

Communication

Nickel Silicide Catalyst from Photovoltaic Waste for the Methanation Reaction

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Abstract: A technology designed for recycling photovoltaic (PV) cells at the end of their life was successfully used for the preparation of a nickel silicide catalyst. PV cells were mixed with magnesium scrap to produce magnesium silicide (Mg_2Si), with almost total conversion under optimized conditions (400 °C, 5 Pa, 25 min), in a constructed semi-open tubular reactor. Subsequently, magnesium silicide was hydrolyzed by 25% phosphoric acid to produce a mixture of silicon hydrides, which were utilized as chemical vapor deposition (CVD) precursors for the preparation of a nickel silicide catalyst. The activity and stability of the prepared catalyst was repeatedly tested for methanation reactions. It was verified that the nickel silicide catalyst showed an approximately 20% higher activity for the methanation reactions compared to the commonly used nickel catalyst.

Keywords: electronic waste utilization; carbon monoxide to SNG; energy from waste; environmentally friendly technology; sustainable energy



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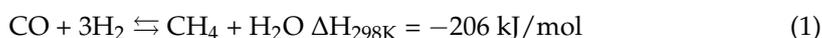
1. Introduction

The 21st century has brought about rapid technological progress, especially in the electronics industry. Breakthrough innovations in existing technologies, and the development of a wide range of new ones, simplify our lives [1]; however, they also stimulate an increase in the consumption of raw materials for both semiconductor and rare earth elements [2]. Nevertheless, this is associated with a strong environmental impact, such as the loss of raw material deposits, pollution caused by the technological processing and refining of raw materials, high energy consumption [3] and, most importantly, increased amounts of electronic waste [4]. In 2016, only 20% of the world's electronic waste was properly recycled, and the fate of the remaining 80% is not documented. It was probably dumped, traded or recycled under worse conditions. [5]. For these reasons, the development of recycling and waste-free technologies, which enable the environmentally friendly and economic regeneration of raw materials, is inevitable [6].

The lifespan of the first generation of PV cells is coming to an end, which will cause a serious problem owing to the fact that commonly used technologies are based on high-temperature processes, leading to the chemical leaching of PV cells. Regrettably, these technologies usually do not allow for regeneration in an efficient and ecological way [7]. For these reasons, a three-step process for the utilization of waste PV cells was designed and verified. The first step includes the milling of entire PV cells and mixing them together with a magnesium scrap. The mixture then reacts after heating under optimized conditions in a semi-open tubular reactor, to form magnesium silicide (Mg_2Si) with almost complete conversion. The last step of the proposed process is the acid hydrolysis of the prepared magnesium silicide, to form silicon hydrides (silanes) [8]. The instability of silanes makes them suitable not only for the regeneration of photovoltaic silicon by decomposition

into electronics-grade silicon and hydrogen [9], but also for chemical vapor deposition (CVD), which is used in the electronics industry and for the preparation of metal silicide catalysts [7,10].

The technological development that has occurred in the 21st century also relates to the replacement of traditional fossil fuel energy sources by renewable ones, e.g., solar and wind. Regrettably, these processes are usually unable to provide energy continuously; thus, a problem with the efficient storage of the produced energy persists [11]. Nowadays, there are various technologies for energy storage, such as direct storage by supercapacitors or superconducting magnetic energy storage (SMES), or even the conversion of chemical energy in batteries into the form of hydrogen from water electrolysis, or into the form of synthetic natural gas (SNG) [11]. The production of SNG seems to be especially promising due to the huge capacity of the grid, which allows for practically unlimited storage [11]. Therefore, methanation, a process based on the reaction of carbon oxides with hydrogen to form methane and water, becomes attractive for the production of sustainable energy from waste; see Equation (1) [12].



This is used as the last stage of processing in most modern ammonia production facilities, not only to purify the synthesised gases, but also to produce synthetic natural gas (SNG) [13]. The source of a methane feedstock can be hydrogen produced by an electrolysis unit at solar or wind power plants [13]. The source of carbon oxides can be the gases produced from coal and biomass combustion, or carbon monoxide formed during the production of silicon [13]. Due to the carbon monoxide content, which is a catalytic poison [11], and the high reaction enthalpy of methanation, a catalyst, which would not only be sufficiently active for the methanation process, but also thermally stable and resistant, is still being sought [9,10]. Commonly used catalysts are based on nickel [14–16], ruthenium [13,17], iron [13,17] or cobalt [13,17]. Nevertheless, their application is accompanied by some difficulties and limitations. In the case of nickel and ruthenium, these problems primarily involve evaporation of the active ingredient in the form of carbonyl compounds, together with their lower resistance to deactivation [18]. Iron-based catalysts are less active, and are prone to the formation of carbonaceous deposits, while cobalt-based catalysts show a lower selectivity to the desired methane. On the other hand, metal silicides exhibit unique chemical and physical properties, such as a high thermal stability, as well as a resistance to inactivation caused by the incorporation of silicon into the crystalline structure [19].

This article applies the proposed technology of recycling photovoltaic cells for the preparation of a new type of catalyst that is suitable for the methanation reaction. The new recycling method, patented by the authors, enables the easy and efficient production of silicon hydrides directly from photovoltaic waste, which can be thermally decomposed into electronic-grade silicon and hydrogen. Silicon hydrides prepared from photovoltaic waste were then employed as a CVD precursor to prepare a thin layer of nickel silicide. The prepared nickel silicide was used as a catalyst for the methanation reaction, and its catalytic activity, together with its resistance, was successfully verified.

2. Materials and Methods

A silicon hydride mixture (99% content of silicon hydrides, see Figure 1a,b) used as CVD precursor for a nickel silicide catalyst was prepared by the hydrolysis reaction between a 25% (w/w) solution of phosphoric acid (85 wt. % in H₂O, 99.99%; Sigma Aldrich, St. Louis, MO, USA) and magnesium silicide (Mg₂Si; 97.9%, see Figure 2), which was synthesized from magnesium (99.9%; particle size under 200 μm; Fichema, Brno-Lisen, Czech Republic) and milled photovoltaic scrap (Si content over 90%; particle size under 200 μm; Solartec Holding, Rožnov pod Radhoštěm, Czech Republic) under optimized conditions (400 °C, 5 Pa, 25 min) by Bumba et al. [7,10], in a designed and constructed semi-opened tube reactor. The hydrolysis reaction was performed in laboratory apparatus

consisting of a two-neck round-bottom flask equipped with a dropping funnel for the acid, and with a connector to the vacuum pump and a cuvette, which enabled the creation of a vacuum inside the flask, and also the collection of silane.

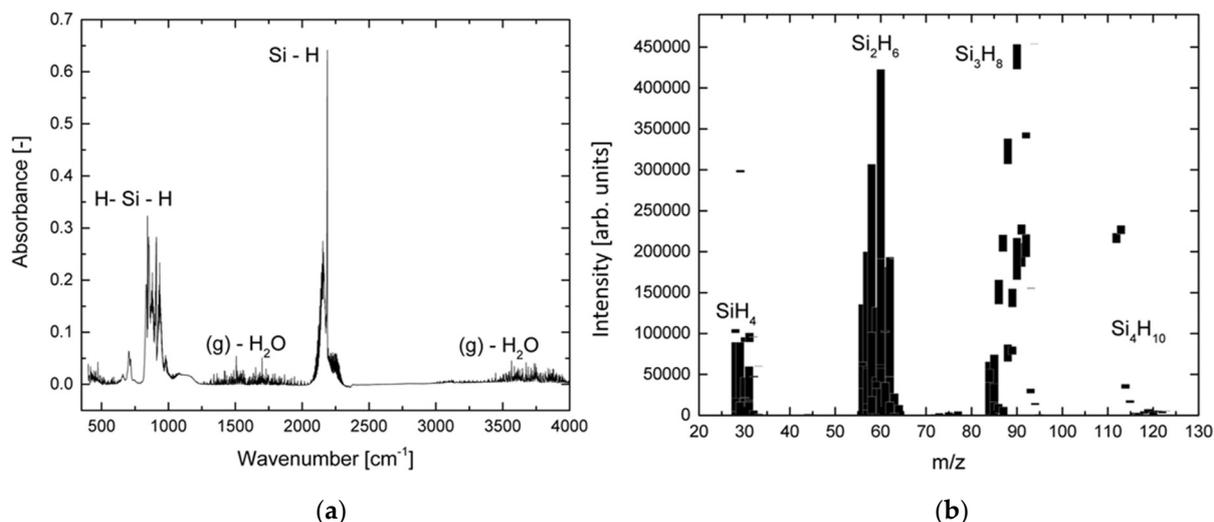


Figure 1. Characterization of silicon hydride mixture prepared by acid hydrolysis of magnesium silicide (a) by FTIR, and (b) by GC/MS.

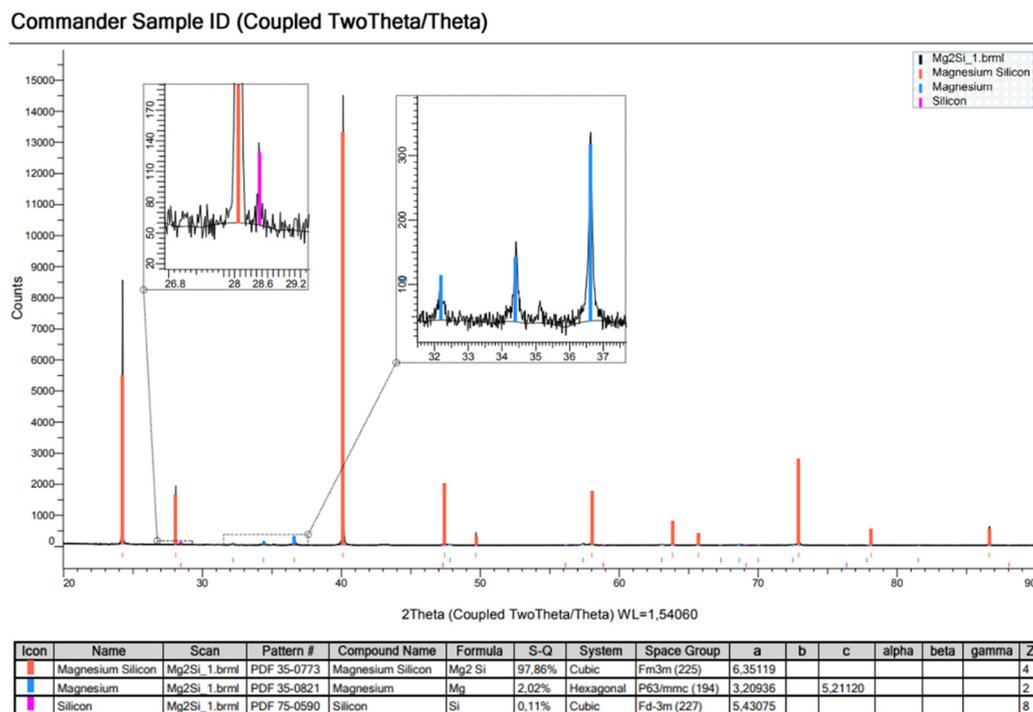


Figure 2. XRD of magnesium silicide (Mg₂Si) prepared from discarded PV cells and magnesium under optimized conditions (400 °C, 5 Pa, 25 min) in the semi-opened tube reactor.

Nickel sieves (99.9% purity; Goodfellow Cambridge Limited) with a thickness of 0.1 mm, diameter of 25 mm, and mesh size of 180 mm were cleaned with acetone in an ultrasonic bath, then dried and placed in a quartz tube, which was inserted into a plug-in furnace (see Figure 3). The quartz tube was subsequently connected to a rotary vacuum pump and vacuumed for 60 min. After reaching a pressure of 10⁻³ Pa, the system was tempered to the final temperature of 400 °C. When the desired temperature was reached,

the silicon hydride mixture flowing at 6 sccm (0.1 mbar L/s), was fed into the quartz tube and a constant pressure of approximately 160 Pa was kept. After 120 min, tempering was turned off, the inlet to the mixture of silicon hydride was closed, and the system was naturally cooled to room temperature.

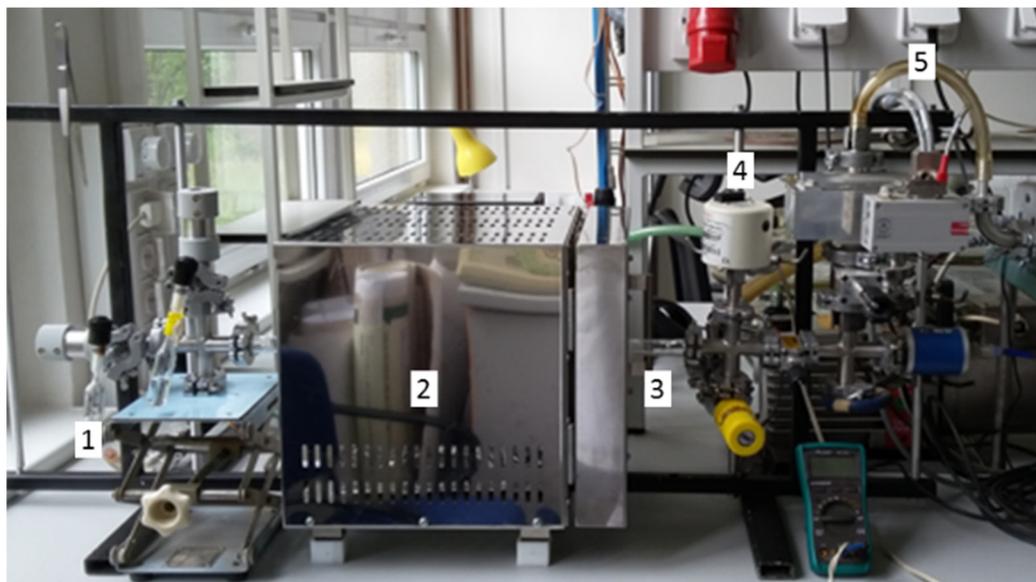


Figure 3. CVD apparatus for Ni_xSi_y catalyst preparation. 1—Cuvette with hydride; 2—plug-in furnace; 3—quartz tube with nickel sieve; 4—manometer; 5—rotary vacuum pump.

Prepared nickel silicide layers were tested as a possible catalyst for the methanation reaction using a raw mixture of carbon monoxide and hydrogen. The catalytic activity of prepared nickel silicide layers (0.163 g nickel sieves with 1.75 mg of nickel silicide) was compared with that of pure nickel sieves (0.163 g). The weight of Ni_xSi_y was determined using laboratory scales, with each sieve being weighed before and after chemical vapor deposition (maximum deviation 5%). Average weight sieves (1.75 mg) were chosen for methanation experiments. All tested sieves were cut into squares with 1 mm sides, and subsequently fed into a flow reactor with an internal diameter of 8 mm. The catalyst bed was fixed on both sides with quartz cotton together with dried silica gel layers, to remove the inlet moisture and reaction water (see Figure 4).



Figure 4. Flow reactor with catalyst bed fitted with a silica gel layer.

Afterwards, the reactor was fastened in the apparatus vertically, a thermocouple was introduced into the catalyst bed, and the reactor was put into a plug-in furnace (see Figure 5). The flow rate of carbon monoxide (99.0%; Linde Gas, Dublin, Ireland) and hydrogen (99.99%; Linde Gas) was separately controlled by mass flow meters, and the reaction mixture was formed in a mixer located above the reactor. The $\text{H}_2:\text{CO}$ molar ratio was 5:1, and the total rate of flow for mixture flowing through the reactor was 120 mL per minute. Before starting the experiment, the catalyst was always reduced for 3 h in a stream of hydrogen at 100 mL/min and 340 °C. After the elapsed time, carbon monoxide was introduced into the reactor, and the output stream was characterized by mass spectrometry (MS) (see Figure 6).



Figure 5. Flow reactor with thermocouple equipped with a plug-in furnace and a mixture of supplied gases. 1—thermocouple; 2—gas mixer; 3—CO supply; 4—H₂ supply; 5—plug-in furnace; 6—reactor outlet.



Figure 6. Methanation apparatus connected to a mass spectrometer (left). 1—flow reactor (see Figure 5); 2—mass flow meters and temperature controller; 3—mass spectrometer.

Analytical Methods

Solid starting materials and prepared products (magnesium silicide, PV cells) were characterized by scanning electron microscopy, with energy dispersive X-ray spectroscopy (SEM/EDX) and/or X-ray diffraction (XRD). The gaseous products (silicon hydrides) were characterized by Fourier transform infrared spectroscopy (FTIR), and gas chromatography with mass spectrometry (GC/MS) detection. The prepared nickel silicide thin films were also characterized by a high-resolution transmission electron microscope equipped with an energy-dispersive spectroscope (HRTEM/EDX).

The purity of starting materials was determined by SEM equipped with EDX (Tescan Indus; Fuveau, France), being used specifically for compositional evaluation of starting materials, and products, based on the ratios of the MgK α and SiK α intensities. The tungsten substrate was used as a carrier for layers measured by the EDX method at an accelerating voltage of 15–30 kV.

The composition of magnesium silicide (Mg₂Si) was also characterized by XRD (PANalytical X'Pert PRO; Malvern, United Kingdom), equipped with an X'Celerator detector

and a PW3050/60 (Theta/Theta) goniometer. Polychromating radiation, i.e., Cu K α 1 ($\lambda = 1.54060 \text{ \AA}$), K α 2 ($\lambda = 1.54443 \text{ \AA}$), K β ($\lambda = 1.39225 \text{ \AA}$) [A], and K α 2/K α 1 (ratio: 0.50000) was measured without a monochromator. XRF measurements were used to determine the elemental composition of the products on the ARL 9400 Rh spectrometer, using a 60 kV LiF200 LiF220 Ge111 TIAP excitation source. The Nicolet Almega XR Raman spectroscope (Waltham, MA, USA) was used to obtain additional information on the structure of the solids. All Raman dispersion spectra were collected at 256 exposures with an excitation wavelength of 473 nm (power 8–10 mW) and resolution of 2 cm^{-1} .

Gaseous products of the magnesium silicide hydrolysis reaction were characterized by FTIR and GC/MS methods. FTIR spectra were measured on a 1 cm^{-1} Nicolet spectrometer (Waltham, MA, USA) with 100 replicates. The gas chromatograph with mass spectrometer detection (GC-Hewlett Packard series 6890; Palo Alto, CA, USA) using the MS-5973 mass-selective protector, was equipped with a 30 m long capillary column (DB-5) with a diameter of 0.25 mm. The temperature range was programmed to 35–90 °C, with a temperature increase of 10 °C/min. Helium with a flow rate of 1 mL/min was used as the carrier gas. The injection was performed with a gas sampling syringe with a split ratio of 1:20, and the injector temperature was set to 130 °C. Ionization of the sample was performed with an EI (Electron Ionization) source with an energy of 70 eV.

Nickel silicide thin films prepared by CVD were also characterized by a JEOL JEM 3010 high-resolution transmission electron microscope (HRTEM) (Tokyo, Japan) operated at 300 kV (LaB6 cathode, 1.7 Å spot resolution), equipped with an Oxford Instruments energy-dispersive X-ray detector (EDX) for elemental analysis, and by a Gatan CCD camera (1024×1024 pixels) for image recording. The images were analyzed using the Digital Micrograph software package. EDX analyses were performed using the INCA software package. Electron diffraction patterns were evaluated using the ICDD-2 database and the ProcessDiffraction V_8.7.1.Q software package.

Regarding methanation, the output current was detected by the MS method (Omnistar200, Pfeiffer Vacuum/Balzers, Wien, Austria), which recorded the signal of selected mass fractions.

3. Results and Discussion

Acetone-cleaned nickel sieves were used as a solid substrate for CVD of the silicon hydride mixture to prepare a thin layer of Ni $_x$ Si $_y$, which is a promising material for use within the field of catalysis. The gaseous precursor (a mixture of silicon hydrides) was prepared by acid hydrolysis of magnesium silicide, which was prepared by thermal synthesis directly from discarded photovoltaic cells and magnesium sawdust under optimized conditions (400 °C, 5 Pa, 25 min). The surface of the nickel sieves was observed using scanning electron microscopy (SEM) (see Figure 7a–c). Figure 7a depicts the pure nickel sieve, used as a solid substrate for subsequent CVD of the prepared silicon hydride mixture. Figure 7b shows the nickel sieve after CVD, where it is obvious that a continuous and homogeneous layer was formed. Figure 7c, which shows the details of the formed layer, allows a deeper look at the structure, which was formed by very fine wires.

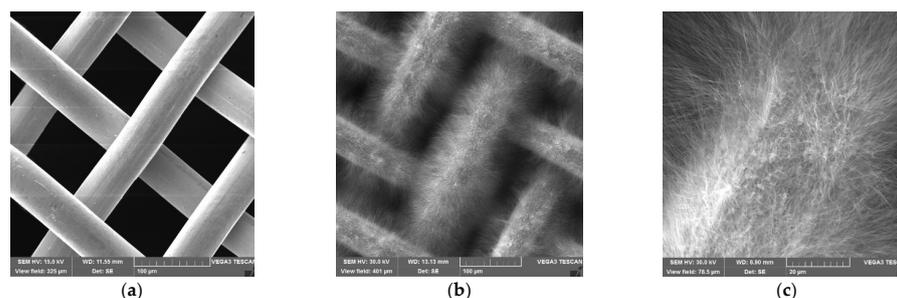


Figure 7. SEM pictures of the nickel sieve surface. (a) Pure nickel sieve before CVD; (b) Nickel sieve covered with layer after CVD; (c) Detail of the prepared layer.

To verify that the formed layer was actually made of fine nickel silicide wires, a sample of this layer was characterized by a high-resolution transmission electron microscope equipped with energy-dispersive X-ray spectroscopy (HRTEM/EDX) (see Figure 8 and Table 1). The selected area diffraction (SAD) included in Figure 8, clearly confirmed that the sample of the examined layer was polycrystalline. Individual evaluation of the diffractograms (see Figure 8) confirmed the formation of the desired nickel silicides, with variable contents of nickel and silicon (Ni_3Si , $\text{Ni}_{74}\text{Si}_{26}$, Ni_3Si_2), together with different crystalline structures. The quantity of specific individual elements was also confirmed by the EDX method, and the results are summarized in Table 1. The quantitative results of the EDX analyses confirmed the varying silicon and nickel contents, from about 4.5 to 37.4 at. % for silicon and 1.4 to 64.3 at. % for nickel. For this reason, the prepared layer is referred to as Ni_xSi_y .

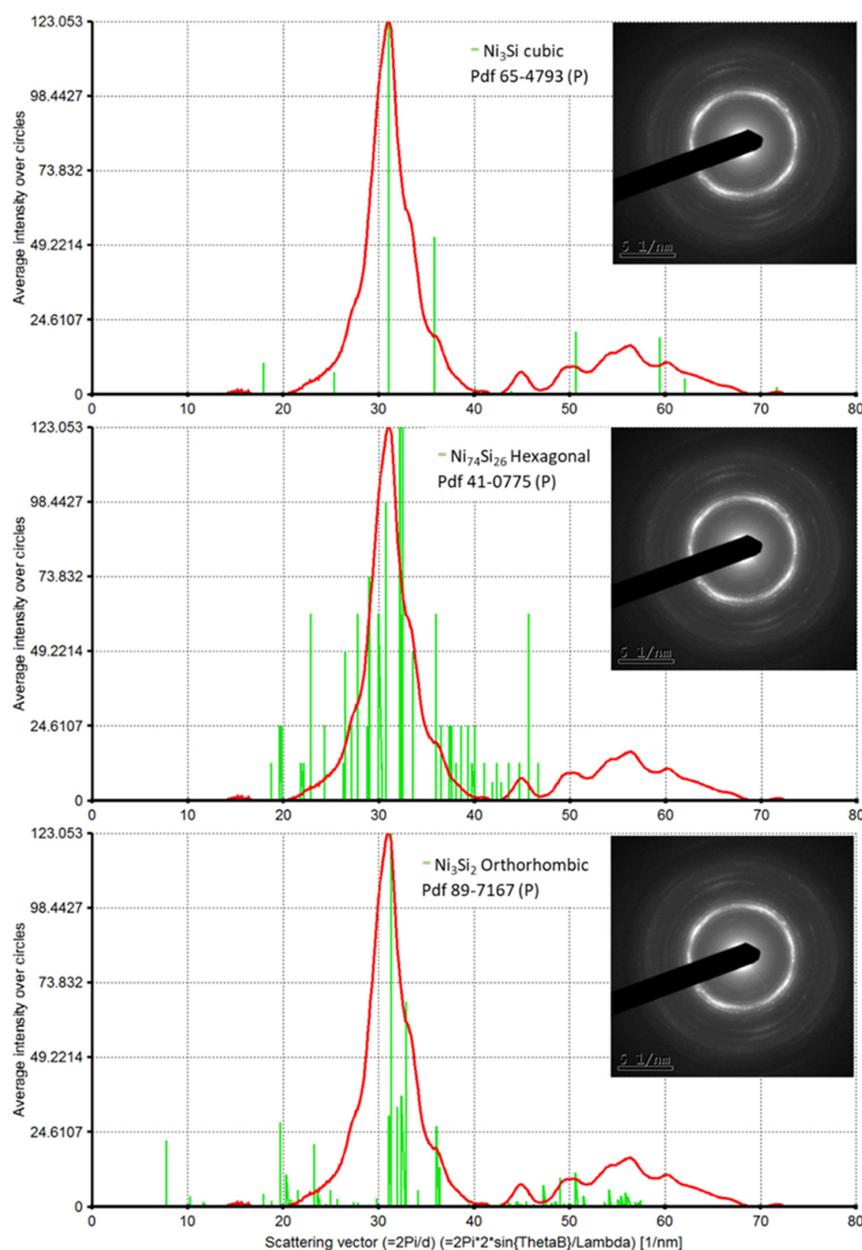


Figure 8. HRTEM-SAD patterns of the prepared Ni_xSi_y thin layer on the nickel sieve surface by CVD.

Table 1. HRTEM/EDX results of the prepared Ni_xSi_y thin layer on the nickel sieve surface by CVD.

Spectrum	C (at. %)	O (at. %)	Si (at. %)	Ni (at. %)
Spectrum 1	-	13.55	34.15	52.30
Spectrum 2	21.32	15.32	26.81	36.56
Spectrum 3	15.07	11.89	28.46	44.58
Spectrum 4	94.07	-	4.51	1.41
Spectrum 5	54.23	16.19	15.53	14.05
Spectrum 6	38.17	7.62	21.84	32.37
Spectrum 7	47.27	14.56	17.85	20.32
Spectrum 8	49.03	17.58	16.86	16.53
Spectrum 9	59.50	13.91	14.26	12.33
Spectrum 10	74.08	17.53	6.82	1.57
Spectrum 11		20.87	33.63	45.50
Spectrum 12	-	19.70	32.03	48.27
Spectrum 13	-	7.21	36.07	56.72
Spectrum 14	-	-	35.67	64.33
Spectrum 15	-	-	37.37	62.63
Max.	94.07	20.86	37.37	64.33
Min.	15.07	7.20	4.51	1.41

Nickel silicide layers were prepared to demonstrate the ecological possibility of reusing waste PV cells. In addition to the decomposition of silanes into electronics-grade silicon and hydrogen. The preparation of a new type of nickel silicide catalyst revealed further possibilities for waste PV cell utilization. As one of the many applications of the newly prepared catalyst, a methanation reaction was introduced, which fits into the ecological cycle of the entire recycling process. The prepared nickel silicide layers possessed high thermal stabilities, as well as a resistance to inactivation caused by the incorporation of silicon into the crystalline structure [19]; thus, it met all the requirements of an efficient and stable methanation catalyst.

The catalytic activity of the prepared nickel silicide layers was compared with pure nickel sieves, which are commonly used as a catalyst for the methanation reaction. After activation of the catalyst, carbon monoxide was introduced into the mixer, and the output stream was continuously measured by a mass spectrometer.

This continually measured data stream was plotted as a graph of the absolute intensity of the methane signal ($m/z = 16$) over time for both tested catalysts: the green nickel silicide sieve [$c\text{CH}_4(\text{Ni}_x\text{Si}_y)$]; and the red pure nickel reference sieve [$c\text{CH}_4(\text{Ni})$]. Figure 9a demonstrates the average time course of catalytic activity (solid lines), together with the maximal standard deviations (green and red lines). The catalytic activity was comparable for both samples at the beginning of the reaction. After approximately 30 min, the catalytic activity of the pure nickel catalyst began to decrease, while the activity of the nickel silicide sieve gradually increased. For a clearer representation of this, the graphical dependence of $c\text{CH}_4(\text{Ni}_x\text{Si}_y)/c\text{CH}_4(\text{Ni})$ over time is shown in Figure 9b, which in fact quantifies the activity of nickel silicides against that of pure nickel sieves, showing that the activity of the nickel silicides was about 20% higher.

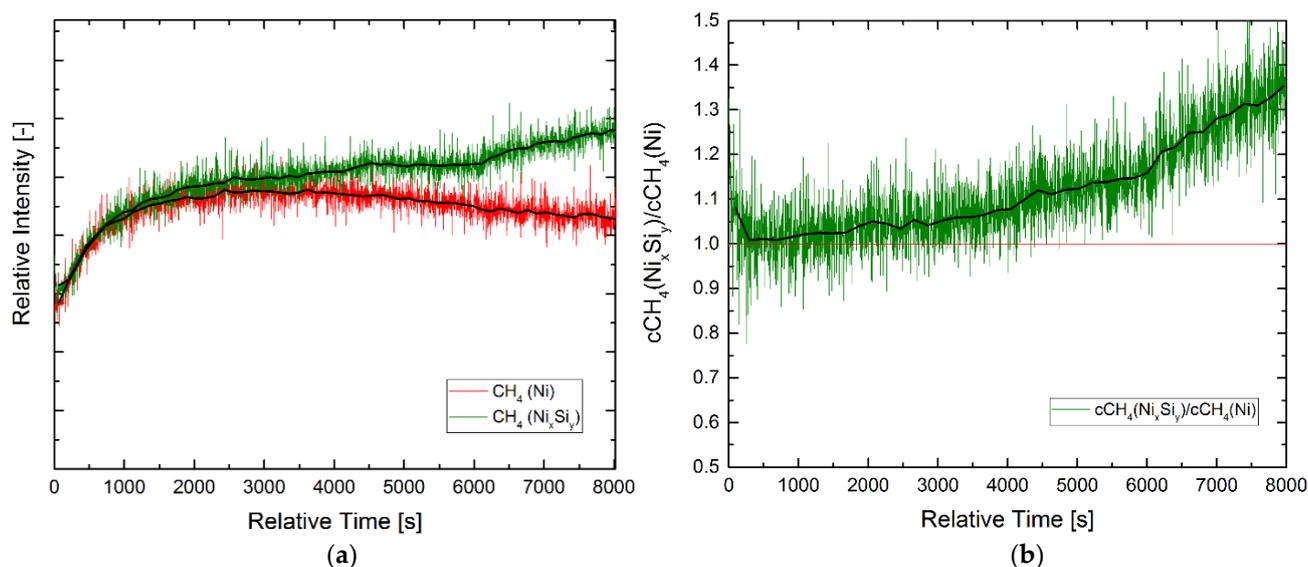


Figure 9. (a) Time course of the methane signal intensity on the Ni_xSi_y -coated nickel sieve (green) and the reference nickel sieve (red) by the MS method; (b) Time dependence of the methane concentrations produced on Ni_xSi_y coated sieve versus nickel sieve ($c\text{CH}_4(\text{Ni}_x\text{Si}_y)/c\text{CH}_4(\text{Ni})$).

The same samples of nickel silicide and pure nickel catalysts were tested repeatedly to verify their stability and catalytic activity, see Figure 10. It was obvious that the activity of the pure nickel sieve progressively declined, whereas the prepared nickel silicide catalyst revealed a stable activity. Based on information from the available literature [12,13,19], in terms of the use of nickel silicide compared to pure nickel, it is not a question of a different methanation mechanism, but rather of the better properties of the silicide catalyst—mainly the higher resistance of nickel silicide to high temperatures (which can cause nickel sintering) due to the strong bond between nickel and silicon, which thermodynamically stabilizes the catalytically active nickel. At the same time, a small amount of silicon interacting with Ni atoms appears to selectively prevent the adsorption of resistant carbon deposits and, thus, prolongs its life. Measured results fully correspond to findings from the literature [20–22].

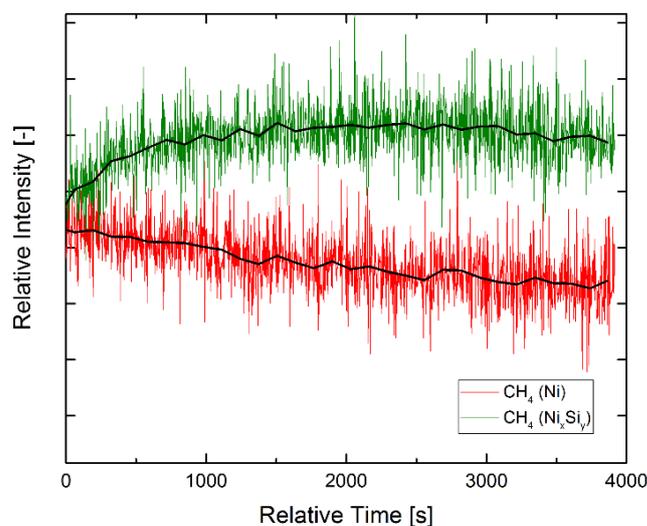


Figure 10. Timeline of the methane signal intensity on the Ni_xSi_y -coated nickel sieve (green) and the reference nickel sieve (red) by the MS method, showing repeated measurements.

4. Conclusions

The mixture of silicon hydrides, which was the product of a newly designed method for the recycling of waste photovoltaic cells, was successfully tested as a CVD precursor for the preparation of nickel silicide layers. The thermal decomposition of silanes on the nickel sieve surfaces resulted in the formation of a nickel silicide layer, in the form of thin wires with a diameter of less than 1 micrometer. The prepared catalyst was characterized by SEM, which confirmed its uniform distribution on the surface of the nickel sieves, and by HRTEM/EDX, which verified the polycrystalline structure of the Ni_xSi_y . The prepared nickel silicide layers were tested for use in the methanation reaction, together with a commonly used nickel catalyst to compare their activities. The obtained results confirmed that the prepared nickel silicide catalyst showed not only a 20% higher activity compared to the common nickel catalyst, but also better a stability with respect to pure nickel. It was verified that the prepared nickel silicide catalyst featured a high activity, together with a resistance to the formation of carbonaceous deposits due to the thermodynamic stabilization of nickel by silicon incorporated into the crystalline structure. Consequently, this catalyst appeared promising even in the demanding conditions associated with the methanation reaction. The primary aim of this manuscript was to demonstrate another possibility for the ecological reuse of waste PV cells, in addition to the decomposition of silanes into electronics-grade silicon and hydrogen. The preparation of a new type of nickel silicide catalyst revealed further possibilities for waste PV cell utilization. As one of the many applications of the newly prepared catalyst, the methanation reaction was successfully introduced, which fits into the ecological cycle of the entire recycling process. The described technology not only solves the issue of recycling photovoltaic waste, but also produces a new type of catalyst for SNG production, thus, it meets two United Nations sustainable development goals (SDGs), namely, SDG 7: affordable and clean energy, SDG 12: responsible consumption and production [23].

Author Contributions: J.B.; conceptualization, investigation, writing—original draft, V.D.; supervision of catalyst preparation, software and formal analysis, P.K.; provided critical feedback and helped to evaluate and edit the manuscript, P.D.; data curation, data visualization, O.S.; conceptualization, supervision, project administration and resources. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no competing financial interest.

References

1. Bomgarden, M.; Scott, A. Recycling Renewables. *C&EN Glob. Enterp.* **2018**, *96*, 34–41. [[CrossRef](#)]
2. Choi, J.-K.; Fthenakis, V. Design and Optimization of Photovoltaics Recycling Infrastructure. *Environ. Sci. Technol.* **2010**, *44*, 8678–8683. [[CrossRef](#)]
3. Tan, Q.; Li, J. Recycling Metals from Wastes: A Novel Application of Mechanochemistry. *Environ. Sci. Technol.* **2015**, *49*, 5849–5861. [[CrossRef](#)] [[PubMed](#)]
4. de Buzin, P.J.W.K.; Ambrós, W.M.; de Brum, I.A.S.; Tubino, R.M.C.; Hoffmann Sampaio, C.; Oliva Moncunill, J. Development of a Physical Separation Route for the Concentration of Base Metals from Old Wasted Printed Circuit Boards. *Minerals* **2021**, *11*, 1014. [[CrossRef](#)]
5. Ilankoon, I.M.S.K.; Ghorbani, Y.; Chong, M.N.; Herath, G.; Moyo, T.; Petersen, J. E-waste in the international context—A review of trade flows, regulations, hazards, waste management strategies and technologies for value recovery. *Waste Manag.* **2018**, *82*, 258–275. [[CrossRef](#)] [[PubMed](#)]
6. Xolo, L.; Moleko-Boyce, P.; Makelane, H.; Faleni, N.; Tshentu, Z.R. Status of Recovery of Strategic Metals from Spent Secondary Products. *Minerals* **2021**, *11*, 673. [[CrossRef](#)]

7. Dytrych, P.; Bumba, J.; Kastanek, F.; Fajgar, R.; Kostejn, M.; Solcova, O. Waste Photovoltaic Panels for Ultrapure Silicon and Hydrogen through the Low-Temperature Magnesium Silicide. *Ind. Eng. Chem. Res.* **2017**, *56*, 12863–12869. [[CrossRef](#)]
8. Hurd, D.T. A General Mechanism for the Formation of Volatile Hydrides by Hydrolysis Reactions. *J. Am. Chem. Soc.* **1947**, *69*, 1647–1651. [[CrossRef](#)] [[PubMed](#)]
9. Hogness, T.R.; Wilson, T.L.; Johnson, W.C. The Thermal Decomposition of Silane. *J. Am. Chem. Soc.* **1936**, *58*, 108–112. [[CrossRef](#)]
10. Bumba, J.; Dytrych, P.; Fajgar, R.; Kastanek, F.; Solcova, O. Total Germanium Recycling from Electronic and Optical Waste. *Ind. Eng. Chem. Res.* **2018**, *57*, 8855–8862. [[CrossRef](#)]
11. Schaaf, T.; Grünig, J.; Schuster, M.R.; Rothenfluh, T.; Orth, A. Methanation of CO₂ - Storage of Renewable Energy in a Gas Distribution System. *Energy Sustain. Soc.* **2014**, *4*, 1–14. [[CrossRef](#)]
12. Baudouin, D.; Szeto, K.C.; Laurent, P.; De Mallmann, A.; Fenet, B.; Veyre, L.; Rodemerck, U.; Copéret, C.; Thieuleux, C. Nickel-Silicide Colloid Prepared under Mild Conditions as a Versatile Ni Precursor for More Efficient CO₂ Reforming of CH₄ Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 20624–20627. [[CrossRef](#)]
13. Miao, B.; Ma, S.; Wang, X.; Su, H.; Chan, S.H. Catalysis Mechanisms of CO₂ and CO Methanation. *Catal. Sci. Technol.* **2016**, *6*, 4048–4058. [[CrossRef](#)]
14. Sehested, J.; Dahl, S.; Jacobsen, J.; Rostrup-Nielsen, J.R. Methanation of CO over Nickel: Mechanism and Kinetics at High H₂/CO Ratios. *J. Phys. Chem. B* **2005**, *109*, 2432–2438. [[CrossRef](#)]
15. Heine, C.; Lechner, B.A.J.; Bluhm, H.; Salmeron, M. Recycling of CO₂: Probing the Chemical State of the Ni(111) Surface during the Methanation Reaction with Ambient-Pressure X-Ray Photoelectron Spectroscopy. *J. Am. Chem. Soc.* **2016**, *138*, 13246–13252. [[CrossRef](#)] [[PubMed](#)]
16. Roiaz, M.; Monachino, E.; Dri, C.; Greiner, M.; Knop-Gericke, A.; Schlögl, R.; Comelli, G.; Vesselli, E. Reverse Water–Gas Shift or Sabatier Methanation on Ni(110)? Stable Surface Species at Near-Ambient Pressure. *J. Am. Chem. Soc.* **2016**, *138*, 4146–4154. [[CrossRef](#)] [[PubMed](#)]
17. Vannice, M.A. The catalytic synthesis of hydrocarbons from H₂CO mixtures over the group VIII metals: I. The specific activities and product distributions of supported metals. *J. Catal.* **1975**, *37*, 449–461. [[CrossRef](#)]
18. Betta, R.A.D. Ruthenium. *Catal. J.* **1974**, *35*, 54. [[CrossRef](#)]
19. Chen, X.; Jin, J.; Sha, G.; Chuang, L.; Zhang, B.; Su, D.; Williams, C.; Liang, C. Silicon-Nickel Intermetallic Compounds Supported on Silica as a Highly Efficient Catalyst for CO Methanation. *Catal. Sci. Technol.* **2014**, *4*, 53–61. [[CrossRef](#)]
20. Premkumar, P.A.; Meersschant, J.; Richard, O.; Moussa, A.; Steenbergen, J.; Schaekers, M.; To, Z.; Elshocht, S.V.; Adelman, C. Phase Formation and Morphology of Nickel Silicide Thin Films Synthesized by Catalyzed Chemical Vapor Reaction of Nickel with Silane. *Chem. Mater.* **2015**, *27*, 245–254. [[CrossRef](#)]
21. Ryabchuk, P.; Agostini, G.; Pohl, M.; Lund, H.; Agapova, A.; Junge, H.; Junge, K.; Beller, M. Intermetallic Nickel Silicide Nanocatalyst—A Non-Noble Metal—Based General Hydrogenation Catalyst. *Sci. Adv.* **2018**, *4*, eaat0761. [[CrossRef](#)] [[PubMed](#)]
22. Dubois, L.H.; Nuzzo, R.G. Small-Molecule Chemisorption in Nickel Disilicide: Implications for Heterogeneous Catalysts. *J. Am. Chem. Soc.* **1983**, *105*, 365–369. [[CrossRef](#)]
23. United Nations—Sustainable Development Goals. Available online: <https://sdgs.un.org/goals> (accessed on 13 December 2021).