

Article

Study of the Metal–Support Interaction and Electronic Effect Induced by Calcination Temperature Regulation and Their Effect on the Catalytic Performance of Glycerol Steam Reforming for Hydrogen Production

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Abstract: Steam reforming of glycerol to produce hydrogen is considered to be the very promising strategy to generate clean and renewable energy. The incipient-wetness impregnation method was used to load Ni on the reducible carrier TiO₂ (P25). In the process of catalyst preparation, the interaction and electronic effect between metal Ni and support TiO₂ were adjusted by changing the calcination temperature, and then the activity and hydrogen production of glycerol steam reforming reaction (GSR) was explored. A series of modern characterizations including XRD, UV-vis DRS, BET, XPS, NH₃-TPD, H₂-TPR, TG, and Raman have been applied to systematically characterize the catalysts. The characterization results showed that the calcination temperature can contribute to varying degrees of influences on the acidity and basicity of the Ni/TiO₂ catalyst, the specific surface area, together with the interaction force between Ni and the support. When the Ni/TiO₂ catalyst was calcined at 600 °C, the Ni species can be produced in the form of granular NiTiO₃ spinel. Consequently, due to the moderate metal–support interaction and electronic activity formed between the Ni species and the reducible support TiO₂ in the NiO/Ti-600C catalyst, the granular NiTiO₃ spinel can be reduced to a smaller Ni⁰ at a lower temperature, and thus to exhibit the best catalytic performance.

Keywords: hydrogen production; glycerol steam reforming; nickel-based supported catalyst; electronic and metal–support interactions

1. Introduction

Hydrogen energy has gradually attracted people's research interest because it is regarded as a promising high-efficiency clean energy and is widely used in the chemical and petroleum industries, especially in fuel cell power generation [1,2]. However, the current primary source of hydrogen production is from fossil energy reforming, contributing to a large amount of carbon dioxide (CO₂) gas emission as well; for example, producing 1 ton of hydrogen from shale gas will release about 10 tons of CO₂ gas [3]. Furthermore, the physical state of hydrogen makes its storage and transportation difficult, which is not conducive to the usage of hydrogen [4]. It has been reported that hydrogen exists in a chemical form and it is then released through a catalytic process, which is a promising method to solve the storage and application of hydrogen [5–7]. Therefore, considering



Citation: Zhu, S.; Wang, Y.; Lu, J.; Lu, H.; He, S.; Song, D.; Luo, Y.; Liu, J. Study of the Metal–Support Interaction and Electronic Effect Induced by Calcination Temperature Regulation and Their Effect on the Catalytic Performance of Glycerol Steam Reforming for Hydrogen Production. *Nanomaterials* **2021**, *11*, 3149. https://doi.org/10.3390/ nano11113149

Academic Editors: Juan Carlos Serrano-Ruiz, Manuel Antonio Diaz-Perez and Diego Cazorla-Amorós

Received: 14 October 2021 Accepted: 16 November 2021 Published: 22 November 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the environmental impact of the hydrogen production process, the use of renewable resources, especially the liquid-phase biomass hydrogen carrier, has attracted extensive attention [8–10]. Among various biomass liquid hydrogen carriers, glycerol is economically attractive and environmentally friendly, because of its advantage of relatively high hydrogen content, non-toxicity, and easy storage. More importantly, the process of producing biodiesel by transesterification animal oil (or vegetable oil) and alcohols will release about 10% of crude glycerin as a byproduct [11-13]. With the increase of global biodiesel production capacity, crude glycerol production is obviously in excess, resulting in the continuous tendency to decrease crude glycerol price [14]. Therefore, the conversion of crude glycerol derived from bio-derived products into valuable chemicals is not only environmentally friendly but also has economic value. Glycerin and methanol are the main components of crude glycerin, among which the content of glycerol is between 40% and 85%, and the content of methanol can be as high as 25% [15]. However, there are some defects in using glycerol and methanol purified from crude glycerol and refined glycerol as biomass hydrogen carriers, such as complex processing technology, low use rate and high cost. Herein, it is of great significance to study the different ratios of glycerol and methanol mixed-alcohol feeds for the high value-added use of crude glycerol.

Noble metal catalysts (such as Pt, Ru) can effectively break the C–C and C–H bonds, lowering the reaction temperature and a considerably better stability, but the high cost limits its large-scale application [16]. Copper-based catalysts have very good low-temperature catalytic activity. They are usually used for Water-Gas Shift (WGS) reaction and CO oxidation reactions or other low-temperature reactions, but they are prone to severe sintering at high temperatures [17–20]. Ni is a non-precious metal with the ability to break C–C bonds and C–H bonds which can be used commercially as an active component for hydrogen production from shale gas and alcohol reforming [21–25]. However, Ni particles are prone to sintering and depositing carbon at high temperatures, leading to a decrease in catalytic performance [26]. Generally, the sintering of Ni particles can be suppressed by increasing the calcination temperature or doping the second metal, especially the rare earth elements (such as Ce, Pr) [27]. Nevertheless, an excessively high calcination temperature will cause a drastic decrease in the specific surface area of the support and the active metal. Moreover, an excessively strong metal-support interaction force will make it difficult to reduce Ni species. For supported metal catalysts, the activity and selectivity of the steam reforming reaction are largely affected by the nature of the support and its interaction with the active metal. Many works have been reported about the carriers and the corresponding reaction processes for hydrogen production reaction of alcohol reforming, including Al₂O₃, ZrO₂, CeO₂, La₂O₃, and TiO₂ [21,23,28–30]. Among them, the non-redox carrier Al₂O₃ was widely used in the hydrogen production reaction of glycerol steam reforming due to its large specific surface area and good hydrothermal stability. However, it is easy to form a strong interaction force between Al₂O₃ and the active metal Ni, forming an inactive NiAl₂O₄ spinel, which is difficult to reduce to catalytically active Ni⁰ species [31]. Extensive research is mainly focused on weakening the interaction between Ni species and Al_2O_3 by adding rare earth elements, therefore promoting the reduction of Ni species [21,32]. Lu et al. found that the addition of rare earth element Pr can change the electronic environment around Ni species, therefore weakening the interaction between nickel and Al₂O₃, and strengthening the low-temperature catalytic activity of methanol steam reforming hydrogen production [21]. Compared with the Al₂O₃ carrier, the reducible support TiO₂ was more widely used in the field of water-gas shift reaction, selective hydrogenation and steam reforming reactions due to the electronic effect and strong interaction between it and the active metal [33–36]. Joseph and co-workers studied the selective hydrogenation of acetophenone on a titanium-supported nickel catalyst, and found that nickel interacts with rutile electrons, resulting in an electron-rich Ni-H active species [35]. Xu et al. recent research has shown that Ti will transfer electrons to nickel, therefore producing electron-rich Ni^{δ} -O_v-Ti³⁺ (O_v denotes oxygen vacancy), which strengthens the activity of the water–gas shift reaction [33,34]. Compared with the non-reducible carrier Al₂O₃, which requires the

addition of additives to control the electronic effect between it and the active metal, there is an obvious electron transfer effect between Ni and the reducible support TiO_2 . However, the influence of the electronic effect of Ni-Ti system catalyst on the catalytic performance of alcohol steam reforming hydrogen production is still unclear.

Promoted by the above demands, we tried to tune the electronic effect between Ni and the support TiO_2 by changing the calcination temperature, and then study its influence on the steam reforming of glycerol. At the same time, considering that the crude glycerol contains a large amount of methanol, we have also studied in detail the influence of different glycerol/methanol/water ratio feeds on the reaction. To the best of our knowledge, there is no report on the electronic effect of Ni/TiO₂ catalyst on its initial catalytic performance, as well as the influence of mixed-alcohol feeds with different volume ratios of glycerol and methanol on the reaction (GMSR).

2. Materials and Methods

2.1. Catalyst Preparation

A commercial TiO₂ (P25, surface area = $50 \text{ m}^2/\text{g}$, Degussa Inc., Hessen, Germany) without further calcination, and nickel nitrate (Ni(NO₃)₂·6H₂O) were obtained from Aladdin Industrial Corporation (Shanghai, China). During the whole experimental process, deionized water was used, and the chemicals were used without further purification and pretreatment.

Typically, 1.0 g of Ni(NO₃)₂·6H₂O was dispersed in 2.4 mL distilled water and then 1.8 g TiO₂ was added into the above solution using incipient-wetness impregnation method with stirring intensely for 20 min and then ultrasonic treatment for 5 min. After impregnation, the slurry was aged at room temperature and dried at 110 °C for 12 h, respectively, and finally thermally decomposed in a static air muffle furnace under different set-temperatures with a dwell time of 5 h (5 °C/min). To explore the effect of calcination temperature on the electronic effect between Ni and reducible oxide supports TiO₂, the catalysts were synthesized according to the above processes except for calcination temperature (500 °C, 600 °C, 700 °C, and 800 °C), which were labeled as NiO/Ti-500C, NiO/Ti-600C, NiO/Ti-800C, respectively. The NiO/Ti-100C sample represents only after being aged without further calcination. The reduced catalysts were marked as Ni/Ti-500R, Ni/Ti-600R, Ni/Ti-600R, Ni/Ti-800R, respectively.

2.2. GSR Catalyst Testing

First, the GSR was used as a probe reaction to study the catalytic performance of the above catalysts, and then GMSR was studied on the best catalyst. Those reactions were performed in a fixed-bed quartz reactor (Chengtai Quartz Inc., Jiangsu, Chnia) with an inner diameter of 8 mm under normal pressure. The reactor was equipped with 200 mg of catalyst (40–60 mesh) and mixed with 100 mg of quartz particles. Prior to each test, the samples were in situ reduced at 500 °C (NiO/Ti-500C) or 600 °C (NiO/Ti-600C), 700 °C (NiO/Ti-700C), 800 °C (NiO/Ti-800C) under a flow of gaseous mixture of H_2/N_2 (50 vol%) with the flow rate of 60 mL/min, then kept for 1 h. Then a glycerol (30 wt. %)/water solution was fed (0.03 mL/min) by a HPLC (Japan Spectroscopy Inc., PU980, Tokyo, Japan) pump and then was vaporized at 220 °C, and the inert N₂ (N₂/feed = 4/1) was also introduced into the vaporizer(Chengtai Quartz Inc., Jiangsu, China) at the same time. The corresponding weight hourly space velocity (WHSV) was fixed at $9 h^{-1}$. The products were first condensed through a cooler, and the incondensable gas species were analyzed online by two gas chromatographs with two thermal conductivity detectors (Fuli Analytical Instrument Inc., Hangzhou, China). For activity testing, reaction temperature ranged from 500 °C to 700 °C with an interval of 50 °C, and the corresponding activity data were averaged from three recorded data at each test temperature range. The stability tests of all samples were performed at 600 °C for 20 h with the same conditions. Considering that in the liquid product obtained by condensation, there are less C_2 and C_{2+} compounds. Therefore, the catalytic performance of the catalyst is presented in terms of the gaseous conversion rate of glycerol and glycerol-methanol mixed alcohol for GSR and GMSR, respectively, the molar yield of H₂ and the selectivity of carbon-containing gas products.

The conversion was calculated by

$$X_{glycerol} = \frac{Carbon_g}{3 \times glycerol_{in}} \times 100\%$$
(1)

$$X_{\text{mixed alcohol}} = \frac{\text{moles of carbon in gas production}}{3\text{glycerol}_{\text{in}} + \text{methanol}_{\text{in}}} \times 100\%$$
(2)

The glycerol_{in}, methanol_{in} and carbon_g mean the moles of glycerol fed in, methanol fed in and carbon detected in gaseous products, respectively.

The H_2 mole yield was calculated by

$$Y_{H_2} = \frac{\text{moles of } H_2 \text{ productions}}{\text{glycerol}_{in}}$$
(3)

The selectivity of carbonaceous gaseous products (CO, CO₂, CH₄) were calculated by

$$S_{i} = \frac{\text{moles of } i}{\text{moles of carbon in gas production}} \times 100\% \tag{4}$$

 S_i represents the selectivity of CO, CO₂, CH₄ in the product, respectively.

2.3. Catalyst Characterization

Structural properties of the catalysts were carried out by N_2 adsorption–desorption (Quantachrome NOVA 4200e, Kantar Technology Inc., New York, NY, USA). All samples were pretreated at 300 °C for 3 h. Specific surface area (BET) was obtained from the data of adsorption branch at -196 °C using the BET method, and pore size distribution was calculated from Barrett-Joyner-Halenda (BJH) method. X-ray powder diffraction (XRD) (Japan Rigaku Inc., Tokyo, Japan) patterns were measured by a Rigaku D/max-1200 diffractometer equipped with Cu K α radiation (λ = 0.15406 nm), operated at 30 mA and 40 kV. The crystalline size of Ni and NiO were calculated with Scherer equation using the Rietveld refinement of Jade 6.0 software. The UV-vis diffuse reflection spectrum was recorded by the TU-1901 UV-vis spectrophotometer(Puxi Technology Inc., Beijing, China) produced by the Persee General Instrument Co., Ltd. and equipped with an integrating sphere. The X-ray photoelectron spectra (XPS) was carried out on an ESCALAB 250 Xi spectrometer (Thermo Scientific Inc., Waltham, MA, USA) equipped with an Al K_{α} (h ν = 1486.6 eV) X-ray source. The charging effect was corrected by adjusting the binding energy of the C 1s peak from carbon pollution to 284.8 eV. Raman spectra were carried out on a micro-Raman system (Dilor Technology Inc., Paris, France) equipped with a 532 nm laser as the excitation source. A thermogravimetric analyzer (TGA 4000, PerKinElmer Inc., TGA 4000, Waltham, MA, USA) was used to analyze coke deposition on the spent catalysts. NH₃-Temperature programmed desorption (NH₃-TPD) experiment was performed on a TCD detect (Fuli Analytical Instrument Inc., Hangzhou, China) to explore the nature of acidity on catalysts. Before recording the TPD profiles, 100 mg of fresh catalyst was pretreated under 450 °C for 1 h and cooled down to 100 °C in the flow of ultra-pure He, then the gas was switched to NH₃ flow at 30 mL/min for 1 h. After that, the gas was switched to ultra-pure He flow at 30 mL/min to purge the material for 2 h, finally, the pretreated sample was heated to $800 \degree \text{C}$ under the ultra-pure He flow at a heating rate of $10 \,^{\circ}\text{C/min}$. H₂-Temperature programmed reduction (H₂-TPR) (Homemade, Kunming, China) experiment was performed to investigate redox properties of catalysts. In short, in a typical test, a sample (50 mg) is first pretreated with a gas mixture (5 vol.% O_2 in Ar) at 400 °C for 1 h to remove moisture and impurities. After cooling down to 100 $^{\circ}$ C, the gas was switched to the mixed gas flow with 10% H₂/Ar (30 mL/min). The pretreated catalyst was heated to 800 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min and the TCD signal was recorded continuously. The H₂ chemisorption experiment was used to measure the ratios of H_2/Ni for the four catalysts. Prior to hydrogen pulse chemisorption, catalysts were pretreated at the reduction temperature under 10% H₂/Ar (30mL/min), and cooled down to

40 °C in the flow of ultra-pure He. The chemisorption was implemented by pulsing of a mixture of 10% H_2/Ar (30 mL/min).

3. Results and Discussion

3.1. Physicochemical Properties of the Samples

UV-vis diffuse reflection spectrum (UV-vis DRS) was performed to investigate the nature of the Ni species within the material with the change of calcination temperature. The DR spectra of the samples with different calcination temperatures are shown in Figure 1A. The peaks of the NiO/Ti-100C sample at 650 nm and 750 nm in the visible region can be attributed to the peak of Ni²⁺ ions adsorbed on the surface of TiO₂, which disappears in the ultraviolet region. Compared with NiO/Ti-100C sample, the peak of the NiO/Ti-500C sample at 720 nm can be attributed the species of NiO [27]. In contrast to the above samples, the NiO/Ti-600C sample shows new peaks at wavelengths 450, 511, and 743 nm, which are attributed to the NiTiO₃ phase [37-39]. The spectra at 450 and 511 nm are due to the splitting of the crystal field of the $3d^8$ band of Ni²⁺ ions into two sub-bands, called $Ni^{2+} \rightarrow Ti^{4+}$ charge transfer (CT) bands. It also shows absorbance at 743 nm as indicated by its yellow color [38]. The reduction catalysts were also characterized by the UV-vis diffuse reflection spectrum shown in Figure 1B. The peaks of NiTiO₃ and NiO disappear, indicating that NiO and NiTiO₃ are completely reduced to Ni⁰. The above observations clearly indicate that the interaction between Ni species and the support TiO_2 gradually increases with the increase of calcination temperature, resulting in the evolution of Ni species from Ni²⁺ species adsorbed on the surface of the carrier to NiO species, and then to NiTiO₃ spinel species.



Figure 1. UV-vis diffuse reflection spectrum of the samples annealing (A) and reduce (B).

We turned to the XRD to further determine the bulk composition and the average crystallite size of the above catalysts. The XRD patterns for the support and samples before and after reduction are shown in Figure 2A,B, and the calculated average crystallite size is listed in Table 1. The anatase (JCPDS#21-1272) and rutile (JCPDS#21-1276) structure existed in all samples. However, the face-centered cubic of structure NiO (JCPDS#47-1049) only appears in NiO/Ti-500C and the NiTiO₃ species (JCPDS#33-0960) is apparent in NiO/Ti-600C, NiO/Ti-700C, NiO/Ti-800C. The characterization results are consistent with those of a UV-vis DR spectrum. It has been reported that higher calcination temperature could enhance the immersion of Ni^{2+} into TiO_2 crystal lattices to form $NiTiO_3$ crystals, which, after activation, could allow the existence of Ni crystallites highly dispersed in the support, as also previously reported [28,40]. As can be seen from Table 1, with the increase of calcination temperature, anatase gradually evolves into rutile, and the proportion of rutile in the reduction process will further increase, but the transformation speed is obviously lower than that of calcination in muffle furnace. The particle size of nickel-containing compounds for the above catalysts increases gradually and is approximated to be 15.0, 33.7, 45.5, and 76.1 nm for NiO/Ti-500C, NiO/Ti-600C, NiO/Ti-700C, NiO/Ti-800C, respectively. After catalyst reduction, the particle size of Ni⁰ increases gradually and is approximated to be 18.80 \pm 1, 19.77 \pm 0.5, 20.83 \pm 1, and 23.25 \pm 2 nm for Ni/Ti-500R, Ni/Ti-600R, Ni/Ti-700R, Ni/Ti-800R, respectively. The XRD spectrum of Ni/TiO₂-500R catalyst after high temperature reaction is shown in Figure S1, the particle size of Ni⁰ increases slightly. However, in the case of TiO₂ crystallite size, a monotonic increase in TiO₂ crystallite size can be observed with increasing calcination temperature from 500 to 800 °C. After catalyst reduction, the particle size of TiO₂ is almost the same as that after calcination, indicating that the carrier TiO₂ is seriously sintered in the process of high-temperature calcination. At the same time, it can be seen from Figure 2B that NiO and NiTiO₃ were not detected in the reduced catalyst, indicating that these two substances can be completely reduced to Ni⁰ specie, and the results were consistent with the UV-vis DRS results.



Figure 2. XRD patterns of the (A) calcined and (B) reduced catalysts.

Table 1. Physicochemical parameters for the samples

Sample	The Pro- portion of Rutile (%)	Crystallite Size of Rutile [110] ^a (nm)	Crystallite Size of NiO [111] ^a (nm)	Crystallite Size of NiTiO3 [104] ^a (nm)	Crystallite Size of Ni [200] ^a (nm)	BET Surface Area (m²/g) ^b	Pore Volume (cm ³ /g)	Pore Diameter (nm)
NiO/Ti-500C	11.5	27.3	14.97	_	_	64.56 ± 1	0.32	13.38
NiO/Ti-600C	54.0	36.2	_ c	33.70	_	33.00 ± 0.5	0.22	15.31
NiO/Ti-700C	100.0	50.0	_	46.50	_	7.46 ± 0.5	0.08	3.25
NiO/Ti-800C	100.0	74.9	_	67.10	_	0.98 ± 0.3	0.02	3.92
Ni/Ti-500R	13.7	33.0	_	_	18.80 ± 1	41.38 ± 1	0.24	11.17
Ni/Ti-600R	71.2	44.3	_	_	19.77 ± 0.5	15.21 ± 0.5	0.11	14.56
Ni/Ti-700R	100.0	49.1	_	_	20.83 ± 1	_	_	_
Ni/Ti-800R	100.0	75.0	-	-	23.25 ± 2	1.18 ± 0.2	0.01	4.28

^a Crystallite size was determined by XRD with the Scherrer equation; ^b Determined by N₂ adsorption–desorption, calcined catalyst/reduced catalyst; ^c no data.

To further investigate the reducibility of Ni species over NiO/Ti-500C, NiO/Ti-600C, NiO/Ti-700C, NiO/Ti-800C, H₂-temperature programmed reduction (H₂-TPR) was performed (Figure 3A). The main peak of NiO/Ti-500C centered at 455 °C is attributed to the reduction of highly dispersed NiO phase [34]. Compared with NiO/Ti-500 sample, hydrogen consumption peak of the NiO/Ti-600 sample shifts to higher reduction temperature and the main peak is approximated to be 535 °C and the peak is attributed to the reduction of granular NiTiO₃ phase in medium intensity interaction with TiO₂ [41,42]. As the calcination temperature increases, hydrogen consumption peaks of the NiO/Ti-700C and the NiO/Ti-800C samples shift to higher reduction temperature and the main peaks are approximated to be 570, 635 °C. The peaks are attributed to the reduction with support TiO₂ or metal–support solid solution [43,44], suggesting the interface NiTiO₃ or metal–support solid

solution phase is more difficulty to reduce than NiO with weaker interaction with support. To better understand the number of active Ni species on the catalyst, H₂ chemisorption characterization was carried out, the data are listed in Table 2. It can be seen from Table 2 that for Ni/Ti-500R, Ni/Ti-600R, Ni/Ti-700R and Ni/Ti-800R, the ratios of the four catalysts are calculated to be 74.4, 110.2, 35.6 and 25.8 $\mu mol_{H2}/g_{cat}$, respectively. The results indicate that Ni/Ti-600R catalyst has the best initial activity. N₂ adsorption/desorption isotherms curves of the NiO/Ti-500C, NiO/Ti-600C, NiO/Ti-700C, NiO/Ti-800C catalysts were displayed as Figure 3B. All samples exhibit the physisorption isotherms of Type II and hysteresis loops of Type H1 [45], indicating a non-porous or macroporous structure of the catalyst particles. The data of Brunauer-Emmett-Teller (BET) surface area and respective pore volume for calcined and reduced samples are shown in Table 1. The BET surface area of NiO/Ti-500C is $64.56 \pm 1 \text{ m}^2/\text{g}$, which is greater than the $0.98 \pm 0.3 \text{ m}^2/\text{g}$ of NiO/Ti-800C sample. Compared with the calcined catalysts, the specific surface area of Ni/Ti-500R sample decreases to $41.38 \pm 1 \text{ m}^2/\text{g}$ and Ni/Ti-600R to $15.21 \pm 0.5 \text{ m}^2/\text{g}$. The specific surface areas of Ni/Ti-700R and Ni/Ti-800R increase slightly, and the pore volume of all samples decreases slightly. N2 adsorption-desorption isotherms profile of Ni/TiO2-500R catalyst after high temperature reaction is shown in Figure S2, and the specific surface area has decreased significantly. Combined with the XRD characterization, it can be seen that increasing the annealing temperature of the sample will cause the sintering of the supported TiO₂ particles, which will further reduce the specific surface area and pore volume of the catalyst.



Figure 3. H₂-TPR (A) and N₂ adsorption–desorption isotherms (B) profiles of the catalysts.

Table 2. NH3 desorbed and H2 uptake of samples.

Samulas	NH	H ₂ Uptake		
Samples	T < 550 °C	T > 550 °C	Total	$(\mu mol_{H2}/g_{cat})$
TiO ₂	313.2	7.1	320.3	-
Ni/Ti-500C	265.2	80.1	345.3	74.4
Ni/Ti-600C	114.7	149.3	264.0	110.2
Ni/Ti-700C	47.8	127.6	175.4	35.6
Ni/Ti-800C	5.4	113.7	119.1	25.8

XPS spectra was used to prove the possible existence of electrons interaction between Ti oxide and separated NiO species. The corresponding Ni 2p, Ti 2p, and O 1s XPS spectra of NiO/Ti-500C, NiO/Ti-600C, NiO/Ti-700C, NiO/Ti-800C catalysts, respectively, are given in Figure 4. For the NiO/Ti-500C catalyst, 855.7 eV can be attributed to Ni³⁺, it may be that NiO is oxidized to Ni₂O₃ during the calcination process, or the interaction between the Ni precursor and the support TiO₂ is weak at a lower calcination temperature, and it decomposes into NiO and Ni₂O₃ [46,47]. The electron cloud density around Ni³⁺ is low, so the binding energy shifts to higher binding energy relative to Ni²⁺ in NiO. The binding energy of 854.1 eV is attributed to the weaker Ni²⁺ peak that interacts with the carrier TiO₂ [46]. As the calcination temperature of the catalysts increases, the interaction between NiO and the support TiO₂ becomes stronger, and the electronic environment around the Ni species changes significantly. Compared with Ni²⁺ (854.1 eV) in NiO/Ti-500C catalyst, the binding energy of Ni²⁺ in Ni 2p XPS spectrum for NiO/Ti-600C (855.0 eV), NiO/Ti-700C and NiO/Ti-800C (ca. 855.4 eV) catalyst shifts to high binding energy but are 0.3 eV lower than Ni³⁺. As for the Ti 2p and O 1s XPS spectra, compared with the NiO/Ti-500C catalyst, with the increase of the catalyst calcination temperature, except for the binding energy of O 1s spectrum for NiO/Ti-600C catalyst slightly shifts to higher binding energy, the binding energies of Ti 2p and O 1s XPS spectra for all catalysts shift to low binding energies. This indicates that when the calcination temperature is increased, there is a stronger electronic activity phenomenon between the carrier TiO₂ and the active metal Ni species. These changes may also be caused by anatase—rutile phase transition in the carrier [48].



Figure 4. XPS spectra of Ni 2p (A), Ti 2p (B) and O 1s (C) for the above samples.

Combined with XRD, UV-vis DRS, H₂-TPR and BET characterization results, increasing the calcination temperature, the interaction force and the electronic effect between the active metal Ni and the support gradually increase, and the interaction force between NiTiO₃ and the support TiO₂ is also enhanced. For NiO/Ti-600C catalyst, the active metal Ni and the support TiO₂ form a medium-strength interaction force and electronic effect, which leads to the existence of the Ni species in the catalyst in the form of granular NiTiO₃, which is easily reduced to small particles of Ni at relatively lower temperatures. However, under high-temperature calcination, a very strong interaction force and electronic effect are formed between interface NiTiO₃ and the support TiO₂, or in the form of a Ni-Ti solid solution, which caused the Ni²⁺ in NiTiO₃ to be reduced at a higher temperature. The higher calcination and reduction temperature will cause severe sintering of the active metal and the carrier, therefore affecting the performance of the catalyst.

It is well known that the acidity of the catalyst has an important influence on the catalytic performance and anti-coking performance during the reforming reaction [49]. Weak acid facilitates the adsorption of reactants, while strong acid easily led to carbon on the catalyst surface. NH₃-Temperature programmed desorption profile was used to study the acid strength characteristics of the Ni-supported TiO₂ catalyst as a function of the calcination temperature. The results are shown in Figure 5 and Table 2. It can be stated that all catalysts are dominated by two desorption regions at lower than 550 °C and higher than 550 °C associated with weak/medium and strong acid sites, respectively [50]. For the support TiO₂, there is a bulky and wide desorption peak ($T_{max} = 220 \degree C$) caused by Ti–OH of the support surface, indicating that the weak acid and medium strong acid coexist in the support TiO_2 and the weak acid is the main one. For the NiO/Ti-500C, the intensity of desorption peak at 350 °C increases gradually, and new desorption peaks appear at ca. $550 \,^{\circ}$ C and ca. $650 \,^{\circ}$ C, indicating that the acidity of the catalyst becomes stronger when the catalyst is calcined at 500 °C. For the NiO/Ti-600C, NiO/Ti-700C, NiO/Ti-800C, when the calcination temperature is further increased, the intensity of desorption peak below 550 °C gradually decreases or even disappears, while the desorption peak above 550 °C shifts to a

higher temperature, indicating that the NiO/TiO₂ catalyst transforms weak/medium acid into strong acid at higher temperature. As we all know, the strong acidity of the catalyst may cause carbon deposition on the surface of the catalyst, which will lead to a decrease in its catalytic activity [51]. The effect of the surface acidity on the catalytic properties will be discussed below.



Figure 5. NH₃-TPD profiles of (**a**) TiO₂, (**b**) NiO/Ti-500C, (**c**) NiO/Ti-600C, (**d**) NiO/Ti-700C, (**e**) NiO/Ti-800C.

3.2. Catalytic Performance Tests

3.2.1. Catalytic Performance Tests of GSR

The effects of reaction temperature on the activity of Ni/Ti-500R, Ni/Ti-600R, Ni/Ti-700R and Ni/Ti-800R in GSR were investigated, and the corresponding results are shown in Figure 6. When the reaction temperature is 500 °C and 550 °C, the glycerol conversion rate and H_2 yield of all catalysts are low, indicating that the Ni particles have a weak ability to break chemical bonds at low temperatures [52]. Moreover, glycerol conversion and H_2 yield of Ni/Ti-500R and Ni/Ti-600R are higher than those of Ni/Ti-700R and Ni/Ti-800R catalysts under the same reaction temperature. At 600 °C, the conversion rate of glycerol reaches 98.5% for Ni/Ti-600R catalyst, but the conversion rate of other catalysts is much lower than that of Ni/Ti-600R catalyst. When the reaction temperature reached 650 $^\circ$ C and 700 °C, the glycerol conversion rate of Ni/Ti-600R catalyst is almost completely achieved, but the glycerol conversion rate of other catalysts was still far lower than Ni/Ti-600R. For all the catalysts, the conversion rate of glycerol and the yield of hydrogen increased gradually with the increase of the reaction temperature. For Ni/Ti-600R catalyst, the conversion rate of glycerol and the yield of hydrogen increased rapidly between 550 $^\circ$ C and 600 $^\circ$ C, and then the increase of temperature did not influence much. With the increase of reaction temperature, the selectivity of CO and methane increases first and then decreases, reaching the maximum at 650 °C. However, the selectivity of CO₂ decreased first and then increased, and the selectivity is the lowest at 650 °C. The above experimental phenomena accord with the reaction thermodynamics. The lower reforming temperature limits the catalytic performance of the catalyst. The feed mainly forms liquid carbon compounds or coke deposits, resulting in a decrease in gaseous products and a decrease in H₂ yield [53].



Figure 6. GSR activity of the catalysts (**A**) glycerol conversion, (**B**) H₂ yield, (**C**) CO selectivity, (**D**) CO₂ selectivity, (**E**) CH₄ selectivity. Reaction conditions: 30 wt.% glycerol/water solution, WHSV = 9 h⁻¹, 1 atm.

As the temperature increased, the more gas was generated, and the reforming process is more favorable. In addition, as the temperature goes up, the WGS reaction and methanation reaction tends to proceed in the opposite direction, since these two reactions are exothermic reactions [54]. Hence, when the temperature is higher than 650 °C, CO selectivity increases and CH₄ selectivity decreases. When the reaction temperature is lower than 650 °C, although the high temperature will inhibit the methanation reaction, the glycerol conversion rate will increase, and more CO will be produced during the reaction. In the process of increasing the temperature from 500 °C to 650 °C, from the perspective

of reaction thermodynamics, increasing the reaction temperature will inhibit the methanation reaction of CO (CO + $3H_2 = H_2O + CH_4 \Delta H_0 = -206.11 \text{ kJ/mol}$). However, as the reaction temperature increases, the glycerol conversion rate increases, and more CO will be produced, resulting in an increase in the selectivity of methane in the product. When the temperature is higher than 650 $^{\circ}$ C, CO selectivity and CH₄ selectivity in the product decreases. Comparing the catalytic performance of the above catalysts, increasing the calcination temperature of the catalyst during the preparation process results in the catalytic activity order of Ni/Ti-600R > Ni/Ti-500R > Ni/Ti-700R > Ni/Ti-800R catalysts and the result is consistent with the H₂/Ni ratio characterized by H₂ chemisorption. Compared with Ni/Ti-600R catalyst, the Ni/Ti-700R and Ni/Ti-800R catalysts have lower glycerol conversion rate and hydrogen production rate, which may be due to their lower specific surface areas and stronger acidity. At the same time, the strong acidity of the catalyst promotes the cracking reaction of glycerol, resulting in a significantly higher CO selectivity in the product than Ni/Ti-500R and Ni/Ti-600R catalysts. Therefore, Ni/Ti-600R and Ni/Ti-500R are used to investigate the stability of the catalyst at the reaction temperature of 600 $^{\circ}$ C, and the hydrogen production capacity is shown as the index listed in Figure 7. In a 20-h test, the Ni/Ti-600R and Ni/Ti-500R catalyst achieved a total turnover number of 2108 mole and 1578 mole hydrogen per kilogram catalyst. In terms of linear correlation and slope for Ni/Ti-600R and Ni/Ti-500R, respectively, R_2^2 (0.9973) is larger than R_1^2 (0.9967), and K₂ (110.8 \pm 1.3) is larger than K₁ (82.7 \pm 1.1), indicating that the stability of hydrogen production capacity of Ni/Ti-600R catalyst is higher than that of Ni/Ti-500R catalyst.



Figure 7. Stability test of (A) Ni/Ti-500R and (B) Ni/Ti-600R catalysts for hydrogen production in 20 h.

3.2.2. Catalytic Performance Tests of GMSR

Considering that the byproduct crude glycerin of biodiesel itself contains about 25% methanol by mass, the adaptability of the Ni/Ti-600R catalyst to reactant systems with different methanol/glycerol/water volume ratios was further investigated. The results are shown in Figure 8. It can be seen from Figure 8, compared with the feed glycerol/methanol/water ratio of 2/0/8 and 2/1/7, adding a certain amount of additional methanol into the original glycerol system will lead to a decrease in the conversion rate of mixed alcohol and an increase in CO selectivity. However, the hydrogen production capacity will not decrease, and the hydrogen production capacity within 20 h is 1.15 times that of the single glycerol system. The decrease of mixed-alcohol conversion rate may be caused by the increase of Ni/Ti-600R catalyst substrate due to the addition of a certain amount of methanol. There is competitive adsorption between small molecule methanol and glycerol may dehydrate to produce aldehydes. This process is likely to cause the formation of graphitized carbon on the surface of the catalyst, which is difficult to remove, resulting the activity of the catalyst gradually decreases [55]. Compared with the feedstock

glycerol/methanol/water ratio of 2/0/8 and 1/2/7, the mixed alcohols of the two feedstocks are almost completely converted within 20 h. However, hydrogen production and CO concentration in gas products increased significantly when methanol content is higher. Therefore, in the mixed-alcohol reaction system, increasing the ratio of methanol to glycerol can increase the concentration and stability of hydrogen in the product, but compared with the single glycerol feed, the selectivity of CO in the gas product will also increase.



Figure 8. The conversion rate (**A**), CO selectivity (**B**) and hydrogen production stability (**C**), (**D**) of mixed alcohol feeds on Ni/Ti-600R catalyst in 20 h.

4. Mechanism Analysis of Catalyst Deactivation

The deactivation of catalysts in the GSR (GMSR) reaction is mainly caused by carbon deposition and sintering of active species Ni, among which many researchers reported that the most important reason is the carbon deposition. Therefore, thermogravimetry and Raman were used to characterize and analyze the amount and type of carbon on the surface area of Ni/Ti-600R catalyst after 20 h reaction in different mixed-alcohol systems.

Thermogravimetric analyzer (TGA) was used to characterize the coking characteristics and coking amount of spent catalyst and the results are shown in Figure 9. The initial losses in the 150–300 °C region are attributed to the removal of easily oxidized carbonaceous species, such as adsorbed reactants or liquid products [56]. Compared with the feedstock glycerol/methanol/water ratio of 2/0/8 and 2/1/7, the glycerol/ methanol/ water ratio of 1/2/7 feedstock with higher methanol ratio appears a loss peak at 367 °C, which can be attributed the gasification of weakly stable amorphous (C_{α}) [57]. The major loss peak located at the range of 300–660 °C, and the corresponding differential peaks are shown in the inset profile in Figure 9. The three feeds have similar differential peak centered at ca. 595 °C, which is probably due to the gasification of the bulky carbonaceous species or the graphitized carbon on spent catalysts [56]. The feedstock of glycerol/methanol/ water ratio of 2/0/8 and 2/1/7 appear an additional shoulder peak at 558 °C which can be attributed to the gasification of filamentous coke (C_β) with different graphitization degree [57]. As listed in Table 3, the mass losses assigned to coke gasification after 20 h reaction on the feedstock glycerol/methanol/ water ratio of 1/2/7, 2/0/7 and 2/1/7 are 5.1%, 9.4% and 12.8% respectively. The above phenomena indicate that the glycerol/methanol/ water ratio of 1/2/7 feedstock with higher methanol ratio forms carbon types that are easier to remove during the reaction process, resulting in lower carbon accumulation.



Figure 9. TGA and DTG (inset) profile of the Ni/Ti-600R catalyst for different mixed-alcohol feed after 20 h stability test.

Feed Glycerol/MeOH/H ₂ O	Weight Loss (%)	Coke/Glycerol (mmol/mol)	Coke Formation Rate mol/gcat/s	Carbon Balance (%)	I _G /I _D
1/2/7	5.1	0.25	$5.9 imes10^{-8}$	99.1	0.53
2/0/8	9.4	0.37	$1.1 imes10^{-7}$	99.1	0.64
2/1/7	12.8	0.44	$1.5 imes10^{-7}$	89.2	0.67

The Raman spectrum was applied to further analyze the type of coke deposition on spent catalysts used in different mixed-alcohol feeding systems, and the Raman spectrum in the range 1100–2000 cm⁻¹ is presented in Figure 10 and Table 3. The spent catalysts used in different mixed-alcohol feeding systems display peaks around 1350 cm⁻¹ and 1590 cm⁻¹ in Raman spectra, which are categorized as D-band and G-band of carbon-based materials, respectively. D-band, which is usually caused by the vibration of carbon atoms with dangling bonds in disordered carbon-like substances, and G-band is attributed to the well-ordered, condensed or graphitic aromatic carbon species as the sp² bonded carbon atoms in a two-dimensional hexagonal lattice [27]. In addition, the ratio of band intensities (I_G/I_D) has been used to characterize the graphitic degree of coke on catalysts [58]. The ratios of I_G/I_D of Ni/Ti-600R after 20 h reaction on the feedstock glycerol/methanol/water ratios of 1/2/7, 2/0/7 and 2/1/7 are 0.53, 0.64 and 0.67, respectively. Raman results are consistent with TG characterization, which indicate that the mixed-alcohol feed with a glycerol/methanol/water ratio of 1/2/7 deposits more unstable amorphous (C_a) and filamentous coke (C_β) on the catalyst. These carbons are easy to gasify and decompose in

the reaction process at high temperature, so TG characterization shows that the amount of carbon deposition is minimal under this feed condition.



Figure 10. Raman spectrum of the Ni/Ti-600R catalyst for different mixed-alcohol feed after 20 h stability test.

5. Conclusions

In our work, we found that the calcination temperature of the Ni/TiO_2 catalyst during the preparation process has a great influence on its physical and chemical properties and the catalytic performance of the corresponding alcohol reforming hydrogen production reaction. During the preparation process of the Ni/TiO₂ catalyst, compared to calcination at 500 °C to form NiO, calcination at 600 °C forms a granular NiTiO3 species with medium intensity interaction and electronic activity between the metal and support. Due to the moderate metal-support interaction and electronic activity for NiO/Ti-600C catalyst, the granular NiTiO₃ spinel can be reduced to a smaller Ni⁰ at a lower temperature, showing the best glycerol conversion rate and the highest hydrogen yield. However, when the catalyst is calcined at 700 and 800 °C, the Ni species exists in the form of interface NiTiO₃ spinel or Ni-Ti solid solution with strong metal-support interaction force and electronic effect, which requires a higher temperature to reduce to Ni⁰ species. The higher calcination and reduction temperature will cause severe sintering of the active metal and the carrier, therefore affecting the performance of the catalyst. At the same time, as the calcination temperature increases, the acidity of the catalyst gradually changes from weak acid to strong acid.

We have also carried out research on hydrogen production by reforming mixed alcohols with different ratios of glycerol/methanol/water as feedstock on Ni/Ti-600R catalyst. It is found that when the concentration of glycerol is the same, adding a certain amount of methanol will increase the amount of carbon deposit on the catalyst, and the conversion rate of mixed alcohol will decrease, but the hydrogen production will increase. When the methanol concentration in the mixed-alcohol feed is the highest, the carbon deposit is the least, and the hydrogen production will further increase. Therefore, for crude glycerin, a byproduct of biodiesel, a certain amount of methanol will help increase hydrogen production. When the volume ratio of glycerol to methanol is less than 50%, it will not only help reduce carbon deposits, but also increase hydrogen production.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.339 0/nano11113149/s1, Figure S1. N₂ adsorption–desorption isotherms profile of the Ni/Ti-500R catalysts after 20 h stability test. Figure S2. XRD pattern of the Ni/Ti-500R catalysts after 20 h stability test.

Author Contributions: Conceptualization: S.H. and J.L. (Jiangping Liu); Data curation: S.Z., J.L. (Jichang Lu) and Y.L.; Formal analysis: S.Z., J.L. (Jichang Lu) and S.H.; Investigation: S.Z. and Y.W.;

Methodology: Y.W. and H.L.; Software: S.Z. and D.S.; Supervision: J.L. (Jiangping Liu), Y.W., S.H. and J.L. (Jichang Lu); Validation: H.L. and D.S.; Visualization: Y.W. and S.H.; Writing—original draft: S.Z.; Writing—review and editing: S.H. and J.L. (Jiangping Liu). All authors have read and agreed to the published version of the manuscript.

Funding: We acknowledged the financial support from National Natural Science Foundation of China (Grant Nos. 42030712, 21666013, 21966018, 2210060708 and 2216060105), Applied Basic Research Foundation of Yunnan Province (Grant Nos. 202101AS070026, 202101AU070025 and 202105AE160019) as well as Yunnan Ten Thousand Talents Plan Young & Elite talents Project (No. YNWR-QNBJ-2018-067).

Data Availability Statement: All data used to support the findings of this study are included within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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