

Deactivation Mechanisms and Mitigation Strategies for Nickel-Based Acetylene Semi-Hydrogenation Catalysts

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Materials and Methods

Catalysts Synthesis

Supported Nickel-based catalysts. A nickel-based catalyst was prepared using incipient-wetness impregnation method. Specifically, a certain amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd.) was weighed and dissolved in 5 ml of deionized water to obtain a homogeneous solution. The solution was then impregnated onto 2 g of white carbon black (SiO_2 , Shanghai Macklin Biochemical Co., Ltd.), yielding a precursor. The precursor was aged for 12 hours and subsequently dried at 70°C for 12 hours. Finally, the precursor was reduced in a 5% H_2/Ar atmosphere at 500°C for 2 hours, resulting in a final nickel-based catalyst with a Ni loading of 10 wt%, which was designated as Ni/SiO_2 .

Supported nickel-based catalysts modified with the support. A) White carbon black support was modified with ammonia. Specifically, a certain amount of white carbon black was placed in a tube furnace, and ammonia gas was introduced at a flow rate of 50 ml/min, a treatment temperature of 500°C , and a treatment time of 2 hours. After obtaining the ammonia-treated support, the incipient-wetness impregnation method was used, following the above steps, to prepare the material, which was named $\text{Ni}/\text{SiO}_2\text{-N}$. The effect of ammonia treatment time (0 hour, 1 hour, 4 hours) on the catalytic performance was also investigated; B) White carbon black support was modified with alkali metals. Taking potassium modification as an example, a certain amount of KHCO_3 (Shanghai Lingfeng Chemical Reagent Co., Ltd.) was weighed and dissolved in 5 ml of deionized water to obtain a uniform solution. The solution was then impregnated onto 2 g of white carbon black, followed by drying at 70°C for 12 hours and calcination in a muffle furnace at 600°C for 2 hours to obtain alkali metal-modified supports, with alkali metal contents of 0.1 wt%, 0.5 wt%, and 1.5 wt%, respectively. After obtaining the alkali metal-modified support, the incipient-wetness impregnation method was used, following the steps described above. The final catalyst obtained was named $\text{Ni}/x\text{K-SiO}_2$. The modification process for sodium was similar, and the resulting catalyst was named $\text{Ni}/x\text{Na-SiO}_2$. For comparison, the $\text{Ni}/0.1\text{K-SiO}_2$ catalyst was synthesized using the co-impregnation method. Specifically, a certain amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and KHCO_3 was dissolved in 5 ml of deionized water to obtain a uniform solution. The solution was then impregnated onto 2 g of white carbon black to prepare the precursor. The precursor was subsequently treated according to the steps outlined above to complete the preparation.

Supported nickel-based catalysts at different reaction stages. To study the structural changes of the samples under reaction conditions, the catalysts (Ni/SiO_2 , $\text{Ni}/\text{SiO}_2\text{-N}$, and $\text{Ni}/0.1\text{K-SiO}_2$) were exposed to a specific reaction atmosphere ($\text{C}_2\text{H}_2/\text{H}_2/\text{C}_2\text{H}_4/\text{N}_2 = 1:2:100:200$) for varying periods of time. The samples were then characterized in a quasi-in-situ manner and named $\text{Ni}/\text{SiO}_2\text{-t}$, $\text{Ni}/\text{SiO}_2\text{-N-t}$, and $\text{Ni}/0.1\text{K-SiO}_2\text{-t}$, where "t" indicates the reaction time.

Catalytic Performance Evaluation

Acetylene semi-hydrogenation was carried out in a fixed-bed reactor with a quartz tube of 6 mm inner diameter. Catalyst powder was pressed into tablets and sieved (60-80 mesh). 100 mg of catalyst and 200 mg of inert quartz sand were mixed uniformly and placed in the fixed-bed reactor. Before testing, the sample was heated to 200°C at a rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere and held until stable. Then, the reactant gas was passed through the reactor at a flow rate of 30 ml/min for catalytic performance evaluation. The gas composition before and after the reaction was analyzed using online gas chromatography (GC-2060) with a FID detector and a separation column of $\text{KB-Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ (30 m \times 0.32 mm \times 10.00 μm) capillary column. The carbon balance in all tests exceeded 95%. Acetylene conversion and ethylene selectivity were calculated based on carbon atomic balance, defined as follows:

$$\text{C}_2\text{H}_2 \text{ conversion}(\%) = \frac{[\text{C}_2\text{H}_2]_{in} - [\text{C}_2\text{H}_2]_{out}}{[\text{C}_2\text{H}_2]_{in}} * 100 \quad (1)$$

$$\text{C}_2\text{H}_4 \text{ selectivity}(\%) = \left\{ 1 - \frac{[\text{C}_2\text{H}_6]_{out} + 2 * [\text{C}_4]_{out}}{[\text{C}_2\text{H}_2]_{in} - [\text{C}_2\text{H}_2]_{out}} \right\} * 100 \quad (2)$$

Catalytic Characterizations

X-ray diffraction (XRD) measurements were performed using a Smart-lab 9 kW advanced powder X-ray diffractometer with a Cu K α radiation source ($\lambda = 0.154$ nm). The 2θ range was scanned from 5° to 90° at a rate of $5^\circ/\text{min}$. **X-ray photoelectron spectroscopy (XPS)** experiments were conducted on a Thermo Scientific K-Alpha instrument. The system utilized monochromatic Al K α radiation ($h\nu = 1486.6$ eV) as the X-ray source, with an operating voltage of 12 kV and a filament current of 6 mA. The analysis chamber vacuum was maintained at better than 5.0×10^{-7} mbar. The binding energy was calibrated using the C1s peak at 284.8 eV. Peak fitting was performed using the Avantage 5.9931 software. **Thermogravimetric analysis (TGA)** (NetzschTGA209F1, Germany) was employed to analyze coke deposition on the catalyst before and after the reaction. The catalyst was heated in an air atmosphere from room temperature to $\sim 800^\circ\text{C}$ at a rate of $10^\circ\text{C}/\text{min}$. **Oxygen-programmed temperature oxidation combined with online mass spectrometry (O₂-TPO-MS)** was conducted using a temperature-programmed instrument (manufactured by Zhengzhou Ketian Instrument Equipment Co., Ltd.) coupled with the SRD200M online mass spectrometer (from Tilon Grp Technology Limited). The process began by heating 50 mg of the catalyst in an argon (Ar) atmosphere at a rate of 10°C per minute to 100°C , where it was held for 1 hour to remove any surface moisture and organic contaminants. Following this, the system was cooled to room temperature, and the mass spectrometer baseline was stabilized. Subsequently, a 1%O₂/Ar gas mixture (flow rate of 20 ml/min) was introduced into the system. The temperature was then increased to 600°C at the same heating rate of 10°C per minute. Throughout this process, the mass spectrometer continuously monitored the signal at $m/z = 44$, which corresponds to CO₂. **Fourier Transform Infrared Spectroscopy (FT-IR)** analysis was conducted using a Thermo Scientific iS50 FT-IR spectrometer. A small amount of dried sample was mixed with KBr at a mass ratio of 1:100, thoroughly ground, dried, and pressed into a pellet for transmission mode testing. **Hydrogen-programmed temperature reduction coupled with online mass spectrometry (H₂-TPR-MS)** was performed using a temperature-programmed device (Zhengzhou Ketian Instrument Equipment Co., Ltd.) coupled with SRD200M online mass spectrometer (Tilon Grp Technology Limited). The procedure involved heating 50 mg of catalyst in an Ar atmosphere at a rate of $10^\circ\text{C}/\text{min}$ to 300°C for 1 hour to remove surface moisture and organic contaminants. After cooling to room temperature and stabilizing the mass spectrometer baseline, a 5% H₂/Ar mixture (20 ml/min) was introduced, and the temperature was ramped to 500°C at $10^\circ\text{C}/\text{min}$. The mass spectrometer monitored the $m/z = 18$ (H₂O) signal. **Diffuse Reflectance Infrared Fourier Transform Spectroscopy with CO or C₂H₂ as Probe Molecules (CO-DRIFTS or C₂H₂-DRIFTS)** Diffuse reflectance infrared Fourier transform spectroscopy was performed using a Thermo Scientific iS50 FT-IR spectrometer combined with a self-made in-situ testing equipment (temperature control system, flow system, reactor system). Prior to testing, the sample was held at 300°C in an inert N₂ atmosphere for 1 hour to remove impurities such as water vapor and organic compounds. After cooling to room temperature, a background spectrum was collected in N₂. Subsequently, a 5% CO/Ar gas mixture was introduced, and the sample was allowed to adsorb CO for 60 minutes at room temperature to ensure saturation. The system was then purged with N₂, and spectra were collected every minute for 15 minutes to record and analyze the characteristic vibrational peaks of CO adsorbed on the catalyst surface. For C₂H₂-DRIFTS experiments, the same procedure was followed, with C₂H₂ gas replacing CO as the probe

molecule. **In-situ Fourier Transform Infrared Spectroscopy under Reaction Conditions (In-situ FT-IR)** analysis was performed using a Thermo Scientific iS50 FT-IR spectrometer combined with a self-made equipment. The sample was first heated to 200°C in an inert atmosphere, followed by purging with the reaction gas for 5 minutes. Background data were collected, and spectra were recorded approximately every 5 minutes for a total duration of 720 minutes using the Series plugin. The collected data were then analyzed.

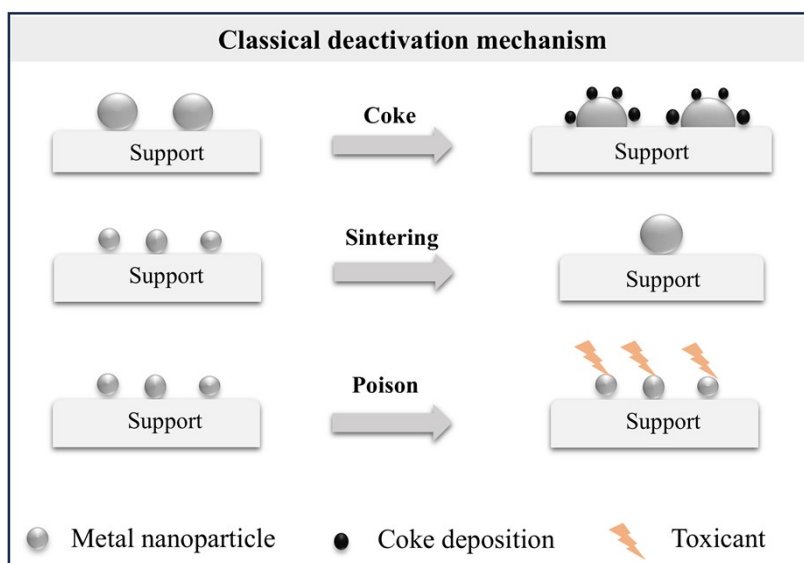


Figure S1. The classical deactivation mechanism of Ni-based catalysts for acetylene Semi-Hydrogenation.

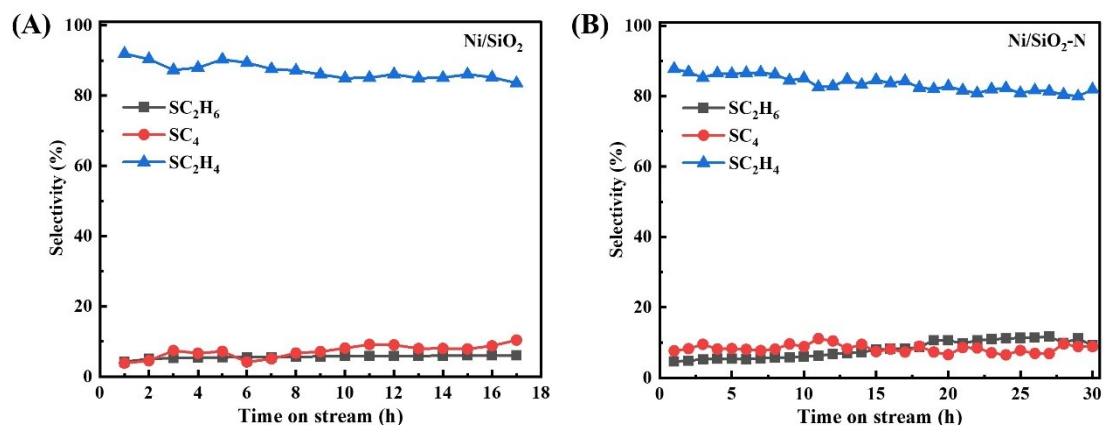


Figure S2. Other product selectivity changes with time for (A) Ni/SiO₂ and (B) Ni/SiO₂-N. Reaction condition: WHSV=18,000 ml/g_{cat}/h; m_{cat}=100 mg; quartz sand=200 mg; Gas Composition: C₂H₂/H₂/C₂H₄/N₂=1:2:100:200; Reaction temperature, ~200°C.

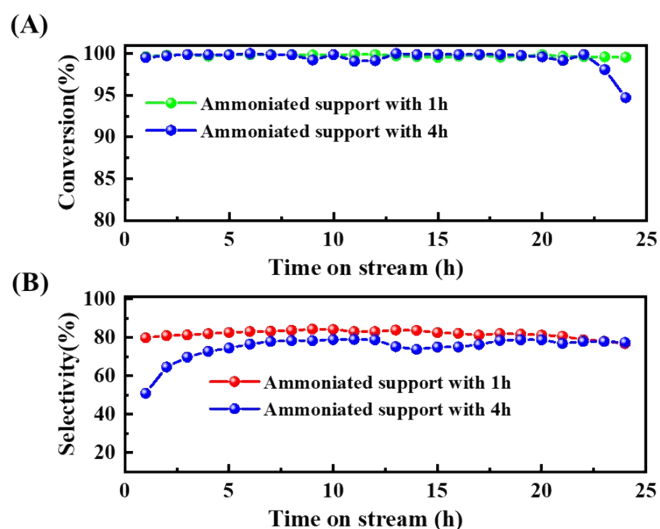


Figure S3. The stability test on ammoniated support with different times. Reaction

condition: WHSV=18,000 ml/g_{cat}/h; m_{cat}=100 mg; quartz sand=200 mg; Gas Composition: C₂H₂/H₂/C₂H₄/N₂=1:2:100:200; Reaction temperature, ~200°C.

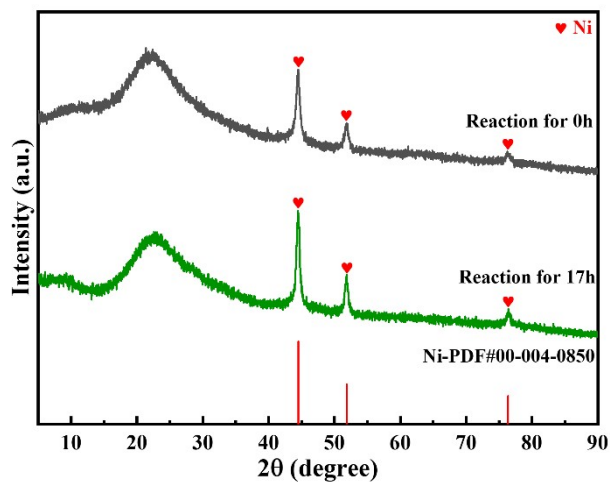


Figure S4. X-ray diffraction (XRD) of Ni/SiO₂ with different reaction times.

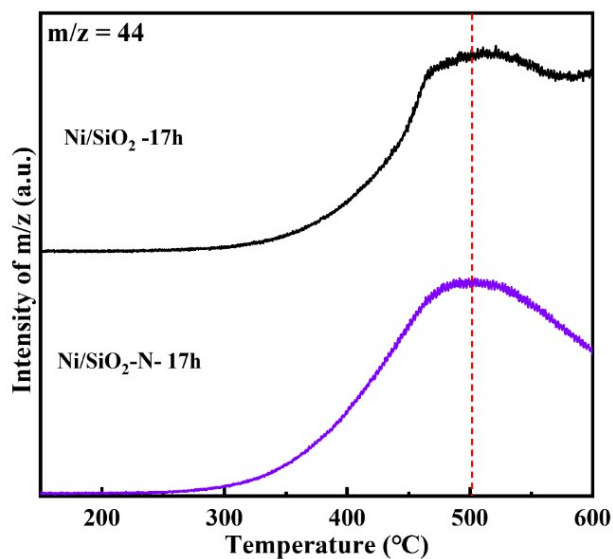


Figure S5. Oxygen-programmed temperature oxidation coupled with mass spectrometry (O₂-TPO-MS) of Ni/SiO₂-17h and Ni/SiO₂-N-17h.

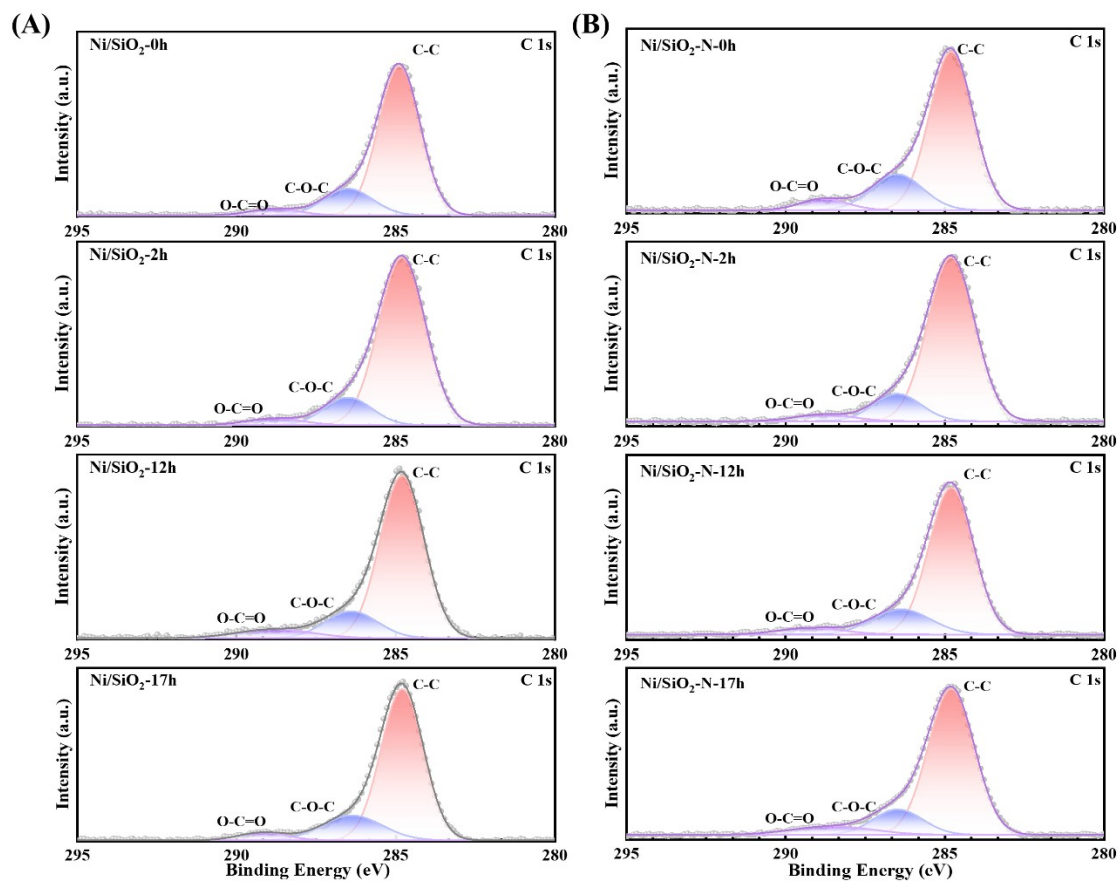


Figure S6. C1s X-ray photoelectron spectroscopy (XPS) spectra of (A) Ni/SiO₂; (B) Ni/SiO₂-N catalysts with different reaction times.

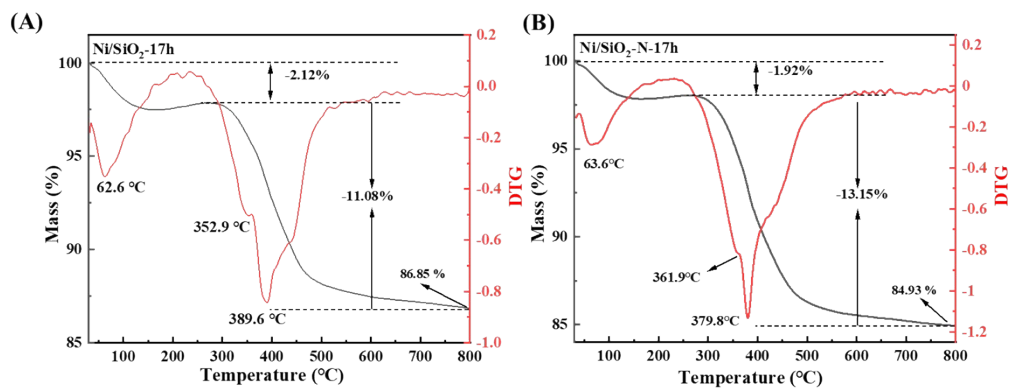


Figure S7. Thermogravimetric analysis (TGA) of (A) Ni/SiO₂-17h and (B) Ni/SiO₂-N-17h.

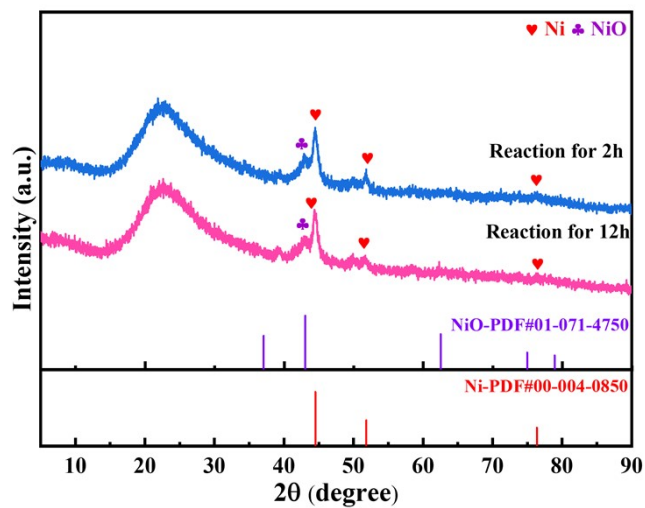


Figure S8. XRD of Ni/SiO₂ with different reaction times.

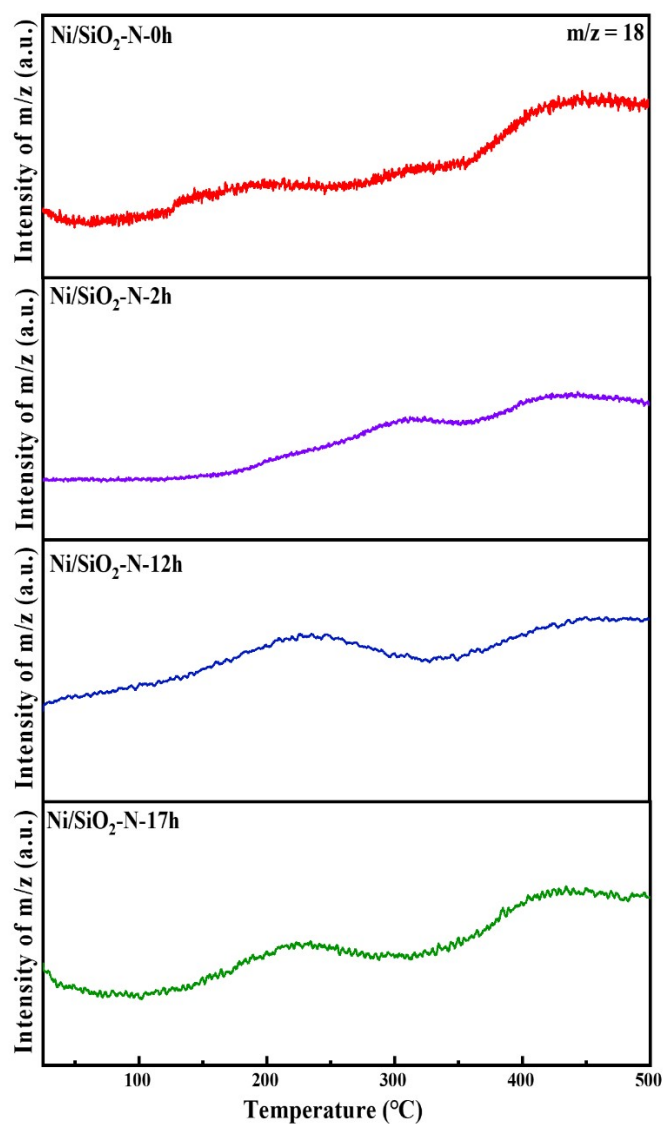


Figure S9. Hydrogen-programmed temperature reduction coupled with mass spectrometry (H₂-TPR-MS) of Ni/SiO₂-N with different reaction times.

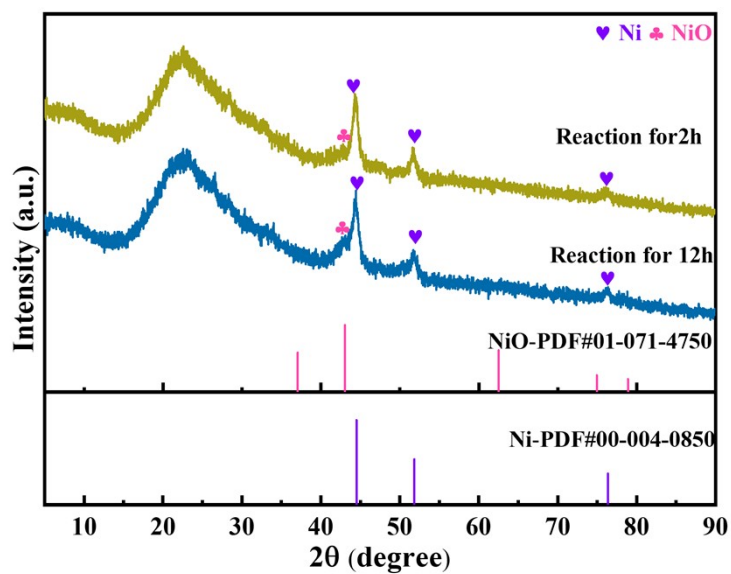


Figure S10. XRD of Ni/SiO₂-N with different reaction times.

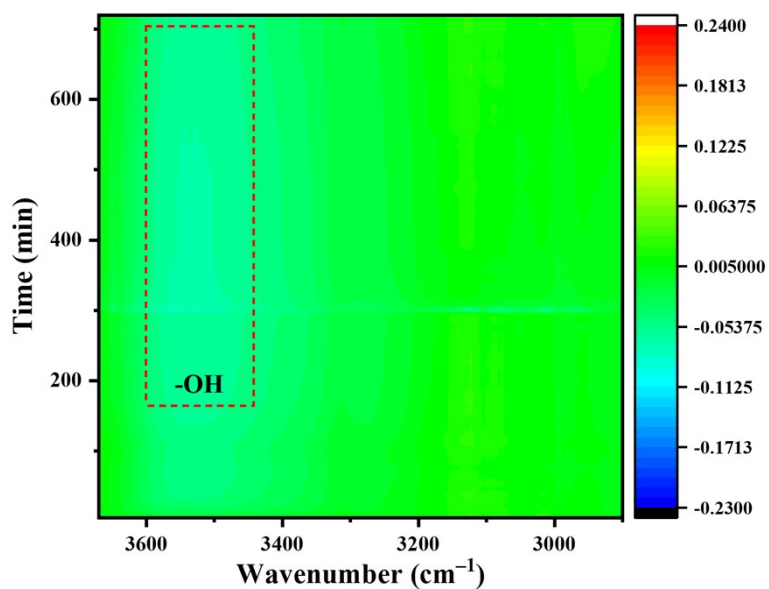


Figure S11. In-situ Fourier transform infrared spectroscopy under acetylene semi-hydrogenation reaction (In-situ FT-IR) on Ni/SiO₂-N. Reaction condition: WHSV=36,000 ml/g_{cat}/h; m_{cat}=50 mg; Gas Composition: C₂H₂/H₂/C₂H₄/N₂=1:2:100:200; Reaction temperature, ~200°C.

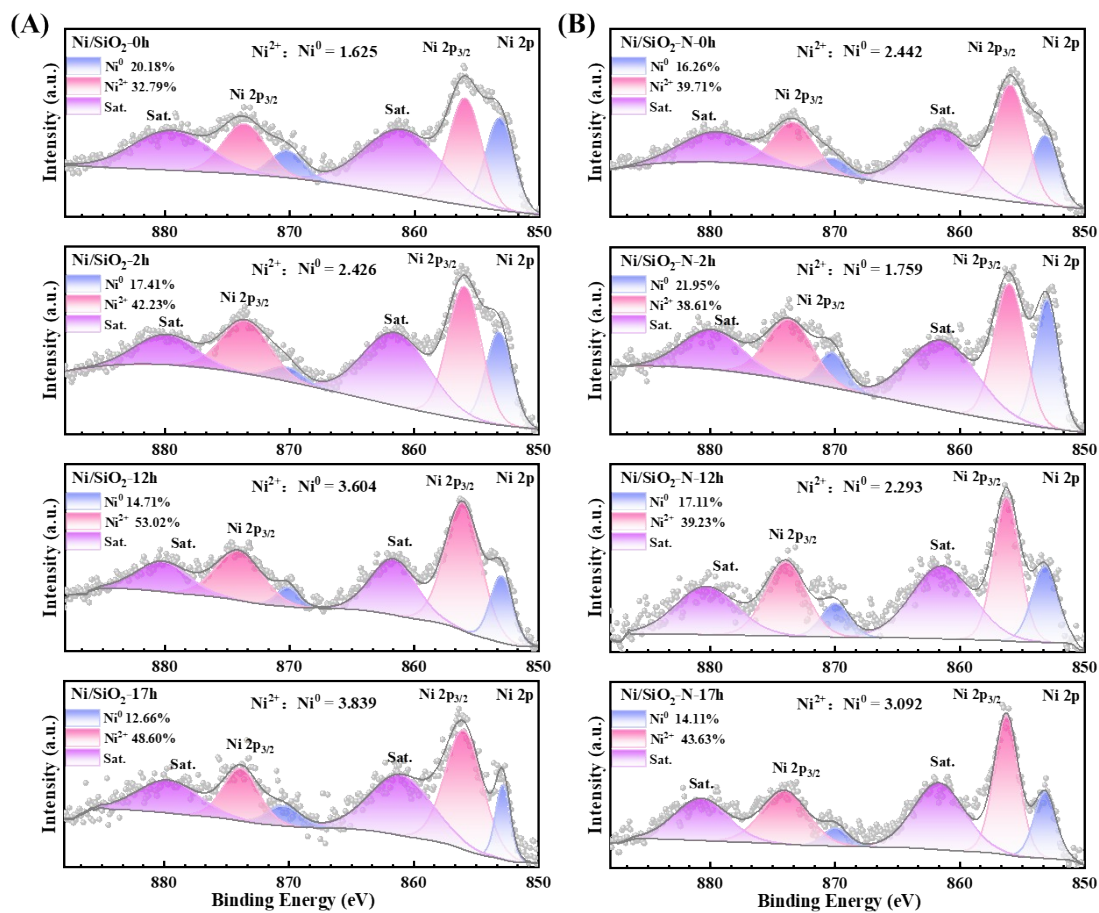


Figure S12. Ni 2p XPS spectra of (A) Ni/SiO₂, (B) Ni/SiO₂-N catalysts with different reaction times.

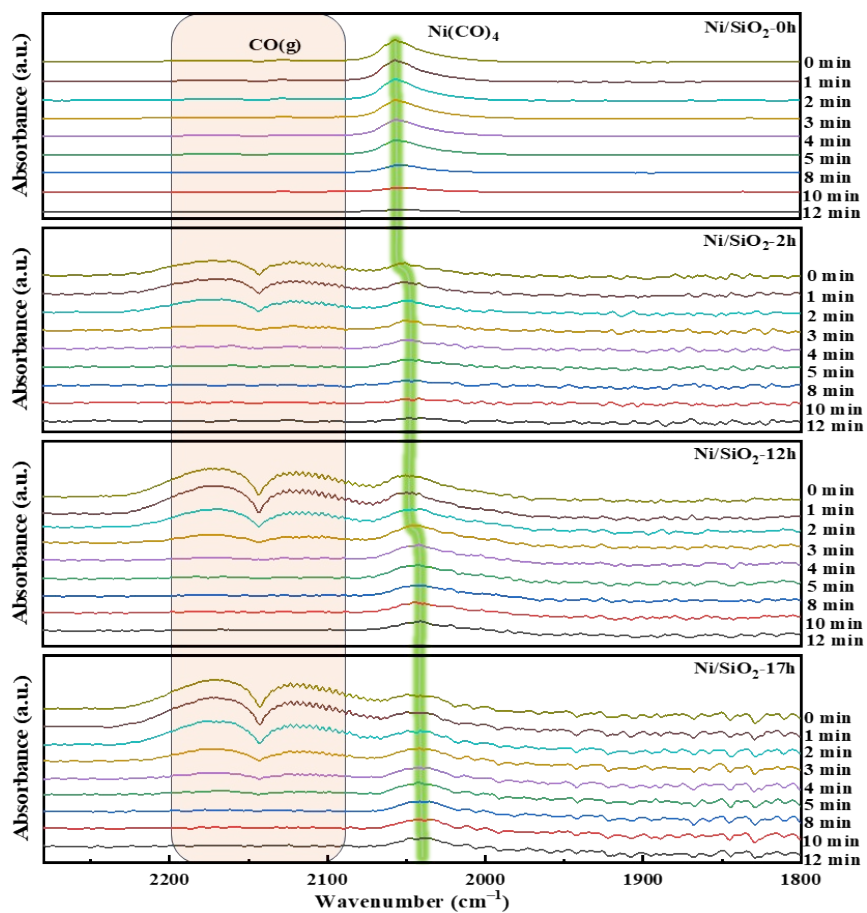


Figure S13. Diffuse reflectance infrared Fourier transform spectroscopy with CO as a probe molecule (CO-DRIFTS) on Ni/SiO₂ catalysts with different reaction times.

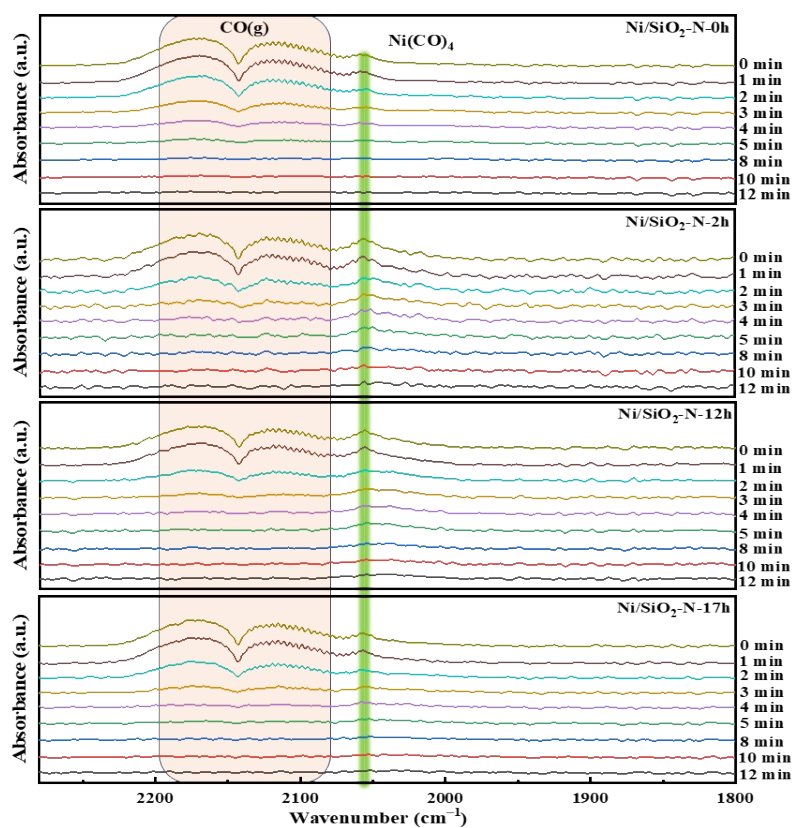


Figure S14. CO-DRIFTS on Ni/SiO₂-N catalysts with different reaction times.

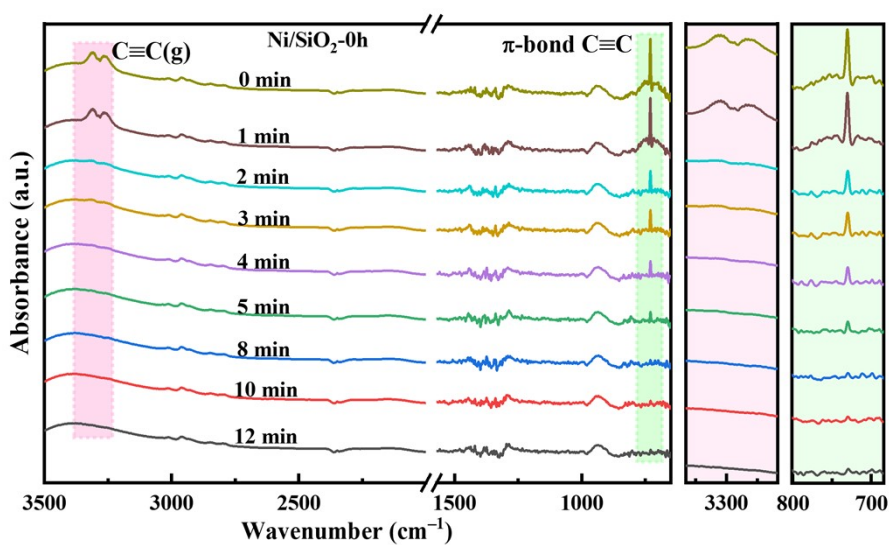


Figure S15. Diffuse reflectance infrared Fourier transform spectroscopy with C₂H₂ as a probe molecule (C₂H₂-DRIFTS) on Ni/SiO₂ for 0 h.

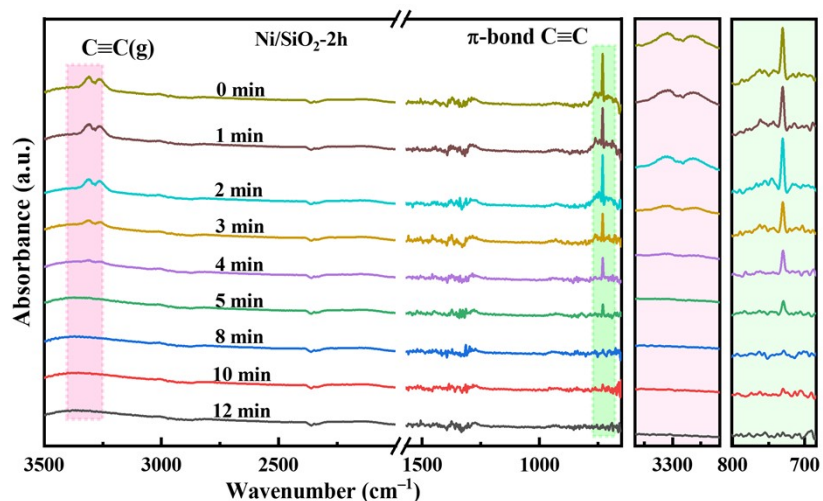


Figure S16. C_2H_2 -DRIFTS on Ni/SiO₂ for 2 h.

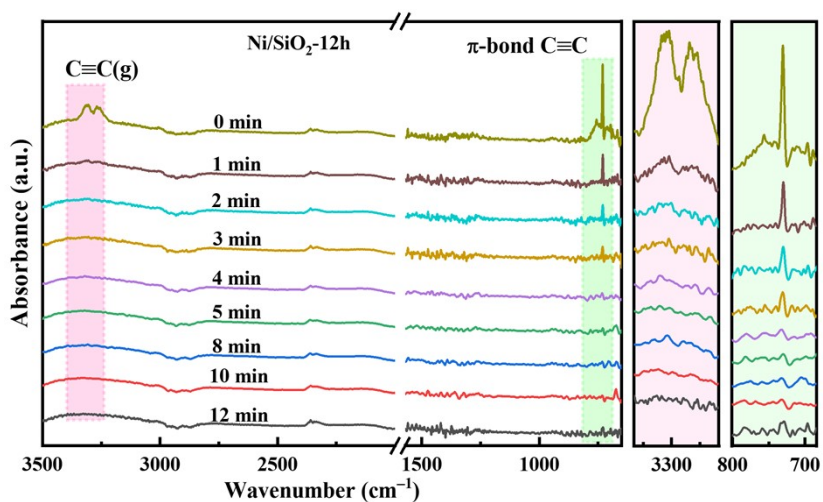


Figure S17. C_2H_2 -DRIFTS on Ni/SiO₂ for 12 h.

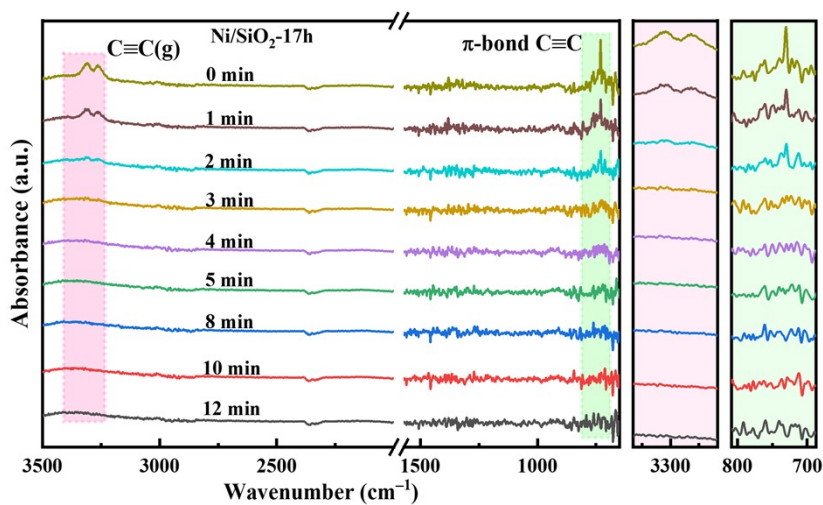


Figure S18. C_2H_2 -DRIFTS on Ni/SiO₂ for 17 h.

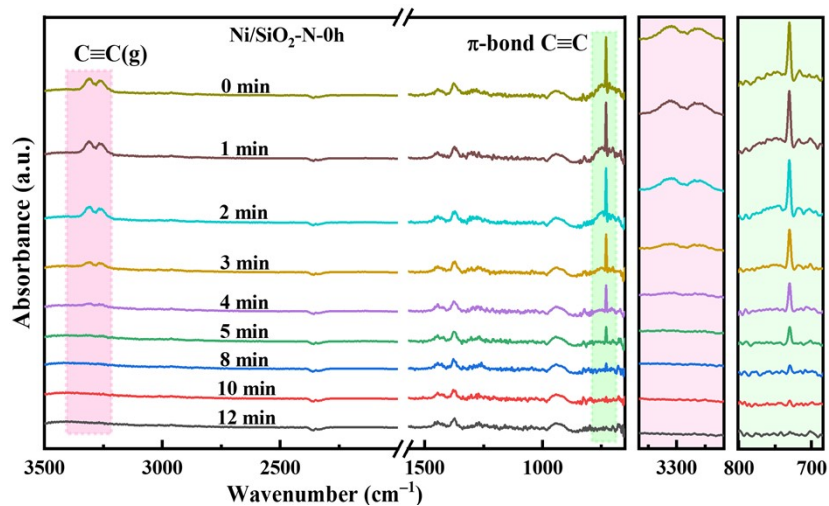


Figure S19. C_2H_2 -DRIFTS on Ni/SiO₂-N for 0 h.

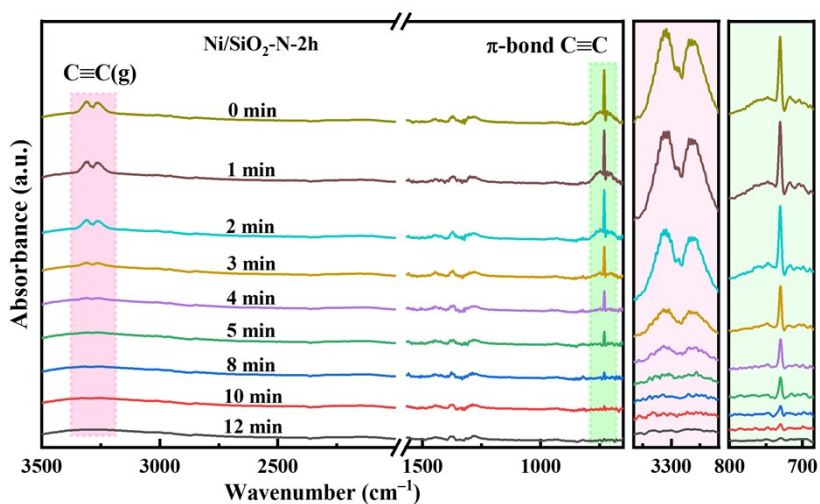


Figure S20. C_2H_2 -DRIFTS on Ni/SiO₂-N for 2 h.

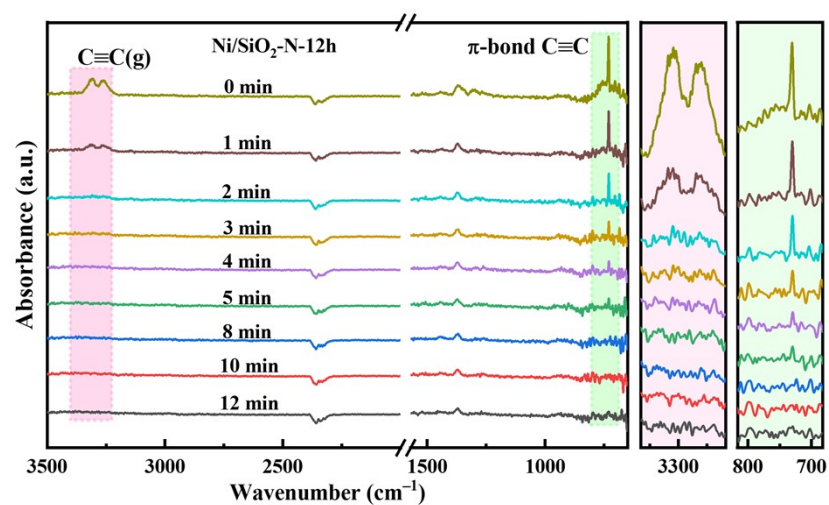


Figure S21. C_2H_2 -DRIFTS on Ni/SiO₂-N for 12 h.

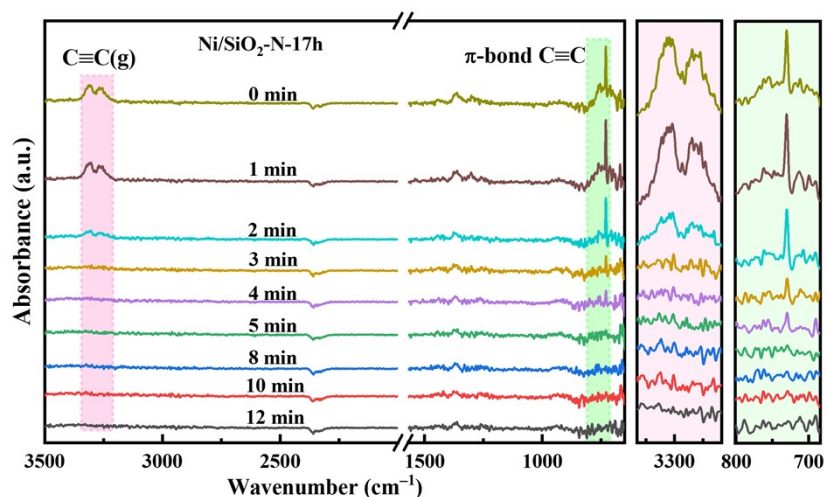


Figure S22. C_2H_2 -DRIFTS on Ni/SiO₂-N for 17 h.

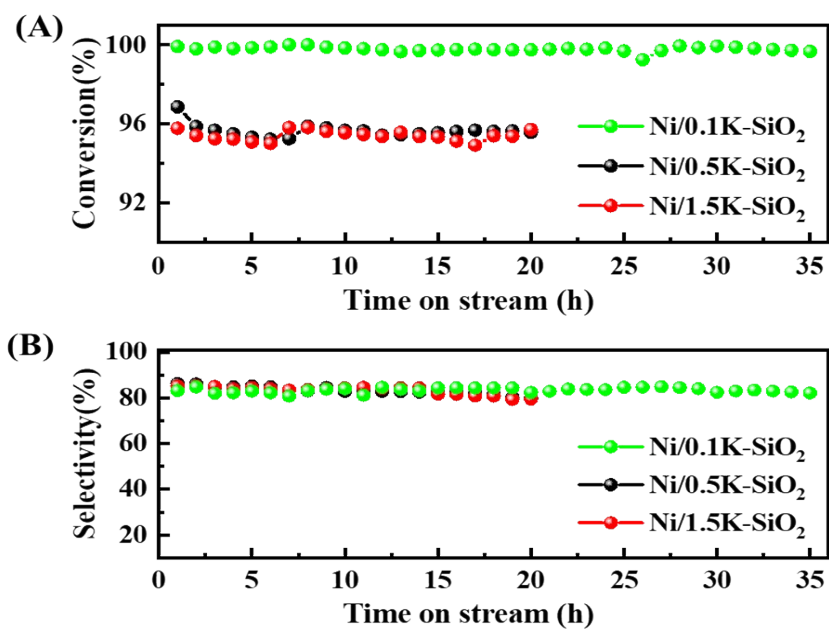


Figure S23. The stability test on Ni/xK-SiO₂ catalysts with different loading of K. Reaction condition: WHSV=18,000 ml/g_{cat}/h; m_{cat}=100 mg; quartz sand=200 mg; Gas Composition: C₂H₂/H₂/C₂H₄/N₂=1:2:100:200; Reaction temperature, ~200°C.

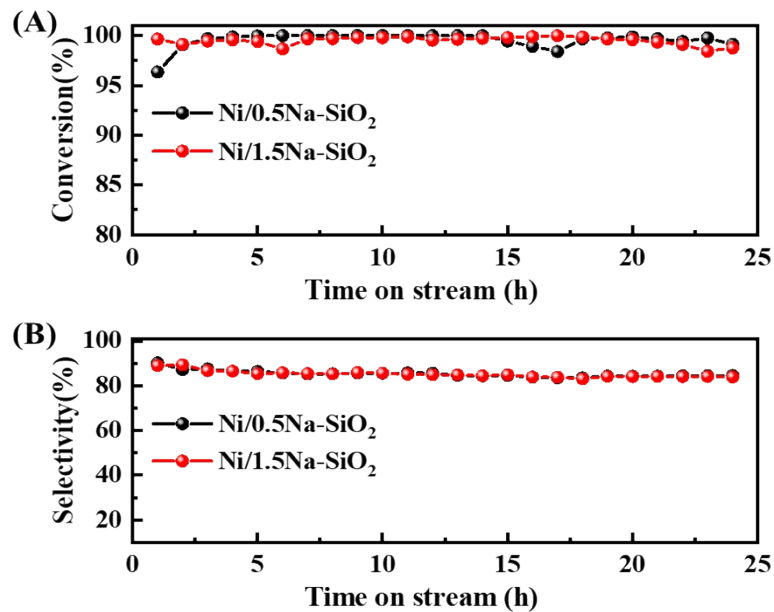


Figure S24. The stability test on Ni/xNa-SiO₂ catalysts with different loading of Na. Reaction condition: WHSV=18,000 ml/g_{cat}/h; m_{cat}=100 mg; quartz sand=200 mg; Gas Composition: C₂H₂/H₂/C₂H₄/N₂=1:2:100:200; Reaction temperature, ~200°C.

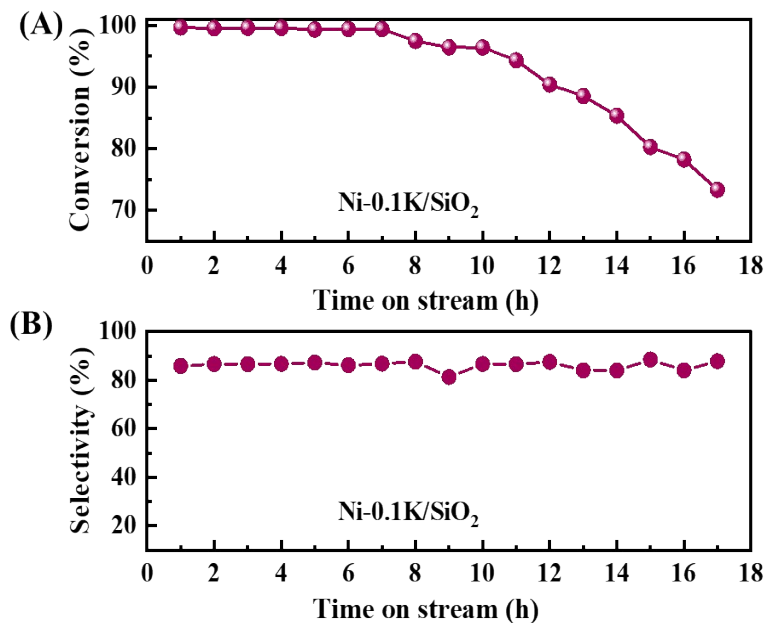


Figure S25. The stability test on Ni-0.1K/SiO₂ catalysts. Reaction condition: WHSV=18,000 ml/g_{cat}/h; m_{cat}=100 mg; quartz sand=200 mg; Gas Composition: C₂H₂/H₂/C₂H₄/N₂=1:2:100:200; Reaction temperature, ~200°C.

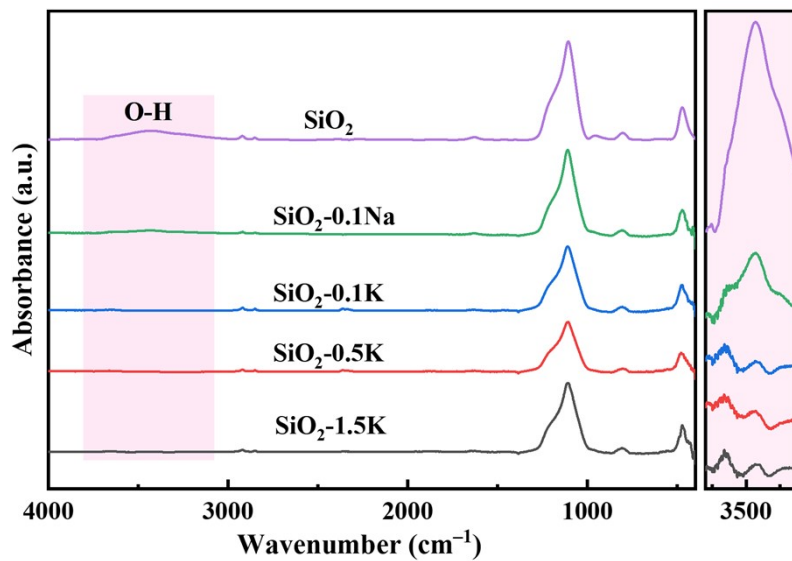


Figure S26. Fourier Transform Infrared Spectroscopy (FT-IR) of SiO₂ with different alkali metal modifications.

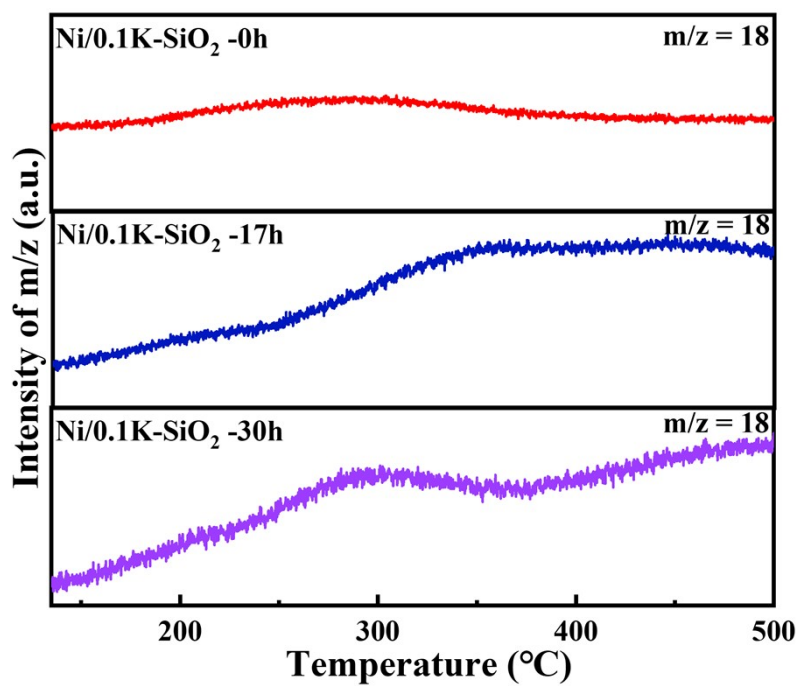


Figure S27. Ni/0.1K-SiO₂ catalysts for H₂-TPR-MS with different reaction times.

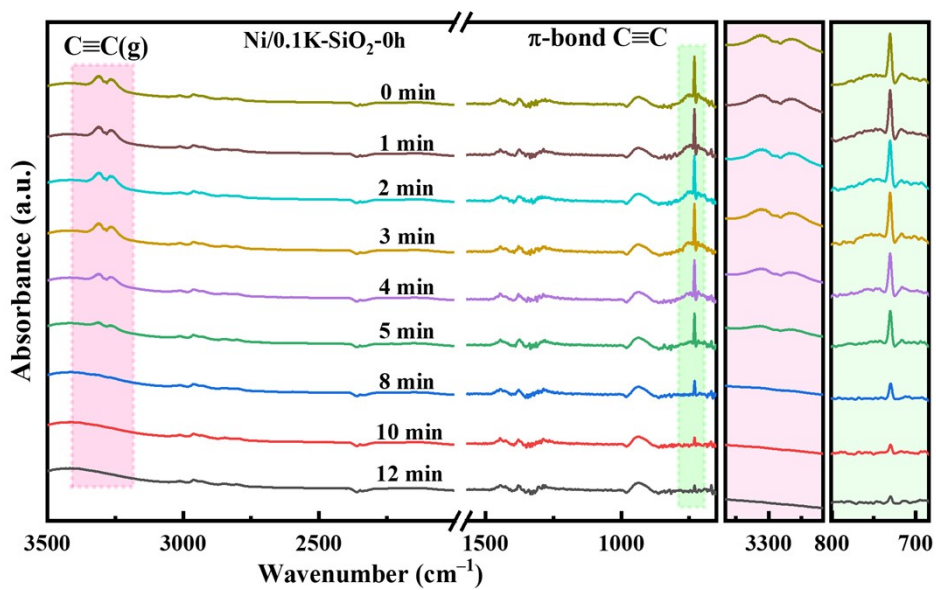


Figure S28. C_2H_2 -DRIFTS on Ni/0.1K-SiO₂ for 0 h.

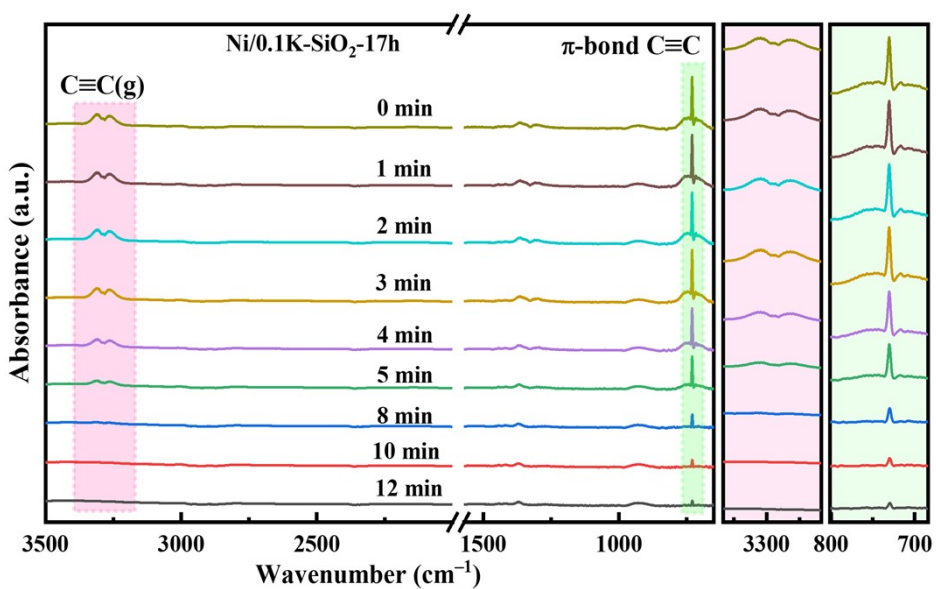


Figure S29. C_2H_2 -DRIFTS on Ni/0.1K-SiO₂ for 17 h

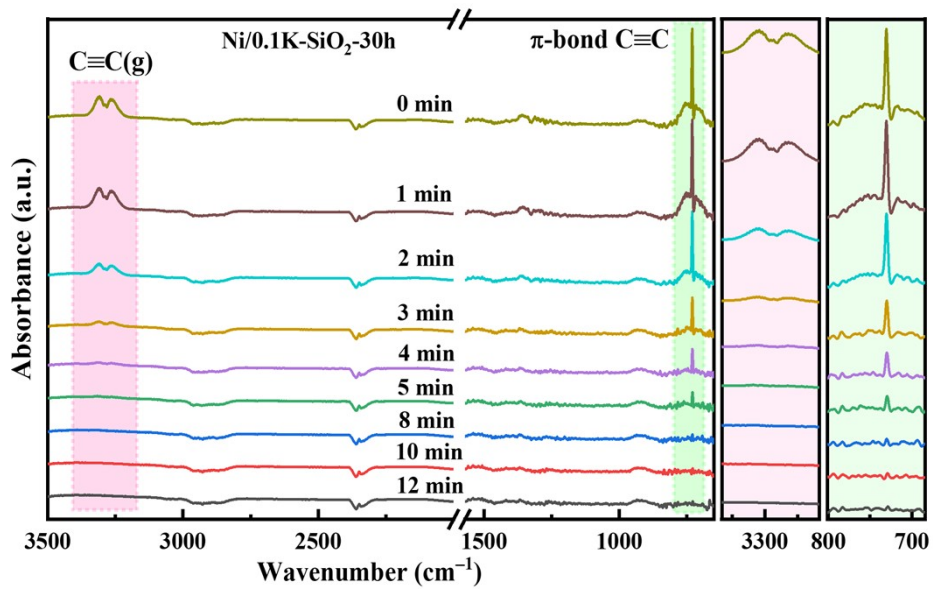


Figure S30. C_2H_2 DRIFTS on $Ni/0.1K-SiO_2$ for 30 h

Table S1. Particle size(nm) of Ni/SiO₂ and Ni/SiO₂-N catalysts before and after reaction.

Samples	Ni/SiO ₂	Ni/SiO ₂ -N
fresh	14.5	12.7
spend	15.0	13.1

The particle size of the catalyst before and after the reaction was calculated from Scheller's equation.

Table S2. Analysis of the type and amount of coke after reaction of Ni/SiO₂ and Ni/SiO₂-N catalysts.

	Ni/SiO ₂ -17h	Ni/SiO ₂ -N-17h
C 1s Binding Energy/eV ^a	284.8 (C-C)	284.8
	286.4 (C-O-C)	286.4
	289.2 (O-C=O)	289.0
starting combustion temperature (°C) ^b	280.0	275.0
Coke deposition amount (%) ^c	11.08	13.15

^a from C1s in Figure S5; ^b from the starting combustion temperature in Figure S4; ^c from TGA in Figure S6.

Table S3. Binding energy(eV) of Ni⁰ for Ni/SiO₂ and Ni/SiO₂-N catalysts with different reaction times

Reaction time (h)	Ni/SiO ₂	Ni/SiO ₂ -N
0	853.2	853.2
2	853.2	853.2
12	853.0	853.2
17	852.9	853.2