Nanoporous Ni/SiC(O)-based nanocomposites are successfully synthesized by the pyrolytic conversion of nickel-modified polycarbosilane precursors, which are obtained by the chemical modification of polycarbosilane with nickel acetylacetonate (Ni-SMP). High-temperature treatment of the produced precursor in argon atmosphere leads to the homogeneously distributed in situ generated crystalline Ni nanoparticles in the amorphous SiC(O) matrix. The obtained Ni/SiC(O)-based nanocomposites show high specific surface area (SSA; 100–200 m² g⁻¹) with in situ generated microporosity. Furthermore, the chemical modification of Ni-SMP precursor with macromolecule poly(ethylene glycol) methacrylate (PEGM) increases the SSA (Ni-SMP-PEGM; 300–350 m² g⁻¹) and generated micro-mesoporosity. In terms of catalytic properties, preliminary results of the catalytic activity of the Ni/SiC(O)-based nanocomposites show that they are active for the methanation of CO₂. The CO₂ conversion increases with increasing reaction temperature and decreases with increasing nanocomposite pyrolysis temperature. The maximum CO₂ conversion efficiency is found for the Ni-SMP-PEGM-600 (46%) at reaction temperature of ≈500 °C.

1. Introduction

Currently, the world’s primary energy sources are fossil fuels, out of which oil and natural gas provide 50% of primary energy supply.¹,² However, burning of fossil fuels increases carbon dioxide gas emission and is the most important cause of global warming.³⁻⁵ Therefore, there is an urgent need for a solution of the aforementioned problem. The recommended strategies include the conversion of CO₂ to value-added product or new energy fuel, for example, CO₂ hydrogenation to CH₄, methanol, or higher alcohols.⁶ Ni-based catalysts have been receiving considerable attentions for catalytic hydrogenation of CO₂ to methane in the industrial field because of their comparable methanation activity and low material cost.⁷ The catalyst often presents as a minor phase dispersed homogeneously in a support. The support provides easy inlets of the reactant and outlets of the product, and avoids the diffusional limitation. The support also helps in the dispersion of the catalyst, which in turn increases the number of accessible active sites.⁸

Polymer-derived ceramics (PDCs) are of great interest for many emerging applications including gas separation and catalysis (as a support).⁹ This class of ceramics show extremely high thermal stabilities, chemical inertness, and high mechanical hardness.¹⁰⁻¹¹ For further catalytic applications, the desired catalyst can be integrated inside the PDCs. However, postfunctionalization methods lead to a heterogeneous dispersion of the catalyst within the matrix, which in turn lowers the catalytic activity.¹²⁻¹³

PDCs have been synthesized by the thermal treatment of preceramic polymer with variable pore geometry, microstructure, and specific surface area (SSA).¹⁴⁻¹⁵ The conversion of preceramic polymers to ceramics occurs through the decomposition of the organic groups with the release of gaseous species, which nucleates microporosity in the formed products. However, the aforementioned microporosity collapses as the thermolysis temperature increases (higher than ≈450 °C).¹⁶ Several works have been reported in the literature to avoid the collapse of micropores and to increase the SSA during polymer-to-ceramic conversion.

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The studies showed that lower pyrolysis temperature (around 500–600 °C), slower heating rate, and longer dwelling time during pyrolysis lead to microporous PDCs with higher SSA.[17,18] However, the allyl-hydrido polycarbosilane-derived ceramics obtained under the aforementioned condition found to be nonporous. Furthermore, the addition of filler reduces the viscous flow of the material at higher temperature and helps to avoid the collapse of microporosity.[11] The mesoporous PDCs were produced by modification of the preceramic polymer with sacrificial templates.[19] The presence of functional group at silicon-based preceramic polymer can help to adjust its chemistry and network architecture, which in turn effects the properties of the obtained ceramics.[20–22] Self-assembled polycarbosilane block copolymers have been applied to the fabrication of mesoporous SiC materials.[23] Micro-mesoporous SiC(O)-based ceramic with high SSA has been obtained by the thermal treatment of macromolecule-modified polycarbosilane. The studies clearly showed that the decomposition of the macromolecular-modified polycarbosilane leads to the formation of porosity with the evolution of gaseous species, whereas better cross-linking helps to retain it up to high temperature.[24] This work focuses on the production of heterogeneous catalysts with high SSA and homogeneously distributed active sites.

In this study, we report the production of homogeneously distributed nanoporous Ni/SiC(O)-based nanocomposites with high SSA using a PDC route. The goal of the current work is to generate porosity by the decomposition of the acetylacetonate and poly(ethylene glycol) methacrylate (PEGM), and collapse of the porosity is avoided by better cross-linking. Furthermore, a direct generation of catalytically active species during the formation of the PDCs helps to generate homogeneously distributed metal particles with controlled particle size. Thus, Ni/SiC(O)-based nanocomposites were synthesized upon the thermal transformation of an allyl-hydrido polycarbosilane (SMP-10) chemically modified with nickel acetylacetonate in an inert gas atmosphere. The prepared precursor and ceramic were investigated with respect to their chemical and phase composition as well as microstructure. The effect of chemical modification of macromolecular precursor PEGM on SSA and porosity of Ni/SiC(O)-based nanocomposites were also examined. Preliminary investigation of the catalytic activity of Ni/SiC(O) nanocomposite for the hydrogenation of CO2 to methane was performed and is briefly introduced.

Therefore, in the current work, we provide a fundamental approach to produce Ni/SiC(O)-based nanocomposites. It states the transformation of modified preceramic polymer into homogeneously distributed Ni catalyst within SiC(O)-based ceramics while achieving a high SSA.

2. Results and Discussion

Samples prepared and investigated contain different amounts of Ni and PEGM as summarized in Table 1. Figure 1 shows the attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of polycarbosilane, PEGM-modified polycarbosilane, nickel acetylacetonate-modified polycarbosilane, and nickel acetylacetonate and PEGM-modified polycarbosilane. The ATR-FTIR spectrum of the preceramic polymer with an absorption band at 1034 cm⁻¹ that can be attributed to the backbone of the SMP-10 (Si–CH₂–Si stretching). The ATR-FTIR shows the existence of Si–CH₃ by the presence of band at ≈1253 and 833 cm⁻¹ related to Si–CH₃ stretching and rocking, respectively. In the Ni-modified samples, additional bands related to the acetylacetonate precursor have been observed for C–O stretch at ≈1593 cm⁻¹, CH₃ symmetric deformation (1396 cm⁻¹), and at 1261 cm⁻¹ for C–C stretch. Moreover, the presence of PEGM in PEGM-modified Ni-SMP precursors has been confirmed by the presence of bands related to C–O–C stretching (≈1100 cm⁻¹), C=C stretch (1631 cm⁻¹); overlap with the band of SMP-10, C=O stretch (1728 cm⁻¹), and ν(O–H) (1000–1200 cm⁻¹).[25]

The precursors without nickel modification show the presence of Si–H groups with strong bands at ≈2119 and 933 cm⁻¹ related to Si–H stretching and Si–H bending, respectively. Furthermore, the presence of allyl bands were confirmed by the absorption bands at 1631 cm⁻¹ (C=C stretch in –CH=CH₂ and 3076 cm⁻¹ (C–H stretch in –CH₂=CH₂). However, the ATR-FTIR spectrum of the Ni acetylacetonate-based precursors shows a relative decrease in the intensity of the Si–H band and disappearance of allyl group (unlike in SMP-pre) indicating that the hydrolysisation occurred at the reaction condition (Figure 2a).

Table 1. SMP-10:Ni(acac)₂:PEGM weight ratio used for the preparation of the modified polycarbosilane precursor.

| Sample assigned | SMP-10 [wt%] | Ni(acac)₂ [wt%] | PEGM [wt%] |
|-----------------|-------------|----------------|------------|
| SMP             | 100         | –              | –          |
| SMP-PEGM        | 75          | –              | 25         |
| 35 Ni-SMP       | 65          | 35             | –          |
| 45 Ni-SMP       | 55          | 45             | –          |
| 45 Ni-SMP-PEGM  | 30          | 45             | 25         |

Figure 1. ATR-FTIR spectra of precursors (SMP-pre, polycarbosilane; SMP-PEGM, PEGM-modified polycarbosilane; Ni-SMP, nickel acetylacetonate-modified polycarbosilane; Ni-SMP-PEGM, nickel acetylacetonate and PEGM-modified polycarbosilane).
Furthermore, the sample shows a relative decrease in the intensity of the band related to Si–H, as the amount of the allyl substituents is markedly lower than that of Si–H bonds, which indicates that dehydrocoupling reactions (Figure 2b) also occurred under these conditions. Therefore, the nickel acetylacetonate helps to increase the cross-linking of the polycarbosilane. In literature, nickel acetylacetonate has been proven as a good catalyst for hydrosilylation and dehydrogenation reactions.[26–28]

In addition, the hydrosilylation and dehydrocoupling reactions have also been observed in case of PEGM-modified Ni-SMP precursors. However, the complete disappearance of the allyl band shows that inter- and intramolecular hydrosilylation occurs in case of PEGM-modified Ni-SMP precursors. The results confirm that the PEGM is chemically bonded to SMP-10 in the produced Ni-SMP-PEGM precursors (Figure 2c).

The polymer-to-ceramic conversion of polycarbosilane occurs by the decomposition of the preceramic polymer and conversion into an inorganic materials.[29] However, better cross-linking degree and the modification of polycarbosilane with Ni(acac)₂ and PEGM might affect the final ceramic yield of produced ceramic nanocomposites. The thermogravimetric analysis (TGA) results of Ni(acac)₂ show a decomposition of the gaseous components with residual mass around 27% in an argon environment (Figure 3). Furthermore, the thermal decomposition of PEGM takes place in the temperature range from 350 to 420 °C with a residual mass of 2%. The ceramic yield of SMP (70.4%) is calculated by the subtraction of the weight loss (100% – mass loss %) and is found to be increased after the chemical modification (PEGM—72.6%; 35 Ni-SMP—74.4%, Table 2).

Nickel acetylacetonate modification helps to increase the cross-linking degree as confirmed by ATR-FTIR results, which in turn increases the ceramic yield. With increasing amount of the nickel acetylacetonate from 35 to 45 wt%, the ceramic yield decreases what is obvious due to the decomposition of a higher content of acetylacetonate. In the same way, the presence of nickel acetylacetonate in PEGM-modified Ni-SMP sample increases the cross-linking of the precursors and increases the ceramic yield of final ceramic.

Furthermore, the ceramics obtained after the pyrolysis of the precursors at 600 °C under argon environment was analyzed to investigate its elemental composition (Table 3). The result shows that the ceramics contain 30–31 wt% of carbon and 19–21 wt% of oxygen (Table 3). The presence of minor amounts of the oxygen in pure SMP-10 has been reported in the literature (3–6.7 wt%).

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**Figure 2.** a) Hydrosilylation, b) dehydrocoupling, and c) reaction of SMP-10 with PEGM occurring during the synthesis process.

**Figure 3.** TG curves of the polymer-to-ceramic transformation for SiC(O) and Ni/SiC(O) precursors.

**Table 2.** Ceramic yield of the obtained ceramic nanocomposites (calculated by the subtraction of the weight loss (100% – mass loss %).

| Sample          | Obtained ceramic yield [%] |
|-----------------|----------------------------|
| 35 Ni-SMP       | 74.4                       |
| 45 Ni-SMP       | 65.0                       |
| 45 Ni-SMP-PEGM  | 65.1                       |

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which might be incorporated during the preceramic polymer synthesis and handling.\textsuperscript{[29]} The higher amount of oxygen can be explained as a consequence of the chemical modification of SMP-10 with oxygen-containing Ni(acac)$_2$ and PEGM. Furthermore, annealing of carbon-rich PEGM precursors at high temperatures might lead to a formation of higher content of segregated carbon in the matrix. The carbon content was estimated by assuming that the oxygen is present in the samples as silica; the remaining silicon is present as SiC (with Si/C ratio of 1:1) and the remaining carbon is present as segregated phase.\textsuperscript{[21]} As expected, the segregated carbon content in the sample increases from $\approx$17 wt% (as for the 45 Ni-SMP sample prepared at 600 °C) to higher than 26 wt% in the 45 Ni-SMP-PEGM sample annealed at 600 °C. Interestingly, by comparing the chemical composition of 45 Ni-SMP with that of 45 Ni-SMP-PEGM, it is clear that the PEGM-modified precursors lead to a higher content of the nickel in the final ceramic. This is due to the amount of the starting precursors used during the synthesis process, in case of PEGM-modified Ni-SMP less content of Si-based polycarbosilane has been used, which is replaced by the C-based PEGM (Table 1).

The X-ray powder diffraction (XRD) patterns of the samples annealed at different temperatures under argon are shown in Figure 4. First, the precursor heated at low temperature was examined to get the information of the nickel particle. It has been found that the samples remain amorphous at 250 °C (Figure S2, Supporting Information). The Ni/SiC(O)-based nanocomposites obtained upon pyrolysis of produced precursor at 600 °C exhibit the presence of metallic Ni dispersed in an amorphous SiC(O) matrix. The presence of metallic nickel phase is more pronounced as the amount of the nickel precursor increases from 35 to 45 wt% and with increasing pyrolysis temperature at 800 °C. Considering the fact that nickel is bounded only to oxygen atoms, we assume that during pyrolysis a phase separation process occurs involving the separation of amorphous nickel oxides, forming an amorphous NiO$_x$/SiC(O) nanocomposites.\textsuperscript{[30]} A further reduction of NiO$_x$ leads to the formation of metallic nickel within the amorphous SiC(O) ceramic matrix. In case of precursors with PEGM modification annealed at higher temperatures, a more pronounced crystallization of metallic nickel is observed. This is due to the production of reducing environment (hydrogen, hydrocarbon, and carbon) due to the decomposition of PEGM structure, which in turn promotes the reduction of NiO$_x$ more efficiently compared with Ni-SMP-based samples.

In the studies, high SSA PDCs with micro-mesoporosity have been synthesized by the thermolysis of precursor polymers (Table 4). The conversion of preceramic polymer to ceramics occurs through the decomposition of the organic groups with the release of gaseous species, which nucleates porosity in the as-formed products.\textsuperscript{[10]} The polymer-to-ceramic conversion of unmodified polycarbosilane occurs by the decomposition step with release of H$_2$, SiH$_4$, and CH$_3$SiH$_3$. These gaseous species generate micropores in the samples but they collapse at high temperature (>450 °C).\textsuperscript{[29]} So, the SSA of polycarbosilane pyrolyzed at 600 °C was found to be $<5$ m$^2$ g$^{-1}$.

However, high SSA SiC(O)-based ceramic nanocomposites can be obtained by the modification of polycarbosilane. The SSA strongly depends on the chemical modification and pyrolysis temperature. The SSA of SMP-10 tends to increase from 5 to 100–200 m$^2$ g$^{-1}$ upon the addition of nickel acetylacetonate, which further increases to 300–350 m$^2$ g$^{-1}$ on PEGM modification of Ni-SMP. The decomposition of organic groups (acetylacetonate and ethylene glycol methacrylate) helps to nucleate porosity in the final ceramic nanocomposites. Furthermore, nickel acetylacetonate helps to increase the cross-linking degree of preceramic precursor and it helps to avoid the collapse of formed porosity up to higher temperature.\textsuperscript{[24]}

Therefore, the results obtained clearly show that high SSA Ni/SiC(O)-based nanocomposites can be prepared by chemical modification of polycarbosilane. The decomposition of the modified precursor increases the surface area of formed ceramic nanocomposites with the evolution of gaseous species, whereas a better cross-linking helps to retain it until high temperature. However, SSA decreases with increasing temperature (from 600 °C: 100–350 m$^2$ g$^{-1}$ to 800 °C: 50–152 m$^2$ g$^{-1}$) due to the

| Sample | Elemental analysis [wt%] | Empirical formula |
|--------|-------------------------|------------------|
| Si     | C                       | O                | Ni | H     |
| 45 Ni-SMP-600 | 36.9 | 30.9 | 19.6 | 10.8 | 1.8 | SiC$_{3.6}$O$_{2.8}$Ni$_{0.14}$H$_{1.16}$ |
| 45 Ni-SMP-PEGM-600 | 28.3 | 30.7 | 20.9 | 15.9 | 4.2 | SiC$_{2.18}$O$_{1.28}$Ni$_{0.27}$H$_{4.13}$ |

| Sample | Pyrolysis temperature [°C] | Specific surface area [m$^2$ g$^{-1}$] |
|--------|---------------------------|--------------------------------------|
| SMP    | 600                       | $<5$                                 |
| SMP-PEGM | 600          | 362                                 |
| 35 Ni-SMP | 600          | 114                                 |
| 45 Ni-SMP | 600         | 200                                 |
| 45 Ni-SMP-PEGM | 600 | 332                                 |
| 45 Ni-SMP     | 800     | 52                                  |
| 45 Ni-SMP-PEGM | 800     | 152                                 |

Table 3. Elemental analysis data and empirical formula of Ni/SiC(O) samples obtained from annealing at 600 °C.

Table 4. SSA of the SiC(O) and Ni/SiC(O) samples with respect to pyrolysis temperature.
collapse of microporous structure, which is further confirmed by N\textsubscript{2} adsorption–desorption isotherms.

Figure 5 shows the N\textsubscript{2} adsorption–desorption isotherms of produced samples pyrolyzed at different temperatures. The SMP-10-based samples without modification and pyrolyzed at 600 °C is a nonporous materials, whereas SMP-10 modified with PEGM leads to a micro-mesoporous materials.[24] Furthermore, the Ni-SMP samples pyrolyzed at 600 °C have a typical type I isotherm for microporous materials. However, the isotherm of sample 45 Ni-SMP-PEGM shows a typical type IV isotherm and display a distinct hysteresis loop in the range of 0.4–1.0 \(P/P_0\) characteristics of mesoporous materials. In addition, the sharp uptake at a relative pressure \((P/P_0) < 0.1\) indicates the presence of microporous structures. Therefore, Ni/SiC(O) ceramics obtained by pyrolysis of 45 Ni-SMP at 600 °C contain micropores, whereas 45 Ni-SMP-PEGM contains micropores as well as mesopores. The reason behind the generation of microporosity is the production of small fragments (H\textsubscript{2}, SiH\textsubscript{4}, CH\textsubscript{3}SiH\textsubscript{3}, CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, and CH\textsubscript{4}), whereas the evolution of monomeric unit of PEGM is the reason behind mesoporosity in the final ceramic.[21,24] On further high-temperature treatment up to 800 °C, microporous structures collapse; however, mesoporosity is still observed.

The Ni/SiC(O) samples prepared from Ni-SMP and Ni-SMP-PEGM by thermal treatment in argon at 600 and 800 °C were also investigated by transmission electron microscopy (TEM). In Figure 6a,b, the microstructure of Ni/SiC(O) obtained at 600 °C is shown, indicating the crystallization of nickel nanoparticles (as shown in XRD) in an amorphous SiC(O) matrix. The sample obtained from Ni-SMP exhibits an average Ni particle

![Figure 5](image_url)  
**Figure 5.** The nitrogen adsorption/desorption isotherms of the SiC(O) and Ni/SiC(O) samples with respect to pyrolysis temperature.

![Figure 6](image_url)  
**Figure 6.** TEM images of 45 Ni-SMP and 45 Ni-SMP-PEGM samples as prepared at a,b) 600 °C and c,d) 800 °C in argon atmosphere.
size of ≈10–15 nm, whereas, in case of Ni-SMP-PEGM-obtained ceramic, the Ni particle size is around 5–10 nm. Furthermore, high-temperature treatment facilitates the increase in the particle size (≈30–35 nm Ni-SMP and ≈25–30 nm Ni-SMP-PEGM; Figure 6c,d).

CO2 methanation measurements were performed to analyze the applicability of the Ni-containing ceramic nanocomposites for catalytic application. The sample was heated in hydrogen environment to remove the surface oxygen prior to the catalytic test. The measurement investigates the influence of the reduction time prior to the measurement, SSA, and particle size on the catalytic activity. The result shows that reduction prior to the measurement increases the catalytic activity of the nanocomposites (Figure S3, Supporting Information). The CO2 conversion and CH4 selectivity are shown as a function of reaction temperature (200–500 °C) in Figure 7. It is clearly observed that CO2 conversion and CH4 selectivity increase with increasing temperature for all samples, reaching its maximum at a reaction temperature of 500 °C. The highest conversion (>46%) and selectivity (>58%) are observed for the 45 Ni-SMP-PEGM pyrolyzed at 600 °C, whereas the values obtained for 45 Ni-SMP sample were 40% and 43%, respectively. High SSA and crystallinity of nickel[31] in PEGM-modified Ni-SMP samples contribute to higher conversion and selectivity. However, a further increase in the pyrolysis of 45 Ni-SMP-PEGM and 45 Ni-SMP to 800 °C reduces the conversion and selectivity. The main factors that contribute to the reduction of CO2 conversion and CH4 selectivity with increasing pyrolysis temperature are the SSA of the ceramic nanocomposites and particle size of catalytic metal. During thermal treatment, the SSA of the nanocomposites decreases (600 °C: from 200 m² g⁻¹ Ni-SMP, 330 m² g⁻¹ Ni-SMP-PEGM to 52 m² g⁻¹ Ni-SMP, 152 m² g⁻¹ Ni-SMP-PEGM), whereas the particle size of Ni increases (from 10–15 nm Ni-SMP, 5–10 nm Ni-SMP-PEGM to 30–35 nm Ni-SMP, 25–30 nm Ni-SMP-PEGM, respectively). High SSA helps in proper dispersion of the catalyst and smaller particles offer a large number of surface atoms, and by that, more catalytic sites, which in turn increases the conversion and selectivity.[32]

Nickel-based catalysts with various supports were used for CO2 methanation and their activities vary with respect to the support materials used. The Ni/ZSM-5 catalyst exhibited the best CO2 conversion of about 76%,[7] which is obviously higher than that of Ni/SiC(O) nanocomposite prepared in this work (46%). The relatively low efficiency of Ni/SiC(O) compared with Ni/ZSM-5 might relate to the relatively low Ni content (and consequently low fraction of accessible nickel nanoparticles). However, the CO2 conversion efficiency of the Ni/SiC(O) nanocomposite seems to be lower but it eliminate the drawbacks of conventionally used alumina, silica, or carbon catalyst supports. These classes of supports face some disadvantages, such as poor heat conductivity, high chemical reactivity of alumina and silica, and weak oxidation resistance of carbon at high temperatures. Therefore, the efficiency of ≈46% concerning the conversion of CO2 represents a rather good value. However, there is still the possibility for further improvement and detailed studies on this type of nanocomposites; e.g., increasing content of nickel or use of bimetallic system might be the solutions.

3. Conclusions

Within the current work, Ni/SiC(O)-based nanocomposites with high SSA were successfully produced. Nickel-modified polycarboalumina precursors were successfully synthesized by chemical modification of commercially available allyl-hydrido polycarbosilane with nickel acetylacetonate. The produced precursors at high temperatures deliver nanocomposites consisting of crystalline nickel nanoparticles homogeneously dispersed within amorphous SiC(O) matrix. Different samples have been prepared to evaluate the influence of the precursor composition as well as the pyrolysis temperature (600 and 800 °C) on the ceramic nanocomposite properties and catalytic activity of the final nanocomposites. Furthermore, the modification of the Ni-SMP precursors with macromolecular precursor PEGM helps to tailor the SSA and
porosity of the final ceramic. The PEGM modification helps to produce homogeneously distributed Ni nanoparticles with an average size of 5–10 nm with high SSA of the final Ni/SiC(O)-based nanocomposites (300–350 m² g⁻¹). The pyrolysis temperature affects the crystallinity, SSA, and particle size of final ceramic nanocomposites. The crystallinity of the nickel particle increases with increasing the pyrolysis temperature from 600 to 800 °C, but, in turn, it decreases the SSA with increase in particle size. The SSA and particle size play a crucial role in the catalytic properties of the final ceramic nanocomposites. Preliminary results of the catalytic activity of the Ni/SiC(O)-based nanocomposites show that they are active for the methanation of CO₂. The maximum carbon conversion of 74% (CH₄ yield 34%) was found at reaction temperature of 600 °C and further annealed at 600 °C argon atmosphere (2 h dwell using 50 °C h⁻¹ heating/cooling rate).

4. Experimental Section

Materials Synthesis: Commercially available chemicals of analytical grade were used in the current study without further purification. Allyl-hydrido polycarbosilane (SMP-10, Starfire Systems, USA) was used as suitable preceramic polymer. Nickel acetylacetonate (Sigma-Aldrich) was used as a nickel precursor and PEGM (Sigma-Aldrich) was used as a macromolecule precursor for further chemical modification (Figure S1, Supporting Information). Nickel-modified polycarbosilane (Ni-SMP) has been synthesized by adding SMP-10 to a solution of nickel acetylacetonate (Ni(acac)₃) in toluene. For the synthesis of Ni-SMP-PEGM, the aforementioned step was followed by the addition of PEGM in the presence of platinum catalyst (platinum(0)-1,3-divinyl-1,2,3,3-tetramethyldisiloxane complex solution, Sigma Aldrich). Furthermore, the obtained solution was stirred for 24 h at room temperature. The solution was then heat-treated at 120 °C for 4 h, and the solvent has been subsequently removed under vacuum. The obtained samples were cross-linked at 250 °C and further annealed at 600 and 800 °C in argon atmosphere (2 h dwell using 50 °C h⁻¹ heating/cooling rate).

Materials Characterization: To investigate the chemical structure of the obtained precursors, ATR-FTIR spectroscopy was performed (Device Alpha II, Bruker, Ettlingen, Germany); crystalline phases of the produced ceramic materials were investigated by the powder X-ray diffractometer (Seifert C 3000 Diffractometer MZ IV ISO, Germany) with Cu Kα radiation. TGA was used to investigate the transformation of polymer to ceramic. The TGA (STA503, Bähr-Thermoanalyse GmbH, Hüllhorst, Germany) was performed under flowing argon (2 L h⁻¹) within a temperature range of 20–1000 °C with a heating rate of 10 °C min⁻¹. Quantitative elemental analysis was performed by Microanalytical Laboratory Pascher (Remagen, Germany) as a double determination. The SSA (S BET) values were determined by the Brunauer, Emmett, and Teller (BET) method from the linear parts of the adsorption isotherms (BELSORP-Mini, Bel Japan, Inc., Toyonaka, Osaka, Japan). To minimize nitrogen diffusion effects during the measurements, the samples were grinded and sieved with a 300 μm mesh, and were degassed at 120 °C for 3 h before the analysis. The morphology and microstructure of ceramics nanocomposites were investigated by transmission electron microscope (FEI Titan 80, at 300 kV).

A tubular fixed-bed reactor was used to conduct catalytic tests at atmospheric pressure to compare the activity and selectivity of each sample. First, a homogeneous mixture of 50 mg of the catalyst powder and 300 mg of Al₂O₃ was made and transferred in a quartz-glass tube reactor (inner diameter of 6 mm). The total flow rate was adjusted to 50 mL min⁻¹ composed of H₂/CO₂/Ar = 1/1/5, resulting in a weight hourly space velocity (WHSV) of 60 L g⁻¹ cat⁻¹ h⁻¹. The catalytic activity was measured between 100 and 500 °C in intervals of 50 °C. The outflowing gas was continuously monitored with an online compact gas chromatograph equipped with a thermal conductivity detector. Furthermore, the CO₂ conversion as well as CH₄ yield and selectivity were determined according to the following equations:

\[ X_{CO_2} = \frac{1 - \frac{C_{CO_2_{out}}}{C_{CO_2_{in}}}}{C_{CH_4_{out}} + C_{CO_2_{out}} + C_{CO_{2{\text{in}}}}} \]  \hspace{1cm} (1)

\[ Y_{CH_4} = \frac{C_{CH_4_{out}}}{C_{CO_2_{out}} + C_{CH_4_{out}} + C_{CO_{2{\text{in}}}}} \]  \hspace{1cm} (2)

\[ S_{CH_4} = \frac{Y_{CH_4}}{X_{CO_2}} \]  \hspace{1cm} (3)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

allyl-hydrido polycarbosilane, nanocomposites, poly(ethylene glycol) methacrylate, preceramic polymers, specific surface areas.

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