

Supporting Information

Nickel-induced morphology change of mesostructured alumina with enhanced catalytic activity for selective CO methanation

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Experimental Section

Mesoporous nickel-aluminum oxides, denoted as MA-xNi, was prepared following the procedure described by Morris et al. by employing a triblock copolymer (Pluronic P123, $M_{av} = 5800$, EO20PO70EO20, Sigma-Aldrich) as a template [1]. In detail, approximately 1.0 g P123 and nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved in 10.0 ml of 99.5 % anhydrous ethanol with stirring at room temperature. Then, aluminum isopropoxide was dissolved in 1.6 ml of 68-70 wt % nitric acid and 10.0 ml anhydrous ethanol. Once dissolved, the two solutions were mixed and 3 ml of anhydrous ethanol was used to thoroughly transfer the aluminum isopropoxide solution. The mixture was covered with PE film, stirred at room temperature for about 5 h. Solvent evaporation was performed at 60 °C for 48 h in air. The resulting sample was calcined at 400 °C with a ramp rate of 1 °C/min and held for 4 h.

In a typical synthesis, MA-10Ni was dispersed in deionized water with concentration of 1wt% at room temperature. Then, the mixture was covered with PE film, stirred for 6 h. Then, the mixture was dried at 110 °C for 12 h. A part of the sample was calcined at 400 °C (1 °C min⁻¹ ramping rate) for 2 h. The general formula MA-xNi-w (w refers to be stirred in deionized water and dried at 110 °C and MA-xNi-c (c refers to the former samples were calcined at 400 °C) are used to represent the products. For instance, MA-10Ni-c refers that MA-10Ni undergoes the whole process mentioned above.

The X-ray powder diffraction of the samples was carried out with a Rigaku D/MAX-2000 diffractometer using Cu K α radiation. Transmission electronic microscopy (TEM) was recorded on a JEOL-2100 or F20 under a working voltage of 200 kV. Scanning electron microscope (SEM) images were recorded by Hitachi S-4800. The nitrogen adsorption and desorption isotherms at 78.3 K were measured using an ASAP 2020 analyzer. The surface areas were calculated by Brunauer-Emmett-Teller (BET) equation. Before measurement, each sample was pretreated at 300 °C for 1 h. MA-20Ni and MA-20Ni-c were reduced by H₂ at 400 °C for 1h (denoted as MA-20Ni* and MA-20Ni-c*, respectively). Affinities of MA-20Ni* and MA-20Ni-c* to

H₂ adsorption were examined with a commercialized chemisorption equipment (BEL-Cat, Bel Japan Inc.). The as-prepared samples were first placed in Pyrex tube, and then they were pretreated at 300°C. After the pretreatment, the samples were cooled down to room temperature in He flow, then H₂ pulse was introduced until the saturated coverage was achieved. The effluent gas through the catalyst bed was detected by TCD. Ar gas for H₂ adsorption was used as the carrier gas. The amount of chemisorbed gas was calculated from the reduced peak area. The H₂-TPR was used PFEIFFER GSD320 Mass Spectrometer to monitor the H₂ fragment as a function of temperature. The samples (100mg) were loaded in a U-shaped quartz reactor. Prior to the TPR measurements, samples were pretreated at 200 °C for 1h in the flowing He (30 ml/min) to remove any moisture and other adsorbed impurities. After cooling to the room temperature, a 5% H₂-N₂ (50 ml/min) gas mixture was introduced. The catalysts were heated from room temperature to 800 °C with a ramp rate of 10 °C/min. The catalytic activity tests were performed through a fixed-bed quartz tubular reactor at atmospheric pressure. The catalyst powder was shaped and sieved into pellets with diameters of 1.2-2.0 mm. Before reaction, the catalyst was pretreated at 400 °C with H₂ for 1 h. An on-line gas chromatograph with a thermal conductivity detector (TCD) and flame ionization detector (FID) was used to analyze the inlet and outlet gas composition.

Reference:

- [1] S.M. Morris, P.F. Fulvio, M. Jaroniec, *J. Am. Chem. Soc.*, 2008, **130**, 15210.

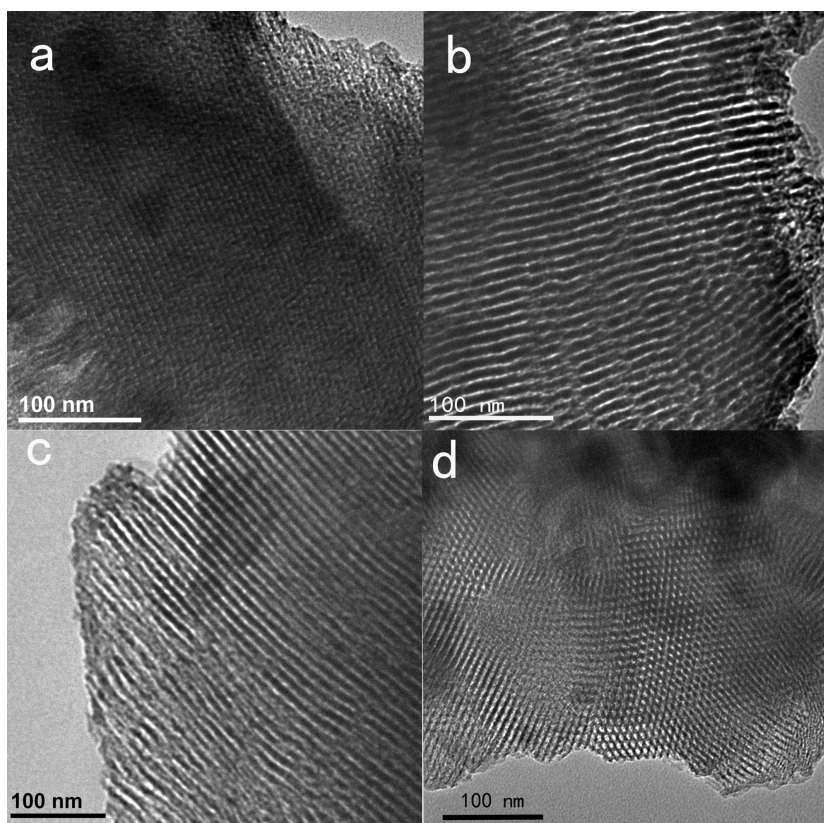


Fig. S1 TEM images of (a) MA-Fe, (b) MA-Co, (c) MA-Ti, and (d) MA.

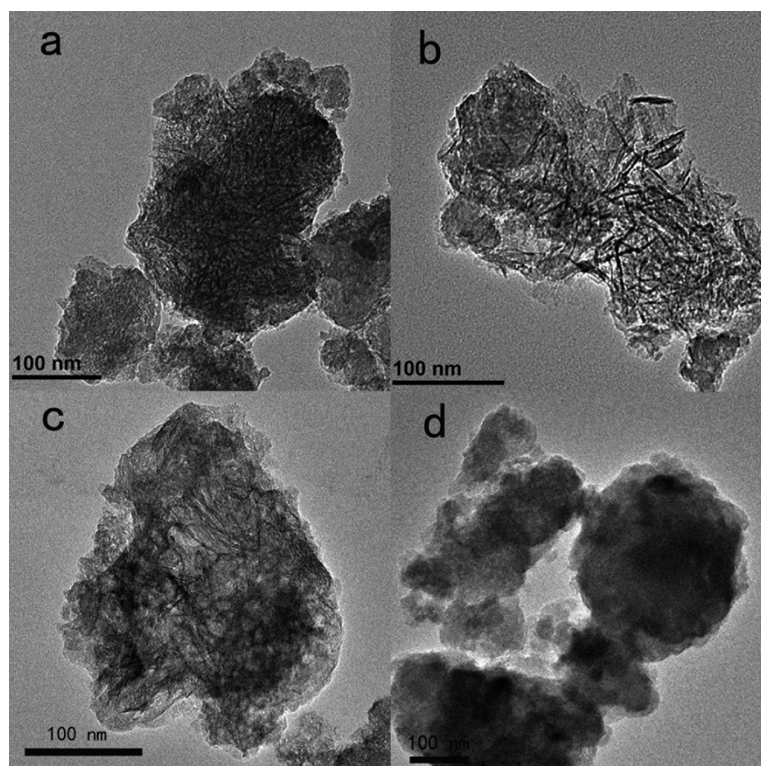


Fig. S2 TEM images of (a) MA-Fe-w, (b) MA-Co-w, (c) MA-Ti-w, and (d) MA-w.

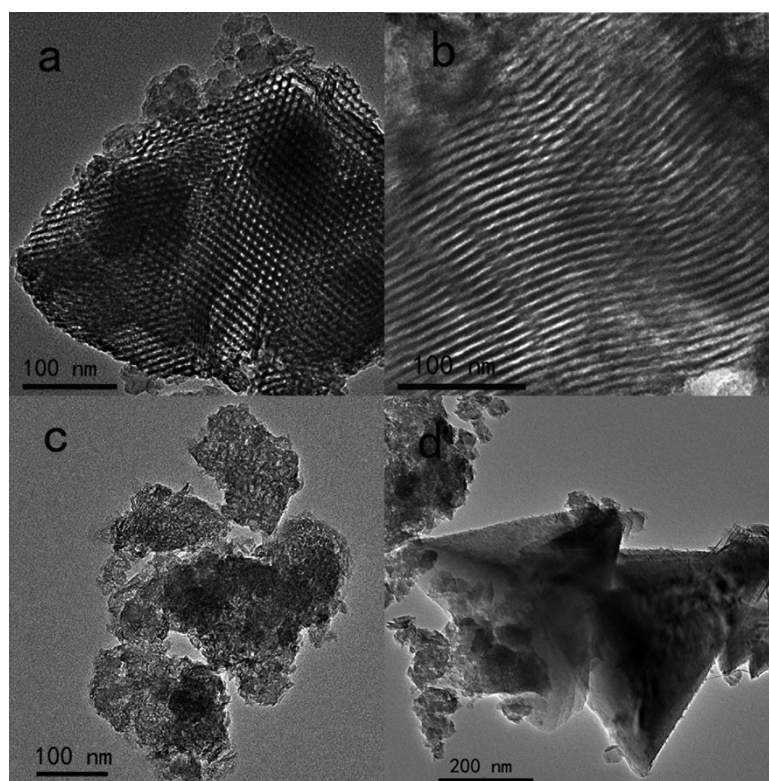


Fig. S3 TEM images of (a) MA-5Ni, (b) MA-8Ni, (c) MA-5Ni-w, and (d) MA-8Ni-w.

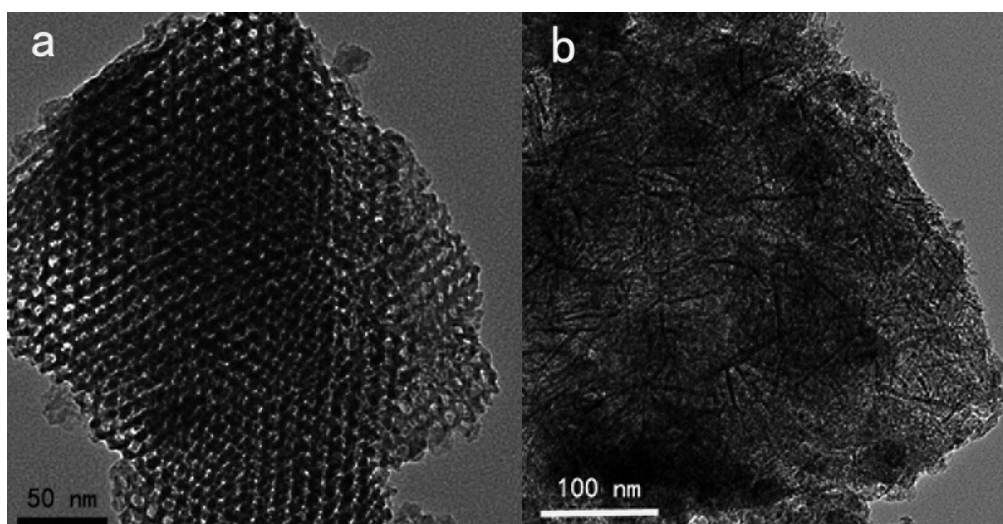


Fig. S4 TEM images of (a) Ni/MA, (b) Ni/MA-w.

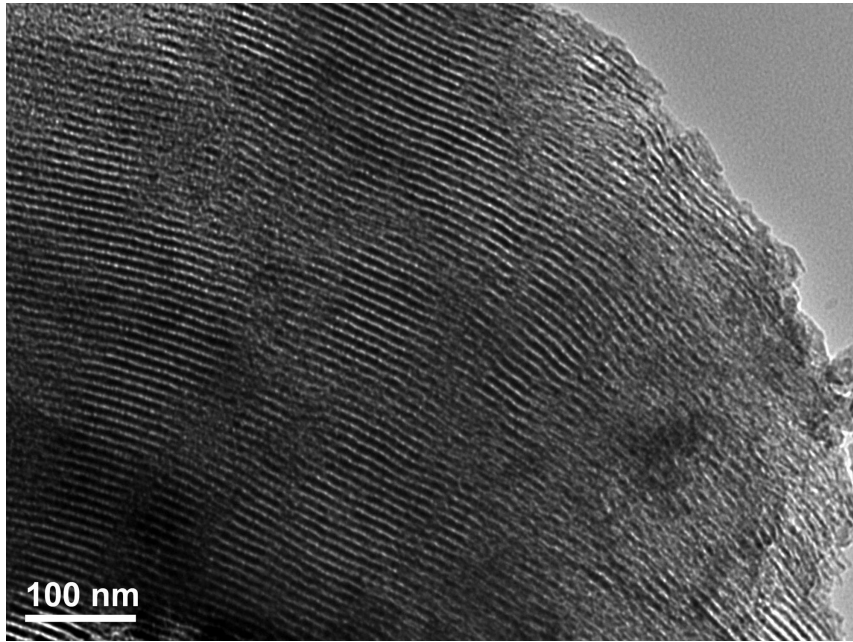


Fig. S5 TEM image of MA-10Ni after treated in ethanol.

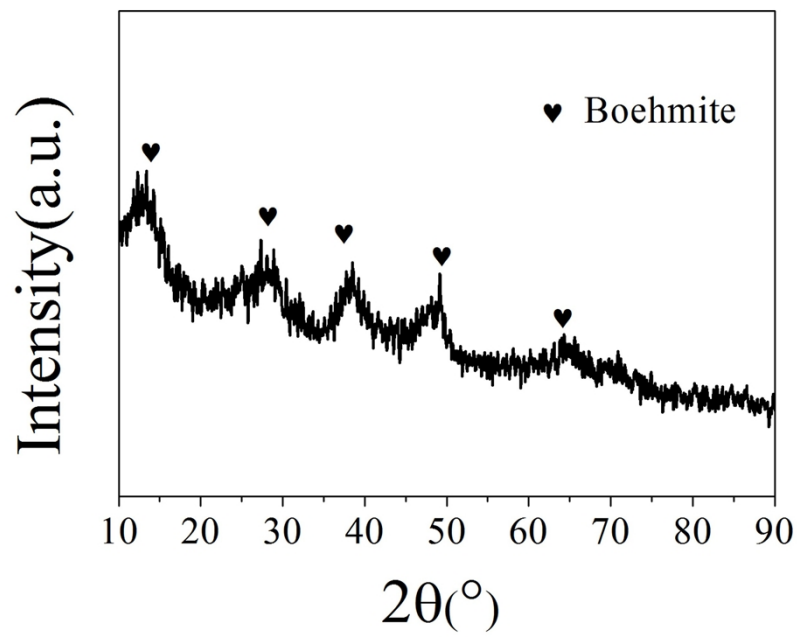


Fig. S6 XRD pattern of MA after treated in water.

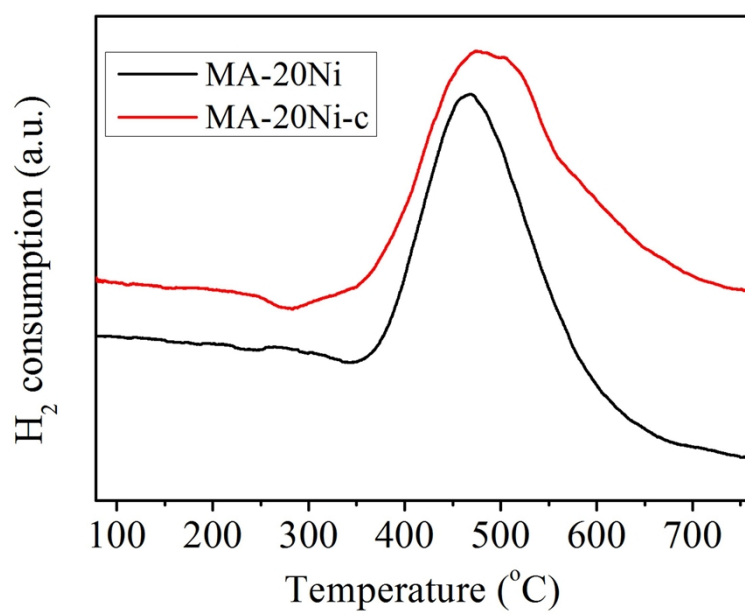


Fig. S7 H₂-TPR profiles of MA-20Ni and MA-20Ni-c.