Electronic Supplementary Information

Enhancing catalytic activity and stability for CO_2 methanation on Ni@MOF-5 *via* controlling active species dispersion

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Experimental section

1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, AR, Xilong Chemical Co., Ltd.), Nickel(II) acetylacetonate ($Ni(acac)_2$, AR, J&K Scientific Ltd.), N,N-dimethylformamide (DMF, 99.5%, Xilong Chemical Co., Ltd.), terephthalic acid (H_2BDC, ≥99.0%, Shanghai KEFENG Chemical Reagent Co., Ltd.), acetone (AR, Xilong Chemical Co., Ltd.), hydrazine solution ($N_2H_4 \cdot H_2O$, AR, Tianjin NO.2 Reagent Co. Ltd), silica (SiO_2, 40 mesh, Shanghai Meryer Chemical Technology Co., Ltd), ethanol (C_2H_5OH, AR, Xilong Chemical Co., Ltd.) were used.

2. Catalysts preparation

2.1 Synthesis of MOF-5.

MOF-5 was synthesized by the solvent-thermal route according to the previous literature [S1]. In a glass reactor equipped with a reflux condenser and a teflon-lined stirrer, 1.025 g of H_2BDC and 4.825 g of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 148.9 mL of DMF and heated up to 130°C for 4 h. After about 45 min, crystallization started and the formerly clear solution turned slightly opaque. After 4 h, the reaction product was cooled down to room temperature. The solid was filtered off, washed three times with 100 mL of dry acetone and dried under a stream of nitrogen. Finally, as-synthesized MOF-5 was calcinated in N_2 flow at 250°C for 6 h to remove the guest molecules from the pores.

2.2 Synthesis of x(wt%)Ni@MOF-5.

A series of x(x=5, 7.5, 10, 12.5)Ni@MOF-5 catalysts was prepared by impregnation methods using Ni(acac)$_2$ and MOF-5. Ni(acac)$_2$ (0.875 g) was dissolved in ethanol (150.0 mL) to form a dark green solution at 60 °C. Subsequently, guest-free MOF-5 (1.8 g) was added into the solution under continuous agitation. The mixture was stirred for 16 h in air, and 5.00 mL of hydrazine solution (80 wt%) was added into the aqueous dispersions. The mixture was maintained at this temperature for 8 h until the color of the solution changed into dark. After complete reduction, the obtained dispersions were filtered, washed with water several times to remove the impurities. Finally, the obtained wet solids were dried at 110 °C for 12 h and calcined at 250 °C for 5 h under inert atmosphere (N_2). This synthesized Ni@MOF-5 catalyst was denoted as 10Ni@MOF-5.

2.3 Synthesis of 10Ni/SiO2.

The catalyst 10(wt%)Ni/SiO_2 was prepared by similar impregnation method. Ni(acac)$_2$ (0.875 g) was dissolved in ethanol (150.0 mL) to form a dark green solution at 60 °C. Subsequently, SiO_2 (1.8 g) was added into the solution under continuous agitation. The mixture was stirred for 16 h in air. Subsequently, 5.0 mL of hydrazine solution (80 wt%) was added into the aqueous dispersions. The mixture was maintained at this temperature for 8 h until the color of the solution changed into dark. After complete reduction, the obtained dispersions were filtered, washed with water several times to remove the impurities. Finally, the obtained wet solids were dried at 110 °C for 12 h and calcined at 450 °C for 5 h under inert atmosphere (N_2). The Ni/SiO_2 catalyst was denoted as 10Ni/SiO_2.

3. Catalytic activity

Catalytic performances tests were conducted at atmospheric pressure in a fixed-bed continuous flow quartz reactor in the temperature range from 180 to 320°C over 200mg catalyst. The reactor was heated in a tube furnace equipped with a temperature controller. All gases were monitored by calibrated mass flow controllers.

The H_2 and CO_2 reactant with a ratio of 4:1 was used and N_2 was added as a carrier gas and internal standard for gas analysis. They were introduced into the reactor at a molar ratio of H_2:CO_2:N_2=12:3:10 and the total flow rate were set to 25 $mL \cdot min^{-1}$. The gas hourly space velocity (GHSV) was $2000h^{-1}$. The gas phase products were analyzed on two on-line chromatographs equipped with thermal-conductivity detectors (TCD). Hydrocarbons as well as oxygenated products were separated with a GC112A (SDPTOP, Shanghai in China; column: HP-5, 30m×0.53mm×0.5μm) and analyzed by means of a flame ionization detector (FID). The detection limit for the products was 1×10^{-2}vol. % at the given conditions. CO_2 conversion, CH_4 yield, CH_4 and CO selectivity were defined as follows:

$$X_{CO_2}(\%) = (1 - \frac{CO_2 \times (N_2)_{in}}{N_2 \times (CO_2)_{in}}) \times 100$$

$$S_{CH_4}(\%) = \frac{CH_4}{CO_2 + CH_4 + CO + 2C_2H_6} \times 100$$

$$S_{CO}(\%) = \frac{CO}{CO_2 + CH_4 + CO + 2C_2H_6} \times 100$$

Where X is the conversion, S is the selectivity, P and $(P)_{in}$ are the reactant/product molar quantities at the exit and at the entrance of the reactor, respectively.

4. Characterization of the catalysts

Temperature-programmed reduction analysis (H_2-TPR) was carried out by heating a sample (50mg) from 25 to 700°C at 10°C min^{-1} in a flow of 5 vol% H_2/Ar mixture (40 mL min^{-1}). The amount of H_2 consumed was measured by a TCD. The X-ray diffraction patterns (XRD) of the samples were recorded on a Rigaku B/Max-RB X-ray diffractometer with a nickel-filtrated Cu Kα radiation over a 2θ range of 15-85° and a position sensitive detector using a step size of 0.017° and a step time of 15s at 40 mA and 40 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB 250Xi-XPS photoelectron spectrometer with an Al Kα X-ray resource. The binding energies were calibrated by the C1s binding energy of 284.7 eV. The specific surface areas (SSA) of the catalysts were determined by N_2 adsorption-desorption measurements at 77 K by employing the Brunauer-Emmet-Teller (BET) method (Micromeritics apparatus ASAP 2020M). Transmission electron microscopy (TEM) and HRTEM images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV. To understand the calcination process, the samples (before calcination) were measured by thermogravimetric and differential scanning calorimetry (TG-DSC) analysis using NETZSCH STA 449F3 instrument. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet Nexus 870 with the wave number from 4000 to 400 cm^{-1}. The dispersion was measured by H_2 chemisorption using a Micromeritics Chemisorb 2750 Pulse Chemisorption System at 25°C.

Table S1 Structural parameters obtained from N_2 adsorption isotherms analysis

Samples	**S_{BET} (m^2/g)[a]**	**pore volume (cm^3/g) [b]**	**Ni concentration (wt%) [c]**	**Ni dispersion (%) [d]**
10Ni@MOF-5	2961	1.037	9.73	41.8
MOF-5	2973	1.182	0	0
10Ni/SiO_2	155.6	0.8245	9.69	33.7

[a] Obtained from BET method.

[b] Total pore volume taken from the nitrogen adsorption volume at a relative pressure (P/P_0) of 0.99.

[c] The data obtained from XPS.

[d] Measured by H_2 chemisorption at 25°C.

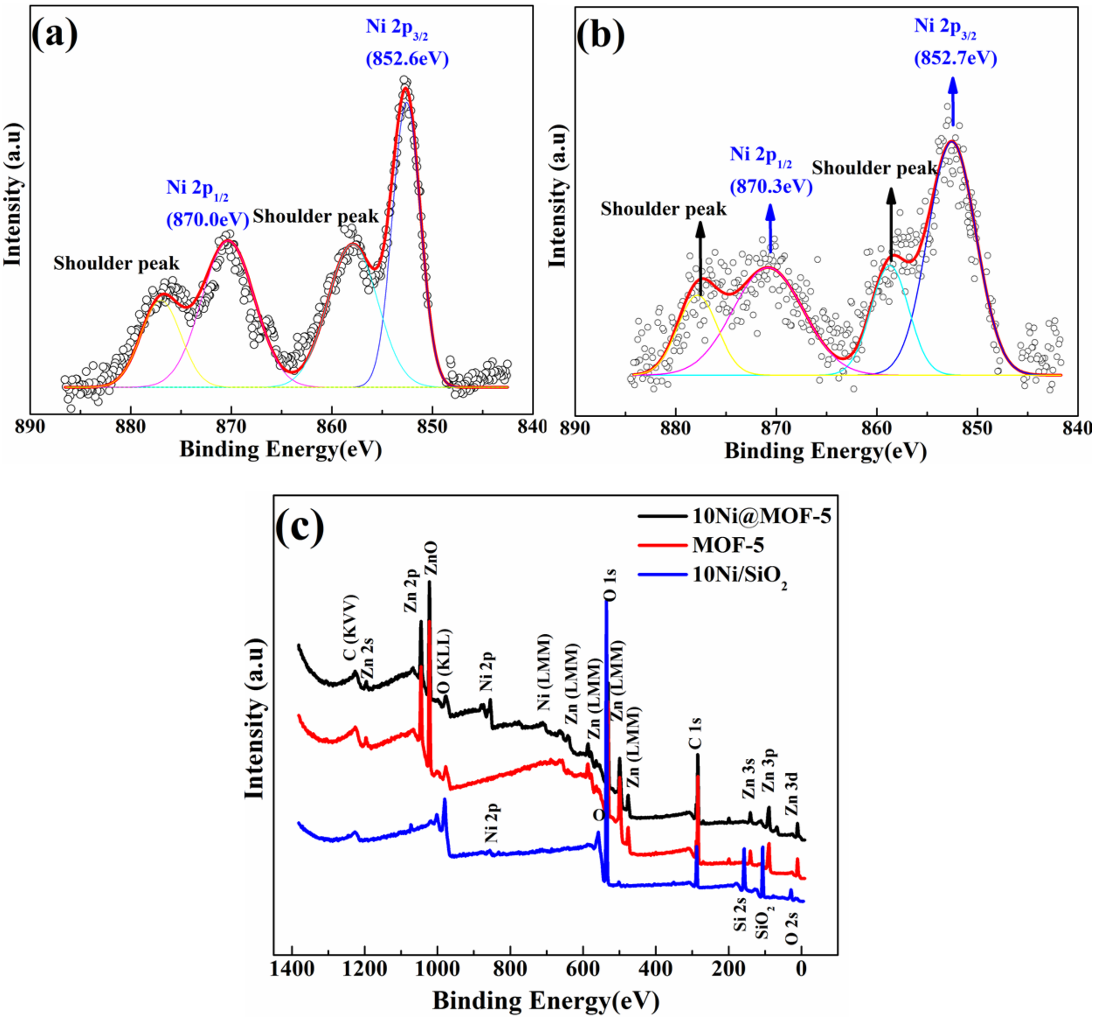

Fig. S1 Ni2p XPS spectra for (a) 10Ni@MOF-5 and (b) 10Ni/SiO_2; (c) XPS survey spectra of MOF-5, 10Ni@MOF-5 and 10Ni/SiO_2.

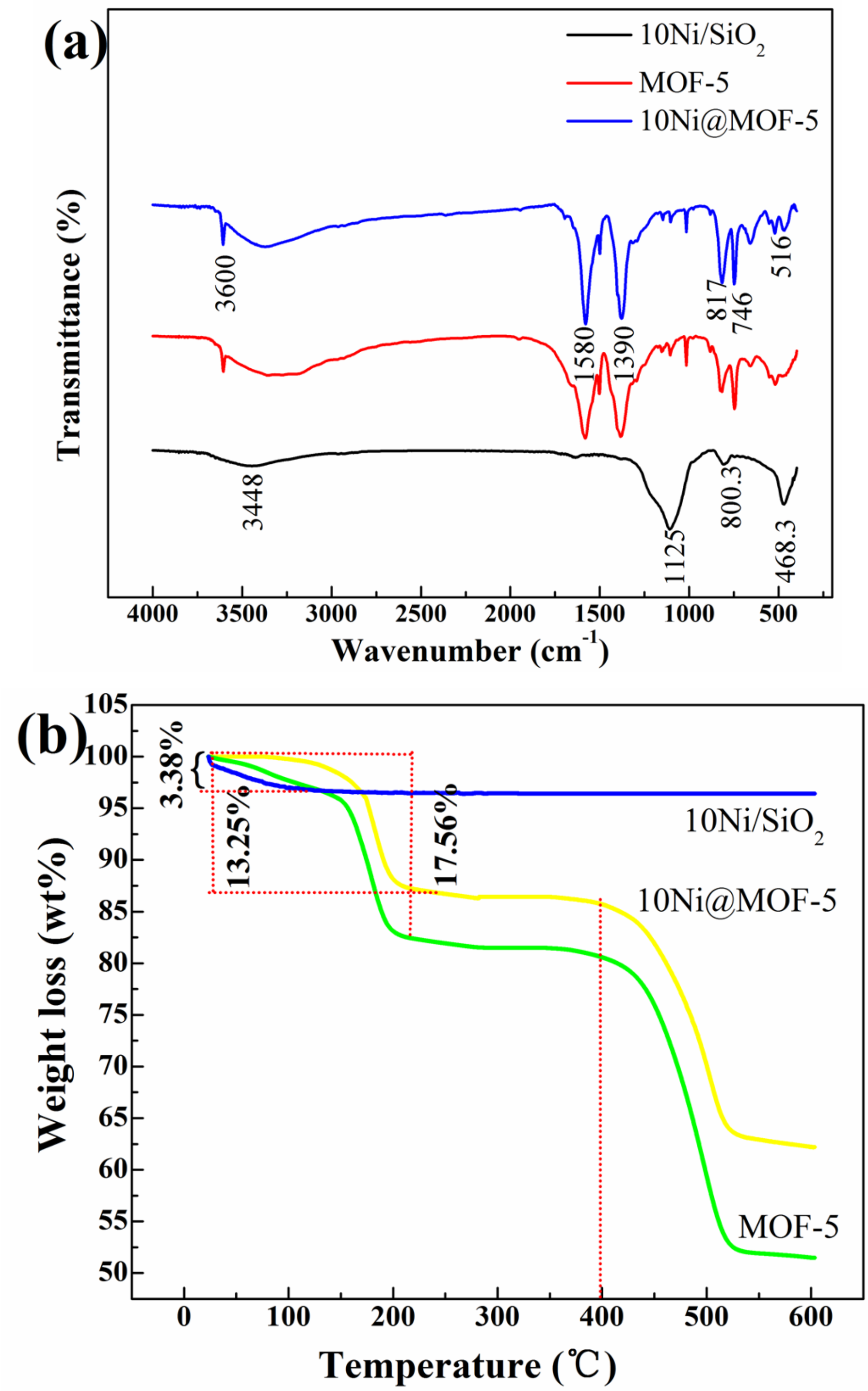

Fig. S2 FT-IR spectra (a) and TGA plot (b) of the as-synthesized MOF-5, 10Ni@MOF-5 and 10Ni/SiO_2.

References

S1 U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastré, *J. Mater. Chem.*, 2006, **16,** 626-636