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Article

Preparation and characterization of Ni/CeO₂-SiO₂ catalysts and their performance in catalytic partial oxidation of methane to syngas

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ABSTRACT

Hexahydrated cerium(III) nitrate (Ce(NO₃)₃·6H₂O) and tetraethyl orthosilicate (C₈H₂₀O₄Si) were used as the precursors for the synthesis of a series of xCeO₂-(1-x)SiO₂ (x = 0, 0.25, 0.5, 0.75, 1) composite oxides using a sol-gel process under acidic conditions. The active component, Ni, was loaded on the as-synthesized composite oxides, producing supported Ni catalysts for catalytic partial oxidation of methane to syngas. The properties of the as-synthesized products, such as textural structure, reduction behavior, surface acidity, and carbon deposition, were determined using N₂ physical adsorption/desorption, X-ray diffraction, scanning electron microscopy, ultraviolet-visible diffuse reflectance spectroscopy, temperature-programmed reduction by H₂, temperature-programmed desorption of NH₃, and thermogravimetric analysis. The effects of catalyst composition, calcination temperature, and reaction time on the catalytic performance were investigated. The characterization results showed that these Ni/CeO₂-SiO₂ catalysts have large surface area, small CeO₂ crystals, weak acidity, and low carbon deposition. Highly dispersed NiO is present and is easy to be reduced. The Ni/CeO₂-SiO₂ catalyst with a Ce/Si molar ratio of 1:1, w(Ni) = 10%, and calcined at 700 °C exhibited good stability and the highest CH₄ conversion (~84%) and CO and H₂ selectivity (> 87%).

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1. Introduction

Syngas is a raw material in the production of numerous chemical products, such as synthetic oils and olefins. Catalytic partial oxidation of methane (POM) is the main method used to produce syngas [1–7]. Designing and developing cheap catalysts with good catalytic performance and high selectivity for POM are important for the production of syngas from CH₄.

Supported noble-metal (Pt [8], Pd [9], and Rh [10]), Ni-based [11,12], and Co-based [5] catalysts are usually used in POM. The support is an important component of the catalyst and significantly affects the catalytic performance. The sup-

ports generally used for POM catalysts include Al₂O₃ [13,14], SiO₂ [15,16], CeO₂ [17], ZrO₂ [18], TiO₂ [19], and CeZrO₂ solid solution [20,21]. Among these, SiO₂ shows good stability because it does not easily react with the other components at high temperature. Moreover, dispersion of the supported active component over SiO₂ is improved as a result of its large surface area. For example, Li et al. [22] reported that a Pd/SiO₂ catalyst exhibited good activity in POM because of high dispersion of Pd. After reaction for 7 h at 700 °C, the Pd particle size was still 4–5 nm. Xia et al. [23] reported a spherical, single-channel Ni/SiO₂ catalyst with good Ni dispersion, synthesized by a sol-gel process. This Ni/SiO₂ catalyst showed high activity, se-

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lectivity, and long life in POM. Another porous, core-shell Ni@SiO₂ catalyst, with a narrow particle size distribution, was synthesized by Li et al. [24]. Activity tests showed that the catalytic performance of this core-shell Ni@SiO₂ catalyst is closely related to the size of the Ni core, the porosity of the SiO₂ shell, and core-shell interactions.

The catalyst promoter is also crucial in POM because the reduction of the active component is greatly influenced by the interactions between the promoter and the active component. Moreover, such interactions also affect the stability of the catalyst. For example, Li et al. [25] found that Ce doping in Ni/SiO₂ effectively inhibited the growth of Ni crystallites and improved Ni dispersion. Moreover, CeO₂ easily reacts with other oxides to produce composite oxides, such as CeO₂-TiO₂, CeO₂-ZrO₂, CeO₂-Al₂O₃, and so on [26,27]. The produced composite oxides always have large surface areas and are rich in oxygen vacancies, enabling better promotion by Ce in POM.

In this work, a series of CeO₂-SiO₂ composite oxides with large surface areas were synthesized using a sol-gel process. The active component, Ni, was loaded on the as-synthesized composite oxides, producing supported Ni catalysts. The effects of the Ce/Si molar ratio in the support, Ni content, calcination temperature, and reaction time on the catalytic performance of Ni/CeO₂-SiO₂ in POM were investigated.

2. Experimental

2.1. Catalyst preparation

All the chemicals used were analytically pure and obtained from the Sinopharm Chemical Reagent Co., Ltd. The CeO₂-SiO₂ composite oxides were synthesized using a sol-gel process. Stoichiometric hexahydrated cerium(III) nitrate (Ce(NO₃)₃·6H₂O) was dissolved in ethanol, and the solution pH was maintained at 2–3 using nitric acid. Stoichiometric tetraethyl orthosilicate (TEOS, C₈H₂₀O₄Si) was then added dropwise to the solution under stirring, producing a transparent gel. The produced gel was aged naturally overnight, dried at 110 °C, ground, and calcined at 700 °C for 4 h in air, giving CeO₂-SiO₂ composite oxide supports. The obtained supports were impregnated for 12 h with a stoichiometric nickel nitrate (Ni(NO₃)₂·6H₂O) solution, dried, and calcined at different temperatures for 4 h in air. The obtained catalysts were denoted by wNi/xCeO₂-(1-x)SiO₂-T, where *w* represents the Ni content (mass fraction, 5%–20%), *x* refers to the Ce molar fraction (*x* = 0–1) in the support, and *T* stands for the calcination temperature (600–900 °C) after impregnation with Ni.

2.2. Catalyst characterization

The Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained from N₂ adsorption/desorption isotherms determined at liquid-N₂ temperature (–196 °C) using an automatic analyzer (V-Sorb 2800P, Beijing Jinaipu Company of Science and Technology). The samples were degassed at 200 °C for 1 h under vacuum before the measurements. X-ray diffraction (XRD) measurements were carried out using a Holland

X'Pert Pro MPD X-ray diffractometer (Philips, the Netherlands) equipped with a monochromatized Co K α radiation source (λ = 0.1790955 nm). The accelerating voltage and the applied current were 40 kV and 120 mA, respectively. Scanning electron microscopy (SEM) was performed using a Nova Nano SEM230 (20 kV) scanning electron microscope (FEI company, USA). Ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) were obtained using a UV-Vis spectrophotometer (UV-2550, Shimadzu). The absorption spectra were referenced to BaSO₄. Temperature-programmed reduction by H₂ (H₂-TPR) was carried out using a chemical adsorption instrument (TP5080, Tianjin Xianquan Industry and Trade Development Co., Ltd.). Samples (0.05 g) were placed in a quartz reactor and treated in situ with a flow of dry N₂ (30 mL/min) at 300 °C for 0.5 h. Before a run, the baseline was stabilized in the gas flow. The reactor was heated in a temperature-programmed furnace from room temperature to 800 °C (10 °C/min). A 10% (volume fraction) H₂ in N₂ mixture was used as the reducing gas. The H₂ consumption as a function of the reduction temperature was continuously monitored using a thermal conductivity detector (TCD) cell and recorded. Temperature-programmed desorption of NH₃ (NH₃-TPD) was carried out using the same chemical adsorption instrument as that used for H₂-TPR. Before the tests, the samples (0.1 g) were degassed in situ under a N₂ stream at 300 °C for 0.5 h and then cooled to room temperature. The samples were then saturated with an NH₃ flow (10 mL/min) at room temperature. The physically adsorbed NH₃ was purged under a N₂ stream until the TCD baseline was stabilized and then TPD was performed from room temperature to 800 °C at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed using a TGA Q50 thermogravimetric analyzer (TA Company, USA) to determine the deposited carbon content. After reaction, about 10 mg of each catalyst was degassed in a N₂ stream (40 mL/min) and then tested from room temperature to 750 °C at a heating rate of 10 °C/min in an air stream (60 mL/min).

2.3. Catalytic performance tests

Catalytic performance tests were carried out using a WFSM-3060 reaction apparatus (Tianjin Xianquan co, China) equipped with a continuous-flow fixed-bed quartz-tube reactor of inner diameter 8 mm, operated under atmospheric pressure. Before the reaction, about 0.15 g of each catalyst was placed in the quartz reactor and reduced at 750 °C for 1 h in pure H₂ stream (20 mL/min), followed by purging with N₂ stream (20 mL/min) for 20 min. The reaction mixture CH₄/O₂ = 20/10 (30 mL/min) was fed to the reactor at a total gas hourly space velocity of 12000 mL/(h·g). After 30 min the reaction began, the composition of the gaseous products was analyzed using an online GC-2060 chromatograph (Tengzhou Lunan Analysis Instrument Co, LTD, China) equipped with a TCD and a TDX-101 packed column. The CH₄ conversion, CO selectivity, H₂ selectivity, and H₂/CO molar ratio were calculated using the following formula, where *A*_{*i*,out} and *F*_{*i*,out} represent the chromatographic peak area and relative molar correction factor of gaseous component *i*, respectively. Here, *F*_{CH₄} = 1, *F*_{CO} = 38.5,

$$F_{\text{CO}_2} = 1.9, F_{\text{H}_2} = 0.35.$$

$$X(\text{CH}_4) = ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) / ([\text{CH}_4]_{\text{out}} + [\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}}) \times 100\% = (A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}}) / (A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}} + A_{\text{CH}_4,\text{out}}F_{\text{CH}_4,\text{out}}) \times 100\%$$

$$S(\text{CO}) = [\text{CO}]_{\text{out}} / ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) \times 100\% =$$

$$A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} / (A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}}) \times 100\%$$

$$S(\text{H}_2) = [\text{H}_2]_{\text{out}} / 2([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) \times 100\% =$$

$$A_{\text{H}_2,\text{out}}F_{\text{H}_2,\text{out}} / 2(A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}}) \times 100\%$$

$$n(\text{H}_2)/n(\text{CO}) = [\text{H}_2]_{\text{out}} / [\text{CO}]_{\text{out}} = A_{\text{H}_2,\text{out}}F_{\text{H}_2,\text{out}} / A_{\text{CO},\text{out}}F_{\text{CO},\text{out}}$$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET surface area

The BET surface area was calculated using the BET equation and the physical adsorption/desorption isotherms of N_2 ; the surface areas of all the supports and catalysts are shown in Table 1. The data in Table 1 show that the surface area is closely related to the Ce molar fraction. The surface areas of the $x\text{CeO}_2-(1-x)\text{SiO}_2$ composite oxide supports are larger than that of CeO_2 alone. As the Ce molar fraction increases (x value from 0 to 1), the surface area decreases (from 470 to 20 m^2/g). The Ce molar fraction is the key factor in obtaining CeO_2 - SiO_2 composite supports with large surface area. Increasing the calcination temperature (from 600 to 900 $^\circ\text{C}$) decreases the BET surface area of $0.50\text{CeO}_2-0.50\text{SiO}_2$ (from 196 to 96 m^2/g). Increasing the Ni loading only leads to a slight decrease in the surface area (10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-700$, 100 m^2/g ; 20%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-700$, 103 m^2/g). The Ni is highly dispersed because of the large surface area of the $0.50\text{CeO}_2-0.50\text{SiO}_2-700$ support (149 m^2/g). The loaded Ni could enter some of the pores, causing minor decreases in the surface area [25,28–30]. It is notable that even after calcination at 900 $^\circ\text{C}$ for 4 h, the surface area of 10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-900$ still maintains 59 m^2/g , which indicates that the high thermal stability and strong anti-sintering capacity of the catalyst.

3.1.2. XRD

Table 1

Surface area of composite oxide supports and catalysts.

Sample	$A_{\text{BET}}^a/(\text{m}^2/\text{g})$
SiO_2-700	470
$0.25\text{CeO}_2-0.75\text{SiO}_2-700$	260
$0.50\text{CeO}_2-0.50\text{SiO}_2-700$	149
$0.75\text{CeO}_2-0.25\text{SiO}_2-700$	68
CeO_2-700	20
$0.50\text{CeO}_2-0.50\text{SiO}_2-600$	196
$0.50\text{CeO}_2-0.50\text{SiO}_2-800$	131
$0.50\text{CeO}_2-0.50\text{SiO}_2-900$	96
10%Ni/ SiO_2-700	546
10%Ni/ $0.25\text{CeO}_2-0.75\text{SiO}_2-700$	137
10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-700$	100
10%Ni/ $0.75\text{CeO}_2-0.25\text{SiO}_2-700$	63
10%Ni/ CeO_2-700	42
20%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-700$	103
10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-600$	140
10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-800$	98
10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-900$	59

^a Calculated from the linear portion of the BET equation.

The phase structure of the as-prepared supports and catalysts was analyzed using XRD; the XRD patterns are shown in Fig. 1. Figure 1(a) shows that no clear diffraction peak from SiO_2 is observed in the single-component SiO_2-700 support, indicating that SiO_2 is amorphous. Strong diffraction peaks from cubic fluorite CeO_2 (Ref. code: 00-034-0394), at around $2\theta = 33.3^\circ, 38.7^\circ, 55.8^\circ$, and 66.5° , are observed for the $x\text{CeO}_2-(1-x)\text{SiO}_2-700$ ($x = 0.25, 0.50, 0.75, 1$) supports, and the peak intensity increases with increasing Ce molar fraction. Figure 1(b) shows that the diffraction peaks of cubic phase NiO (Ref. code: 01-078-0423), at around $2\theta = 43.7^\circ, 50.8^\circ$, and 74.7° , are detected for 10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2-700$, and, as shown in Fig. 1(c), the peak intensity increases with increasing Ni content (from 10% to 20%). The XRD patterns of the $0.50\text{CeO}_2-0.50\text{SiO}_2$ and 10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2$ catalysts calcined at different temperature are shown in Fig. 1(d) and 1(e), respectively. The intensity of the CeO_2 and NiO diffraction peaks increase with increasing calcination temperature.

Fig. 1. XRD patterns of composite oxide supports and catalysts. (a) $x\text{CeO}_2-(1-x)\text{SiO}_2$ supports with different x values calcined at 700 $^\circ\text{C}$; (b) 10%Ni/ $x\text{CeO}_2-(1-x)\text{SiO}_2$ catalysts with different x values calcined at 700 $^\circ\text{C}$; (c) Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2$ catalysts with different Ni contents calcined at 700 $^\circ\text{C}$; (d) $0.50\text{CeO}_2-0.50\text{SiO}_2$ supports calcined at different temperatures; (e) 10%Ni/ $0.50\text{CeO}_2-0.50\text{SiO}_2$ catalysts calcined at different temperatures.

Table 2

 Average crystallite size and CeO₂ lattice parameters in composite supports and catalysts.

Sample	Integral FWHM width ^a (rad)		Average crystallite size ^b (nm)		CeO ₂ lattice parameter ^c (nm)
	CeO ₂	NiO	CeO ₂	NiO	
SiO ₂ -700	—	—	—	—	—
0.25CeO ₂ -0.75SiO ₂ -700	0.01609	—	10.32	—	0.5396
0.50CeO ₂ -0.50SiO ₂ -700	0.01613	—	10.30	—	0.5408
0.75CeO ₂ -0.25SiO ₂ -700	0.01282	—	12.96	—	0.5403
CeO ₂ -700	0.00665	—	24.97	—	0.5414
0.50CeO ₂ -0.50SiO ₂ -600	0.01753	—	8.068	—	0.5392
0.50CeO ₂ -0.50SiO ₂ -800	0.01068	—	13.24	—	0.5402
0.50CeO ₂ -0.50SiO ₂ -900	0.00726	—	22.89	—	0.5407
10%Ni/SiO ₂ -700	—	0.01415	—	12.25	—
10%Ni/0.25CeO ₂ -0.75SiO ₂ -700	0.01292	0.01419	12.86	12.42	0.5412
10%Ni/0.50CeO ₂ -0.50SiO ₂ -700	0.01452	0.00973	11.44	18.12	0.5405
10%Ni/0.75CeO ₂ -0.25SiO ₂ -700	0.01078	0.01388	15.41	12.70	0.5404
10%Ni/CeO ₂ -700	0.00656	0.01365	25.32	12.92	0.5416
20%Ni/0.50CeO ₂ -0.50SiO ₂ -700	0.01722	0.00843	9.641	20.89	0.5413
10%Ni/0.50CeO ₂ -0.50SiO ₂ -600	0.01971	0.01013	8.427	17.39	0.5410
10%Ni/0.50CeO ₂ -0.50SiO ₂ -800	0.01383	0.00916	12.01	19.67	0.5396
10%Ni/0.50CeO ₂ -0.50SiO ₂ -900	0.01023	0.00875	16.24	20.74	0.5406

^a Obtained from X-ray line broadening analyzed by X'pert Highscore Plus software. ^b Calculated from X-ray line broadening of CeO₂(111) and NiO(200) reflection analyzed by Scherrer formula. ^c Calculated from CeO₂(111) plane reflection by using Bragg equation.

—: Not determined because of the phase nature.

The Scherrer equation, $D = 0.89\lambda/\beta\cos\theta$, was used to estimate the average crystallite size of the samples, where β is the width in radians of the XRD peak at half-height for the plane peak, λ is the X-ray wavelength in nanometers ($\lambda = 0.1790955$ nm), θ is the angle between the incident and diffracted beams in degrees, and D is the average crystallite size of the powder sample in nanometers. The strongest diffraction peaks of CeO₂ ($2\theta = 33.3^\circ$) and NiO ($2\theta = 50.8^\circ$) were used in the calculation. The obtained results are summarized in Table 2. The CeO₂ and NiO particles are nanoscale. According to the literature [26,31], a mixture of CeO₂ and SiO₂ first forms a Ce_{9.33}(SiO₄)₆O₂ intermediate phase. During calcination, Ce_{9.33}(SiO₄)₆O₂ decomposes to nanoscale CeO₂ particles, and the produced CeO₂ is highly dispersed on the SiO₂ matrix. The average crystallite size of CeO₂ in catalysts is slightly larger than that in supports; this may be caused by the second calcination. High-temperature (900 °C) calcination causes an increase in the size of the CeO₂ and NiO crystallites, suggesting that aggregation or sintering of these particles occurs, and this could also be a major factor in the decrease in the BET surface area. The average crystallite size of CeO₂ in CeO₂-700 and 10%Ni/CeO₂-700 is 0.5414 and

0.5416 nm, respectively, which are slightly larger than that of CeO₂ in the CeO₂-SiO₂ composite. This could be attributed to lattice constriction of CeO₂ when Si⁴⁺ enters the CeO₂ lattice and forms the CeO₂-SiO₂ composite oxide, because the Si⁴⁺ radius ($r = 0.042$ nm) is smaller than the Ce⁴⁺ radius ($r = 0.087$ nm) [26].

Scheme 1 shows a proposed mechanism for the formation of the CeO₂-SiO₂ composite oxide. The formation process could include several steps such as hydrolysis of TEOS, condensation, calcination, and dehydration [32,33]. First, under acidic conditions, hydrolysis of TEOS takes place, producing orthosilicic acid. The orthosilicic acid is transformed into a silicate polymer by condensation and dehydration. Ce³⁺ could be adsorbed by the hydroxy (–OH) groups in the silicate polymer. Drying and calcination produce a CeO₂-SiO₂ composite oxide with good dispersion and a large BET surface area.

3.1.3. SEM

The morphology of typical supports and catalysts was analyzed using SEM; the SEM images are shown in Fig. 2. As shown in Fig. 2(a), the SiO₂-700 support consists of a large number of aggregated particles. It can be seen from Fig. 2(b) that there are

Scheme 1. Proposed mechanism of CeO₂-SiO₂ composite oxide formation.

Fig. 2. SEM images of typical supports and catalysts. (a) SiO_2 -700; (b) 0.50CeO_2 - 0.50SiO_2 -700; (c) $10\%\text{Ni}/0.50\text{CeO}_2$ - 0.50SiO_2 -700.

no obvious morphological differences between SiO_2 -700 and the 0.50CeO_2 - 0.50SiO_2 -700 composite support. Figure 2(c) shows that after Ni loading ($w = 10\%$), small particles appear on the surface of 0.50CeO_2 - 0.50SiO_2 -700. These are NiO particles that were reduced to metallic Ni^0 by H_2 before POM.

3.1.4. UV-Vis DRS

DRS was used to identify Ni species on the catalyst surface. Fig. 3 shows the UV-Vis DR spectra of typical catalysts. The UV-Vis DR spectrum of pure CeO_2 is also shown. It can be seen from this figure that CeO_2 has an obvious absorption peak at around 343 nm, and NiO absorption peaks are observed in the region from 297 to 350 nm. The characteristic absorption peaks of NiO are attributed to charge transfer by octahedral Ni^{2+} among NiO lattices [25,34,35]. A comparison of Fig. 3(a) with Fig. 3(b)–(e) shows that the peaks in the UV-Vis DR spectra of the Ni species in $10\%\text{Ni}/x\text{CeO}_2$ – $(1-x)\text{SiO}_2$ -700 ($x = 0.25, 0.50, 0.75, 1$) shift to slightly longer wavelengths, indicating that less energy is needed for charge transfer, as a result of interactions between Ni species and the $x\text{CeO}_2$ – $(1-x)\text{SiO}_2$ -700 composite support [25,30]. These interactions also affect the reduction performance of the catalysts.

3.1.5. H_2 -TPR

The H_2 -TPR profiles of the catalysts are shown in Fig. 4. The reduction of the CeO_2 - SiO_2 composite support was first tested to determine whether its reduction peaks overlap with the

Fig. 3. UV-Vis DR spectra of catalysts. (1) $10\%\text{Ni}/\text{SiO}_2$ -700; (2) $10\%\text{Ni}/0.25\text{CeO}_2$ - 0.75SiO_2 -700; (3) $10\%\text{Ni}/0.50\text{CeO}_2$ - 0.50SiO_2 -700; (4) $10\%\text{Ni}/0.75\text{CeO}_2$ - 0.25SiO_2 -700; (5) $10\%\text{Ni}/\text{CeO}_2$ -700; (6) CeO_2 -700.

reduction peaks of NiO. Figure 4(a) shows that 0.50CeO_2 - 0.50SiO_2 -700 has a weak H_2 consumption peak at around 490 °C. This peak results from the reaction between H_2 and surface lattice oxygen on CeO_2 or adsorbed oxygen [28–31,36]. The reduction peak at 780 °C is ascribed to reduction of bulk CeO_2 containing large crystallites [36–41] because SiO_2 cannot be reduced below 800 °C [36]. The NiO reduction peaks appear at 325–580 °C, and they become stronger with increasing Ni content.

Fig. 4. H_2 -TPR profiles of catalysts. (a) $\text{Ni}/0.50\text{CeO}_2$ - 0.50SiO_2 -700 with different Ni contents; (b) $10\%\text{Ni}/x\text{CeO}_2$ – $(1-x)\text{SiO}_2$ -700 with different x values; (c) $10\%\text{Ni}/0.50\text{CeO}_2$ - 0.50SiO_2 calcined at different temperatures.

The effects of the Ce/Si molar ratio on the reduction performance of the catalysts are shown in Fig. 4(b). Two reduction peaks are observed at 365–670 °C for 10%Ni/SiO₂-700 and at 250–470 °C for 10%Ni/CeO₂-700. The reduction temperature of NiO supported on the xCeO₂-(1-x)SiO₂-700 composite support ($x = 0.25, 0.50, 0.75$) is lower than that for Ni/SiO₂-700, suggesting that Ni is more easily reduced over xCeO₂-(1-x)SiO₂-700. The interactions between CeO₂ and NiO could benefit NiO reduction. Moreover, oxygen vacancies in CeO₂-SiO₂ could increase the lattice oxygen mobility, making the reduction of Ni species easier [20].

Figure 4(c) shows the influence of the calcination temperature on the reduction performance of 10%Ni/0.50CeO₂-0.50SiO₂. An increase in the calcination temperature causes the reduction peak of NiO to shift toward higher temperature. This shift indicates that reduction of NiO is difficult; this could be a result of the strong interactions between CeO₂ and SiO₂ formed during high-temperature calcination [29,42]. Increases in the size of the CeO₂ and NiO crystallites (see Table 2) could also help to make NiO reduction difficult.

3.1.6. NH₃-TPD

The surface acidity of typical supports and catalysts was tested using NH₃-TPD; the TPD profiles are shown in Fig. 5. For SiO₂-700, two NH₃ desorption peaks are observed at around 90 °C and 450 °C, corresponding to weak and strong acid sites, respectively. The TPD profile of 10%Ni/SiO₂-700 is consistent with that of SiO₂-700. Compared with SiO₂-700, the 0.50CeO₂-0.50SiO₂-700 has a smaller weak acid desorption peak, and the strong acid desorption peak almost disappears, indicating that the acidity is weakened by the formation of the composite support; this could be caused by the alkalinity of Ce. Ni loading (10%) on 0.50CeO₂-0.50SiO₂-700 causes no obvious difference in the TPD profile. In POM, carbon species and coke are easily deposited on strong acid centers [2]. The weak acidity of the 10%Ni/0.50CeO₂-0.50SiO₂-700 catalyst could contribute to its low carbon deposition in POM.

3.1.7. TGA

Typical catalysts were analyzed after POM using TGA; the TG profiles are shown in Fig. 6. The mass losses below 130 °C, in the region 130–350 °C, and above 600 °C are produced by

Fig. 5. NH₃-TPD profiles of typical supports and catalysts.

Fig. 6. TG profiles of the catalysts after reaction. (1) 10%Ni/SiO₂-700; (2) 10%Ni/0.50CeO₂-0.50SiO₂-700; (3) 20%Ni/0.50CeO₂-0.50SiO₂-700.

desorption of adsorbed water and amorphous carbon, combustion of filamentous carbon, and graphitic carbon combustion, respectively [43,44]. However, a mass increase is also observed in the region 350–570 °C; this is caused by oxidation of Ni⁰. The smaller mass losses below 130 °C for 10%Ni/0.50CeO₂-0.50SiO₂-700 and 20%Ni/0.50CeO₂-0.50SiO₂-700 compared with that for 10%Ni/SiO₂-700 imply that smaller amounts of water and amorphous carbon are adsorbed on these catalysts, and their more obvious mass increases indicate that there are larger numbers of active Ni⁰ centers in these two catalysts after reaction. Above 450 °C, no obvious mass loss is observed for 10%Ni/0.50CeO₂-0.50SiO₂-700, whereas above 440 °C, a mass loss of about 7.1% occurs for 20%Ni/0.50CeO₂-0.50SiO₂-700, suggesting that there is a large amount of deposited carbon on 20%Ni/0.50CeO₂-0.50SiO₂-700. Previous research [45–47] showed that the average coke formation rate is closely related to the crystallite size and dispersion of Ni. Smaller Ni crystallites and higher dispersion of Ni could significantly decrease coke formation. Moreover, Fig. 6 also shows that carbon deposition increased with increasing Ni content. The increase in Ni content increases the Ni crystallite size, and large Ni crystallites easily become active centers for carbon deposition reactions.

3.2. Catalytic performance

3.2.1. Effects of Ni content

Table 3 shows the CH₄ conversion and CO and H₂ selectivity

Table 3

Catalytic performance of Ni/0.50CeO₂-0.50SiO₂-700 with different Ni contents in POM reaction.

Sample	X(CH ₄) /%	S(CO) /%	S(H ₂) /%	S(CO ₂) /%	n(H ₂) /n(CO)
0.50CeO ₂ -0.50SiO ₂ -700	23.7	8.6	4.5	91.4	—
5%Ni/0.50CeO ₂ -0.50SiO ₂ -700	71.6	79.3	87.1	20.7	1.93
10%Ni/0.50CeO ₂ -0.50SiO ₂ -700	84.3	87.4	93.3	12.6	2.04
15%Ni/0.50CeO ₂ -0.50SiO ₂ -700	74.1	80.3	88.4	19.7	2.06
20%Ni/0.50CeO ₂ -0.50SiO ₂ -700	70.9	77.8	84.1	22.2	2.11

Reaction conditions: 150 mg catalyst, CH₄/O₂ = 20/10 (30 mL/min), gas hourly space velocity = 12000 mL/(h·g), reaction temperature 750 °C, reaction time 190 min.

Table 4

Catalytic performance of 10%Ni/ x CeO₂-(1- x)SiO₂-700 with different x values in POM reaction.

Sample	$X(\text{CH}_4)$ /%	$S(\text{CO})$ /%	$S(\text{H}_2)$ /%	$S(\text{CO}_2)$ /%	$n(\text{H}_2)$ / $n(\text{CO})$
10%Ni/SiO ₂ -700	76.1	81.9	87.0	18.1	2.12
10%Ni/0.25CeO ₂ -0.75SiO ₂ -700	78.3	84.1	89.0	15.9	2.05
10%Ni/0.50CeO ₂ -0.50SiO ₂ -700	84.3	87.4	93.3	12.6	2.04
10%Ni/0.75CeO ₂ -0.25SiO ₂ -700	82.2	85.0	90.9	15.0	2.03
10%Ni/CeO ₂ -700	77.2	81.0	87.9	19.0	1.98

Reaction conditions: 150 mg catalyst, CH₄/O₂ = 20/10 (30 mL/min), gas hourly space velocity = 12000 mL/(h·g), reaction temperature 750 °C, reaction time 190 min.

for 0.50CeO₂-0.50SiO₂-700-supported catalyst with different Ni contents. From the data in Table 3, it can be seen that the 0.50CeO₂-0.50SiO₂-700 support gives low activity. The CH₄ conversion is 23.7%, and the CO and H₂ selectivity is only 8.6% and 4.5%, respectively, indicating that the major reaction on this support is CH₄ combustion. A loading of 5% Ni greatly improves the activity and selectivity: the CH₄ conversion is 71.6%, and the CO and H₂ selectivity increases to 79.3% and 89.0%, respectively. Loading of 10% Ni gives the highest CH₄ conversion (84.3%), CO selectivity (87.4%), and H₂ selectivity (93.3%). With further increases in the Ni content (20% Ni), the activity and selectivity decrease again. A very low Ni content (5%) does not provide enough active Ni⁰ centers for POM. However, a very high Ni content (20%) leads to large Ni crystallites (see Table 2) and higher carbon deposition (in Fig. 6), which impair the catalytic performance.

3.2.2. Effects of Ce/Si molar ratio

The effects of Ce/Si molar ratio on the catalytic performance in POM are shown in Table 4. 10%Ni/SiO₂-700 and 10%Ni/CeO₂-700 show low catalytic activity, but 10%Ni/0.50CeO₂-

Table 5

Catalytic performance of 10%Ni/0.50CeO₂-0.50SiO₂ calcined at different temperatures in POM reaction.

Sample	$X(\text{CH}_4)$ /%	$S(\text{CO})$ /%	$S(\text{H}_2)$ /%	$S(\text{CO}_2)$ /%	$n(\text{H}_2)$ / $n(\text{CO})$
10%Ni/0.50CeO ₂ -0.50SiO ₂ -600	77.2	83.3	90.3	16.7	1.94
10%Ni/0.50CeO ₂ -0.50SiO ₂ -700	84.3	87.4	93.3	12.6	2.04
10%Ni/0.50CeO ₂ -0.50SiO ₂ -800	73.2	80.3	87.8	19.7	2.01
10%Ni/0.50CeO ₂ -0.50SiO ₂ -900	71.4	78.6	85.1	22.4	2.05

Reaction conditions: 150 mg catalyst, CH₄/O₂ = 20/10 (30 mL/min), gas hourly space velocity = 12000 mL/(h·g), reaction temperature 750 °C, reaction time 190 min.

0.50SiO₂-700, which has the same Ni content (10%), shows the highest CH₄ conversion and CO and H₂ selectivity. The BET surface area, H₂-TPR, and NH₃-TPD results show that 10%Ni/0.50CeO₂-0.50SiO₂-700 has a large surface area and weak acidity, and the loaded Ni is easily reduced to Ni⁰; these are the main reasons for its high catalytic performance.

3.2.3. Effects of calcination temperature

Table 5 shows the catalytic performance over the catalysts calcined at different temperatures. The highest CH₄ conversion and product selectivity were obtained over 10%Ni/0.50CeO₂-0.50SiO₂-700. A very high calcination temperature results in an obvious decrease in the BET surface area and growth of CeO₂ and NiO crystallites. Moreover, after very-high-temperature calcination, reduction of NiO becomes difficult, and the number of Ni⁰ active centers decreases. The catalytic performance of 10%Ni/0.50CeO₂-0.50SiO₂-900 was therefore poor.

3.2.4. Stability tests

The changes in CH₄ conversion, and CO and H₂ selectivity with increasing reaction time over 10%Ni/0.50CeO₂-0.50SiO₂-700 and 10%Ni/SiO₂-700 are shown in Fig. 7. For 10%Ni/SiO₂-

Fig. 7. Comparison of catalytic performance of 10%Ni/0.50CeO₂-0.50SiO₂-700 (1) and 10%Ni/SiO₂-700 (2) in POM reaction. (a) CH₄ conversion; (b) CO selectivity; (c) CO₂ selectivity; (d) H₂ selectivity; (e) H₂/CO molar ratio. Reaction conditions: 150 mg catalyst, CH₄/O₂ = 20/10 (30 mL/min), gas hourly space velocity = 12000 mL/(h·g), temperature 750 °C, reaction time 900 min.

700, when the reaction time is prolonged to 390 min, the CH_4 conversion and CO and H_2 selectivity decrease sharply, suggesting poor stability. However, for 10%Ni/0.50CeO₂-0.50SiO₂-700, there is almost no change in the CH_4 conversion and CO and H_2 selectivity during POM for 900 min, implying good stability.

4. Conclusions

A series of CeO₂-SiO₂ composite oxide supports with large surface area were synthesized using a sol-gel process. After Ni loading, the produced Ni/CeO₂-SiO₂ catalysts exhibited high catalytic performance in POM. The catalytic performance of Ni/CeO₂-SiO₂ was closely related to the Ni content, Ce/Si molar ratio, and calcination temperature. The experimental results showed that the highest CH_4 conversion and product selectivity and good stability were obtained over Ni/CeO₂-SiO₂ calcined at 700 °C, with a Ce/Si molar ratio of 1:1 and a Ni content of 10%. The large BET surface area, weak acidity, ease of NiO reduction, and low carbon deposition are the main reasons for its high catalytic performance.

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Graphical Abstract

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Preparation and characterization of Ni/CeO₂-SiO₂ catalysts and their performance in catalytic partial oxidation of methane to syngas

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A catalyst consisting of Ni (10%) loaded on a CeO₂-SiO₂ composite support synthesized using a sol-gel process exhibited high performance in the catalytic partial oxidation of methane to syngas, as a result of its large BET surface area, weak acidity, high dispersion, easy of Ni reduction, and low carbon deposition.

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Ni/CeO₂-SiO₂催化剂的制备、表征及其甲烷部分氧化制合成气性能

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摘要: 以硝酸亚铈(Ce(NO₃)₃·6H₂O)和正硅酸四乙酯(C₈H₂₀O₄Si)为前驱体, 采用溶胶-凝胶法合成了系列具有大比表面积 of $x\text{CeO}_2\text{-(1-x)SiO}_2$ ($x = 0, 0.25, 0.50, 0.75, 1$) 复合氧化物载体, 然后浸渍活性组分Ni制得用于甲烷部分氧化制合成气的Ni催化剂. 运用N₂物理吸附-脱附、X射线粉末衍射、扫描电镜、紫外-可见漫反射光谱、氢程序升温还原、氨程序升温脱附和热重等手段对所得催化剂的组织结构、还原性、表面酸性和积炭行为等进行了表征; 同时考察了催化剂的组成、焙烧温度和反应时间等对催化剂在甲烷部分氧化制合成气中催化性能的影响. 表征结果表明, 该系列Ni/CeO₂-SiO₂催化剂具有大比表面积, CeO₂晶粒较小, NiO的分散性好且易被还原, 表面酸性弱, 不容易积炭. 当Ce/Si摩尔比为1:1, 活性组分Ni的质量分数为10%, 焙烧温度为700 °C时, 所制备的Ni/CeO₂-SiO₂催化剂表现出较好的稳定性、最高的CH₄转化率(~84%)和对产物CO及H₂的选择性(>87%).

关键词: 溶胶-凝胶法; 铈-硅复合氧化物; 负载型镍催化剂; 甲烷部分氧化; 合成气

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1. 前言

合成气(CO+H₂)被认为是制备合成油和烯烃等众多化工产品的枢纽原料. 而催化甲烷部分氧化(POM)是生产合成气的主要途径, 具有重要的经济和理论意义^[1-7]. 目前, 研发低成本、高催化活性和高产物选择性的催化剂仍是甲烷部分氧化制合成气的关键.

POM反应通常使用的是负载型贵金属(Pt^[8], Pd^[9], Rh^[10]), Ni基^[11,12]或Co基^[5]催化剂. 载体是催化剂的重要组成部分, 并影响其催化性能. 通常使用的载体有

Al₂O₃^[13,14], SiO₂^[15,16], CeO₂^[17], ZrO₂^[18], TiO₂^[19]和CeZrO₂固溶体^[20,21]等. 其中SiO₂在高温条件下不易和其它组分发生固相反应, 具有较好的稳定性, 同时SiO₂的比表面积较大, 能够提高活性组分的分散性能. 如Li等^[22]报道了Pd/SiO₂催化剂在POM反应中具有优异的活性, 原因是SiO₂负载的Pd具有良好的分散性和热稳定性, 经700 °C反应7 h后的Pd粒子的粒径仅为4–5 nm. Xia等^[23]采用溶胶-凝胶法制备了易使Ni颗粒分散的单通道、球状Ni/SiO₂催化剂, 该催化剂具有较高的POM反应活性和较长的使用寿命. Li等^[24]则合成了具有多孔核-壳结

构、粒径分布窄的Ni@SiO₂催化剂,其催化性能与Ni核的尺寸、SiO₂壳的孔隙率及核-壳间相互作用密切相关。另一方面,助剂在POM反应中的作用也极为关键,因为助剂与活性组分的相互作用可以改变活性组分的还原性能,并影响催化剂的稳定性。Li等^[25]考察了助剂对Ni/SiO₂催化剂在CH₄和CO₂重整反应中的影响。结果表明Ce的掺杂效果最佳,Ce能够很好地抑制Ni晶粒的高温长大并提高Ni的分散性。另外,CeO₂易与其它氧化物结合形成复合氧化物,如CeO₂-TiO₂,CeO₂-ZrO₂和CeO₂-Al₂O₃等^[26,27]。这些复合氧化物通常具有大比表面积,易产生丰富的缺陷氧中心,在POM反应中常表现出最佳的载体作用。

本论文采用溶胶-凝胶法合成了系列大比表面积的CeO₂-SiO₂复合氧化物,然后负载活性组分Ni,制得Ni/CeO₂-SiO₂催化剂。考察了载体中Ce/Si摩尔比、Ni的质量分数、焙烧温度及反应时间等对催化剂在甲烷部分氧化制合成气反应中催化性能的影响。

2. 实验部分

2.1. 催化剂的制备

所使用的试剂均来自上海国药集团,均为分析纯。首先,采用溶胶-凝胶法制备CeO₂-SiO₂复合氧化物载体。按计量比称取硝酸亚铈(Ce(NO₃)₃·6H₂O)溶解于适量的乙醇溶液中,并滴加一定浓度的HNO₃,调节溶液的pH至2–3。然后以1滴/s的速率滴加正硅酸四乙酯(C₈H₂₀O₄Si, TEOS),同时搅拌形成透明凝胶,待凝胶自然老化过夜后,于110 °C干燥,研磨,700 °C焙烧4 h,即得到复合氧化物载体CeO₂-SiO₂。将载体等体积浸渍于计量的Ni(NO₃)₂溶液中,12 h后进行干燥,于不同温度下焙烧4 h,自然冷却至室温,即得到载Ni催化剂,命名为wNi/xCeO₂-(1-x)SiO₂-T其中w表示负载Ni的质量分数(5%–20%),x为复合载体中Ce的摩尔分数(x=0–1),T为负载Ni后进行焙烧的温度(600–900 °C)。

2.2. 催化剂的表征

比表面积测定(BET, N₂物理吸附)在北京金埃谱公司生产的V-Sorb 2800P型比表面积分析仪上进行,相对压力(p/p_0)介于0.05–0.25。测试前,样品于150 °C下抽气真空处理2 h,然后在–196 °C下进行N₂等温多点吸附。依据BET法计算比表面积。X射线衍射(XRD)在荷兰飞利浦公式生产的X'Pert Pro MPD型衍射仪(Co K α , λ = 0.1790955 nm)上进行,电压40 kV,电流120 mA,扫描范围 2θ = 10°–90°,扫描步长0.02°。此外,样品的平均晶粒

粒径依据Scherrer公式计算,CeO₂的晶胞参数则运用Bragg公式估算。催化剂的表面形貌在美国FEI公司生产的Nova Nano SEM230型扫描电镜(SEM)仪上观察。紫外-可见漫反射(DRS)吸收光谱在日本岛津UV-2550型紫外分光光度计上进行室温测试。波长范围为200–800 nm,狭缝宽度5 nm,参照材料为BaSO₄。氢程序升温还原(H₂-TPR)测试在天津先权公司产TP-5080型多用吸附仪上进行,催化剂的用量为50 mg。测试前,升温至300 °C并通入N₂气吹扫样品表面物理吸附的水分和杂质。30 min后冷却至室温,再通入组成为10%H₂-90%N₂的混合气体(30 mL/min)作还原气。待基线调零后以10 °C/min的速率开始还原并升温至800 °C。氮程序升温脱附(NH₃-TPD)测试也在TP-5080型多用吸附仪上进行,样品装载量为100 mg。表征前的步骤与H₂-TPR的一致,然后以10 mL/min的流量通入NH₃进行吸附。待吸附饱和后关闭NH₃,打开N₂吹扫体系约30 min并调零基线,最后以10 °C/min的速率开始脱附并升温至800 °C。反应后催化剂的热重(TG)分析在美国TA公司提供的TGA Q50型热重分析仪上进行,以确定其反应过程中的相对积炭量。样品在N₂气流中吹扫后,再在空气气流中以10 °C/min的速率开始测试并升温至750 °C。

2.3. 催化性能测试

催化剂的POM反应在天津先权公司生产的WFSM-3060型反应装置中进行,石英反应管的内径为8 mm,催化剂的装填量为150 mg。反应前将催化剂于750 °C下还原1 h,还原气体为20 mL/min的纯氢。还原完成后,用20 mL/min的高纯N₂吹扫反应装置20 min。随后切换成组成为CH₄/O₂配比为2:1的原料反应气体(30 mL/min),总空速为12000 mL/(h·g)。反应10 min后,经六通阀每30 min取样一次,联接GC-2060型气相色谱仪分析反应后的尾气组成。色谱检测条件为:TCD检测器,TDX-01色谱填充柱,热导池桥电流为70 mA,载气为高纯N₂。催化剂上CH₄转化率、CO和H₂选择性及合成气组分的摩尔比按照以下公式计算得出:

$$\begin{aligned} X(\text{CH}_4) &= ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) / ([\text{CH}_4]_{\text{out}} + [\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}}) \\ &\times 100\% = (A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}}) / (A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + \\ &A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}} + A_{\text{CH}_4,\text{out}}F_{\text{CH}_4,\text{out}}) \times 100\% \\ S(\text{CO}) &= [\text{CO}]_{\text{out}} / ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) \times 100\% = \\ &A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} / (A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}}) \times 100\% \\ S(\text{H}_2) &= [\text{H}_2]_{\text{out}} / 2([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) \times 100\% = \\ &A_{\text{H}_2,\text{out}}F_{\text{H}_2,\text{out}} / 2(A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} + A_{\text{CO}_2,\text{out}}F_{\text{CO}_2,\text{out}}) \times 100\% \\ n(\text{H}_2)/n(\text{CO}) &= [\text{H}_2]_{\text{out}} / [\text{CO}]_{\text{out}} = A_{\text{H}_2,\text{out}}F_{\text{H}_2,\text{out}} / A_{\text{CO},\text{out}}F_{\text{CO},\text{out}} \end{aligned}$$

式中, A_i 和 F_i 分别表示尾气组分*i*的色谱峰面积和相对摩尔校正因子, F_{CH_4} = 1, F_{CO} = 38.5, F_{CO_2} = 1.9, F_{H_2} = 0.35。

3. 结果与讨论

3.1. 催化剂表征结果

3.1.1. 比表面积结果

催化剂的比表面积由 N_2 物理吸附结合BET方程计算得到, 表1列出了所有载体和催化剂的比表面积. 可以看出, 复合氧化物载体 $x\text{CeO}_2-(1-x)\text{SiO}_2$ 的比表面积远大于单一 CeO_2 的比表面积, 其比表面积与Ce摩尔分数密切相关, 随着Ce含量的增大, 比表面积逐渐下降. 当Ce摩尔分数 x 由0增大至1时, 载体的比表面积由 $470\text{ m}^2/\text{g}$ 逐渐降低至 $20\text{ m}^2/\text{g}$. 为了得到大比表面积的 $\text{CeO}_2\text{-SiO}_2$ 复合载体, 控制Ce/Si比是非常关键的. 固定Ce的摩尔分数 x 为0.50, 当焙烧温度分别为600, 700, 800和900 °C时, $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2$ 的比表面积分别为196, 149, 131和96 m^2/g , 可见随着焙烧温度的升高, 复合载体的比表面积逐渐下降. 负载10%的Ni后, 催化剂10%Ni/ $x\text{CeO}_2-(1-x)\text{SiO}_2$ ($x = 0.25, 0.50, 0.75$)的比表面积相对于其载体而相应下降, 这是因为负载的Ni可能占据载体的孔道, 造成催化剂的比表面积下降^[25,28–30]. 当Ni的含量由10%增大至20%时, 催化剂10%Ni/ $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2\text{-}700$ ($100\text{ m}^2/\text{g}$)和20%Ni/ $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2\text{-}700$ ($103\text{ m}^2/\text{g}$)的比表面积仅略微变化, 这是因为复合载体 $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2\text{-}700$ 具有较大的比表面积($149\text{ m}^2/\text{g}$), 能够有效地促进Ni的分散. 催化剂10%Ni/ $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2$ 在900 °C的高温焙烧4 h后, 其比表面积仍然维持在59 m^2/g , 表明该催化剂具有较好的热稳定性能.

3.1.2. XRD

利用XRD对所制备的载体和催化剂进行了物相分析, 结果示于图1. 图1(a)为不同Ce/Si比载体的XRD谱, 图1(b)为不同Ce/Si比的载体负载10%Ni后催化剂的XRD谱. 由图1(a)可知, 单一载体 $\text{SiO}_2\text{-}700$ 的XRD谱线中未发现其衍射峰, 表明 SiO_2 呈现无定形态; 其它载体 $x\text{CeO}_2-(1-x)\text{SiO}_2\text{-}700$ ($x = 0.25, 0.50, 0.75, 1$)均在 2θ 为 $33.3^\circ, 38.7^\circ, 55.8^\circ$ 与 66.5° 处出现立方萤石型 CeO_2 的衍射峰(Ref. code: 00-034-0394), 并且衍射峰随 x 的增大而变强和尖锐; 在复合载体中未发现 SiO_2 的衍射峰, 主要原因是 SiO_2 处于无定形态, 衍射峰较弱. 由图1(b)可知, 负载10%Ni后催化剂的XRD谱线中除了 CeO_2 的衍射峰外, 在 $2\theta = 43.7^\circ, 50.8^\circ$ 与 74.7° 附近还出现了立方相NiO的衍射峰(Ref. code: 01-078-0423). 当负载Ni的含量增大至20%后, NiO的衍射峰逐渐变强而尖锐(图1(c)). 不同温度焙烧后的载体 $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2$ 和催化剂10%Ni/ $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2$ 的XRD谱图见图1(d)和图1(e).

可以发现, 随焙烧温度升高, 载体和催化剂中 CeO_2 和NiO的衍射峰均逐渐变强.

根据上述XRD谱中 CeO_2 ($2\theta \approx 33.3^\circ$)和NiO ($2\theta \approx 50.8^\circ$)的晶面衍射峰, 利用Scherrer公式和Bragg公式计算分别得到 CeO_2 和NiO的平均晶粒粒径和 CeO_2 的晶胞参数, 结果列于表2. 由计算结果发现, 所有载体和催化剂中的 CeO_2 和NiO均为纳米级晶粒. 已有研究表明, CeO_2 和 SiO_2 之间可形成一种组成为 $\text{Ce}_{9.33}(\text{SiO}_4)_6\text{O}_2$ 的中间相态, 该物种在焙烧处理时进一步分解成纳米级的 CeO_2 颗粒和无定形的 SiO_2 , 且 CeO_2 高度分散在 SiO_2 的网格中^[26,31]. 此外, 催化剂中 CeO_2 的晶粒粒径略大于载体中 CeO_2 的晶粒粒径, 可能由负载Ni后经过二次焙烧所引起. 焙烧温度影响载体和催化剂的晶粒粒径, 尤其是经过900 °C高温焙烧后, CeO_2 和NiO的晶粒粒径增大更为明显, 说明900 °C高温焙烧造成晶粒间发生了一定程度的聚集或烧结, 这也是造成其比表面积降低的主要因素. 另外, 载体 $\text{CeO}_2\text{-}700$ 和催化剂10%Ni/ $\text{CeO}_2\text{-}700$ 中 CeO_2 的晶胞参数分别0.5414和0.5416 nm, 而其它载体和催化剂中 CeO_2 的晶胞参数均略小. 这是由于 Si^{4+} 半径($r = 0.042\text{ nm}$)比 Ce^{4+} 半径($r = 0.087\text{ nm}$)小, 形成的凝胶在焙烧过程中部分 Si^{4+} 进入 CeO_2 的晶格, 形成 $\text{CeO}_2\text{-SiO}_2$ 复合氧化物, CeO_2 的晶格发生收缩所致^[26].

$\text{CeO}_2\text{-SiO}_2$ 复合氧化物的形成机理见图式1所示, 该过程包括正硅酸四乙酯的水解、缩合和焙烧脱水等^[32,33]. 首先, 正硅酸四乙酯在酸性环境中水解成原硅酸, 然后原硅酸经缩合失水形成硅酸聚合物, 同时硅酸聚合物表面的 -OH 与吸附 Ce^{3+} 表面的 -OH 产生氢键作用力, 连接在一起. 最后经干燥、焙烧等过程进一步脱水, 产生共价键, 使Ce固定在 SiO_2 相的网格中, 形成分散均匀、具有大比表面积的 $\text{CeO}_2\text{-SiO}_2$ 复合氧化物.

3.1.3. SEM

利用扫描电镜对典型样品的表面形貌进行了分析, 结果如图2所示. 可以看出, 载体 $\text{SiO}_2\text{-}700$ 的表面由大量尺寸不一的颗粒团聚而成, 复合载体 $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2\text{-}700$ 的表面形貌没有明显变化. 当载体 $0.50\text{CeO}_2\text{-}0.50\text{SiO}_2\text{-}700$ 负载10%Ni后, 催化剂的整体形貌虽没有变化, 但其表面有更多细小的颗粒, 这些细小颗粒为沉积的NiO颗粒.

3.1.4. UV-Vis DRS

典型催化剂的UV-Vis DRS吸收光谱如图3所示, 同时示出纯 CeO_2 的UV-Vis DRS吸收光谱. 由图可见, 纯 CeO_2 的吸收峰在343 nm左右, 而催化剂中NiO的吸收峰出现在297–350 nm, 此特征吸收谱带归属于NiO晶胞中

八面体 Ni^{2+} 的电荷跃迁^[25,34,35]。比较谱线(a)和(b)–(e)发现,复合载体负载Ni后的10%Ni/ $x\text{CeO}_2$ –(1– x) SiO_2 –700 ($x = 0.25, 0.50, 0.75, 1$)催化剂的表面Ni物种的吸收谱带向长波方向移动。这表明催化剂10Ni/ $x\text{CeO}_2$ –(1– x) SiO_2 –700中的NiO与复合载体产生了相互作用,使 Ni^{2+} 的电荷跃迁所需的能量更低^[25,30]。这种相互作用还将影响到NiO的还原性能。

3.1.5. H_2 -TPR

图4是催化剂的 H_2 -TPR曲线。由于复合载体 CeO_2 – SiO_2 可能产生耗氢峰,因此先对其进行TPR分析以判断其还原峰与NiO的还原峰是否发生重叠。由图4(a)可以看出,载体0.50 CeO_2 –0.50 SiO_2 –700在490 °C左右出现了一个很弱的耗氢峰,这是 CeO_2 表面晶格氧及吸附氧同 H_2 作用引起的^[28–31,36]。由于800 °C以下的 SiO_2 不能被 H_2 还原^[36],因此780 °C附近出现的高温耗氢峰可能是由体相大粒径 CeO_2 的还原所致^[36–41]。负载活性组分Ni后,NiO的还原峰出现在325–580 °C,该还原峰随Ni含量的增加而逐渐变大,但还原峰的位置没有明显改变。复合载体中 x 值对催化剂还原性能的影响见图4(b)。单一载体 SiO_2 –700负载Ni后的催化剂仅在365–670 °C出现NiO的还原峰;而10%Ni/ CeO_2 –700在250–470 °C出现NiO的还原峰,高于800 °C的峰为大粒径 CeO_2 的还原耗氢峰。复合载体 $x\text{CeO}_2$ –(1– x) SiO_2 –700 ($x = 0.25, 0.50, 0.75$)负载Ni后的催化剂中NiO还原峰的峰温明显低于10%Ni/ SiO_2 –700中NiO还原峰的峰温,表明Ni负载在 $x\text{CeO}_2$ –(1– x) SiO_2 复合载体上更容易被还原。焙烧温度对10%Ni/0.50 CeO_2 –0.50 SiO_2 还原性能的影响见图4(c)。可以看出,NiO还原峰的峰温随焙烧温度的升高而逐渐向高温方向移动,NiO的还原变得更难。经900 °C焙烧后催化剂的NiO还原峰移动得最明显。NiO还原峰向高温移动的主要原因在于高温焙烧促进了 CeO_2 与 SiO_2 之间强烈的相互作用^[29,42],导致NiO还原更困难。同时表2数据也显示,随焙烧温度的升高,催化剂中 CeO_2 和NiO的粒径均有所增大,NiO粒径的增大也是造成还原峰向高温移动的原因之一。

3.1.6. NH_3 -TPD

利用 NH_3 -TPD分析了典型载体和催化剂表面酸性的强弱,结果见图5。图5表明,单一载体 SiO_2 –700的 NH_3 -TPD曲线中存在两个明显的 NH_3 脱附峰,分别位于90 °C和450 °C左右,可分别归属为弱酸和强酸中心吸附氨的脱附峰。比较发现,0.50 CeO_2 –0.50 SiO_2 –700复合载体的弱酸中心脱附峰更小,且强酸中心的脱附峰消失,

说明形成复合载体后其酸性减弱,这可能由Ce的碱性所引起的。载体负载10%Ni后,催化剂10%Ni/ SiO_2 –700的脱附曲线与其载体的基本保持一致,同样也存在弱酸中心和强酸中心的脱附峰,但峰温略微向高温方向偏移;10%Ni/0.50 CeO_2 –0.50 SiO_2 –700的脱附曲线的峰形与其载体相似,但是弱酸中心脱附峰明显减小。在POM反应中,积炭优先在催化剂表面强酸位置产生和积淀,且强酸中心的强度和数量越大,积炭量也相应增加^[2]。对比两个催化剂的 NH_3 -TPD曲线可以看出,10%Ni/0.50 CeO_2 –0.50 SiO_2 –700的酸性比10%Ni/ SiO_2 –700更弱且几乎没有强酸中心。因此,10%Ni/0.50 CeO_2 –0.50 SiO_2 –700在POM反应过程中可能产生更少的表面积炭。

3.1.7. TG

将反应后的典型催化剂进行了热重测试,其热重曲线如图6所示。10%Ni/ SiO_2 –700在低于130 °C,130–350 °C和高于600 °C的失重分别来自催化剂表面吸附水的脱除、表面无定形炭的脱除和石墨化炭的燃烧^[43,44],而350–570 °C的增重则由反应后催化剂中活性中心 Ni^0 被氧化所致。10%Ni/0.50 CeO_2 –0.50 SiO_2 –700和20%Ni/0.50 CeO_2 –0.50 SiO_2 –700在低于130 °C时的失重较小,说明其表面吸附的水和无定形炭较少。另外,两者测试过程中出现更明显的增重,说明这两个催化剂反应后仍具有更多的活性中心 Ni^0 。10%Ni/0.50 CeO_2 –0.50 SiO_2 –700在高于450 °C没有明显的失重,即表面积炭量很小,然而20%Ni/0.50 CeO_2 –0.50 SiO_2 –700在高于440 °C时出现了大约7.1%的失重,说明该催化剂表面生成了大量积炭。据文献[45–47]报道,催化剂的平均积炭速率与Ni颗粒粒径和分散性紧密相关,Ni颗粒粒径越小,分散性越好,其表面的积炭速率也越低。此外,图6还显示,增大Ni的负载量可产生更多的积炭,因为随着Ni负载量的增加,Ni晶粒粒径变大,而大颗粒的Ni更易成为积炭反应的活性中心。

3.2. 催化剂的催化性能

3.2.1. 负载Ni质量分数的影响

表3列出的是载体0.50 CeO_2 –0.50 SiO_2 –700及其负载不同质量分数的Ni后催化剂的 CH_4 转化率和目的产物CO和 H_2 的选择性。由该表可知,载体0.50 CeO_2 –0.50 SiO_2 –700对 CH_4 转化也具有一定的活性,其 CH_4 转化率为23.7%,但CO和 H_2 的选择性仅分别为8.6%和4.5%,说明在载体表面主要发生的是 CH_4 燃烧反应。负载5%的活性Ni后催化剂上 CH_4 转化率(71.6%),CO(79.3%)和 H_2 (89.0%)的选择性明显提高;继续增大Ni质量分数至

10%时, CH_4 转化率(84.3%), CO (87.4%)和 H_2 (93.3%)的选择性达到最高值; 但是进一步加大Ni的质量分数至20%时, CH_4 转化率及 CO 和 H_2 的选择性开始下降. CH_4 转化率和目的产物选择性的变化表明, 较低的Ni含量虽然使Ni的分散性能提高, 但由于总体活性中心 Ni^0 的数量较少, 难以提供足够的POM所需的活性中心, 因此甲烷转化率较低; 但过高的Ni含量容易造成Ni晶粒变大(表2)和分散性降低, 生成更多的表面积炭(图6), 同样不利于催化剂整体性能的提高.

3.2.2. 载体中Ce/Si摩尔比的影响

不同的载体负载10%Ni后催化剂在POM反应中的催化性能列于表4. 可以看出, 单一载体负载10%Ni后的催化剂10%Ni/ SiO_2 -700和10%Ni/ CeO_2 -700的催化活性均较低; 而复合氧化物载体负载10%Ni后催化剂的 CH_4 转化率和 CO , H_2 选择性大幅度提高, 其中, 10%Ni/0.50 CeO_2 -0.50 SiO_2 -700表现出最高的 CH_4 转化率和 CO , H_2 选择性. 前面的比表面积、 H_2 -TPR和 NH_3 -TPD表征结果表明, 10%Ni/0.50 CeO_2 -0.50 SiO_2 -700具有大比表面积和弱酸性, 同时该催化剂中的NiO较容易被还原成活性中心 Ni^0 , 这是10%Ni/0.50 CeO_2 -0.50 SiO_2 -700催化性能最高的主要原因.

3.2.3. 焙烧温度的影响

经不同温度焙烧制备的催化剂10%Ni/0.50 CeO_2 -0.50 SiO_2 对POM反应的催化性能见表5. 由表可知, 焙烧温度对催化剂的催化性能具有显著影响. 其中, 经过700 °C焙烧后的催化剂10%Ni/0.50 CeO_2 -0.50 SiO_2 -700表现出最高的 CH_4 转化率和目的产物选择性. 对比这四个

催化剂的比表面积(表1)、晶粒粒径(表2)和还原性能(图4(c))可以看出, 过高的焙烧温度导致催化剂比表面积下降和 CeO_2 , NiO 粒子变大, 同时使NiO的还原更加困难, 不能产生充足的催化反应活性中心 Ni^0 , 这是高温焙烧造成催化性能下降的主要原因.

3.2.4. 催化剂的稳定性

将典型催化剂10%Ni/0.50 CeO_2 -0.50 SiO_2 -700和10%Ni/ SiO_2 -700的反应时间延长至900 min, 考察了 CH_4 转化率和 CO , H_2 选择性随反应时间的变化, 结果见图7. 催化剂10%Ni/ SiO_2 -700在前390 min内催化性能的变化较小, 但随后催化性能迅速下降, 当反应时间为660 min时, 该催化剂 CH_4 转化率及 CO 和 H_2 的选择性分别降低至58.2%, 67.0%和75.3%, 且 H_2 / CO 摩尔比由2.0降至1.54, 说明10%Ni/ SiO_2 -700上的POM反应稳定性较差. 相反, 催化剂10%Ni/0.50 CeO_2 -0.50 SiO_2 -700在900 min的反应时间内, 其 CH_4 转化率基本维持在84%左右, H_2 / CO 摩尔比也一直保持为2.04, 表现出较好的稳定性.

4. 结论

采用溶胶-凝胶法合成了大比表面积的 CeO_2 - SiO_2 复合氧化物载体. 该系列载体负载Ni后, 对甲烷部分氧化反应具有较高的催化活性. 在Ce/Si摩尔比1:1, Ni的负载质量分数10%, 700 °C焙烧时所得的催化剂Ni/ CeO_2 - SiO_2 具有最高的 CH_4 转化率和目的产物选择性, 同时该催化剂的稳定性较好. 所得催化剂具有大的比表面积和较弱的酸性, NiO分散性较好且易被还原, 催化剂不容易发生积炭.