Barium-Promoted Yttria–Zirconia-Supported Ni Catalyst for Hydrogen Production via the Dry Reforming of Methane: Role of Barium in the Phase Stabilization of Cubic ZrO2

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ABSTRACT: Developing cost-effective nonprecious active metal-based catalysts for syngas (H2/CO) production via the dry reforming of methane (DRM) for industrial applications has remained a challenge. Herein, we utilized a facile and scalable mechanochemical method to develop Ba-promoted (1−5 wt %) zirconia and yttria–zirconia-supported Ni-based DRM catalysts. BET surface area and porosity measurements, infrared, ultraviolet−visible, and Raman spectroscopy, transmission electron microscopy, and temperature-programmed cyclic (reduction−oxidation−reduction) experiments were performed to characterize and elucidate the catalytic performance of the synthesized materials. Among different catalysts tested, the inferior catalytic performance of 5Ni/Zr was attributed to the unstable monoclinic ZrO2 support and weakly interacting NiO species whereas the 5Ni/YZr system performed better because of the stable cubic ZrO2 phase and stronger metal−support interaction. It is established that the addition of Ba to the catalysts improves the oxygen-endowing capacity and stabilization of the cubic ZrO2 and BaZrO3 phases. Among the Ba-promoted catalysts, owing to the optimal active metal particle size and excess ionic CO3\(^{2−}\) species, the 5Ni4Ba/YZr catalyst demonstrated a high, stable H2 yield (i.e., 79% with a 0.94 H2/CO ratio) for up to 7 h of time on stream. The 5Ni4Ba/YZr catalyst had the highest H2 formation rate, 1.14 mol g\(^{−1}\) h\(^{−1}\) and lowest apparent activation energy, 20.07 kJ/mol, among all zirconia-supported Ni catalyst systems.

1. INTRODUCTION

The Paris Agreement set a goal for this century of keeping global warming below 2 °C and preferably at 1.5 °C. Aside from reducing anthropogenic greenhouse gas emissions (e.g., CO2 and CH4), turning these gases into value-added chemical feedstock is a more enticing way to accomplish this aim. In this context, the dry reforming of methane (DRM) is a potential and viable option because it yields hydrogen from the conversion of two major greenhouse gases (i.e., CH4 and CO2). Catalysts based on noble metals have been reported to be effective for DRM.1−5 The total methane dissociation energy among the transition metals was found to follow the order Ni < Pd = Pt, so the experimental order of methane conversion was observed to be Ni > Pd = Pt.6 Among Ni and Co, Gallego et al. found that the electronic configuration of Ni in Ni−CH4 is s\(^{3}\)d\(^{8}\)s\(^{2}\)d\(^{8}\) (with respect to the d\(^{8}\)s\(^{2}\) electronic configuration of metallic Ni), indicating smaller steric repulsion between a closed shell of Ni and CH4.7 However, the electronic configuration of Co remains the same (either in Co−CH4 or in metallic Co), causing a large repulsion between a closed shell of Co and CH4. Importantly, the interaction energy of CH4 with Ni is 18 kcal/mol, and with Co it is 0.7 kcal/mol. As a result, from a catalytic activity standpoint, Ni-based catalysts are more appealing for industrial applications than Co catalysts. However, high-temperature Ni sintering, which induces pronounced coke deposition and, eventually, catalyst deactivation, is a major challenge.

To stabilize the Ni, it has been dispersed on several metal oxides including Al2O3,8 SiO2,9 zeolites,10 ZrO2,11 TiO2,12 and MgO.13 Furthermore, the addition of a promoter over supported Ni catalysts had brought about major physiochemical changes over the catalyst surface in favor of DRM. In brief, Mg incorporation added alkalinity to the catalyst system,1,4,14−17

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and produced fewer exposed active metal sites. However, by interaction feature but required a costly synthetic procedure.

Subsequently, the adsorbed oxygen oxidizes the formed support interface/boundary as well as oxygen vacancies. On the other hand, is adsorbed over basic surface sites and dissociates after reductive treatment, metallic Ni sites (i.e., Ni<sup>0</sup>) and oxygen vacancies are formed. The reaction scheme over the Ni-supported catalyst system is shown in Figure 1. Generally, C–H cleavage occurs at Ni<sup>0</sup> sites, whereas CO<sub>2</sub> dissociation occurs preferably at oxygen vacancies. Because Ni has a strong interaction with CH<sub>x</sub> and CH<sub>4</sub> is decomposed over Ni<sup>0</sup> into CH<sub>2–x</sub>H<sub>x</sub> (where x = 1, 2, 3, 4). CO<sub>2</sub> on the other hand, is adsorbed over basic surface sites and dissociates into CO and atomic oxygen/adsorbed oxygen at the Ni-support interface/boundary as well as on oxygen vacancies. Subsequently, the adsorbed oxygen oxidizes the formed CH<sub>(4–x)</sub> species into CO and (4–x)(1/2)H<sub>2</sub>. At the same time, the carbon deposit is oxidized by lattice oxygen from the support, leaving an oxygen vacancy behind. Following that, the oxygen vacancy is replenished by CO<sub>2</sub>. This emphasizes the significance of adsorbed oxygen, which is directly involved in the oxidation of CH<sub>(4–x)</sub> species.

According to the literature, the conventionally synthesized Ni-impregnated ZrO<sub>2</sub> catalyst exhibited good DRM activity initially. However, because of a lack of optimal metal–support interactions, it underwent a high degree of graphitization and continuous catalyst deactivation. On the other hand, sol–gel-derived catalysts demonstrated a strong metal–support interaction feature but required a costly synthetic procedure and produced fewer exposed active metal sites. However, by applying high Ni loading (10 wt %) and high-volume expansive carrier gas argon (8 times the feed gas volume), good catalytic activity was noticed.

The ultimate challenges needed for a DRM reaction are the inhibition of carbon deposition on the catalyst surface and active metal sintering. Numerous approaches have been used by researchers to improve stability and to circumvent coke formation over Ni-based catalysts. It has been proposed that basicity improves the catalyst’s ability to adsorb CO<sub>2</sub>, facilitating coke gasification via the reverse Boudouard reaction (i.e., 2CO ↔ C + CO<sub>2</sub>). The addition of alkali or alkaline earth metals as promoters can improve the basic properties of the catalysts. These promoters may also enhance other features such as active metal dispersion and the metal–support interaction. For instance, 0.6% Na addition to a ZrO<sub>2</sub>-supported Ni catalyst was found to increase the metal–support interaction by the formation of NiO–ZrO<sub>2</sub> species and to inhibit the hydrogenation of carbon deposits. Similarly, adding Ca to a Ni/ZrO<sub>2</sub> catalyst improves its basicity and textural properties, which in turn helps to avoid carbon deposition.

Among other basic promoters, barium (Ba) has previously been used to improve the thermal and catalytic properties of Ni-based materials. For instance, when Ni was deposited by chemical vapor deposition over the BaO-ZrO<sub>2</sub> support, it demonstrated the self-decoking ability of a carbon deposit by –OH and –O species with a negligible sign of Ni sintering for up to 50 h TOS at 700 °C. Similarly, when barium is added to alumina, barium hexa-aluminate is formed, which has excellent thermal stability.

You et al. demonstrated that the addition of Ba to γ-Al<sub>2</sub>O<sub>3</sub> can significantly neutralize the acidity of alumina. Gomes et al. found that by substituting La with Ba in LaNiO<sub>3</sub> perovskite, resistance against deactivation had been improved. BaO (4 wt %) addition over SiO<sub>2</sub>-supported Ni enhanced the CO<sub>2</sub> methanation activity. The BaO/Ni interface is known for the water-mediated oxidation of carbon deposits to CO<sub>2</sub>. Ersoy demonstrated that BaCO<sub>3</sub> is effective at oxidizing carbon through the formation of complexes between BaCO<sub>3</sub> and C, which can be decomposed to CO at higher temperatures. A barium zirconate-supported Ni catalyst has been utilized for a dry reforming reaction by Seo et al. When BaO is combined with the ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> support, it forms the BaZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub><sup>δ−</sup> mixed oxide, which has a higher basicity than ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>. BaZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub><sup>δ−</sup> also exhibits a high proton conductivity, which may accelerate H-abstraction from the methyl group on the surface.

Promotional loading of BaCO<sub>3</sub> over the ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>-supported Ni catalyst was well utilized in solid-oxide fuel cells for the direct utilization of methane and the electrolysis of H<sub>2</sub>O to H<sub>2</sub> and CO<sub>2</sub> to CO. On the basis of these findings, we anticipate that BaO-promoted ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>-supported Ni materials will have well-dispersed catalytically active sites (Ni<sup>0</sup>), improved basic properties, high proton conductivity, and coke resistance in favor of DRM.

Among the various synthesis methods, mechanochemical synthesis has received a considerable amount of attention because of its simplicity and use of cheap precursors as well as...
the possibility of realizing phases with different properties. Herein, we have systematically developed Ba-promoted (1–5 wt %) yttria–zirconia-supported Ni-based catalysts (SNiBa/YZr; x = 1–5 wt %). These materials were tested for DRM and characterized by surface area porosity measurements, infrared, ultraviolet–visible and Raman spectroscopy, and transmission electron microscopy. We demonstrated that adding a Ba promoter to the Ni/YZr catalyst inhibits carbon formation.

Figure 2. N₂ adsorption isotherm and porosity distribution profiles of (A) 5Ni/Zr, (B) 5Ni/YZr, (C) 5Ni1Ba/YZr, (D) 5Ni2Ba/YZr, (E) 5Ni3Ba/YZr, (F) 5Ni4Ba/YZr, and (G) 5Ni5Ba/YZr.
During the DRM reaction, catalyst surfaces are exposed to reducing gas (H\textsubscript{2}) as well as oxidizing gas (CO\textsubscript{2}). The reduction–oxidation–reduction cycles over catalyst surfaces are regulated during the entire DRM reaction. To establish the function–activity correlations, we performed cyclic H\textsubscript{2}TPR-CO\textsubscript{2}TPR-H\textsubscript{2}TPR experiments in this study. These findings will contribute to advancing the knowledge spectrum of surface science toward DRM.

2. EXPERIMENT

2.1. Materials. Nickel nitrate hexahydrate (98%, Alfa Aesar), zirconia (gifted by Kagaku Daiichi Kogyo Co. Ltd Osaka), yttria (obtained from China), and deionized water were used.

2.2. Catalyst Preparation. The catalysts were prepared by the mechanochemical mixing of Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (equivalent to 5 wt % Ni loading), Ba(NO\textsubscript{3})\textsubscript{2} (equivalent to 0, 1, 2, 3, 4, 5 wt % BaO loadings), and a mesoporous yttria-stabilized zirconia (8 wt % yttria, 92 wt % zirconia) support, followed by drying and calcination at 600 °C for 3 h. For convenience, the prepared catalysts are abbreviated as 5Ni\textsubscript{x}Ba/YZr, where Ni loading is fixed at 5 wt % and the Ba loading “x” varies from 0 to 5 wt % (i.e., x = 0, 1, 2, 3, 4, 5).

2.3. Catalyst Characterization. The catalysts that were synthesized were characterized using the Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–vis), transmission elec-
electron microscopy (TEM), H2 temperature-programmed reduction (H2-TPR), CO2 temperature-programmed desorption (CO2-TPD) and thermogravimetric analysis (TGA). Detailed descriptions of the instruments and characterization procedures are provided in Supporting Information S1.

2.4. Catalyst Activity Test. The DRM experiments were carried out in a tubular stainless-steel reactor at a space velocity of 42 000 mL/h gcat by passing a 30:30:10 mL/min volume ratio of a CH4/CO2/N2 gas feed through 0.1 g of prereduced catalyst. All of the catalysts were prereduced under H2 flow for 1 h at a flow rate of 30 mL/min at 600 °C. The DRM reaction was performed at 1 atm and 800 °C. The effluent was examined with an online GC equipped with molecular sieves 5A, Porapak Q columns, and a TCD detector using Ar carrier gas. The H2 yield % was estimated with the following expression:

\[
H_2 \text{ yield}\% = \frac{\text{moles of } H_2 \text{ produced}}{2 \times \text{moles of } CH_4} \times 100
\]

3. RESULTS

3.1. Characterization Results. A N2 adsorption isotherm and the porosity distribution, BET surface area, pore volume, and pore diameter results of 5Ni/Zr and 5Ni\(x\)Ba/YZr (\(x = 0\)–5) catalysts are depicted in Figure 2, Figure S1, and Table S1. All materials have typical type IV isotherms with an H1 hysteresis loop indicating the presence of cylindrical mesopores. The \(dV/d\log W\) vs \(W\) plot (where \(V\) is volume and \(W\) is the pore width) shows a rapid view of micropore, mesopore, and macropore distributions over the catalyst surface. The obtained results show that our catalysts have a bimodal pore size distribution. The marked change appeared in the lower pore width range of 10–50 nm and the intermediate pore width range of 100–150 nm, where the intensity of the earlier one was higher than that of the later.69 The average pore size over Ni/YZr catalyst is 17.88 nm (Table S1). Interestingly, when yttria is incorporated, the pore size of the respective catalyst is increased to 24.78 nm. It is worth noting that the yttria–zirconia-supported Ni catalyst system has ~50% less surface area but an ~40% larger average pore size than the zirconia-supported Ni catalyst. However, no substantial structural changes in terms of pore volume and pore width are observed upon the incorporation of Ba into the Ni/YZr catalyst. In a Ba-promoted catalyst system, the pore size was typically in the 24–27 nm range (Table S1).

The X-ray diffraction pattern of different catalyst samples and the NiO and BaZrO3 crystallite sizes are shown in Figure 3 and Table S2. The zirconia-supported Ni catalyst (Ni/Zr) has a monoclinic zirconia phase (at 2\(\theta\) = 23.93, 28.18, 31.48, 34.78, 38.58, 40.85, 44.70, 49.37, 50.16, 54.04, 55.34, 58.14, 59.98, 61.68, 62.92, 65.60, 69.13, 71.20, 75.39, 78.97, and 83.56°; JCPDS reference no. 00-007-0343) and a cubic NiO phase (at 2\(\theta\) = 37.12, 43.24, 62.92, 75.39, and 78.97°; JCPDS reference no. 00-004-0835). The presence of the monoclinic ZrO2 phase in the 5Ni/Zr catalyst is also verified by Raman spectra (Figure 4A). The Raman bands related to the monoclinic ZrO2 phase appeared at 179, 335, 379, 476, and 610 cm\(^{-1}\). Interestingly, over the yttria–zirconia-supported Ni catalyst were found more intense peaks of the cubic ZrO2 phase (at 2\(\theta\) = 30.08, 34.97, 50.10, 59.64, 62.59, 74.07, 75.39, 78.97, and 83.56°; JCPDS reference no. 00-003-0640) than of monoclinic ZrO2. This indicates that yttria stabilizes the cubic phase of ZrO2. The crystallite size of cubic NiO is increased to 38.8 nm in 5Ni/YZr (against 18.4 nm in the 5Ni/Zr catalyst) (Table S2). The 1 wt % barium-promoted yttria–zirconia-supported Ni catalyst mainly contains the cubic ZrO2 phase. However, cubic BaZrO3 Bragg reflections at 2\(\theta\) = 30.10, 43.26, and 62.67° (JCPDS reference no. 00-006-0399) were also evident in this catalyst (Figure 3B). The presence of Ba–O in the
structure is also verified by the Raman spectra of the 5Ni1Ba/YZr catalyst. The Raman band at around 220−280 cm\(^{-1}\) over 5Ni1Ba/YZr is due to the overtones of TA, TA + TO, and TO of Ba−O vibrational modes\(^ {72}\) (Figure 4A). It can be said that Ba incorporation stabilizes the cubic phase of ZrO\(_2\) pronouncedly. On increasing the Ba loading up to 4 wt %, the minimum sizes of NiO (18.7 nm) and BaZrO\(_3\) (28.4 nm) crystallites were found. At 5 wt % Ba loading, selected planes (111, 200, 220, and 311) of cubic ZrO\(_2\) peaks are shifted to a higher Bragg’s angle, indicating a decrease in interplanar spacing (Figure 3C−F).

IR spectra, UV−vis spectra, and corresponding band-gap energy profiles of SNi/Zr and SNiBa/YZr (x = 0, 1, 2, 3, 4, and 5 wt %) catalyst systems are shown in Figure 4B−D, respectively. IR peaks due to the bending and stretching vibration of O−H are present at 1630 and 3444 cm\(^{-1}\), respectively, in all catalysts.\(^ {22,73}\) The zirconia-supported Ni catalyst has vibrational peaks of Zr−O at 497 and 750 cm\(^{-1}\),\(^ {22}\) a broad peak of the bidentate format at 1355 cm\(^{-1}\),\(^ {174}\) and a unidentate carbonate peak at 1380 cm\(^{-1}\).\(^ {37,73}\) Interestingly, in the yttria−zirconia-supported Ni catalyst, the vibrational peaks of Zr−O and bidentate format peaks disappeared, indicating that the addition of yttria brought about major changes in the bonding pattern. At higher Ba loadings (4 to 5 wt %), the stretching vibrations of CO\(_3^{2−}\) are observed at 851 and 1460 cm\(^{-1}\).\(^ {75}\) However, at 2 wt % Ba, the symmetric stretching vibrational peak of CO\(_3^{2−}\) (C\(_2\)v or C\(_1\)v symmetry) at 1084 cm\(^{-1}\) and the stretching vibration of C═O at 1712 cm\(^{-1}\) are also noticed.\(^ {77}\)

The zirconia-supported Ni catalyst had O\(^{2−}\) (2p, valence band) to M\(^{n+}\) (4d, conduction band) charge-transition bands at 229 and 290 nm in the UV−vis spectra.\(^ {22}\) In comparing the UV spectra of Ni/Zr to those of ZrO\(_2\), it is found that the peak intensity at 229 nm remains the same but the peak intensity at about 290 nm is increased as well as broadened upon Ni anchoring over ZrO\(_2\) (Figure S2). This indicates that the peak at 229 nm is due to the charge-transfer band from O\(^{2−}\) to Zr\(^{4+}\) and that the peak at 290 is due to the charge-transfer band from O\(^{2−}\) to Ni\(^{2+}\) as well as that from O\(^{2−}\) to Zr\(^{4+}\). On the other hand, for the yttria−zirconia-supported catalyst, the peak at 229 nm disappears, which indicates that yttria incorporation into the support changes the coordination environment of Zr\(^{4+}\)
exclusively. For most of these catalysts, the d–d transition bands at 378 and 418 nm for the d–d transition from the 3A2g(F) energy state to the 3T1g(P) energy state of Ni2+ (in the octahedral environment) and at 718 nm for the d–d transition from the 3A2g(F) energy state to the 3T1g(F) energy state of Ni2+ (in an octahedral environment) are found. Indeed, these findings confirm the octahedral environment of Ni2+ in the 5Ni_xBa/YZr (x = 0−5 wt %) catalyst system. Interestingly, at a 4 wt % Ba loading, the charge transition from the O2− (2p, valence band) to the Zr4+/Ni2+ peak has the highest intensity but the d–d transition band for the 3A2g(F) energy state to the 3T1g(P) energy state of the Ni2+ octahedral environment disappeared. However, in this catalyst, the band gap was not affected by the addition of the Ba promoter (Figure 4D).

Figure 5 depicts TEM images of fresh and spent catalysts as well as their particle size distributions. Mean NiO particle sizes of 3.25, 3.75, and 3.91 nm are observed for 5Ni/Zr, 5Ni/YZr, and 5Ni4Ba/YZr catalysts, respectively. After the reaction, the particle sizes (Ni species) are grown to 7.16, 7.60, and 7.64 nm, respectively. For spent catalysts, the formation of carbon nanotubes is easily visible.

H2-TPR, H2-TPR followed by CO2-TPD, and H2-TPR-CO2-TPD-H2-TPR cyclic profiles of different catalyst samples are shown in Figure 6 and Figure S3. The H2-TPR profile of the zirconia-supported Ni catalyst (Ni/ZrO2) shows a small reduction peak shoulder at about 235 °C for the reduction of free NiO, a sharp reduction peak at 335 °C for the reduction of NiO weakly interacting with the support, and a relatively smaller but broader peak at 490 °C for the reduction of NiO moderately interacting with the support (Figure 6A). When yttria was combined with the ZrO2 support, the reduction peak for weakly interacting NiO species almost vanished, whereas the reduction peaks for NiO moderately interacting with the support remained. This indicates that the catalyst had a smaller quantity of reducible, weakly interacting NiO species and that the addition of yttria resulted in a stronger metal–support interaction. Importantly, the reduction profile of Ba-promoted catalysts is identical to that of 5Ni/YZr. The CO2-TPD experiments were performed in conjunction with H2-TPR over reduced 5Ni/Zr, 5Ni/YZr, and 5Ni5Ba/YZr catalysts in order to estimate the basic sites in these materials (Figure 6B). During the H2-TPR, the reducible metal oxides are reduced to the respective metals and the surface hydroxyls are converted to water. As a result, the reducible NiO and surface hydroxyl ions should be eliminated during H2-TPR treatment for these catalysts. The reduced 5Ni/Zr catalyst had a significant concentration of weak basic sites (surface hydroxyls) at low temperatures, moderate-strength basic sites (surface oxide ions) at intermediate temperatures, and strong basic sites (thermally stable surface carbonates) at high temperatures. This indicates that the surface anion that is present on 5Ni/Zr may not be reducible but basic. The yttria–zirconia-supported Ni catalyst had a good quantity of moderately interacting reducible NiO species, and during H2-TPR treatment, they must be reduced to metallic Ni (by removing oxygen). Thus, the CO2 TPD profile of the reduced 5Ni/YZr catalyst showed the absence of moderate strength basic sites. It also indicates the greater oxygen-endowing capacity of the YZr-supported Ni catalyst than the ZrO2-supported Ni catalyst. The 5Ni4Ba/YZr catalyst had a good quantity of reducible, moderately interacting NiO species. However, a substantial number of intermediate-strength basic sites are present over the reduced
SNi4Ba/YZr catalyst. These results imply that the basic nature of BaO contributes to retaining the high surface basicity of the SNi4Ba/YZr catalyst.

H2-TPR reduces NiO to metallic Ni while also creating oxygen vacancies in the underlying metal oxide support because of H2 spillover from adjacent metallic Ni species. In general, such oxygen vacancies could be refilled when CO2-TPD is combined with H2-TPR. In this CO2-TPD process, the reduced Ni is reoxidized to NiO. It is important to know the type of NiO that is regenerated following oxygen replenishment by CO2. This can be achieved by performing another H2-TPR over the H2TPR-CO2TPD treated catalyst (Figure 6C). The cyclic experiment (H2TPR-CO2TPD-H2TPR) will provide evidence of the CO2 replenishment capacity and the stability of Ni species across different catalyst systems. In the case of the zirconia-supported Ni catalyst, abundant reducible peaks for free NiO species and reducible moderately interacting NiO species are observed. Prominent reducible peaks for free NiO species indicate pronounced Ni sintering during the reduction–oxidation–reduction cycle, which may be the major cause of the inferior performance of the catalytic activity of the zirconia-supported Ni catalyst. In contrast, there is no free NiO reducible peak in the SNi/YZr catalyst, although there are peaks attributable to moderately and strongly interacting NiO species, which indicates that the yttria has improved the sintering resistance and strong metal–support interaction properties. Likewise, the broad reduction peak associated with strongly interacting NiO species is mainly observed in the case of the Ba-promoted catalyst.

The TGA profiles of the spent catalysts are shown in Figure 6D. The zirconia- and yttria–zirconia-supported Ni spent catalysts showed a significant weight loss due to the oxidation of surface carbon deposits. Notably, increasing the Ba loading reduces weight loss. It implies that the incorporation of Ba in the catalytic system decreases the extent of coke formation on the catalyst surface during the DRM reaction.

3.2. Catalytic Activity Results. The catalytic activity of SNi/YZr and SNixBa/YZr (x = 1–5 wt %) catalyst systems for DRM in terms of hydrogen yield is shown in Figure 7. The H2 yield for a zirconia-supported catalyst (5Ni/Zr) is the lowest and is unstable with respect to the time on stream (TOS). It is 50% initially, which decreases to 45% within 420 min. In contrast, the yttria–zirconia-supported Ni catalyst (5Ni/YZr) has a higher stable H2 yield for up to 420 min on TOS. It remains nearly stable at around 71% for 420 min. This suggests that incorporating yttria into the ZrO2 support is beneficial to the catalyst system. Interestingly, when 1–5 wt % Ba promoter is added to a yttria–zirconia-supported Ni catalyst (5NiBa/YZr; x = 1–5 wt %), prominent changes in the H2 yield are observed. The H2 yield remains more or less at about 72.5, 73, and 77% (for up to 420 min) over 1, 2, and 3 wt % BaO-promoted catalysts, respectively. The H2 yield is highest (i.e., 78%) for a catalyst with 4 wt % Ba loading (5Ni4Ba/YZr), and it remains constant for up to 420 min on TOS. The 5Ni4Ba/YZr catalyst also maintains the highest H2/CO ratio (i.e., 0.94) throughout the TOS (Figure 7B). The H2/CO and H2 yields increase as the reaction temperature increases from 500 to 800 °C, confirming the endothermic nature of the DRM reaction. Upon 5 wt % Ba, the H2 yield drops sharply to 70% (even less
Table 1. Comparison of Apparent Activation Energies for H₂ Formation across Various Catalyst Systems

| catalyst system   | Ni wt % | reaction temp (°C) | $R_{H}$ | slope    | apparent activation energy (kJ/mol) | ref    |
|-------------------|---------|--------------------|---------|----------|-------------------------------------|--------|
| 5Ni4Ba/YZr        | 5       | 500                | 0.21    | −2.41    | 20.07                               | our work |
|                   | 5       | 550                | 0.30    |          |                                     |        |
|                   | 5       | 600                | 0.48    |          |                                     |        |
|                   | 5       | 650                | 0.70    |          |                                     |        |
|                   | 5       | 700                | 0.90    |          |                                     |        |
|                   | 5       | 750                | 1.08    |          |                                     |        |
|                   | 5       | 800                | 1.13    |          |                                     |        |
| Ni/Zr             | 5       | 500                | 0.11    | −3.27    | 27.19                               | 43     |
|                   | 5       | 550                | 0.29    |          |                                     |        |
|                   | 5       | 600                | 0.44    |          |                                     |        |
|                   | 5       | 650                | 0.56    |          |                                     |        |
|                   | 5       | 700                | 0.79    |          |                                     |        |
| Ni-CeO₂/ZrO₂      | 5       | 500                | 0.13    | −3.08    | 25.61                               | 43     |
|                   | 5       | 550                | 0.26    |          |                                     |        |
|                   | 5       | 600                | 0.46    |          |                                     |        |
|                   | 5       | 650                | 0.57    |          |                                     |        |
|                   | 5       | 700                | 0.79    |          |                                     |        |
| Ni-La₂O₃/ZrO₂     | 5       | 500                | 0.22    | −2.56    | 21.28                               | 43     |
|                   | 5       | 550                | 0.35    |          |                                     |        |
|                   | 5       | 600                | 0.54    |          |                                     |        |
|                   | 5       | 650                | 0.69    |          |                                     |        |
|                   | 5       | 700                | 0.98    |          |                                     |        |
| Ni-K₂O/ZrO₂       | 5       | 500                | 0.22    | −2.62    | 21.78                               | 43     |
|                   | 5       | 550                | 0.33    |          |                                     |        |
|                   | 5       | 600                | 0.56    |          |                                     |        |
|                   | 5       | 650                | 0.70    |          |                                     |        |
|                   | 5       | 700                | 0.98    |          |                                     |        |
| Ni/ZrO₂-P         | 10      | 600                | 0.48    | −1.57    | 13.05                               | 133    |
|                   | 10      | 650                | 0.57    |          |                                     |        |
|                   | 10      | 700                | 0.67    |          |                                     |        |
|                   | 10      | 750                | 0.80    |          |                                     |        |
|                   | 10      | 800                | 0.92    |          |                                     |        |
| Ni/ZrO₂-C         | 10      | 600                | 0.38    | −2.16    | 17.96                               | 133    |
|                   | 10      | 650                | 0.43    |          |                                     |        |
|                   | 10      | 700                | 0.55    |          |                                     |        |
|                   | 10      | 750                | 0.74    |          |                                     |        |
|                   | 10      | 800                | 0.91    |          |                                     |        |
| 5Ni/8PZr          | 5       | 600                | 0.05    | −0.78    | 6.48                                | 86     |
|                   | 5       | 650                | 0.71    |          |                                     |        |
|                   | 5       | 700                | 0.07    |          |                                     |        |
|                   | 5       | 750                | 0.10    |          |                                     |        |
|                   | 5       | 800                | 0.18    |          |                                     |        |
| 10Ni/8PZr         | 10      | 500                | 0.01    | −4.28    | 35.58                               | 86     |
|                   | 10      | 550                | 0.05    |          |                                     |        |
|                   | 10      | 600                | 0.12    |          |                                     |        |
|                   | 10      | 650                | 0.11    |          |                                     |        |
|                   | 10      | 700                | 0.24    |          |                                     |        |
|                   | 10      | 750                | 0.28    |          |                                     |        |
|                   | 10      | 800                | 0.37    |          |                                     |        |
| 15Ni/8PZr         | 15      | 500                | 0.07    | −2.20    | 18.29                               | 86     |
|                   | 15      | 550                | 0.13    |          |                                     |        |
|                   | 15      | 600                | 0.14    |          |                                     |        |
|                   | 15      | 650                | 0.25    |          |                                     |        |
|                   | 15      | 700                | 0.29    |          |                                     |        |
|                   | 15      | 750                | 0.32    |          |                                     |        |
|                   | 15      | 800                | 0.40    |          |                                     |        |
| 20Ni/8PZr         | 20      | 500                | 0.07    | −2.23    | 18.54                               | 86     |
|                   | 20      | 550                | 0.13    |          |                                     |        |
|                   | 20      | 600                | 0.14    |          |                                     |        |
|                   | 20      | 650                | 0.25    |          |                                     |        |
than for the 1 wt % Ba-promoted sample) and decreases further to 65% within 420 min on TOS. Excess BaO may cover the available catalytic active sites at a high Ba loading (5 wt %), resulting in inferior performance compared to that of its counterparts. It appears that 4 wt % Ba is the optimal promotor loading for the yttria−zirconia-supported Ni catalyst to obtain the maximal H₂ yield and high H₂/CO. The hydrogen-formation rate over the 5Ni4Ba/YZr catalyst was found to be 1.14 (molH₂/gCat/h). The effect of temperature on the H₂-formation rate was also investigated in the temperature range of 500−800 °C. The apparent activation energy of 20.07 kJ/K/mol was estimated for H₂ formation over the 5Ni4Ba/YZr catalyst.

4. DISCUSSION

The catalytic activity of the zirconia-supported Ni catalyst in DRM is due to Ni²⁺ in octahedral coordination, a large surface area, the pore volume, and the bidentate format/monodentate
carbonate species. However, the presence of a reducible free/weakly interacting NiO species, a small pore size, and unstable monoclinic ZrO₂ phases limits the activity. The H₂TPR-CO₂TPD-H₂TPR cyclic experiment displayed a prominent quantity of a reducible free NiO species/weakly interacted NiO species. Weak metal-support interaction leads to Ni sintering at high temperatures, which causes a prominent carbon deposit. The 5Ni/Zr catalyst exhibited only 45% H₂ yield on TOS, and the TGA results showed a huge weight loss due to coke removal from this catalyst.

On the other hand, the yttria-zirconia-supported Ni catalyst had a small surface area but a relatively larger pore size. Furthermore, it mainly featured a cubic ZrO₂ phase and reducible Ni³⁺ species that were in octahedral coordination and strongly interacted with the support. This strong metal-support interaction, together with cubic ZrO₂ phase stabilization, resulted in a 71% H₂ yield over the 5Ni/YZr catalyst. The H₂-TPR followed by the CO₂-TPD experiment showed that the 5Ni/YZr catalyst has a higher oxygen-endowing capacity than the Ni/Zr catalyst. Although the 5Ni/YZr catalyst experienced similar weight loss due to carbon removal as the 5Ni/Zr catalyst, it demonstrated stable catalytic performance (71% H₂ yield) for up to 420 min, which indicates that the type of carbon deposit is amorphous and oxidizable and so does not block the catalytic active sites.

Upon addition of Ba promoter, the cubic BaZrO₃ phase additionally stabilizes the cubic ZrO₂ phase. When the Ba loading increases, the TGA result shows less weight loss in the spent catalysts. This indicates a greater oxygen-endowing capacity of the catalyst upon increasing the Ba loading to oxidize carbon deposits during the DRM. Among all Ba-promoted samples, 5Ni4Ba/YZr possesses the smallest NiO crystals (18.7 nm), excess CO₃²⁻ ionic species, a high-intensity charge-transition band from O²⁻ (2p, valence band) to Zr⁴⁺/Ni²⁺, and an optimal metal-support interaction. H₂-TPR followed by the CO₂-TPD experiment showed that the reduced 5Ni4Ba/YZr sample has a relatively more basic site concentration than the 5Ni/YZr catalyst. The H₂TPR-CO₂TPD-H₂TPR cyclic experiment shows the presence of only reducible NiO species strongly interacting with the support. It can be said that the metallic Ni species anchored on the cubic zirconia support facilitates CH₄ decomposition and that the resultant hydrocarbon intermediates are then oxidized by oxygen-containing surface species (e.g., ionic CO₃²⁻) or lattice oxygen. It conveys the highest H₂ yield of 78% commonly up to 420 min on TOS. The 4 wt % Ba is the optimum loading for the highest H₂ yield. When the Ba loading is increased to 5 wt %, the lattice planes are compacted and the NiO crystallite size increases. The excess Ba covers the accessible catalytic active sites, which in turn lowers the catalytic activity and stability. The 5Ni5Ba/YZr catalyst shows an inferior H₂ yield even below that of the 5Ni1Ba/YZr catalyst.

The catalytic activity of the above-discussed DRM catalysts and the other set of 54 DRM catalysts in terms of the H₂ yield, H₂ formation rate, and CO formation is shown in Table S3. The calculation details for hydrogen and CO formation rates are described in Supporting Information S2. Among the different catalysts synthesized in this study, the 5Ni4Ba/YZr catalyst showed the highest hydrogen formation rate (1.14 mol g⁻¹ h⁻¹). On the basis of the results in Table S3, it seems that the Ba promoter is a better choice than Ga, Mn, Al, Pr, Sm, and Nd promoters in terms of achieving a high hydrogen formation rate. At a ≤5 wt % Ni loading, a >0.9 H₂/CO ratio, and a ≤0.1 g catalyst weight, Sc, La, Gd, and Ce promoted ordered mesoporous silica-supported Ni catalyst systems demonstrated a higher rate of H₂ formation than our catalyst system. Nevertheless, the additional cost of structure-directing agents and complex catalyst preparation procedures may limit the industrialization potential of these materials. Following silica, some zirconia-based Ni catalysts were found to be more competent than our catalyst system in terms of H₂ production via DRM, such as the Cr-promoted lanterna-zirconia-supported Ni catalyst85 Ce-promoted lanta-nia-zirconia catalyst, and tungstate-zirconia-supported Ni catalyst. They showed 1.18 mol g⁻¹ h⁻¹, 1.23 mol g⁻¹ h⁻¹, 1.14 mol g⁻¹ h⁻¹ H₂ formation rate, respectively. Furthermore, we compared the apparent activation energy for H₂ formation among closely related zirconia-supported Ni catalyst systems (Table 1). Among 5 wt % Ni-loaded catalysts, the apparent activation energies of the 5Ni4Ba/YZr catalyst (this work) and phosphate-zirconia-supported catalyst (5Ni/8PZr)96 were 20.07 and 6.48 kJ/mol, respectively. However, in terms of activity, the 5Ni/8PZr catalyst had a much lower rate of hydrogen formation than our 5Ni4Ba/YZr catalyst.

5. CONCLUSIONS
Yttria-zirconia-supported Ni-based catalysts and 1–5 wt % Ba-promoted yttria-zirconia-supported Ni-based catalysts are characterized and tested in the dry reforming of methane. The 5Ni/Zr catalyst shows low catalytic activity of a 45% H₂ yield due to an unstable monoclinic ZrO₂ support and the presence of free/weakly interacting reducible NiO species. The high activity (71%) of the 5Ni/YZr catalyst is correlated with larger crystal size than the 5Ni/Zr catalyst. The 5Ni/YZr catalyst experienced lower weight loss due to carbon removal as the 5Ni/Zr catalyst, it demonstrated stable catalytic performance (71% H₂ yield) for up to 420 min, which indicates that the type of carbon deposit is amorphous and oxidizable and so does not block the catalytic active sites.

ASSOCIATED CONTENT
+ Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00471.

Catalyst characterization; pore size distribution of different catalyst samples; surface area, pore volume, and pore size of different catalyst samples; crystalline size of NiO and BaZrO₃ for different catalyst samples; UV−vis spectra of ZrO₂ and 5Ni/Zr catalysts; H₂-TPR profile of catalyst samples 5Ni/Zr and 5Ni6Ba/YZr (x = 0, 1, 2, 3, 4, and 5 wt %); catalyst activity of different catalyst (reported across the literature as DRM catalysts).
in terms of the conversion of CH₄ and the conversion of CO₂; yield of H₂, H₂/CO ratio; rates of hydrogen formation and CO formation; expression for calculating the rates of H₂ formation and CO formation from CO₂ conversion and CH₄ conversion data; and chromatograms of DRM product analysis over the SNI/Zr catalyst at 800 °C, DRM product analysis over the SNI/YZr catalyst at 800 °C, and DRM product analysis over the SNI4Ba/YZr catalyst at 800 °C. 

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Notes

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