

Supplementary Information: Controllable Acid/Base Propriety of Sulfate Modified Mixed Metal Oxide Derived from Hydrotalcite for Synthesis of Propylene Carbonate

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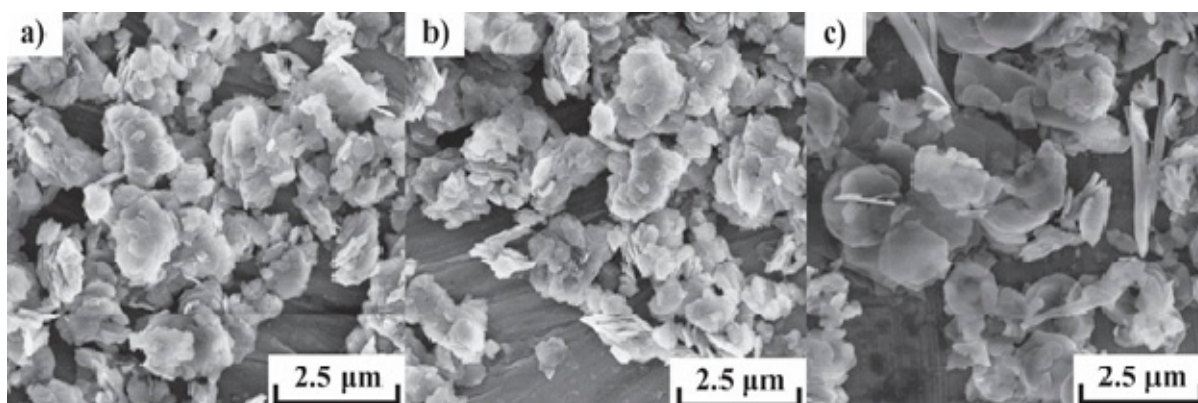


Figure S1. SEM of (A) SMgAlO-1; (B) SMgAlO-3; and (C) SMgAlO-7.

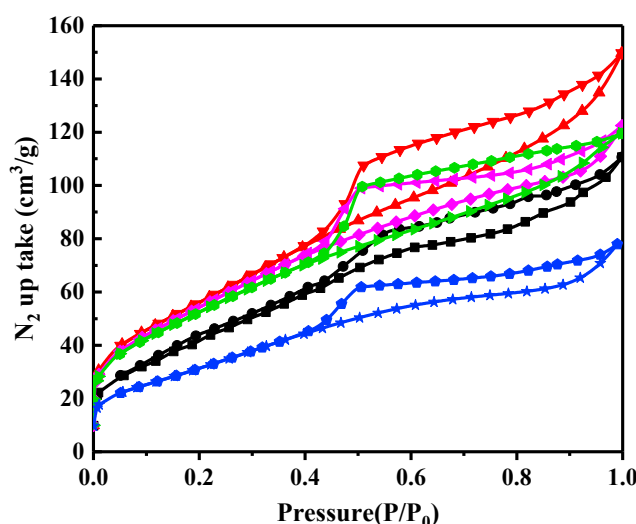


Figure S2. N₂ adsorption and desorption isotherms (77K) for MgAlO (blue), SMgAlO-1 (black), SMgAlO-3 (green), SMgAlO-5 (red), and SMgAlO-7 (magenta).

Table 1. The properties of the probes.

Probe	Character	$\alpha \times 10^{22} / \text{m}^2$	$\gamma_l^d / \text{mJ} \cdot \text{m}^{-2}$	$\text{AN}^* / \text{KJ} \cdot \text{mol}^{-1}$	$\text{DN} / \text{KJ} \cdot \text{mol}^{-1}$	$2\alpha\text{N}(\gamma_l^d)^{0.5}$
n-hexane	apolar	0.515	18.4	--	--	2.6598
n-heptane	apolar	0.570	20.3	--	--	3.0921
n-octane	apolar	0.630	21.3	--	--	3.4896
n-nonane	apolar	0.690	22.7	--	--	3.9581
DCM	acidic	0.315	27.6	16.32	0.00	1.9925
TCM	acidic	0.440	25.9	22.60	0.00	2.6960
Acet	amphoteric	0.425	16.5	10.5	71.13	2.0785
THF	basic	0.450	22.5	2.09	83.72	2.5700
DEE	amphoteric	0.470	47.0	5.86	80.37	2.1916

DCM: dichloromethane; TCM: chloroform; Acet: acetone; THF: tetrahydrofuran; DEE: diethylether.

Table S2. The retention time, Vn and RTlnVn of the MgAlO catalyst at various temperatures.

Temperature	Probe	Retention time/min	Vn	RTlnVn
343.15 K	n-hexane	0.757	1.264	0.234
	n-heptane	2.098	3.503	1.253
	n-octane	5.832	9.739	2.276
	n-nonane	15.048	25.130	3.224
	DCM	0.762	1.273	0.241
	TCM	1.990	3.324	1.201
	Acet	7.538	12.588	2.532
	THF	6.653	11.111	2.407
	DEE	2.019	3.372	1.215
353.15 K	n-hexane	0.607	0.983	-0.0168
	n-heptane	1.432	2.319	0.841
	n-octane	3.748	6.071	1.803
	n-nonane	9.515	15.414	2.735
	DCM	0.593	0.961	-0.039
	TCM	1.307	2.117	0.750
	Acet	5.599	9.070	2.205
	THF	4.732	7.666	2.036
	DEE	1.523	2.467	0.903
363.15 K	n-hexane	0.465	0.734	-0.308
	n-heptane	1.048	1.655	0.504
	n-octane	2.621	4.141	1.421
	n-nonane	6.173	9.753	2.277
	DCM	0.448	0.708	-0.344
	TCM	0.866	1.369	0.3144
	Acet	4.067	6.426	1.860
	THF	3.369	5.323	1.672
	DEE	1.128	1.782	0.577
	n-hexane	0.407	0.624	-0.470
	n-heptane	0.815	1.251	0.223
	n-octane	1.798	2.759	1.015

373.15 K	n-nonane	4.198	6.443	1.863
	DCM	0.399	0.611	-0.491
	TCM	0.643	0.984	-0.016
	Acet	3.464	5.301	1.667
	THF	2.702	4.134	1.419
	DEE	0.968	1.481	0.392

343.15 K, $y = 6.628x - 16.891$, $R^2 = 0.996$; 353.15 K, $y = 6.296x - 16.843$, $R^2 = 0.997$; 363.15 K, $y = 6.091x - 17.163$, $R^2 = 0.997$; 373.15 K, $y = 5.627x - 16.531$, $R^2 = 0.997$.

Table S3. γ_s^d / $\text{mJ}\cdot\text{m}^{-2}$ values of the MgAlO catalyst versus temperature.

γ_s^d / $\text{mJ}\cdot\text{m}^{-2}$				
Temperature/K	343.15	353.15	363.15	373.15
LDO-2	43.930	39.639	37.100	31.663

Table S4. Adsorption free energy and adsorption enthalpy of polar probes on the surface of the MgAlO catalyst.

$-\Delta G^{SP} / \text{KJ}\cdot\text{mol}^{-1}$					$-\Delta H_a^s / \text{KJ}\cdot\text{mol}^{-1}$
Temperature/K	343.15 K	353.15 K	363.15 K	373.15 K	
DCM	4.373	4.181	3.987	3.793	11.016 ($R^2 = 0.999$)
TCM	2.446	2.069	1.689	1.308	15.481 ($R^2 = 0.999$)
Acet	10.336	10.226	10.116	10.006	14.121 ($R^2 = 0.999$)
THF	6.722	6.638	6.554	6.469	9.627 ($R^2 = 0.999$)
DEE	5.830	5.694	5.556	5.415	10.577 ($R^2 = 0.997$)

$y = 0.098x + 0.681$ ($R^2 = 0.997$); $K_a = 0.098$; $K_b = 0.681$; $K_a + K_b = 0.779$; $K_a/K_b = 0.144$.

Table S5. The retention time, V_n , and $RT\ln V_n$ of the SMgAlO-1 catalyst at various temperatures.

Temperature	Probe	Retention time/min	V_n	$RT\ln V_n$
343.15 K	n-hexane	0.728	1.216	0.559
	n-heptane	2.514	4.198	4.093
	n-octane	7.853	13.116	7.343
	n-nonane	30.068	50.213	11.173
	DCM	0.377	0.630	-1.317
	TCM	0.666	1.113	0.306
	Acet	0.839	1.401	0.962
	THF	1.694	2.829	2.967
	DEE	0.930	1.554	1.258
353.15 K	n-hexane	0.480	0.778	-0.736
	n-heptane	1.510	2.447	2.628
	n-octane	4.333	7.019	5.721
	n-nonane	15.002	24.303	9.368
	DCM	0.285	0.462	-2.261
	TCM	0.391	0.634	-1.334
	Acet	0.508	0.823	-0.571
	THF	0.991	1.605	1.389
	DEE	0.548	0.888	-0.346
363.15 K	n-hexane	0.467	0.737	-0.917
	n-heptane	1.359	2.148	2.308
	n-octane	3.632	5.739	5.275
	n-nonane	11.565	18.273	8.772
	DCM	0.253	0.400	-2.759

	TCM	0.314	0.496	-2.114
	Acet	0.491	0.777	-0.760
	THF	0.884	1.398	1.012
	DEE	0.560	0.885	-0.365
373.15 K	n-hexane	0.387	0.593	-1.619
	n-heptane	1.0705	1.637	1.530
	n-octane	2.723	4.166	4.427
	n-nonane	8.186	12.525	7.842
	DCM	0.207	0.316	-3.566
	TCM	0.226	0.346	-3.284
	Acet	0.378	0.579	-1.693
	THF	0.664	1.017	0.053
	DEE	0.440	0.673	-1.227

343.15 K, $y = 8.175x - 21.1845$, $R^2 = 0.990$; 353.15 K, $y = 7.783x - 21.4378$, $R^2 = 0.987$; 363.15 K, $y = 7.463x - 20.7693$, $R^2 = 0.987$; 373.15 K, $y = 7.288x - 21.005$, $R^2 = 0.985$.

Table S6. γ_s^d / mJ·m⁻² values of the SMgAlO-1 catalyst versus temperature.

	γ_s^d / mJ·m ⁻²			
Temperature/K	343.15	353.15	363.15	373.15
LDO-2	66.830	60.575	55.696	53.114

Table S7. Adsorption free energy and adsorption enthalpy of polar probes on the surface of the SMgAlO-1 catalyst.

Temperature/K	$-\Delta G^{SP}$ / KJ·mol ⁻¹				$-\Delta H_{ad}^s$ KJ·mol ⁻¹
	343.15 K	353.15 K	363.15 K	373.15 K	
DCM	3.879	3.669	3.457	3.244	11.162
TCM	-0.425	-0.879	-1.336	-1.794	15.255
Acet	5.022	4.689	4.354	4.018	16.518
THF	3.096	2.825	2.552	2.278	12.470
DEE	4.280	4.033	3.785	3.537	12.795

$y = 0.132x + 0.679$ ($R^2 = 0.991$); $K_a = 0.132$; $K_b = 0.679$; $K_a + K_b = 0.811$; $K_a/K_b = 0.194$.

Table S8. The retention time, V_n , and $RT \ln V_n$ of the SMgAlO-3 catalyst at various temperatures.

Temperature	Probe	Retention time/min	V_n	$RT \ln V_n$
343.15 K	n-hexane	0.600	1.003	0.008
	n-heptane	1.625	2.714	2.849
	n-octane	4.060	6.781	5.461
	n-nonane	11.946	19.949	8.539
	DCM	0.543	0.906	-0.278
	TCM	0.758	1.265	0.672
	Acet	1.155	1.929	1.875
	THF	2.339	3.906	3.887
	DEE	1.173	1.959	1.919
	n-hexane	0.471	0.763	-0.791
	n-heptane	1.218	1.974	1.997
	n-octane	2.918	4.728	4.561
	n-nonane	8.169	13.234	7.583

353.15 K	DCM	0.411	0.665	-1.193
	TCM	0.512	0.830	-0.545
	Acet	0.808	1.309	0.790
	THF	1.608	2.606	2.812
	DEE	0.935	1.515	1.221
363.15 K	n-hexane	0.291	0.460	-2.343
	n-heptane	0.723	1.142	0.402
	n-octane	1.668	2.636	2.926
	n-nonane	4.471	7.064	5.902
	DCM	0.244	0.385	-2.877
	TCM	0.274	0.434	-2.518
	Acet	0.445	0.703	-1.061
	THF	0.875	1.383	0.980
	DEE	0.528	0.834	-0.545
	n-hexane	0.263	0.403	-2.816
	n-heptane	0.629	0.963	-0.116
	n-octane	1.401	2.144	2.367
	n-nonane	3.600	5.508	5.293
	DCM	0.207	0.316	-3.566
373.15 K	TCM	0.226	0.346	-3.284
	Acet	0.378	0.579	-1.693
	THF	0.664	1.017	0.052
	DEE	0.439	0.673	-1.228

Note: 343.15 K, $y = 6.571x - 17.469$, $R^2 = 0.990$; 353.15 K, $y = 6.4507x - 17.949$, $R^2 = 0.994$; 363.15 K, $y = 6.352x - 19.239$, $R^2 = 0.994$; 373.15 K, $y = 6.247x - 19.432$, $R^2 = 0.993$.

Table S9. γ_s^d / $\text{mJ}\cdot\text{m}^{-2}$ values of the SMgAlO-3 catalyst versus temperature.

γ_s^d / $\text{mJ}\cdot\text{m}^{-2}$				
Temperature/K	343.15	353.15	363.15	373.15
LDO-2	43.178	41.611	40.347	39.025

Table S10. Adsorption free energy and adsorption enthalpy of polar probes on the surface of the SMgAlO-3 catalyst.

Temperature/K	$-\Delta G^{\text{SP}}/\text{KJ}\cdot\text{mol}^{-1}$				$-\Delta H_{\text{a}}^{\text{S}}/\text{KJ}\cdot\text{mol}^{-1}$
	343.15 K	353.15 K	363.15 K	373.15 K	
DCM	4.097	3.902	3.705	3.508	10.852
TCM	0.426	0.012	-0.404	-0.822	14.735
Acet	5.686	5.332	4.975	4.616	17.944
THF	4.469	4.183	3.895	3.606	14.353
DEE	4.987	5.032	4.772	4.512	14.214

$y = 0.156x + 0.659$ ($R^2 = 0.996$); $K_a = 0.156$; $K_b = 0.659$; $K_a + K_b = 0.815$; $K_a/K_b = 0.237$.

Table S11. The retention time, Vn, and RTlnVn of the SMgAlO-5 catalyst at various temperatures.

Temperature	Probe	Retention time/min	Vn	RTlnVn
343.15 K	n-hexane	0.379	0.632	-1.304
	n-heptane	0.932	1.556	1.261
	n-octane	2.532	4.228	4.111
	n-nonane	6.59	11.005	6.839
	DCM	0.373	0.623	-1.346
	TCM	0.655	1.094	0.257
	Acet	0.913	1.524	1.203
	THF	1.885	3.148	3.271
	DEE	1.010	1.687	1.492
353.15 K	n-hexane	0.348	0.564	-1.677
	n-heptane	0.787	1.275	0.714
	n-octane	1.664	2.697	2.913
	n-nonane	4.025	6.520	5.505
	DCM	0.392	0.635	-1.330
	TCM	0.521	0.844	-0.496
	Acet	0.853	1.383	0.952
	THF	1.539	2.493	2.681
	DEE	0.943	1.529	1.246
363.15 K	n-hexane	0.225	0.356	-3.118
	n-heptane	0.492	0.777	-0.758
	n-octane	1.010	1.595	1.411
	n-nonane	2.356	3.722	3.968
	DCM	0.241	0.380	-2.913
	TCM	0.292	0.462	-2.326
	Acet	0.480	0.759	-0.832
	THF	0.859	1.358	0.924
	DEE	0.545	0.862	-0.448
373.15 K	n-hexane	0.198	0.302	-3.703
	n-heptane	0.423	0.647	-1.349
	n-octane	0.823	1.259	0.714
	n-nonane	1.832	2.802	3.196
	DCM	0.207	0.316	-3.566
	TCM	0.226	0.346	-3.284
	Acet	0.378	0.579	-1.692
	THF	0.664	1.017	0.053
	DEE	0.440	0.673	-1.227

343.15 K, $y = 6.4389x - 18.223$, $R^2 = 0.997$; 353.15 K, $y = 5.5323x - 16.392$, $R^2 = 0.994$; 363.15 K, $y = 5.4586x - 17.637$, $R^2 = 0.998$; 373.15 K, $y = 5.3033x - 17.785$, $R^2 = 0.999$

Table S12. γ_s^d / mJ·m⁻² values of the SMgAlO-5 catalyst versus temperature.

	γ_s^d / mJ·m ⁻²			
Temperature/K	343.15	353.15	363.15	373.15
LDO-2	41.459	30.606	29.796	28.124

Table S13. Adsorption free energy and adsorption enthalpy of polar probes on the surface of the SMgAlO-5 catalyst.

	$-\Delta G^{SP}$ /KJ·mol ⁻¹				$-\Delta H_a^s$ KJ·mol ⁻¹
Temperature/K	343.15 K	353.15 K	363.15 K	373.15 K	
DCM	4.228	4.037	3.846	3.653	10.803 (R ² = 0.999)
TCM	1.364	0.980	0.593	0.205	14.644 (R ² = 0.995)
Acet	6.230	5.845	5.458	5.070	19.517 (R ² = 0.994)
THF	5.177	4.856	4.533	4.209	16.266 (R ² = 0.991)
DEE	5.801	5.514	5.225	4.936	15.715 (R ² = 0.989)

$$y = 0.179x + 0.653 \text{ (R}^2 = 0.998\text{); } K_a = 0.179; K_b = 0.653; K_a + K_b = 0.832; K_a/K_b = 0.274$$

Table S14. The retention time, Vn, and RTlnVn of the SMgAlO-7 catalyst at various temperatures.

Temperature	Probe	Retention time/min	Vn	RTlnVn
343.15 K	n-hexane	0.409	0.684	-1.081
	n-heptane	1.017	1.699	1.512
	n-octane	2.347	3.920	3.898
	n-nonane	6.289	10.503	6.709
	DCM	0.371	0.620	-1.359
	TCM	0.653	1.090	0.247
	Acet	0.901	1.504	1.165
	THF	1.858	3.103	3.230
	DEE	0.998	1.667	1.458
353.15 K	n-hexane	0.327	0.531	-1.858
	n-heptane	0.741	1.200	0.536
	n-octane	1.569	2.542	2.739
	n-nonane	3.798	6.154	5.335
	DCM	0.308	0.499	-2.040
	TCM	0.471	0.764	-0.790
	Acet	0.683	1.106	0.297
	THF	1.215	1.969	1.990
	DEE	0.767	1.242	0.638
363.15 K	n-hexane	0.262	0.415	-2.654
	n-heptane	0.550	0.869	-0.422
	n-octane	1.086	1.715	1.630
	n-nonane	2.419	3.823	4.049
	DCM	0.252	0.398	-2.774
	TCM	0.312	0.493	-2.134

	Acet	0.503	0.794	-0.692
	THF	0.911	1.439	1.100
	DEE	0.573	0.905	-0.299
373.15 K	n-hexane	0.218	0.333	-3.404
	n-heptane	0.433	0.662	-1.276
	n-octane	0.814	1.245	0.681
	n-nonane	1.712	2.620	2.988
	DCM	0.206	0.316	-3.567
	TCM	0.226	0.346	-3.285
	Acet	0.378	0.579	-1.693
	THF	0.664	1.017	0.053
	DEE	0.439	0.673	-1.227

343.15 K, $y = 6.001x - 17.043$, $R^2 = 0.994$; 353.15 K, $y = 5.541x - 16.596$, $R^2 = 0.999$; 363.15 K, $y = 5.163x - 16.387$, $R^2 = 0.992$; 373.15 K, $y = 4.924x - 16.501$, $R^2 = 0.990$.

Table S15. γ_s^d / $\text{mJ}\cdot\text{m}^{-2}$ values of the SMgAlO-7 catalyst versus temperature.

	γ_s^d / $\text{mJ}\cdot\text{m}^{-2}$			
Temperature/K	343.15	353.15	363.15	373.15
LDO-2	36.012	30.702	26.656	24.245

Table S16. Adsorption free energy and adsorption enthalpy of polar probes on the surface of the SMgAlO-7 catalyst.

Temperature/K	$-\Delta G^{SP}/\text{KJ}\cdot\text{mol}^{-1}$				$-\Delta H_{av}^s$ $\text{KJ}\cdot\text{mol}^{-1}$
	343.15 K	353.15 K	363.15 K	373.15 K	
DCM	3.112	3.314	3.516	3.716	10.640
TCM	0.092	0.480	0.867	1.252	14.531
Acet	4.602	4.990	5.377	5.761	19.048
THF	3.699	4.023	4.346	4.667	15.756
DEE	4.512	4.802	5.090	5.377	15.291

$y = 0.172x + 0.649$ ($R^2 = 0.992$); $K_a = 0.172$; $K_b = 0.649$; $K_a + K_b = 0.821$; $K_a/K_b = 0.265$.