

The Active Phase of Nickel/Ordered $\text{Ce}_2\text{Zr}_2\text{O}_x$ Catalysts with a Discontinuity ($x = 7-8$) in Methane Steam Reforming**

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In recent years, there has been a surge in interest in syngas (H_2/CO) and H_2 production technologies, which utilize a wide variety of hydrocarbon feed stocks, such as gasoline, diesel, LPG, natural gas, methanol, and bio-ethanol. Among fossil fuels, natural gas (≥ 90 vol % CH_4) is the ideal fuel, owing to its ready availability, high energy density, and wide distribution network; CH_4 activation and reforming provide attractive ways to produce syngas, which can be transformed to useful larger hydrocarbons. Catalysts based on both noble metals and other metals have been extensively studied for CH_4 steam reforming.^[1,2] Noble-metal (Rh, Ru, Ir, Pd, and Pt) catalysts are active and stable; however, because of the limited supply and high cost of noble metals, much attention has been paid to the development of non-noble metal catalysts, among which nickel-based catalysts have attracted particular attention because of their similar mechanistic features to noble-metal catalysts.^[3]

The strong C–H bonds of CH_4 (439 kJ mol^{-1})^[4] and endothermic heat of reforming reactions necessitate high temperatures for practical CH_4 conversion, and thus stable

catalysts that resist sintering under extreme operating conditions. In CH_4 steam reforming, coke formation that deactivates the catalyst is thermodynamically favored at a $\text{H}_2\text{O}/\text{CH}_4$ ratio less than 1.4. Thus, industrial CH_4 steam reforming is usually carried out at a $\text{H}_2\text{O}/\text{CH}_4$ ratio of 1.4 or greater.^[5] Although catalytic CH_4 steam reforming at low $\text{H}_2\text{O}/\text{CH}_4$ ratios have many advantages from operational and energy-consuming viewpoints, conventional nickel-based catalysts suffer from severe carbon deposition under such conditions. Supports and additives (for example, CeO_2 , ZrO_2 , $\text{CeO}_2\text{-ZrO}_2$, and La_2O_3) have been used to confer catalysts with kinetic resistance to carbon deposition and Ni sintering because they enhance redox activity and thermal stability, thereby promoting steam reforming.^[6] The efficient CH_4 upgrading has long been a challenge in fundamental research.^[7]

Herein, we report the unique properties and active phase of a new Ni/ordered $\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x = 7-8$) catalyst with a regular arrangement of Ce and Zr ions in CH_4 steam reforming to produce H_2 and CO at $\text{H}_2\text{O}/\text{CH}_4 = 1$. The catalytic performance of Ni/ $\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x = 7-8$) strongly depends on the phase and oxygen content of $\text{Ce}_2\text{Zr}_2\text{O}_x$, and it shows a unique discontinuity in catalytic activity at $x = 7.5$.

The 2 wt % Ni/pyrochlore- $\text{Ce}_2\text{Zr}_2\text{O}_7$ catalyst showed a remarkable performance in CH_4 steam reforming at 923 K at $\text{H}_2\text{O}/\text{CH}_4 = 1$ (Table 1). Ni/ CeO_2 , Ni/ ZrO_2 , and Ni/ $\text{CeO}_2\text{-ZrO}_2$ reduced by H_2 were much less active and selective than Ni/ $\text{Ce}_2\text{Zr}_2\text{O}_7$, and significant deactivation was observed probably owing to Ni sintering and carbon deposition. On the other hand, the Ni/pyrochlore- $\text{Ce}_2\text{Zr}_2\text{O}_7$ catalyst was stable, resulting in a remarkably high catalytic performance (for a typical 50 h performance, see the Supporting Information, Figure S4). At 973 K, the Ni/ $\text{Ce}_2\text{Zr}_2\text{O}_7$ catalyst exhibited high CO selectivity of 96–98% and high H_2 selectivity of 96–99% at CH_4 and H_2O conversions of 92–94% and > 96%, respectively.

Platinum, a typical noble metal active for CH_4 steam reforming, was supported on CeO_2 , ZrO_2 , or $\text{Ce}_2\text{Zr}_2\text{O}_7$, but the performance was not significantly enhanced by these types of supports, and the CH_4 conversion on these Pt-based catalysts ranged between 29% and 39%. For Pt-based catalysts, CH_4 steam reforming may be controlled by Pt rather than by the nature of the support.^[1,8]

In the presence of 0.8% O_2 in the reaction feed, the Ni/ $\text{Ce}_2\text{Zr}_2\text{O}_7$ catalyst also exhibited high H_2 selectivity (97–99%) at a CH_4 conversion of 93–94% for at least 10 h. No significant deactivation was observed. These are great advan-

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Table 1: Catalytic performance of CeO₂, ZrO₂, Ce₂Zr₂O₈, and supported Ni catalysts (2 wt % Ni) in CH₄ steam reforming.^[a]

Catalyst	CH ₄ conv. [%]	H ₂ O conv. [%]	Selec. C [%] (CO/CO ₂)	Selec. H [%] (H ₂)
CeO ₂	0	0	–/–	–
ZrO ₂	0	0	–/–	–
Ce ₂ Zr ₂ O ₈	0	0	–/–	–
Ce ₂ Zr ₂ O ₇	0	0	–/–	–
NiO/CeO ₂ ^[b]	0	0	–/–	–
Ni/CeO ₂ ^[c]	26.0	33.5	71.2/28.8	93.6
NiO/ZrO ₂ ^[b]	0	0	–/–	–
Ni/ZrO ₂ ^[c]	30.2	40.2	67.0/33.0	92.9
NiO/CeO ₂ - ZrO ₂ ^[b,d]	0	0	–/–	–
Ni/CeO ₂ -ZrO ₂ ^[c,d]	42.1	44.9	93.3/6.7	95.5
NiO/Ce ₂ Zr ₂ O ₈ ^[b]	0	0	–/–	–
Ni/Ce ₂ Zr ₂ O ₇ ^[c,e]	74.0	80.9	90.7/9.3	91.0
Ni/Ce ₂ Zr ₂ O ₇ ^[c]	81.8	91.5	88.1/11.9	94.0
Ni/Ce ₂ Zr ₂ O ₇ ^[c,f]	94.2	96.2	97.9/2.1	95.9

[a] Catalyst 0.1 g, total flow rate = 24.5 mL min^{−1}, CH₄/H₂O/He = 2.8/2.8/94.4 (molar ratio), 923 K. Analyzed at 1 h on time-on-stream. H₂O conv. was calculated as (CO + 2 × CO₂)/supplied H₂O × 100%. CO selectivity = CO/(CO + CO₂) × 100%. CO₂ selectivity = CO₂/(CO + CO₂) × 100%. H₂ selectivity = (H₂)/(2 × consumed CH₄ + consumed H₂O) × 100%. [b] Calcined at 773 K. [c] Reduced with H₂ at 773 K. [d] CeO₂ and ZrO₂ were physically mixed and then Ni was supported. [e] 873 K. [f] 973 K.

tages over other Ni catalysts, such as a Ni/co-precipitated CeO₂-ZrO₂ catalyst, whose CH₄ conversion decreased with reaction time (91 → 87 %) and H₂ selectivity was as low as 74–78 % in the presence of 0.8 % O₂ in the reaction feed.

CeO₂-ZrO₂ materials have oxygen storage/release capacity (OSC) and are widely used as promoters of automobile three-way catalysts. The most efficient CeO₂-ZrO₂ material in terms of OSC is a solid solution, which has an atomically ordered arrangement of Ce and Zr assigned to the κ-Ce₂Zr₂O₈ fluorite phase.^[9] The κ-Ce₂Zr₂O₈ phase transforms to the pyrochlore-Ce₂Zr₂O₇ phase by H₂ reduction, and the redox transformation is reversible (Supporting Information, Figure S1). In the Ce₂Zr₂O₇, Ce³⁺ ions are 8-fold coordinated and Zr⁴⁺ ions are 6-fold coordinated.^[10] In the transformation from κ-Ce₂Zr₂O₈ to pyrochlore-Ce₂Zr₂O₇, the number of coordinated oxygen atoms at Zr sites changes without a change in Zr valence, whereas at Ce sites, the valence of Ce changes without a change in the number of coordinated oxygen atoms. These observations were made by analyzing the time-resolved XAFS.^[11] Thus, Ni nanoparticles may be affected by the oxygen content of Ce₂Zr₂O_x (x = 7–8), while the nature of Ce₂Zr₂O_x may also change depending on the oxygen content.

The CH₄ steam reforming activity of Ni/Ce₂Zr₂O_x (x = 7–8) was found to strongly depend on the oxygen content x of the Ce₂Zr₂O_x solid solution, and a discontinuous change was found at x = 7.5. Figure 1 shows the variation in the CH₄ steam reforming performance with oxygen content x, where the samples with x < 7.5 were active under the steady-state conditions, whereas those with x ≥ 7.5 were inactive. The structures and electronic states of the Ni/Ce₂Zr₂O_x catalysts with different oxygen contents were characterized by XRD,

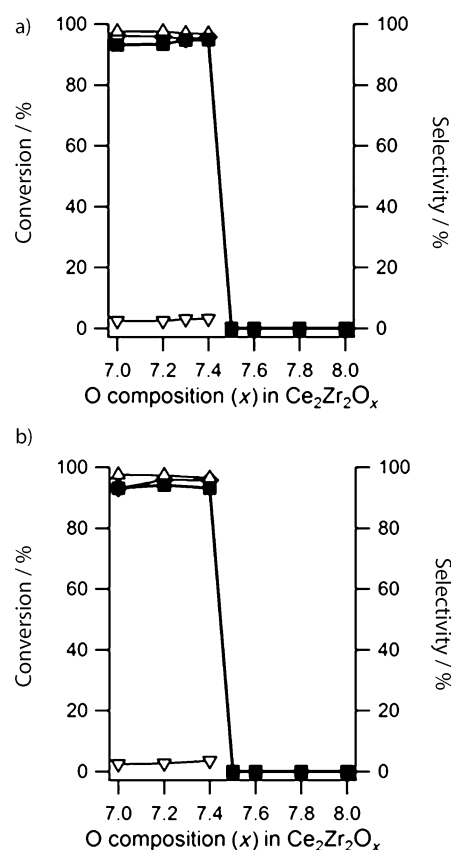


Figure 1. Catalytic performance of Ni/Ce₂Zr₂O_x in CH₄ steam reforming at 973 K. a) Catalysts with different O content x prepared by the oxidation of Ni/pyrochlore-Ce₂Zr₂O₇ with a given amount of O₂ at 773 K, and b) catalysts with different O content x prepared by the reduction of NiO/κ-Ce₂Zr₂O₈ with a given amount of H₂ at 773 K. ■ (with bold line) CH₄ conversion [%], △ CO selectivity [%], ▽ CO₂ selectivity [%], ◇ H₂ selectivity [%].

Ni K-edge XANES and EXAFS, and Ce L_{III}-edge XANES and EXAFS.

TEM images for Ni (1 wt % and 2 wt %)/Ce₂Zr₂O₇ and Ni and Ce EDS profiles for Ni (2 wt %)/Ce₂Zr₂O₇ (Supporting Information, Figure S5) showed that Ni particles on the crystalline Ce₂Zr₂O₇ (roughly 700 nm size in average) with a low surface area of about 1 m² g^{−1} were as large as about 30 nm (average) even in the case of low Ni loadings of 1–2 wt %. It was hard to regulate Ni particle sizes to much smaller particles on the Ce₂Zr₂O_x crystals.

Figure 2a shows the Ce L_{III}-edge XANES spectra of the Ce₂Zr₂O_x phases in Ni/pyrochlore-Ce₂Zr₂O₇, NiO_y/Ce₂Zr₂O_{7.4} prepared by oxidation of NiO/pyrochlore-Ce₂Zr₂O₇, NiO_y/Ce₂Zr₂O_{7.4} prepared by reduction of NiO/κ-Ce₂Zr₂O₈ with a given amount of H₂ at 773 K, NiO_y/Ce₂Zr₂O_{7.4} and NiO_y/Ce₂Zr₂O_{7.6} prepared by oxidation of Ni/pyrochlore-Ce₂Zr₂O₇ with a given amount of O₂ at 773 K, and NiO/κ-Ce₂Zr₂O₈. The active Ni/Ce₂Zr₂O₇ catalyst showed no change in its XANES spectra before or after CH₄ steam reforming at 923 K. The Ce L_{III}-edge XANES data revealed that Ce₂Zr₂O_{7.4} prepared by oxidation of Ni/Ce₂Zr₂O₇ was reduced to Ce₂Zr₂O₇ after CH₄ steam reforming. A similar change was observed for NiO_y/Ce₂Zr₂O_{7.4} prepared by reduction of NiO/κ-Ce₂Zr₂O₈.

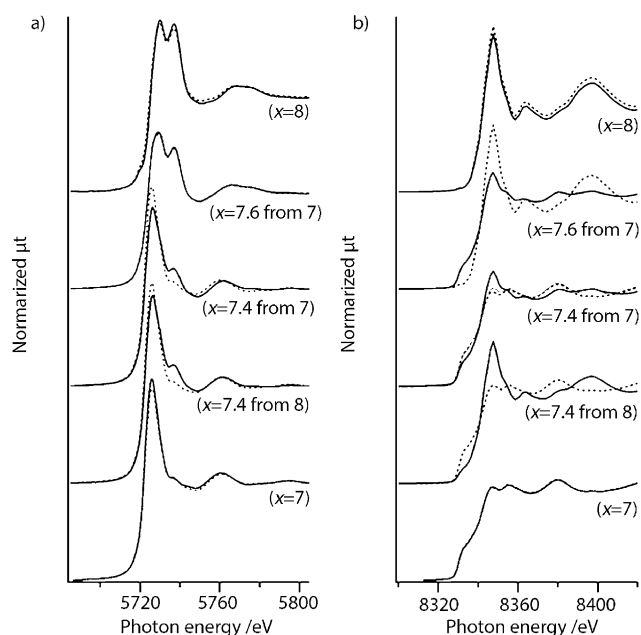


Figure 2. a) Ce L_{III}-edge and b) Ni K-edge XANES spectra of NiO_y/Ce₂Zr₂O_x catalysts before and after CH₄ steam reforming. (*x* = 7) Ni/pyrochlore-Ce₂Zr₂O₇, (*x* = 7.4 from 8) NiO_y/Ce₂Zr₂O_{7.4} prepared by H₂ reduction of NiO/κ-Ce₂Zr₂O₈, (*x* = 7.4 from 7) NiO_y/Ce₂Zr₂O_{7.4} prepared by O₂ oxidation of Ni/pyrochlore-Ce₂Zr₂O₇, (*x* = 7.6 from 7) NiO_y/Ce₂Zr₂O_{7.6} prepared by O₂ oxidation of Ni/pyrochlore-Ce₂Zr₂O₇, and (*x* = 8) NiO/κ-Ce₂Zr₂O₈. Solid line: fresh catalyst; dotted line: catalyst after CH₄ steam reforming at 923 K; and gray solid line for (*x* = 7.4 from 7) of (b): NiO_y/Ce₂Zr₂O_{7.4} catalyst after treatment with CH₄ at 923 K in the absence of H₂O.

The phase transformation of Ce₂Zr₂O_{7.4} after CH₄ steam reforming was also observed by XRD analysis (Figure 3). Fresh NiO_y/Ce₂Zr₂O_{7.4} samples prepared by Ni/Ce₂Zr₂O₇ oxidation and by NiO/Ce₂Zr₂O₈ reduction showed almost the same XRD peaks at intermediate positions between

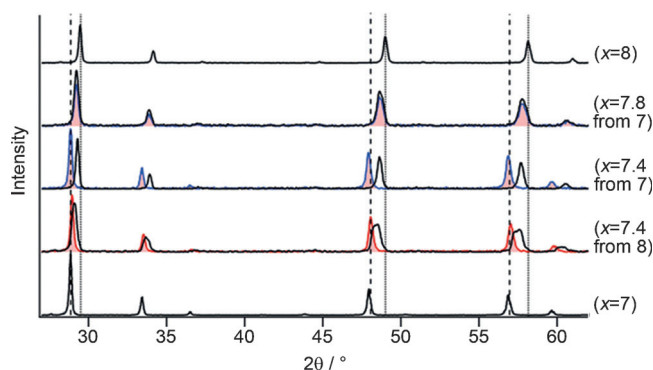


Figure 3. XRD patterns of NiO_y/Ce₂Zr₂O_x. (*x* = 7) Ni/pyrochlore-Ce₂Zr₂O₇, (*x* = 7.4 from 8) NiO_y/Ce₂Zr₂O_{7.4} prepared by H₂ reduction of NiO/κ-Ce₂Zr₂O₈, (*x* = 7.4 from 7) NiO_y/Ce₂Zr₂O_{7.4} prepared by O₂ oxidation of Ni/pyrochlore-Ce₂Zr₂O₇, (*x* = 7.8 from 7) NiO_y/Ce₂Zr₂O_{7.8} prepared by O₂ oxidation of Ni/pyrochlore-Ce₂Zr₂O₇, and (*x* = 8) NiO/κ-Ce₂Zr₂O₈. Black lines: fresh catalyst; red lines, red shading: catalyst after CH₄ steam reforming at 923 K; blue line: catalyst after the treatment with CH₄ at 923 K. Dashed and dotted lines: peak positions of pyrochlore-Ce₂Zr₂O₇ and κ-Ce₂Zr₂O₈, respectively.

pyrochlore-Ce₂Zr₂O₇ and κ-Ce₂Zr₂O₈. These XRD peaks shifted to the position corresponding to pyrochlore-Ce₂Zr₂O₇ after CH₄ steam reforming at 923 K. A similar transformation of Ce₂Zr₂O_{7.4} to pyrochlore-Ce₂Zr₂O₇ also occurred with exposure to CH₄ without H₂O at 923 K.

In contrast, the Ce L_{III}-edge XANES spectrum of NiO_y/Ce₂Zr₂O_{7.6} remained unchanged after CH₄ steam reforming (Figure 2a). The XRD of NiO_y/Ce₂Zr₂O_{7.8} also showed no change after the reforming (Figure 3). There was also no change in the XANES spectrum of NiO/Ce₂Zr₂O₈ under the reforming conditions. Thus, the Ce₂Zr₂O_x phase transformation proceeded depending on the oxygen content *x* of Ce₂Zr₂O_x, and the pyrochlore-Ce₂Zr₂O₇ phase was crucial for the high reforming activity. No XRD peak corresponding to crystalline Ni or NiO_y was observed in any sample.

The surface layers of Ni nanoparticles on Ce₂Zr₂O_x should be oxidized to NiO in samples prepared by the O₂ oxidation of Ni/Ce₂Zr₂O₇, whereas these layers should be reduced to metallic Ni in samples prepared by the H₂ reduction of NiO/Ce₂Zr₂O₈. Thus, Ni nanoparticle surfaces in NiO_y/Ce₂Zr₂O_x can have different Ni phases even in the same *x*. We characterized the Ni phase in NiO_y/Ce₂Zr₂O_x by Ni K-edge XANES (Figure 2b). The XANES of Ni/Ce₂Zr₂O₇ was almost the same as that of Ni foil, which indicates that Ni nanoparticles on pyrochlore-Ce₂Zr₂O₇ are metallic. The Ni K-edge EXAFS analysis also revealed that the Ni nanoparticles were metallic Ni species, the Ni–Ni coordination number of which was 11.1 ± 1.3 at 0.249 ± 0.001 nm (Supporting Information, Table S1 and Figure S3).

As the white-line intensity at the Ni K-edge corresponds to the vacancy of Ni 3d levels, the Ni K-edge XANES spectra of the two NiO_y/Ce₂Zr₂O_{7.4} samples indicate that Ni nanoparticles in NiO_y/Ce₂Zr₂O_{7.4} prepared by the reduction of NiO/Ce₂Zr₂O₈ are more strongly oxidized than those in NiO_y/Ce₂Zr₂O_{7.4} prepared by the oxidation of Ni/Ce₂Zr₂O₇. These results suggest that Ni nanoparticles in NiO_y/Ce₂Zr₂O_{7.4} prepared by the oxidation of metallic Ni nanoparticles on pyrochlore-Ce₂Zr₂O₇ form a core-shell structure with a metallic Ni core and a NiO shell. On the other hand, Ni nanoparticles in NiO_y/Ce₂Zr₂O_{7.4} prepared by the reduction of NiO nanoparticle on κ-Ce₂Zr₂O₈ form another core-shell structure with a NiO core and a metallic Ni shell. Although the core-shell phases in the two NiO_y/Ce₂Zr₂O_{7.4} samples were different, both their Ni K-edge XANES spectra changed to that of metallic Ni nanoparticles in Ni/Ce₂Zr₂O₇ under the CH₄ steam reforming conditions (Figure 2b). Both NiO_y/Ce₂Zr₂O_{7.4} catalysts also exhibited similar performance as shown in Figure 1. The activity of both NiO_y/Ce₂Zr₂O_{7.4} catalysts was similar to that of Ni/Ce₂Zr₂O₇.

The Ni K-edge XANES spectrum of fresh NiO_y(*y* = 0.4)/Ce₂Zr₂O_{7.6} prepared by Ni/Ce₂Zr₂O₇ oxidation was not much different from that of fresh NiO_y(*y* = 0.3)/Ce₂Zr₂O_{7.4} prepared by Ni/Ce₂Zr₂O₇ oxidation (Figure 2b), where *y* was estimated from Ni K-edge white-line intensity. However, the NiO_y/Ce₂Zr₂O_{7.6} catalyst showed no activity for the CH₄ steam reforming (Figure 1). The NiO_y(*y* = 0.3)/Ce₂Zr₂O_{7.4} sample was reduced to metallic Ni/Ce₂Zr₂O₇ under the CH₄ steam reforming conditions, whereas the NiO_y(*y* = 0.4)/Ce₂Zr₂O_{7.6} sample behaved similarly to NiO/Ce₂Zr₂O₈; that is, Ni

nanoparticles were oxidized to NiO under the CH₄ steam reforming conditions (Figure 2b).

The high catalytic activity, robustness against deactivation, and newly found discontinuity may be related to the reactivity of lattice oxygen in Ce₂Zr₂O_x ($7 \leq x < 7.5$), to water activation to form protons and oxygen anions on the support surface, and to the strong interaction at the interface between Ni/NiO_y nanoparticles and the Ce₂Zr₂O_x support ($7 \leq x < 7.5$). On NiO_y/Ce₂Zr₂O_x ($7.5 \leq x \leq 8$), an anti-phase boundary in the Ce₂Zr₂O_x bulk suppresses oxygen diffusion and makes it difficult for water activation to occur.^[12]

The discontinuity in catalytic performance at $x = 7.5$ may be related to the OSC of Ce₂Zr₂O_x^[11] because it was not observed in the case of only NiO_y. The reduction of NiO_y strongly depended on the nature of the Ce₂Zr₂O_x support. In the range of $7 \leq x < 7.5$, Ni and Ce₂Zr₂O_x were reduced to the metallic state and the pyrochlore-Ce₂Zr₂O₇ phase, respectively, under the reaction conditions; the reduction was due to CH₄. Indeed, the NiO_y/Ce₂Zr₂O_{7.4} prepared from Ni/Ce₂Zr₂O₇ reacted with CH₄ in the absence of H₂O and was converted to Ni/Ce₂Zr₂O₇, as shown in Figure 2b and Figure 3. In the range of $7.5 \leq x \leq 8$, however, NiO_y was converted into NiO, and Ce₂Zr₂O_x remained unchanged under the reaction conditions. The oxidation of Ni nanoparticles on Ce₂Zr₂O_x ($7.5 \leq x \leq 8$) was due to H₂O.

In the range of $7 \leq x < 7.5$, the reduction of the catalyst to Ni/Ce₂Zr₂O₇ by CH₄ was preferred over other reactions, whereas in $7.5 \leq x \leq 8$, the oxidation of the catalyst to NiO/Ce₂Zr₂O_x by H₂O was preferred. No data for the Ellingham diagram of Ce₂Zr₂O_x ($7 \leq x \leq 8$) are available,^[13] but the dependence of the equilibrium pressure of oxygen (p_{O_2}) on the oxygen content x of Ce₂Zr₂O_x shows different aspects at $x \geq 7.5$ and $x < 7.5$.^[14] The oxygen storage and release processes rapidly occur at $x < 7.5$ compared with $x \geq 7.5$. A feature of kinetic catalyst bistability is seen in the present system, namely the tendency of the system to flip into two competing different redox states despite the presence of apparently unchanged thermodynamic gas phase conditions. In the range of $7 \leq x < 7.5$, lattice oxygen atoms in Ce₂Zr₂O_x readily migrate from the bulk to the surface, at which they react with CH₄ to form the resultant Ce₂Zr₂O₇ phase. This event occurs at the start of the reforming, followed by the catalytic CH₄ steam reforming that proceeds on the Ni/pyrochlore Ce₂Zr₂O₇ (produced in situ or initially prepared). NiO_y on Ce₂Zr₂O_x may react directly with CH₄, but NiO_y on Ce₂Zr₂O_{7.6} is not reduced. Thus, the direct reduction of NiO_y by CH₄ may be minor.

The transport of oxygen atoms at the interface between NiO_y nanoparticles and a Ce₂Zr₂O_x support and/or the spillover of oxygen atoms at the boundary may be key issues in the chemical event of interest.^[15] The NiO_y nanoparticles possess a disordered structure owing to strong interaction at the interface between the NiO_y and the Ce₂Zr₂O_x, which gives some strain to the nanoparticle structures (Supporting Information, Figure S5). Oxygen atoms move from NiO_y to Ce₂Zr₂O_x at 923 K, thereby reducing NiO_y to metallic Ni, and Ce₂Zr₂O_x to Ce₂Zr₂O₇, with CH₄. In the range of $7.5 \leq x \leq 8$, oxygen transport may be difficult owing to an increase in the energy barrier for oxygen

diffusion in the bulk as a result of the anti-phase boundary.^[13] CH₄ activation is difficult on the fluorite-type Ce₂Zr₂O_x and the NiO produced on it.

CH₄ decomposition to C atoms may occur on the Ni surface, more preferably at the boundary of Ni nanoparticle and Ce₂Zr₂O_x O-vacancy, followed by the reaction of C with H₂O or O anions produced by H₂O activation on the Ce₂Zr₂O_x ($x < 7.5$) surface. The catalytic activity is considered to be a synergetic effect of the Ni and Ce₂Zr₂O_x phases. The stable activity without significant coking may also be due to the OSC of the Ce₂Zr₂O_x solid solution. Kinetic criticality phenomena are difficult to confirm and are usually highly resistant against monocausal explanations. Despite the macroscopic interpretation for the critical behavior, further study is needed for a micro-mechanistic unequivocal explanation of the observed discontinuity at $x = 7.5$. Nevertheless, the present finding of the discontinuous aspect and active phase in the new Ni/pyrochlore Ce₂Zr₂O₇ catalysis provides some implication to bifunctional catalyst design by synergetic interface, improving reactant activation and spillover of oxidizing/reducing species.

Experimental Section

Pyrochlore Ce₂Zr₂O₇ was prepared by co-precipitation using an aqueous NH₃ solution of Ce(NO₃)₃·6H₂O and ZrO(NO₃)₂·2H₂O, followed by reduction with pure CO at 1673 K for 4 h.^[9] The sample was calcined in air at 773 K for 3 h and impregnated with an aqueous solution of Ni(NO₃)₂·6H₂O, followed by calcination at 773 K for 3 h to prepare NiO/Ce₂Zr₂O₈. Ni/Ce₂Zr₂O₇ was prepared by the reduction of NiO/Ce₂Zr₂O₈ with H₂ at 773 K for 3 h. CeO₂-ZrO₂ mixed oxides were prepared by co-precipitation of ZrOCl₂ and (NH₄)₂Ce(NO₃)₂ with CO(NH₂)₂ in a Teflon autoclave at 433 K for 4 h or by physical mixing of CeO₂ and ZrO₂, followed by calcination at 773 K, to which Ni was impregnated in a similar manner. Before use, the samples were reduced with H₂ at 773 K for 3 h. The details of the synthesis and characterization methods are described in the Supporting Information. XAFS spectra for the samples were measured at 293 K at KEK-PF (BL9A in a transmission mode (Ce L_{III}-edge) and BL12C in a fluorescence mode (Ni K-edge)).

CH₄ steam reforming reactions were conducted in a fixed-bed down-flow quartz-tube reactor of 6 mm inner diameter, typically using 0.1 g of catalyst at atmospheric pressure. The flow rates of H₂, CH₄, O₂, and He were regulated by mass flow controllers, and H₂O was supplied by bubbling of He. Reactants and products were analyzed two on-line GCs with columns packed with molecular sieves 5 A for H₂, O₂, CO, and CH₄ and Porapak-S for CO₂ and H₂O.

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