

## Ni/CeO<sub>2</sub> catalysts synthesized by SCS with a porous $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support for efficient H<sub>2</sub> production via aqueous-phase glycerol reforming

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**ABSTRACT** Aqueous-phase reforming (APR) of glycerol for H<sub>2</sub> production was evaluated over a supported Ni/CeO<sub>2</sub> (CeNi) catalyst prepared by introducing a porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support into the reaction mixture during solution combustion synthesis. This approach enables the preparation of a catalyst with improved pore volume and average pore size, which is crucial for facilitating reactant diffusion. Unlike the bulk CeNi system, the presence of alumina increases the availability of active nickel nanoparticles and enhances ceria and nickel dispersion. The glycerol APR results show that CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> provides higher glycerol conversion and hydrogen yield compared to the bulk system. Notably, halving the active component content leads to a 2.3-fold increase in activity, which is independent of the feed flow rate and, consequently, of the extent of diffusion limitations. The catalyst obtained in this study outperformed known analogs in terms of H<sub>2</sub> formation rate, while maintaining high glycerol conversion and H<sub>2</sub> selectivity.

**KEYWORDS** nickel, ceria, alumina, solution combustion synthesis, aqueous-phase reforming, glycerol, hydrogen

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### 1. Introduction

Crude glycerol is the main by-product of biodiesel production, resulting from the transesterification of plant-based substances (100 g of glycerol *per* 1 kg of biodiesel) [1, 2]. Increased biodiesel manufacturing capacity is driving efforts to recycle glycerol to improve profitability and reduce waste, aided by lower glycerol prices [3, 4].

Aqueous phase reforming (APR) of glycerol [5] is one of the efficient and promising methods for converting it into valuable hydrogen, which is the main energy source of the future world [6]. In APR, reactants remain in the liquid phase, unlike steam reforming (SR), thus avoiding an energetically demanding vaporization-step [7]. In an ideal APR reaction, up to 7 moles of H<sub>2</sub> can be obtained from one mole of glycerol [8] by combining glycerol decomposition followed by the water-gas shift (WGS) reaction [9]. Mild APR conditions (200 – 260 °C; 20 – 50 bar) promote the WGS reaction [6, 10], which prevents the formation of excess CO [7]. Nevertheless, the immaturity of this technology requires ongoing research into active and stable catalysts that will increase the attractiveness of the process for industry [7, 11].

In order to facilitate the cleavage of C–C, C–H and O–H bonds in the glycerol molecule during the APR process, the catalyst should contain noble metals or nickel [7]. Nickel-based systems, known for their high availability and cost-effectiveness, have also attracted considerable attention as an alternative to more expensive metals. In addition to the main APR reaction, Ni nanoparticles are effective in C–O hydrogenolysis and CO/CO<sub>2</sub> methanation [12], because under H<sub>2</sub>-rich conditions, the metal sites rapidly hydrogenate these fragments to alkanes [13]. Collectively, this diminishes the production of hydrogen and consequently mitigates the necessity for regulating the distribution and accessibility of nickel particles.

The efficiency of this process is ensured by the selection of an appropriate catalyst support material. In particular, the use of CeO<sub>2</sub> is the most promising due to the increased oxygen mobility and the acceleration of the WGS reaction instead of methanation [12]. It was previously shown that the Ni–Ce–O system can successfully compete with noble metal-based catalysts (Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) in glycerol APR [5]. This was achieved using the solution combustion method (SCS) with a high glycine-to-oxidizer ratio. A similar advantage of this method over classical catalyst preparation methods (coprecipitation, impregnation) for glycerol APR was shown in [14], as well as in [15–20] for other processes. Moreover, this method ensures high dispersion and homogeneity of nanoparticles, as well as a spongy porous structure.

However, APR involves numerous side reactions: oxidation to dihydroxyacetone/glyceraldehyde/glyceric acid [21], hydrogenolysis into glycols [22], etherification [23], and esterification [24–26]. These reactions lead to the consumption

of  $H_2$ , which is formed during the main reaction. This requires the development of a more selective catalyst with respect to  $H_2$ -forming reactions. Furthermore, intense agglomeration of the material during SCS leads to sintering of the primary nanoparticles into dense conglomerates, which reduces the availability of active Ni nanoparticles and destroys useful open porosity [27]. To improve the economic efficiency of the APR process, it is essential to reduce the amount of active Ni/CeO<sub>2</sub> without compromising  $H_2$  yield.

These problems can be solved by switching from a bulk Ni/CeO<sub>2</sub> catalyst to supported catalysts in combination with the SCS method. This is achieved by introducing an external microstructural template (a porous oxide support), into the SCS reaction mixture. Using a template allows to significantly moderate combustion by reducing the maximum temperature and to localize the reaction in nanodomains between particles and in the nanopores of the support [28]. It has previously been shown that deposition of CeFeO<sub>3</sub> and LaFeO<sub>3</sub> perovskites on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> improves CO<sub>2</sub> hydrogenation catalyst performance.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acted as a support with a large surface area, which promotes finer dispersion of crystallites, increases oxygen defectiveness, and enhances the adsorption capacity for  $H_2$  and CO<sub>2</sub> [29, 30]. This combination of approaches made it possible to reduce the amount of active ferrite without losing catalytic activity and stability. More complex diffusion phenomena in the APR process, occurring in a three-phase system, are an additional argument in favor of using porous supports. Thus, this study aims to assess the potential of the solution combustion method for producing a Ni/CeO<sub>2</sub> catalyst in combination with a porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support to improve the efficiency of  $H_2$  production by aqueous-phase reforming of glycerol.

## 2. Experimental

### 2.1. Synthesis

NiO/CeO<sub>2</sub>-based systems (denoted as CeNi), both supported and bulk, were prepared by solution combustion synthesis (SCS) using glycine and nitrates.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, obtained by calcining AlOOH (Pural SB Lot. N. 233,144, Sasol) at 700 °C for 2 hours, was used as the support.

In a wide glass beaker (250 mL), an appropriate amount of glycine (99.2 %, LenReactiv, Russia) and the corresponding metal nitrates (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.0 %, NevaReactiv, Russia) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.1 %, LenReactiv, Russia)) were dissolved in deionized water (1 ml *per* 1 g of precursors) to obtain 1 g of NiO/CeO<sub>2</sub>. The theoretical NiO content was 30.3 wt % (or 23.8 wt % Ni). The fuel-to-oxidizer ratio ( $\varphi$ ) was taken 2 and calculated through the reducing and oxidizing valence states according to [5]. In the supported system, in addition to nitrates and glycine, 1 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (and 1 ml of water) was added to the initial solution, resulting in lower nickel concentration in final CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The aqueous solution or suspension with alumina was heated on an electric plate (1 kW) until boiling, after which spontaneous combustion occurred. In the final stage, the samples were heat treated at a temperature of 350 – 450 °C to burn off most of the remaining fuel and nitrates.

### 2.2. Characterization

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a DTG-60A analyzer (Shimadzu, Japan) by heating the sample in static air at a heating rate of 10 °C/min.

Infrared transmission spectra were determined using an IRTracer-100 spectrophotometer (Shimadzu, Japan) in the range from 4000 to 350 cm<sup>-1</sup>. One to two mg of each solid sample were mixed with 200 – 210 mg of vacuum-dried IR-grade KBr. The mixture was dispersed in an agate mortar and then formed into tablets under 12 tons of pressure and vacuum pumping in a steel die 13 mm in diameter.

X-ray diffraction (XRD) analysis was performed on an XRD-6100 diffractometer (Shimadzu, Japan) equipped with a Fe filter and a CoK $\alpha$  radiation source ( $\lambda_1 = 1.78897$  Å). The settings included 40 kV voltage, 30 mA current, a scan speed of 1 °/min, a step width of 0.02 °, and D(divergence):S(scatter):R(receiving) = 1:1:0.3. The diffraction data were analyzed using Crystallographica Search-Match ver. 2.0.3.1. The mean crystallite size was calculated using the Scherrer equation.

N<sub>2</sub> physical adsorption was carried out using an Autosorb-6iSA instrument (Quantachrome, USA) (for the supported CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and alumina) and an ASAP 2020 device (Micromeritics, USA) (for bulk CeNi). The samples were pre-degassed at 200 – 250 °C in vacuum. The specific surface area and total pore volume were determined using the BET equation. The NLDT method was used to calculate pore size distributions.

To obtain high-resolution images and conduct elemental microanalysis of solid samples, a VEGA 3 SBH microscope (Tescan, Czech Republic) equipped with an EDS INCAx-act detector (Oxford Instruments, England) was used.

Temperature-programmed reduction with hydrogen ( $H_2$ -TPR) and temperature-programmed desorption of  $H_2$  ( $H_2$ -TPD) were performed on a SOLO Chemosorb unit (Russia) equipped with a thermal conductivity detector and a MC7-200D quadrupole mass analyzer (Institute for Analytical Instrumentation of Russian Academy of Sciences).

In  $H_2$ -TPR tests, from 13 to 42 mg of a powder was reduced from 70 – 150 to 800 °C at a 10 °/min rate under 20 mL/min of 10 vol %  $H_2$ /Ar (99.9999 vol % purity) in the presence of a water vapor trap.

In  $H_2$ -TPD, 50 – 100 mg of a sample was first reduced *in situ* by a  $H_2$ /Ar flow (50:50 vol %, 40 mL/min) at a ramp rate of 20 °/min to 450 or 550 °C (for supported systems) and 10 °/min to 500 or 600 °C (for supported systems) and held

for 30 min. Then it was cooled to 60 °C and saturated with H<sub>2</sub> (H<sub>2</sub>/Ar flow, 50:50 vol %, 20 mL/min) for 20 min. The removal of physically adsorbed H<sub>2</sub> was monitored using a mass spectrometer by purging with argon (20 mL/min), after which the sample was heated to 600 °C at a ramping rate of 10 °C/min.

The nickel dispersion (%), specific metal surface area (m<sup>2</sup>/g-Ni), and the average Ni diameter (nm) were calculated by assuming a stoichiometry ratio of H/Ni using equations from [5].

### 2.3. Catalytic tests

Catalyst tests in aqueous phase reforming (APR) of glycerol (99.3 %, NevaReactiv, Russia) were carried out using a fixed bed reactor in the downflow (top-down) mode. The reactor was a cylindrical stainless-steel tube 46 cm in length, with an inner diameter of 4 mm, and a wall thickness of 1 mm. A two-zone furnace was used to heat and expand the isothermal zone of the reactor. The separator volume is 47 ml.

The required amount of catalyst granules (660±3 mg) of fraction 0.1 – 0.3 mm was mixed with quartz granules of fraction 0.45 – 0.90 mm to a total volume of 2 mL. The upper unfilled part of the reactor was packed with quartz granules of the same fraction. The installation was considered hermetically sealed if the pressure drop in it did not exceed 0.10 bar in 10 minutes at an excess pressure of 39.00 bar for N<sub>2</sub>.

Before testing, the samples were preliminarily reduced in H<sub>2</sub> flow (40 mL/min) for 30 min at a temperature in accordance with the results of H<sub>2</sub>-TPR. All tests were performed at an excess pressure of 35.00 ± 0.05 bar and a temperature of 231 ± 2 °C measured under the catalyst bed. For all tests, the reactor was fed with a flow of N<sub>2</sub> (99.999 vol % purity, 32 mL/min) and liquid feedstock (a mixture of 10 wt % of glycerol and water; total liquid flow 0.05 or 0.12 mL/min). Liquid sampling was performed after 3 hours of accumulation at a feed flow rate of 0.05 ml/min, and after 1 hour of accumulation at 0.12 mL/min.

### 2.4. Method for determining the composition of APR products

A Test-1 gas analyzer (BONER, Russia) was used for online monitoring of H<sub>2</sub>, CO<sub>2</sub>, and CO concentrations in the gaseous products. The detailed composition of the gaseous products was analyzed using a Crystallux-4000M gas chromatograph (Meta-Chrom, Russia) equipped with two thermal conductivity detectors and two packed columns: a CaA column (3 m × 3 mm) and a Haysep Q column (3 m × 2 mm). Hydrogen and argon were used as carrier gases, and the column temperature was maintained constant at 80 °C throughout the analysis. The following compounds were detected in the chromatograms: H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>.

The method for calculating glycerol conversion into gaseous products ( $X(G)_{gas}$ , %), the yield of hydrogen ( $Y(H_2)$ , % of stoichiometry), and selectivity ( $S(i)$ , %) is similar to that used in the previous study [5, 15, 31].

The residual concentration of glycerol in the liquid products was determined using the external standard method on the same gas chromatograph, equipped with a TRB WAX capillary column (30 m × 0.32 mm × 0.5 μm) and a flame ionization detector. The method described in [32] was used as the reference conditions. The residual glycerol concentration,  $C(G)_\tau$ , in liquid APR products was determined using the known concentration of 1,4-butanediol in the sample and a dilution factor.

The total conversion of glycerol  $X(G)_{sum}$  was calculated as:

$$X(G)_{sum} = \frac{C(G)_0 - C(G)_\tau}{C(G)_0}, \quad (1)$$

where  $C(G)_0$  is the initial concentration of glycerol in the feedstock (10 wt %).

## 3. Results and discussion

### 3.1. Combustion efficiency and surface functional groups

The total weight change upon heating in air (Fig. 1) and IR spectroscopy data (Fig. 2) indicate that some amount of unburned fuel and nitrates remained in the as-prepared bulk and supported NiO–CeO<sub>2</sub> systems (designated as CeNi and CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively). Overall, excluding physical water, the residual glycine-nitrate precursor ranged from 2.1 to 3.7 wt % (Fig. 1). Combustion in the presence of alumina leads in increased weight loss compared to the bulk CeNi system. This phenomenon can be explained by a decrease in the peak combustion temperature as a result of partial absorption of the released heat by the support. Accordingly, DTA revealed a shift of the exothermic peak upon the addition of alumina from 323 to 314 °C attributed to the combustion-type decomposition of free glycine and its complexes [33]. Water desorption is accompanied by thermal degradation of nitrate ions at a temperature of approximately 163 °C.

Prior to FTIR analysis, the samples were further heat-treated at 350 – 450 °C to remove the majority of residual fuel and nitrates. The presence of the most intense absorption bands in the far-infrared region indicates the formation of metal–oxygen bonds (Fig. 2). For the bulk nanocomposite, an absorption band was found at 414 cm<sup>−1</sup>, which can be attributed to O–Ce–O stretching vibrations [34, 35]. For the alumina-based system, two peaks can be identified at 452 and 733 cm<sup>−1</sup>, which are associated with vibrations of the Al–O bonds in octahedral [AlO<sub>6</sub>] and tetrahedral units [AlO<sub>4</sub>], respectively [36, 37]. It is clear that nickel and cerium oxides provide a significant signal enhancement in the region of 452 cm<sup>−1</sup> relative to the 733 cm<sup>−1</sup> peak, which is not typical for pure alumina.

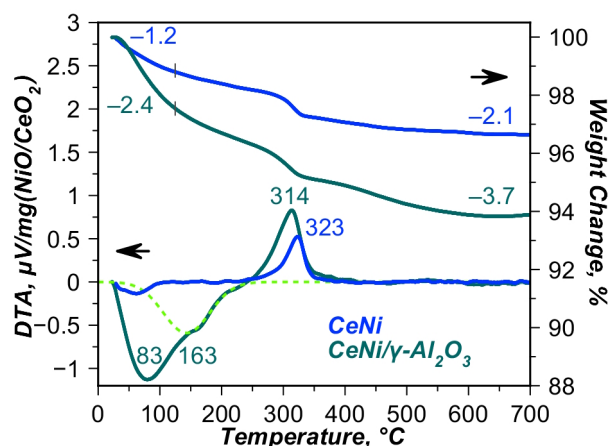


FIG. 1. DTA–TGA data of the as-prepared bulk and alumina-supported CeNi-based samples obtained by glycine-nitrate combustion method (SCS)

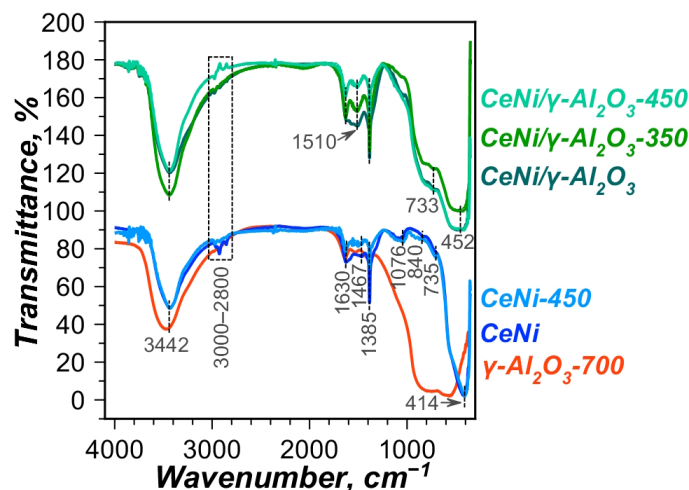


FIG. 2. IR spectra of the as-prepared and calcined samples produced using glycine-nitrate combustion (SCS)

Peaks observed in the ranges of 1630 and 3442  $\text{cm}^{-1}$  are due to bending and stretching vibrations of surface hydroxyl groups or molecular water. The presence of nitrate groups is confirmed by peaks at 840, 1385, and 1510  $\text{cm}^{-1}$ . The bands at 1467 and 2800–3000  $\text{cm}^{-1}$  indicate the presence of stretching and bending vibrations of aliphatic C–H bonds, while the peak at 1076  $\text{cm}^{-1}$  confirms the absorption of the amino acid group.

### 3.2. Phase composition and crystallinity

Figure 3 shows XRD patterns of bulk and supported CeNi systems, as well as  $\gamma\text{-Al}_2\text{O}_3$ . In the CeNi-alumina system, no noticeable shift in the position of the 440 peak was detected, indicating minimal structural changes in the crystal lattice of alumina. Based on the obtained values of the average size of  $\text{CeO}_2$  crystallites (Table 1), it can be concluded that the combustion of nickel–ceria in the presence of alumina occurs under milder conditions (than for the bulk CeNi system, confirmed by DTA–TGA), which makes it possible to obtain smaller particles.

TABLE 1. Peak positions and average crystallite size for the synthesized materials

| Sample                                    | $\text{CeO}_2$ (111)           |                      | $\text{NiO}$ (200)             |                      |
|-------------------------------------------|--------------------------------|----------------------|--------------------------------|----------------------|
|                                           | Peak position, $2\theta^\circ$ | Crystallite size, nm | Peak position, $2\theta^\circ$ | Crystallite size, nm |
| CeNi-350                                  | 33.227                         | 6.2                  | 50.692                         | 5.0                  |
| CeNi/ $\gamma\text{-Al}_2\text{O}_3$ -350 | 33.342                         | 2.8                  | 51.248                         | 5.2                  |

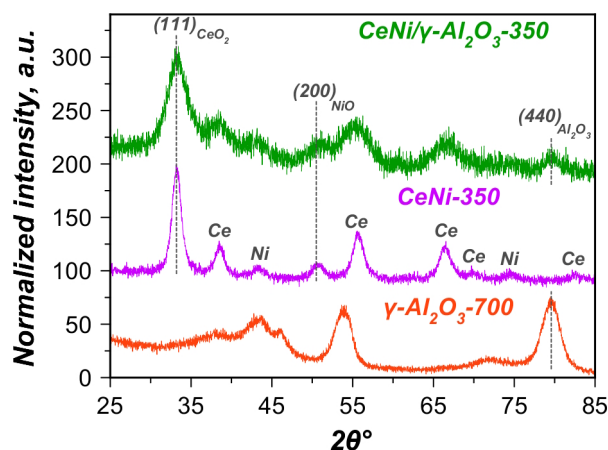


FIG. 3. XRD patterns of  $\gamma$ -alumina and materials synthesized by the glycine-nitrate combustion method (SCS) (additionally calcined at 350 °C), where reflections designated as Ni and Ce represents their oxides according to PDF cards No. 44-1159 (cubic) and 75-120 (cubic), respectively

### 3.3. Morphology and porosity

Alumina and all synthesized samples exhibit an IUPAC type IV(a) isotherm, characteristic of a mesoporous structure (Fig. 4a). The small total pore volume  $\Sigma V_{\text{pores}}$  (0.09 cm<sup>3</sup>/g) and moderate specific surface area  $S_{\text{BET}}$  (27 m<sup>2</sup>/g) in the bulk CeNi sample is probably due to secondary porosity and aggregation of small crystalline particles. This is also confirmed by the H4 hysteresis loop, a phenomenon often observed in aggregated crystals. In contrast, the support exhibits an H1-type loop (almost parallel vertical adsorption and desorption branches), which is typical for materials with well-defined cylindrical mesopores or a narrow pore size distribution.

In the supported CeNi system obtained by the SCS method, a combined hysteresis loop of H1 and H4 is observed, because parallelism is broken at high relative pressures, and at  $P/P_0 = 0.4$ , compared to alumina, a characteristic sharp step-down the desorption branch appears. In this case, a decrease in  $S_{\text{BET}}$  and  $\Sigma V_{\text{pores}}$  is also observed (Table 2).

TABLE 2. Textural characteristics of the obtained CeNi-based systems and comparison with alumina and literature data

| Sample                                                  | Synthesis method                | Temperature calcination, °C | Ni, wt % | Ce, wt % | $S_{\text{BET}}$ , m <sup>2</sup> /g | $\Sigma V_{\text{pores}}$ , cm <sup>3</sup> /g | Average pore diameter, nm |
|---------------------------------------------------------|---------------------------------|-----------------------------|----------|----------|--------------------------------------|------------------------------------------------|---------------------------|
| $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -700           | —                               | 700                         | 0        | 0        | 200                                  | 0.50                                           | 10.0                      |
| CeNi                                                    | SCS with glycine, $\varphi = 2$ | —                           | 23.8     | 56.8     | 27                                   | 0.09                                           | 13.3                      |
| CeNi/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -450     | SCS with glycine, $\varphi = 2$ | 450                         | 11.9     | 28.4     | 119                                  | 0.38                                           | 12.8                      |
| Ni/Al <sub>2</sub> O <sub>3</sub> [38]                  | Wet impregnation                | 600                         | 15       | 0        | 175                                  | 0.57                                           | —                         |
| Ni <sub>20</sub> Al <sub>2</sub> O <sub>3</sub> -M [39] | Microwave method                | 400                         | 20       | 0        | 163                                  | 0.49                                           | 10.0                      |
| Ni <sub>20</sub> Al <sub>2</sub> O <sub>3</sub> -I [39] | Improved impregnation           | 400                         | 20       | 0        | 144                                  | 0.42                                           | 12.3                      |
| NiCeAl (R=4) Ce:Al = 4.9 [40]                           | EISA method                     | 700                         | 7        | 10.8     | 64                                   | 0.24                                           | 11.5                      |
| Ni/10Ce-Al [41]                                         | Incipient wetness impregnation  | 600                         | 10       | 9.1      | 198                                  | 0.36                                           | 6.8                       |
| Ni/CeAl [42]                                            | Wet impregnation                | 500                         | 10.0     | 14.8     | 141                                  | 0.31                                           | 6.1                       |
| Ni-IS [43]                                              | Impregnation                    | 500                         | 20       | 9.8      | 121                                  | 0.21                                           | 7.0                       |

The pore size distribution for the bulk CeNi system is relatively wide compared to the system containing alumina (Fig. 4b). It is evident that wider pores of alumina become clogged more strongly than smaller ones. In addition, in the alumina-supported CeNi system, the pore distribution pattern repeated the long tail of the bulk system at large diameters (Fig. 4c).

A comparison with literature data shows that cerium-free samples have higher surface areas (144 – 175 m<sup>2</sup>/g) and pore volumes (0.42 – 0.57 cm<sup>3</sup>/g); these values, however, depend on the alumina properties, synthesis conditions, and

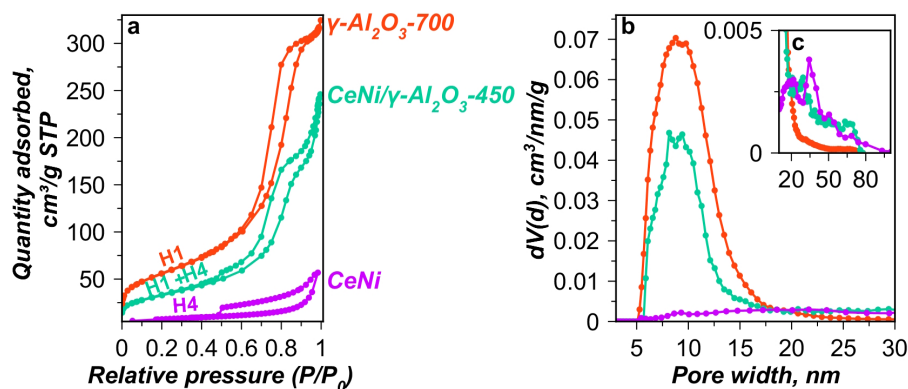


FIG. 4.  $N_2$  adsorption–desorption isotherms (a) and DFT pore size distribution (b,c) for CeNi-based systems and alumina support

nickel content (Table 2). Compared to  $Ni/Al_2O_3$ ,  $\Sigma V_{pores}$  of cerium-containing systems drops more significantly, falling to  $0.21 - 0.36 \text{ cm}^3/\text{g}$ . An even more significant influence was observed for the average pore diameter, which diminished to mostly  $6 - 7 \text{ nm}$ . This is in contrast to  $CeNi/\gamma-Al_2O_3-450$  synthesized in this study, which has an average pore diameter of  $12.8 \text{ nm}$ . Therefore, the SCS method including the support is preferable to retain the significant pore volume and average pore size of  $CeNi/\gamma-Al_2O_3$ , which may be crucial to facilitate the diffusion of reactants.

According to SEM and EDX mapping of morphologically distinct regions, the  $CeNi/\gamma-Al_2O_3$  sample consisted of dense dark sub-round particles and a light foam-like phase (Fig. 5b,c). Foam was observed around and on the surface of dark particles with high aluminum and low nickel-cerium content compared to light particles (Fig. 5b, Table 3), which suggests the formation of a variable-thickness Ce–Ni–O layer on the alumina surface. Analysis of the distribution of elements in numerous particles reveals large areas where alumina predominates (Fig. 5d).

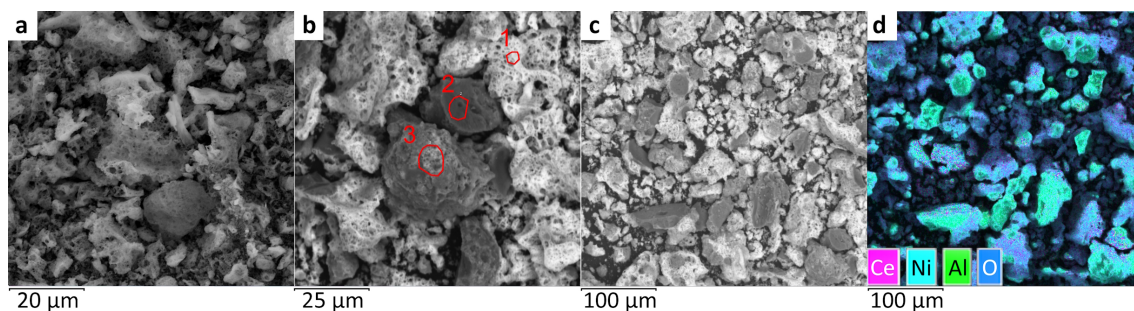


FIG. 5. SEM images (a–c) and EDX elemental mapping (d) and of bulk (a) and alumina-supported (b–d) NiCe-based systems obtained by SCS

TABLE 3. EDX results for different areas of  $CeNi/\gamma-Al_2O_3-350$  presented in Fig. 5b

| Area | Ni   | Ce   | Al   | O    |
|------|------|------|------|------|
| 1    | 19.2 | 47.7 | 4.2  | 28.9 |
| 2    | 18.2 | 40.4 | 18.7 | 22.8 |
| 3    | 10.4 | 25.3 | 30.3 | 34.1 |

### 3.4. Reducibility and nickel dispersion

$H_2$ -TPR analysis clearly shows that the obtained bulk and supported CeNi-based systems begin to react with hydrogen at  $150 - 200^\circ\text{C}$  (Fig. 6a). The most symmetrical peak of hydrogen consumption with a maximum of  $329^\circ\text{C}$  is observed in the bulk CeNi system, which is even  $15^\circ\text{C}$  less than that of the reference NiO obtained from nickel nitrate by calcination. Increasing the heat treatment temperature from  $350$  to  $450^\circ\text{C}$  cleans the surface of the studied systems from residual organic compounds or incompletely decomposed nitrates, which changes  $H_2$ -TPR profiles. In contrast,  $CeNi/\gamma-Al_2O_3$  exhibits more complex reduction spectra with peaks shifted towards higher temperatures. Moreover, when normalized by  $NiO/CeO_2$  mass, the bulk composite system exhibits a peak intensity 1.8 times higher than the alumina-based system.

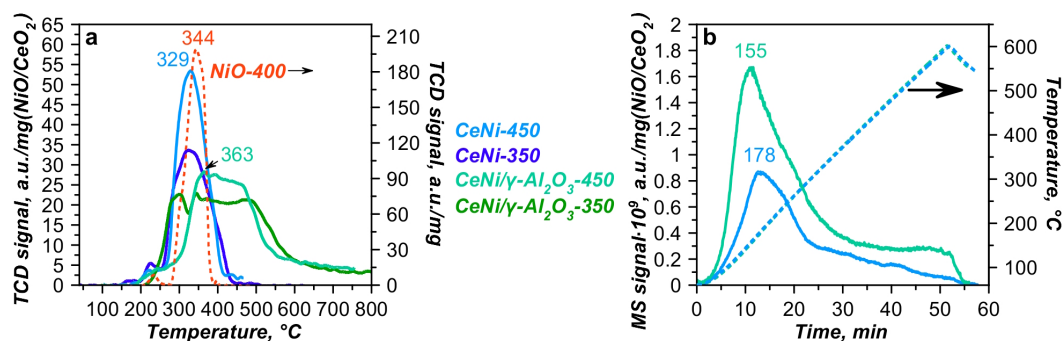


FIG. 6. H<sub>2</sub>-TPR profiles (a) and H<sub>2</sub>-TPD spectra (b) for calcined samples produced using SCS. Nickel oxide reference was prepared from nickel nitrate by calcination at 400 °C

To further investigate the influence of support presence on the H<sub>2</sub> adsorption capacity, an H<sub>2</sub>-TPD analysis was performed (Fig. 6b). The results show that the main temperature range of desorption occurs for weakly bound hydrogen. The desorption intensity in the bulk system is significantly lower compared to the system containing alumina. Thus, the SCS synthesis using alumina ensured high accessibility of the active sites. The principal difference between the bulk and supported systems is in the region of strongly bound hydrogen (above 200 °C). The large signal areas observed for the supported system indicate that nickel is dispersed as smaller nanoparticles, unlike the bulk system.

Direct comparison of the samples shows that using of alumina has a positive effect on nickel dispersion (Table 4). In the unsupported system, the Ni dispersion decreases sharply to 7.1 %, while the particle size increases to 14.3 nm, highlighting the important role of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a spatial spacer to achieve a highly dispersed state of nickel. The larger particle sizes of Ni detected by H<sub>2</sub>-TPD compared to NiO determined by XRD indicate that although individual Ni crystallites are small, they aggregate together.

TABLE 4. Ni dispersion, particle size, and surface area for the obtained CeNi-based samples and comparison with literature data

| Sample                                                         | Synthesis method                | Temperature calcination, °C | Ni, wt % | Ce, wt % | Ni dispersion, % | Ni surface area, m <sup>2</sup> /g | Ni particle size, nm |
|----------------------------------------------------------------|---------------------------------|-----------------------------|----------|----------|------------------|------------------------------------|----------------------|
| CeNi-450                                                       | SCS with glycine, $\varphi = 2$ | 450                         | 23.8     | 56.8     | 7.1              | 47.3                               | 14.3                 |
| CeNi/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -450            | SCS with glycine, $\varphi = 2$ | 450                         | 11.9     | 28.4     | 13.8             | 92.1                               | 7.3                  |
| Ni/Al <sub>2</sub> O <sub>3</sub> -450 [44]                    | Wet impregnation                | 450                         | 9.6      | 0        | 4.3              | —                                  | 12.6                 |
| Ni/Al <sub>2</sub> O <sub>3</sub> [38]                         | Wet impregnation                | 600                         | 15       | 0        | 4.3              | 4.3                                | 23.7                 |
| Ni <sub>20</sub> Al <sub>2</sub> O <sub>3</sub> -M [39]        | Microwave method                | 400                         | 20       | 0        | 25.3             | —                                  | 10                   |
| Ni <sub>20</sub> Al <sub>2</sub> O <sub>3</sub> -I [39]        | Improved impregnation           | 400                         | 20       | 0        | 16.6             | —                                  | 15                   |
| Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (N-N) [46] | Incipient wetness impregnation  | 500                         | 9.9      | 2.5      | 3.2              | 21.4                               | —                    |
| NiCeAl (R=4) Ce:Al = 4.9 [40]                                  | EISA method                     | 700                         | 7        | 10.8     | 11.7             | 1.9                                | 6.2                  |
| Ni/10Ce-Al [41]                                                | Incipient wetness impregnation  | 600                         | 10       | 9.1      | 23.7             | —                                  | 2.7                  |
| 20 %Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> [45]   | Wet impregnation                | 400                         | 20       | 42.5     | 1.2              | 7.7                                | —                    |

It is evident that cerium-free conventional impregnation leads to low dispersion (4.3 %) and the generation of large nickel particles (12.6 nm) [44]. Under more severe conditions (600 °C and higher loading), the particle size increases further to 23.7 nm [38]. The effect of cerium inclusion on nickel dispersion is not straightforward. In the Ni/10Ce-Al sample with 9.1 % Ce [41], a very high dispersion (23.7 %) and extremely small nickel particle size (2.7 nm) are achieved, which is explained by the ability of CeO<sub>2</sub> to stabilize the metal and prevent sintering. Nevertheless, achieving such high

dispersion entails a trade-off in the form of diminished transport properties. With a significant excess of cerium (42.5 % in the study [45]), dispersion decreases to 1.2 %, presumably because ceria layers cover the nickel surface and block the active sites. Microwave synthesis and improved impregnation method of Ni/Al<sub>2</sub>O<sub>3</sub> [39] in the absence of cerium yield high dispersion of 16.6 – 25.3 % and particle size of 10 – 15 nm, demonstrating that there are alternative routes to obtain highly dispersed nickel without the addition of Ce.

The CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-450 sample synthesized in this study occupies an intermediate position: it exhibits moderate dispersion with the most favorable pore properties of all cerium-containing materials. This makes it attractive for practical applications requiring a combination of good active site accessibility and efficient mass transfer, such as steam/aqueous-phase reforming or hydrodesulfurization reactions involving large molecules.

### 3.5. Catalytic performance in APR

The results obtained from testing the synthesized catalysts in APR are shown in Fig. 7 and Table 6. These data clearly indicate that CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-450 achieved the highest conversion of glycerol into gaseous products (Fig. 7a) and the highest hydrogen yield (Fig. 7b). Accounting for the absolute nickel content, the H<sub>2</sub> formation rate (Fig. 7c) enables a more meaningful catalyst activity comparison. It is evident that halving the active component loading resulted in a 2.3-fold increase in activity that was unaffected by WHSV and, hence, by the extent of diffusion limitations. Thus, the combination of SCS method and porous support provided a synergistic effect on the catalytic activity in APR.

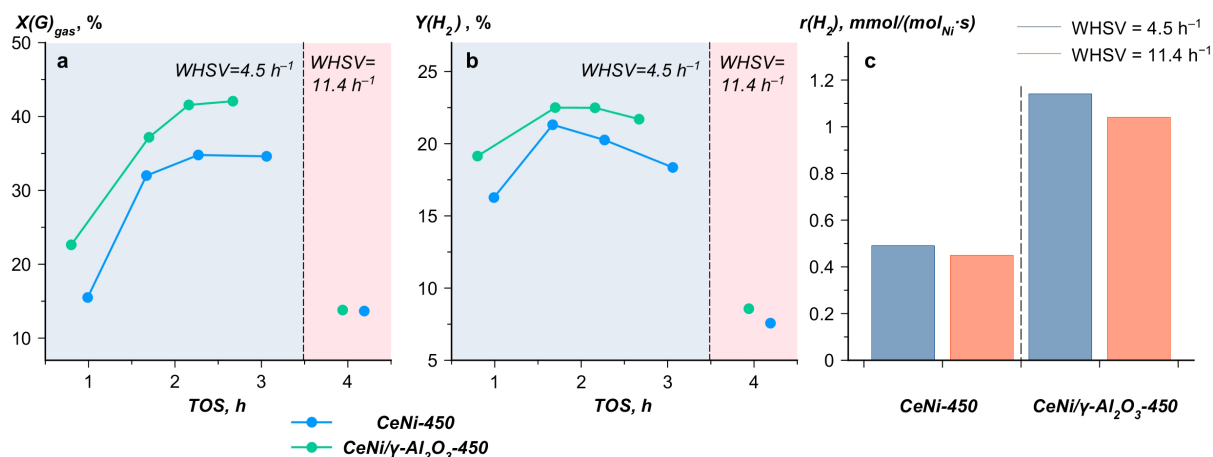


FIG. 7. Glycerol conversion into gaseous products (a), hydrogen yield (b) over time-on-stream and the rate of H<sub>2</sub> formation *per* mole of Ni (c)

Table 5 presents a comparison of the catalyst behavior of CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-450 catalyst with literature analogues. Catalysts containing similar active components and support were selected under comparable APR testing conditions ( $T = 225 - 250$  °C,  $P = 20 - 41$  bar, 10 – 15 wt % glycerol in the feedstock). Clearly, the catalyst obtained in this study outperformed known analogs in terms of H<sub>2</sub> formation rate  $r(H_2)$ , while maintaining high glycerol conversion and H<sub>2</sub> selectivity. Moreover, this advantage remained consistent across various feed flow rates.

As expected, increasing WHSV led to lower values for total glycerol conversion, conversion of glycerol into gaseous products, and hydrogen yield. This phenomenon is due to the reduced role of the primary reaction between glycerol and water, which produces H<sub>2</sub> and CO<sub>2</sub>, a characteristic of glycerol transformation processes [5, 31]. In addition, there was also a general increase in  $S(H_2)$  and  $S(CO_2)$ , but selectivity towards other products decreased (Table 6).

Two factors explain the above-mentioned effect. Firstly, increasing the pressure with an excess H<sub>2</sub> relative to CO<sub>2</sub> promotes an increase in the yield of methane [51]. This route is also supported by the fact that methane formation increases with increasing conversion of glycerol to gaseous products during glycerol SR [5, 31]. The same trend is seen in the present study when comparing glycerol conversion and  $S(CH_4)$  at varying feed flow rates (Table 6). However, this route does not explain the formation of other hydrocarbons [52]. Therefore, secondly, CO and hydrocarbons can be by-products in a complex chain of consequence-parallel reactions of glycerol (de)hydrogenation and dehydration [5, 10, 53] involving metallic nickel nanoparticles and the acid sites of the catalyst. During glycerol SR, the formation of ethane and propane occurs predominantly with decreasing conversion of glycerol to gaseous products [5, 31]. In this study, as glycerol conversion diminished, selectivity to CO and hydrocarbons also declined. This finding underscores the significant influence of liquid by-products on selectivity.

Therefore, with increasing the feed flow rate, the observed increase in  $S(H_2)$  and  $S(CO_2)$  can be explained by a decrease in the contribution of CO<sub>2</sub> hydrogenation to CH<sub>4</sub> and CO, as well as a decrease in H<sub>2</sub> consumption for the hydrogenation of intermediate liquid products. Evidently, the decrease in  $S(H_2)$  and  $S(CO_2)$  coupled with the increase

TABLE 5. The catalyst performance of CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SCS-450 in APR compared with literature data

| Catalyst                                                                     | Synthesis method   | Ni <sup>0</sup> , nm      | Reactor and reaction conditions                                              | Results                                                                                                                                                                                                    | Reference  |
|------------------------------------------------------------------------------|--------------------|---------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| 11.9 %34.9 %CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -450 | SCS, $\varphi = 2$ | 7.3 (H <sub>2</sub> -TPD) | Fixed bed, 231 °C, 35 bar, 2 – 2.5 h, 4.5 h <sup>-1</sup> , 10 wt % glycerol | $X(G)_{\text{sum}} = 100\%$ ;<br>$X(G)_{\text{gas}} = 42.1\%$ ;<br>$Y(\text{H}_2) = 21.7\%$ ;<br>$r(\text{H}_2) = 1.14 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$ ;<br>$S(\text{H}_2) = 54.1\%$ | This study |
| 11.9 %34.9 %CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -450 | SCS, $\varphi = 2$ | 7.3 (H <sub>2</sub> -TPD) | Fixed bed, 231 °C, 35 bar, 3.9 h, 11.4 h <sup>-1</sup> , 10 wt % glycerol    | $X(G)_{\text{sum}} = 25\%$ ;<br>$X(G)_{\text{gas}} = 13.8\%$ ;<br>$Y(\text{H}_2) = 8.6\%$ ;<br>$r(\text{H}_2) = 1.04 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$ ;<br>$S(\text{H}_2) = 61.9\%$   | This study |
| 14.24 %Ni/CeO <sub>2</sub> [47]                                              | Precipitation      | 5.3 (XRD)                 | Fixed bed, 250 °C, 20 bar, 20 h, 5 h <sup>-1</sup> , 15 wt % glycerol        | $X(G)_{\text{gas}} = 17.3\%$ ;<br>$S(\text{H}_2) = 95.7\%$                                                                                                                                                 | [47]       |
| 33.2 %Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> [48]                      | Sol-gel            | 25.7 (XRD)                | Batch, 250 °C, 41.4 bar, 3.9 h, 1.8 wt % glycerol                            | $X(G)_{\text{gas}} = 49.0\%$ ;<br>$Y(\text{H}_2) = 31.0\%$ ;<br>$S(\text{H}_2) = 62.0\%$                                                                                                                   | [48]       |
| NiAl <sub>2</sub> O <sub>4</sub> (33.2 % Ni) [49]                            | Precipitation      | 16.0 (XRD)                | Fixed bed, 235 °C, 35 bar, 3 h, 24.5 h <sup>-1</sup> , 10 wt % glycerol      | $X(G)_{\text{sum}} = 65.0\%$ ;<br>$X(G)_{\text{gas}} = 27.0\%$ ;<br>$Y(\text{H}_2) = 8.0\%$ ;<br>$r(\text{H}_2) = 0.68 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$ ;<br>$S(\text{H}_2) = 37.0\%$ | [49]       |
| 1.3 %Ni4.6 %Co/6.0 %CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>         | CCMU               | —                         | Fixed bed, 225 °C, 25 bar, 2.5 h, 4.9 h <sup>-1</sup> , 10 wt % glycerol     | $X(G)_{\text{sum}} = 23 \pm 1.2\%$ ;<br>$r(\text{H}_2) = 0.12 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$ ;<br>$S(\text{H}_2) = 83.0\%$                                                          | [50]       |

TABLE 6. Gas product selectivity in the APR process

| Sample                                              | $X(G)_{\text{sum}}, \%$ | $S(\text{H}_2), \%$ | $S(\text{CO}_2), \%$ | $S(\text{CH}_4), \%$ | $S(\text{C}_2\text{H}_6), \%$ | $S(\text{C}_3\text{H}_8), \%$ | $S(\text{CO}), \%$ |
|-----------------------------------------------------|-------------------------|---------------------|----------------------|----------------------|-------------------------------|-------------------------------|--------------------|
| $WHSV = 4.5 \text{ h}^{-1}$ and TOS = 2 – 2.5 h     |                         |                     |                      |                      |                               |                               |                    |
| CeNi-450                                            | 100                     | 58.2                | 70.3                 | 15.8                 | 1.4                           | 1.8                           | 10.7               |
| CeNi/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -450 | 100                     | 54.1                | 68.0                 | 20.9                 | 1.0                           | 0.9                           | 9.3                |
| $WHSV = 11.4 \text{ h}^{-1}$ and TOS = 3.9 – 4.2 h  |                         |                     |                      |                      |                               |                               |                    |
| CeNi-450                                            | 39.3                    | 55.1                | 74.2                 | 15.0                 | 1.2                           | 1.4                           | 8.1                |
| CeNi/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -450 | 25.0                    | 61.9                | 74.6                 | 17.1                 | 0.5                           | 0.5                           | 7.4                |

in  $S(\text{CH}_4)$  observed for CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-450 can be attributed to the increased dispersion of nickel particles, which in turn enhanced the hydrogenation function of the catalyst.

The importance of the various catalyst functions also becomes apparent when assessing its deactivation. This is difficult to determine definitively, as glycerol conversion to gaseous products does not decrease with increasing TOS. The drop in hydrogen yield observed with increasing TOS can be explained by the increasing role of RWGS, which produces CO. This is supported by the observed increase in  $S(\text{CO})$  and decrease in  $S(\text{CO}_2)$  as a function of TOS (data not shown). An additional contribution could potentially come from side reactions of hydrogenation of liquid intermediates; however, the decrease in selectivity to ethane and propane indicates deactivation of acid sites responsible for these reactions. The smallest decrease in hydrogen yield and formation of undesirable hydrocarbons are observed over CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-450.

The catalyst test results show a distinct period of increasing conversion and hydrogen yield. This effect is primarily due to the filling of the catalytic unit volume with gaseous products of the APR process, which has also been shown in other studies [5, 50]. However, the varying periods of stabilization of the parameters in Fig. 7 suggest an additional effect associated with an induction period of catalysts under process conditions.

#### 4. Conclusions

The methods used to develop catalysts significantly influence their structure, surface properties, and catalytic performance. Solution combustion synthesis (SCS) has proven to be a reliable and versatile method for the rapid production of catalytic materials, allowing the creation of highly dispersed and porous structures that are crucial for achieving high catalytic efficiency in complex chemical reactions. Specifically, in aqueous-phase reforming (APR) of glycerol for hydrogen production, the Ni/CeO<sub>2</sub> (CeNi) system developed using this method shows potential to compete with noble metal-based catalysts.

In this study, glycerol APR was evaluated over a supported Ni/CeO<sub>2</sub> catalyst prepared by introducing a porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support into the SCS reaction mixture. This approach enables the preparation of a catalyst with improved pore volume and average pore size, which is crucial for facilitating reactant diffusion. Unlike the bulk CeNi system, the presence of alumina increases the availability of active nickel nanoparticles and enhances nickel dispersion. This underscores the important role of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a spatial spacer for achieving a highly dispersed nickel state. Because the support partially absorbs the released heat, the peak combustion temperature is reduced, thereby explaining this phenomenon.

The glycerol APR results show that CeNi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> provides higher glycerol conversion and hydrogen yield compared to the bulk system. Notably, halving the active component content leads to a 2.3-fold increase in activity, which is independent of the feed flow rate and, consequently, of the extent of diffusion limitations. The catalyst obtained in this study outperformed known analogs in terms of H<sub>2</sub> formation rate, while maintaining high glycerol conversion and H<sub>2</sub> selectivity. Thus, reducing the amount of Ni/CeO<sub>2</sub> without reducing the H<sub>2</sub> yield increases the economic efficiency of the APR process.

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