Hydrochar-Supported, *in Situ*-Generated Nickel Nanoparticles for Sorption-Enhanced Catalytic Gasification of Sewage SludgeChao Gai,^{†,‡} Fang Zhang,[§] Yanchuan Guo,^{‡,||} Nana Peng,^{†,‡} Tingting Liu,^{†,‡} Qianqian Lang,^{†,‡} Yu Xia,^{†,‡} and Zhengang Liu^{*,†,‡,||}[†]Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China[‡]University of Chinese Academy of Sciences, Beijing 100049, China[§]Analytical and Testing Center, Beijing Institute of Technology, Beijing 100081, China^{||}Key Laboratory of Photochemical Conversion and Optoelectronic Material, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 29 Zhongguancun East Road, Beijing 100190, China

S Supporting Information

ABSTRACT: Conversion of sewage sludge into hydrogen-rich syngas is highly attractive but is frequently hampered by low hydrogen selectivity and low gasification efficiency. In the present study, a new strategy was developed that could greatly promote hydrogen production and markedly suppress the formation of undesired byproducts. A hydrochar (HC)-supported Ni nanoparticles (NPs) composite was initially synthesized via a facile, one-step hydrothermal carbonization of Ni-preloaded sewage sludge. A sorption-enhanced steam gasification process was then probed to shift the equilibrium of the water–gas shift (WGS) reaction toward hydrogen production using calcined eggshell as the natural CO₂ sorbent. During the catalytic gasification process, uniformly dispersed NiO NPs were generated *in situ* and provided the active sites for the adsorption of tar molecules for catalytic conversion. The resulting Ni_{0.1}@HC composite showed the highest catalytic activity in promoting hydrogen production and tar reduction under mild conditions due to the strong interactions between the metal cations and the carbonaceous support. Excellent catalytic results (72.5% selectivity for hydrogen and 78.7 g H₂/kg hydrochar for hydrogen yield) were achieved, and little or no tar was formed, even at moderately low temperatures (700–800 °C). Successful utilization of sewage sludge via the proposed catalytic strategy has the potential to enhance hydrogen-rich syngas production and simplify cleanup of the syngas without extra energy consumption.

KEYWORDS: Sewage sludge, Nickel nanoparticles, Hydrothermal carbonization, Hydrochar, Hydrogen, Steam gasification

■ INTRODUCTION

Against the backdrop of global energy crisis and environmental pollution, the significant promise of hydrogen as an alternative energy carrier has led to the question of how to produce hydrogen more efficiently and sustainably. This question has arisen in parallel with the development of innovative, sustainable nanomaterials that achieve desirable performance in this area with limited environmental impact. From a sustainability and availability standpoint, derivation of hydrogen-rich syngas from renewable, abundant, and inexpensive waste biomass rather than fossil fuels via pyrolysis/gasification may provide an economically viable and environmentally responsible option.

Sewage sludge from municipal or industrial wastewater treatment processes contains large amounts of organic components and harbors great potential for hydrogen production via steam gasification.^{1,2} Nevertheless, the efficient conversion of sewage sludge to hydrogen-rich syngas still

represents a key challenge because of its complex composition and high moisture content. In this context, synthesis of highly active, low cost, robust, and coke-resistant catalysts for gasification of sewage sludge has garnered increasing attention. Ni-based catalysts are among the most promising for tar removal and syngas reforming during biomass gasification.^{3–6} The catalytic activity of Ni-based catalysts is greatly affected by the porous support on which the active phase (Ni metal or Ni metal oxide) is finely dispersed. Although various types of supports are accessible for nickel catalysts, including metal oxides (e.g., MgO, ZrO₂, and Al₂O₃) or natural materials (e.g., zeolite, dolomite, and olivine), the facile use of low toxic and inexpensive carbon-based materials as the support for the synthesis of Ni-based nanomaterials for catalysis deserves

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priority due to the tailored porous structure and surface functional groups, which in turn affect the redox properties and the strength of the metal–support interaction that pertain primarily to the catalytic activity and stability.

Nickel nanoparticles (NPs) may be fabricated to be strongly or weakly anchored to the carbon layers, depending on the preparation approach. The catalyst prepared by surface precipitation or impregnation of metal precursor to the pyrochar derived from biomass exhibited desirable performance in the biomass conversion.^{7,8} As the pyrochar cannot effectively anchor all metal NPs and the uncoated metal NPs are prone to agglomerate, modulation of both the carbon support and the preparation approach has been probed to strengthen the interaction between the metal NPs and the carbonaceous support. Progress has been made recently in synthesizing carbonaceous supports via a hydrothermal carbonization (HTC) process. A high-temperature HTC process (>300 °C) is applied to synthesize activated carbon, graphite, and carbon nanotubes.^{9,10} Alternatively, a low-temperature HTC process, which is generally carried out under milder conditions (<300 °C), is used to generate monodispersed colloidal carbonaceous spheres (hydrochar, HC).^{11,12} Hydrochar prepared by the moderate hydrothermal processing of biomass is rich in various oxygenated functional groups (e.g., hydroxyl, carbonyl, carboxyl, and lactone),^{13–15} which could enhance the carbon–metal precursor interaction and may contribute to a better catalytic ability for hydrogen-rich syngas production via the gasification process. In previous work, we have demonstrated that a facile, one-pot HTC synthesis of Fe NPs immobilized in the hydrochar¹⁶ assisted uniform dispersion of metal NPs on the surface of hydrochar through surface-mediated chemistry, possessing high catalytic activity and stability for biomass tar reduction.

According to Pentsak et al.,¹⁷ modulation of the carbon support may take place not only during the catalyst preparation but also during the operation of the catalysts in the reaction. The development of a new catalytic strategy is therefore desirable to further simplistically modulate the cleanup of the syngas produced during the gasification process. For example, to promote process intensification in syngas production from biomass gasification, Richardson and co-workers^{18,19} probed the integration of Ni-based nanocatalysts in the biomass feedstock and observed that the Ni NPs generated *in situ* during biomass pyrolysis exhibited high catalytic activity for biomass tar reduction. This novel catalytic strategy, relying on the *in situ* conversion of reactive intermediates by *in situ*-generated metal NPs, was also successfully applied to other biomass pyrolysis/gasification processes.²⁰ To further increase the selectivity of H₂ formation during the catalytic gasification process, the equilibrium of water–gas shift (WGS) reactions and steam reforming toward H₂ production should be further promoted. To this end, the *in situ* removal of CO₂ by the carbonation reaction of CaO-based sorbents is necessary.²¹ For example, Feroso and co-workers²² achieved both desirable selectivity (>99 vol %) and good yield (up to 90%) of H₂ from wood sawdust by a sorption-enhanced catalytic steam gasification process. Separately, the production of H₂ with substantially suppressed CO₂ formation was achieved when Group I and II hydroxides were applied in the alkaline thermal treatment of cellulose.²³

Therefore, to maximize hydrogen-rich syngas production from sewage sludge, we postulated a catalytic strategy that combined *in situ*-generated Ni NPs during the gasification with

the sorption-enhanced steam gasification process. Although extensive work on Ni-doped biomass/biochar as the feedstock and their effect on pyrolysis/gasification performance has been reported in the literature, to the best of our knowledge the inclusion of nickel into the hydrochar structure has not been shown, and there is no clear understanding of the effect of nickel loading on the interaction between the nickel cations and the hydrochar as the carbonaceous support. In addition, given that the hydrochar as the carbonaceous support can promote the dispersion of the crystallites and increase the number of active sites,¹⁶ optimization of the Ni dispersion and Ni–support interaction could provide a basis for exploring a novel gasification strategy.

In this work, we describe a facile, one-pot hydrothermal synthesis of Ni-doped hydrochar and explore its use as a precursory feedstock for hydrogen-rich syngas production via an integrated sorption-enhanced catalytic gasification process. The purpose of the current work was to provide new insight into the complex catalytic mechanisms involved in this pathway, which is not quite clear to date. To that end, we focused on the following: (i) preparing the Ni-based hydrochar via a one-pot hydrothermal process, (ii) characterizing the resulting *in situ*-generated Ni NPs in the gasification process using a variety of analytical techniques, (iii) probing how the reaction variables control the selectivity and yields of hydrogen in product streams during the gasification process, and (iv) elucidating underlying mechanistic issues of the proposed catalytic strategy.

■ EXPERIMENTAL SECTION

Preparation of Nickel-Doped Hydrochar. Raw sewage sludge was collected from a municipal sewage treatment plant in Beijing, China. The initial moisture content of the raw sewage sludge was 81.9%. The physical and chemical properties of the sewage sludge are presented in Table 1. The raw sewage sludge was oven-dried at 105 °C

Table 1. Proximate and Ultimate Analysis of the Sewage Sludge

strain	sewage sludge
Proximate Analyses (% Dry Basis)	
Fc	11.46
Vm	57.78
ash	30.76
Ultimate Analyses (% Dry Ash-Free Basis)	
C	33.98
H	6.02
N	6.24
O ^a	52.84
S	0.92

^aBy difference.

for 24 h, and then 20 g samples of dried sewage sludge were mixed with 200 mL portions of nickel nitrate solutions with different concentrations. The mixture was placed in a stainless steel autoclave which was then sealed, and heated to 200 °C for 1 h. After the reaction, the reactor was cooled to ambient temperature. The solid products were then filtered off from the resultant mixture, washed with 200 mL of deionized water, and then dried in an oven at 105 °C for 12 h. The resulting samples were sieved through a 120-mesh screen, and the particles smaller than 0.125 mm were reserved for further testing. All the experiments were repeated three times, and the samples produced under identical conditions were mixed to reduce the error. Three metal concentrations were applied in the solutions: 0.1, 0.5, and 1.0 M. The resulting composites are denoted as Ni_{0.1}@HC_{Op}, Ni_{0.5}@

Figure 1. Preparation of the nickel-impregnated hydrochar derived from sewage sludge by one-pot synthesis and steam gasification test.

HC_{Op}, and Ni_{1.0}@HC_{Op}, respectively. As a control, a blank hydrochar sample was prepared under identical conditions using water instead of nickel nitrate solutions, and it was labeled as HC.

Catalytic Gasification. The performance of the prepared composites for hydrogen-rich syngas production was determined as follows: Steam gasification of the nickel-impregnated hydrochar was conducted with a laboratory-scale fixed-bed reaction system.²⁴ It included a steam generation kit, quartz tubular reactor, gas pipeline, and gas purification unit. A schematic illustration of hydrochar preparation and steam gasification of sewage sludge for the production of hydrogen-rich syngas is shown in Figure 1. During the experiment, N₂ (100 mL min⁻¹) was applied as carrier gas. Around 1 g of the feedstock was placed inside a quartz boat. The quartz tube was initially heated to the desired temperature, and then the steam generation kit was turned on. After 20 min, the quartz boat was sent into the heating zone of the tube, and the nitrogen gas was switched off. The produced gas was cooled and dried by the gas purification unit and then collected using a gas sampling bag throughout the entire reaction time. The main noncondensable gas composition, including H₂, CH₄, CO, and CO₂, was analyzed using a gas chromatograph (GC 3420A) equipped with a thermal conductivity detector (TCD), a GDX-104 column, and a 5A column. Argon was used as the carrier gas, and standard gas mixtures were used for quantitative calibration. The catalytic performance was evaluated in terms of the hydrogen yield, gasification efficiency, and energy recovery efficiency (ERE).^{24,25}

Characterization. A Hitachi SU-8020 field-emission scanning electron microscope (FE-SEM, Hitachi, Japan) operated at an accelerating voltage of 5 kV was applied to observe the surface morphology of the prepared materials. High-resolution transmission electron microscopy (HR-TEM) images of the composites were observed using a JEOL JEM-2100 instrument (JEOL, Japan) equipped with a Gatan SC1000 ORIUS camera. The composite samples were finely dispersed in ethanol, followed by ultrasonic processing, and then dropped onto a copper grid coated with a holey carbon film. The crystalline phases of the samples were evaluated by using a wide-angle X-ray diffractometer (Bruker D8 Advance, Bruker, Germany) with graphite monochromated copper radiation (Cu K α) at 40 kV and 30 mA. The sample was scanned from 20° to 80° at a scanning rate of 5°/min.

RESULTS AND DISCUSSION

Characteristics of the Nickel-Doped Hydrochar. The surface morphologies of hydrochar and the composites of Ni_{0.1}@HC, Ni_{0.5}@HC, and Ni_{1.0}@HC were initially examined

by FE-SEM measurements (Figure 2). Porous surfaces and irregular structures were observed for all the samples, including

Figure 2. FE-SEM images of the pristine hydrochar (a,e), Ni_{0.1}@HC (b,f), Ni_{0.5}@HC (c,g), and Ni_{1.0}@HC (d,h).

trenches and cracks with small carbonaceous microspheres. This may be ascribed to the hydrolysis/decomposition of the organic components in sewage sludge, accompanied by the formation of amorphous carbon during the HTC process. Micrometer-sized particles with forms such as honeycombs, fluffies, or spherical shaped were also observed, mainly derived from the carbohydrates in sewage sludge.²⁶ Moreover, compared to the HC and Ni_{0.1}@HC, a structure comprising multiple carbonaceous layers with a curved or flat upper edge were observed in the FE-SEM images of Ni_{0.5}@HC, and part of Ni_{1.0}@HC. These results indicate that the structure of the prepared Ni@HC composite depends strongly on the concentration of the precursor nickel ions during the one-pot HTC process. The different catalytic activities are expected because of the different structures of the prepared composites. The distribution of O and Ni elements in the Ni_{0.1}@HC was probed via SEM mapping (Figure S1), and these elements were found to be uniformly dispersed throughout the prepared Ni@HC composite.

Fourier transform infrared (FTIR) spectroscopy can be used to study the nature of the metal cation adsorption sites inside the biochar matrix.^{18,20} FTIR spectra of HC and the composites

of $\text{Ni}_{0.1}\text{@HC}$, $\text{Ni}_{0.5}\text{@HC}$, and $\text{Ni}_{1.0}\text{@HC}$ are shown in Figure 3. The band at 3320 cm^{-1} is ascribed to the O–H stretching

Figure 3. FTIR spectra of the pristine hydrochar, $\text{Ni}_{0.1}\text{@HC}$, $\text{Ni}_{0.5}\text{@HC}$, and $\text{Ni}_{1.0}\text{@HC}$.

vibration in hydroxyl or carboxyl functional groups. The band between 3000 and 2800 cm^{-1} is assigned to the $-\text{CH}_x$ stretching vibration of alkyl groups. The peaks between 1710 and 950 cm^{-1} are attributed to the presence of oxygen-containing functionalities. FTIR spectra of the nickel-doped hydrochar reveal that, during the one-pot HTC process, the

nickel ions are anchored to the hydrochar surface by linking to functional groups such as $-\text{OH}$ and $-\text{COOH}$.

The crystalline structure of the $\text{Ni}_x\text{@HC}$ composites before and after gasification was examined by wide-angle X-ray diffraction (XRD) analysis (Figure 4). In the XRD patterns of the spent $\text{Ni}_{0.1}\text{@HC}$, $\text{Ni}_{0.5}\text{@HC}$, and $\text{Ni}_{1.0}\text{@HC}$ composites, the diffraction peaks at 37.30° , 43.29° , 62.84° , 75.41° , and 79.37° are assigned to NiO, corresponding to the following crystallographic planes: (003), (202), (220), (223), and (042), respectively (PDF card #01-89-3080). No characteristic peaks for NiO NPs were observed in the XRD patterns of the fresh $\text{Ni}_x\text{@HC}$ ($x = 0.1, 0.5, 1.0$) composites (Figure 4A). This observation provides strong evidence for the *in situ*-generated NiO NPs during the gasification process.

Further insights into the morphology of the NiO NPs were gained from the HR-TEM micrographs (Figure 5). Taking the $\text{Ni}_{0.5}\text{@HC}$ composite as an example, the HR-TEM of the spent $\text{Ni}_{0.5}\text{@HC}$ at 700 , 800 , and 900°C reveals that well-dispersed NiO NPs were formed after the gasification process. Location of the metal NPs inside or outside of the support greatly affects the catalytic activity of the composite.²⁷ Wu et al.²⁸ probed the effect of Ni location within the support for hydrogen production from the catalytic gasification of biomass. During the gasification process, for the catalysts that had NiO particles located inside the pores of the support, more hydrogen and less tar were generated compared to the catalysts that had NiO particles located outside the pores. This can probably be

Figure 4. XRD patterns of the fresh nickel-doped hydrochar (A), spent $\text{Ni}_{0.1}\text{@HC}$ (B), spent $\text{Ni}_{0.5}\text{@HC}$ (C), and spent $\text{Ni}_{1.0}\text{@HC}$ (D) composites according to PDF card #01-89-3080.

Figure 5. TEM images of the spent $\text{Ni}_{0.5}\text{@HC}$ at 700 (a), 800 (b), and 900 °C (c) and $\text{Ni}_{1.0}\text{@HC}$ at 900 °C (d).

ascribed to the longer residence time of the pyrolysis reactants inside the pores of the support, resulting in a longer contact time between the reactants and active Ni sites. In this work, the *in situ*-generated NiO NPs were all encapsulated in the nanosized pores/channels of the hydrochar support, which may enhance the metal–support interaction. According to Moussa et al.,²⁷ electrons are more significant factors affecting the metal–support interaction than geometric factors, as the charge transfers between the carbonaceous support and metal NPs. Shi et al.²⁹ reported that doped graphite nitrogen into a carbonaceous support could lead to a non-uniform electron distribution, thus promoting charge transfer and enhancing the catalytic activity. In this work, sewage sludge is a natural nitrogen-rich precursor due to its large fraction of proteins. Therefore, we envision that the *in situ*-generated NiO NPs on the hydrochar derived from nitrogen-rich sewage sludge may promote high catalytic activity and selectivity toward hydrogen during the gasification process, which will be probed in the next section.

Catalytic Gasification Performance. The catalytic activities of HC and the composites of $\text{Ni}_{0.1}\text{@HC}$, $\text{Ni}_{0.5}\text{@HC}$, and $\text{Ni}_{1.0}\text{@HC}$ were examined via the gasification tests. In a previous study,²⁴ the steam-to-biomass (S/B) mass ratio was optimized to enhance hydrogen production, and the optimum ratio was 1.0, which was applied in this work. Figure 6 depicts the selectivity of the main gas compositions (dry and N_2 -free basis) from the catalytic gasification of the $\text{Ni}_x\text{@HC}$ ($x = 0.1, 0.5$, and 1.0) at different reaction temperatures ranging from 600 to 900 °C. The hydrogen yield, gasification efficiency, and ERE calculated for each test are summarized in Table 2. The control reaction exhibited lower selectivity toward H_2 yield (21–42%) and contained significant amounts of CO_2 (30–58%), especially at lower temperatures (600–700 °C). For comparison, we tested the activity of the $\text{Ni}_x\text{@HC}$ ($x = 0.1, 0.5, 1.0$) composites under identical conditions, and as expected, the nickel-doped hydrochar exhibited higher catalytic activity and selectivity for H_2 (40–67%) than the pristine hydrochar. For example, at the temperature of 800 °C, the selectivity of H_2 for the hydrochar was markedly increased from 40% for HC to 67% for $\text{Ni}_{0.1}\text{@HC}$, 54% for $\text{Ni}_{0.5}\text{@HC}$, and 52% for $\text{Ni}_{1.0}\text{@HC}$. Moreover, the H_2 yields of the $\text{Ni}_x\text{@HC}$ ($x = 0.1, 0.5, 1.0$) were 2 or 3 times higher than that of HC at relatively lower temperatures (600–700 °C). Overall, the $\text{Ni}_x\text{@HC}$ composites markedly outperformed the pristine HC for the gasification. It is well known that the intrinsic catalytic activity of the catalyst is

Figure 6. Selectivity of the main gaseous products from the catalytic gasification of $\text{Ni}_x\text{@HC}$ ($x = 0.1, 0.5, 1.0$) composites at 600 (a), 700 (b), 800 (c), and 900 °C (d).

Table 2. Hydrogen Yield, Gasification Efficiency, and Energy Recovery Efficiency of the Catalytic Gasification of Sewage Sludge

entry	composite	temp (°C)	hydrogen yield (g H_2 /kg biochar)	gasification efficiency (%)	ERE
1	HC	600	12.85	25.95	0.27
2	HC	700	21.12	38.60	0.40
3	HC	800	36.01	58.28	0.60
4	HC	900	41.65	63.21	0.66
5	$\text{Ni}_{0.1}\text{@HC}$	600	37.01	85.25	0.96
6	$\text{Ni}_{0.1}\text{@HC}$	700	58.05	88.39	0.99
7	$\text{Ni}_{0.1}\text{@HC}$	800	72.34	97.47	1.09
8	$\text{Ni}_{0.1}\text{@HC}$	900	67.22	93.46	1.05
9	$\text{Ni}_{0.5}\text{@HC}$	600	36.79	96.34	1.10
10	$\text{Ni}_{0.5}\text{@HC}$	700	50.65	92.62	1.06
11	$\text{Ni}_{0.5}\text{@HC}$	800	53.35	93.24	1.07
12	$\text{Ni}_{0.5}\text{@HC}$	900	46.75	87.83	1.00
13	$\text{Ni}_{1.0}\text{@HC}$	600	39.11	94.26	1.10
14	$\text{Ni}_{1.0}\text{@HC}$	700	49.22	98.50	1.15
15	$\text{Ni}_{1.0}\text{@HC}$	800	49.41	94.26	1.10
16	$\text{Ni}_{1.0}\text{@HC}$	900	42.90	88.17	1.03

more related to the phase than to the structure. As verified by the XRD patterns (Figure 4) and HR-TEM images (Figure 5) of the spent $\text{Ni}_x\text{@HC}$ composites, we find that the high catalytic activity and selectivity toward hydrogen of the $\text{Ni}_x\text{@HC}$ composites are more related to the *in situ*-generated NiO NPs on the hydrochar derived from nitrogen-rich sewage sludge.

The effects of reaction temperature and nickel loading on the catalytic activity of the *in situ*-generated NiO NPs toward the hydrogen-rich syngas production were further probed. As for the control test (HC), the selectivity (Figure 6) and yield (Table 2) of H_2 gradually increased with the increased temperature from 600 to 900 °C. The significant increase of the hydrogen selectivity with the increasing temperature is probably due to the favored endothermic WGS reaction and steam reforming of the hydrocarbons. Interestingly, the selectivity (Figure 6) and yield (Table 2) of H_2 for the $\text{Ni}_{0.5}\text{@HC}$ composite continuously increased at temperatures up to 800 °C. A further increase of the reaction temperature had negative effects on the catalytic activity of the $\text{Ni}_{0.5}\text{@HC}$.

Figure 7. Selectivity of the main gaseous products from the sorption-enhanced steam gasification. (a) Effect of loading of CaO as the CO₂ sorbent. (b) Comparison of CaO and calcined eggshell as the natural CO₂ sorbent. (c) Gasification of Ni_{0.1}@HC at 700 °C. (d) Gasification of Ni_{0.1}@HC at 800 °C.

Although Ni has been reported to be an active site for the WGS reaction,³⁰ it appears that the catalytic reactivity of the Ni_{0.5}@HC is not obvious at relatively high gasification temperature in this study. The turnover temperatures for Ni_{0.1}@HC and Ni_{1.0}@HC were also observed at around 800 °C. As shown in the XRD patterns of the Ni_x@HC composites (Figure 4), the (202) diffraction peak for patterns of the three materials appeared at somewhat lower 2θ angles and became narrower and stronger with the increasing gasification temperature, indicating the growth of the crystal size of NiO NPs. The effects of Ni²⁺ cation concentration and temperature on the crystal size of the *in situ*-generated NiO NPs in the Ni_x@HC (*x* = 0.1, 0.5, 1.0) composites determined by XRD are shown in Table S1. For the Ni_{0.5}@HC composite, based on the (202) diffraction peak (Figure 4B) and Scherrer's formula, the average size of the crystallites was calculated to be 33.78 nm at 600 °C, and the crystals grew to 67.44 nm at 900 °C. Moreover, the grain size of the NiO NPs rapidly increased from 37.48 nm at 700 °C to 56.18 nm at 800 °C. This calculation coincides with the values observed by HR-TEM (Figure 5a–c). The changes in the grain size as presented in Table S1 are consistent with the temperature affecting the selectivity and yield of H₂ for the

Ni_{0.5}@HC. Moreover, such consistency was also observed in the XRD patterns of the spent Ni_{0.1}@HC and Ni_{1.0}@HC (Figure 4, Table S1). Similarly, Chen et al.³¹ also observed that increasing the NiO fraction in the catalyst did not enhance the WGS reaction. Consequently, we anticipate that the grain size of the NiO NPs significantly affects the catalytic activity of the prepared nickel-doped hydrochar. The catalytic activity of the hydrochar-supported Ni NPs composite could be enhanced when the crystal size was lower than 50 nm. It was observed that, at the same temperature, small modifications of the crystal size were obtained for the nickel-doped hydrochar with different amounts of Ni doping. Gasification temperature is a more important factor modulating the grain size of the NiO NPs. The metal NPs are usually described by three mechanisms in terms of (i) particle migration, (ii) Ostwald ripening, and (iii) vapor transport between the particles, notwithstanding that a comprehensive knowledge of this process is currently not available. Sehested et al.³² reported that Ostwald ripening dominated the Ni NPs growth during the steam reforming of Ni-based catalysts. The above results reveals that the inclusion of nickel in the hydrochar via a one-pot HTC synthesis allows the hydrogen-rich syngas production via gasification at a

Table 3. Hydrogen Yield, Gasification Efficiency, and Energy Recovery Efficiency of the Sorption-Enhanced Steam Gasification Process

entry	composite	temp (°C)	absorbent	loading (wt%)	hydrogen yield (g H ₂ /kg biochar)	gasification efficiency (%)	ERE
1	Ni _{0.1} @HC	700	CaO	10	52.36	85.12	0.96
2	Ni _{0.1} @HC	700	eggshell	10	61.36	97.87	1.10
3	Ni _{0.1} @HC	700	eggshell	20	68.09	96.75	1.09
4	Ni _{0.1} @HC	700	eggshell	50	50.46	92.36	1.04
5	Ni _{0.1} @HC	800	CaO	10	65.32	89.83	1.01
6	Ni _{0.1} @HC	800	eggshell	10	69.30	92.41	1.04
7	Ni _{0.1} @HC	800	eggshell	20	78.67	97.28	1.10
8	Ni _{0.1} @HC	800	eggshell	50	46.17	75.88	0.86
9	Ni _{0.5} @HC	700	CaO	0	50.65	92.62	1.06
10	Ni _{0.5} @HC	700	CaO	20	57.16	98.04	1.12
11	Ni _{0.5} @HC	700	CaO	50	54.88	96.35	1.10
12	Ni _{0.5} @HC	700	CaO	75	21.92	74.70	0.86
13	Ni _{0.5} @HC	700	CaO	100	14.74	68.49	0.78
14	Ni _{1.0} @HC	800	eggshell	20	60.18	93.92	1.08
15	Ni _{1.0} @HC	800	eggshell	20	42.20	54.80	1.01

relatively lower temperature than the conventional feedstock precursors.

A ERE of 1 indicates that the total energy consumption during the one-step HTC treatment combined with gasification is equal to the energy involved in the product gas. We calculated ERE values of the four materials and found that, at the same temperature, the ERE values of the Ni_x@HC ($x = 0.1, 0.5, 1.0$) composites (entries 5–16, Table 2) were all higher than those of HC (entries 1–4, Table 2). This suggests that the conversion of nickel-impregnated hydrochar is a more energy-saving approach for hydrogen-rich syngas production compared with that of the pristine hydrochar. Moreover, the ERE values of Ni_{0.5}@HC and Ni_{1.0}@HC were higher than 1 at different temperatures, implying that increasing nickel loading on the hydrochar helps to save more energy during the hydrogen-rich syngas production from sewage sludge.

Promoting tar conversion is one of the key factors to increase the H₂ yield.^{22,33} We also probed the effect of reaction temperature and nickel loading on tar conversion (Figure S2). As shown in Figure S2, the color of the liquid phase from reaction of HC was golden yellow, which suggested the presence of tar in terms of phenolic, alkylated aromatic, polycyclic aromatic hydrocarbons, and other high-molecular-weight compounds. The color of the liquid phase from reactions of Ni_x@HC ($x = 0.1, 0.5, 1.0$) was much lighter than that of HC under identical reaction conditions. With the increased Ni²⁺ concentration, the color changed to pale yellow, and for Ni_{0.5}@HC, it became completely colorless, even at the relatively low temperature of 700 °C. This observation implies that increasing concentration of nickel salt during the one-pot hydrothermal synthesis helps to promote tar conversion during the gasification process, thus leading to a higher H₂ yield. Similarly, Richardson et al.¹⁸ observed that the *in situ*-generated Ni NPs exhibited higher catalytic efficiency for aromatic tar during the biomass pyrolysis process. However, it should be noted that increasing temperature from 800 to 900 °C darkened the color of the liquid phase from Ni_x@HC ($x = 0.1, 0.5, 1.0$), implying that the tar reduction ability of the Ni_{1.0}@HC was decreased at high temperatures. As revealed by XRD (Figure 4), it is proposed that NiO NPs played an important role to provide active sites for tar reforming when the grain size was lower than 50 nm in this study. Therefore, the one-pot HTC process is a promising strategy for *in situ* tar

reduction during the gasification process, and future research should be focused on the development of more active catalysts.

Sorption-Enhanced Steam Gasification. The *in situ* generation of Ni NPs is independent of the CO₂ sorption-enhanced catalytic strategy. To probe whether the combination of the two sides will affect each other, we carried out a sequence of experiments of the sorption-enhanced steam gasification of the nickel-doped hydrochar in the presence of different CO₂ sorbents including CaO and calcined eggshell.

The desirable loading of CaO-based sorbents for enhancing hydrogen production was initially probed in a series of tests in which the mixtures of Ni_{0.5}@HC and CaO were gasified at 700 °C with different mixture ratios: 0, 20, 50, 75, and 100 wt%. The selectivity for the gaseous products is illustrated in Figure 7a. The corresponding hydrogen yield, gasification efficiency, and ERE calculated for each experiment are presented in Table 3. It was found that a mixture ratio lower than 20 wt% increased the selectivity toward H₂, while a further increase of the mixture ratio displayed a negative effect (entries 9–13, Table 3). The optimum activity and selectivity toward hydrogen were observed with a CaO loading of 20 wt%. The mixture ratio of 100 wt% (entry 13, Table 3) showed the highest selectivity toward CO but the lowest selectivity toward H₂. The high selectivity for CO from the addition of excess CaO may be attributed to the favored reaction ($C + CO_2 \rightarrow CO$) by the decarbonation reaction ($CaCO_3 \rightarrow CaO + CO_2$).³⁴

Eggshell is a desirable CaO-based CO₂ sorbent from the waste resources for reasons of low cost and safety and because it is environmentally benign. To make sure the calcite in eggshell was transformed to CaO and maintain the strength, the eggshell was calcined at 800 °C for 2 h.³⁵ FE-SEM images of the CaO and calcined eggshell (Figure S3) illustrated that various irregular particles were present on the surface of CaO, while more uniform spherical particles were clearly observed on the calcined eggshell with a more porous structure. To illustrate the usefulness of this natural material, we subsequently conducted the sorption-enhanced gasification reaction of Ni_{0.1}@HC at two temperatures (700 and 800 °C) using the calcined eggshell as the natural CO₂ sorbent in the sorption-enhanced steam gasification process. The hydrogen selectivity and yield are shown in Figure 7b and Table 3, respectively. At the temperature of 700 °C, better selectivity for hydrogen (64%) and higher hydrogen yield (61.36 g H₂/kg hydrochar)

were observed accordingly with the presence of calcined eggshell versus CaO (58% hydrogen selectivity and 52.36 g H₂/kg hydrochar hydrogen yield). We also tested the activity of Ni_{0.1}@HC at 800 °C and found that the calcined eggshell resulted in a higher selectivity and yield toward H₂. Therefore, calcined eggshell as the natural CO₂ sorbent has the potential to deliver higher hydrogen selectivity and yield than CaO. The XRD patterns of the spent Ni_{0.1}@HC with 20 wt% loading of eggshell and 20 wt% CaO (Figure 8) showed the diffraction

Figure 8. XRD patterns of the spent Ni_{0.1}@HC and Ni_{0.1}@HC composites after the sorption-enhanced steam gasification.

peaks of NiO and CaO, indicating the generation of NiO NPs during the sorption-enhanced gasification process. The grain size of the NiO NPs in the spent Ni_{0.1}@HC with 20 wt% eggshell was 44 nm, which was remarkably smaller than that of the 20 wt% loading of CaO, 62 nm. As a hypothesis, we speculated that the well-defined structure of the calcined eggshell may impart higher thermal stability against the growth of the NiO NPs, and therefore maintain their high catalytic activity.

The effects of loading of calcined eggshell on the selectivity of hydrogen at 700 and 800 °C were further probed (Figure 7c,d and entries 2–4 and 6–8 in Table 3). Similar to the result with CaO, a loading of 20 wt% calcined eggshell delivered higher hydrogen selectivity (67% at 700 °C and 72% at 800 °C) than the control reaction without calcined eggshell at 700 and 800 °C, respectively. In addition, the corresponding hydrogen yield was greatly increased to 68.09 g H₂/kg hydrochar at the temperature of 700 °C and 78.67 g H₂/kg hydrochar at the temperature of 800 °C. The Ni_{0.1}@HC was compared with Ni_{0.5}@HC and Ni_{1.0}@HC in terms of hydrogen selectivity and yield under identical reaction conditions. The hydrogen selectivity and yield of the Ni_{0.1}@HC were also higher than those of Ni_{0.5}@HC and Ni_{1.0}@HC. Based on the XRD results (Figure 8), the grain size of the NiO NPs in the spent Ni_{0.1}@HC with 20 wt% eggshell (44 nm) was relatively smaller than that of Ni_{1.0}@HC (48 nm). We postulated that the smaller particle size of the *in situ*-generated NiO NPs contributed to the higher catalytic activity. From these results, the Ni_{0.1}@HC clearly exhibited excellent selectivity toward H₂ in the syngas, especially at a moderate temperature (800 °C), as shown in Figure 6c,d, and the Ni_{0.1}@HC exhibited more excellent catalytic performance than Ni_{0.5}@HC and Ni_{1.0}@HC.

At the temperature of 800 °C, combining *in situ*-generated NiO NPs with *in situ* removal of CO₂ using calcined eggshell as the CaO-based CO₂ sorbent delivered a higher H₂ yield (78.67 g H₂/kg hydrochar in Table 3) and higher hydrogen selectivity (72% in Figure 7d) than the steam gasification of nickel-doped hydrochar alone without the CO₂ sorption process (72.34 g H₂/kg hydrochar of H₂ yield, shown in Table 2, and 67% H₂ selectivity, shown in Figure 6c). It proved that the combination of hydrochar-supported NiO NPs catalyst with CO₂ sorption-enhanced gasification process significantly increased the catalytic activity and selectivity toward H₂, leading to a higher yield and selectivity of hydrogen. Based on the XRD results, we found that the grain size (44 nm) of the NiO NPs in the spent Ni_{0.1}@HC combined with 20 wt% eggshell as the natural CO₂ sorbent was smaller than that of the spent Ni_{0.1}@HC (56 nm) alone (Table S1), which may account for this interaction.

Previous studies have suggested that the hydrochar derived from sewage sludge yielded more hydrogen than the pyrochar derived from sewage sludge and raw sludge.^{24,25} A comparison of H₂ selectivity and yield from gasification of sewage sludge in previous work and the present study is shown in Table 4. These

Table 4. Comparison of Hydrogen Selectivity and Yield from Gasification of Sewage Sludge

entry	type of gasification experiment	H ₂ selectivity (%)	H ₂ yield (g H ₂ /kg sample)	ref
1	sewage sludge	29.8	15.2	21
2	pyrochar derived from sewage sludge	49.1	64.1	20
3	hydrochar derived from sewage sludge	57.3	76.7	20
4	hydrochar-supported Ni NPs composite derived from sewage sludge	66.7	72.3	this work
5	hydrochar-supported Ni NPs composite derived from sewage sludge combined with sorption-enhanced steam gasification	72.5	78.7	this work

results demonstrate that the hydrogen selectivity and yield are strongly associated with the morphology and composition of the precursory hydrochars, which can be controlled by hydrothermal conditions. The *in situ*-generated Ni NPs on the hydrochar during the gasification combined with the sorption-enhanced steam gasification process exhibited much higher hydrogen selectivity and yield than the hydrochar alone.

Mechanistic Interpretation. Building on earlier reports, mechanistic studies³⁶ on the model that mostly mirror the formation and growth of precursory hydrochar via the HTC process have established with a core (hydrophobic)–shell (hydrophilic) Lamer model. Pentsak and co-authors¹⁷ probed the non-innocent nature of the carbon support in metal/carbon catalysts. They proposed a modulation of the carbon surface with a metal-mediated etching (mostly on smooth surface)/pitting (mostly on defective surface) mechanism, and the hypothesis has been experimentally confirmed and verified by FE-SEM analysis. These structures can be further decorated by various metal NPs based on redox chemistry and HTC surface functionality.^{37–39}

Figure 9 proposes a schematic illustration of the reaction routes for the *in situ*-generated NiO NPs combined with sorption-enhanced catalytic steam gasification of sewage sludge. As a working hypothesis in this study, a series of hydrochar

Figure 9. Schematic illustration of the reaction routes for the *in situ*-generated NiO NPs combined with the sorption-enhanced steam gasification of sewage sludge.

surface modifications occurred during the one-pot HTC process and varied with the reaction conditions (temperature, residence time, and pressure). In the one-pot hydrothermal synthesis route, we postulated the formation of nanosized channels or pits on the hydrophilic shell of the hydrochar and coating of the metal NPs into the hydrophobic core of the hydrochar under a relatively high pressure. The uniformly distributed pores on the hydrochar surface promote the penetration of reactive species and Ni^{2+} cations. The nickel NPs will be preferentially dispersed *in situ* in the hydrophobic core of the hydrochar to form the inner-sphere surface complexes, which contribute to the enhanced interaction between the nickel NPs and the supports during the preparation process and restrain the rapid growth of the nickel NPs during the gasification process.

Furthermore, the grain size of the *in situ*-generated NiO NPs decorating the hydrothermal carbon nanospheres could be tailored by varying the concentration of the precursory nickel ions during the one-pot HTC process (as revealed by the XRD patterns in Figure 4). These nickel-based nanomaterials offered promising potential for the hydrogen-rich syngas production from sewage sludge. In fact, other metal NPs can be fabricated on the hydrochar by this synthetic strategy, endowing the hydrothermal carbon spheres with high catalytic activity in fields such as biofuel production. Further structural characterization of the crystalline model of our nanomaterials is complicated, but first-principles density functional theory calculations together with powder neutron diffraction, especially combining Rietveld refinement with pair distribution function analysis, might provide direct structural evidence of coating the hydrothermal carbon spheres with metal NPs and elucidate the specific conversion pathways of the nanomaterials during the gasification process.

CONCLUSIONS

We have developed a quantitative conversion of sewage sludge to hydrogen-rich syngas via a facile and controllable hydrothermal carbonization process followed by sorption-enhanced catalytic steam gasification using an eggshell-based CO_2 sorbent. Multiple characterization techniques demonstrated that the monodispersed NiO NPs can be generated *in situ* on the hydrochar as the support during the gasification process. Compared to the pristine hydrochar, the surface-mediated hydrochar facilitated the uniform dispersion of NiO NPs and promoted a strong metal–support interaction. Moreover, the

gasification temperature and concentration of the precursory nickel cations played a key role in controlling the morphology and particle size of the NiO NPs, which in turn significantly affected its catalytic activity during the gasification process. As expected in the sorption-enhanced steam gasification, the surface-mediated hydrochar derived from sewage sludge significantly increased the catalytic activity and selectivity toward H_2 . A high yield (78.7 g H_2 /kg hydrochar) and selectivity (72.5%) of hydrogen were achieved, and little or no tar was formed, even at moderate temperatures (700–800 °C).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b00924.

SEM images of $\text{Ni}_{0.1}\text{@HC}$ and corresponding mapping of elemental O and Ni in $\text{Ni}_{0.1}\text{@HC}$; photograph of the liquid phases from catalytic gasification at different temperatures; SEM images of the CaO and calcined eggshell; effect of Ni^{2+} cation concentration and temperature on the crystal size of the *in situ*-generated NiO NPs in the $\text{Ni}_x\text{@HC}$ ($x = 0.1, 0.5, 1.0$) composites determined by XRD (PDF)

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REFERENCES

- (1) Sikarwar, V. S.; Zhao, M.; Clough, P.; Yao, J.; Zhong, X.; Memon, M. Z.; Shah, N.; Anthony, E. J.; Fennell, P. S. An overview of advances in biomass gasification. *Energy Environ. Sci.* **2016**, 9, 2939–2977.
- (2) Zhao, P.; Ge, S.; Ma, D.; Areeprasert, C.; Yoshikawa, K. Effect of hydrothermal pretreatment on convective drying characteristics of paper sludge. *ACS Sustainable Chem. Eng.* **2014**, 2, 665–671.
- (3) Laprun, D.; Theodoridi, C.; Tuel, A.; Farrusseng, D.; Meunier, F. C. Effect of polyaromatic tars on the activity for methane steam reforming of nickel particles embedded in silicalite-1. *Appl. Catal., B* **2017**, 204, 515–524.
- (4) Ashok, J.; Kawi, S. Nickel-Iron alloy supported over Iron-Alumina catalysts for steam reforming of biomass tar model compound. *ACS Catal.* **2014**, 4, 289–301.
- (5) Ashok, J.; Kathiraser, Y.; Ang, M. L.; Kawi, S. Bi-functional hydrotalcite-derived $\text{NiO-CaO-Al}_2\text{O}_3$ catalysts for steam reforming of

biomass and/or tar model compound at low steam-to-carbon conditions. *Appl. Catal., B* **2015**, 172–173, 116–128.

(6) Rownaghi, A. A.; Huhnke, R. L. Producing hydrogen-rich gases by steam reforming of syngas tar over CaO/MgO/NiO catalysts. *ACS Sustainable Chem. Eng.* **2013**, 1, 80–86.

(7) Yao, D.; Hu, Q.; Wang, D.; Yang, H.; Wu, C.; Wang, X.; Chen, H. Hydrogen production from biomass gasification using biochar as a catalyst/support. *Bioresour. Technol.* **2016**, 216, 159–164.

(8) Wang, D.; Yuan, W.; Ji, W. Char and char-supported nickel catalysts for secondary syngas cleanup and conditioning. *Appl. Energy* **2011**, 88, 1656–1663.

(9) Salvador, F.; Sánchez-Montero, M. J.; Izquierdo, C. C/H₂O reaction under supercritical conditions and their repercussions in the preparation of activated carbon. *J. Phys. Chem. C* **2007**, 111, 14011–14020.

(10) Hirose, T.; Fujino, T.; Fan, T.; Endo, H.; Okabe, T.; Yoshimura, M. Effect of carbonization temperature on the structural changes of woodceramics impregnated with liquefied wood. *Carbon* **2002**, 40, 761–765.

(11) Hu, B.; Wang, K.; Wu, L.; Yu, S. H.; Antonietti, M.; Titirici, M. M. Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv. Mater.* **2010**, 22, 813–828.

(12) Zhou, K.; Li, Y. Catalysis based on nanocrystals with well-defined facets. *Angew. Chem., Int. Ed.* **2012**, 51, 602–613.

(13) Liu, Z.; Zhang, F.; Hoekman, S. K.; Liu, T.; Gai, C.; Peng, N. Homogeneously dispersed zerovalent iron nanoparticles supported on hydrochar-derived porous carbon, simple, in situ synthesis and use for dechlorination of PCBs. *ACS Sustainable Chem. Eng.* **2016**, 4, 3261–3267.

(14) Grigoras, I. F.; Stroe, R. E.; Sintamarean, I. M.; Rosendahl, L. A. Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow. *Bioresour. Technol.* **2017**, 231, 116–123.

(15) Garcia Alba, L.; Torri, C.; Fabbri, D.; Kersten, S. R. A.; Brilman, D. W. F. Microalgae growth on the aqueous phase from hydrothermal liquefaction of the same microalgae. *Chem. Eng. J.* **2013**, 228, 214–223.

(16) Gai, C.; Zhang, F.; Lang, Q.; Liu, T.; Peng, N.; Liu, Z. Facile one-pot synthesis of iron nanoparticles immobilized into the porous hydrochar for catalytic decomposition of phenol. *Appl. Catal., B* **2017**, 204, 566–576.

(17) Pentsak, E. O.; Gordeev, E. G.; Ananikov, V. P. Noninnocent nature of carbon support in metal/carbon catalysts, etching/pitting vs nanotube growth under microwave irradiation. *ACS Catal.* **2014**, 4, 3806–3814.

(18) Richardson, Y.; Motuzas, J.; Julbe, A.; Volle, G.; Blin, J. Catalytic investigation of in situ generated Ni metal nanoparticles for tar conversion during biomass pyrolysis. *J. Phys. Chem. C* **2013**, 117, 23812–23831.

(19) Richardson, Y.; Blin, J.; Volle, G.; Motuzas, J.; Julbe, A. In situ generation of Ni metal nanoparticles as catalyst for H₂-rich syngas production from biomass gasification. *Appl. Catal., A* **2010**, 382, 220–230.

(20) Yan, Q.; Wan, C.; Liu, J.; Gao, J.; Yu, F.; Zhang, J.; Cai, Z. Iron nanoparticles in situ encapsulated in biochar-based carbon as an effective catalyst for the conversion of biomass-derived syngas to liquid hydrocarbons. *Green Chem.* **2013**, 15, 1631–1640.

(21) Wang, J.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O'Hare, D.; Zhong, Z. Recent advances in solid sorbents for CO₂ capture and new development trends. *Energy Environ. Sci.* **2014**, 7, 3478–3518.

(22) Feroso, J.; Rubiera, F.; Chen, D. Sorption enhanced catalytic steam gasification process, a direct route from lignocellulosic biomass to high purity hydrogen. *Energy Environ. Sci.* **2012**, 5, 6358–6367.

(23) Stonor, M. R.; Ferguson, T. E.; Chen, J. G.; Park, A. H. A. Biomass conversion to H₂ with substantially suppressed CO₂ formation in the presence of Group I & Group II hydroxides and a Ni/ZrO₂ catalyst. *Energy Environ. Sci.* **2015**, 8, 1702–1706.

(24) Gai, C.; Chen, M.; Liu, T.; Peng, N.; Liu, Z. Gasification characteristics of hydrochar and pyrochar derived from sewage sludge. *Energy* **2016**, 113, 957–965.

(25) Gai, C.; Guo, Y.; Liu, T.; Peng, N.; Liu, Z. Hydrogen-rich gas production by steam gasification of hydrochar derived from sewage sludge. *Int. J. Hydrogen Energy* **2016**, 41, 3363–3372.

(26) Titirici, M. M.; Antonietti, M.; Baccile, N. Hydrothermal carbon from biomass, a comparison of the local structure from poly to monosaccharides and pentoses/hexoses. *Green Chem.* **2008**, 10, 1204–1212.

(27) Moussa, S. O.; Panchakarla, L. S.; Ho, M. Q.; El-Shall, M. S. Graphene-supported, iron-based nanoparticles for catalytic production of liquid hydrocarbons from synthesis gas, The role of the graphene support in comparison with carbon nanotubes. *ACS Catal.* **2014**, 4, 535–545.

(28) Wu, C.; Dong, L.; Onwudili, J.; Williams, P. T.; Huang, J. Effect of Ni particle location within the mesoporous MCM-41 support for hydrogen production from the catalytic gasification of biomass. *ACS Sustainable Chem. Eng.* **2013**, 1, 1083–1091.

(29) Shi, J.; Wang, Y.; Du, W.; Hou, Z. Synthesis of graphene encapsulated Fe₃C in carbon nanotubes from biomass and its catalysis application. *Carbon* **2016**, 99, 330–337.

(30) Carrasco, J.; López-Durán, D.; Liu, Z.; Duchoň, T.; Evans, J.; Senanayake, S. D.; Crumlin, E. J.; Matolín, V.; Rodríguez, J. A.; Ganduglia-Pirovano, M. V. In situ and theoretical studies for the dissociation of water on an active Ni/CeO₂ catalyst, importance of strong metal-support interactions for the cleavage of O–H bonds. *Angew. Chem., Int. Ed.* **2015**, 54, 3917–3921.

(31) Chen, F.; Wu, C.; Dong, L.; Vassallo, A.; Williams, P. T.; Huang, J. Characteristics and catalytic properties of Ni/CaAlO_x catalyst for hydrogen-enriched syngas production from pyrolysis-steam reforming of biomass sawdust. *Appl. Catal., B* **2016**, 183, 168–175.

(32) Sehested, J.; Gelten, J. A. P.; Remediakis, I. N.; Bengaard, H.; Norskov, J. K. Sintering of nickel steam-reforming catalysts, effects of temperature and steam and hydrogen pressures. *J. Catal.* **2004**, 223, 432–443.

(33) Gai, C.; Dong, Y. Experimental study on non-woody biomass gasification in a downdraft gasifier. *Int. J. Hydrogen Energy* **2012**, 37, 4935–4944.

(34) Zamboni, I.; Courson, C.; Kiennemann, A. Fe–Ca interactions in Fe-based/CaO catalyst/sorbent for CO₂ sorption and hydrogen production from toluene steam reforming. *Appl. Catal., B* **2017**, 203, 154–165.

(35) Guan, G.; Chen, G.; Kasai, Y.; Lim, E. W. C.; Hao, X.; Kaewpanha, M.; Abuliti, A.; Fushimi, C.; Tsutsumi, A. Catalytic steam reforming of biomass tar over iron- or nickel-based catalyst supported on calcined scallop shell. *Appl. Catal., B* **2012**, 115–116, 159–168.

(36) Lamer, V. K.; Dinegar, R. H. Theory, production and mechanism of formation of monodispersed hydrosols. *J. Am. Chem. Soc.* **1950**, 72, 4847–4854.

(37) Titirici, M. M.; White, R. J.; Brun, N.; Budarin, V. L.; Su, D. S.; del Monte, F.; Clark, J. H.; MacLachlan, M. J. Sustainable carbon materials. *Chem. Soc. Rev.* **2015**, 44, 250–290.

(38) Sun, X.; Li, Y. Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angew. Chem., Int. Ed.* **2004**, 43, 597–601.

(39) Wright, C. S.; Walton, R. I.; Thompson, D.; Fisher, J.; Ashbrook, S. E. One-step hydrothermal synthesis of nanocrystalline ceria-zirconia mixed oxides: the beneficial effect of sodium inclusion on redox properties. *Adv. Mater.* **2007**, 19, 4500–4504.