Morphology-Dependent Ni/TiO₂ Catalysts for CO₂

Hydrogenation

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Experimental section

Materials

All the chemicals and reagents used in this study were sourced from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

Anatase TiO₂{001} Nanocrystals Synthesis ^{1,2,3}

To synthesize anatase TiO₂{001} nanocrystals, 3 mL of aqueous HF (40 wt%) and 25 mL of Ti(OBu)₄ were combined under magnetic stirring. The mixture was then transferred into a dried Teflon autoclave (50 mL) and heated at 180 °C for 24 hours. After the reaction, the resulting precipitate was washed several times with ethanol and water, then dried at 70 °C overnight. To remove F^- , the powder was immersed in 0.1 mol/L NaOH solution (700 mL) at room temperature for 24 hours, followed by washing with ultrapure water until the suspension reached a pH of 7-8.

Anatase TiO₂{100} and TiO₂{101} Nanocrystals Synthesis ^{1,2,3}

For the preparation of Ti(OH)₄ precursor. TiCl₄ (6.6mL) was slowly added to 0.43 mol/L aqueous HCl (20mL) while stirring at 0 °C. The resulting TiCl₄ was then added dropwise to 50 mL of 5.5 wt% aqueous NH₃ under stirring at room temperature. The pH of the suspension was adjusted to 6-7 using 4 wt% aqueous NH₃. The mixture was stirred at room temperature for 2 hours, and the Ti(OH)₄ precursor was filtered, washed multiple times with ultrapure water to remove Cl⁻, and dried at RT. Ti(OH)₄ (2.0 g) and (NH₄)₂SO₄ (0.5 g for TiO₂{100}) or NH₄Cl (0.2g for TiO₂{101}) were added to a mixture of iPrOH (15 mL) and ultrapure H₂O (15 mL) under stirring; The mixture was poured into a 50 mL dried Teflon autoclave and kept at 180 °C for 24 h. The obtained precipitate was centrifuged and washed with ultrapure H₂O several times.

Synthesis of Ni/TiO₂ Catalysts

The preparation of Ni/TiO₂ catalysts was carried out through a conventional incipient wetness impregnation approach. Typically, a calculated amount of Ni(NO₃)₂.6H₂O was dissolved to form a solution. Then, 2 mL of the solution was impregnated onto 500 mg of pre-synthesized TiO₂ nanocrystals with different facets, followed by drying at 30 °C. Subsequently, the sample was reduced in 5% H₂/Ar at 420 °C for 1 hour to obtain a fresh catalyst. The catalyst loaded with Ni on TiO₂{001} was named Ni/TiO₂{001}, the one on TiO₂{100} was named Ni/TiO₂{100}, and the one on TiO₂{101} was named Ni/TiO₂{101}. Ni/TiO₂{100} was further impregnated with 0.5 mol/L NaOH solution, dried at 30 °C, and then reduced with H₂. The resulting catalyst was named Ni/TiO₂{100}-OH.

Catalyst Characterization

Transmission electron microscopy (TEM) images of various representative Ni/TiO₂ catalysts were acquired using a JEOL JEM-2100F microscope operating at 200 kV. BET surface area measurements were performed on a Micromeritics ASAP 2460 after the TiO₂ was degassed at 300 °C under vacuum. X-ray diffraction (XRD) patterns were recorded on a multifunctional rotating anode X-ray diffractometer (Cu K α radiation, $\lambda = 0.15406$ nm) operating at 40 kV and 15 mA. The loading of nickel was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). *Quasi in situ* X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer with a reaction chamber, using monochromatic Al anode K α radiation (hv = 1486.6 eV). The analysis pressure is 6.6*10⁻¹⁰ torr. Charging effects were corrected by aligning the C 1s binding energy of adventitious carbon to 284.8 eV.

The specific operational procedure is as follows: the samples were pretreated in 5% H₂/Ar at a flow rate of 20 mL/min at 420 °C for 1 hour, then cooled to RT and directly transferred to the analysis chamber without air exposure. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Nicolet 6700 FTIR spectrometer equipped with a Harrick high-temperature reaction chamber with ZnSe windows. For in situ DRIFTS measurements of NO adsorption at room temperature, Ni/TiO₂ catalysts were reduced in 5% H₂/Ar at 420°C for 90 min, then cooled to room temperature RT and evacuated to 0.01 Pa to record the back-ground spectrum. Subsequently, NO was introduced into the sample through a leaking valve, and spectra were recorded until a steady state was achieved at a specific pressure. For in situ DRIFTS measurements of CO₂ hydrogenation reactions, Ni/TiO₂ catalysts were reduced at 420°C in 5% H₂/Ar (20 mL/min) atmosphere for 60 min. After reduction, the catalysts were naturally cooled to room temperature in reducing atmosphere, then purged by pure Ar (20 mL/min) until a steady state. After the background spectrum was collected under Ar at 400°C, the mixed gas containing 25% CO₂ and 25% H₂, balanced with pure Ar, was introduced into the reaction cell at a flow rate of 20 mL/min at 400 °C for 120 min, whose spectra were recorded regularly. The H₂-TPR experiments were conducted on a Huasi chemisorption instrument equipped with a TCD detector to detect H₂ consumption. 50 mg fresh Ni/TiO₂ catalyst was first pretreated under Ar at 300 °C for 1 h and cooled to room temperature, and then was heated from room temperature to 700 °C at a heating rate of 10 °C/min in 5% H₂/Ar (30 mL/min). The CO₂-TPD experiments were conducted on a Huasi adsorption instrument. 50mg of the fresh Ni/TiO₂ catalyst was reduced at 420 °C in 5% H₂/Ar (30 mL/min) atmosphere for 60 min, followed by purging with pure He (30 mL/min) for another 30 min before cooling to room temperature. Subsequently, it was exposed to pure CO₂ (30 mL/min) at room temperature for 60 min, followed by switching to pure He (30 mL/min). Finally, the sample was heated to 400 °C at a heating rate of 10 °C/min under pure He (30 mL/min). The CO₂ desorption signal was recorded by an online mass spectrometer.

Catalyst Performance Testing

Catalytic performance was evaluated in a fixed-bed quartz reactor. Fresh catalysts (50 mg) diluted with 550 mg of SiC were reduced in 5%H₂/Ar with a flow rate of 20 mL/min at 420 °C for 60 min, followed by cooling to room temperature. A reaction gas mixture (25% CO₂, 25% H₂,50% Ar) was introduced at a flow rate of 20 mL/min for activity testing. The sample was directly heated to 400 °C at a rate of 10 °C/min and maintained at this temperature for 120 min. The gas compositions were analyzed by online gas chromatography (GC9790 Plus, Fuli Instruments) equipped with a TCD detector and a flame ionization detector (FID). The CO₂ conversion and product selectivity were calculated as following equations:

 $CO_2 Conversion = (n_{CO2,in}-n_{CO2,out}) / n_{CO2,in}$

CO or CH₄ selectivity = $n_{CH4 \text{ or } CO}/(n_{CH4} + n_{CO})$

The hydrogenation performance of CO was tested under the same conditions as described above. A reaction gas containing 24% CO and 60% H₂, balanced with Ar, was fed at a flow rate of 20 mL/min for activity testing. The apparent activation energy (Ea) for CO_2 hydrogenation over the Ni/TiO₂ catalysts was determined from Arrhenius plots by varying the reaction temperatures between 300 and 380 °C, with CO_2

conversions below 20%.

Catalyst	Ni content(wt.%)		
Ni/TiO ₂ {001}	1.78		
Ni/TiO ₂ {100}	1.32		
Ni/TiO ₂ {101}	3.14		

Table S1 : Ni content measured by ICP-AES

Catalyst	Conv.CO ₂	Sel.CO
$TiO_{2}\{001\}$	0.1%	100%
$TiO_2\{100\}$	0.2%	100%
$TiO_2\{101\}$	0.1%	100%

Table S2: Catalytic activity and product selectivity of CO_2 hydrogenation at 400°C of different TiO₂ supports.

Catalyst	Т	Р	X _{CO2}	S _{CO}	$H_2: CO_2$	WHSV	STY
	(°C)	(MPa)	%	%	ratio	$(ml g_{cat}^{-1}h^{-1})$	$(mol/g_{Ni}/h)$
Ni/TiO ₂ {001}	400	0.1	21.0	72.0	1:1	24000	2.38
Ni-SAs/N-CNTs4	400	0.1	16.0	100.0	3:1	12000	1.00
NiAlIn ₃ ⁵	400	0.1	20.0	99.8	4:1	30000	0.12
7Ni-M1 ⁶	400	0.1	14.0	79.0	1:1	15000	0.53
Ni ₅ NC/CO ⁷	400	0.1	19.0	95.0	1:1	40000	0.13
Ni ₅ NC/CO ⁷	450	0.1	45.0	85.0	4:1	40000	0.27
Ni/ZnO ⁸	400	0.1	21.0	99.3	4:1	36000	1.34
Ni ₃ Fe9/ZrO ₂ ⁹	400	0.1	18.6	95.8	2:1	24000	1.58
Ni0.07/Ce0.9La010	700	0.1	57.0	99.0	2:1	300000	0.54
Pristine Ni ¹¹	519	0.1	54.7	20.1	1:1	600	0.13
NiIn(4)/CeO ₂ ¹²	370	0.1	23.9	99.1	4:1	5000	0.62
Ni/SiO ₂ ¹³	660	0.1	67.5	98.7	4:1	40000	9.91
10Ni/TiO ₂ -OH ¹⁴	400	0.1	20.0	90.0	3:1	400000	6.77

 Table S3 : Comparison of CO production rate for the reported catalysts and present catalysts

Catalyst	Ni content(wt.%)
1%Ni/TiO ₂ {001}	0.87
2%Ni/TiO ₂ {001}	1.78
5%Ni/TiO ₂ {001}	4.83

 Table S4 : Ni content measured by ICP-AES

Table S5: Activity, product selectivity, activation energy, pre-exponential factor, and the number of weak basic sites for CO_2 hydrogenation catalyzed by Ni/TiO₂{001} and Ni/TiO₂{100} catalysts.

Sample	Ni/TiO ₂ {001}	Ni/TiO ₂ {100}
conv.CO ₂ (%)	21.5	1.9
Sel. CO (%)	71.5	99.7
Ea (kJ/mol)	44.3 ± 2.9	43.5 ± 1.3
A (mol/g _{cat} /s)	95.6 ± 1.8	18.1 ± 1.3
S weakly alkaline sites (E^{-10})	26.7	6.5



Figure S1. TEM images of the (A1-A2) $TiO_2\{001\}$, (A3) $Ni/TiO_2\{001\}$, (B1-B2) $TiO_2\{100\}$, (B3) $Ni/TiO_2\{100\}$, (C1-C2) $TiO_2\{101\}$, (C3) $Ni/TiO_2\{101\}$



Figure S2. XRD patterns of the Ni/TiO_{2}{001}, Ni/TiO_{2}{100} and Ni/TiO_{2}{101} catalysts



Figure S3. TEM images of the (A) Ni/TiO₂{001}, (B) Ni/TiO₂{100}, (C) Ni/TiO₂{101}



Figure S4. Stability testing of (A)Ni/TiO₂{001}, (B)Ni/TiO₂{100}, (C)Ni/TiO₂{101}



Figure S5. Ni 2p XPS spectra under exposed air of Ni/TiO₂{001} catalyst



Figure S6. H₂-TPR spectra of various Ni/TiO₂ catalysts.



Figure S7. In situ time-resolved DRIFTS spectra of Ni/TiO₂{001} under the reaction atmosphere (CO₂/H₂ = 1:1) at 400 °C



Figure S8. TEM image and metal Ni particle size distribution of the 5%Ni/TiO₂{001}



Figure S9. TEM image, magnified TEM image and metal Ni particle size distribution of the 1%Ni/TiO₂{001}

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