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Kaur, S, Fischer, S, Falta, J, Rezwan, K, Wilhelm, M

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High surface area SiC(O)-based ceramic by pyrolysis of poly (ethylene glycol) methacrylate-modified polycarbosilane

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Funding information
Deutsche Forschungsgemeinschaft

Abstract

In the present work, a high surface area SiC(O)-based ceramic powder was synthesized upon thermal transformation of a polymer-derived macromolecular precursor, which was obtained by the chemical modification of a allylhyldrido polycarbosilane with poly(ethylene glycol) methaacrylate under argon environment. The pyrolysis of developed precursor led to the formation of amorphous and high surface area SiC(O)-based ceramic powder with in situ generated micro/meso-porosity. The specific surface area of the obtained powders depends on the processing temperature. It decreases from 363 to 122 m^2/g as the pyrolysis temperature increases from 600 to 1200°C, respectively. Furthermore the promising samples were fabricated using pressing technique, which led to crack-free SiC(O) monoliths on subsqunt heat treatment. The present study also emphasizes the potential of produced SiC(O) ceramic powder to support NiO catalyst. The impregnation method were used to produce high surface area NiO@SiC(O) ceramic powder (NiO as a catalyst; SiC(O) as a catalyst support) for further catalytic applications. Interestingly, the distribution of the NiO was shown to strongly depend on the oxygen content present in the SiC(O) matrix. Thus, larger oxygen contents induce homogeneously distributed flower-like NiO catalyst onto SiC(O).

KEYWORDS
allylhydrido polycarbosilane, poly(ethylene glycol) methaacrylate, polymer-derived ceramics (PDCs), porosity, SiC

1 | INTRODUCTION

The challenge of "Going Green" has sought the attention of researchers during the last decades. Catalysis is a key technology to achieve the objectives, as it helps to improve the environmental issues and to save the energy consumption in many of the chemical processes.[1] However, with increasing demand of environmental protection and economic benefit, the development of modern and highly efficient catalysts are necessary. The target can be achieved either by the development of new catalyst or improvement in the currently used catalyst.[2]

Most of the catalysts are supported on porous materials, which help in improving the properties of a catalyst. In addition it also address the goals of saving the energy consumption by providing the ease of separation of product and catalyst, thereby eliminating the need for separation through distillation or extraction.[3] Alumina, silica, or carbon are the most common commercially used 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. Nowadays, great efforts have made in order to improve the efficiency of catalyst

supports, and silicon carbide (SiC) might be a solution of the above-mentioned drawbacks. SiC is well known for its superior hardness, high thermal conductivity, high resistance toward oxidation, high thermal stability, high resistance to aggressive media (acidic or basic), high chemical inertness, and its low density.[4] SiC has already proved to be a very effective candidate in many chemical processes, for example, gas phase selective oxidation, liquid phase benzoylation (Fridel craft reaction), and Fischer Tropsch synthesis.[5–9] Still commercialization of silicon carbide is restricted due to limited specific surface area and difficulties to process it into desired shapes. With the conventional Acheson synthesis, it is only possible to yield material with a surface area of 0.1 to 1 m^2/g. Solid-state reactions, gas phase reactions, and gas-solid reactions have developed during the last two decades to prepare silicon carbide with a higher surface area (>20 m^2/g) for subsequent use as a catalyst support. But all synthesis methods exhibit significant drawbacks for example relatively expensive starting raw materials, the inability to prepare SiC with controlled size and shape for subsequent use and the fabrication of the ceramic in desired shapes.[4,10]

Other issues which are necessary to be addressed at this point are (a) the deposition of metal nanoparticles directly onto SiC, as metal particles are prone to aggregate or sinter because the SiC surface has low reactivity, making the metal-SiC interaction quite weak and (b) the formation of metal silicides during the catalytic reaction. This results in low activities of the catalyst during the reaction and the performance of the supports was significantly deterioted. However, modification of the SiC surface with a thin layer of SiO_xC_y/SiO_2 could enhance the interaction between the applied metals and SiC, and also suppress the formation of the silicides, thereby improving the catalyst stability.[10,11]

Micro-mesoporous polymer-derived ceramics with variable pore geometry and specific surface area have been synthesized by the thermolysis of preceramic polymers. The polymer-to-ceramic transformation occurs through the cross-linking and decomposition of the organic groups, accompanied by the release of gaseous species, which nucleates porosity in the as-formed products. Allyl-hydrido polycarbosilane (SMP-10) is a preceramic polymeric precursor, which leads to the near stoichiometric SiC. However, the SMP-10-derived material under similar conditions was found to be non-porous, by gas adsorption techniques.[12] In situ evolved gas analysis study of polycarbosilane indicates that the decomposition step involves mainly the release of hydrogen and small polymer fragments. These generate micropores in the samples but they collapse at high temperature.[13] However, the allyl and hydrido substituents at silicon in the SMP-10 can help to adjust its chemistry and network architecture.[14] Therefore, the challenge is to develop macromolecular-based SMP-10 precursors, which upon heat treatment decompose and help to develop micro and meso-porous SiC(O) and do not collapse at high temperature for the aforementioned application.

Hence, the present study focuses on the (a) synthesis of macromolecular precursor by chemical modification of the allyl-hydrido polycarbosilane with poly(ethylene glycol) methacrylate (PEGM) via hydrosilylation reactions (PEGM also contain oxygen in the network help to enrich the surface of SiC with oxygen); (b) shaping using pressing technique; (c) ceramization process (pyrolysis) of the powder and shaped material at temperatures ranging from 600°C to 1200°C and (d) synthesis of NiO@SiC(O) ceramic powder by impregnation method.

2 | MATERIAL AND METHODS

2.1 | Synthesis of macromolecular precursor using allyl-hydrido polycarbosilane and poly(ethylene glycol) methacrylate

A commercially available allyl-hydrido polycarbosilane (SMP-10, Starfire Systems, USA) was used as suitable preceramic polymer for the preparation of near-stoichiometric silicon carbide. Poly (ethylene glycol) methacrylate (PEGM; Sigma-Aldrich) was used as a precursor for chemical modification of the polycarbosilane. In a typical experiment, macromolecule-based polycarbosilane has been synthesized by adding PEGM to a solution of SMP-10 in toluene, followed by stirring for 24 hours in the presence of platinum catalyst (platinum(0)-1,3-divi-nyl-1,2,3,3,-tetramethyldisiloxan complex solution, Sigma Aldrich). The sample without PEGM has also been synthesized using the above-mentioned steps. The sample was refluxed for 4 hours and then the solvent has subsequently removed under vacuum. The obtained samples were cross-linked upon annealing at 250°C in argon for 3 hours and ceramized in argon at 600, 1000, and 1200°C (2 hours dwell) (Table 1).

2.2 | Processing of obtained macromolecular precursor using pressing technique

The powder obtained from the heat treatment of macromo-lecular precursor (300°C and 600°C, 3 hours) was uniaxi-ally pressed in a steel dye (diameter 10 mm) under different

TABLE 1 SMP-10:PEGM weight ratio used for the preparation of the macromolecular precursor

Sample assigned	SMP-10	PEGM	Catalyst[a]
SMP	2 g	0.0	0.0
CSMP	2 g	0.0	10 μL
CSMP-25-PEGM	1.50 g	0.50 g	10 μL
CSMP-50-PEGM	1.00 g	1.00 g	10 μL

[a]Catalyst for hydrosilylation reaction.

pressures applied (Table 2). The optimized green-body fabrication process involved addition of two drops polyvinylalcohol as a binder (10 vol% solution of PVA) to 226.3 mg of precursor powder, followed by compaction pressure of 128 MPa applied at room temperature.

The obtained optimized green bodies were converted into ceramic upon heat treated at 600°C under argon environment and were further pyrolyzed at 1000°C, and 1200°C for 2 hours in argon atmosphere to study the high-temperature behaviors.

2.3 | Synthesis of NiO@SiC(O) ceramic powder by impregnation method

Nickel-based catalysts supported on prepared SiC(O) ceramic were synthesized by the impregnation method. For the present study the ceramic obtained after pyrolysis of CSMP and CSMP-25-PEGM precursors at 600°C were impregnated with solution of commercial $Ni(NO_3)_2 \cdot 6H_2O$ (≥98.5%, Sigma Aldrich) nickel source. Nickel-based catalysts were obtained with 10 wt % Ni loading by the impregnation method. For the impregnation, nickel nitrate was dissolved in deionized water at room temperature. Then the aqueous solution was added into the SiC(O) support material. After 24 hours, the samples were dried in an oven for further 24 hours at 70°C before calcination in air by a temperature program (5°C/min) from room temperature to 500°C and then maintained at 500°C for 5 hours.

2.4 | Materials characterization

Attenuated-total-reflectance FTIR spectroscopy measurements were performed on an ATR-FTIR; powder X-ray diffraction studies were done on a Seifert device (Seifert C 3000 Diffraktometer MZ IV ISO, Germany). The polymer-to-ceramic transformation of PEGM-containing SSPs was investigated by thermogravimetric analysis. Thermogravimetric analysis (TGA; STA503, Bähr-Thermo-analyse GmbH, Hüllhorst, Germany) was performed at a temperature range of 20°C-1000°C under flowing argon (2 L/h) with a heating rate of 10°C/min. Quantitative measurement of elements was performed by elemental analysis (Microanalytical laboratory Pascher Remagen, Germany) as a double determination.

The specific surface area (SBET) 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). The materials were ground and sieved with a 300 µm mesh in order to minimize nitrogen diffusion effects during the measurements, and were degassed at 120°C for 3 hours before the analysis. The chemical state of the amorphous PEGM-modified SMP-10 heat treated at 600°C and 1200°C was analyzed by X-ray photoelectron spectroscopy (XPS) using an Omicron EA 125 XPS system. Water vapor and n-heptane adsorption measurements carried out by placing vessels with ~0.5 g of sample powder (particle sizes ≤300 µm) into closed Erlenmeyer flasks filled with the solvents at equilibrium with their vapor phase at room temperature. Samples were weighed at the start and end of a 24-hour measurement period in order to determine the vapor uptake of the material. The uptake was then recalculated into g/m^2 using the specific surface area of the materials (measured by nitrogen adsorption). Scanning electron microscopy (SEM) studies were performed on a Supra 40-Carl Zeiss, Germany with an acceleration voltage of 10–15 kV.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of obtained macromolecular precursors and ceramics

The presence of allyl- and hydrido-substituents at the silicon atom in the allyl-hydrido polycarbosilane (SMP-10) help to adjust its chemistry and network architecture. The incorporation of poly(ethylene glycol) methacrylate (contain allyl group) within the network of SMP-10 was achieved upon hydrosilylation reactions of the silane groups of SMP-10 (Figure 1).

The prepared polymeric samples were investigated by means of ATR-FTIR spectroscopy. The ATR-FTIR spectrum of the macromolecular precursor shows an absorption band related to SMP-10 at 1034 cm^{-1} which was attributed to the backbone of the SMP-10 (Si-CH_2-Si stretching); furthermore, two bands

TABLE 2 Fabrication of monoliths from the heat treated macromolecular precursor (300 and 600°C, 3 h) using two drops polyvinylalcohol (PVA) as a binder)

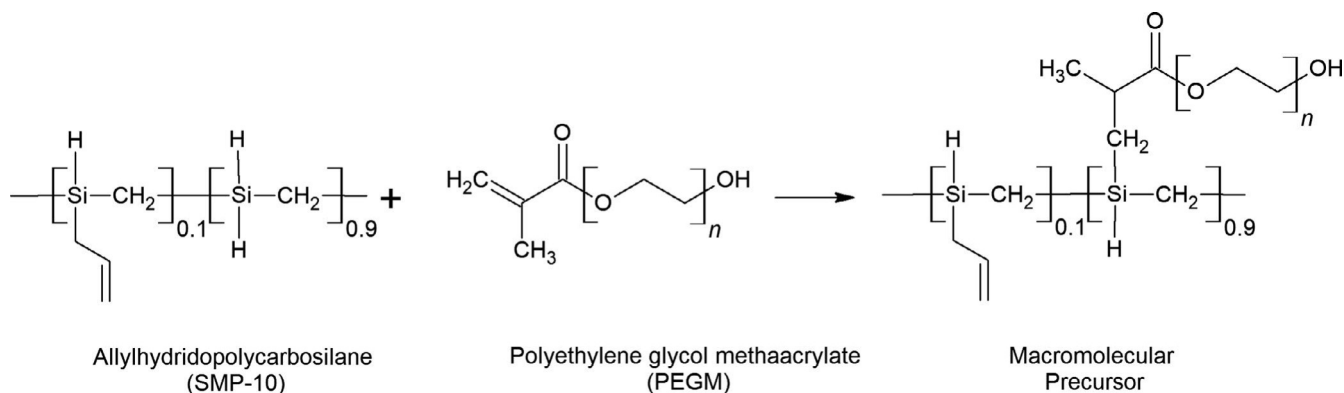| No.	Temperature [°C]	PVA (10 vol%)	Pressure [MPa]	Holding Time [min.]	Remark	Pyrolysis (600°C)
1	300	—	128	2	No compaction	—
2	300	2 drops	128	2	compaction	Crack
3	600	—	128	2	No compaction	—
4	600	2 drops	128	2	compaction	Crack free

FIGURE 1 Possible hydrosilylation reaction of SMP-10 with PEGM

at 1360 and 2900 cm^{-1} were assigned to C-H bending and stretching, respectively, in Si-CH$_2$. The band at ca. 1253 cm^{-1} shows the existence of Si-CH$_3$ stretching. The strong bands at ca. 2119 cm^{-1} (Si-H stretching) and 933 cm^{-1} (Si-H bending) were assigned to Si-H groups, whereas the bands at 1631 (C = C stretch in -CH = CH$_2$) and 3,076 cm^{-1} (C-H stretch in -CH = CH$_2$) were assigned to the allyl-groups. The absorption at 747 and 833 cm^{-1} was attributed to Si-C stretching and Si-CH$_3$ rocking. Moreover, ν(COC) at ~1100 cm^{-1} and ν(O-H) (1000–1200 cm^{-1}) whereas the bands at 1631 cm^{-1} (C = C stretch; overlap with the band of SMP-10) and 1728 cm^{-1} C = O stretch were observed and assigned to the poly(ethylene glycol) methacrylate in the precursors.[15]

The ATR-FTIR spectrum shows a relative decrease in the intensity of the vibrational band corresponding to Si-H band and allyl-group (unlike in SMP-10; as with respect to Si-CH$_3$, ~1,253 cm^{-1}). The rate of the peak intensities between 1631 cm^{-1}(C = C stretch) and 1253 cm^{-1} (Si-CH$_3$ group) was 51/49 and 52/48 for SMP and CSMP respectively sample as shown in Figure 2. This result shows that hydrosilylation reaction between the allyl and silane group of SMP-10 is not started at the reaction condition. When the PEGM is added to the sample, hydrosilylation reaction occurs and most probable it happens in between of allyl group of PEGM and silane group of SMP-10 because the rate of the peak intensities between 1631 cm^{-1} and 1253 cm^{-1} was found to be 42/58. This proved that the macromolecular precursor contain SMP-10 chemically bonded with PEGM. As the allyl and silane group is still observable in the precursor, this indicates that the completion of hydrosilylation reaction need temperatures as high as 250°C. Accordingly, after the complete hydrosilylation process, subsequent cross-linking is expected to rely on dehydrocoupling reactions (Si-H + H-Si = Si-Si + H$_2$). Hence, the obtained precursor after heat-treated at 250°C are highly cross-linked (Figure S2) which in further helps to increase the ceramic yield of the ceramic and prevents the collapse of formed porosity (helps to maintain specific surface area even at high temperature).

The polymer-to-ceramic conversion of precursors was studied by means of TGA. Figure 3 shows the preceramic
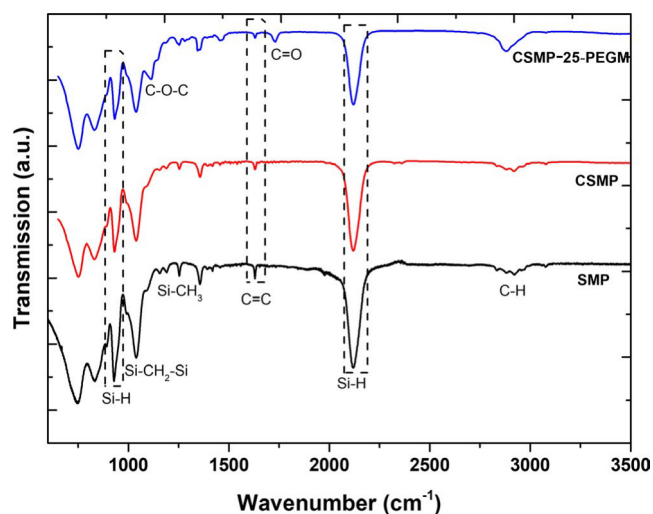

FIGURE 2 ATR-FTIR spectra of precursor of SMP-10 (SMP), SMP-10 with catalyst (CSMP) as well as PEGM-modified SMP-10 in presence of catalyst (CSMP-25-PEGM) [Color figure can be viewed at wileyonlinelibrary.com]

precursors weight loss as a function of temperature with and without catalyst. It indicates that the ceramic yield was increased by addition of catalyst in SMP-10. The ceramic yield of the SMP-10 without catalyst was found to be 71% when heated in argon to 900°C. Whereas the yield of SMP-10 mixed with Pt catalyst was 75%. The TGA curves also demonstrated that the initial weight-loss temperature of the samples shifted to a higher value with a slow rate in the presence of catalyst. These results suggest that the presence of the catalyst control the degree of cross-linking of SMP-10 and increases the ceramic yield.

Furthermore, the yield of SMP-10 mixed with Pt catalyst was 75% and yields of PEGM-modified SMP-10 in the presence of catalyst were 73% and 52%, for samples contained 25 and 50 wt% PEGM, respectively. As the amount of the PEGM increases, the ceramic yield decreases. Hence, for further studies only CSMP-25-PEGM was considered. The FTIR results of the CSMP-25-PEGM precursor cross-linked at 250°C shows that the precursor undergoes hydrosilylation
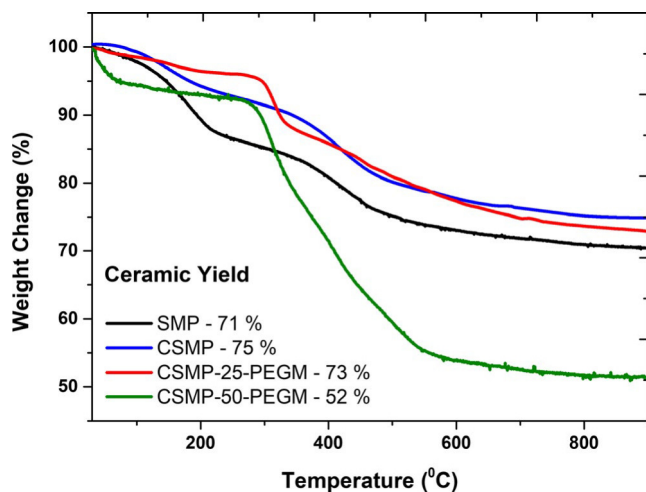
FIGURE 3 TGA curve of the precursor of SMP-10 (SMP), SMP-10 with catalyst (CSMP) and PEGM-modified SMP-10 with catalyst (CSMP-25-PEGM and CSMP-50-PEGM) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Specific surface area of the precursors pyrolyzed at different temperatures

Sample assigned	Pyrolysis temperature (°C)	Specific surface area (m^{2}g^{-1})
CSMP-600	600	<5
CSMP-25-PEGM-600	600	363
CSMP-25-PEGM-1000	1000	129
CSMP-25-PEGM-1200	1200	122

reaction and dehydrocoupling reaction. Therefore, the main reason of the weight loss of the macromolecular precursor until around 250°C is the dehydrocoupling reaction with evolution of hydrogen, as hydrosilylation is a zero weight loss reaction. The FTIR studies also assure the presence of the PEGM in the CSMP-25-PEGM-250. Then the decomposition of the PEGM attached to SMP-10 is suspected which might be the reason of the further weight loss. The thermal degradation of the cross-linked methacrylate is accomplished with the evolution of the monomer during the thermal treatment (250°C –450°C).[16] Additionally in the temperature range of 450°C –850°C the conversion of the preceramic polymer into inorganic materials take place, which is accompanied by the decomposition of the preceramic unit.[13]

The ceramic obtained by heat treatment was X-ray amorphous until 1200°C for 2 hours (Figure S3). Furthermore, the ceramics obtained via pyrolysis of the PEGM-modified SMP-10 at 600°C handled completely under argon analyze with respect to its elemental composition. The result shows a carbon content of 26–27 wt% and 18–19 wt% of oxygen present in the ceramic. The presence of minor amounts of the oxygen has been reported in the literature to range from 3 to 6.7 wt% and might be related to polymer synthesis and handling issues.[13] The higher amount of oxygen can be explained as a consequence of the chemically modification of SMP-10 with oxygen containing PEGM. This result shows that SiC(O)-based ceramic obtained from PEGM-containing samples exhibits a higher oxygen content compared to SMP-10 without modification. This will in turn further help in order to (a) ease to impregnate metal catalyst and (b) enhance the catalytic activity.

Table 3 summarizes the specific surface areas for the obtained samples at different temperatures. The results show that a high specific surface area SiC(O) ceramic can be obtained by using the above mentioned techniques. In order to understand the effect of crosslinking on the specific surface area of the final ceramic. Homogeneous mixture of SMP-10 and PEGM has been formed which further pyrolyzed at 600°C was also produced. In addition, the results clearly shows the effect of crosslinking as the produced ceramic shows <10 m^{2}g^{-1} of specific surface area. The formation of high specific surface area at 600°C by chemical modification. The specific surface area strongly depends on the pyrolysis temperature and shows gradual decreases with increasing temperature (600°C −363 m^{2}g^{-1} to 1,200°C −122 m^{2}g^{-1}) due to the collapse of microporous structure which is further observable in N$_2$ adsorption-desorption isotherms. Highly ordered mesoporous SiC ceramics was also synthesized using polycarbosilane as a precursor using template-assisted method. Compared with a typical two-step casting procedure and removal of template, this method helps to produce high specific surface area SiC(O)-based ceramics in one pot synthesis.[17,18]

Figure 4 shows the N$_2$ adsorption-desorption isotherms of produced samples pyrolyzed at different temperatures. It can be seen clearly that all the samples pyrolyzed at different temperatures have a typical Type IV isotherm and display a distinct hysteresis loop in the range of 0.4–1.0 P/Po characteristics of mesoporous materials. Additionally, the sharp uptake at a relative pressure (p/po) <0.1 indicates the presence of microporous structures. Hence, SiC(O)-ceramics obtained after pyrolysis at 600°C contain micropores and mesopores. This can be concluded in this way that the evolution of hydrogen and small fragment is the reason of microporosity whereas the evolution of monomeric unit of PEGM is the reason behind mesoporosity in the final ceramic. On further high-temperature treatment, microporous structures collapse, however, mesoporosity is still observed.[19] The mesoporosity was further analyzed using the BJH model. The mesopore diameter was found to be in the range of 5–25 nm for sample pyrolyzed at 600°C. On further high temperature treatment at 1000°C, a reduction in the number of mesopores was observed. At a temperature of 1200°C, a decrease in the size of mesoporous diameter is observed in addition to a reduction in the number of mesopores.

The elemental analysis of the ceramics obtained via pyrolysis of the PEGM-modified SMP-10 at 600°C shows the
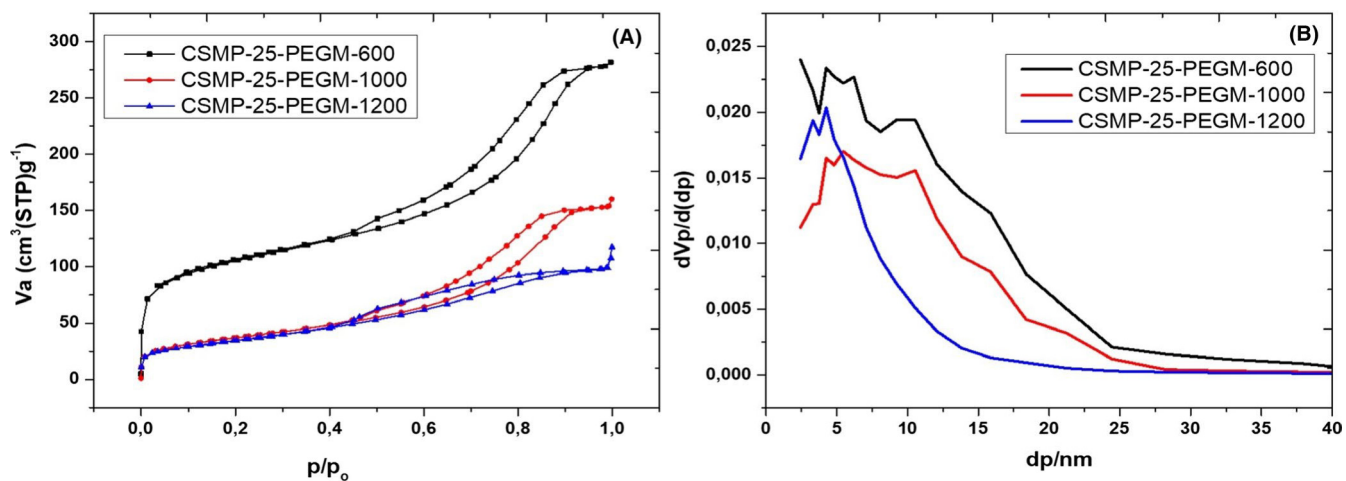
FIGURE 4 (A) The nitrogen adsorption/desorption isotherms (B) the BJH analysis of samples pyrolyzed at different temperatures [Color figure can be viewed at wileyonlinelibrary.com]
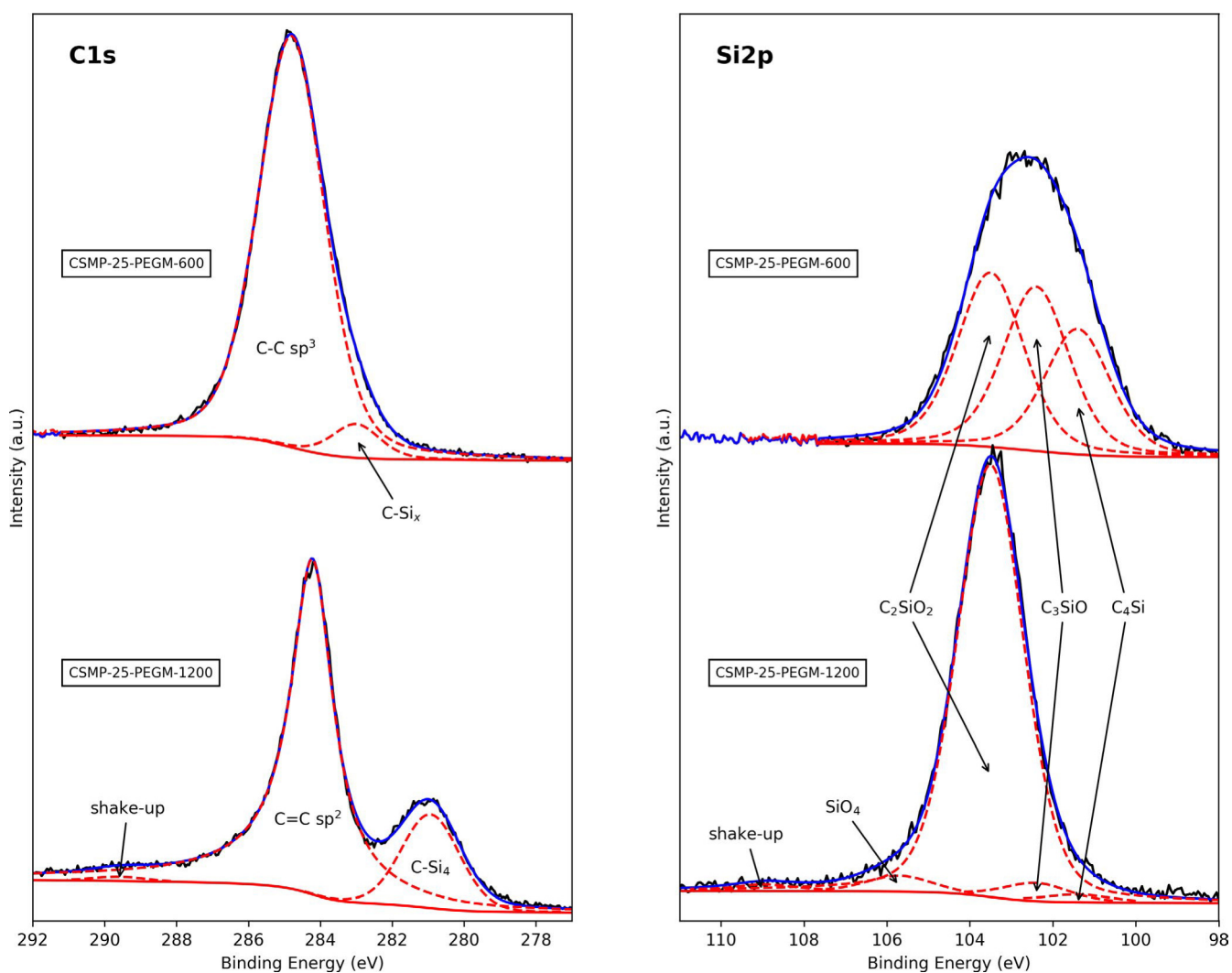

FIGURE 5 X-ray photoemission spectra of the C1s and Si2p core levels of PEGM-modified SMP-10 pyrolyzed 600°C and 1200°C [Color figure can be viewed at wileyonlinelibrary.com]
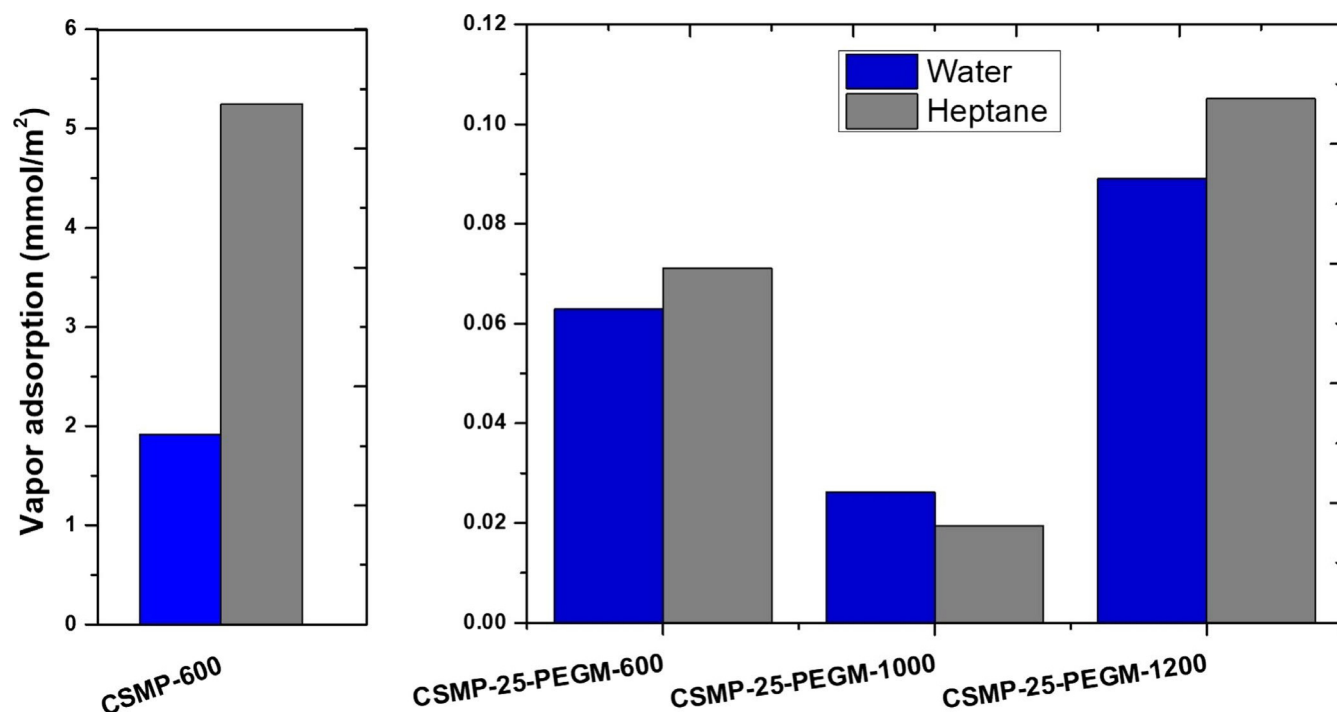
FIGURE 6 Water and n-heptane vapor adsorption at 25°C for precursors pyrolysis at different temperature under argon environment [Color figure can be viewed at wileyonlinelibrary.com]

incorporation of oxygen within the ceramic which in turn might produces oxygen-containing (C_xSiO_y) surface layer. So a detailed surface analysis of PEGM-modified SMP-10 pyrolyzed at 600 and 1200°C was performed using X-ray photoelectron spectroscopy (XPS) as shown in Figure 5. The XPS analysis of the pyrolyzed PEGM-modified SMP-10 confirms the presence of several C_xSiO_y components in the Si2p core level spectrum. The C_4Si- and C_3SiO-type bonding was observed in the sample pyrolyzed at 600°C whereas on further heat treatment at 1200°C, silicon exists almost exclusively as C_2SiO_2-type bonding together with component related to silica (SiO_4 bonding).[20–22] Furthermore, in the C1s spectrum, an increased chemical shift of the C-Si component can be observed which indicates that the corresponding carbon atoms form more bonds to silicon, that is, CSi_4. This does not contradict the decreased C_4Si component as the silicon can be bond not only to carbon but also to oxygen at the same time. As the C/Si ratio does not significantly change and in fact even increases from 0.35 to 0.39, this leaves some carbon not bound to the silicon anymore. In fact, the main C-C peak in the C1s spectrum indicates the presence of sp^2-hybridized carbon because of its asymmetric shape modeled by a Doniach-Sunjic line profile[20] and because of the shake-up visible at slightly higher energies.[21] This suggests the presence of graphene at the surface.[22] Overall, this leads to the conclusion that during pyrolysis, the carbon-rich C_xSiO_y oxidizes further, even forming energetically favorable silica, while the carbon partially segregates to the surface to form grapheme.[23]

The XPS results clearly shows the presence of an oxygen-containing (SiOxCy) surface layer on the SiC(O) surface might affect the surface properties of the formed silicon carbide. Therefore, hydrophilicity and hydrophobicity of the pyrolyzed samples are determined using water and n-heptane vapor adsorption at 22°C (Figure 6). The vapor adsorption was recalculated based on the SSA values and given in mmol/m². The surface characteristic was reflected by the ratio of water/ heptane adsorption, instead of the absolute value of the water or vapor adsorption.[23] All the samples (except samples pyrolyzed at 1000°C) have a higher n-heptane adsorption than water vapor adsorption, displaying hydrophobic surface characteristics. Firstly, the sample produced without chemical modification shows hydrophobic character and the ratio of water/heptane/ was found to be 0.36. With chemical modification, the ratio of water/heptane/(0.88) is relatively high as compared to the sample obtained without modification. The fact is related to the presence of oxygen containing surface layer, which form hydrophilic C_xSiO_y on the surface and probably in the matrix of silicon carbide. On further high temperature treatment, it decreases again to 0.48 (1500°C) due to the carbothermal reduction of silica (deposited on SiC), which starts at above 1450°C ($SiO_2 + 3C = SiC + 2CO$).

The control over the surface wettability is widely known to be of great importance in the regulation of interactions between heterogeneous catalysts and reactants and thus the activity and selectivity of the catalyst. For instance, hydrophobic solid catalysts were proven to be excellent catalysts for epoxidation, hydrogenation, condensation, and esterification or trans-esterification reaction. Moreover, a number of

TABLE 4 Mass loss, volume shrinkage, density, and surface area of CSMP-25-PEGM-based ceramic monoliths annealed at different temperatures (the sample at 600°C was set as reference sample)

Sample	Temperature (°C)	Holding Time [h]	Mass loss [%]	Volume shrinkage [%]	Skeletal Density [g/cm³]	Surface area (m²g⁻¹)
CSMP-25-PEGM	600	2	—	—	1.08	170
	1000	2	10	8.6	0.95	86
	1200	2	26	8.1	0.83	51

metal catalyst reactions face the drawbacks of agglomeration of metal nanoparticles, which can be stabilized by different porous materials. The catalytic performance of such material can further be boosted by hydrophobic modification of the pore surface.[24,25]

Overall, the obtained ceramics in the present study are hydrophobic in nature and they can overcome the issue of deactivation of catalytic sites or hydrolysis of the frameworks by the adsorption of typical solvent, or byproduct in a variety of reactions.

3.2 | Processing of SiC(O)-based monoliths

In order to obtain compacted green bodies, several experiments were done using different parameters. At ambient temperatures and without use of the binder polyvinyl alcohol no compaction of the powders was observed. This is because the binder created a sorbed viscoplastic shells which in turn help to compact. Thus, the compaction of the powder occurred with the use of binder only. However, the optimization of several parameters like amount and concentration of PVA, uniaxial pressure applied to form the green bodies was investigated. The optimization of the process led to the fabrication of crack-free monoliths (Figure S4). Mass loss, volume shrinkage, skeletal density and surface area of SiC(O)-based ceramic pellets at higher temperature are indicated in Table 4. The results show that the mass loss and volume shrinkage of the ceramic monoliths increase with the temperature. The specific surface area of the monolithic sample was found to be 170 m²g⁻¹. However, the surface area of the monolithic sample is lower when compared to powdered sample but still high enough for the intended use as monoliths for catalytic purposes.
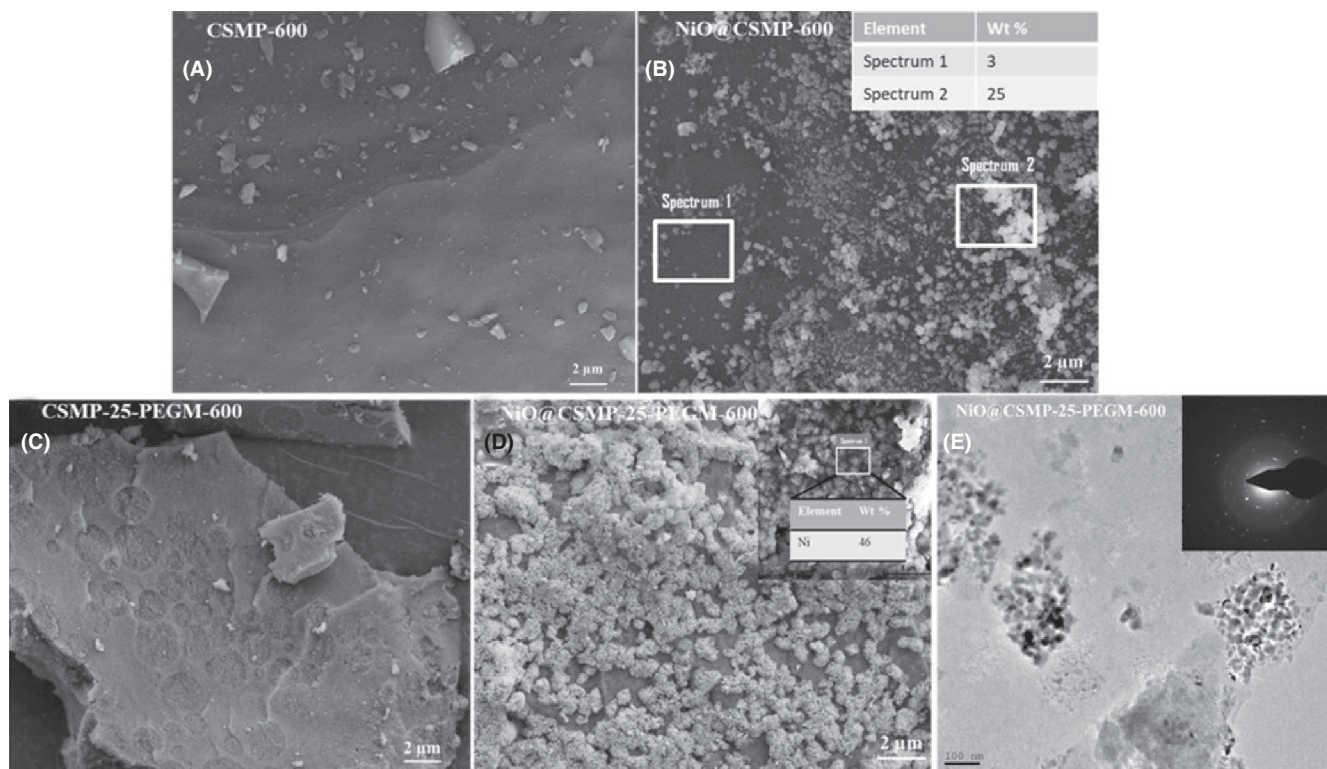

FIGURE 7 SEM images of (A) SiC(O) powder, (B) NiO@SiC(O) powder, (C) PEGM modified SiC(O) and (D) NiO@ PEGM modified SiC(O) powder obtained after calcined at 500°C for 5 h whereas (E) TEM images of NiO@ PEGM modified SiC(O) powder obtained after calcined at 500°C for 5 h with the SAED pattern

3.3 | Characterization of NiO@SiC(O) ceramic powder obtained by impregnation method

The sample obtained after calcination in air at 500°C for 5 hours were first characterized with respect to its phase formation. The XRD results show that the support stayed amorphous whereas $NiNO_3$ leads to the formation of NiO after calcination in air (Figure S6). The corresponding SEM images and EDX results are presented in Figure 7. It can be observed that, after annealing for 5 hours in air, the dispersion, morphology, and structure of the developed NiO strongly depend on the properties of the surface of the support. In case of the sample obtained without chemical modification of SMP-10 with low surface area and low content of oxygen on the surface, the crystal structure was found to be mostly irregular. The EDX results also show that the dispersion of the NiO is not homogeneous. However, in case of sample obtained after impregnation on CSMP-25-PEGM-600 and calcination a different result was found. Homogeneously distributed flower-like architecture of NiO were observed. The high dispersion of the nickel phase on the SiC(O) surface was attributed to the presence of an oxygen-containing (SiO_2-SiO_xC_y) surface layer on the SiC surface which helps in anchoring and dispersing of the deposited metal particles.[26–28] Than the newly formed nuclei with a high surface energy, prefer to aggregate, driven by the minimization of surface energy and self-assembly process, which is followed by further growth and lead to the formation of flower-like structure. Furthermore, the NiO@CSMP-25-PEGM-600 were further characterized by HRTEM and the TEM images with the selected area electron diffraction (SAED) patterns shown in Figure 7E, reveal that the matrix is amorphous whereas NiO are present as a form of clusters. Existence of several halo rings in SAED of NiO@CSMP-25-PEGM-600 is a good evidence for their polycrystalitte state, because diffraction pattern of a single crystal just shows light dots without recognizable halo rings.[29] The produced NiO can also be further reduced to nickel particles as reported in the literature.[30]

The obtained NiO@CSMP-25-PEGM-600 powder after calcined at 500°C for 5 hours was further subjected to the analysis of porosity by the N_2 adsorption method. The analysis data clearly indicated that the nickel impregnated samples also possess typical Type IV isotherm for mesoporous materials (Figure 8A). As discussed earlier, the CSMP-25-PEGM pyrolysis at 600°C contain micropores and mesopores but on nickel impregnation and calcination micropore structures collapse, however mesoporosity still remained. As the microporosity collapsed due to the impregnation of nickel precursor, it is assumed that NiO was mainly formed in the micropores. Furthermore, the mesoporosity was further analyzed using the BJH model. The mesopore diameter was found to be in range of 5-25 nm. The specific surface area of nickel-impregnated sample was found to be 101 m^2g^{-1} which is a reasonable value when intending to use the material for catalytic purposes. Another possible reason for the decrease in the specific surface area and collapse of the microporosity is the stability of the support in air. In order to understand the stability of the CSMP-25-PEGM, the sample without nickel impregnation was calcined at 500°C in air. The specific surface area was found to be 161 m^2g^{-1} and higher than the sample with nickel impregnated. Therefore, the nickel impregnation and instability of support in air are the reason behind the decrease in the specific surface area and collapse of the microporosity.

4 | CONCLUSION

The present study has proved high specific surface area SiC(O)-based ceramic can be produced by thermal treatment of chemical modified preceramic polymer SMP-10
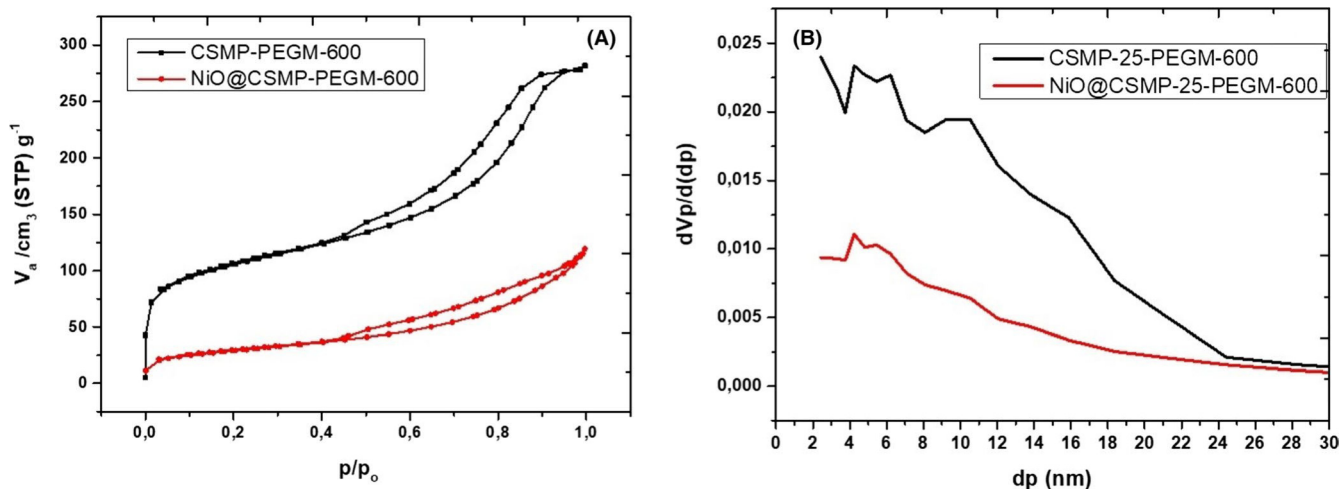

FIGURE 8 (A) The nitrogen adsorption/desorption isotherms (B) the BJH analysis of SiC(O)-600 impregnated with nickel based solution and calcined at 500°C in air [Color figure can be viewed at wileyonlinelibrary.com]

with PEGM. The obtained materials is a micro/mesoporous SiC(O) based ceramic. The reason behind the increase in surface area is the decomposition of the macromolecular precursor with the evolution of gaseous species whereas crosslinking helps to retain it till high temperature. Corroborated spectroscopic and diffraction studies indicate that the macromolecular precursor converts at high temperatures into an amorphous ceramic and were shown to be thermally stable toward crystallization up to 1200°C. Moreover, the study also shows that the oxygen containing PEGM helps to increase the oxygen content on the surface of SiC ceramic. The produced high surface area SiC(O) ceramic is a promising candidate to support homogeneously distributed flower like NiO catalyst. It also opens up the possibilities to introduce different metal salt into the home made SiC(O) support for further catalytic application.

ACKNOWLEDGMENTS

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