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1	Low-temperature hydrogen production from waste polyethylene by nonthermal plasma (NTP)-assisted
2	catalytic pyrolysis using NiCeOx/β catalyst
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10	Abstract: Conventional catalytic pyrolysis of waste plastics for H <sub>2</sub> production faces challenges due to
11	excessively high reaction temperatures. This study introduced a NiCeOx/ $\beta$ catalyst for low-temperature H <sub>2</sub>
12	production from polyethylene (PE), aiming to enhance H <sub>2</sub> yield through nonthermal plasma (NTP) and catalytic
13	active sites. Experimental results confirmed the efficacy of NTP in promoting collision between high-potential-
14	energies active species and plasma-catalyst interactions, identifying acidic sites as primary catalytic active sites.
15	Both experiments and density functional theory (DFT) calculations confirmed NiO and CeO <sub>2</sub> particles as
16	metallic active sites, exhibiting thermodynamic and kinetic benefits for primary products from PE pyrolysis.
17	Under optimal conditions, the highest $H_2$ yield and selectivity respectively reached 32.71 mmol/g and 82.10%
18	at a PE/(NiCeOx/ $\beta$ ) ratio of 1:4, reaction temperature of 400 °C, and NTP discharge power of 210 W. The
19	$NiCeOx/\beta$ catalyst facilitated low-temperature pyrolysis of waste plastics, enhancing H <sub>2</sub> selectivity and yield.
20	Keywords: Polyethylene; Plastic wastes; Non-thermal plasma; Hydrogen; Catalytic pyrolysis;
21	1. Introduction
22	Plastics play a significant role in our daily lives and various industries [1-3]. Despite a period of stagnation

caused by the Covid-19 pandemic, global plastic production has rebounded in 2021, reaching 390.7 million tons.
China, accounting for almost one-third of the world's plastic production, is the largest contributor [4]. Most
plastic products have a short service life and eventually become part of municipal solid wastes, with more than
90% not disposed of properly [5]. For example, as the most widely used plastic (accounting for 26.9% of total
plastic production), the recycling rate of polyethylene (PE) in 2021 is only 8.58%. Proper disposal of plastic
waste has become a major environmental issue and attracted widespread attention.

29 The conversion of non-recyclable waste plastics into high-value hydrogen through catalytic pyrolysis (without steam addition) or catalytic pyrolysis reforming (with steam addition) is considered a promising 30 31 method for the disposal of waste plastics [6-9]. However, the drawbacks of the above methods are significant, as the reaction temperatures are high (750-1000 °C), leading to reduced catalyst lifespan, increased energy 32 consumption, and a higher occurrence of side reactions [10, 11]. The high-temperature conditions are primarily 33 34 advantageous for the dehydrogenation reaction and effective activation of the catalyst. Therefore, it is possible to reduce the reaction temperatures by promoting dehydrogenation reactions and developing catalysts that can 35 be activated at lower temperatures. 36

The energy range of active substances in non-thermal plasma (NTP) nitrogen discharge was 6-11 eV, which 37 38 is sufficient to meet the energy required for breaking C-H [12, 13]. Hence, introducing NTP can promote dehydrogenation reactions, thereby lowering the reaction temperature. Aminu et al. compared the  $H_2$  yield using 39 thermal reforming and NTP-assisted thermal reforming of PE primary pyrolysis products at 250 °C. They found 40 41 that, compared to single thermal reforming, introducing NTP increased the H<sub>2</sub> yield from 0.12 mmol/g to 1.04 mmol/g [14]. Similar conclusions were drawn by Xiao et al. for PP primary pyrolysis products, where no H<sub>2</sub> 42 was produced after single thermal reforming at 400 °C, but the H<sub>2</sub> yield was approximately 0.80 mmol/g after 43 NTP-assisted thermal reforming [15]. Although existing research has achieved H<sub>2</sub> production at low 44

45 temperatures of less than 500 °C, there is room for further improvement in H<sub>2</sub> yield. It is essential to develop
46 efficient catalysts suitable for NTP-assisted catalytic pyrolysis systems.

47 Ni-based catalysts doped with noble metals (Ce, La, Ru, etc.) exhibit high reaction activity and coking resistance, demonstrating the potential for  $H_2$  production at low temperatures. Zhang et al. found that the Ni-La 48 49 bimetallic-based catalyst catalyzed the co-pyrolysis of PE and straw at 700 °C, resulting in a H<sub>2</sub> yield of approximately 13.5 mmol/g. Moreover, this catalyst remained stable, with H<sub>2</sub> selectivity only decreasing by 50 around 22.7% after six repeated uses [16]. Zeolites possess abundant surface area and acidic sites, and a suitable 51 52 pore structure, which can effectively disperse metal particles and provide catalytic active sites [17]. Among the 53 widely used zeolites (Hβ, HZSM-5, HY, and MCM-41), β zeolite has been proven to be more suitable for H<sub>2</sub> production. Navlani-García et al. studied the effect of Pd loading on different zeolites (HB, HZSM-5, and HY) 54 in catalyzing the dehydrogenation of formic acid. The results indicated that  $\beta$  zeolite exhibited the best H<sub>2</sub> 55 56 production performance [18]. Furthermore, our previous research demonstrated that compared to USY, HZSM-5, and MCM-41,  $\beta$ -catalyzed plastic pyrolysis gas yields higher, with H<sub>2</sub> being the major component of the 57 pyrolysis gas [13, 19]. Based on these considerations, this paper proposes a novel catalyst, NiCeOx/ $\beta$ , which 58 59 exhibits high catalytic activity under low-temperature conditions. The rationality of the catalyst design is further 60 verified through density functional theory (DFT) calculations.

This study addresses the critical issue of high temperatures in existing catalytic pyrolysis H<sub>2</sub> production from waste plastics by introducing NTP and a novel bimetallic catalyst, NiCeOx/ $\beta$ . We investigated the role of NTP on H<sub>2</sub> production by comparing the gas products obtained through different treatment methods, including NTP alone, NTP catalysis, pyrolysis alone, NTP-assisted pyrolysis, catalytic pyrolysis, and NTP-assisted catalytic pyrolysis. A combined experimental and DFT calculation approach was employed to explore the roles of metal and acidic active sites in H<sub>2</sub> production. Moreover, we studied the H<sub>2</sub> production under different PE/(NiCeOx/ $\beta$ )

67	ratios, discharge powers, and reaction temperatures. Finally, a H <sub>2</sub> production mechanism for PE in the low-
68	temperature NTP-assisted catalytic pyrolysis system was proposed. This study introduces a highly effective and
69	robust catalyst to realize the efficient hydrogen production from plastics at low temperatures, representing a
70	potential approach for managing plastic waste.
71	
72	2. Materials and methods
73	2.1 Materials and catalyst
74	The PE samples were obtained from Meisheng Engineering Plastics Co., China. The $\beta$ zeolite (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =
75	25) came from Nankai University Catalyst Plant, China. The Nickel (II) nitrate hydrate and Cerium (IV) nitrate
76	hydrate were provided by Aladdin.
77	The catalyst with metal modification was prepared through the wet impregnation method. Typically, 4 g of $\beta$
78	zeolite support was added to 30 mL of $Ni(NO_3)_2$ and $Ce(NO_3)_3$ hydrate solution, with a loading ratio of 10 wt.%
79	of Ni and 2 wt.% of Ce. The mixture was stirred at 80 °C for 5 h, followed by drying at 100 °C for 4 h and
80	calcination with a heating rate of 10 °C/min up to 550 °C for 5 h under air. Finally, the acquired catalyst was
81	sieved into 100 mesh and denoted as NiCeOx/ $\beta$ .
82	
83	2.2 Catalyst characterization
84	To illustrate the surface area and pore size of the catalyst before and after use, a surface area and porosity
85	analyzer (ASAP 2460) was used to analyze the surface and porosity of both fresh and used catalyst samples.
86	The specific surface was determined through the Brunauer-Emmett-Teller (BET) equation. Pore volume was

obtained using the t-plot method and pore size distribution was analyzed using the DFT model.

88 To demonstrate the morphological changes of the catalyst before and after use, a scanning electron

89 microscope (SEM, Hitachi SU8230) operating at 2 kV was employed to examine the morphologies of both the 90 fresh and used catalysts. For cross-section analysis, we employed an FEI Helios G4 CX DualBeam SEM 91 equipped with a focused ion beam (FIB). Energy-dispersive X-ray spectroscopy was used to obtain the metal 92 mappings.

To identify the changes in the types and quantities of acidic sites after the catalytic reaction, ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD, Bel Cata II) was used to analyze the acidic sites of both fresh and used catalyst samples. Prior to measurement, the samples underwent pretreatment with helium flow at 550 °C for 30 min. Subsequently, NH<sub>3</sub> was introduced to the sample for 60 min after cooling down to 180 °C, followed by helium filling for 1.5 h. Finally, the NH3-TPD curve was recorded by programmed heating from 180 to 800 °C at a heating rate of 10 °C/min.

To characterize the changes in the acidic properties (Lewis and Brønsted) of the catalyst after the catalytic 99 100 reaction, pyridine adsorption Fourier-transform infrared (Py-IR) spectroscopy using a Tensor 27 instrument was employed to study the Lewis and Brønsted acidic properties of both fresh and used catalysts. Samples were 101 subjected to a high vacuum at 350 °C for 2 h. After cooling down to 40 °C, the catalysts were exposed to 102 103 pyridine volatiles for 30 min at temperatures of 200 and 400 °C before conducting the IR spectra measurements. To characterize the changes in the crystal phase structure of the catalyst after the catalytic reaction, X-ray 104 105 diffusion (XRD) was used to characterize the crystal phases of both fresh and used catalysts. The angle scanning rate was  $10^{\circ}$ /min, within a 2 $\theta$  range from 5° to 90°. 106

107 To characterize the oxidation states of the catalyst before and after use, X-ray photoelectron spectroscopy 108 (XPS) analysis was conducted on a Thermo Scientific K-Alpha spectrometer using Al K $\alpha$  (1486.60 eV) source 109 radiation. To account for charging effects, the binding energies were calibrated using the adventitious C 1s line 110 at 284.80 eV. To determine the type of carbon deposition formed on the catalyst, Raman spectroscopy analysis was conducted on the carbon deposition. The Raman spectroscopy was performed using the Horiba LabRAM HR Evolution, with a laser wavelength of 532 nm.

114

#### 115 2.3 Experimental setup

Figure 1 depicts the experimental reactor system. A detailed description of the key components of the system can be found in our earlier studies [19, 20]. The furnace served as the heat source for the sample and catalyst, which were separately suspended by quartz wool and placed in a ceramic alundum tube. A mesh outer electrode was wound around the alundum tube (dielectric constant of 8–11), and at the core of the tube, a rod (stainless steel) worked as the inner electrode. Monitoring of electrical signals was carried out using a digital oscilloscope (MDO3014, Tektronix, America).

In a typical run, quartz wool was used to separately fix 0.15 g of the sample and 0.6 g of the catalyst within the discharge area. Nitrogen was purged into the reactor before each experiment to ensure an inner atmosphere. The furnace was gradually heated to the target temperature at 20 °C/min and retained for 20 min. Activation of the NTP was initiated when the generator reached the desired power level, and the experiment began. Nitrogen functioned as the carrier gas with 100 mL/min. The product gases were directed through a gas bottle surrounded by ice water and collected within a gas sample bag eventually.

The gas products were qualified and quantified using gas chromatographs (Agilent 490 Micro GC). For the analysis of permanent gases (H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>), an MS5A column maintained at 80 °C was employed, with carrier gas of argon.  $C_2H_4$  and  $C_2H_6$  were analyzed using a PPU column at 80 °C with helium as the carrier gas, while hydrocarbons  $C_3-C_4$  were analyzed using an Al<sub>2</sub>O<sub>3</sub>/KCl column, maintained at 100 °C with the carrier gas of helium. The oil product underwent analysis with a gas chromatography/mass spectrometer (GC/MS-QP2010 SE,
Shimadzu, Japan). Detailed program settings were previously outlined [19]. The mass loss attributes of the used
catalyst were analyzed using Q500 V20.13. The temperature was increased at 10 °C/min from 50 to 800 °C.
During the catalyst regeneration process, the spent catalyst (20 mg) used under the conditions of 180 W,
400 °C, and an HDPE/(NiCeOx/β) ratio of 1:4, is heated to 550 °C at a heating rate of 10 °C/min and calcined
for 5 h under an oxygen atmosphere. The oxygen flow is 100 mL/min [20, 21].



139 140

Figure 1 Schematic diagram of the experimental device.

141

## 142 **2.4 DFT calculations**

We conducted all DFT calculations by the Vienna Ab initio Simulation Package (VASP) [22]. The exchange-143 correlation interactions were described using the generalized gradient approximation (GGA) in the Perdew-144 145 Burke-Ernzerhof functional (PBE) [23]. A plane-wave basis set with a cut-off kinetic energy of 400 eV, and the projector-augmented wave (PAW) method as implemented in the VASP [24]. The electronic convergence 146 criterion was 10–5 eV, and the force criterion for structure relaxation was 0.05 eV Å–1 for all forces. Weak 147 interactions were accounted for using the DFT + D3 method with empirical corrections following Grimme's 148 scheme [25]. A vacuum space of at least 15 Å was employed to prevent interactions in the periodic structure. 149 The Brillouin zone was sampled with a  $3 \times 3 \times 1$  Monkhorst-Pack grid. The reaction Gibbs free energy changes 150 151  $(\Delta G)$  for each elementary step were determined based on the computational hydrogen electrode model, which 152can be calculated using the following equation:

where $\Delta E$ represents the total energy, $\Delta ZPE$ is the change in zero-point energies (ZPE), T represents the
temperature, and $\Delta S$ represents the change in entropy of products and reactants. VASPKIT was utilized to
further analyze the result from wavefunction [26]. the climbing image elastic band (CI-NEB) method was
conducted to investigate the energy barrier of transition states [27].
3. Results and discussion
3.1 Catalyst characterizations
Table 1 provides an overview of the textural characteristics of the fresh and used catalysts. It shows that after
use, the inner surface area and pore volume of the catalyst decreased significantly, which was caused by the

coke blockage. The increased average pore diameter of the catalyst was also observed after the reaction. This is because during the reaction, the interaction between the active sites on the catalyst and the reactants leads to thermodynamic and kinetic changes in the catalyst structure. Typically, these interactions result in changes in the lattice parameters of the catalyst, causing an expansion in the size of the pores, thereby increasing the average pore diameter. Similar results have been reported in related studies [15, 28]. The DFT pore diameter distributions of the catalysts are shown in figure S1. The micropore and macropore volume of the used catalyst changed slightly in comparison to those of the fresh one. The volume of the micropores around 0.59 nm was increased, which was caused by the migration of metal particles from micropores to larger pores and external surfaces [29]. The metal migration and coke blockage led to a decrease in the macropore volume. Therefore, the catalytic reactions mainly underwent inside the micropores and macropores. 

173 Table 1 Textural properties of the catalysts.

Properties	Fresh NiCeOx/β	Used NiCeOx/β
BET surface area (m <sup>2</sup> /g)	474.35±0.73	436.59±1.18

Internal surface area (m <sup>2</sup> /g)	373.78±0.39	330.32±1.22
External surface area (m <sup>2</sup> /g)	100.57±0.47	106.27±1.13
Total pore volume (cm <sup>3</sup> /g)	0.15±0.01	0.13±0.01
Average pore diameter (nm)	3.17±0.02	3.39±0.07

Figure S2 shows the surface morphology and Ce and Ni mappings of the fresh and used NiCeOx/ $\beta$ . The fresh one displayed a uniform spherical crystal measuring approximately 0.2  $\mu$ m in size, along with a few agglomerates no longer than 5.5  $\mu$ m. The Ce and Ni metals were evenly distributed on the catalyst surface, except for slight aggregation in the agglomerated region. Ni aggregation was more evident than Ce, likely due to the higher Ni loading. The used catalyst showed serious agglomeration, with a maximum agglomeration length of about 31  $\mu$ m, and a larger amount of Ni and Ce concentrated in the agglomeration area.

Figure 2 shows the cross-section morphology and Ce and Ni mappings of the catalysts. Figure 2 (a) and (b) show that the fresh NiCeOx/ $\beta$  exhibited a loose structure, both on the surface and inside, suggesting its porous nature. The metal mappings in figure 2(c) and (d) show that both Ni and Ce metals were highly concentrated in the porous structure and evenly distributed throughout the cross-sectional area. The used catalyst also maintained its porous structure with well-dispersed Ni and Ce metals.



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Figure 2 Cross-section images of (a) and (b) fresh catalyst in different magnification, (c) Ni mapping of the fresh catalyst (d) Ce mapping of the fresh catalyst, (e) and (f) used catalyst in different magnification, (g) Ni mapping of the used

191	In figure S3, NH <sub>3</sub> -TPD profiles of the catalysts are displayed. Three distinct desorption peaks were noted
192	centered at ~144 °C, ~340 °C, and ~515 °C, corresponding to the weak, medium, and strong acid sites
193	desorption, respectively [30]. The strong acidic sites were formed due to the introduction of Ni <sup>2+</sup> and Ce <sup>4+</sup> [31].
194	After use, all three peaks shifted to lower temperatures, indicating a decrease in the acidity of the NiCeOx/ $\beta$
195	[19]. In addition, the area of those peaks decreased, indicating a reduction in the number of acid sites,
196	particularly weak acidic sites (1.46 to 1.01 mmol/g) and strong acidic sites (0.32 to 0.07 mmol/g). To indirectly
197	demonstrate whether the reduction in the number of acidic sites is caused by their involvement in the reaction
198	or by coverage with coke, the used catalyst underwent thermal regeneration, and the regenerated catalyst was
199	also characterized using NH <sub>3</sub> -TPD. The comparison of acidic site numbers among fresh, used, and regenerated
200	catalysts is presented in Table S1. After catalyst regeneration, there was a recovery in the number of weak and
201	strong acidic sites, indicating that carbon deposition on the catalyst surface led to partial deactivation of acidic
202	sites, with a more pronounced effect on weak acidic sites. A comparison of acidic site numbers between fresh
203	and regenerated catalysts illustrates that both weak and strong acidic sites are the primary catalytic active sites.
204	Figure S4 illustrates the pyridine IR spectra of the catalysts at different temperatures. Pyridines coordinated
205	to Lewis acidic sites were indicated by adsorption bands at ~1446, ~1581, ~1596, and ~1606 cm <sup>-1</sup> . The presence
206	of pyridine adsorbed at the Brønsted acidic sites was denoted by the band at ~1539 cm <sup>-1</sup> . Additionally, the band
207	at 1490 cm <sup>-1</sup> indicated the presence of pyridine adsorbed at either Lewis or Brønsted acidic sites. The decrease
208	in the signal intensity means less acidity after heating to higher temperatures under vacuum [32]. The count of
209	acids at distinct temperatures is presented in table 2. The reduction in the number of acidic sites indicated the
210	involvement of both Lewis and Brønsted acidic sites in the reaction. Additionally, the B/L ratio of the catalysts
211	at each temperature decreased after use.

Samples	Temperature	Total acid sites	B acid sites	L acid sites	B/L
	°C	µmol/g	µmol/g	µmol/g	
Fresh NiCeOx/β	40	564.75	45.37	519.38	0.09
	200	141.28	24.11	117.17	0.21
	400	44.83	9.35	35.48	0.26
Used NiCeOx/β	40	440.37	25.98	414.39	0.06
	200	114.97	9.40	105.57	0.09
	400	42.78	4.82	37.96	0.13

212 Table 2 Acidity from pyridine IR measurements.

214 Figure 3 illustrates the XRD patterns of the fresh and used NiCeOx/ $\beta$ . The strongest peak at  $2\theta = 22.5^{\circ}$ corresponds to the characteristic diffraction peak of the  $\beta$  zeolite crystal structure [33]. The peaks located at  $2\theta$ 215 216 = 37.3°, 43.3°, 62.9°, 75.5°, and 79.4° are observed on the fresh NiCeOx/ $\beta$  and identified as NiO [34, 35]. Additionally, the diffraction peaks at  $2\theta = 28.7^{\circ}$ ,  $33.2^{\circ}$ ,  $48.0^{\circ}$ , and  $55.9^{\circ}$  are identified as CeO<sub>2</sub> [36, 37]. After 217 use, the signal intensity of the NiO and CeO<sub>2</sub> peaks of the catalyst decreased significantly while the new Ni 218 219 peaks at  $2\theta = 44.4^{\circ}$ ,  $51.8^{\circ}$ , and  $76.5^{\circ}$  and new Ce peak at  $2\theta = 33.1^{\circ}$  appeared, suggesting that NiO and CeO<sub>2</sub> 220 served as catalytically active sites and were reduced to the corresponding metal products during the reaction. 221 The Scherrer formula was employed to calculate the size of metal particles on the catalyst before and after usage. 222 The findings indicated that the average size of metal crystals on the catalyst before participating in the reaction was 9.22 nm, which increased to 12.13 nm after the reaction. This increase may be attributed to metal 223 aggregation, consistent with the aggregation phenomenon observed in TEM images. 224



Figure 3 XRD patterns of the fresh and used NiCeOx/ $\beta$ .

The Ni 2p and Ce 3d XPS spectra of the fresh and used NiCeOx/ $\beta$  are shown in figure 4. In figure 4(a), there 228 229 were six diffraction peaks in the Ni 2p XPS spectra of the catalyst. Binding energies at ~872.1 and ~854.5 eV were assigned to Ni<sup>0</sup> 2p1/2 and Ni<sup>0</sup> 2p3/2, respectively [38, 39]. Binding energies of ~874.6 and ~856.8 eV 230 represented Ni<sup>2+</sup> 2p1/2 and Ni<sup>2+</sup> 2p3/2, respectively [40, 41]. The peaks at ~881.1 and ~861.9 eV were satellite 231 peaks of Ni [42, 43]. Compared with the Ni<sup>0</sup> species on the fresh NiCeOx/ $\beta$ , the Ni<sup>0</sup> species on the used 232 233 NiCeOx/ $\beta$  were transferred to a lower binding energy, indicating that the Ni<sup>0</sup> species donated fewer electrons to  $\beta$  support catalyst [44]. In addition, the proportion of Ni<sup>2+</sup> peaks to the total peak area decreased after use, 234 suggesting that a large amount of Ni<sup>2+</sup> species on the catalyst surface participated in the chemical reaction, 235aligning with the XRD findings. The Ce 3d spectra in figure 4(b) could be deconvoluted into seven diffraction 236 peaks. The five Ce 3d 3/2 peaks primarily ranged from 895 to 930 eV, and the two Ce 3d 5/2 peaks were mainly 237 at 870-905 eV. The peaks at 917.3, 903.1, 897.9, 888.3, and 881.5 eV were identified for the Ce<sup>4+</sup> oxidation 238 state, and the Ce<sup>3+</sup> oxidation state was described by the two peaks at 907.6 and 899.9 eV [45-47]. There were 239 fewer Ce<sup>4+</sup> species on the used NiCeOx/ $\beta$  compared with that of the fresh NiCeOx/ $\beta$ , suggesting that the Ce<sup>4+</sup> 240 241 species on the catalyst surface were the main active sites.



242 243

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Figure 4 XPS spectra of the fresh and used NiCeOx/ $\beta$  for (a) Ni 2p, and (b) Ce 3d.

12

#### 3.2 The role of NTP in the hydrogen production

To get a better understanding of the role of plasma in hydrogen production, six different treatment methods: pyrolysis alone (400 °C), NTP-assisted pyrolysis (180 W, 400 °C), NTP alone (180 W), NTP catalysis (180 W, HDPE/(NiCeOx/ $\beta$ ) ratio of 1:4), catalytic pyrolysis (400 °C), and NTP-assisted catalytic pyrolysis (180 W, 400 °C, HDPE/(NiCeOx/ $\beta$ ) ratio of 1:4) were compared. Figure 5 shows the gas yield and composition under different treatment methods.

251Figure 5(a) shows that only small amounts of gas components were produced through the pyrolysis alone 252 method, each less than 0.15 mmol/g. However, introducing plasma into the pyrolysis alone system significantly 253enhanced the yields of gas products, with 18.56 mmol/g of H<sub>2</sub> and 2.93 mmol/g of CH<sub>4</sub>. This increase was attributed to the collision between the high-potential-energies active species in NTP (such as electrons, charged 254particles, and electronically neutral excited substances) and primary pyrolysis products can produce radicals, 255256which can recombine to form H<sub>2</sub> and other gas products [19]. The yield of H<sub>2</sub> and CH<sub>4</sub> were 18.04 mmol/g and 1.64 mmol/g, respectively, through the NTP alone method. The energy range of active substances within the N<sub>2</sub> 257discharge was mainly at 6-11 eV, surpassing the energy thresholds for C-C and C-H bond cleavage [12]. Hence, 258 259 the reaction can occur at room temperature. Introducing the catalyst to the NTP alone system led to an increase 260 in H<sub>2</sub> yield to 21.93 mmol/g, with the yields of other gas products showing minimal change. The catalytic pyrolysis method only produced small amounts of gas components, each less than 1 mmol/g. However, the 261 application of NTP in the catalytic pyrolysis system substantially increased the yield of gas components, 262 263 resulting in the production of 31.41 mmol/g of H<sub>2</sub> and 3.91 mmol/g of CH<sub>4</sub>. The introduction of NTP into the catalytic pyrolysis system resulted in a significant improvement in  $H_2$  yield, primarily due to the plasma-catalyst 264 265interactions. The plasma was capable of modifying the physicochemical characteristics of the catalyst, changing the surface reaction pathways, and prolonging the reaction time. Meanwhile, the catalyst could enhance the 266

electric field and change the discharge type, thereby facilitating the H<sub>2</sub> production process [48, 49]. Furthermore, Bacariza et al. demonstrated that the higher the dielectric constant of the catalyst, the more pronounced the interaction between the NTP and the catalyst. Therefore, loading CeO<sub>2</sub> ( $\epsilon$ =24) and NiO ( $\epsilon$ =7-10) on zeolites( $\epsilon$ <5) is beneficial for enhancing the interaction between NTP and the catalyst [50].

271 Figure 5(b) shows the gas composition under different treatment methods. It is noteworthy that the vertical 272 axis is in logarithmic scale. The H<sub>2</sub> selectivity was only 37.81% in the pyrolysis alone system. In the NTPassisted pyrolysis system, the H<sub>2</sub> selectivity increased to 73.26%. The H<sub>2</sub> selectivity was 88.83% in the NTP-273 alone system, much higher than that in the pyrolysis-alone system, suggesting that NTP showed good selectivity 274 towards H<sub>2</sub> during the reaction. Upon the introduction of the catalyst into the NTP-alone system, the H<sub>2</sub> 275 selectivity increased to 92.62%, resulting in a total relative content of H<sub>2</sub> and CH<sub>4</sub> as high as 99.38%. The further 276 277 addition of NTP in the catalytic pyrolysis system enhanced the H<sub>2</sub> selectivity to 80.03%. In conclusion, both 278NTP and catalyst had good performance in enhancing H<sub>2</sub> selectivity.





Figure 5. The gas yield (a), and gas composition (b) under different treatment methods.

Figure S5(a) and figure S5(b) present the TG and DTG curves of used NiCeOx/ $\beta$  under different treatment 282 283 methods, respectively. As displayed in figure S5(a), there were two weight loss stages in the TG curves of the catalysts in the NTP catalysis and catalytic pyrolysis system, located at 100-200 °C and 375-550 °C, 284 respectively. The first weight loss below 200 °C was because of water release and the oxidation of light coke. 285 The second weight loss resulted from the burning of heavy carbon deposits [19]. The weight gain stage at 200-286 287550 °C was due to the oxidation of Ni [51-53]. Another weight gain stage was observed only in the NTP-assisted catalytic pyrolysis system, indicating that the combined effect of plasma and thermal could maximize the 288 catalytic activity of the Ni<sup>2+</sup> species, leading to its reduction to Ni during the catalytic process. Overall, the 289 290 weight loss of the catalysts under all three methods was low, indicating the excellent anti-coking ability of the 291 NiCeOx/ $\beta$  catalyst. Figure S5(b) shows that the maximum weight loss rate of the catalyst using the NTP 292 catalysis method was higher than that in the other two methods.

293 To further determine the type of carbon deposition formed on the catalysts, the carbon deposition was characterized using Raman spectroscopy. As shown in Figure S6, peaks corresponding to the D band at 1380 294 295 cm<sup>-1</sup> and the G band at 1600 cm<sup>-1</sup> were observed in both the NTP catalysis and catalytic pyrolysis system. The D band represents disordered carbon, while the G band represents the ideal graphite lattice [54-56]. In the NTP-296 assisted catalytic pyrolysis system, only the G band was observed, indicating that the simultaneous presence of 297 298 plasma and heat leads to the formation of carbon deposits with ordered graphite structures only, with minimal 299 carbon defects. The intensity ratio of the D band to the G band (ID/IG) was highest in the NTP catalysis system, indicating the highest degree of carbon defects in the carbon deposition. 300

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# 302 3.3 H<sub>2</sub> enhancement by different HDPE/(NiCeOx/ $\beta$ ) ratios

At a reaction temperature of 400 °C and discharge power of 180 W, figure 6(a) and figure 6(b) display the 303 gas yield and gas composition, respectively, under different HDPE/(NiCeOx/ $\beta$ ) ratios. As depicted in figure 304 305 6(a), the NiCeOx/ $\beta$  catalyst exhibited good catalytic ability for H<sub>2</sub> production. The findings of NH<sub>3</sub>-TPD and 306 Py-IR suggested that acidic sites were the primary catalytic active sites. Furthermore, the XRD and XPS results 307 demonstrated that NiO and CeO<sub>2</sub> particles were the main metallic active sites. With the increase in the catalyst, the H<sub>2</sub> yield increased first and then decreased, with the maximum value of 31.41 mmol/g at the 308 309 HDPE/(NiCeOx/ $\beta$ ) ratio of 1:4. This suggested that there existed an optimal HDPE/(NiCeOx/ $\beta$ ) ratio which can maximize hydrogen production through the synergistic effect of plasma and catalyst. This ratio is determined 310 311 by the interaction between the catalyst and plasma. The volume of the catalyst influenced the electric field in the discharge, and the electric field, in turn, affected the properties of the catalyst, thereby resulting in an optimal 312

catalyst ratio to maximize the  $H_2$  yield [57]. Figure 6(b) suggests that the main pyrolysis gas products from HDPE in the NTP-assisted catalytic pyrolysis system were  $H_2$  and  $CH_4$ . The  $H_2$  selectivity increased first and



then decreased, having the maximum value of 80.03% at the HDPE/(NiCeOx/ $\beta$ ) ratio of 1:4.



Figure 6 The gas yield (a), and gas composition (b) under different HDPE/(NiCeOx/ $\beta$ ) ratios.

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Figure S7 displays the TG and DTG profiles of the fresh catalysts under different HDPE/(NiCeOx/ $\beta$ ) ratios. As displayed in figure S7(a) when the HDPE/(NiCeOx/ $\beta$ ) ratio changed from 1:2 to 1:5, the weight loss of the catalysts reduced to 3.65%. Figure S7(b) shows that the increase of the catalyst led to a decrease in the maximum weight loss rate of the DTG curves.

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#### 324 3.4 H<sub>2</sub> enhancement by different temperatures

The results of the gas yield and gas composition under different temperatures, with a discharge power of 180 W and an HDPE/(NiCeOx/ $\beta$ ) ratio of 1:4, are presented in figure 7. Figure 7(a) illustrates that when the temperature increased from 100 to 300 °C, the H<sub>2</sub> yield enhanced significantly. With the further increase in temperature to 400 °C, the H<sub>2</sub> yield was increased slightly to 31.41 mmol/g. Two main reasons contributed to the enhancement of H<sub>2</sub> yield. First, higher temperatures increased the catalyst activity. Second, higher temperatures provided more energy, which promoted the chemical reaction. Figure 7(b) suggests that with increasing the temperature, the H<sub>2</sub> selectivity increased first and then decreased, with the maximum value of 81.80% at the temperature of 300 °C. At this temperature, the total relative content of H<sub>2</sub> and CH<sub>4</sub> was as high as 93.01%.







Figure 7 The gas yield (a), and gas composition (b) under different temperatures.

<sup>337</sup> The TG and DTG profiles of the used NiCeOx/ $\beta$  under different temperatures are displayed in figure S8. The <sup>338</sup> minimum weight loss (3.96%) and weight loss rate were obtained on the catalyst used at the temperature of <sup>339</sup> 400 °C. In addition, both the weight loss (5.44%) and the weight loss rate of the catalyst used at the temperature <sup>340</sup> of 200 °C were the highest.

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# 342 3.5 H<sub>2</sub> enhancement by different discharge power

When investigating the H<sub>2</sub> enhancement under different discharge power at a reaction temperature was 400 °C and an HDPE/(NiCeOx/ $\beta$ ) ratio was 1:4, the gas yield and gas composition are shown in figure 8. Figure 8(a) shows a significant increase in the H<sub>2</sub> yield as discharge power increases, up to a maximum value of 32.71 mmol/g at 210 W. Similar results were reported by Aminu et al., who demonstrated that increasing power from 0 to 60 W led to a rise in H<sub>2</sub> yield from 0.13 to 1.04 mmol/g [58]. This could be attributed to the higher electric field strength associated with higher discharge power. High electric field strength provided a source of highenergy electrons, promoting the cracking reaction and generating more H free radicals. Additionally, higher electric field strength could improve the metal distribution across the catalyst surface, enhance the acidity of the catalyst, and thus promote  $H_2$  generation [19, 20]. However, the yields of other gas products were slightly affected by the discharge power, potentially due to the lower energy required to break the C-H bond compared to the energy needed to break the C-C bond. Figure 8(b) suggests that the maximum  $H_2$  selectivity of 82.10% was obtained at 210 W. With increasing the discharge power,  $CH_4$  selectivity decreased first and then increased.





Figure 8 The gas yield (a), and gas composition (b) under different discharge power.

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Figure S9 shows the TG (figure S9(a)) and DTG (figure S9(b)) curves of used NiCeOx/ $\beta$  under different discharge power. The weight gain stage of the catalyst was notably impacted by the discharge power. The weight gain caused by Ni oxidation was the most at 210 W, and that was the least at 120 W. The weight loss of the catalyst was decreased as the discharge power increased, with a value of 3.24% at 210 W. This suggested higher discharge power enhanced the anti-coking ability of the catalyst. Additionally, from figure S9(b), it can be seen that increasing the discharge power reduced the maximum weight loss rate of the catalyst.

364

365 **3.6 Catalyst stability test** 

To demonstrate the cycling stability of the catalyst, the catalyst was tested under the operating conditions of
 HDPE/(NiCeOx/β) ratio of 1:4, discharge power of 180 W, and reaction temperature of 400 °C. Within 5 cycles,

the gas yield and gas composition are shown in figure 9. It is worth noting that the y-axis in figure 9 is in 368 logarithmic scale. As shown in figure 9(a), the H<sub>2</sub> yield slightly increased after the first cycle. This may be 369 370 attributed to the partial reduction of NiO and CeO<sub>2</sub> particles to their corresponding metallic forms during the catalytic reaction, and Ni and Ce metals also have good catalytic hydrogen production effects [59, 60]. The H<sub>2</sub> 371 372 yield significantly decreased after the third cycle, followed by a gradual decline. The decrease in H<sub>2</sub> yield is attributed to the accumulation of catalyst carbon deposition, leading to a decrease in catalyst activity [15]. After 373 5 cycles, the H<sub>2</sub> yield decreased by 26.45% compared to the original H<sub>2</sub> yield. Compared to the H<sub>2</sub> yield, the 374 375 decrease in CH<sub>4</sub> yield was more pronounced, especially after the fourth cycle.

As shown in figure 9(b), the selectivity of each gas fluctuates up and down within different cycle numbers. Among them, the selectivity of  $H_2$  for each cycle number was higher than the original  $H_2$  selectivity. After 2 cycles, the catalyst had the highest selectivity for  $H_2$ , reaching 85.87%. This indicates that even though the catalytic hydrogen production activity of the catalyst decreases after repeated uses, its selectivity for  $H_2$  remains relatively high.



381

382

Figure 9 The gas yield (a), and gas composition (b) under different cycle numbers.

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385 To further understand the catalytic dehydrogenation mechanism during the pyrolysis process of PE on the

386	catalysts, were performed DFT calculations and focused on typical alkanes (CH <sub>4</sub> ) and olefins (C <sub>2</sub> H <sub>4</sub> ) as the
387	subjects of study. The thermodynamic and kinetic (transition state, TS) energy barriers of CH4 dehydrogenation
388	are listed in table S2 and table S3, respectively. Compared to pure CeO <sub>2</sub> (3.79 eV), NiCeOx exhibited a reduced
389	thermodynamic energy barrier (2.62 eV), resulting in a more favorable spontaneous reaction tendency of CH <sub>4</sub>
390	decomposition on NiCeOx (table S2). Furthermore, NiCeOx also displayed a smaller kinetic reaction energy
391	barrier (3.38 eV) compared to NiO (3.55 eV) and CeO <sub>2</sub> (5.98 eV), indicating a higher $H_2$ production rate at the
392	same reaction condition (table S3). This indicated that both NiO and CeO <sub>2</sub> played key roles in the reaction,
393	confirming the rationality of the catalyst design. The free energy of CH <sub>4</sub> dehydrogenation is shown in figure 10
394	and the reaction pathway of CH <sub>4</sub> dehydrogenation is illustrated in figure 11. The process of CH <sub>4</sub>
395	dehydrogenation was as follows: $*CH_4 \rightarrow *CH_3 + *H \rightarrow *CH_2 + *H \rightarrow *CH + *H \rightarrow *C + *H$ . The thermodynamic
396	and kinetic barriers for $C_2H_4$ dehydrogenation are listed in table S4 and table S5, respectively. In comparison to
397	NiO and CeO <sub>2</sub> with an associated thermodynamic energy barrier of 2.82 eV and 3.73 eV, NiCeOx exhibited a
398	noteworthy modulation with a reduced of 1.75 eV (table S4). While NiCeOx also displayed a considerably
399	reduced kinetic reaction energy barrier, quantified at 3.24 eV, in comparison to the corresponding values for
400	NiO (3.91 eV) and CeO <sub>2</sub> (4.97 eV) (table S5). As a result, NiCeOx possessed distinct thermodynamic and kinetic
401	benefits for both alkanes and olefins intermediate during plastic decomposition, serving as the foundational
402	driving force behind the catalytic activity of our catalysts. The free energy and reaction pathways for $C_2H_4$
403	dehydrogenation are shown in figure 12 and figure 13, respectively. The C <sub>2</sub> H <sub>4</sub> dehydrogenation process
404	followed the sequence: $*C_2H_4 \rightarrow *C_2H_3 + *H \rightarrow *C_2H_2 + *H \rightarrow *C_2H + *H \rightarrow *C_2 + *H.$



Figure 10 Free energy diagram of the dehydrogenation from CH<sub>4</sub> to \*C.





\*C<sub>2</sub>H<sub>2</sub>+\*H

\*C<sub>2</sub>H<sub>3</sub>+\*H \*C<sub>2</sub>H<sub>3</sub>

\*C<sub>2</sub>H<sub>2</sub>

\*C<sub>2</sub>H+\*H

NiCeOx

 $*C_2H$ 

NiO

CeO<sub>2</sub>

411

412

405

406

407

408

409

410

2

1

0

 $C_2H_4$ 



414 415

Figure 13 Reaction pathway of the dehydrogenation from  $C_2H_4$  to  $*C_2$ .

417 Based on DFT calculations of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, we have created a probable reaction mechanism diagram for the in-situ reforming of primary pyrolysis products of PE with NTP-assisted catalysis, as shown in figure 14. 418 Initially, the NTP-assisted pyrolysis of PE occurred according to random-chain scission, forming primary 419 420 pyrolysis products primarily composed of chain hydrocarbons. Among these products, the liquid fraction was predominantly made up of diolefins, mono-olefins, and alkanes (see table S6), while the gaseous fraction was 421 422 as shown in figure 5. The NTP and catalyst then facilitated the in-situ reforming of these intermediate products. 423 Studies have shown that the NTP can penetrate the mesopores and stabilize the active species, thus enhancing the reaction time [61]. The active particles in the NTP, such as electrons,  $N_2^+$ , and the second positive bands of 424 N<sub>2</sub>, collided with the intermediate products, generating unstable radicals that further reacted to form gas products 425 [62]. The NiCeOx/ $\beta$  catalyst had three types of active sites: Lewis and Brønsted acidic sites of  $\beta$  support, NiO 426 427 active sites, and CeO<sub>2</sub> active sites, all of which exhibited good performance in H<sub>2</sub> production. Finally, in the NTP-assisted catalytic pyrolysis system, the H<sub>2</sub>-rich gaseous products were produced as a result of the combined 428 429 effect of thermal energy, plasma, and catalysis.





- This study aims to enhance H<sub>2</sub> yield using the NiCeOx/ $\beta$  catalyst at low temperatures. The study examined 434 the role of NTP and catalyst in H<sub>2</sub> production, as well as the effects of PE/(NiCeOx/β) ratio, discharge power, 435 and reaction temperature on H<sub>2</sub> production. Finally, based on DFT calculations, a hydrogen production 436 437 mechanism was proposed. The main conclusions were as follows:
- (1) NTP enhanced H<sub>2</sub> production by promoting collision between high-potential-energies active species and 438
- by creating plasma-catalyst interactions. 439

- (2) The NiCeOx/ $\beta$  catalyst showed excellent performance in H<sub>2</sub> production due to its catalytic acidic sites, as 440
- well as the main metallic active sites of NiO and CeO<sub>2</sub> particles. 441
- (3) The DFT calculations indicated that both NiO and CeO<sub>2</sub> exhibited significant thermodynamic and kinetic 442
- 443 benefits for the primary pyrolysis products of PE.
- 444 (4) The yield and selectivity of H<sub>2</sub> increased first and then decreased with increasing catalyst, peaking at a

- 445 PE/(NiCeOx/ $\beta$ ) ratio of 1:4 with maximum values of 31.41 mmol/g and 80.03%, respectively.
- 446 (5) Increasing the pyrolysis temperature and discharge power led to increased  $H_2$  yield. The maximum  $H_2$
- 447 yield, reaching 32.71 mmol/g, was achieved at a temperature of 400 °C and a discharge power of 210 W.

# 448 Authorship contribution

- Jiaxing Song: Writing original draft, Investigation, Methodology, Writing review & editing.
- 450 Jiabao Lv: Conceptualization.
- 451 Yuhan Pan: Writing review & editing.
- 452 Jingyu Wang: Writing review & editing.
- 453 Jun Wang: Methodology.
- 454 Ang Cao: Conceptualization.
- 455 Angjian Wu: Conceptualization.
- 456 Paul T. William: Investigation.
- 457 Qunxing Huang: Supervision, Project administration.

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- 463 **Note**
- 464 The author declares no competing financial interest.

465

466 **Declaration of competing interest** 

The authors declare that they have no known competing financial interests or personal relationships that could
 have appeared to influence the work reported in this paper.

469

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