Electronic Supplementary Information (ESI)

Coke- and sintering-resistant monolithic catalysts derived from *in-situ* supported hydrotalcite-like films on Al wires for dry reforming of methane

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Experimental Section:

HT-NiMgAl catalysts: Aluminum wires (purity: 99.9%; diameter: 0.1 mm)) was carefully immersion in the with dilute NaOH aqueous solution (0.10 M) for 30 s in order to remove the surface oxidation layer, and then deionized water and absolute ethanol were successively used in ultrasonic bath for 10 min**.** $Ni(NO_3)_2\cdot6H_2O$ (0.006 mol), $Mg(NO_3)_2\cdot6H_2O$ (0.014 mol) and NH_4NO_3(0.06 mol) were dissolved in deionized water (70 mL), and the pH was adjusted to 6.5 by addition of 1% ammonia solution. Then the resulting soltion and the aluminum wires (0.1g) were transferred to the Teflon-lined stainless autoclave and it was kept at 150^oC for 12h. Finally, the collected aluminum wires were rinsed with ethanol several times**.** After drying at 80 °C, the resultant HTLcs films on aluminum wires were calcined at 600 ^oC for 4 h, and then they were reduced *in situ* at 700 °C for 1 h in a mixed flow of H_2 and N_2 (H_2, vol%: 10%). The as-prepared catalysts are the HT-NiMgAl monolithic catalysts.

IM-NiMgAl catalysts: The Mg-Al hydrotalcites were prepared by following the route described in the previous literature.[1] The as-prepared Mg-Al hydrotalcites were transformed into mixed oxides after the calcination at 600 ^oC for 4 h. The IM-NiMgAl catalysts was prepared by wetness impregnation of mixed oxides with an aqueous solution of $Ni(NO_3)_2\cdot6H_2O$ followed by drying at 80 °C for 12 h, calcination at 400 °C for 2 h and reduction at 700 °C for 1 h in a mixed flow of H_2 and N_2 (H_2, vol%: 10%). The Ni loadings of the IM-NiMgAl catalysts were controlled at 5 wt% and 0.65 wt%.

Characterization: The XRD measurements were performed with a Rigaku D/MAX-RB X-ray diffractometer by using Cu Kα (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The morphologies and structures were observed by a TEM (JEOL JEM-200CX), a HRTEM (JEOL JEM-2010F), and a SEM (JEOL JSM-6700F). Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was performed on a Plasma-400.

The H_2-TPR measurements were carried out in a quartz tube reactor equipped with a thermal conductivity detector (TCD). First of all, the catalysts (0.25 g) were pretreated at 300 ^oC for 30 min in a flowing stream of high-purity nitrogen. After cooling to room temperature, a 10 % H_2 of N_2 gas mixture (40 mL/min) was introduced and the programing temperature was controlled from room temperature to 950 °C with a rate of 10 ^oC/min. The TPO measurements were carried out with the same procedure of H_2-TPR. The difference was that the amount of the used catalysts was 50 mg and a 10% O_2 of N_2 gas mixture was applied.

The CO_2-TPD tests were also performed to study the basic sites on the catalysts. The samples were firstly pretreated at 300 ^{o}C for 30 min. After cooling to 50 ^{o}C, CO_2 was injected for 1h. Then, the purity nitrogen was introduced to purge the catalysts to remove the CO_2 in physisorption. Finally, the temperature was increased at a ramp of 10 ^{o}C/min to 700 ^{o}C under N_2, and the desorbed gas was monitored by a TCD detector.

Catalyst Evaluation: The CO_2 reforming of methane reactions was carried out in a fixed bed reactor with a quartz tube (inner diameter of 8 mm). The quartz tube was filled with the catalysts (0.50 g) and fed a mixture of CH_4 and CO_2 (CH_4:CO_2 = 1:1, 15 mL/min per reactor). The catalytic tests were carried out from 450 to 800 °C with a heating rate of 8 ^{o}C/min. The effluent product gases were cooled in an ice–water bath and analyzed by online gas chromatography with a TCD, using a TDX-01 packed column. To study the coke-resistant properties, the durability tests were also carried out at 750 °C for 360 min.

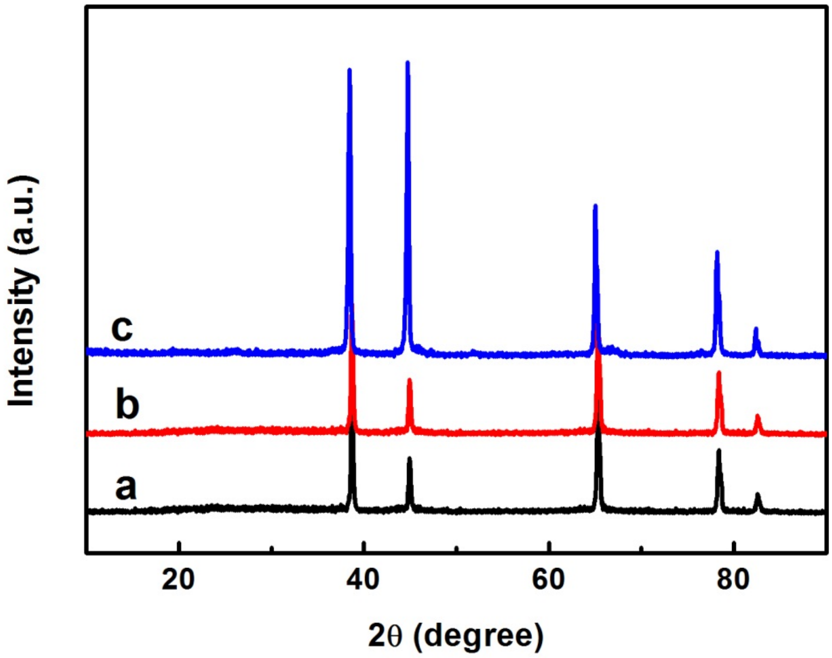

Fig. S1. XRD patterns of the monolithic HT-NiMgAl catalysts (b), the catalysts before reduction (a) and the used catalysts (c).

Beacause the diameter of the Al wires we selected only 0.1mm, it is very difficult to scrap the powder from the substrate. Therefore, the XRD patterns only show strong reflections of the aluminum substrate.

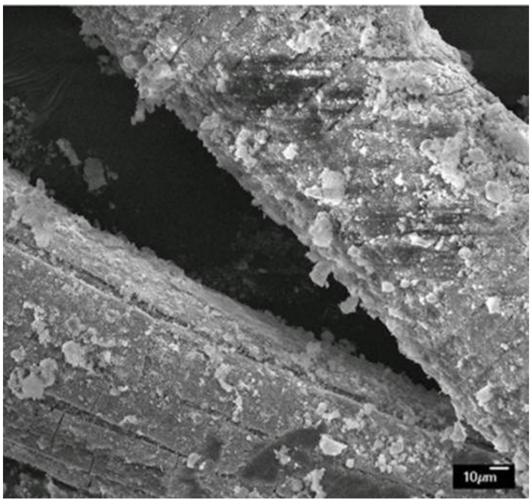

Fig. S2. The surface morphology of the monolithic catalysts.

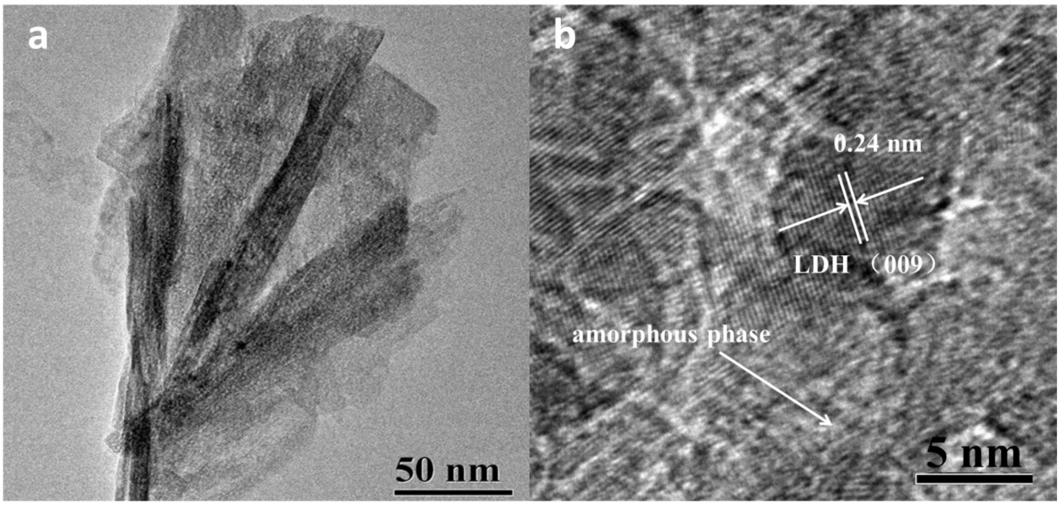

Fig. S3. TEM (a) and HRTEM (b) images of the HTLcs nanosheet films before the calcination.

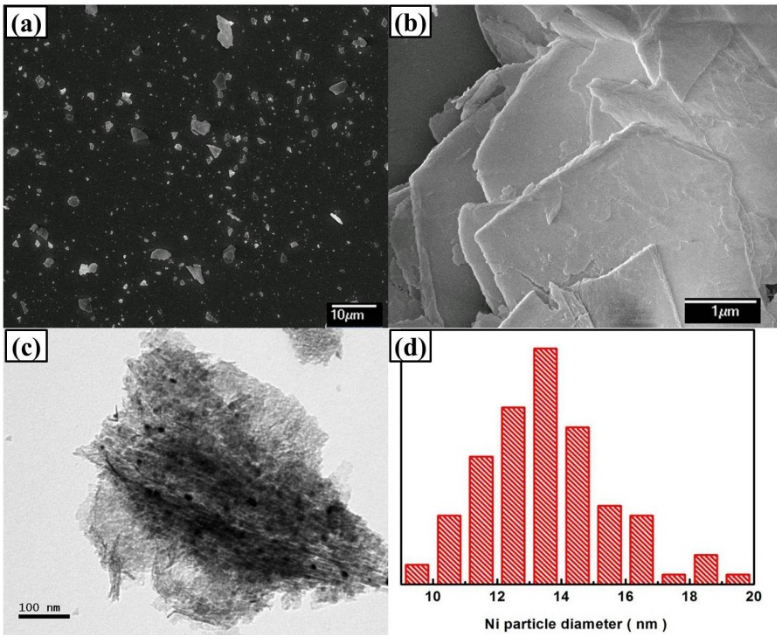

Fig. S4. Low (a), high (b) magnification SEM and TEM (c) images of the IM-NiMgAl catalysts, and the size distribution of Ni nanoparticles on the catalysts (d).

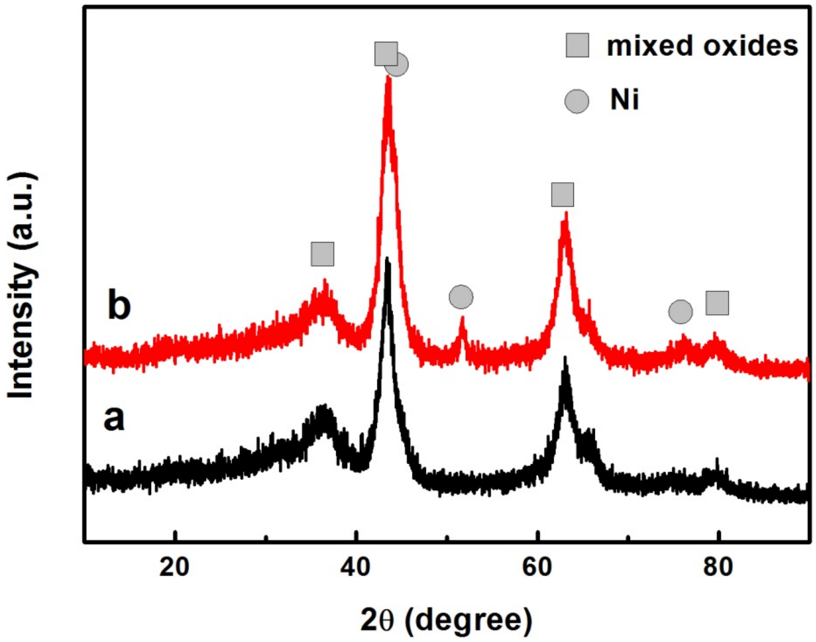

Fig. S5. XRD patterns of the IM-NiMgAl catalysts (b) and the catalysts before reduction (a).

Before reduction, the XRD partern only display reflections of the mixed oxides. After the reduction , the XRD partern of the IM-NiMgAl catalysts presents the evident reflection peaks belong to Ni. The peak at 44^o relates to typical reflection of the (111) plane (JCPDS 70-1849).

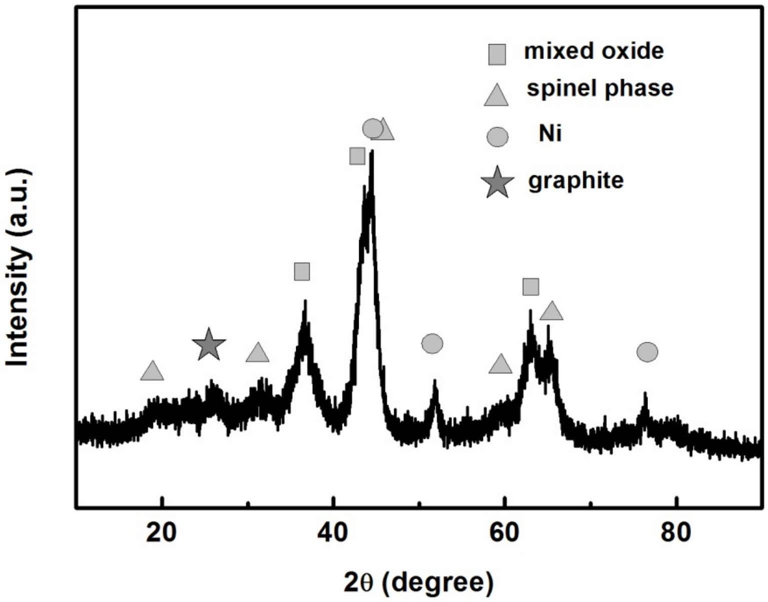

Fig. S6 XRD pattern of the used IM-NiMgAl catalysts after stability tests.

After the stability tests, XRD pattern of the used IM-NiMgAl catalysts suggest the presence of fibrous carbon species.[2] Besides, under the long-term test at a high temperature, part of the mixed oxides can be transformed into spinel phase.[3]

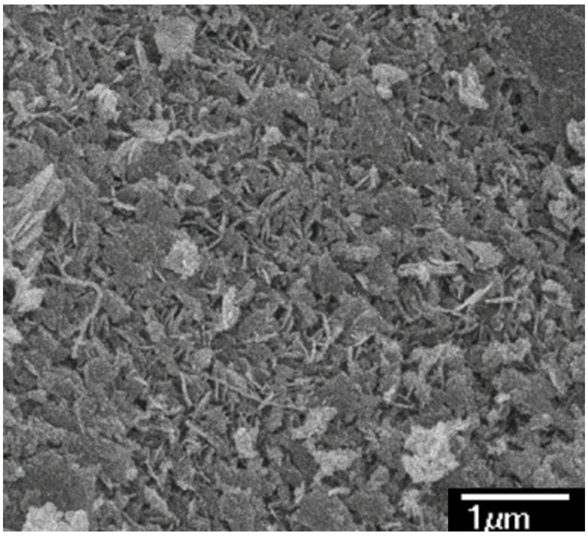

Fig. S7 SEM image of the used HT-NiMgAl after the stability tests.

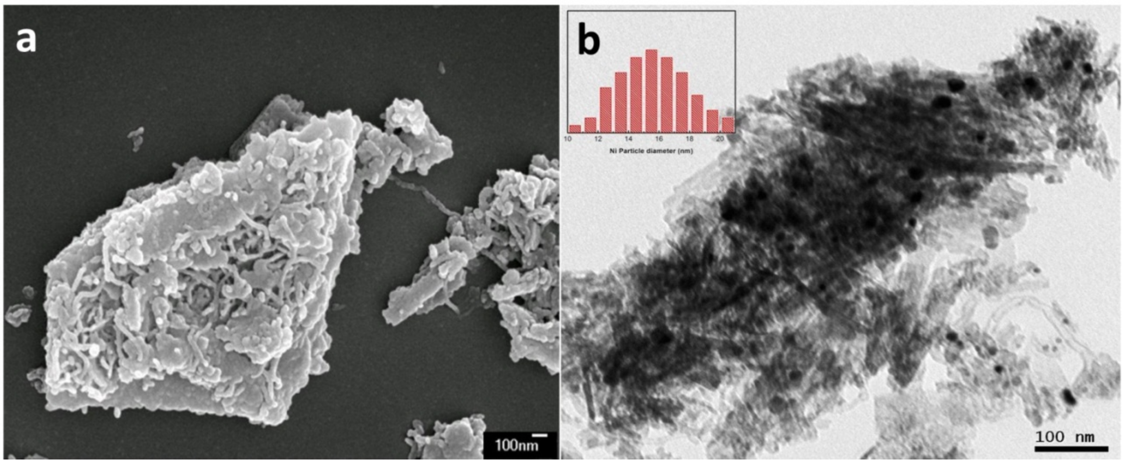

Fig. S8 SEM (a) and TEM (b) images of the used IM-NiMgAl catalysts after the stability tests (inset: size distribution of the Ni nanoparticles).

References

1. S. Huang, H. Peng, W. W. Tjiu, Z. Yang, H. Zhu, T. Tang and T. Liu, *J Phys Chem B*, 2010, **114**, 16766-16772.
2. L. Li, S. He, Y. Song, J. Zhao, W. Ji and C.-T. Au, *J Catal*, 2012, **288**, 54-64.
3. B. Rebours, J.-B. d'Espinose de la Caillerie and O. Clause, *J Am Chem Soc*, 1994, **116**, 1707-1717.