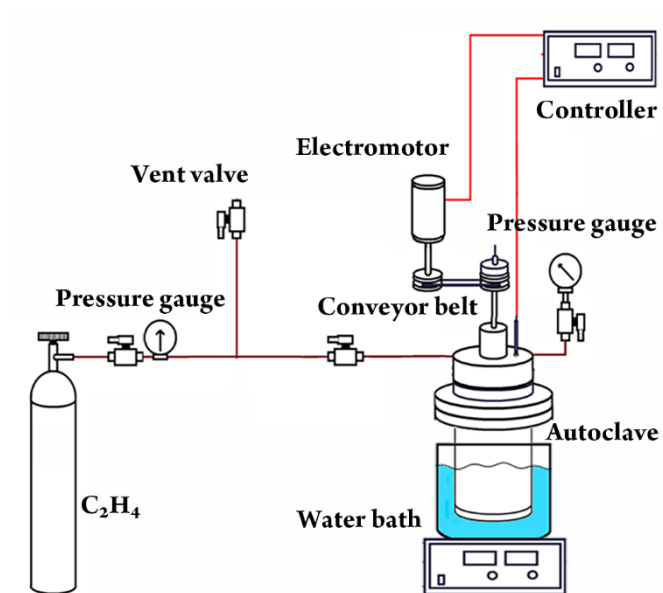


Fig. S1. Schematic diagram of the ethylene dimerization reactor.

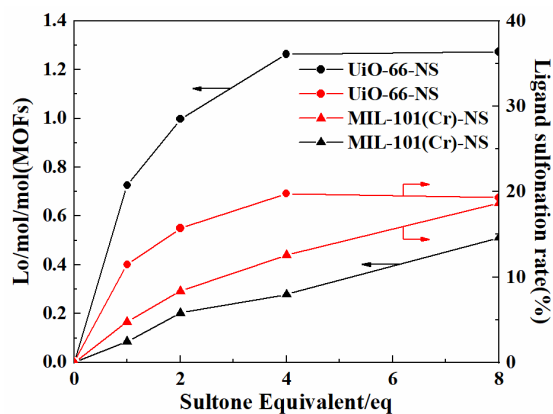


Fig. S2. The loading amounts and the ligand sulfonation rates of UiO-66-NS_x and MIL-101(Cr)-NS_x

With the increase of propanesultone equivalent, the sulfonation rate of ligands also increases. When the equivalent of propanesultone reaches 4eq, the sulfonation rate of UiO-66-NS₄ reaches saturation, and the maximum sulfonation rate is about 20%. The sulfonation rate of MIL-101(Cr)-NS is slower than that of UiO-66-NS. When the equivalent of propanesultone reaches 8eq, the sulfonation rate of MIL-101(Cr)-NS₈ is close to 20%. The coordination number of ligands on the metal center of UiO-66 is 6, while that of MIL-101 (Cr) is 3. Therefore, at the same sulfonation rate, the loading amount of UiO-66-NS in the repeating unit is twice than that of MIL-101(Cr)-NS.

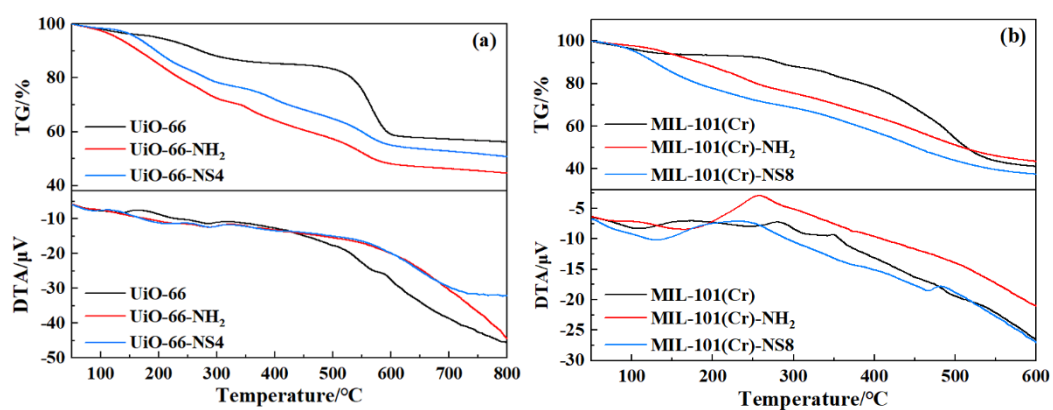


Fig. S3. TGA and DTA curves of (a) UiO-66-NS and (b) MIL-101(Cr)-NS.

Table S1. The effect of the SA concentration on catalytic performance of SA/MIL-101(Cr).^a

Cat.	SA/% ^b	Activity/ g/(mol(cat.)·h)	Selectivity/%		
			C ₆	C ₈	C ₁₀₊
SA	-	0	0	0	0
MIL-101(Cr)	-	2205	38.66	48.59	12.75
10SA/MIL-101(Cr)	10	11489	10.16	67.70	22.15
30SA/MIL-101(Cr)	30	9761	4.45	78.51	17.04
50SA/MIL-101(Cr)	50	8292	2.04	88.54	9.42
70SA/MIL-101(Cr)	70	5544	0	77.41	22.59
90SA/MIL-101(Cr)	90	6976	7.58	89.52	2.90

^aReaction conditions: catalyst 10 μ mol (based on the MOFs), 25 °C, 1 MPa, 1 h, toluene as solvent, GC measurement. ^bThe concentration of aqueous solution of SA, n(SA)/n(MIL-101(Cr)).

Table S2. The effect of the sultone equivalent on catalytic performance of UiO-66-NS.^a

Cat.	Sultone equivalent/eq ^b	Activity/ g/(mol(cat.)·h)	Selectivity/%			
			C ₄	C ₆	C ₈	C ₁₀₊
UiO-66	-	940	19.48	51.53	28.99	0
UiO-66-NH ₂	-	943	10.34	52.88	36.78	0
UiO-66-NS1	1	3046	0	23.47	56.38	20.15
UiO-66-NS2	2	9041	0	1.43	79.65	18.92
UiO-66-NS4	4	13472	0	10.11	68.01	21.88
UiO-66-NS8	8	11105	0	2.56	63.82	33.62

^aReaction conditions: catalyst 10 μmol (based on the MOFs), 25 °C, 1 MPa, 1 h, toluene as solvent, GC measurement. ^bThe concentration of aqueous solution of 1,3-propanesultone, n(sultone)/n(UiO-66-NH₂).

Table S3. The effect of the sultone equivalent on catalytic performance of MIL-101(Cr)-NS.^a

Cat.	Sultone equivalent/eq	Activity/ g/(mol(cat.)·h)	Selectivity/%		
			C ₆	C ₈	C ₁₀₊
MIL-101(Cr)	-	2205	38.66	48.59	1275
MIL-101(Cr)-NH ₂	-	2485	39.77	32.40	27.83
MIL-101(Cr)-NS1	1	2212	3.86	96.14	0
MIL-101(Cr)-NS2	2	2620	16.87	83.13	0
MIL-101(Cr)-NS4	4	4211	7.67	68.63	23.70
MIL-101(Cr)-NS8	8	9010	27.14	43.43	29.43

^aReaction conditions: catalyst 10 μmol (based on the MOFs), 25 °C, 1 MPa, 1 h, toluene as solvent, GC measurement. ^bThe concentration of aqueous solution of 1,3-propanesultone, n(sultone)/n(MIL-101(Cr)-NH₂).

Table S4. The effects of the reaction temperature and the ethylene pressure on catalytic performance of SA/MIL-101(Cr).^a

Reaction temperature/°C	Ethylene pressure/MPa	Activity/ g/(mol(cat.)·h)	Selectivity/%		
			C ₆	C ₈	C ₁₀₊
25	0.5	16127	2.95	48.31	48.75
25	1	11489	10.16	67.70	22.15
25	1.5	3413	0	74.40	25.6
15	1	21953	3.42	70.32	26.26
35	1	7501	19.48	57.69	22.83

^aReaction conditions: catalyst: 10SA/MIL-101(Cr), 10 μmol (based on the MOFs), 1 h, toluene as solvent, GC measurement.

Table S5. The effects of the reaction temperature and the ethylene pressure on catalytic performance of UiO-66-NS.^a

Reaction temperature/°C	Ethylene pressure/MPa	Activity g/(mol(cat.)·h)	Selectivity/%		
			C ₆	C ₈	C ₁₀₊
15	1	980	46.60	44.62	8.78
20	1	1197	29.32	64.62	5.76
25	1	13472	10.11	68.01	21.88
30	1	7923	1.81	25.19	73.00
35	1	2977	13.05	13.70	73.25
25	0.5	3665	6.87	91.55	1.58
25	0.75	7406	1.66	72.29	26.05
25	1.25	20853	3.79	24.69	71.52
25	1.5	25128	4.37	5.53	90.10

^aReaction conditions: catalyst: UiO-66-NS4, 10 μ mol (based on the MOFs), 1 h, toluene as solvent, GC measurement.

Table S6. The effects of the reaction temperature and the ethylene pressure on catalytic performance of MIL-101(Cr)-NS.^a

Reaction temperature/°C	Ethylene pressure/MPa	Activity/ g/(mol(cat.)·h)	Selectivity/%		
			C ₆	C ₈	C ₁₀₊
15	1	1103	92.26	0	7.74
20	1	4486	11.94	40.49	47.57
30	1	6095	3.28	91.66	5.07
25	1	9010	27.14	43.43	29.43
35	1	775	18.30	79.11	2.58
25	0.5	248	28.66	71.34	0
25	0.75	1896	32.98	45.77	21.26
25	1.25	9466	10.15	2.58	87.27
25	1.5	17353	2.58	25.66	71.76

^aReaction conditions: catalyst: MIL-101(Cr)-NS8, 10 μmol (based on the MOFs), 1 h, toluene as solvent, GC measurement.

Table S7. The effects of the reaction time on catalytic performance of SA/MIL-101(Cr).^a

Reaction time/h	Activity/g/(mol(cat.)·h)	Selectivity/%		
		C ₆	C ₈	C ₁₀₊
0.5	9847	1.99	72.61	25.40
1	11489	10.16	67.70	22.15
1.5	2599	9.42	29.06	61.53

^aReaction conditions: catalyst: 10SA/MIL-101(Cr), 10 μmol (based on the MOFs), 25 °C, 1 MPa, toluene as solvent, GC measurement.

Table S8. The effects of the reaction time on catalytic performance of UiO-66-NS.^a

Reaction time/h	Activity g/(mol(cat.)·h)	Selectivity/%			
		C ₄	C ₆	C ₈	C ₁₀₊
0.5	14610	90.76	0.15	6.90	2.19
1	13472	0	10.11	68.01	21.88
1.5	15184	0	0	30.73	69.27
2	2101	0	29.16	30.05	40.79

^aReaction conditions: catalyst: UiO-66-NS4, 10 μmol (based on the MOFs), 25 °C, 1 MPa, toluene as solvent, GC measurement.

Table S9. The effects of the reaction time on catalytic performance of MIL-101(Cr)-NS.^a

Reaction time/h	Activity/g/(mol(cat.)·h)	Selectivity/%		
		C ₆	C ₈	C ₁₀₊
0.5	11370	32.10	61.23	6.67
1	9010	27.14	43.43	29.43
1.5	9527	3.93	8.28	87.79
2	7583	4.73	4.73	90.53

^aReaction conditions: catalyst: MIL-101(Cr)-NS8, 10 μmol (based on the MOFs), 25 °C, 1 MPa, toluene as solvent, GC measurement.

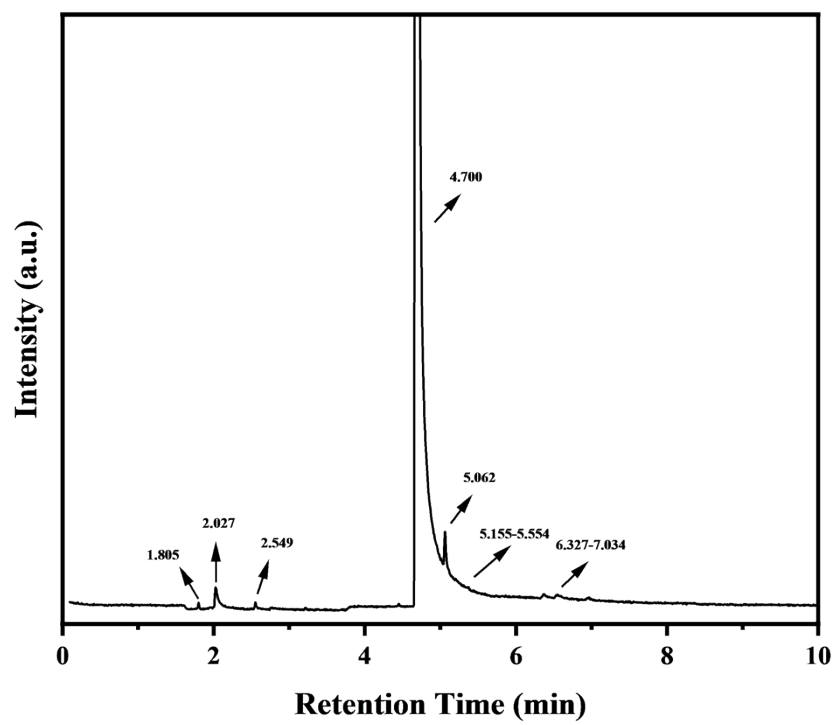


Fig. S4. GC of the ethylene oligomerization products

Table S10. Retention time corresponds to the substance

Enter	Retention Time/min	Substance
1	1.805	Ethylene
2	2.027	Ethanol
3	2.549	Hexene (C6)
4	4.700	Toluene
5	5.062	1-Octene (1-C8)
6	5.155-5.554	Octene isomer
7	6.327-7.034	C10+

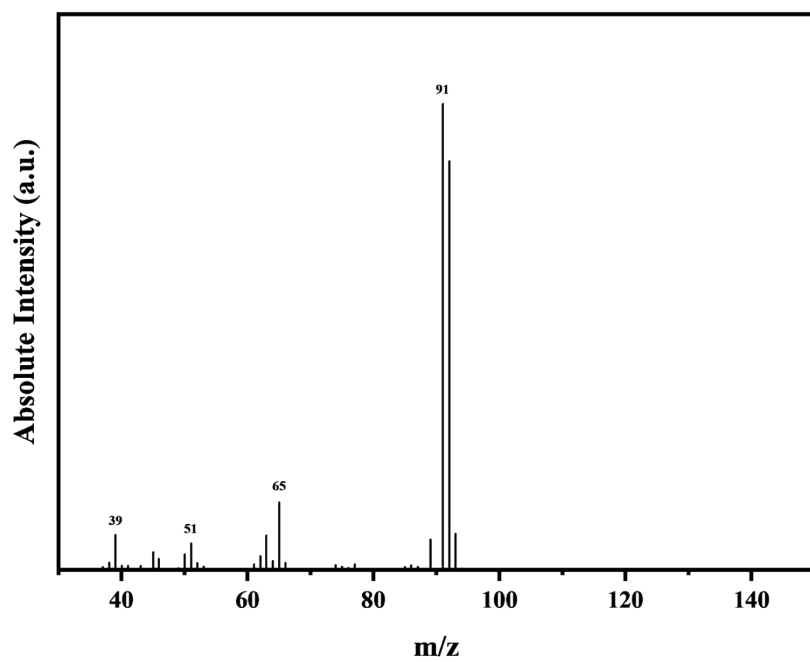


Fig. S5. Mass spectrum at the retention time of 4.700 min

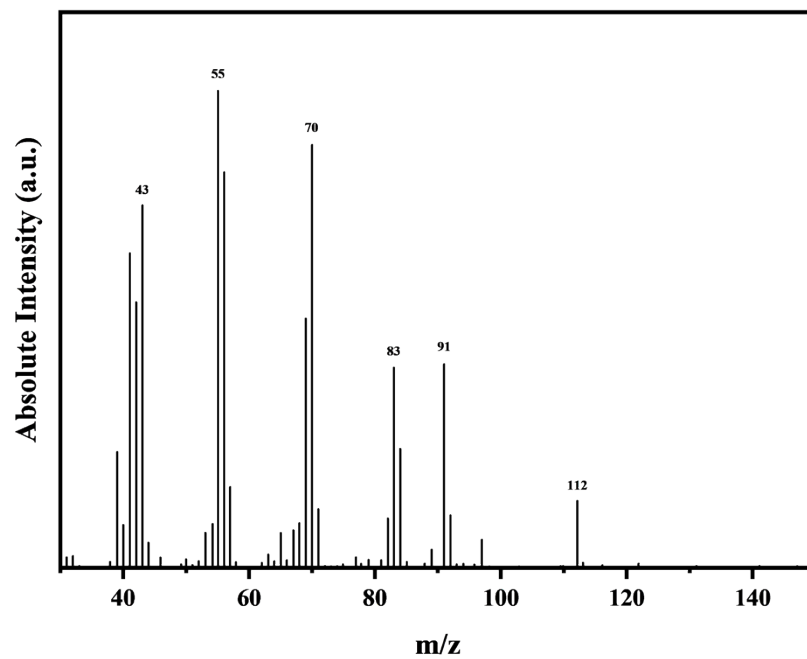


Fig. S6. Mass spectrum at the retention time of 5.062 min