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Three-Dimensional Mesoporous Ni-CeO₂ Catalysts with Ni Embedded in the Pore Walls for CO₂ Methanation

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Abstract: Mesoporous Ni-based catalysts with Ni confined in nanochannels are widely used in CO₂ methanation. However, when Ni loadings are high, the nanochannels are easily blocked by nickel particles, which reduces the catalytic performance. In this work, three-dimensional mesoporous Ni-CeO₂-CSC catalysts with high Ni loadings (20–80 wt %) were prepared using a colloidal solution combustion method, and characterized by nitrogen adsorption–desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM) and H₂ temperature programmed reduction (H₂-TPR). Among the catalysts with different Ni loadings, the 50% Ni-CeO₂-CSC with 50 wt % Ni loading exhibited the best catalytic performance in CO₂ methanation. Furthermore, the 50% Ni-CeO₂-CSC catalyst was stable for 50 h at 300° and 350 °C in CO₂ methanation. The characterization results illustrate that the 50% Ni-CeO₂-CSC catalyst has Ni particles smaller than 5 nm embedded in the pore walls, and the Ni particles interact with CeO₂. On the contrary, the 50% Ni-CeO₂-CP catalyst, prepared using the traditional coprecipitation method, is less active and selective for CO₂ methanation due to the larger size of the Ni and CeO₂ particles. The special three-dimensional mesoporous embedded structure in the 50% Ni-CeO₂-CSC can provide more metal–oxide interface and stabilize small Ni particles in pore walls, which makes the catalyst more active and stable in CO₂ methanation.

Keywords: CO₂ methanation; Ni-CeO₂; metal–oxide interface; embedded catalyst; colloidal solution combustion

1. Introduction

In recent years, CO_2 conversion has attracted much attention [1,2]. CO_2 methanation can convert CO_2 and renewable H_2 to storable and transportable CH_4 , which is of great significance for greenhouse gas control and the chemical storage of renewable H_2 [3,4]. Although the exothermic methanation is thermodynamically favorable at low temperatures, there are significant kinetic limitations for converting CO_2 into methane due to the stability of CO_2 .

A large number of studies have shown that the Rh [5], Ru [6,7], Pd [8] and Ni [9] catalysts are active in CO_2 methanation. Precious metal catalysts have a higher activity than Ni catalysts, but the high cost of precious metal catalysts limits their large-scale application in industry. Ni catalysts



have a relatively low cost and have attracted extensive attention in the field of CO₂ methanation. To improve the methanation activity of Ni catalysts, many methods have been proposed to prepare highly dispersed Ni catalysts [10–14]. The general strategy to improve the dispersion of Ni is to load the Ni onto a support with a high specific surface area [15–17]. However, small particles of Ni with high dispersion tend to aggregate and grow into large particles in a long-time reaction, leading to catalysts deactivation [11,18]. Embedded structures can improve the thermal stability of Ni-based catalysts. Embedded Ni catalysts, such as Ni@HZSM-5 [19], Ni@MOF [20,21] and Ni@C [22], have been used for carbon dioxide methanation and shown good stability.

Mesoporous materials are widely used to prepare embedded catalysts [23–26]. Metal particles can be embedded in the pore channels [25] or pore walls [27]. Metal particles embedded in the pore channels are a conventional structure of embedded catalysts, but the high metal load can lead to channel blockage, which is not conducive to mass transfer [26]. On the contrary, the metal particles embedded in the pore wall can not only improve the thermal stability of the catalyst, but also avoid the blockage of the channel, which is conducive to mass transfer. Moreover, the metal particles embedded in the pore wall are in close contact with the support and have abundant metal–support interfaces, which is conducive to improving the methanation activity [28].

As CeO_2 can adsorb and activate CO_2 , Ni-CeO₂ catalysts prepared by different methods have been applied to CO_2 methanation and exhibit excellent catalytic performance [28–32]. Small nickel particles and abundant Ni–CeO₂ interfaces are important for improving the carbon dioxide activity of the catalyst [28,32]. Recently, a facial colloidal solution combustion (CSC) method was reported for the synthesis of three-dimensional mesoporous materials [33–35]. In this paper, in order to increase the Ni–CeO₂ interface and improve the thermal stability of a highly dispersed Ni-CeO₂ catalyst, three-dimensional mesoporous Ni-CeO₂-CSC catalysts with Ni embedded in the pore walls were prepared using a colloidal solution combustion method. The catalysts had abundant metal–support interfaces and small nickel particles, showing good catalytic performance in CO_2 methanation.

2. Results and Discussion

2.1. Characterization of Fresh and Reduced Catalysts

The N₂ adsorption–desorption isotherms and pore size distributions of the fresh Ni-CeO₂-CSC catalysts are shown in Figure 1. As shown in Figure 1a, all the catalysts display type IV isotherms with a hysteresis loop, indicating the presence of a mesoporous structure. When the relative pressure (P/P₀) approaches 1, the adsorption branch of the isotherm rises, which is due to the adsorption of nitrogen in the macropore. This indicates that a certain amount of macropore exists in these catalysts. In Figure 1b, all the catalysts exhibit a probable pore diameter centered at 20–25 nm. The probable pore diameter is similar to that of the colloidal SiO₂ (about 22 nm) used to prepare the catalyst, indicating that the mesoporous structure is mainly produced by etching the SiO₂ particles.



Figure 1. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of the fresh Ni-CeO₂-CSC catalysts.

Table 1 lists the Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) of the fresh Ni-CeO₂ catalysts prepared by the CSC and coprecipitation (CP) methods. For the mesoporous Ni-CeO₂-CSC catalysts, the S_{BET} of the catalyst decreases with the increase in nickel content. The S_{BET} of the 50% Ni-CeO₂-CSC is 121.5 m²/g, which is more than three times that of the 50% Ni-CeO₂-CP catalyst prepared by the coprecipitation method. The results show that the mesoporous Ni-CeO₂-CSC catalysts have larger S_{BETs} than the 50% Ni-CeO₂-CP catalyst.

Samples	S_{BET} (m ² /g)	CeO ₂ (nm) ^a	NiO (nm) ^a
20% Ni-CeO ₂ -CSC	134.0	3.9	/ b
50% Ni-CeO ₂ -CSC	121.5	3.1	/ b
80% Ni-CeO ₂ -CSC	94.9	/ ^b	3.7
50% Ni-CeO ₂ -CP	38.7	8.2	8.9

Table 1. Physicochemical properties of the fresh Ni-CeO₂.

^a Crystal size was calculated using the Scherrer equation according to the XRD result. ^b The diffraction peak is too weak.

The X-ray diffraction patterns of the fresh Ni-CeO₂ are shown in Figure 2a. The fresh 20% Ni-CeO₂-CSC exhibits the characteristic diffraction peaks of CeO₂, and no peaks of NiO are observed. The broad diffraction peaks and low intensity could indicate small crystallites or solids with low crystallinity, such as amorphous phase. From the following HRTEM image, we found small crystallites, and no amorphous phase was observed. Therefore, the broad diffraction peaks and low intensity are due to the small crystallites. The XRD result indicates that NiO is highly dispersed in the 20% Ni-CeO₂-CSC catalyst. When the Ni loading increased to 50%, the weak and broad diffraction peaks of CeO₂ and NiO were observed, indicating that NiO and CeO₂ particle sizes are small in the catalyst. The 80% Ni-CeO₂-CSC catalyst exhibits an obvious NiO diffraction peak, and no peaks of CeO₂ are observed in the catalyst. The 50% Ni-CeO₂-CP catalyst shows sharp diffraction peaks of NiO and CeO₂, indicating that the 50% Ni-CeO₂-CP catalyst has large NiO and CeO₂ crystal particles.

Table 1 presents the crystal sizes of NiO and CeO₂ calculated by the Scherrer equation. The sizes in the Ni-CeO₂-CSC catalyst are less than 5 nm. When the Ni loading is less than or equal to 50%, the diffraction peak of the NiO in the Ni-CeO₂-CSC is too weak to calculate the crystal size. Even when the nickel content reaches 80%, the average NiO size is only 3.7 nm. In contrast, the NiO and CeO₂ size in the 50% Ni-CeO₂-CP catalyst are 8.2 and 8.9 nm, respectively. The results indicate that the colloidal solution combustion is an effective method for preparing highly dispersed Ni-CeO₂ catalysts with NiO and CeO₂ particles smaller than 5 nm.



Figure 2. X-ray diffraction (XRD) patterns of Ni-CeO₂: (a) fresh catalysts, (b) reduced catalysts.

The XRD patterns of the reduced 50% Ni-CeO₂-CSC and 50% Ni-CeO₂-CP are shown in Figure 2b. The reduced 50% Ni-CeO₂-CP presents sharp Ni peaks, indicating that the crystal size of the Ni in it was large. Table 2 shows that the Ni size of the reduced 50% Ni-CeO₂-CP was 24.8 nm, which is 2.8 times the NiO size of the fresh catalyst. This indicates that the Ni particles were unstable and

sintered in the process of catalyst reduction, thus forming large Ni particles. For the reduced 50% Ni-CeO₂-CSC catalyst, the crystal size of the Ni cannot be calculated using the Scherrer equation because the diffraction peaks of the Ni are too weak, suggesting that the particle size of the Ni is small. The results indicate that the 50% Ni-CeO₂-CSC catalyst is more stable than the 50% Ni-CeO₂-CSC catalyst in the reduction process.

Catalysts	CeO ₂ (nm) ^a	Ni (nm) ^a	
Reduced 50% Ni-CeO ₂ -CSC	3.2	/ b	
Reduced 50% Ni-CeO ₂ -CP	11.8	24.8	

Table 2. Cristal size of the reduced 50% Ni-CeO₂ catalysts.

^a Crystal size was calculated using the Scherrer equation according to the XRD result. ^b The diffraction peak is too weak.

The transmission electron microscopy (TEM) images of the colloidal SiO_2 and the 50% Ni-CeO₂-CSC are shown in Figure 3. As shown in Figure 3a, the spherical colloidal SiO_2 is about 22 nm in diameter.

Figure 3b,c present the TEM images of the fresh 50% Ni-CeO₂-CSC. For the fresh 50% Ni-CeO₂-CSC catalyst, an ordered mesopore of about 20 nm in diameter is observed in Figure 3b. During the catalyst preparation, the mesoporous structure was formed after etching the SiO₂. The diameter of the mesopore is basically the same as that of the colloidal SiO₂. Figure 3c shows that the pore wall thickness is about 5 nm, and the pore wall is composed of nanoparticles smaller than 5 nm. This is consistent with the XRD results. Figure 3d reveals that the pore wall contains small NiO and CeO₂ particles. As shown in Figure 3d, the particles with a d-spacing of 0.312 and 0.209 nm are associated with CeO₂(111) and NiO(200) planes, respectively. These results indicate that the NiO in the mesoporous 50% Ni-CeO₂-CSC catalyst is embedded in the pore wall rather than filled in the pore channel.

Figure 3e,f present the TEM images of the reduced 50% Ni-CeO₂-CSC catalyst. Figure 3e shows the mesoporous structure of the reduced catalyst, indicating that the mesoporous structure is stable during the reduction process. As shown in Figure 3f, small particles of Ni embedded in the pore wall are in close contact with CeO₂, which can provide more Ni–CeO₂ interface and is conducive to improving the CO₂ methanation activity [32].

Figure 4 shows the H₂ programmed temperature reduction (H₂-TPR) profiles of the NiO and Ni-CeO₂ catalysts. NiO was prepared by calcining nickel nitrate hexahydrate at 450 °C for 4 h. For pure NiO, only one hydrogen consumption peak located at 355 °C was observed. Combined with the XRD characterization results, the reduction peak at 403 °C of the 50% Ni-CeO₂-CP can be assigned to the reduction in the large NiO particles that interacted weakly with CeO₂ [32]. However, the Ni-CeO₂-CSC catalysts exhibit a broad peak between 300 and 600 °C, which is attributed to the reduction in the surface CeO₂ and the small NiO particles that interacted with CeO₂ [36].

Because of the low nickel content, the reduction peak of the 20% Ni-CeO₂-CSC catalyst is small. In addition, the reduction temperature of the catalyst is higher, which may be because the nickel particles in the catalyst were smaller and the interaction with CeO₂ was stronger. Shan et al. reported that the highly dispersed NiO strongly interacted with CeO₂ and had a higher reduction temperature [36].

Compared with the 50% Ni-CeO₂-CP, the Ni-CeO₂-CSC catalysts exhibit an obviously higher reduction temperature, indicating that the Ni–CeO₂ interaction in the Ni-CeO₂-CSC is stronger. The strong interaction in the Ni-CeO₂-CSC catalysts could be due to the small NiO particles embedded in the pore wall and in contact with CeO₂.

In previous reports, it has been shown that Ni^{2+} can be incorporated into the CeO₂ lattice and form a Ce_{1-x}Ni_xO₂ solid solution, which leads to the formation of an oxygen vacancy [36]. The oxygen adsorbed on the oxygen vacancy in the solid solution can be reduced below 300 °C [32,36,37]. However, in the TPR patterns shown in Figure 4, there is no obvious reduction peak below 300 °C, which indicates that it is difficult to generate a solid solution in our Ni-CeO₂ catalysts.



Figure 3. Transmission electron microscopy images of (**a**) the colloidal SiO₂, (**b**–**d**) the fresh 50% Ni-CeO₂-CSC and (**e**,**f**) the reduced 50% Ni-CeO₂-CSC.



Figure 4. H₂ programmed temperature reduction profiles of the NiO, the 50% Ni-CeO₂-CP and the Ni-CeO₂-CSC.

2.2. Catalytic Performance

Figure 5 shows the catalytic performance of the Ni-CeO₂-CSC catalysts. At low temperatures, the CO₂ conversion and CH₄ selectivity of the 20% Ni-CeO₂-CSC catalyst were low. This could be due to most of the Ni surface being covered by CeO₂ in the 20% Ni-CeO₂-CSC catalyst. When the nickel content increased from 20% to 50%, the CO₂ conversion and CH₄ selectivity of the Ni-CeO₂-CSC increased significantly. When the nickel content further increased to 80%, the conversion and selectivity of the catalyst decreased. The Ni-CSC catalyst with 100% Ni content showed low CO₂ conversion and CH₄ selectivity, especially at low temperatures. The 50% Ni-CeO₂-CSC catalyst had the best catalytic performance among the Ni-CeO₂-CSC catalysts. At temperatures higher than 400 °C, the conversion and selectivity of the catalyst decreased slightly, due to the limitation of the thermodynamic equilibrium of CO₂ methanation and the formation of CO in the reverse water–gas shift reaction [38,39].



Figure 5. (a) CO₂ conversion and (b) CH₄ selectivity of the Ni-CeO₂-CSC catalysts in CO₂ methanation.

The comparison of the catalytic activities of the 50% Ni-CeO₂-CP and 50% Ni-CeO₂-CSC catalysts is shown in Figure 6. Compared with the 50% Ni-CeO₂-CP, 50% Ni-CeO₂-CSC had a higher CO₂ conversion and CH₄ selectivity in the temperature range of 250 to 450 °C. At 250 °C, the CO₂ conversions of the 50% Ni-CeO₂-CSC and the 50% Ni-CeO₂-CP were 33% and 4%, respectively. The former is about eight times the latter, indicating that the 50% Ni-CeO₂-CSC catalyst has better low-temperature activity.



Figure 6. (a) CO₂ conversion and (b) CH₄ selectivity over the 50% Ni-CeO₂-CSC and 50% Ni-CeO₂-CP catalysts in CO₂ methanation.

Small Ni particles can absorb and dissociate H_2 , and CeO_2 can absorb and activate CO_2 . The Ni–CeO₂ interface facilitates further reactions between the two adsorbed species to form methane [32]. The three-dimensional mesoporous catalyst prepared by the CSC method can keep the particle size of the Ni and CeO₂ less than 5 nm in the catalyst with a high Ni content, and at the same time the Ni embedded in the pore wall provides an abundant Ni–CeO₂ interface, meaning that the 50% Ni-CeO₂-CSC catalyst has excellent activity and selectivity for CO₂ methanation. On the contrary, due to the larger size of the Ni and CeO₂ particles, the 50% Ni-CeO₂-CP catalyst is less active and selective for CO₂ methanation. The excellent catalytic performance of the 50% Ni-CeO₂-CSC catalyst is related to the large number of small Ni particles and abundant Ni–CeO₂ interfaces in the three-dimensional mesoporous structure.

A comparison of catalyst activity with other Ni-based catalysts found in the literature is listed in Table 3. Compared with the Ni-based catalysts reported in the literature, the 50% Ni-CeO₂-CSC catalyst exhibits an excellent CO₂ conversion rate in low-temperature CO₂ methanation.

Catalyst	WHSV (mL.g _{cat} ⁻¹ .h ⁻¹)	Reaction Temperature (°C)	X _{CO2} (%)	CO ₂ Conversion Rate (×10 ⁻⁵ mol _{CO2} /g _{cat} /s)	Ref.
50% Ni-CeO2-CSC	120,000	250	33	4.91	This Work
		300	70	10.42	This Work
20% Ni-Ce/RGO	36,000	250	20	1.79	[40]
		300	80	7.14	[40]
25% Ni/Al ₂ O ₃	9000	250	7	0.17	[41]
		300	50	1.24	[41]
15% Ni/ZrO ₂	48,000	250	15	1.61	[42]
		300	60	6.43	[42]
10% Ni/CeO2-ZrO2	20,000	250	46	0.91	[43]
		300	55	1.09	[43]
6% Ni/ZrO ₂	15,000	250	84	2.50	[11]
6% Ni-MgO/ZrO ₂	15,000	250	90	2.68	[11]

Table 3. CO_2 conversion rate and CH_4 selectivity of the 50% Ni-CeO₂-CSC catalyst and recently reported low-temperature CO_2 methanation catalysts in the literature at 0.1 MPa.

The stability test of the 50% Ni-CeO₂-CSC catalyst was conducted at 300 and 350 °C, and the results are shown in Figure 7. The catalytic performance was stable for 50 h, and the CO₂ conversions at 300 and 350 °C remained around 68% and 82%, respectively. The CH₄ selectivity was higher than 99%. The results show that the 50% Ni-CeO₂-CSC catalyst has good stability. The embedded structure of the 50% Ni-CeO₂-CSC catalyst can prevent the sintering or aggregation of the highly dispersed Ni during the methanation reaction, thus improving the stability of the catalyst. The excellent stability of the catalyst could be due to the pore wall embedded structure of the catalyst.



Figure 7. Stability of the 50%Ni-CeO₂-CSC in CO₂ methanation: (**a**) stability at 300 °C, (**b**) stability at 350 °C.

2.3. Characterization of the Used Catalyst

The 50% Ni-CeO₂-CSC catalyst after the stability test at 300 °C was characterized by TEM and XRD. The three-dimensional mesoporous structure with the spherical pores of the catalyst is clearly visible in Figure 8a. As can be seen from the high-resolution TEM image (Figure 8b), Ni and CeO₂ particles less than 5 nm constituted the pore wall, and the metal Ni particles were embedded in the pore wall and in close contact with CeO₂. The TEM results show that the mesoporous structure and particle size did not change significantly, which further confirms the stability of the three-dimensional mesoporous structure. The XRD pattern of the used 50% Ni-CeO₂-CSC catalyst is shown in Figure 8c: the Ni and CeO₂ peaks are broad and very weak, indicating that the Ni and CeO₂ particles were small and stable in the 50% Ni-CeO₂-CSC catalyst during the methanation reaction. This result further confirms that the three-dimensional embedded structure can prevent the small nickel particles from sintering or aggregating, thus making the catalyst stable in the CO₂ methanation reaction.



Figure 8. Cont.



Figure 8. (**a**,**b**) Transmission electron microscopy images and (**c**) X-ray diffraction pattern of the used 50% Ni-CeO₂-CSC catalyst.

3. Experimental

3.1. Synthesis of Catalysts

A series of Ni-CeO₂-CSC catalysts were prepared with the CSC method, as shown in Scheme 1. In the solution combustion reaction, metal nitrates were used as the oxidizers, and glycine as the fuel. When preparing 1 g Ni-CeO₂-CSC catalyst, 0.6 g glycine and an amount of Ce(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O were dissolved in 6.3 mL deionized water, and the solution was ultrasonic for 20 min. A 1.26 mL colloidal SiO₂ LUDOX TMA (Sigma-Aldrich, Saint Louis, USA; 34 wt %, diameter of 22 nm) was added to the solution and continued to be ultrasonic for 20 min. Then, the solution was heated over a hot plate at 210 °C. After a few minutes of evaporation, a combustion reaction occurred, releasing large amounts of gas and forming a solid powder. The powder was calcined at 450 °C in air for 4 h, and was then treated with a 2 M NaOH solution at 80 °C for 4 h. After washing with ethanol and water 3 times and drying for 12 h at 80 °C, the catalyst was obtained and named as xNi-CeO₂-CSC, where x represents the weight percentage of the nickel. Three catalysts with nickel content of 20%, 50% and 80% were prepared. A pure NiO catalyst, denoted as Ni-CSC, was prepared with the same method.



Scheme 1. Synthesis route of the Ni-CeO₂-CSC catalysts.

The 50% Ni-CeO₂-CP catalyst was prepared with a coprecipitation method. An NaOH solution was fed dropwise into an aqueous mixture of Ce(NO₃)₂ and Ni(NO₃)₂ until the pH of the mixture was 10. The mixture was aged at room temperature for 24 h. The obtained precipitate was filtered and washed with water, and then dried at 80 °C for 12 h. Finally, the 50% Ni-CeO₂-CP was obtained by calcining the precipitate at 450 °C for 4 h.

3.2. Characterization of Catalysts

The N₂ isotherms of the calcined catalyst were performed at -196 °C on a gas sorption instrument (Quantachrome, Autosorb-iQ). Before the test, the sample was degassed at 300 °C for 8 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The pore size

distribution was calculated from the quenched solid density functional theory (QSDFT) method using the calculation model of N₂ adsorbed on carbon (slit/cylindrical/spherical pores, adsorption branch).

The X-ray diffractometer (XRD) experiments were conducted on a powder X-ray diffractometer (DX-2700, Haoyuan Corporation, Dandong, China) with a Cu K α anode. The transmission electron microscopy (TEM) experiments were performed on a Tecnai G2 F20 microscope (FEI Company, Hillsboro, OR, USA) at 200 kV. The H₂ temperature programmed reduction was performed on a TP-5080 apparatus (Xianquan, Tianjin, China) using 5% H₂/Ar (30 mL min⁻¹).

3.3. Catalytic Performance

The catalytic test was performed in a fixed-bed quartz reactor (8 mm i.d.) at 0.1 MPa. Before the reaction, a 50 mg sample mixed with 200 mg inert silica was reduced at 450 °C for 40 min with 20% H₂/Ar (50 mL min⁻¹). The reaction feed was a mixed gas (CO₂/ H₂/ Ar = 1/4/5, 100 mL min⁻¹). The weight hourly space velocity (WHSV) was 120,000 mL g_{cat}⁻¹ h⁻¹. The Ar was used as the internal standard gas for calculating the CO₂ conversion. After the removal of the water by a cold trap, at each rection temperature, the exit gases were sampled and analyzed four times by gas chromatography (Techcomp GC-7900) with an error of less than 2%.

4. Conclusions

In this study, three-dimensional mesoporous Ni-CeO₂-CSC catalysts with different Ni contents, prepared using the CSC method, were used for CO₂ methanation. The Ni-CeO₂-CSC catalysts had high S_{BETs} . In the Ni-CeO₂-CSC catalysts, small Ni particles were embedded in the pore walls which interacted with CeO₂. This special embedded structure enables the catalyst to have more Ni-CeO₂ interface, while maintaining a particle size of less than 5 nm, even when the nickel content reaches 50%. Among the Ni-CeO₂-CSC catalysts with different nickel contents, the 50% Ni-CeO₂-CSC catalyst showed the best catalytic performance. Compared to the 50% Ni-CeO₂-CP catalyst, the 50% Ni-CeO₂-CSC catalyst had a higher CO₂ conversion and CH₄ selectivity due to its smaller Ni particle size and more Ni-CeO₂ interface. In addition, the 50% Ni-CeO₂-CSC catalyst exhibited excellent stability due to the confinement effect of the embedded structure.

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