

Highly efficient Ni/Ac-Al₂O₃ catalysts in the dry reforming of methane: Influence of acetic acid treatment and Ni loading

Han Xiao ^{a,b}, Jiaming Dong ^{a,b}, Yimin Zhang ^a, Xiaohua Cao ^{a,b}, Yanhong Li ^a,
Dedong He ^{a,b}, Yongming Luo ^{a,b}, Pingyan Wang ^{a,*}, Hao Wang ^{a,b,*}

^a Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, P. R. China;

^b The Higher Educational Key Laboratory for Odorous Volatile Organic Compounds Pollutants Control of Yunnan Province, The Innovation Team for Volatile Organic Compounds Pollutants Control and Resource Utilization of Yunnan Province, Kunming University of Science and Technology, Kunming 650500, P. R. China;

^c Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, P. R. China.

* Corresponding author.

xiaohuacao@kust.edu.cn (X. Cao)

liyh_2004@163.com (Y. Li)

Catalysts characterization

X-Ray Diffraction (XRD). The Rigaku D/Max-1200 diffractometer was used to record XRD patterns. The scan rate was 5°/min with a 2 θ range of 10-80° using Cu-K α radiation at 40 kV and 30 mA.

Hydrogen Temperature Programmed Reduction (H₂-TPR). The experiment was conducted using the Tianjin Golden Eagle instrument with a plate number PX200. The instrument was equipped with a thermal conductivity detector (TCD). The objective of the experiment was to determine the chemical composition of the sample. To begin with, 100 mg of the sample was placed between quartz wool in a U-tube. The sample was then treated with Ar (30 mL/min) at 150°C for 1 hour to remove physically adsorbed water. After cooling the sample down to 50°C, H₂-TPR was performed by flowing 10% H₂/Ar (30 mL/min) at a heating rate of 10°C/min from 50°C to 800°C.

X-ray photoelectron spectroscopy (XPS). XPS measurements were conducted using an ultrahigh-vacuum setup equipped with a non-monochromatic Al X-ray source (h ν =1486.6 eV) and a hemispherical electron analyzer (Phoibos 100, SPECS GMBH). The uncalcined sample was loaded into the reaction chamber and heated to 300°C at a rate of 10°C/min under an airflow of 10 mL/min, this is to exclude the effect of adsorbed water. For each treatment, the sample was cooled to room temperature and then transferred directly to the analytical chamber in a vacuum to avoid exposure to air. X-ray photoelectron spectroscopy was then collected, and the positive charge effect was corrected by adjusting the binding energy (BE) peak of the reference carbon in the C1s region to 284.6 eV.

Transmission Electron Microscopy (TEM). The morphology of metal particles, including their size, shape, and lattice fringe, was examined using transmission electron microscopy (TEM, Tecnai G2 TF30) for both fresh and spent catalysts.

CO₂ Temperature Programmed Desorption (CO₂-TPD). The chemisorption apparatus was used to perform CO₂-TPD analysis to investigate the concentration and strength of the basic surface sites of the catalysts'. The sample, weighing 100 mg, was reduced at 700 °C for 1 hour under a 10 vol% H₂/Ar stream (30 mL/min). After cooling the system to 50°C, a stream of CO₂ gas (30 mL/min) was introduced. Subsequently, a stream of He gas (30 mL/min) was introduced, and the temperature was increased to 100 °C to remove residual CO₂ in the stream. The temperature was programmed to increase from 50 to 900 °C with a ramping rate of 10°C /min while keeping the baseline of the CO₂ signal in TCD stable.

Fourier transform infrared (FT-IR). FT-IR spectra were taken using a BRUKER VERTEX 70 spectrometer with a homemade high-temperature reaction chamber to examine the hydroxyl species in the samples. A 15 mg sample was placed in an in-situ vacuum cell and degassed at 150 °C for an hour. Afterward, the spectra were obtained with 4 cm⁻¹ spectral resolution, with 32 scans of the sample between 4000 and 1200 cm⁻¹.

Pyridine-dosing FTIR (Py-FTIR). The acidity level of the samples was determined by conducting an analysis using in situ FT-IR with pyridine adsorption at a temperature of 150°C under vacuum conditions for half an hour. The sample that was saturated with the adsorption was then desorbed at either 150°C or 400°C for an hour. The final spectra were scanned between 4000 and 1200 cm⁻¹ with a spectral resolution of 4 and 32 scans on a Bruker VERTEX 70 spectroscopy instrument.

In situ diffuse reflectance Fourier transform infrared spectroscopy (In-situ DRIFT).

In-situ DRIFT spectra were recorded using a Nicolet Nexus 6700 DRIFTS spectrometer equipped with an MCT detector. The sample cell was fitted with ZnSe windows and a heating chamber. The DRIFTS spectra were obtained with a resolution of 8 cm and 64 scans. Before the measurements, the sample was loaded into the IR cell and reduced in H₂ at 650 °C for 2 h. The system was then purged with pure Ar and cooled down to 50 °C. Following the recording of the background spectrum, N₂ was substituted with a mixed gas of CH₄/CO₂/N₂=1:1:8 (10 mL/min). The temperature was then raised from 50 to 700 °C, and in-situ DRIFT spectra of the adsorbed species on the catalyst surface were collected.

²⁷Al-solid state nuclear magnetic resonance (²⁷Al-NMR). The hydroxyl groups of the ²⁷Al MAS NMR spectra were recorded on an Agilent 600 DD2 spectrometer (Agilent, USA, magnetic field strength 14.1 T) at resonance frequency of 130.28 MHz for ²⁷Al using the magicangle spinning (MAS), and a high-power 1H decoupling. The powder samples were placed in a pencil-type zirconia rotor of 4.0 mm o.d. The spectra were obtained at a spinning speed of 8 kHz (4 μs 90° pulses), and a recycle delay of 10 s. Each spectrum (i.e., the 0 ppm position) was calibrated using 1 mol/l aqueous AlCl₃ as an external standard. ²⁷Al MAS spectra with the same total NMR peak area were normalized for comparison.

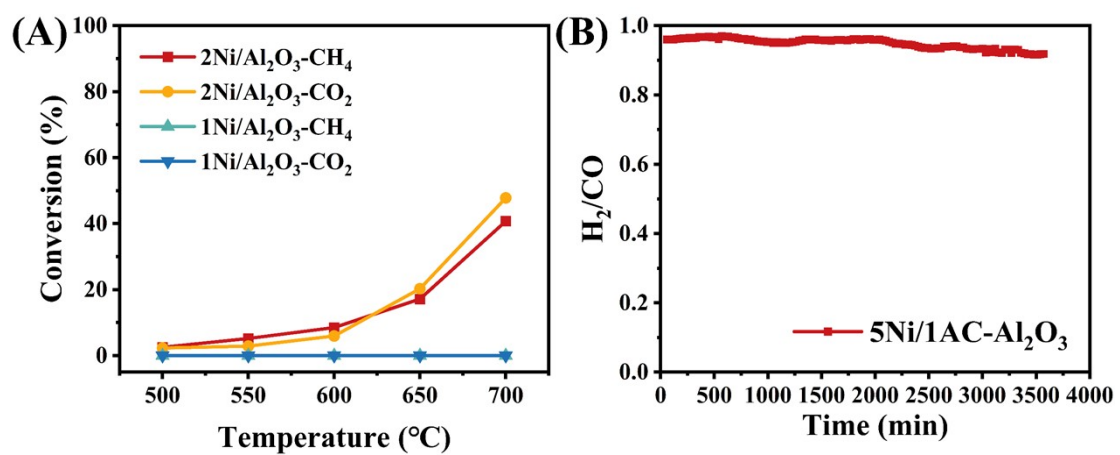


Fig.S 1 CH₄ and CO₂ conversions of yNi/AC-Al₂O₃ (y=1, and 2) (A) and H₂/CO ratio of 5Ni/AC-Al₂O₃ (B)

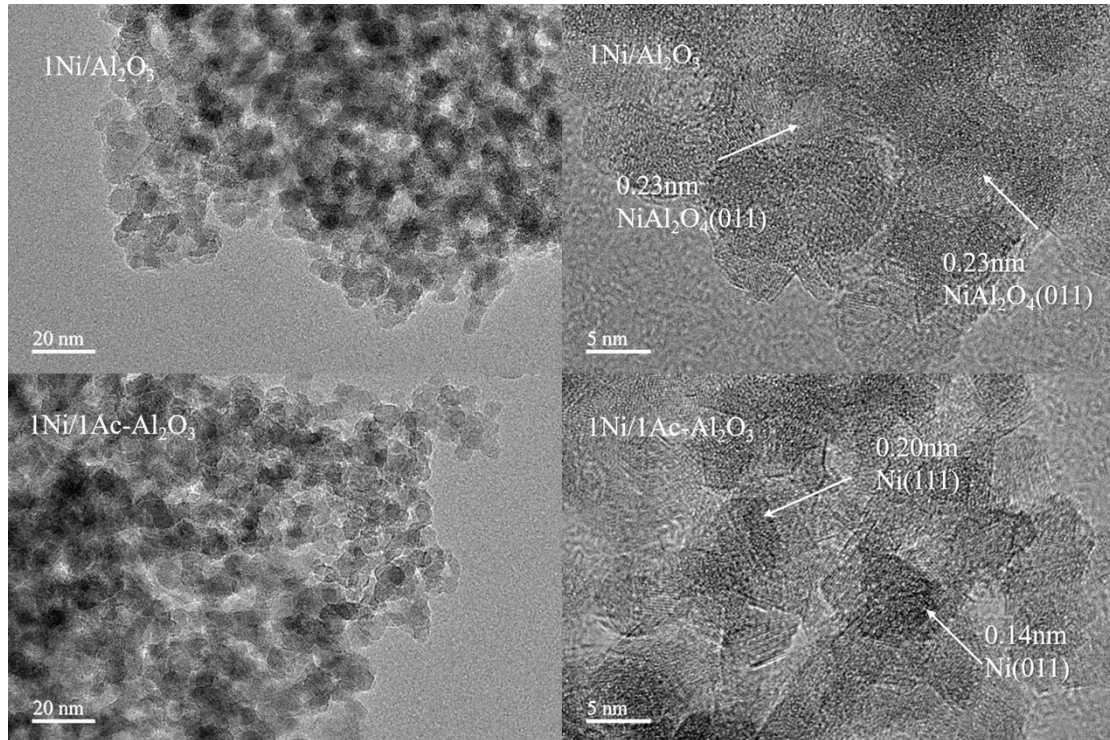


Fig.S 2 TEM image after loading nickel on fresh 1Ni/1Ac-Al₂O₃ and 1Ni/Al₂O₃ catalyst

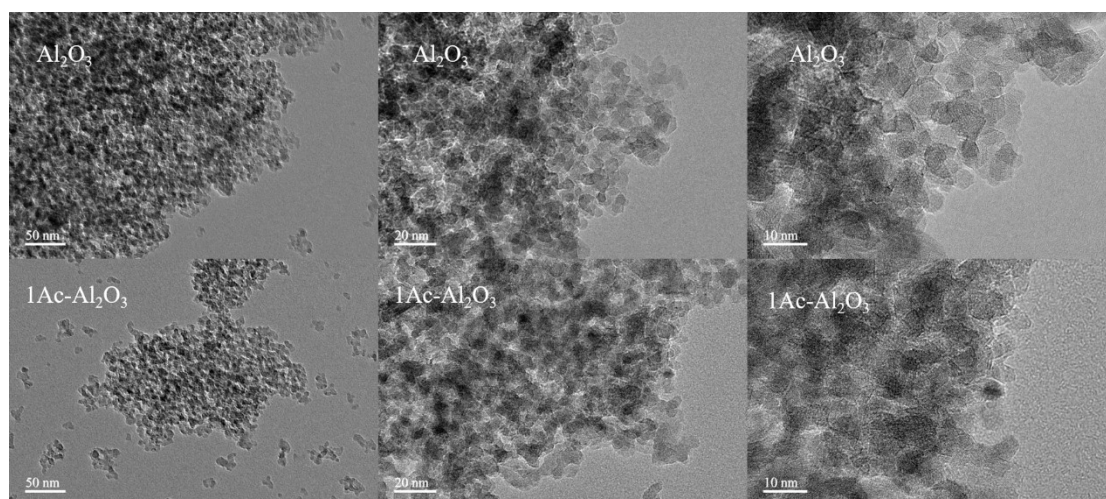


Fig.S 3 TEM images of Al_2O_3 support before and after acetic acid treatment.

Table S1. textural data of Al₂O₃

Chemical formula	PDF-#	P.S.	Space Group	a	b	c	c/a	α	β	γ	Z	Vol	Density
Al ₂ O ₃	10-0425	cF53.5	Fd-3m(227)	7.9	7.9	7.9	1.000	90.0	90.0	90.0	10.7	493.0	3.670