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Size-tunable Ni nanoparticles supported on surfacemodified, cage-type mesoporous silica as highly active catalysts for CO₂ hydrogenation

Ching-Shiun Chen,^{*a,b**} *Canggih Setya Budi*,^{*c*} *Hung-Chi Wu*,^{*a*} *Diganta Saikia*,^{*c*} *and Hsien-Ming Kao*^{*c**}

^aCenter for General Education, Chang Gung University, 259, Wen-Hua 1st Rd., Guishan Dist., Taoyuan City 33302, Taiwan, Republic of China.

^bDepartment of Pathology, Chang Gung Memorial Hospital, 5, Fusing St., Guishan Dist., Taoyuan City 33302, Taiwan, Republic of China.

^cDepartment of Chemistry, National Central University, Chung-Li, 32001, Taiwan, Republic of China.

*Corresponding authors

KEYWORDS mesoporous silicas; SBA-16; nickel nanoparticles; CO₂ hydrogenation

ABSTRACT

In this study, ultra-small Ni nanoparticles (Ni NPs) were controllably supported in the cage-type mesopores of -COOH functionalized mesoporous silica SBA-16 (denoted as Ni(x)@S16C, where x is the Ni loading) via wet impregnation under alkaline conditions, followed by thermal reduction. The particle sizes of the Ni NPs ranged from 2.7 to 4.7 nm depend on the Ni loading. Under the appropriate alkaline conditions, i.e., pH 9, deprotonation of the carboxylic acid groups on the cage-type mesopore surfaces endowed the effective incorporation of Ni²⁺ precursors via favorable electrostatic interactions, and thus well-dispersed Ni NPs confined in the cage-type mesopores of SBA-16 were achieved. The combination of the cage-type mesopores and the surface functionality provided dual beneficial features to confine the immobilized Ni NPs and to tune their particle sizes. The remarkably enhanced catalytic activities of the Ni(x)@S16C materials for CO₂ hydrogenation and CH₄ formation were demonstrated. The cage-type SBA-16 support provided a positive effect for the Ni NPs to enrich the surface sites that can strongly adsorb CO and CO₂, thus leading to high catalytic rates for CO₂ and CO hydrogenation. The reaction mechanism, catalytic kinetics and active sites were investigated to correlate to the high reaction rate for CO₂ hydrogenation to form CH₄.

Keywords: Carboxylic acid functionalized mesoporous silica SBA-16, cage-type mesopore, CO₂ hydrogenation, Ni particles, Carbon monoxide, Methane

1. Introduction

The greenhouse effect raised by carbon dioxide (CO_2) , which is typically generated from the combustion of natural gas, fuels, coal, oil, and wood, has become the worldwide concern. Thus, the chemical conversion of CO₂ as a reactant has attracted great interests due to sustainability and environmental issues. Currently, the literature reports indicate that heterogeneous hydrogenation of CO₂ typically involves the generation of a wide range of organic compounds, e.g., carbon monoxide (CO), methanol, formic acid, methane (CH₄), and hydrocarbons.¹ However, the CO₂ molecule is difficult to activate due to its thermodynamic stability, leading to a high energy demand in the process of chemical conversion. As a result, the catalytic hydrogenation of CO₂ into CO and CH₄ is the prime target. The hydrogenation of CO₂ can produce CO via the reverse water gas shift (RWGS) reaction (i.e., $H_2 + CO_2 \rightarrow CO + H_2O$; ΔH^0 = 41.2 kJ mol⁻¹). A variety of industrial catalytic technologies, such as methanol synthesis, CH_4 reforming with CO₂, ammonia synthesis, the Fischer-Tropsch reaction, and steam reforming of hydrocarbons, makes the use of the RWGS reaction.²⁻⁹ On the other hand, the Sabatier reaction, namely $(4H_2 + CO_2 \rightarrow CH_4 + 2H_2O; \Delta H^0 = -292.9 \text{ kJ mol}^{-1})$ has recently attracted considerable attention to produce CH₄ as a green fuel to fulfill the requests for renewable carbon sources and sustainable processes.¹⁰⁻¹³ Although the Sabatier reaction is thermodynamically favorable ($\Delta G^0 =$ -130.8 kJ mol⁻¹), the high kinetic barrier associated with this conversion hinders its industrial applications.

In recent years, metal nanoparticles (NPs) have been extensively applied in catalytic applications since these NPs are more catalytically active than their bulk materials.¹⁴ However, the unique properties of NPs, such as their large surface-area-to-volume ratio, leads to easy aggregation of metal NPs, often resulting in harmful effects on their activity and selectivity. One

effective methodology to alleviate this aggregation problem is to utilize an ideal support, either an inorganic support or an organic capping agent, to stabilize highly dispersed metal NPs. Apart from organic stabilizing agents, various types of solid supports, including zeolites, TiO₂, mesoporous silicas, hollow silicas, silicon nanotubes, mesoporous carbons, polymers, metalorganic frameworks (MOFs) and graphene oxide, have been extensively utilized to immobilize Ni NPs.¹⁵⁻³¹ By offering high surface areas, unique pore architectures, and pore-size confinement, mesoporous silica materials are ideal scaffolds to immobilize metal NPs. However, one main drawback for the use of pure mesoporous silica is that their mesopores do not provide sufficiently strong affinity with metal precursors. Therefore, additional surface modifications with organic functional groups on the mesopores of mesoporous silicas are essential. Nevertheless, the incorporation of high numbers of highly dispersed, small-sized metal NPs onto mesoporous silica materials remains a challenge.

Conventionally, transitional metals such as Ni, Ru, Rh, Pd, Pt, Cu and their bimetallic alloys have been demonstrated to be catalytically active in CO₂ hydrogenation for formation of CO and CH₄.³²⁻³⁷ Among them, Ni-based catalysts have been reported as promising candidates for CO₂ hydrogenation due to the low cost, high activity, and earth abundance associated with Ni, which can be viewed as effective alternatives to noble metal catalysts. Moreover, Ni NPs have been demonstrated to possess high activities in various hydrogenation processes.

Extensive studies have focused on the search for silica-based supports to immobilize Ni NPs.³⁸⁻⁴⁵ When 2D hexagonal mesoporous silicas, such as MCM-41 and SBA-15, are used as supports, however, the aggregation of Ni NPs cannot be avoided.⁴⁴⁻⁴⁶ One way to improve this aggregation problem is to employ 3D cage-like mesoporous silicas, e.g., SBA-16, to confine the Ni NPs and thus control their growth. Our previous work demonstrated that cage-like mesoporous SBA-16

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can confine the growth of Ni NPs down to approximately 4 nm, exhibiting exceptionally high reactivity and CH₄ selectivity in CO₂ hydrogenation.⁴⁷ However, the methods to enhance the reaction rate of CO₂ hydrogenation and the CH₄ selectivity are still ambiguous. Moreover, the effective trapping of Ni²⁺ ions into the cage-like mesostructure of SBA-16 was believed to contribute to the high reactivity and selectivity. In continuation of our previous work, a strategy to combine the carboxylic functionality and cage-type characteristics of mesoporous silica SBA-16 to confine Ni NPs was systematically evaluated in this study. Under the appropriate alkaline conditions (at pH 9), a high amount of the Ni²⁺ precursor was effectively incorporated via electrostatic interactions induced by the -COO⁻ groups. On the other hand, no effective Ni incorporation was observed under acidic conditions. Scheme 1 illustrates the effect of pH on the fabrication of Ni NPs on the -COOH functionalized SBA-16 support. In view of this pH effect, the Ni(x)@S16C materials, where x is the Ni loading and S16C stands for the support, i.e., -COOH functionalized SBA-16, were prepared in the solution at pH 9 to achieve a maximum incorporation of Ni. With the aid of the organic functional groups on the cage-like mesopores, the present synthesis strategy provided a facile route for the fabrication of well-dispersed Ni NPs with ultra-small particle sizes down to 2.7 nm and high Ni loadings up to 21.7 wt%. Most importantly, the effective size control of the Ni NPs was achieved.

Herein, the Ni(x)@S16C catalysts were used to improve the activity and CH₄ selectivity in CO_2 hydrogenation, displaying considerably superior activity as compared to the cases of the Ni(x)@SiO₂ catalysts where the amorphous SiO₂ was used as a support instead. The catalytic kinetics, reaction pathways, mechanisms and active sites for the catalytic hydrogenation of CO_2 and CO on the SBA-16-supported Ni NPs were investigated in details. The correlation between the enhanced catalytic activity and the particle sizes of Ni NPs was made.



Scheme 1. Synthesis of Ni(x)@S16C under (a) basic (with formation of Ni NPs) and (b) acidic (without formation of Ni NPs) conditions.

2. Experimental

2.1. Preparation of SBA-16 functionalized with carboxylic acid groups

Carboxylic acid functionalized cubic mesoporous silica SBA-16 was first synthesized following a previously reported procedure.⁴⁸ The –COOH functionality was introduced into SBA-16 via a carboxyethylsilanetriol sodium salt (abbreviated as CES, Gelest, 25% in water), a silicon precursor bearing the carboxylic acid moiety. Briefly, a triblock copolymer blend of 0.93 g of Pluronic F127 (Sigma-Aldrich) and 0.19 g of Pluronic P123 (Sigma-Aldrich), both functioning as structure-directing agents, and 4 g of KCl were dissolved in 2 M HCl aqueous solution (60 mL), followed by the addition of a premixed solution of tetraethyl orthosilicate (TEOS, Sigma-Aldrich) and CES with a CES/(TEOS + CES) mole ratio of 20%. Then, the solution was vigorously stirred at 308 K for 4 h. In this study, the functionalization level was fixed at 20% based on the amount of silica. The molar ratio of the reaction mixture for the synthesis of SBA-16 was 0.2/0.8/0.0016/0.0037/2.7/4.4/144 for CES/TEOS/P123/F127/KCl /HCl/H₂O. The reaction mixture was then subjected to hydrothermal treatment at 373 K for 24 h.

After filtration and washed with deionized water, the precipitate was collected and air dried at 343 K. The templates (Pluronic F127 and P123) were removed by acid extraction. Typically, the as-synthesized sample (0.35 g) was dispersed in 125 mL of a H₂SO₄ solution (48 wt%) with vigorous stirring at 368 K for 24 h. The final mesoporous silica denoted as S16C was used as the support to fabricate the Ni NPs.

2.2. Preparation of Ni(x)@S16C and Ni(x)@SiO₂

Fabrication of the Ni NPs inside the mesopores of -COOH functionalized SBA-16 (i.e., S16C) was performed by wet impregnation of 0.1 g of S16C with 10 mL of Ni(NO₃)₂·6H₂O (Sigma-Aldrich) with different concentrations (0.01, 0.025, and 0.05 M), followed by a thermal reduction process under a flow of Ar/H_2 (95%/5%). The pH of the mixture was subsequently controlled by the dropwise addition of a 0.1 M NaOH aqueous solution. A pale green precipitate only formed at a solution pH of 9. The pale green precipitate was then filtered, washed with deionized water, and dried at room temperature. In general, both -COOH and -SiOH functional groups on the surface of S16C can be deprotonated to become -COO⁻ and -SiO⁻ functional groups to attract Ni²⁺ ions under appropriate conditions. Figure S1a shows the titration curve of the S16C support obtained by using a 0.01 M NaOH_(aq) solution. The support S16C (0.04 g) was initially dispersed in 10 mL of pure water (pH 7.0) could generate a weakly acid solution with a pH value of 3.8. According to the acid-base titration experiments, the equivalent point of the support S16C titrated by 0.1 M NaCl aqueous solution was around pH 7.3. As reported in the literature, the –SiOH group can become –SiO⁻ species when the pH value is higher than ~ 7.5 .⁵¹ In addition, as revealed by the zeta potential measurements, as shown in Figure S2b, the surface of the support S16C became negatively charged when the solution pH was increased from 3 to 9 due to deprotonation of both carboxylic acid and silanol groups on the surface of S16C under

alkaline conditions. The preparation of Ni(x)@S16C by wet impregnation at different pHs (i.e., 3, 5, 7 and 9) was performed. It was found that a pale green precipitate was not well formed unless by keeping the solution pH to be 9, as shown in Figure S3c. On the other hand, only few green solid products were formed at low pHs, e.g., at pHs 3 and 6. The intensity of XRD pattern of each reduced powder obtained at different pHs also gradually increased as the pH was increased (Figure S3d). In view of this pH effect, the Ni(x)@S16C materials were prepared at solution of pH 9 in order to achieve the maximum incorporation levels of Ni precursors. The alkaline condition allows the –COOH groups to be deprotonated, confirmed by the zeta potential measurements shown in Figure S2b, and therefore have favorable electrostatic interactions with the Ni²⁺ precursors. At pH 9, the optimum adsorption of Ni ions can be achieved with the Ni loading, measured by ICP-AES, which is consistent with the theoretical Ni amount. The detailed characterization methods for these Ni(x)@S16C samples are described in Supporting Information (SI).

All the samples were ground and thermally treated at 873 K for 6 h under an atmosphere of flowing Ar/H₂ (95%/5%) with a heating rate of 1 K min⁻¹. The resulting dark gray powder was then kept under vacuum to dry. The Ni amount (wt%) was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For comparison purposes, the Ni(x)@SiO₂ catalysts were prepared with similar Ni loadings as the cases of the Ni(x)@S16C catalysts. Typically, 1 g of SiO₂ (Sigma-Aldrich, surface area = 300 m² g⁻¹) was impregnated with 20 mL of a Ni(NO₃)₂ aqueous solution with 0.044 M for 5.9 wt%, 0.094 M for 12 wt% and 0.16 M for 20 wt%, respectively. Afterward, the Ni(x)@SiO₂ catalysts were calcined in air and reduced under H₂ at 773 K for 5 h before use.

2.3. Catalytic CO₂ hydrogenation tests

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The Ni(x)@S16C and Ni(x)SiO₂ catalysts were reduced at 673 K for 5 h before reactions. A fixed-bed reactor (0.95 cm outer diameter) was equipped to perform all catalytic tests for CO₂ and CO hydrogenation over the Ni(x)@S16C and Ni(x)@SiO₂ catalysts at atmospheric pressure. The CO₂ and CO hydrogenation reactions were conducted by feeding streams of H₂/CO₂ (1:1) and H₂/CO (3:1), respectively, at a rate of 100 mL min⁻¹ into the reaction vessel. The gas for reaction after 30 min was sampled for analyzing the product distribution as reaction rate. All the products were analyzed via gas chromatography (GC) quipped with a thermal conductivity detector (TCD) through a 12 ft Porapak-Q column. The turnover frequencies (TOFs) were calculated based on the formula: TOF = [conversion × mL s⁻¹ for CO₂ or CO × 6.02 × 10²³ (molecules mol⁻¹)]/[24400 (mL mol⁻¹) × Ni sites]. The peak areas corresponding to CH₄ and CO were used to obtain the carbon balance data, which reached approximately 95-100%.

2.4. Measurements for Fourier transform infrared (FTIR) spectroscopy

The in-situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy were conducted with a 1 cm⁻¹ resolution for 256 scans by using a Nicolet 5700 FTIR spectrometer, which was equipped with a mercury cadmium telluride (MCT) detector. A heating cartridge was attached on the DRIFT cell (Harrick) with ZnSe windows to heat the sample to 773 K. A stream of CO was passed through the Ni-based catalysts for 30 min at room temperature, and then the IR spectra of the Ni-based catalysts with adsorbed CO were obtained. Finally, the residual gaseous CO was purged for 60 min using a He stream. In a similar way, the IR spectra of the co-adsorption of H₂ and CO₂ were obtained after passing CO₂ through the Ni-based catalysts for 30 min at room temperature. The residual gaseous CO₂ was ensured to be purged out for 60 min using a He stream, followed by reaction with a H₂ stream. At the end, the IR spectra were recorded in a H₂ stream at elevated temperatures.

2.5. Temperature-programmed desorption (TPD) and temperature-programmed hydrogenation (TPH)

All TPD and TPH experiments were performed under pure He and H₂/He (20/80) streams at a flow rate of 100 mL min⁻¹ in a fixed-bed flow system, respectively. The CO and CO₂ streams (100 mL min⁻¹) were fed over the catalysts for 30 min at room temperature to achieve saturation for the TPD and TPH experiments. A K-type thermocouple inserted into the catalyst bed was used to measure the temperature, which was increased from 300 to 650 K at a rate of 10 K min⁻¹ for obtaining TPD and TPH profiles. All signals were measured with a VG Smart IQ+ 200D mass spectrometer and the desorbed products were carried to the vacuum chamber through a leak valve. The operating pressure in the chamber was approximately 3×10^{-7} mbar, and the base pressure in the chamber was approximately 5×10^{-10} mbar.

2.6 Measurements of Ni surface area

The H₂-TPD technique was employed to measure the number of surface Ni sites per unit mass of catalyst, which was carried out on a TPD system equipped with a thermal conductivity detector (TCD). The sample (0.2 g) was used and reduced in H₂ stream at 673 K for 5 h, and then was cooled to room temperature from 673 K under the H₂ environment for saturated adsorption. An Ar stream was used to remove the physically addsorbed H₂ at room temperature for 2 h. The Ni sample with H₂ chemisorption was heated to 773 K ramping at 10 K min⁻¹ in the Ar flow (30 mL min⁻¹). The desorbed H₂ was detected continuously with increasing temperature by a TCD. The area of H₂ detected by TCD was quantified by sampling 1 mL of 10% H₂/Ar to calculate the amount of H₂ desorption. The number of Ni sites was determined by means of peak area assuming the adsorption stoichiometry of H/Ni = 1:1. The average surface density of the Ni metal was 1.54×10^{19} Ni atoms m⁻².

2.7 X-ray photoelectron spectroscopy (XPS)

The oxidation state of the catalyst surface was examined by XPS, using a Thermo VG-Scientific Sigma Probe spectrometer at the Precision Instrument Center of the College of Engineering at the National Central University, Taiwan. The spectrometer was equipped with anAl K α X-ray source (1486.6 eV; 1 eV = 1.602×10^{-19} J) operated at 108 W and a hemispherical analyzer operated at a pass energy of 50 eV. The instrument was typically operated with an analysis chamber pressure of approximately 1×10^{-9} Torr.

3. Results and Discussion

3.1. Structural characterization of the Ni(x)@S16C samples

The wide-angle X-ray diffraction (XRD) patterns of the Ni NPs deposited on -COOH functionalized SBA-16, as shown in Figure 1A, exhibited three major peaks at 20 values of 44.5°, 51.8°, and 76.4°, which can be indexed to the (111), (200), and (220) characteristic facets of crystalline Ni, respectively. The average size of the Ni NPs was estimated from the Scherrer equation using the full-width at half-maximum (FWHM) value of the (111) peak and listed in Table1. The Ni particle size was strongly dependent on the initial concentration of the Ni precursor used in the preparation of the Ni catalyst. The particle size of the Ni NPs immobilized on S16C slightly grew with the increase in the Ni loading from 5.9 to 21.7 wt%. For comparison purposes, the XRD patterns of Ni(x)@SiO₂ with similar Ni loadings (5.6-20.0 wt%) are shown in Figure S2 (SI). Large Ni particles with sizes between 7.4 and 15.8 nm were formed on SiO₂ using a wide range of Ni loadings from 5.6 to 20.0 wt%. Based on the above observations, it can be inferred that the SBA-16 support functionalized with -COOH groups may provide strong interactions between Ni²⁺ and the -COO⁻ groups, leading to a confinement effect on the formation of Ni NPs due to the cage-like mesopores of SBA-16. Thus, the cage-type mesopores

 of –COOH functionalized SBA-16 can effectively confine the Ni nanoparticles down to small sizes ranging from 2.7-4.7 nm, even if the Ni amount was increased to 21.7 wt%. The Ni surface area and dispersion for all the Ni(x)@SiO₂ and Ni(x)@S16C catalysts are also compared in Table S1, revealing that Ni NPs confined in the cage-type mesopores of S16C apparently exhibited higher values than Ni deposited on SiO₂.

The small-angle XRD patterns (Figure 1B) of Ni(x)@S16C and pristine SBA-16 show one major diffraction peak at $2\theta = 0.8^{\circ}$ for the (110) plane, corresponding to cubic SBA-16 with cage-type mesopores (*Im3m* symmetry). As the Ni loading was increased, the intensity of the diffraction peak gradually decreased. It suggests that incorporation of Ni NPs in –COOH functionalized SBA-16 causes some degradation on the mesostructure. The other possible reason is that the formed Ni nanoparticles partially fill the pores, resulting in reduction of the electronic contrast between the mesopores and the silica framework. As a result, a less intense (110) diffraction peak was observed for Ni(x)@S16C.

All the nitrogen adsorption-desorption isotherms, as shown in Figure 1C, of the Ni(x)@S16C samples belong to type IV isotherms with H2 hysteresis loops according to IUPAC classifications. The characteristic shape of hysteresis indicated the presence of mesopores. The width of the hysteresis loops was affected by the amounts of Ni NPs, and became narrower when more Ni NPs were loaded. The pore size distribution curves are provided in Figure 1D. The surface area, pore volume, and pore size of Ni(x)@S16C are summarized in Table 1. As seen in Table 1, when the amount of Ni NPs was increased, the surface area decreased from 664 m² g⁻¹ for pristine SBA-16 to 231 m² g⁻¹ for Ni(21.7)@S16C and the pore volume also decreased from 0.68 to 0.24 cm³ g⁻¹, accordingly. The cage pore size has the similar trend due to the blockage of cages as the Ni loading was increased.



Figure 1. (A) Wide and (B) small angle XRD patterns of Ni(x)@S16C as a function of Ni loading, (C) N₂ adsorption-desorption isotherms and (D) cage pore size distribution curves of Ni(x)@S16C with different Ni loading amounts.

The successful surface functionalization of the SBA-16 support with carboxylic acid functional groups was confirmed by ¹³C cross polarization-magic angle spinning (CPMAS) NMR, as depicted in Figure S3A (SI). As seen in Figure S3A, the peaks at 7 ppm and 27 ppm are attributed to the C₁ and C₂ carbons of ethyl groups from CES, while the peak at 178 ppm is contributed from the carboxylic acid moiety from CES, demonstrating the presence of –COOH functional groups in the S16C support. Furthermore, the absence of the characteristic NMR signals of the copolymer Pluronic templates revealed that the surfactants were completely removed from the S16C silica framework. The characteristic ¹³C NMR signals of –CH₂–CH₂– COOH detected in solid state ¹³C CPMAS NMR spectrum of S16C matched well to the ¹³C

solution NMR spectrum of the liquid CES itself. The triplet peaks at 76-78 ppm are due to the CDCl₃ solvent, as shown in Figure S3(B).

There are no peaks related to the T species detected for the support SBA-16, as shown in the ²⁹Si MAS NMR spectra (Figure S3(C)). The ²⁹Si MAS NMR spectra of S16C (Figure S3(D)) consists of two different peak regions. One region is for the O^n sites consisting of O^4 (-112) ppm), Q^3 (-102 ppm) and Q^2 (-92 ppm), which are attributed from the TEOS condensation.⁴⁵ The other region corresponds to different T^m sites, namely $T^3[(CSi(OSi)_3)]$, $T^2[CSi(OH)(OSi)_2]$, and $T^{1}[CSi(OH)_{2}(OSi)]$ species centered at -67, -60 and -52 ppm, respectively, which are generated from CES that bears the -COOH moiety. The appearance of the T^m sites in the ²⁹Si MAS NMR spectrum gives direct support of the successful incorporation of carboxylic acid functional group into the mesopore surfaces of cage-type SBA-16. The quantitative assessment of the degree of functionalization of the organic moiety can be estimated from the relative integrated intensities of Qⁿ and T^m NMR signals (ca. 20.2 %), which is in good agreement with that expected according to the composition of initial mixture (20% CES). T groups are clearly observed in the S16C sample, which confirm the presence of the CES moiety. Therefore, both ¹³C and ²⁹Si solid-state NMR results confirm the presence of the CES moiety in the support S16C. The carboxylic acid groups on the mesopores of SBA-16 were converted to -COO⁻ groups at pH 9 and, therefore, could have effective electrostatic interactions with the Ni²⁺ ions. The Ni ions could bind to the negatively charged surfaces of the mesopores and then confine in the cagetype mesopores at nanoscale dimensions even with a high loading of 21.7 wt%.

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Table 1.	Textural	properties	of $Ni(x)$ (a) S16C
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Ni loading	A _{BET}	V _p	Cage size	Entrance size	Ni particle size	Ni particle size
(wt %) ^a	$(m^2 g^{-1})^b$	$(cm^3 g^{-1})^c$	$(nm)^d$	(nm) ^e	(nm) ^f	(nm) ^g
0	664	0.68	7.7	3.5	—	—
5.9	414	0.46	6.5	3.4	2.7	2.6±0.9
14.2	366	0.42	5.0	3.2	3.6	3.7±0.9
21.7	231	0.24	4.9	3.2	4.7	5.1±0.9

^aNi loading determined by ICP-AES; ^bA_{BET} is the surface area; ^cV_p is the pore volume; ^dCage pore sizes were obtained from the nitrogen adsorption isotherms; ^eEntrance pore sizes were obtained from the nitrogen desorption isotherms; ^fAverage particle size of Ni NPs estimated from XRD patterns; ^gAverage particle size of Ni NPs estimated from TEM images.

The successful incorporation of the Ni NPs as well as their particle-size distribution as a function of the Ni loading was further explored by transmission electron microscopy (TEM) measurements. A well-ordered unfilled pore structure was clearly observed for the pristine SBA-16 sample in the TEM image shown in Figure 2(a). For all the Ni(x)@S16C samples (Figure 2(b-d)), ultra-small Ni NPs were well confined within the cage pores of the S16C support. The Ni NP size was tuned down to approximately 3 nm for Ni(5.9)@S16C by lowering the initial molar concentration of the Ni precursor, and tuned to approximately 5 nm for Ni(21.7)@S16C by a high initial molar concentration of the Ni precursor. The average particle sizes of Ni NPs with standard deviations, estimated from the TEM images, are also listed in Table 1.



Figure 2. TEM images of Ni(x)@S16C, where x = (a) 0, (b) 5.9, (c) 14.2, and (d) 21.7 wt%.

The mesostructure of Ni(14.2)@S16C was further analyzed by high-resolution TEM (HRTEM), as shown in Figure 3. The magnified HRTEM image and SAED pattern in Figure 3(b-c) clearly demonstrate that the Ni NPs in the S16C support are highly crystalline, indicating distinct lattice fringes with a spacing of 0.203 nm and consistent with the (111) lattice plane of the metallic Ni. The energy dispersive X-ray spectrum (EDS) of Ni(14.2)@S16C clearly

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indicated that the Ni(14.2)@S16C sample mainly contains Si, O and Ni elements (Figure 3d-g) and confirmed well dispersion of Ni NPs in the S16C matrix.



Figure 3. TEM images of (a) the Ni NPs in Ni(14.2)@S16C, (b) displaying the d-spacing of the Ni NPs; (c) selected-area electron diffraction (SAED) pattern of Ni(14.2)@S16C; (d-g) energy dispersive spectroscopy (EDS) selected area and mapping of silicon, oxygen and nickel.

Notably, the Ni NPs were immobilized in the mesopores of SBA-16, which suggested that the presence of the –COOH functionality facilitated the formation of size-controllable Ni NPs without aggregation. The role of the carboxylic acid groups during the formation of the Ni NPs was probed by FTIR spectroscopy (Figure S4, SI). The vibrational band at 1725 cm⁻¹, corresponding to the –COOH groups in SBA-16, disappeared after fabrication of the Ni NPs. We anticipate that the –COOH groups deprotonated at pH 9 and attracted the cationic Ni²⁺ precursor to enter the mesopores via electrostatic interactions during the initial experimental procedure. Most of the –COOH groups decomposed when a high reduction temperature was employed to ensure the formation of the Ni NPs.

Although we have observed from TEM images (Figures 2 and 3) that most of the Ni nanoparticles are uniformly distributed in the pores of S16C support, still it is possible that some nanoparticles may be deposited outside the pores. A close examination of the TEM images indicated very few aggregated Ni nanoparticles outside the pores. The nitrogen adsorption-desorption data listed in Table 1 also confirm the formation of Ni nanoparticles inside the pores as the surface area and pore volumes decrease with the increase in the loading of Ni nanoparticles. The $-COO^{-}$ and $-SiO^{-}$ functional groups on S16C can effectively attract the positive Ni²⁺ ions into the cage structure. For example, the Ni(21.7)@S16C provided larger Ni size with 5.1 ± 0.9 nm than a low Ni loading catalysts, but was apparently smaller than the cage size of pure S16C (7.7 nm). Therefore, our results suggested that most of the Ni nanoparticles were well distributed within the S16C matrix.

The oxidation state associated with the different size and loading amount of Ni NPs immobilized in the mesoporous silica frameworks can be further explored by XPS measurements. The Ni XPS spectra of Ni(x)@S16C were compared and depicted in Figure S5 (SI). As observed in Figure S5, the binding energy of Ni $2p_{3/2}$ signal exhibited at 854.5 eV for 5.9 wt%, at 854.5 eV for 14.2 wt% and slightly shifted to 854.9 eV for 21.7 wt%, respectively. The surface of reduced Ni(x)@S16C might be partially oxidized under atmosphere environment during the sample transfer process before XPS measurements. Thus, the binding energy of Ni $2p_{3/2}$ signals in Figure S5 was likely toward the formation of NiO.⁵⁰⁻⁵² However, the relative shift for Ni $2p_{3/2}$ signal to higher energy could also provide the clue for Ni NPs interacting with the S16C support, when the Ni loading was increased to 21.7 wt%. The Ni(21.7)@S16C sample with higher loading and larger particle size might lead to higher likelihood that the Ni NPs were situated outside the cage pores of S16C than other samples with low Ni loading. In this case, it is

possible that most of –COOH groups were sacrificially decomposed after reduction treatment, therefore the interaction of Ni NPs with oxygen bonded Si-OH group might influence the oxidation state of Ni NPs. For low Ni loadings of 5.9 wt% and 14.2 wt%, the majority of Ni NPs should confine inside the cage pore and weakly interact with the small amount of Si-OH groups in pore structure. Increasing the Ni loading up to 21.7 wt% could cause the additional supportmetal interaction for Ni NPs located on the surface of the mesoporous silica, As a result, the XPS peak slightly shifted to a higher energy for Ni(21.7)@S16C.

3.2. Catalytic hydrogenation of CO₂ on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts The hydrogenation of CO_2 was employed to examine the catalytic efficiencies of the Ni(x)@S16C and $Ni(x)@SiO_2$ catalysts. The TOFs were estimated for all the Ni catalysts based on the number of Ni surface sites, as measured by H₂ chemisorption at room temperature. The overall TOFs for CO₂ hydrogenation on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts are achieved at 598-773 K, as revealed in Figure 4A. The major products detected during CO_2 hydrogenation were CO and CH₄. The Ni(x)@S16C catalysts exhibited higher TOFs for CO₂ hydrogenation than the Ni(x)@SiO₂ catalysts at all the investigated temperatures. The catalytic activity of Ni(x)@S16C increased with a decrease of the Ni loading and particle size. The temperature-dependent TOFs for the formation of CO and CH₄ analyzed from Figure 4A are shown in Figures 4B and 4C. The TOFs for CO on the Ni(x)@S16C catalysts followed the order of 5.9 wt% (2.7 nm) > 14.2 wt% (3.6 nm) > 21.7 wt% (4.7 nm), but the rate for CH₄ formation was enhanced upon increasing the Ni particle size. Figure S6 compares the CO₂ conversion, selectivity of CO and CH₄ as a function of temperature, based on the results in Figure 4. As seen in Figure S6, a larger Ni loading might lead to higher reaction conversion since the overall surface sites increased with the Ni loading. Although both Ni(x)@S16C and Ni(x)@SiO₂ with

similar Ni loadings exhibited similar CH₄ selectivity at all temperatures, the Ni size of the former was significantly smaller than that of the latter.

The Weisz-Prater criterion (N_{W-P}) was frequently used for negligible diffusion limitation.^{53,54} The number of N_{W-P} smaller than 0.3 should have negligible mass transfer limitations.^{53,54} The values of N_{W-P} for both Ni(21.7)@S16C and Ni(20) @SiO₂ catalysts for CO₂ hydrogenation at 673 and 773 K were calculated to obtain extremely small numbers as listed in Table S2, indicating that the turnover rates in this study were not affected by diffusion limitations of reactants.



Figure 4. Comparison of the reaction rates for CO_2 hydrogenation on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts as a function of temperature: (A) overall CO₂ hydrogenation; (B) CO formation and (C) CH₄ formation. A H₂/CO₂ stream with a 1:1 ratio at a total flow rate of 100 mL min⁻¹ was passed over 5 mg of the catalysts.

The CO₂ conversion and selectivity of both products as a function of time at 773 K is revealed in Figure 5. All Ni(x)@S16C catalysts appeared high stability within 48 h. The XRD spectra of

 Ni(x)@S16C catalysts after the time-on-stream tests were shown in Figure S7, revealing the Ni particle size of 2.7 nm for 5.9 wt%, 4.1 nm for 14.2 wt% and 5.5 nm for 21.7 wt%. The particle size of Ni did not seem to be influenced by the long-term catalytic reaction at 773 K.



Figure 5 Time-dependent CO₂ hydrogenation for (A) overall CO₂ conversion; (B) CO selectivity and (C) CH₄ selectivity. A H_2/CO_2 stream with a 1:1 ratio at a total flow rate of 30 mL min⁻¹ was passed over 50 mg of the catalysts at 773 K.

The Arrhenius plots for CO₂ hydrogenation, which provided the apparent activation energies, on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts were further investigated, as shown in Figure 6. All the experiments were performed in the temperature range of 598-673 K. The apparent activation energies were estimated from the slopes, obtaining values of 48.4 kJ/mol for Ni(5.9)@S16C, 52.6 kJ/mol for Ni(14.2)@S16C and 56.8 kJ/mol for Ni(21.7)@S16C, as shown in Figure 6. For comparison, the apparent activation energies for the Ni(x)@SiO₂ catalysts with 5.6-20.0 wt% Ni loadings were ~82.9–94.0 kJ mol⁻¹, which were significantly higher than the cases of the Ni(x)@S16C catalysts.



Figure 6. Arrhenius plots for the TOFs of CO_2 hydrogenation on the Ni(x)@S16C andNi@SiO₂ catalysts.

Figure S8 (SI) shows the CH₄ selectivity versus the CO₂ conversion on the reduced Ni(x)@S16C catalysts. The CO₂ conversion was changed using different flow rate of the reactants and the weight of catalyst. It can obtain that the selectivity of CH₄ decreased with a decreasing CO₂ conversion and approached approximately zero at very low conversion on all the Ni(x)@S16C catalysts. It was indicative of a typical stepwise reaction in which CO is an intermediate in the process of CH₄ formation.⁵⁵ Therefore, CO₂ hydrogenation on the Ni(x)@S16C catalysts is proposed to follow a consecutive pathway, where CO is the key intermediate in CO₂ methanation. According to our previous investigations, the consecutive pathway of CO₂ \rightarrow CO \rightarrow CH₄ was assumed to be the essential steps during CO₂ hydrogenation on the Ni(x)@S16C catalysts, regardless of the Ni particle size.⁵⁶ Thus, the enhancement of the CH₄ formation on Ni(x)@S16C might depend on the reaction pathway for CO hydrogenation.

Figure 7A compares the catalytic activities of CO hydrogenation to CH_4 on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts at different temperatures. The CO methanation reaction was performed in the temperature range of 573-673 K. As expected, all the Ni(x)@S16C catalysts possessed higher rates of CO hydrogenation than the Ni(x)@SiO₂ catalysts, where increasing the Ni loading and particle size led to considerable improvements to the TOF. The Arrhenius plots for CO hydrogenation on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts are shown in Figures 7B and 7C. On the Ni@SiO₂ catalysts, the apparent activation energies displayed similar values regardless of the Ni loading, but the apparent activation energies on the Ni(x)@S16C catalysts decreased from 78.3 kJ/mol to 62.1 kJ/mol when the Ni loading was increased from 5.6 to 21.7 wt%.



Figure 7. (A) Comparison of the reaction rates for CO hydrogenation for the Ni(x)@S16C and Ni(x)@SiO₂ catalysts as a function of temperature; (B) and (C) Arrhenius plots for the TOFs of CO hydrogenation on the Ni(x)@S16C and Ni(x)@SiO₂ catalysts. A H₂/CO stream with a 3:1 ratio at a total flow rate of 100 mL min⁻¹ was passed over 5 mg of the catalysts.

3.3. CO₂- and CO-TPD on the Ni(x)@S16C catalysts

In this study, small Ni NPs with sizes of 2.7-4.7 nm confined in S16C that could induce high catalytic activities for CO₂ hydrogenation and effectively enhance CH₄ formation compared to the Ni(x)@SiO₂ catalysts. In our previous studies, small Ni NPs typically decreased CH₄ formation due to low H₂ coverage on the small Ni NPs.⁵⁶ This special phenomena on the Ni(x)@S16C catalysts might result from the relationship between the active sites and CO₂ and CO adsorption. We used TPD to study the desorption behavior of CO₂ and CO from the active sites on Ni(x)@S16C catalysts. Figure 8 compares the TPD profiles of CO₂ and CO desorbed from the Ni(x)@S16C catalysts under a He stream. As shown in Figure 8A, CO₂ desorbed at ~355 K from Ni(5.6)@S16C, and a new peak associated with CO₂ desorption appeared at 460 K upon increasing the Ni loading.



Figure 8. TPD plots of (A) CO_2 and (B) CO desorbed from the Ni(x)@S16C catalysts in a He stream with a 10 K min⁻¹ heating rate. All CO_2 and CO adsorptions were performed in a pure 100 mL min⁻¹ stream at atmospheric pressure and 298 K for 40 min.

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The TPD results of CO₂ desorption from the Ni(x)@SiO₂ catalysts are also shown in Figure S9A (SI), revealing similar desorption behavior for all the Ni loadings. The desorption peak at ~360 K retained similar intensities for all the Ni(x)@SiO₂ catalysts, but the intensity of the second peak at high temperatures was markedly enhanced as well as the desorption temperature shifted from 520 K to 476 K as Ni loading increased from 5.6 wt% to 20 wt%. In general, CO₂ can be considered as an acidic gas, and thus the desorption temperature represents the strength of the basic sites to bind CO₂. Literature reports have indicated that the CO₂-TPD profiles on Ni surfaces show the desorption temperatures between 373-423 K for weakly basic sites, 423-573 K for moderately basic sites and above 773 K for strongly basic sites.^{57,58} As shown in Figures 8A and S9A, the CO₂ desorbed from Ni(x)@S16C and Ni(x)@SiO₂ might indicate the existence of weakly and moderately basic sites on these surfaces. Notably, the relative intensities for CO₂ catalysts, implying that the Ni(x)@S16C catalysts might induce higher CO₂ coverage.

The formation of CH₄ during CO₂ hydrogenation likely depended on the efficiency for CO hydrogenation due to the reaction following the consecutive pathway. Thus, the CO-TPD results might shed light on the active sites for CO adsorption. Figure 8B reveals the TPD profiles for saturated CO adsorption on the Ni(x)@S16C samples. Small amounts of CO desorption were observed from Ni(5.9)@S16C at ~365 and 478 K, and then three intense desorption bands gradually formed at ~365, 405 and 478 K upon increasing the Ni concentration to 14.2 wt% and 21.7 wt%. Figure S9B (SI) compares the CO-TPD on the Ni(x)@S16C offers a larger number of sites and greater CO adsorption ability than Ni(x)@SiO₂. Assignments of the CO desorption temperature from the Ni surface to specific adsorption sites have been reported in the literature.

The peaks observed at approximately 365 and 405 K were likely ascribed to linear CO chemisorption, and the desorption peak at 478 K might be derived from a bridging-type of CO adsorption.⁵⁹

3.4. CO₂- and CO-TPH on the Ni(x)@S16C catalysts

To identify the relationship between the CO₂ desorption state and CO/CH₄ formation, TPH was further investigated on the CO₂- and CO-adsorbed Ni(x)@S16C catalysts under a H₂/He (20/80) stream. Figure 9 shows the CO₂-TPH results, where CO₂, H₂O, CO and CH₄ molecules are detected at elevated temperature. On Ni(5.9)@S16C, adsorbed CO₂ was hydrogenated to desorbed CO at 360 K. Upon increasing the Ni content to 14.2 wt% and 21.7 wt%, a weak CO₂ signal was observed at ~360 K, while the desorption temperatures of CO derived from CO₂ hydrogenation appeared at ~360, 423 and 500 K. The temperatures for CO desorption were similar to the results of the CO-TPD profiles in Figure 8B, implying that the step of CO₂ hydrogenated to CO might occur below 360 K, before desorbing CO at increased temperatures. However, the relative intensity of desorbed CO at 500 K, corresponding to CO bound to the bridging sites, was small compared to that in the CO-TPD results in Figure 8B. The obvious CH₄ desorption peak at ~ 520 K in the TPH of CO₂ for all the Ni(x)@S16C likely corresponded to the hydrogenation of a bridging CO intermediate.



Figure 9. TPH plots of CO₂ desorbed from the Ni(x)@S16C catalysts in a 100 mL min⁻¹ H₂/He (20/80) stream with a 10 K min⁻¹ heating rate. CO₂ adsorption was performed in a pure 100 mL min⁻¹ CO₂ stream at atmospheric pressure and 298 K for 40 min.

The CH₄ formation correlated to adsorbed CO species on Ni(x)@S16C was further identified using the TPH experiments for CO adsorption, as shown in Figure 10. As expected, the marked CH₄ desorption was also present at 520 K via the hydrogenation of adsorbed CO, but the peaks for CO desorption at 365 K and 405 K persisted, and the peak at 478 K associated with the adsorption of bridging CO completely disappeared. This observation suggests that the adsorption of bridging CO on Ni(x)@S16C may be the important species for CH₄ formation. Thus, CH₄ likely formed from the hydrogenation of adsorbed bridging CO. The CO₂-TPH profiles of Ni(20)@SiO₂ are shown in Figure S10 (SI) to compare with the reactions on Ni(x)@S16C, revealing that the weak CO and CH₄ peaks occurred at ~500 K. The results were attributed to the

simultaneous formation of CO and CH_4 at ~500 K resulting from intermediate dissociation in the process of CO_2 hydrogenation.



Figure 10. TPH plots of CO desorbed from the Ni(x)@S16C catalysts in a 100 mL min⁻¹ H₂/He (20/80) stream with a 10 K min⁻¹ heating rate. CO₂ adsorption was performed in a pure 100 mL min⁻¹ CO stream at atmospheric pressure and 298 K for 40 min.

3.5. IR spectra of CO adsorbed on Ni(x)@S16C

Figure 11A shows the IR spectra of CO adsorbed on Ni(x)@S16C to investigate the active sites associated with CO₂ hydrogenation. CO initially adsorbed on all the Ni(x)@S16C catalysts at 298 K, exhibiting wide IR bands with peaks centered at 2042, 2013, 1900 and 1830 cm⁻¹. The relative intensities of the CO peaks increased upon increasing the Ni loading. The vibrational stretching bands of CO adsorbed on the Ni surfaces have been reported in several literature reports.⁶⁰⁻⁶² The peaks at 2042 and 2013 cm⁻¹ are attributed to linear CO adsorption on the Ni surface. The 1900 and 1830 cm⁻¹ peaks may correspond to bridging Ni₂CO species and 3-fold or

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4-fold CO adsorption, respectively.⁶⁰⁻⁶² Temperature-dependent IR spectra of CO adsorbed on Ni(14.2)@S16C are shown in Figure 11B. The bands for linear CO at ~ 2042 and 2013 cm⁻¹ and bridging CO at ~1900 cm⁻¹ greatly diminished as the temperature increased to 573 K, but the peak at 1830 cm⁻¹, assigned to multi-bonded Ni₄CO or Ni₃CO species, remained intense even at 573 K due to the strong adsorption for the multi-bonded CO species. The IR results are in reasonable accordance with the CO-TPD measurements on Ni(x)@S16C shown in Figure 8B, indicating that the desorbed peaks at 365 and 405 K might be associated with linear CO and that the peak at 478 K corresponds to bridging CO. However, multi-bonded CO might strongly bind to the Ni surface, causing difficultly for observation in the TPD profiles.



Figure 11. (A) IR spectra of CO adsorbed on the Ni(x)@S16C catalysts and (b) temperaturedependent IR spectra of CO on the Ni(14.2)@S16C catalyst.

The vibrational frequency of the multi-bonded CO exhibited a red shift when the temperature was increased. Such a behavior is very characteristic of CO adsorbed onto a Ni surface and is usually explained by dipole–dipole interactions. The decreasing CO coverage on the Ni surface at high temperature can have weak dipole–dipole interactions among CO molecules.⁶³ The CO₂ adsorption site on Ni(x)@S16C was further investigated by IR spectra of the co-adsorption of CO₂ and CO. Figure 12 shows the IR spectra of CO adsorbed on the Ni(14.2)@S16C surface that was pre-saturated with CO₂ at 298 K. The relative intensity of the bridging CO band at 1900 cm⁻¹ markedly disappeared due to the presence of pre-adsorbed CO₂. Thus, the results suggest that the bridging sites on Ni(x)@S16C might play an essential role for CO₂ adsorption.



Figure 12. IR spectra of (a) CO adsorbed on the Ni(14.2)@S16C catalyst and (b) CO adsorbed on the CO₂ pre-adsorbed Ni(14.2)@S16C catalyst.

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3.7. IR spectra of H₂ and CO₂ co-adsorbed on the Ni(x)@S16C catalyst

Figure 13 displays the IR spectra of co-adsorbed H₂ and CO₂ on the Ni(14.2)@S16C catalyst at increasing temperatures. The experiments were performed by passing a pure CO_2 stream (20) mL/min) over the catalysts for 20 min at 298 K, followed by purging residual CO₂ with a pure H₂ stream (20 mL/min). The IR spectra were recorded to monitor adsorbed CO₂ on the Ni(x) @S16C surface under a H_2 stream at elevated temperatures. The IR band at 2338 \mbox{cm}^{-1} corresponds to adsorbed CO₂, which is assigned to the asymmetric stretching (v_{as}) mode of linearly adsorbed CO₂. Linear CO bands at ~2050 and 2027 cm⁻¹ were clearly observed. The broad absorbance band in the region of 1960-1200 cm⁻¹ was deconvoluted into several bands at ~1897, 1778, 1700, 1648, 1591, 1518, 1386 and 1295 cm⁻¹. The peak at 1897 and 1778 cm⁻¹ may be associated with bridging CO and multi-bonded CO with 3-fold or 4-fold adsorption, respectively. The formation of adsorbed CO strongly depended on the decomposition of the intermediates during CO₂ hydrogenation to CO at 298 K. Fingerprint intermediates may be generated on the Ni(x)@S16C surface, thus resulting in a broad absorbance band. However, clearly identifying the major species might be difficult. The peaks for $v_{as}(OCO)$ at 1591 cm⁻¹ and $v_s(OCO)$ at 1295 cm⁻¹ revealed in this figure might be assigned to adsorbed formic acid species.⁶⁴ The peaks at 1518 and 1386 cm⁻¹ might be due to a bidentate formate complex, as the frequency difference (Δv) between $v_s(OCO)$ and $v_{as}(OCO)$ is less than 220 cm⁻¹.⁵⁶ The bands at 1700 and 1648 cm⁻¹ may correspond to the carbonyl group in molecular formic acid and the bending mode of adsorbed H₂O, respectively.⁶⁴ The peaks at 2847 cm⁻¹ and 2954 cm⁻¹ are attributed to the v(CH) mode of a formate or formic acid species.^{56,64} Upon increasing the temperature to 473 K, a v(CH) mode of CH₄ at \sim 3015 cm⁻¹ was observed with the disappearance of bridging CO at 1897 cm⁻¹. The adsorbed bidentate formate and formic acid species likely

contributed for the intermediates during CO_2 hydrogenation. However, it was reasonably suggested that the formic acid species should be the major species for CO formation because of their intensive characteristic peaks in relative intensity.



Figure 13. IR spectra of H_2 and CO_2 co-adsorbed on the Ni(14.2)@S16C catalyst at various temperatures. A pure CO_2 stream (20 mL min⁻¹) was passed over the catalyst for 20 min at 298 K, followed by purging CO_2 with a He stream (20 mL min⁻¹) and adsorbing CO_2 on Ni(x)@S16C under a H_2 stream at different temperatures.

3.8 Active sites for CO₂ hydrogenation

The synthesized –COOH functionalized SBA-16 materials proved to be highly capable of removing Ni^{2+} ions from water through electrostatic interactions. The actual amount of Ni^{2+} adsorption might be limited by the number of carboxylic groups present. The adsorbed Ni^{2+} ions in the cage-type structure were transformed into Ni^{0} NPs through reduction at 873 K.

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Interestingly, the size of the Ni NPs were effectively restricted to less than 5 nm, even if the concentration of impregnated Ni²⁺ ions increased to 21.7 wt%. Notably, Ni NPs formed in the cage-type structure of SBA-16 enriched the surface sites to strongly adsorb CO and CO₂, as evidenced by the CO- and CO₂-TPD profiles. Based on the results of the CO₂-TPD measurements in Figure 8A, Ni(x)@S16C led to a substantially enhanced CO_2 coverage that directly induced a high reaction rate for CO₂ hydrogenation. The high catalytic rate of CO₂ hydrogenation was further observed in the IR spectra of co-adsorbed H₂ and CO₂ on Ni(x)@S16C in Figure 13, revealing that a considerable amount of CO was formed at room temperature. The same IR observation of co-adsorbed H₂ and CO₂ on the Ni(x)@SiO₂ catalyst was investigated in our previous study, indicating that a monodentate intermediate was formed at low temperature, which dissociated to CO at 473 K.⁵⁶ In this case, the fingerprint intermediates for CO₂ hydrogenation on Ni(x)@S16C, which likely contained bidentate formate and formic acid species (as evidenced by the IR spectra in Figure 12), were very different than those on Ni(x) $@SiO_2$. The decomposition of these intermediates might induce the formation of CO on the Ni(x)@S16C catalysts. The Ni(x)@S16C catalysts provided many types of sites for CO adsorption, including linear, bridging and multi-bonding sites. In this study, CO adsorption on Ni@SiO₂ was too weak to observe from IR spectroscopy, even with the 20 wt% Ni loading. In Figures S9B (SI), the TPD profiles of CO desorption from $Ni(x)@SiO_2$ also displayed a single, weak band. We reasonably assumed that linear, bridging and multi-bonded sites should exist on $Ni(x)@SiO_2$ due to the large particle size. However, all the Ni sites of $Ni(x)@SiO_2$ possessed poor binding abilities for CO. Similar phenomena was also found in the CO_2 adsorption studies.

In general, the effect of the metal particle size has been frequently discussed based on the dependence between CO/CH_4 selectivity in CO_2 hydrogenation and the particle size of metal

NPs, such as Ni-, Ru- and Pd-based catalysts.³²⁻³⁴ Literature studies have reported that CO formation is favored on small particles and/or single atoms and that larger particles lead to a considerable enhancement of CH₄ production.³²⁻³⁴ In this case, the Ni NPs with small sizes of 2.7-4.7 nm confined in the SBA-16 structure surprisingly enhanced the CH₄ formation rate of in CO₂ hydrogenation compared to the same reaction on the Ni@SiO₂ catalysts. The high CH₄ formation rate on the Ni(x)@S16C catalysts should depend on the reaction efficiency of CO hydrogenation to CH₄, as the CO₂ hydrogenation followed a consecutive pathway of CO₂ \rightarrow CO \rightarrow CH₄. The IR spectra of co-adsorbed H₂/CO₂ and the CO₂- and CO-TPH profiles further indicated that CO bound to the bridging sites, which might be the primary factor contributing to the enhanced CO hydrogenation to CH₄. On the Ni(x)@S16C catalysts, the relative intensity of the IR band for bridging CO adsorption was enhanced upon increasing the Ni loading, and thus the high Ni loading on SBA-16 effectively accelerated CH₄ formation. On the other hand, CO₂ hydrogenation to CO may also occur on the bridging sites of Ni(x)@S16C, because CO₂ molecules preferred to occupy the bridge sites, based on the results in Figure 12.

The possible consecutive reaction of CO₂ hydrogenation can be described:

$$(1) H_2 + CO_2 \rightarrow CO + H_2C$$

(2)
$$3H_2+CO \rightarrow CH_4+H_2O$$

In this study, the TOF rates for CO formation were markedly higher than that for CH₄ formation, as revealed in Figure 4. The formation of CH₄ from CO hydrogenation undoubtedly demanded more H₂ than the reaction for CO₂ converted to CO, based on the viewpoint of chemical equilibrium. However, the H₂ coverage of the Ni surface should be the essential factor for determining the rates of CO and CH₄ formation.⁵⁶ It was reasonably interpreted that CO product could be rapidly formed in the initial CO₂ hydrogenation reaction with CO₂/H₂ =1, but the rate of

 CH_4 formation was usually slow. On the other hand, we also have shown that the formation of CH_4 may mainly derive from the hydrogenation of CO occupied on the bridge Ni sites. Thus, the process of CO hydrogenated to CH_4 might be attributed to the rate-determining step in the consecutive reactions. The large Ni particles may lead to enhancement of H_2 coverage and in the likelihood of hydrogenation of CO intermediate to CH_4 .

3.9 Comparison with Ni(x)@SBA-16

The TOF rates of CO₂ hydrogenation on Ni(x)@S16C were further compared to the other Ni based catalysts in the literatures.^{65,66} As seen in Table S3, the Ni(x)@S16C catalysts could significantly have higher intrinsic TOF rate than other Ni based catalysts. Comparing to our previous study,⁴⁷ we can also find that the intrinsic TOF rates of CO₂ hydrogenation on various Ni(x)@S16C catalysts were apparently better than that on the Ni NPs deposited on pure SBA-16 without –COOH groups, as shown in Figure S11. The selectivity of CH₄ on the Ni(x)@SBA-16 and Ni(x)@S16C catalysts for CO₂ hydrogenation at 673 K was also compared in Table S4, when all reaction conversions were kept at ~5%. It was found that the CH₄ selectivity on Ni(x)@S16C was higher than that on Ni(x)@SBA-16.

It is clearly observed from both wide angle XRD and TEM measurements that tunable size of Ni NPs can be formed within the cage pores of the –COOH functionalized SBA-16 support by varying the Ni(NO₃)₂· $6H_2O$ concentration. With the increase in the Ni(NO₃)₂· $6H_2O$ concentration, the size of Ni NPs increases. In our previous study, we have found that the particle size of Ni NPs showed less dependence on the Ni loading.⁴⁷ Instead, the cage-like mesopore of SBA-16 is beneficial to confine the growth of Ni NPs, but the size of Ni NPs is not tunable. On the other hand, with the help of –COOH functionalization on the mesopore surface, the control of particle size with the Ni loading becomes possible. From the analysis of N₂

adsorption-desorption isotherms, it was found that the BET surface area (A_{BET}) and pore volume (V_p) of S16C (S_{BET} = 664 m² g⁻¹; $V_p = 0.68$ cm³ g⁻¹) were apparently higher as compared to those of pure silica SBA-16 ($A_{BET} = 511 \text{ m}^2 \text{ g}^{-1}$; $V_p = 0.47 \text{ cm}^3 \text{ g}^{-1}$). In addition to the main role of – COOH functionality in trapping Ni²⁺ ions, such a relatively higher surface area and pore volume of S16C might also contribute to increase the dispersion of Ni nanoparticles, and thus smaller sized Ni particles could be obtained. In particular, it was demonstrated that the Ni dispersion could be achieved up to 35.6 % with the Ni particle size of 2.7 nm for Ni(5.9)@S16C, which was smaller as compared to that of 4.0 nm for Ni(5.8)@SBA-16, at a low Ni loading. It was also reported by Niu et al. that the increased surface area and pore volume of Ni/SiO₂ hollow spheres could lead to the increase in the Ni dispersion and lower the dimension of the Ni particles.⁶⁷ In another work, Varkolu et al. also demonstrated that interconnected mesoporous support possessed higher surface area, pore volume and pore size induced higher Ni dispersion and resulted in slightly smaller size Ni nanoparticles than that on mesoporous silica supports with less textural properties.⁶⁸ At a lower Ni loading, both confinement effect and interactions between the Ni²⁺ ions and -COO⁻ groups work together so that the particle size of Ni NPs in the support S16C can be effectively reduced. In contrast, with the increase in Ni loadings, not all the Ni particles can be confined within the mesopores and the degradation of the mesostructure also occurs. Meanwhile, the same amount of -COO⁻ groups is present in all the cases. It is thus anticipated that the interactions between the Ni²⁺ ions and -COO⁻ groups are not as strong as the cases of lower Ni loadings and cannot control the particle size of Ni NPs effectively at higher Ni loadings. Therefore, the particle size of Ni NPs increases with the increase in Ni loadings. To explore the role of -COOH functionality for the fabrication of Ni NPs in the support S16C, a

series of the H₂-TPR experiments were employed to investigate the degree of Ni reduction and

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the efficiency of Ni²⁺ confined into the cage structure for all the Ni(x)@S16C and Ni(x)@SBA-16 samples that were impregnated but without reduction, i.e., as-impregnated samples. All the as-impregnated samples have been washed by deionized water before their use for the H₂-TPR experiments. The H₂-TPR profiles of the as-impregnated Ni(x)@S16C samples, as shown in Figure S12A, revealed that the Ni^{2+} precursors were directly reduced to Ni^{0} in the temperature range of ~623-800 K. Therefore, the Ni²⁺ ions should be fully reduced to Ni⁰ at 873 K in H₂ for 6 h during the synthesis procedures for the as-impregnated Ni(x)@S16C samples. For comparison purposes, the H₂-TPR profile of the as-impregnated Ni(21.7)@S16C sample that underwent air calcination at 673 K for 5 h was also compared in this figure. It was observed that the reduction band for the calcined Ni(21.7)@S16C became broader and strongly shifted to high temperatures. The results implied that the calcined Ni(x)@S16C sample through air calcination at 673 K and then H₂ reduction at 873 K could still lead to incomplete reduction of Ni²⁺. Thus, it can be inferred that the air calcination should be not a suitable pretreatment process for the Ni(x)@S16C samples. In comparison to the Ni(x)@S16C samples, the H₂-TPR experiments of the as-impregnated Ni(x)@SBA-16 samples were performed and the results are shown in Figure S12B. As shown in Figure S12B, weaker reduction bands for all the Ni(x)@SBA-16 samples were observed as compared to the H₂-TPR profiles shown in Figure S12A. The weaker reduction band for Ni(x)@SBA-16 should directly depend on the low Ni²⁺ concentration in the cage pore. The weak interaction between -SiO⁻ group of SBA-16 and Ni²⁺ might lead to a low amount of Ni²⁺ that can be incorporated into the cage structure, and thus restricted the size of Ni particle to be ~4 nm. On the other hand, the particle sizes of Ni NPs in the Ni(x)@S16C samples with low Ni loadings, i.e., x = 5.9 and 14.2, were smaller than the cases in the Ni(x)@SBA-16 with similar Ni loadings.⁴⁷ The presence of –COOH functionality facilitated the trapping of Ni²⁺ ions into the

cages of S16C and thus resulted in Ni NPs with high dispersion as well as smaller dimensions. In general, when a large amount of Ni^{2+} ions was impregnated into the support, either S16C (x = 21.7) or SBA-16 (x = 22.9), there was higher possibility that the Ni NPs were located outside the cage structure since the average particle sizes of Ni NPs were larger than the entrance size of the cages (\sim 3.2 nm). In the case of S16C, the reduction in surface area and pore volume reached 64.3% and 64.7%, respectively, after a Ni loading amount of 21.7 wt%. However, the Ni(22.9)@SBA-16 sample exhibited 54.4% and 51.0% reduction in surface area and pore volume, respectively, in comparison to the support SBA-16.⁴⁷ A significantly larger reduction in textural properties of the support after similar high Ni loadings suggested that the cage pores in S16C were more partially occupied by the Ni NPs than the case of SBA-16. Based on the description, it was assumed that the pure SBA-16 may give lower ability to effectively trap Ni²⁺ ions into the cage-type mesopores than the SBA-16 with -COOH group (S16C). The S16C material undoubtedly may significantly improve the drawback on pure SBA-16 and give a positive effect to confine a large amount of Ni NPs into the cage-type mesopores due to the electrostatic interaction between Ni²⁺ and $-COO^{-}$. Thus, the Ni(x)@S16C catalysts could enhance high activity toward CO₂ hydrogenation.

3.10 Comparison with directly reduced Ni(x)@SiO₂

The particle size and TOF rates of CO₂ hydrogenation on the impregnated Ni(x)@S16C samples undergoing direct reduction in H₂ without air-calcination treatment were also compared with that on the Ni(x)@S16C catalysts. Figure S13 displays the XRD patterns of the directly reduced Ni(x)@SiO₂ samples, revealing that the particle size of Ni NPs was slightly smaller than the same samples with calcination and reduction treatments shown in Figure S2. However, the process of direct reduction achieved on Ni(x)@SiO₂ did not significantly reduce the Ni particle

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size less than 4.7 nm, as the Ni NPs on S16C. On the other hand, the directly reduced $Ni(x)@SiO_2$ catalysts still appeared low TOF rates of CO₂ hydrogenation in comparison to the Ni(x)@S16C catalysts, as shown in Figure S14.

4. Conclusion

In summary, our results showed that the combined advantageous effects from the confinement of the cage-type mesopores of SBA-16 and the surface functionality made the present SBA-16 material an ideal support to effectively control the growth of Ni NPs in the range of 2.7 to 4.7 nm within the cage-type mesopores. In the series of Ni(x)@S16C samples, the Ni NP size was tuned down to 2.7 nm at a low Ni loading, and a maximum Ni loading up to 21.7 wt% was achieved at high Ni loadings. In view of the relatively low cost of Ni compared to noble metals, the current study demonstrated the use of the unique pore architecture of mesoporous silica as a robust support to control the size of metal NPs in a cost-effective way, which can be readily applied to other transition-metal-based NPs for mesoporous silicas.

The ultra-small Ni NPs confined in the cage-type mesopores provided the Ni(x)@S16C catalysts with remarkably high catalytic activity for CO₂ and CO hydrogenation compared to the Ni@SiO₂ catalysts. The catalytic hydrogenation on the Ni(x)@S16C catalysts followed a consecutive pathway of CO₂ \rightarrow CO \rightarrow CH₄, where CO was assumed to be the intermediate for CH₄ formation during CO₂ hydrogenation. The Ni NPs formed in the cage-type mesopores of – COOH functionalized SBA-16 enriched the surface sites to strongly adsorb CO and CO₂, thus leading to high catalytic rates for CO₂ and CO hydrogenation. The IR spectra of adsorbed CO₂ and CO on Ni(x)@S16C indicated that the bridging sites were mainly responsible for CO₂ adsorption. The fingerprint intermediates, likely including bidentate formate and formic acid species, might be formed during H₂ and CO₂ co-adsorption on Ni(x)@S16C; these intermediates

rapidly dissociated to CO at room temperature. On the other hand, CO formed from the RWGS reaction also bound to the bridging sites for hydrogenation to CH₄.

ASSOCIATED CONTENT

Supporting Information. Comparison for Ni surface and dispersion of Ni(x)@SiO₂ and Ni(x)@S16C; Weisz-Prater criterion calculation for CO₂ and H₂ over Ni(21.7)@S16C and Ni(20)@SiO₂ catalysts; Comparison of TOF of CO₂ hydrogenation on Ni based catalysts; Comparison of selectivity of CH₄ for CO₂ hydrogenation on Ni(x)@SBA-16 and Ni(x)@S16C; XRD spectra of Ni(x)@SiO₂; MAS NMR spectra of S16C support; acid-base titration, zeta potentials of the support S16C, color change and wide angle XRD patterns of the Ni@S16C prepared as a function of pH; FTIR of Ni(x)@S16C; Solid state NMR; XPS spectra of Ni(x)@S16C; Comparison of the conversion and product selectivity for CO₂ hydrogenation; wide-angle XRD patterns of Ni(x)@S16C catalysts undergoing CO₂ hydrogenation; CH₄ selectivity versus the reaction conversion on the Ni(x)@S16C catalysts; TPD profiles of CO₂ and CO desorbed from the Ni(x)@SiO₂ catalysts; TPH profiles of CO₂ desorbed from the Ni(x)@SiO₂ catalysts and H₂-TPR of impregnated Ni(x)@S16C catal Ni(x)@SBA-16.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cschen@mail.cgu.edu.tw (Ching-Shiun Chen)

* E-mail: hmkao@cc.ncu.edu.tw (Hsien-Ming Kao)

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The ultra-small Ni nanoparticles are controllably supported in the cage-type mesopores of – COOH functionalized mesoporous silica SBA-16 and can remarkably enhance catalytic activities for CO_2 hydrogenation.