

Article

Enhanced CH₄ Production from Corn-Stalk Pyrolysis Using Ni-5CeO₂/MCM-41 as a Catalyst

Fang Huang, Weizun Li, Qidong Hou * and Meiting Ju *

Tianjin Engineering Research Center of Biomass Solid Waste Resources Technology, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, China; vanccx@163.com (F.H.); liweizun@nankai.edu.cn (W.L.)

* Correspondence: houqidong@nankai.edu.cn (Q.H.); jumeit@nankai.edu.cn (M.J.)

Received: 19 December 2018; Accepted: 19 February 2019; Published: 26 February 2019



Abstract: Production of syngas from lignocellulosic biomass through pyrolysis is a promising solution for the large-scale utilization of biomass. However, current pyrolysis approaches suffer from the relative low product yield and selectivity, limiting their practical application. To solve this problem, a series of nickel-based catalysts including Ni/MCM-41, Ni-5CeO₂/MCM-41, and Ni-5La₂O₃/MCM-41 were prepared and characterized by transmission electron microscopy (TEM), N₂ adsorption–desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and H₂-temperature-programmed reaction (TPR) analysis. It was observed that the simultaneous addition of Ni and CeO₂ to MCM-41 could increase the reducibility of Ni and the number of active Ni⁰ sites on the surface of the catalyst. Consequently, Ni-5CeO₂/MCM-41 gave a CH₄ yield of 14.6 mmol/g, which is remarkably higher than that (10.5 mmol/g) obtained in the absence of the catalyst. Meanwhile, the CO and H₂ yields increased slightly, while the CO₂ yield decreased slightly. Therefore, the improved CH₄ yield and selectivity was mainly due to the increased decomposition of tarry compounds catalyzed by Ni/MCM-41 with the assistance of CeO₂.

Keywords: corn stalk; pyrolysis; methane; Ni-5CeO₂/MCM-41

1. Introduction

According to Ministry of Agriculture of China, over 900 million tons of biomass stalk are produced every year in China, and around 60% of stalk is arbitrarily stacked, discarded, or burned as solid waste [1,2]. The improper dispositions of lignocellulosic biomass caused serious air, soil, and water environmental problems. In order to alleviate these problems, the conversion of the biomass resource into alternative fine chemicals, bio-fuels, and novel materials is a sustainable and promising solution [3,4]. Numerous approaches, such as combustion, pyrolysis, pyro-gasification, fermentation, and catalytic conversion, were developed to convert biomass into value-added products [5–10]. Pyrolysis is a promising way to transform biomass into renewable energy in the form of H₂, CO, and CH₄ [11].

Nickel-based catalysts were proven to be effective to enhance the biomass pyrolysis via promoting the C–C bond cleavage of biomacromolecules during biomass pyrolysis [12,13]. Nickel-based catalysts are also capable to reform tars and, thus, decrease the need for their removal from producer gas [14]. In addition, nickel-based catalysts are more economically viable than noble metals [15,16]. The challenges in the application of nickel-based catalysts are their rapid deactivation due to coke deposition, sintering, and morphological transformations [14,17], especially when the temperature exceeds 600 °C [18]. Therefore, much efforts were devoted to improve the applicability and lifetime of nickel-based catalysts in a series of catalytic processes, such as water-gas shift reaction, tar cracking, light hydrocarbon reforming, and methanol steam reforming [19].

When Ni species are loaded onto the appropriate support, the positive metal/support synergistic effect will remarkably improve their catalytic performance and stability. For example, Choi et al.

demonstrated that the addition of CeO_2 to Al_2O_3 prior to loading Ni species increased the dispersion of the Ni species on the support due to improved CeO_2 –Ni interaction, leading to increased hydrogen yield and longer lifetime of the catalyst during auto-thermal reforming of iso-octane [20]. Sánchez-Sánchez et al. showed that the existence of Ni–Ce species Ni/ CeO_2 – Al_2O_3 could enhance adsorption and dissociation of water molecules, thus improving their catalytic activity for ethanol reforming [21]. MCM-41 has a large specific surface area and uniform large pore size, which can aid the easy diffusion of reactant molecules in and out of its mesopores [22]. Du et al. reported that Ni/MCM-41 gives a CH_4 selectivity of 96.0% from the methanation of CO at 400 °C under atmospheric pressure [23]. Zhang et al. reported that Ni/MCM-41 is also effective to produce substitute natural gas from the methanation of syngas [24]. Recent studies showed that the use of CeO_2 as an additive could effectively promote the adsorption and the activation of CO_2 molecules on the catalysts, owing to the oxygen exchange capacity of CeO_2 [25,26]. Moreover, the addition of CeO_2 could promote the interaction between support and metal active component, so as to adequately control the growth of the Ni particles and then improve the catalytic performance of Ni-based catalysts [27]. Although the addition of CeO_2 and La_2O_3 was demonstrated to be effective to promote the CO_2 methanation over Ni/ Al_2O_3 and Ni/MCM-41, limited research was conducted on their application for reforming the gases from biomass pyrolysis.

In this study, a series of a series of nickel-based catalysts including Ni/MCM-41, Ni-5 CeO_2 /MCM-41, and Ni-5 La_2O_3 /MCM-41 were prepared via the deposition–precipitation method. The synthesized catalysts were analyzed by transmission electron microscopy (TEM), N_2 adsorption–desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and H_2 -temperature-programmed reaction (TPR), and then used to reform the gases from corn-stalk pyrolysis. The effect of CeO_2 and La_2O_3 on the catalytic performance of Ni-5 CeO_2 /MCM-41 and Ni-5 La_2O_3 /MCM-41 for the reforming of the gases from corn-stalk pyrolysis was investigated.

2. Materials and Methods

Corn stalk was obtained from a crop processing company (Jiangsu, China). The corn stalk was sieved with a 180–380- μm mesh and then dried at 105 °C for 7 h before use as feedstock. The proximate (air-dry base) and ultimate analyses (dry-ash-free base) of the pine sawdust sample were conducted in a muffle furnace (SX-11-4, China) and an elemental analyzer (Vario EL cube, Elementaranalyse, Germany), respectively. The volatile matter, fixed carbon, and ash contents of the corn stalk were 77.4%, 16.86%, and 6.02%, respectively, and the contents of carbon, hydrogen, oxygen, nitrogen, and sulfur in the corn stalk were 41.18%, 4.98%, 39.51%, 0.78%, and 0.19%, respectively.

MCM-41 silica was purchased from Beijing Huawei Ruike Corp. (Beijing, China). Al_2O_3 was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Both MCM-41 and Al_2O_3 were calcined at 600 °C for 4 h to eliminate the impurities adsorbed onto the surface prior to the preparation of the catalysts. Ni-5 CeO_2 /MCM-41 was prepared according to the following steps: firstly, 4.94 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.52 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to 250 mL of deionized water to get a uniform solution, and then 4.0 g of MCM-41 was added to the solution, followed by stirring for 1 h at ambient temperature. Subsequently, 0.2 mol/L K_2CO_3 solution was added dropwise into the suspension as a precipitant until the pH value reached 9–10, followed by stirring for 2 h at 90 °C. The suspension was filtered and washed with deionized water until reaching a neutral state. The obtained precipitate was dried at 110 °C overnight and calcined at 600 °C in air for 4 h. Ni-5 La_2O_3 /MCM-41 was prepared using a similar procedure, except for the replacement of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 2.658 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Ni-5 CeO_2 / Al_2O_3 was prepared using the following steps: firstly, 2.47 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.26 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to 5.4 mL of deionized water to get a uniform solution, and then the solution was dropwise added to 4.5 g Al_2O_3 and mixed well. Next, the mixture solution was stirred at 35 °C for 4 h, and then dried at 80 °C overnight and calcined at 600 °C in air for 4 h. Ni-5 La_2O_3 / Al_2O_3 was prepared using a similar procedure, except for the replacement of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 1.329 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

The XPS spectra were recorded on a PHI 5000 VersaProbe III-Scanning XPS Microprobe equipped with a focused monochromatic aluminum X-ray source with photon energy of 1486.6 eV and X-ray beam size of 100 μm . The binding energy (BE) was corrected by aligning the peak positions with reference to the standard adventitious carbon peak (C1s) at 284.6 eV. The N_2 adsorption–desorption isotherms were recorded at -196°C using a Quadrasorb SI apparatus. Before the measurement, the sample was degassed at 300°C for 3 h. The specific surface area and pore size were obtained using the Brunauer–Emmett–Teller (BET) method, while the pore volume was calculated using the Barrett–Joyner–Halenda (BJH) model using the desorption isotherm branch. The XRD pattern was measured on a Rigaku Miniflex diffractometer operating at 40 kV and 20 mA. Each sample was scanned at a rate of $2^\circ/\text{min}$ every 0.02° for 2θ angles between 10° and 90° . The morphology of catalysts was observed by transmission electron microscopy (TEM, Philips-FEI, Tecnai G2F30). Temperature-programmed reaction of hydrogen (H_2 -TPR) was carried out on an AutoChem II 2920 instrument (Micromeritics Instrument). Each sample (30 mg) was pretreated with argon at 200°C for 1 h, and then cooled down to 50°C . The reduction was carried out with a heating rate of $10^\circ\text{C}/\text{min}$ up to 900°C . The H_2 consumption amount was recorded with a thermal conductivity detector (TCD).

The pyrolysis of corn stalk was performed in a fixed-bed horizontal tubular furnace (length: 100 cm; inner diameter: 2.5 cm), as shown in Figure 1. Initially, 2.3 g of corn stalk was placed on the left side of the feedstock bin and then covered by an asbestos-free wire gauze. A layer of silica sand (30 g) was placed in the middle of the feedstock bin and then covered by another asbestos-free wire gauze to separate biomass and catalyst. Then, 0.2 g of Ni-based catalyst was added to the right side of the feedstock bin. Nitrogen gas was employed to maintain an anaerobic environment in the reactor. Typically, the feedstock bin was placed out of the tubular furnace to keep the feedstock at low temperature during the heating process of the tubular furnace. The blank experiment demonstrated that no gas products were detected when the feedstock bin was placed out of the tubular furnace. When the temperature of the furnace reached 600°C , the feedstock bin was immediately pushed into the reactor in the middle of the furnace. The pyrolysis of biomass was conducted at 600°C for 30 min. After the reaction, the gas product was pushed out by a nitrogen gas (40 L/h) for 8 min and collected by a 10-L air bag. The absorption and filtration devices were used to cool down the formed bio-oil and tar, and they retained these products in the liquid phase to avoid their adverse effect on the measurement of gas composition. The concentrations of H_2 , CO , CO_2 , and CH_4 were determined by gas chromatography (GC; Thermo Fisher TRACE 1310) and then their yields and CH_4 selectivity were calculated.

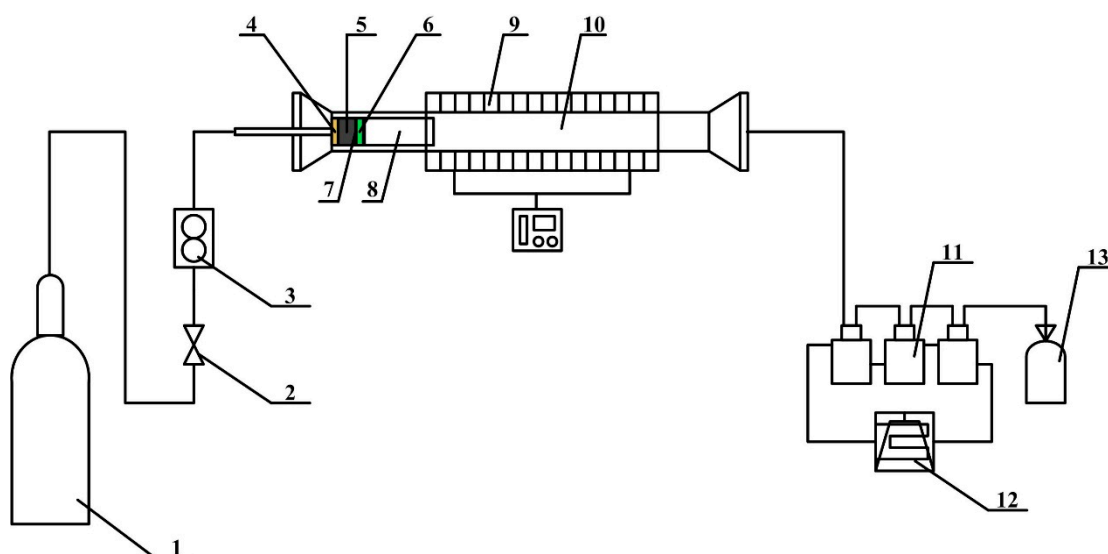


Figure 1. Schematic diagram of the reactor system. 1, nitrogen; 2, regulating valve; 3, gas flowmeter; 4, corn stalk; 5, quartz sand; 6, catalyst; 7, asbestos-free wire gauze; 8, feedstock bin; 9, horizontal tubular furnace; 10, reactor; 11, absorption and filtration devices; 12, cooling pump; 13, air bag.

3. Results and Discussions

3.1. Characterization of Catalysts

3.1.1. Textural Properties of the Catalysts

The TEM images and energy-dispersive X-ray spectroscopy (EDS) elementary mapping images of Ni/MCM-41, Ni-5La₂O₃/MCM-41, and Ni-5CeO₂/MCM-41 are shown in Figure 2. The TEM images and EDS elementary mapping images of Ni/Al₂O₃, 5La₂O₃/Al₂O₃ and 5CeO₂/Al₂O₃ are shown in. The successful loadings of Ce, La, and Ni onto the corresponding support were confirmed by EDS elementary mapping images. It was observed that Ce, La, and Ni were highly dispersed on the corresponding catalysts. The actual loadings of CeO₂ and La₂O₃ were 3.46 wt.% and 1.02 wt.% for Ni-5CeO₂/MCM-41 and Ni-5La₂O₃/MCM-41, respectively.

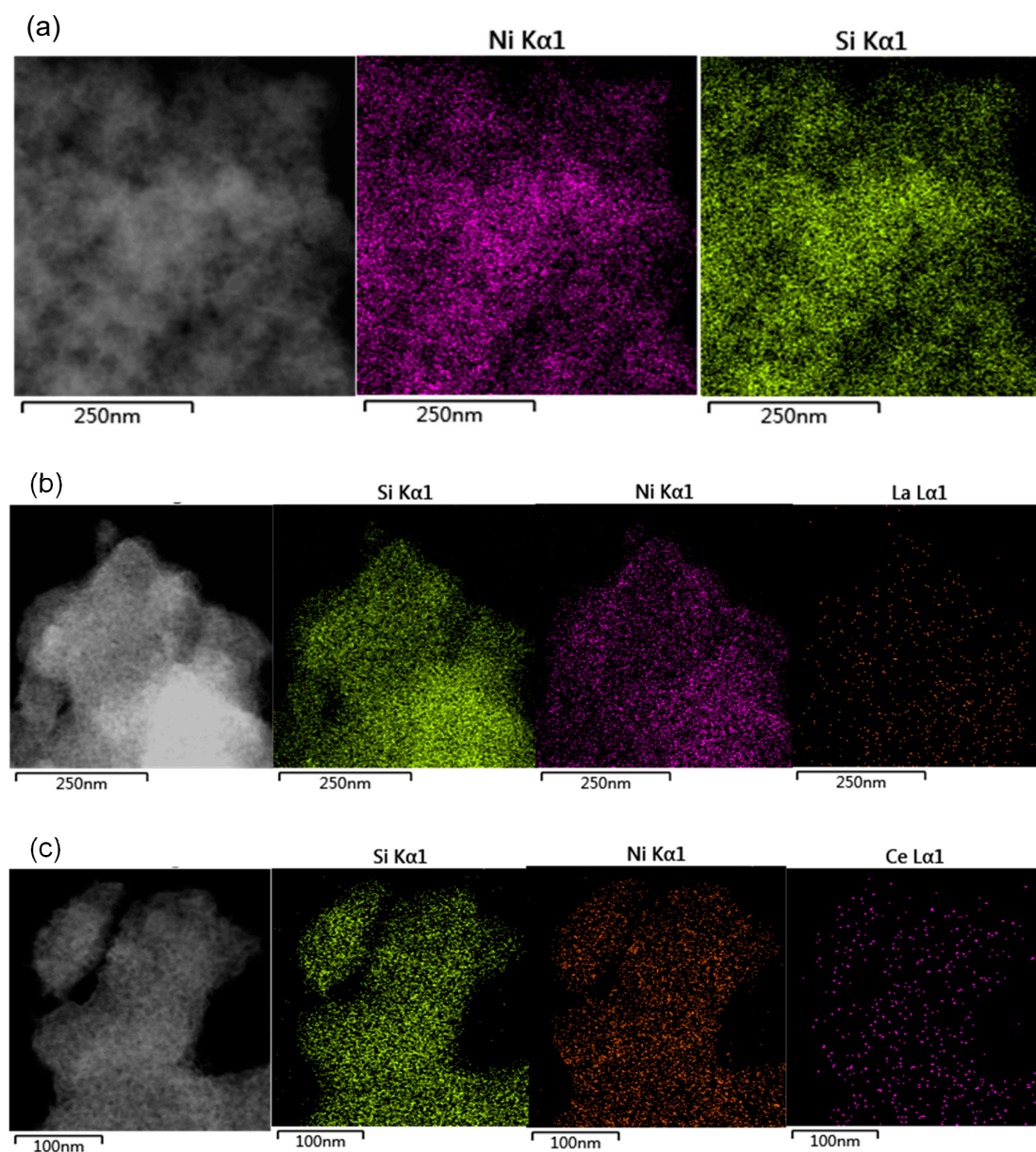


Figure 2. Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) elementary mapping images of Ni/MCM-41 (a), Ni-5La₂O₃/MCM-41 (b), and Ni-5CeO₂/MCM-41 (c).

N₂ adsorption–desorption isotherms of the synthesized catalyst were performed to analyze their textural properties. As displayed in Figure 3a, the isotherms exhibited type IV curves with H4 hysteresis loops (IUPAC International Union of Pure and Applied Chemistry). The pore size distribution displayed in Figure 3b indicated that these catalysts have a typical mesoporous structure. Based on the nitrogen adsorption–desorption data, the specific surface area (S_{BET}), pore volume (V_{pore}), and average pore size (D_{meso}) of these materials were computed and are listed in Table 1. Compared with Al₂O₃-based catalysts, the MCM-41-based materials exhibited remarkably higher specific surface area and pore diameter, while their pore volumes were comparable. The specific surface areas of the synthesized catalysts increased in the following order: 5CeO₂/MCM-41 < Ni/MCM-41 < Ni-5CeO₂/MCM-41 < 5La₂O₃/MCM-41 < Ni-5La₂O₃/MCM-41. The specific surface areas of Ni-5La₂O₃/MCM-41 and Ni-5CeO₂/MCM-41 were higher than that of Ni-5CeO₂/MCM, indicating that the simultaneous loading of Ni and metal oxide was effective to maintain the relatively high specific surface area of the catalyst. Both the pore volume and the average pore size of Ni-5CeO₂/MCM and Ni-5La₂O₃/MCM were lower than those of the corresponding 5CeO₂/MCM and 5La₂O₃/MCM materials, suggesting that the loading of Ni species was responsible for the decrease in pore volume and pore diameter.

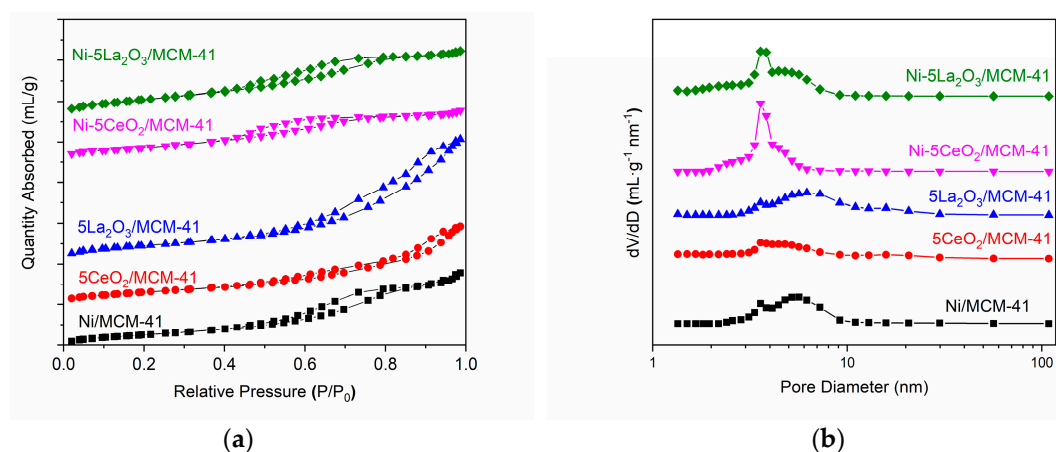


Figure 3. N₂ adsorption–desorption isotherms (a) and pore size distribution (b) of the synthesized catalysts.

Table 1. Textural properties of the catalysts. BET—Brunauer–Emmett–Teller.

Catalysts	S_{BET} (m ² /g)	V_{Pore} (mL/g)	D_{Pore} (nm)
Ni/Al ₂ O ₃	50.3	0.45	35.6
5CeO ₂ /Al ₂ O ₃	44.6	0.38	34.1
5La ₂ O ₃ /Al ₂ O ₃	42.9	0.45	41.9
Ni/MCM-41	276.8	0.59	8.6
5CeO ₂ /MCM-41	237.8	0.6	10
5La ₂ O ₃ /MCM-41	332.1	0.95	11.4
Ni-5CeO ₂ /MCM-41	282.8	0.39	5.6
Ni-5La ₂ O ₃ /MCM-41	407.2	0.53	5.3

3.1.2. XRD

The XRD patterns of the synthesized catalysts were determined to analyze their crystal structure. As displayed in Figure 4, only one broad diffraction peak attributed to MCM-41 was clearly observed in the XRD patterns of 5La₂O₃/MCM-41 and 5CeO₂/MCM-41, while the characteristic peaks of La₂O₃ and CeO₂ were not observable owing to the relative low loading (less than 5 wt.%), suggesting the highly dispersibility of La₂O₃ and CeO₂ in 5La₂O₃/MCM-41 and 5CeO₂/MCM-41. When Ni species were introduced to MCM-41, 5CeO₂/MCM-41, and 5La₂O₃/MCM-41, the characteristic peaks of NiO appeared at $2\theta = 35.6^\circ$ and 60.8° in the XRD patterns of Ni-5CeO₂/MCM-41 and

Ni-5La₂O₃/MCM-41, respectively [28,29]. The diffraction peaks were very weak and broad, suggesting that the nickel-oxide particles formed in the synthesis process were small and sufficiently dispersed. The XRD pattern of Ni-5La₂O₃/MCM-41 also exhibited a diffraction peak at $2\theta = 44.4^\circ$, corresponding to metallic nickel (Ni⁰), indicating that some metallic nickel was formed during the synthesis process. Moreover, the diffraction peak at 29.6° corresponding to La₂O₃ became obvious in the XRD pattern of Ni-5La₂O₃/MCM-41, indicating that the introduction of Ni species may have resulted in the agglomeration of small La₂O₃ particles [30].

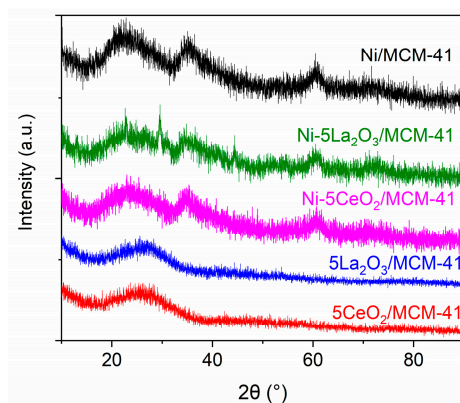


Figure 4. X-ray diffraction (XRD) patterns of the synthesized catalysts.

3.1.3. XPS

The XPS spectra of the synthesized catalysts were measured to analyze their surface elemental composition and chemical state of the transition metal. As displayed in Figure 5a, the wide XPS spectra of all the materials exhibited the characteristic peak of Si 2*p* and O 1*s*, centered at 104.4 and 533.8 eV, respectively. The presence of Ce in 5CeO₂/MCM-41 and Ni-5La₂O₃/MCM-41 was confirmed by the peak at 902 eV, attributed Ce 3*d* [31]; the presence of La in 5La₂O₃/MCM-41 and Ni-5La₂O₃/MCM-41 was confirmed by the peak at 836.0 eV, attributed La 3*d* [28,32]. Eight peaks were observed on the high-resolution Ce 3*d* XPS spectra (Figure 5b). The four peaks of Ce 3*d*_{5/2} at 883.9, 886.0, 890.2, and 899.4 eV were attributed to V, V', V'', and V''', respectively [33]. The four peaks of Ce 3*d*_{3/2} at 902.7, 905.5, 909.1, and 917.7 eV were attributed to U, U', U'', and U''', respectively [34]. The characteristic peaks attributed to La 3*d*_{2/3} and La 3*d*_{5/3} appeared at 851.7 and 835.0 eV, respectively, consistent with La–O bonding in La₂O₃ (Figure 5c) [35,36]. As shown in Figure 5d,e, the Ni 2*p* XPS spectra of Ni-MCM-41 and Ni-5CeO₂/MCM-41 exhibited Ni 2*p*_{1/2} and Ni 2*p*_{3/2} emission lines. The peaks at around 855.8 eV were attributed to octahedral Ni²⁺ present in NiO clusters or nanoparticles, while the peaks at round 857.7 eV were attributed to some isolated Ni²⁺ ions or Ni²⁺ present in small clusters inside the mesopore channels of MCM-41 [28]. Compared with Ni-MCM-41, Ni-5CeO₂/MCM-41 showed a new Ni 2*p*_{3/2} signal between 853.2 and 852.7 eV, confirming the presence of metallic nickel in Ni-5CeO₂/MCM-41 [37].

3.1.4. H₂-TPR

The H₂-TPR profiles of Ni-MCM-41, 5CeO₂/MCM-41, 5La₂O₃/MCM-41, Ni-5CeO₂/MCM-41, and Ni-5La₂O₃/MCM-41 were measured to investigate their reducibility. As shown in Figure 6, only one weak reduction peak at around 493 °C was observed on the H₂-TPR profiles of 5CeO₂/MCM-41, while almost no reduction peak was observed on the H₂-TPR profiles of 5La₂O₃/MCM-41. The predominant peak corresponding to the reduction of NiO particles interacting strongly with the support appeared at 675, 648, and 637 °C in the H₂-TPR profiles of Ni-MCM-41, Ni-5CeO₂/MCM-41, and Ni-5La₂O₃/MCM-41, respectively. In addition, the shoulder peaks between 450 and 520 °C in the H₂-TPR profiles of Ni-5CeO₂/MCM-41 and Ni-5La₂O₃/MCM-41 were attributed to the reduction of NiO particles interacting weakly with the support. The NiO reduction peak shifted to lower

temperature compared with that of other tested catalysts, indicating the high dispersity of metal components on the support. The enhanced dispersity in Ni-5CeO₂/MCM-41 was mainly attributed to that CeO₂ phase, which could weaken the strong NiO–support interactions [38]. These results indicated that the addition of CeO₂ could increase the reducibility of Ni and the number of active Ni⁰ sites on the catalyst surface, in accordance with the conclusion of the XRD and XPS analysis.

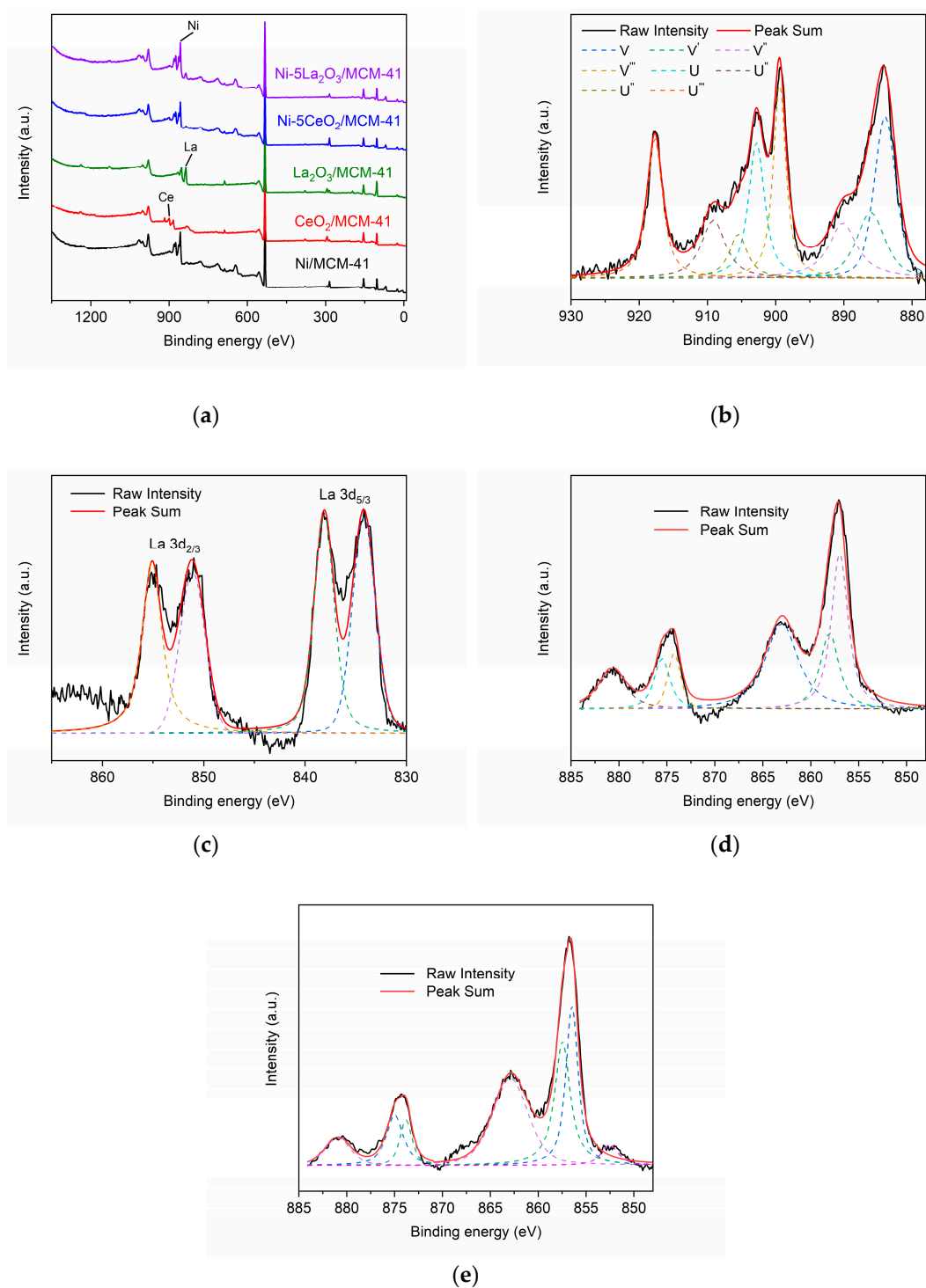


Figure 5. Wide X-ray photoelectron spectroscopy (XPS) spectra of the synthesized catalysts (a); high-resolution Ce 3d XPS spectra of Ni-5CeO₂/MCM-41 (b); La 3d XPS spectra of Ni-5La₂O₃/MCM-41 (c); and Ni 2p XPS spectra of Ni-MCM-41 (d) and Ni-5CeO₂/MCM-41 (e).

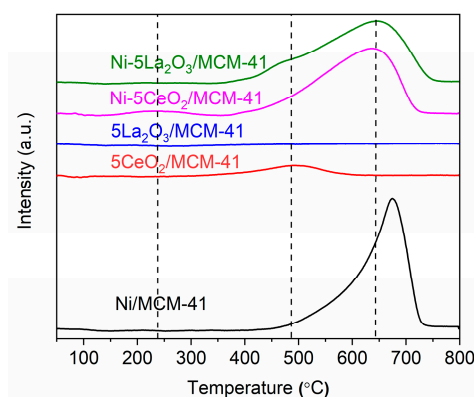


Figure 6. The H_2 -temperature-programmable reaction (TPR) profiles of the synthesized catalysts.

3.2. Gasification of Corn Stalk

3.2.1. Effect of Temperature and Time on the Gas Yield

The pyrolysis of corn stalk (2.30 g) was performed under different temperatures in the absence of catalyst, with a constant pyrolysis time of 30 min. As shown in Figure 7a, the CO yields were between 1.9 and 3.3 mmol/g, and the CO_2 yields were between 3.0 and 4.0 mmol/g when the reaction temperature lower than 500 °C. H_2 started to form at 500 °C, while CH_4 started to form at 550 °C. With the increase of reaction temperature from 500 to 700 °C, the H_2 yield increased continuously from 0.1 to 1.8 mmol/g, the CH_4 yield increased from 5.8 to 14.0 mmol/g, and the CO yield increased slightly from 2.6 to 3.3 mmol/g, while the CO_2 yield ranged between 3.5 and 4.0 mmol/g. Since CH_4 was identified as the main pyrolysis product, the CH_4 selectivity was also analyzed in the subsequent process. It is interesting to note that the CH_4 selectivity also increased with the increasing temperature except that the CH_4 selectivity at 600 °C was slightly higher than that obtained at 650 °C. To avoid the effect of the decomposition of asbestos-free wire gauze, we calcined the asbestos-free wire gauze prior to use. When the asbestos-free wire gauze was calcined at a temperature lower than 650 °C, the gas yields were not affected by the asbestos-free wire gauze. However, when the asbestos-free wire gauze was calcined at a temperature higher than 700 °C, the asbestos-free wire gauze broke down after calcination and then could not be used to separate the catalyst and feedstock. The control experiment indicated that the increased CH_4 yield obtained at 700 °C was mainly attributed to the decomposition of asbestos-free wire gauze at 700 °C. Since the effect of asbestos-free wire gauze could not be precluded at 700 °C, we only investigated the effect of the catalysts on biomass pyrolysis at 600 °C in the subsequent experiment.

In the subsequent experiment, the influence of reaction time on the pyrolysis of corn stalk was investigated to confirm the appropriate pyrolysis time. The H_2 , CO, CO_2 , and CH_4 yields were low when the corn stalk was loaded into the reactor before heating. In this manner, the heating process required about 120 min, owing to the relatively low heating rate of the reactor, thus leading to the low product yields [28]. To solve this problem, rapid loading of biomass was used in the subsequent pyrolysis experiment. The feedstock was placed outside during the heating of the reactor. Once the temperature of the reactor reached the stated value, the biomass in the feedstock bin was pushed into the middle of the reactor immediately to start the pyrolysis process. With pyrolysis times from 10 to 30 min, the H_2 , CO, CO_2 , and CH_4 yields, as well as CH_4 selectivity, increased continuously (Figure 7b). However, the further increase of pyrolysis time from 30 to 40 min did not lead to an obvious increase in product yields and CH_4 selectivity. Based on the above results, the pyrolysis was performed at 600 °C for 30 min in the subsequent experiment to compare the catalytic performance of different catalysts.

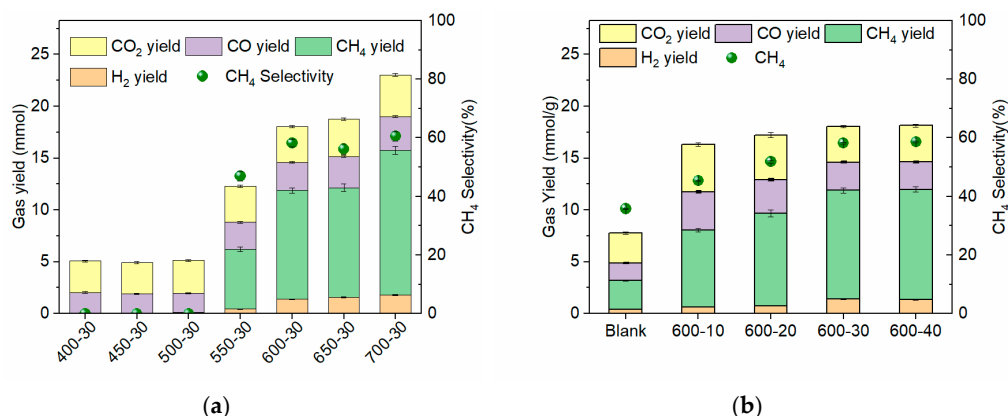


Figure 7. Influence of temperature and time on the gas yields. (a) Temperature, (b) Time.

3.2.2. Effect of Catalyst on the Gas Yield

A series of monometallic catalysts, including Ni-MCM-41, 5CeO₂-MCM-41, Ni-Al₂O₃, 5CeO₂/Al₂O₃, and 5La₂O₃/Al₂O₃, were investigated for the catalytic reforming of pyrolysis gases. As shown in Figure 8a, the gas yields and CH₄ selectivity obtained with Ni/MCM-41 and Ni/Al₂O₃ were slightly higher than those obtained in the absence of the catalyst, indicating the catalytic activity of the Ni species. However, both the gas yields and CH₄ selectivity obtained with 5CeO₂/MCM-41 and 5La₂O₃/Al₂O₃ were not obviously improved when compared to the control group, indicating that these materials were incapable of improving the quality of gas products. In addition, a series of bimetallic catalysts, including Ni-5CeO₂/MCM-41, Ni-10CeO₂/MCM-41, Ni-5La₂O₃/MCM-41, and Ni-10La₂O₃/MCM-41, were tested to further improve the catalytic performance. When Ni-5CeO₂/MCM-41 was used as a catalyst (Figure 7b), the CH₄ yield increased considerably from 10.5 to 14.6 mmol/g, and the CO and H₂ yields increased slightly from 1.4 and 2.9 to 1.7 and 3.2 mmol/g, respectively, while the CO₂ yield reduced slightly from 3.4 to 2.8 mmol/g. As a consequence, the CH₄ selectivity increased from 58.2 to 65.6%. When the CeO₂ loading was increased to 10 wt.%, the gas yields were slightly higher than those obtained with Ni/MCM-41, but lower than those obtained with Ni-5CeO₂/MCM-41. In contrast, the gas yields obtained with Ni-5La₂O₃/MCM-41 and Ni-10La₂O₃/MCM-41 were even lower than those obtained with Ni/MCM-41. The H₂ yield increased slightly when Ni-5CeO₂/MCM-41 was used as a catalyst, suggesting that CO₂ methanation did not occur in this condition. Many recent studies showed that nickel-based catalysts are also capable of reforming tars [14]. Therefore, the increased CH₄ yield was mainly due to the decomposition of tarry compounds on the catalyst, instead of the methanation of CO₂.

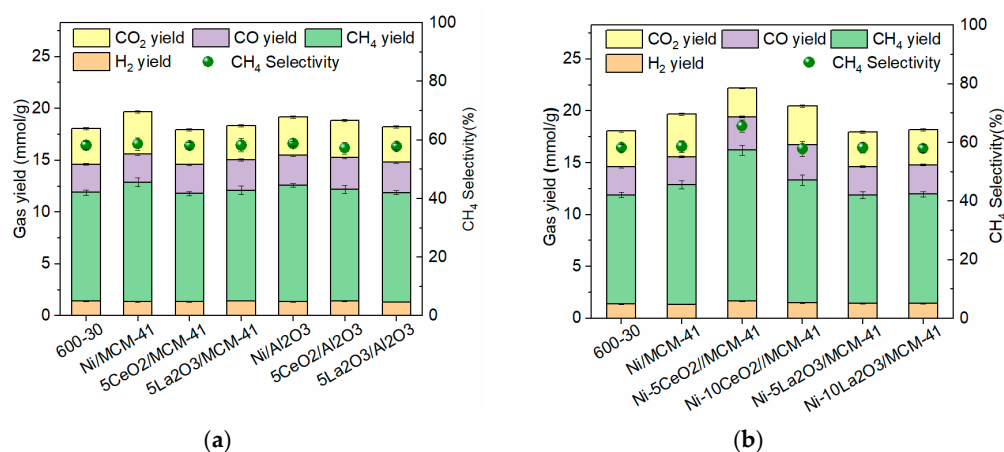


Figure 8. Gas yields over monometallic (a) and bimetallic catalysts (b).

4. Conclusions

In the present work, a series of Ni-based catalysts including Ni/MCM-41, Ni-5CeO₂/MCM-41, and Ni-5La₂O₃/MCM-41 were investigated to improve the product yield and selectivity from biomass pyrolysis. The textural properties, surface element composition, chemical state, crystal structure, and reducibility of these catalysts were characterized by SEM, N₂ adsorption–desorption, XRD, XPS, and H₂-TPR analysis, respectively. These results showed that the simultaneous addition of Ni and CeO₂ to MCM-41 could improve the dispersity of metal components and then increase the reducibility of Ni and the number of active Ni⁰ sites on the surface of the catalyst. Compared with the other catalysts, Ni-5CeO₂/MCM-41 gave much higher CH₄ yield and selectivity, with slightly increased CO and H₂ yields, as well as slightly decreased CO₂ yield. The increased CH₄ yield and selectivity was attributed to the fact that Ni-5CeO₂/MCM-41 could promote the decomposition of tarry compounds.

Author Contributions: F.H. and W.-Z.L. were responsible for the overall experiment and arrangement. Q.-D.H. was responsible for the data analysis and manuscript preparation. M.-T.J. was primarily responsible for the data and manuscript confirmation. All authors were equally responsible for finalizing the manuscript for submission.

Funding: This research was funded by the National Natural Science Foundation of China (21878163), the China Postdoctoral Science Foundation (2018M640231), the Fundamental Research Funds for the Central Universities, the Natural Science Foundation of Tianjin, China (17JCZDJC39500), the National Key Research Project (2018YFD080083-03), the Science and Technology Demonstration Project of Industrial Integration and Development of Tianjin, China (17ZXYENC00100), the National Natural Science Foundation of China (51708301), the Natural Science Foundation of Tianjin, China (17JCZDJC39500), and the Jinnan District Science and Technology Project of Tianjin, China (20171505).

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

References

1. Zhang, W.; Lu, Z.; Xu, Y.; Wang, C.; Gu, Y.; Xu, H.; Streets, D.G. Black carbon emissions from biomass and coal in rural China. *Atmos. Environ.* **2018**, *176*, 158–170. [[CrossRef](#)]
2. Hou, Q.; Meiting, J.U.; Weizun, L.I.; Liu, L.; Yang, Q.; Chen, Y. Research progress on biomass fractionation using ionic liquids. *Chem. Ind. Eng. Prog.* **2016**, *35*, 3022–3031. [[CrossRef](#)]
3. Hou, Q.; Li, W.; Ju, M.; Liu, L.; Chen, Y.; Yang, Q.; Wang, J. Separation of polysaccharides from rice husk and wheat bran using solvent system consisting of BMIMOAc and DMI. *Carbohydr. Polym.* **2015**, *133*, 517–523. [[CrossRef](#)] [[PubMed](#)]
4. Hou, Q.; Ju, M.; Li, W.; Liu, L.; Chen, Y.; Yang, Q. Pretreatment of lignocellulosic biomass with ionic liquids and ionic liquid-based solvent systems. *Molecules* **2017**, *22*, 490. [[CrossRef](#)] [[PubMed](#)]
5. Hou, Q.; Li, W.; Ju, M.; Liu, L.; Chen, Y.; Yang, Q. One-pot synthesis of sulfonated graphene oxide for efficient conversion of fructose into HMF. *RSC Adv.* **2016**, *6*, 104016–104024. [[CrossRef](#)]
6. Hou, Q.; Li, W.; Zhen, M.; Liu, L.; Chen, Y.; Yang, Q.; Huang, F.; Zhang, S.; Ju, M. An ionic liquid–organic solvent biphasic system for efficient production of 5-hydroxymethylfurfural from carbohydrates at high concentrations. *RSC Adv.* **2017**, *7*, 47288–47296. [[CrossRef](#)]
7. Dong, C.; Chen, J.; Guan, R.; Li, X.; Xin, Y. Dual-frequency ultrasound combined with alkali pretreatment of corn stalk for enhanced biogas production. *Renew. Energy* **2018**, *127*, 444–451. [[CrossRef](#)]
8. Xiong, Q.A.; Li, J.; Guo, S.; Li, G.; Zhao, J.; Fang, Y. Ash fusion characteristics during co-gasification of biomass and petroleum coke. *Bioresour. Technol.* **2018**, *257*, 1–6. [[CrossRef](#)] [[PubMed](#)]
9. Zhu, Y.; Yang, W.; Fan, J.; Kan, T.; Zhang, W.; Liu, H.; Cheng, W.; Yang, H.; Wu, X.; Chen, H. Effect of sodium carboxymethyl cellulose addition on particulate matter emissions during biomass pellet combustion. *Appl. Energy* **2018**, *230*, 925–934. [[CrossRef](#)]
10. Hou, Q.; Zhen, M.; Liu, L.; Chen, Y.; Huang, F.; Zhang, S.; Li, W.; Ju, M. Tin phosphate as a heterogeneous catalyst for efficient dehydration of glucose into 5-hydroxymethylfurfural in ionic liquid. *Appl. Catal. B Environ.* **2018**, *224*, 183–193. [[CrossRef](#)]
11. Sikarwar, V.S.; Zhao, M.; Clough, P.; Yao, J.; Zhong, X.; Memon, M.Z.; Shah, N.; Anthony, E.; Fennell, P. An overview of advances in biomass gasification. *Energy Environ. Sci.* **2016**, *9*, 2927–3304. [[CrossRef](#)]
12. Manzour, P.A. Hydrogen Production Using Catalytic Supercritical Water Gasification of Lignocellulosic Biomass. Ph.D. Thesis, University of Toronto, Toronto, ON, Canada, 2012.

13. Byrd, A.J.; Pant, K.; Gupta, R.B. Hydrogen production from glycerol by reforming in supercritical water over Ru/Al₂O₃ catalyst. *Fuel* **2008**, *87*, 2956–2960. [\[CrossRef\]](#)
14. Chan, F.L.; Tanksale, A. Review of recent developments in Ni-based catalysts for biomass gasification. *Renew. Sustain. Energy Rev.* **2014**, *38*, 428–438. [\[CrossRef\]](#)
15. Wu, C.; Williams, P.T. A novel nano-Ni/SiO₂ catalyst for hydrogen production from steam reforming of ethanol. *Environ. Sci. Technol.* **2010**, *44*, 5993–5998. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Yang, R.-X.; Chuang, K.-H.; Wey, M.-Y. Effects of nickel species on Ni/Al₂O₃ catalysts in carbon nanotube and hydrogen production by waste plastic gasification: Bench-and pilot-scale tests. *Energy Fuels* **2015**, *29*, 8178–8187. [\[CrossRef\]](#)
17. Miranda, B.; Chimentão, R.; Santos, J.; Gispert-Guirado, F.; Llorca, J.; Medina, F.; Bonillo, F.L.; Sueiras, J. Conversion of glycerol over 10% Ni/γ-Al₂O₃ catalyst. *Appl. Catal. B Environ.* **2014**, *147*, 464–480. [\[CrossRef\]](#)
18. Ashik, U.; Daud, W.W. Probing the differential methane decomposition behaviors of n-Ni/SiO₂, n-Fe/SiO₂ and n-Co/SiO₂ catalysts prepared by co-precipitation cum modified Stöber method. *Rsc Adv.* **2015**, *5*, 67227–67241. [\[CrossRef\]](#)
19. Ji, G.; Xu, X.; Yang, H.; Zhao, X.; He, X.; Zhao, M. Enhanced hydrogen production from sawdust decomposition using hybrid-functional Ni-CaO-Ca₂SiO₄ materials. *Environ. Sci. Technol.* **2017**, *51*, 11484–11492. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Choi, S.O.; Ahn, I.Y.; Moon, S.H. Effect of CeO₂-addition sequence on the performance of CeO₂-modified Ni/Al₂O₃ catalyst in autothermal reforming of iso-octane. *Korean J. Chem. Eng.* **2009**, *26*, 1252–1258. [\[CrossRef\]](#)
21. Sánchez-Sánchez, M.; Navarro, R.; Fierro, J. Ethanol steam reforming over Ni/MxOy–Al₂O₃ (M = Ce, La, Zr and Mg) catalysts: Influence of support on the hydrogen production. *Int. J. Hydrogen Energy* **2007**, *32*, 1462–1471. [\[CrossRef\]](#)
22. Pattiya, A.; Titiloye, J.O.; Bridgwater, A.V. Fast pyrolysis of cassava rhizome in the presence of catalysts. *J. Anal. Appl. Pyrolysis* **2008**, *81*, 72–79. [\[CrossRef\]](#)
23. Du, G.; Lim, S.; Yang, Y.; Wang, C.; Pfefferle, L.; Haller, G.L. Methanation of carbon dioxide on Ni-incorporated MCM-41 catalysts: The influence of catalyst pretreatment and study of steady-state reaction. *J. Catal.* **2007**, *249*, 370–379. [\[CrossRef\]](#)
24. Zhang, J.; Xin, Z.; Meng, X.; Tao, M. Synthesis, characterization and properties of anti-sintering nickel incorporated MCM-41 methanation catalysts. *Fuel* **2013**, *109*, 693–701. [\[CrossRef\]](#)
25. Corthals, S.; Van Nederkassel, J.; Geboers, J.; De Winne, H.; Van Noyen, J.; Moens, B.; Sels, B.; Jacobs, P. Influence of composition of MgAl₂O₄ supported NiCeO₂ZrO₂ catalysts on coke formation and catalyst stability for dry reforming of methane. *Catal. Today* **2008**, *138*, 28–32. [\[CrossRef\]](#)
26. Liu, D.; Lau, R.; Borgna, A.; Yang, Y. Carbon dioxide reforming of methane to synthesis gas over Ni-MCM-41 catalysts. *Appl. Catal. A Gen.* **2009**, *358*, 110–118. [\[CrossRef\]](#)
27. Li, D.; Zeng, L.; Li, X.; Wang, X.; Ma, H.; Assabumrungrat, S.; Gong, J. Ceria-promoted Ni/SBA-15 catalysts for ethanol steam reforming with enhanced activity and resistance to deactivation. *Appl. Catal. B Environ.* **2015**, *176*, 532–541. [\[CrossRef\]](#)
28. Carraro, P.M.; Blanco, A.A.G.; Soria, F.A.; Lener, G.; Sapag, K.; Eimer, G.A.; Oliva, M.I. Understanding the role of nickel on the hydrogen storage capacity of Ni/MCM-41 materials. *Microporous Mesoporous Mater.* **2016**, *231*, 31–39. [\[CrossRef\]](#)
29. Lensveld, D.J.; Gerbrand Mesu, J.; Jos van Dillen, A.; de Jong, K.P. Synthesis and characterisation of MCM-41 supported nickel oxide catalysts. *Microporous Mesoporous Mater.* **2001**, *44–45*, 401–407. [\[CrossRef\]](#)
30. Gangwar, B.P.; Maiti, S.C.; Sharma, S. Modifying the hygroscopic property of La₂O₃ by Pr, Sm and Nd doping. *J. Solid State Chem.* **2017**, *256*, 109–115. [\[CrossRef\]](#)
31. Beche, E.; Peraudeau, G.; Flaud, V.; Perarnau, D. An XPS investigation of (La₂O₃)_{1-x} (CeO₂)_{2x} (ZrO₂)₂ compounds. *Surf. Interface Anal.* **2012**, *44*, 1045–1050. [\[CrossRef\]](#)
32. Reddy, B.M.; Chowdhury, B.; Smirniotis, P.G. An XPS study of La₂O₃ and In₂O₃ influence on the physicochemical properties of MoO₃/TiO₂ catalysts. *Appl. Catal. A Gen.* **2001**, *219*, 53–60. [\[CrossRef\]](#)
33. Cheng, D.-G.; Chong, M.; Chen, F.; Zhan, X. XPS Characterization of CeO₂ Catalyst for hydrogenation of benzoic acid to benzaldehyde. *Catal. Lett.* **2008**, *120*, 82–85. [\[CrossRef\]](#)
34. Holgado, J.P.; Alvarez, R.; Munuera, G. Study of CeO₂ XPS spectra by factor analysis: Reduction of CeO₂. *Appl. Surf. Sci.* **2000**, *161*, 301–315. [\[CrossRef\]](#)

35. Yang, C.; Fan, H.; Qiu, S.; Xi, Y.; Fu, Y. Microstructure and dielectric properties of La_2O_3 films prepared by ion beam assistant electron-beam evaporation. *J. Non Cryst. Solids* **2009**, *355*, 33–37. [[CrossRef](#)]
36. Wang, N.; Liu, J.; Gu, W.; Song, Y.; Wang, F. Toward synergy of carbon and La_2O_3 in their hybrid as an efficient catalyst for the oxygen reduction reaction. *RSC Adv.* **2016**, *6*, 77786–77795. [[CrossRef](#)]
37. Eliche-Quesada, D.; Mérida-Robles, J.; Maireles-Torres, P.; Rodríguez-Castellón, E.; Jiménez-López, A. Hydrogenation and ring opening of tetralin on supported nickel zirconium-doped mesoporous silica catalysts. influence of the nickel precursor. *Langmuir* **2003**, *19*, 4985–4991. [[CrossRef](#)]
38. Wang, X.; Zhu, L.; Liu, Y.; Wang, S. CO_2 methanation on the catalyst of Ni/MCM-41 promoted with CeO_2 . *Sci. Total Environ.* **2018**, *625*, 686–695. [[CrossRef](#)] [[PubMed](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).