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Supporting Information

Seeded-growth preparation of high-performance Ni/MgAl2O4 catalysts

for tar steam reforming

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Text S1

The crystal structures of the catalysts were obtained by X-ray diffraction analysis (XRD) on a X'TRA diffractometer (ARL, Switzerland) using a Cu K α radiation source (λ =1.540562 Å) at a scan rate of 5°·min⁻¹ in a 2 θ range of 10~90° under atmospheric pressure. The crystallite size of Ni was calculated according to the Scherrer equation. Before the measurement, each catalyst was reduced in the H₂ stream at 700°C for 3 h.

The texture structures of the catalysts were determined by the N2 adsorption-desorption isotherm

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measurements at 77 K on a JW-BK122W static nitrogen adsorption system (JWGB Science and Technology Company, China). Brunauer-Emmett-Teller (BET) standard equation was used to calculate the specific surface areas (S_{BET}). The cumulative pore volumes (V_p) and the average pore diameters (D_p) were calculated by the Barrett-Joyner-Halenda (BJH) model.

Temperature-programmed reduction of H₂ (H₂-TPR) experiments were conducted to explore the interaction between Ni and the support on an Auto Chem II 2920 chemisorption instrument (Micromeritics, USA) with a TCD. Prior to the reduction, around 100 mg of catalyst was pretreated by helium (He) at 250°C for 60 min, followed by cooling down to room temperature in He flow. The sample was then heated to 900°C at a heating rate of 10 °C·min⁻¹ in 5% of H₂/Ar atmosphere at a gas flowrate of 30 mL·min⁻¹. The H₂ consumption profile was recorded.

 H_2 pulse chemisorption was performed on the same instrument of H_2 -TPR to determine the metallic (Ni) dispersion. 100 mg of catalyst was reduced in situ under 5% of H_2 /Ar stream for 3 h at 700°C, and then purged with Ar for 1 h at 300°C to remove the remaining unabsorbed H_2 . When the sample was cooled down to 50 °C, 5% of H_2 /Ar was injected into the reactor for several pulses and the amount of adsorbed H_2 was recorded. The gas flowrate was set at 20 mL·min⁻¹ during the whole period of the experiment. Ni dispersion (D_{Ni}) was calculated from the amount of H_2 chemisorbed by assuming a stoichiometric ratio of H_2 /Ni =1.

Temperature programmed desorption of carbon dioxide (CO₂-TPD) measurements were performed on the same instrument of H₂-TPR. 100 mg of catalyst was firstly reduced in situ by 5% of H₂/Ar, and then purged by He at 250°C for 30 min. After that, the sample was exposed to 10 vol% of CO₂/He for 45 min at 50°C, and the weakly adsorbed CO₂ was removed with He at 50°C for 30 min. Finally, the temperature was increased to 900°C at a heating rate of 10° C·min⁻¹ in a He flow, and the CO₂ desorption signal was monitored by TCD.

The morphologies of the catalysts were observed by transmission electron microscopy (TEM) on a

JEM-200CX microscope.

The amount and type of coke deposited on the catalysts which had been used in STR experiments

for 10 h were measured by the thermogravimetric analysis (TGA) on a SDT 650 synchronous thermal

analyzer (Waters Corporation, USA). In each case, the temperature programmed from ambient

temperature to 800°C at a heating rate of 20 °C min⁻¹ in the air stream at a flowrate of 50 mL min⁻¹.

Text S2 The results and the analysis of CAD for both Ni₅-H₂O and Ni₅-C₇H₈ system Table S2 the result of CAD for Ni₅-H₂O system

				,
Orb.	Occ.	d	b	r
47	2.0	0.000099	0.018626	0.006017
48	2.0	-0.000055	0.003577	0.011963
49	2.0	-0.000409	0.038428	0.038206
50	2.0	-0.000807	0.043169	0.043531
51	2.0	-0.001207	0.005371	-0.044872
52	2.0	0.000536	0.000036	-0.001400
53	2.0	-0.003615	-0.000419	-0.034831
54	2.0	0.001228	-0.000049	-0.008160
55	2.0	0.000202	0.000692	-0.007503
56	2.0	0.004305	0.000839	-0.012966
57	2.0	0.000116	0.000277	-0.009371
58	2.0	0.000368	0.000245	-0.014425
59	2.0	-0.000105	0.000020	-0.002019
60	2.0	0.000616	0.000293	-0.004689
61	2.0	0.000115	-0.000017	-0.000859
62	2.0	0.000902	-0.000343	-0.004079
63	2.0	0.001195	0.000008	0.000032
64	2.0	-0.000316	0.000036	-0.011486
65	2.0	0.002236	-0.001509	-0.006192
66	2.0	0.000149	0.000093	-0.001114
67	2.0	0.000311	0.001992	-0.006635
68	2.0	0.000168	0.001535	-0.005622
69	2.0	-0.000067	0.001395	-0.006626
70	2.0	-0.000061	0.003437	-0.011260
71	2.0	0.001743	0.001425	-0.004958
72	2.0	-0.000048	0.001678	-0.010834
73	2.0	0.000107	0.000194	-0.000828

74	2.0	-0.000357	0.001394	-0.014187
75	2.0	0.005280	-0.000879	-0.012548
Sum	150.0	0.008275	0.120339	-0.139200

Orb.	Occ.	d	b	r
53	2.0	-0.000081	0.004720	0.002178
54	2.0	-0.000078	0.025757	0.008555
55	2.0	-0.000007	0.000136	0.000432
56	2.0	-0.000151	0.032206	0.010764
57	2.0	-0.000064	0.005037	0.002619
58	2.0	-0.000127	0.010418	0.004806
59	2.0	-0.000125	0.004768	0.003374
60	2.0	-0.000608	0.030441	0.014393
61	2.0	-0.000353	0.006882	0.007349
62	2.0	0.000370	0.019787	0.056079
63	2.0	-0.000746	0.010861	0.008827
64	2.0	-0.000198	0.010776	0.009605
65	2.0	-0.001368	0.028659	0.019094
66	2.0	0.000188	0.001240	0.008528
67	2.0	-0.001196	0.005376	0.016807
68	2.0	-0.000505	0.003221	0.007788
69	2.0	0.000658	0.007197	-0.082959
70	2.0	0.001215	0.000450	-0.002654
71	2.0	0.000116	0.001405	0.002451
72	2.0	0.001489	0.002688	0.017086
73	2.0	0.002584	0.001544	-0.025988
74	2.0	0.006608	0.000063	-0.007896
75	2.0	0.001795	0.000030	-0.001338
76	2.0	0.010815	0.003747	-0.043113
77	2.0	0.002168	0.001097	-0.028099
78	2.0	0.007079	0.000325	-0.006544
79	2.0	0.000433	-0.000512	-0.004746
80	2.0	0.001953	-0.000073	-0.013400
81	2.0	0.000156	-0.000035	-0.001346
82	2.0	0.002034	-0.000181	-0.004272
83	2.0	0.000458	-0.000505	0.000376
84	2.0	0.005032	0.001482	-0.036054
85	2.0	0.011350	-0.003251	-0.001695
86	2.0	0.001896	0.000130	-0.009640
87	2.0	0.003305	0.001035	-0.005700
88	2.0	0.003785	0.009587	-0.024831
89	2.0	0.001289	0.000087	-0.001315
90	2.0	0.001553	0.000301	-0.002719

Table S3 the result of CAD for Ni_5 - C_7H_8 system

91	2.0	0.007240	-0.000016	-0.006641
92	2.0	0.007161	0.000903	-0.015058
93	2.0	0.000415	-0.000247	-0.002839
94	2.0	0.010010	0.000012	-0.072841
95	2.0	0.003931	0.000422	-0.012579
Sum	190.0	0.080182	0.226495	-0.220618
Sum	190.0	0.080182	0.226495	-0.220618

"Orb." denotes the indices of the orbitals of the complex; "occ. " is corresponding occupation number. "d(i)" stands for the amount of donated electrons from fragment 1 to 2 via corresponding complex orbital "b(i)" stands for the amount of electrons back donated from fragment 2 to 1 via corresponding complex orbital. "r(i)" corresponds to the overlap population between the occupied fragment orbitals (FOs) of the two fragments in corresponding complex orbital; its positive and negative signs imply that in this complex orbital, the electrons of occupied FOs are accumulated to and depleted (mainly due to Pauli repulsion) from the overlap region between the two fragments respectively. The sum of r(i) reveals that repulsive effect dominates the overall interaction between occupied FOs, which results in corresponding electrons moved away towards nonoverlapping regions from overlap regions

In the Ni₅-H₂O system, Ni₅ cluster is the fragment 1, the H₂O is the fragment 2. From the data, it can be seen that the r(49) and r(50) is a large negative value, which indicate that in this complex orbital, more electrons of occupied FOs are accumulated form the overlap region between Ni₅ cluster and H₂O, thus orbital 49 and 50 is the significantly bonding orbital.

In the Ni₅-C₇H₈ system, Ni₅ cluster is the fragment 1, the C₇H₈ is the fragment 2. From the data, it can be seen that the r(62) is a large negative value, which indicate that in this complex orbital, more electrons of occupied FOs are accumulated form the overlap region between Ni₅ cluster and C₇H₈, thus orbital 62 is the significantly bonding orbital.



Fig. S1. Schematic diagram of steam reforming of toluene over the as-prepared catalysts.



Fig. S2. N₂ adsorption-desorption isotherms and pore size distributions of the as-prepared catalysts. **Fig. S3.** Geometries and the energy difference of the Ni₅ cluster optimized at the B3LYP/def2TZVP



Reactions	Equations	$\Delta H_{298K}^{0} (kJ \cdot mol^{-1})$
	$C_7H_8(g)$ +7 $H_2O(g)$ \rightarrow 7 $CO(g)$ +11 $H_2(g)$	869
I oluene Steam reforming	$C_7H_8(g)$ + 14 $H_2O(g)$ ->7 $CO_2(g)$ +18 $H_2(g)$	581
Water gas shift reaction	$\mathrm{CO}(g)\text{+} \mathrm{H}_2\mathrm{O}(g) {\longleftrightarrow} \mathrm{CO}_2(g)\text{+} \mathrm{H}_2(g)$	-41
Hydrodealkylation reaction	$C_7H_8(g) + H_2(g) {\rightarrow} C_6H_6(g) + CH_4(g)$	-42
Hydrocracking reaction	$C_6H_6(g) \rightarrow CH_4(g) + H_2(g)$	>0
	$CH_4(g)$ + $H_2O(g)$ \rightarrow $CO(g)$ + $3H_2(g)$	206
Methane steam reforming	$CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$	165
Methane CO ₂ reforming	$CH4(g)+CO_2(g)\rightarrow 2CO(g)+2H2(g)$	247
Thermal cracking	$CH_4(g) \leftrightarrow C(s) + H_2(g)$	74.9
Boudouard reaction	$2CO(g) \leftrightarrow CO_2(g) + C(s)$	-172
W	$\mathrm{C}(s) \!\!\!\!+ \mathrm{H}_2\mathrm{O}(g) \!\!\longleftrightarrow \mathrm{CO}(g) \!\!\!+ \!\!\!\mathrm{H}_2(g)$	131
water gas reaction	$C(s)+2H_2O(g) \leftrightarrow CO_2(g)+2H_2(g)$	90

Table S1. Other reactions occurred in the process of the SRT experiment.