

Ni/ZrO₂-CeO₂ Catalysts for the Simultaneous Production of Hydrogen and Carbon Nanotubes

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Abstract: The catalytic methane decomposition (CMD) using Ni/ZrO₂-CeO₂ catalysts for the simultaneous production of hydrogen and carbon nanotubes, was studied on samples prepared by different synthesis methods. The catalysts were synthesized by the impregnation and coprecipitation methods with or without ultrasound treatment. X-ray diffraction (XRD), Raman spectroscopy and high resolution transmission electron microscopy (HRTEM) were the main characterization techniques. It was observed that the Ni impregnated catalyst with ultrasound treatment increases significantly the production of hydrogen and carbon nanotubes in the CDM at 500 °C. The results also indicated that the synthesis of catalysts via coprecipitation generates a higher number of encapsulated Ni particles by both, the ZrO₂-CeO₂ support and the produced carbon at the end of the reaction.

Keywords: Hydrogen Production; Carbon Nanotubes; Catalytic Methane Decomposition; Ultrasound Irradiation Treatment.

1. INTRODUCTION

In the last years, the world faces a global energy crisis both in the electricity and the hydrocarbons sectors, mainly due to a decline in the availability of fossil fuels. Subsequently, the development of new technologies to produce renewable energy has been extensively promoted. There has been much interest in producing hydrogen for electricity generation in fuel cells which are considered as a potential source of renewable and sustainable energy without pollution [1].

The demand for hydrogen is ever increasing also due to its use in various hydrotreating processes in petroleum industries. Currently, hydrogen is mainly produced by steam reformation of hydrocarbons with water; however, the H₂ obtained by this route is not suitable for direct applications in some fuel cells due to poisoning of those that produce carbon monoxide. Among the possible hydrogen sources, methane is still a good option because it is abundant, clean and it can be easily converted to hydrogen by catalytic decomposition, by which hydrogen CO and CO₂-free is produced, besides the reduction of the temperature at which thermal cracking of methane occurs: CH₄ (g) → 2H₂ (g) + C (s) [2,3].

Another advantage of the catalytic decomposition of methane

(CDM) is the production of nanofibers and carbon nanotubes (CNTs), which have attracted attention for its many applications such as electronics, nanosensors, supports for electrocatalysts in fuel cells [4,5] without pollution production. Several studies have been reported in the CDM in different Ni catalysts such as Ni/Al₂O₃, Ni/TiO₂, Ni/ZrO₂, and mainly in Ni/ZrO₂-CeO₂ due to the high reactivity of Ni on this support [6-10]. All these studies have reported active catalysts for hydrogen production; however the deactivation of these solids remains a fundamental problem for catalysts for the CDM. The activity and life of the supported Ni catalysts for CDM strongly depend on the particle size of Ni metal and the textural properties of the support. Unfortunately, rapid deactivation of Ni-based catalyst results at temperatures in excess of 600 °C, leading to a low yield of hydrogen. The catalyst deactivation occurs when the metallic particles are encapsulated by non-reactive carbon compounds [11].

The catalytic properties of these Ni/ZrO₂-CeO₂ materials can be improved by the synthesis process. In this regard it has been found that the use of ultrasound irradiation (US) in the catalysts preparation presents significant advantages such as higher yields, the reduction of the induction periods in the reactions, as well as the synthesis time, the decreased in the particle size, in addition to the increase in the specific surface and surface cleaning [12]. Cavita-

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tion-induced sonochemistry provides a unique interaction between energy and matter, with hot spots inside the bubbles of about 5000 K and pressures of 1000 bar approximately, heating and cooling rates of $>1010\text{K s}^{-1}$; these extraordinary conditions permit access to a range of chemical reaction space normally not accessible, which allows for the synthesis of a wide variety of unusual nanostructured materials [13]. Therefore, in this work we have studied different methods of synthesis assisted by ultrasound irradiation as a new synthesis method of Ni/ZrO₂-CeO₂ catalysts, in order to study the effect of the preparation methods on the activity and stability of these catalysts in the CDM to produce hydrogen and carbon nanotubes.

2. EXPERIMENTAL

2.1. Catalysts Preparation

Four catalysts were synthesized with 15 wt. % of Ni supported on zirconia-ceria in which Ni was deposited by two different methods: coprecipitation and impregnation, with and without ultrasound pretreatment. The synthesized samples are described in Table 1.

ZrO₂-CeO₂ mixed oxides (80 wt.% ZrO₂-20 wt.% CeO₂) were prepared by surfactant-assisted coprecipitation and they were used as supports for the catalysts prepared by impregnation. These materials were prepared from zirconyl chloride and ZrOCl₂·8H₂O and cerium (III) hexa-hydrated nitrate Ce(NO₃)₃·6H₂O. The surfactant used was a 0.4 M aqueous solution of cetyl-trimethyl ammonium bromide (CTAB). Aqueous solutions of zirconyl chloride and cerium nitrate were mixed in adequate concentrations of surfactant solution to obtain a surfactant-zirconia molar ratio of 2 and the mixture was stirred at 60 °C for 1 h. Then, the coprecipitation was carried out using NH₄OH at pH 11. All reagents were supplied by Aldrich.

The precipitates were handled with different pre-treatments: conventional aging for 16 h at 80 °C and an ultrasonic irradiation with 25 KHz of power during 1 h at room temperature. After the pre-treatment, the precipitate was washed repeatedly using distilled water and dried at 110 °C for 16 h. Finally the obtained powders were calcined in static air at 800 °C for 4 h.

An aqueous solution of Ni (NO₃)₂·6H₂O was used as Ni precursor for all the catalysts. For the catalysts synthesized by coprecipitation Ni was precipitated with zirconyl chloride and cerium nitrate, while for the catalyst prepared by impregnation Ni was deposited by impregnation with ultrasonic irradiation with 25 KHz of power during 1 h at room temperature, after calcining the mixed oxide at 800 °C for 4 h in static air.

2.2. Catalyst characterization

Ni/ZrO₂-CeO₂ catalysts were characterized by diverse techniques. X-ray diffraction patterns were obtained in a Bruker-Axs

Table 1. Ni/ZrO₂-CeO₂ catalysts synthesized by different methods

Catalyst	Ni incorporation	Pre-treatment
NZC-CC	Coprecipitation	Conventional
NZC-CU	Coprecipitation	Ultrasound irradiation
NZC-IC	Impregnation	Conventional
NZC-IU	Impregnation	Ultrasound irradiation

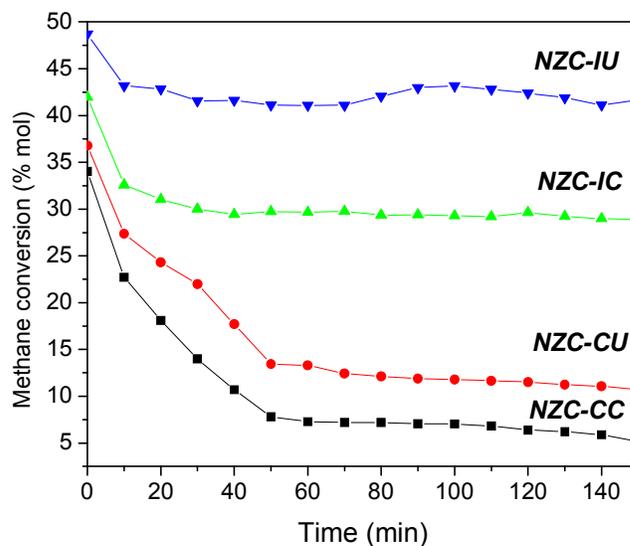


Figure 1. Catalytic activity in the CDM at 500 °C of Ni/ZrO₂-CeO₂ samples prepared by different methods.

D8 Discover with GADDS (General Area Detector Diffraction Systems, two-dimensional detector) diffractometer fitted with a Cu tube (40 kV, 40 mA). These materials were also studied by HRTEM using a JEOL JEM2200FS microscope with Schottky type field emission gun, operating at 200 kV and integrated with a CEOS aberration corrector. The elemental composition was determined by EDS with a NORAN spectrometer fitted to the TEM. In order to prepare the materials for observation, the powder samples were dispersed in ethanol and supported on holey carbon coated copper grids. HRTEM digital images were obtained using Digital Micrograph Software from GATAN.

Temperature programmed reduction (TPR) analyses were conducted in a Micromeritics TPD/TPR equipped with a conductivity detector. The reduction was carried out by using 50 mg sample from 30 to 900 °C (10 °C/min) using a 5% H₂/Ar mixture. The BET analyses were also performed in a Micromeritics TPD/TPR equipment, prior to the measurements the samples were out-gassed at 350 °C for 2 h in vacuum. Finally, Raman spectra were recorded in the 100–1200 cm⁻¹ wave number range using a Horiba, Jobin Yvon Raman apparatus using the excitation laser line of 633 nm.

2.3. Catalytic testing

Catalytic activity was measured in the methane decomposition reaction over the Ni/ZrO₂-CeO₂ catalysts. This evaluation was accomplished in a stainless steel microreactor (Advanced Scientific Designs, RXM-100). This reaction system consists of a microreactor of approximately 4 mm of inner diameter and 15 cm length. The reactor heads is connected to an Agilent gas chromatograph (Agilent 6890) equipped with a capillary column Molosieve (Perkin Elmer), a thermal conductivity detector, TCD (H₂) and a flame ionization detector, FID (CH₄) for the analysis of products. A catalyst sample of 100 mg was loaded into the reactor and the pre-treatment of the catalysts was carried out in situ prior to the activity test. The pretreatment consisted in a drying-reduction program,

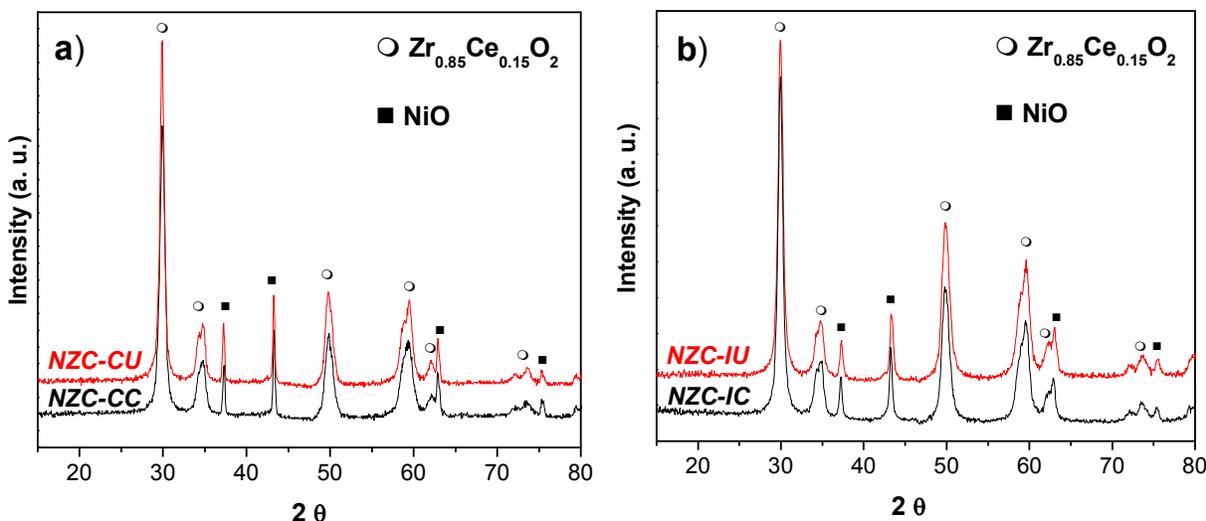


Figure 2. Crystalline phases of the Ni/ZrO₂-CeO₂ catalysts synthesized by different methods: a) Coprecipitation b) impregnation.

drying the samples at 100 °C for 1h in Ar (70 cm³ min⁻¹) followed by reduction in a hydrogen flow (30 cm³ min⁻¹) at 500 °C for 1 h. The reaction was conducted at 500 °C and using a mixture of 10% CH₄-90% Ar in volume at atmospheric pressure.

3. RESULTS AND DISCUSSION

The catalytic activity results of Ni/ZrO₂-CeO₂ samples synthesized by different methods are shown in Figure 1. It can be seen that catalysts prepared by impregnation (N-ZC-IU and N-ZC-IC) presented the highest methane conversion into hydrogen and carbon than those prepared by coprecipitation (N-ZC-CC and N-ZC-UC), with an initial maximum conversion of 48.7% for the catalyst prepared by impregnation, pretreated with ultrasound irradiation. It was also observed that this last catalyst also presents a higher resistance to deactivation.

Due to the high purity (99.9%) of the methane used as reactant and the low reaction temperature (500 °C), the main deactivation processes that occurs in our Ni catalysts is the encapsulation by non-reactive carbon compounds. In this sense, it is also observed that the catalysts treated with ultrasound during the synthesis increase their activity compared to those who did not receive this pretreatment, so that the characterization was performed in order to look for possible changes in their physicochemical features produced by different synthesis methods.

The diffractograms of the Ni/ZrO₂-CeO₂ catalysts are shown in Figure 2. The identification of crystalline phases by XRD indicates that both synthesis methods lead to the formation of Zr_{0.85}Ce_{0.15}O₂ mixed oxides in tetragonal phase with the main diffractions at 2θ = 30, 35, 50 and 60; no reflections corresponding to ceria or zirconia are observed indicating the formation of a solid solution, since there is no segregation of these oxides in these materials. It is also observed the formation of nickel oxide with reflections at 2θ = 37, 43 and 63. All of these catalysts present similar crystalline features, however it is noted that the catalysts synthesized by coprecipitation show slightly thinner NiO peaks, suggesting that this method produces a larger crystallite size, due to the simultaneous precipitation

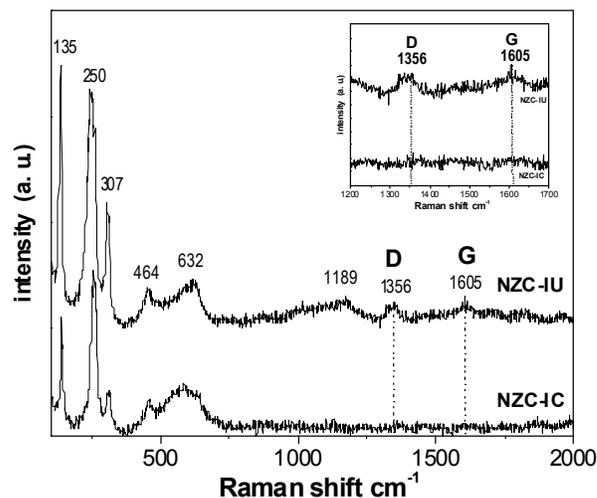


Figure 3. Raman spectra of used catalysts after reaction in CDM at 500 °C.

of Ni with zirconia-ceria, preventing further dispersion of Ni oxide. However, in all catalysts, these reflections are very thin; indicating that both methods produce a high NiO crystallite size. The crystallite size measurements calculated with the Scherrer equation indicates an average size of about 29 nm, and this result was confirmed by HRTEM analysis.

On the other hand, the catalysts characterization after reaction by Raman laser spectroscopy, HRTEM and XRD showed the presence of ZrO₂-CeO₂ mixed oxide and the formation of amorphous carbon and Ni⁰ (Metallic nickel is not detected by Raman, since this metal do not present activity in this technique). These results are shown in Figures 3 to 5.

Figure 3 shows the Raman spectra of the catalysts used in catalytic decomposition of methane at 500 °C, synthesized by impregnation. In both cases we observe the presence of characteristic

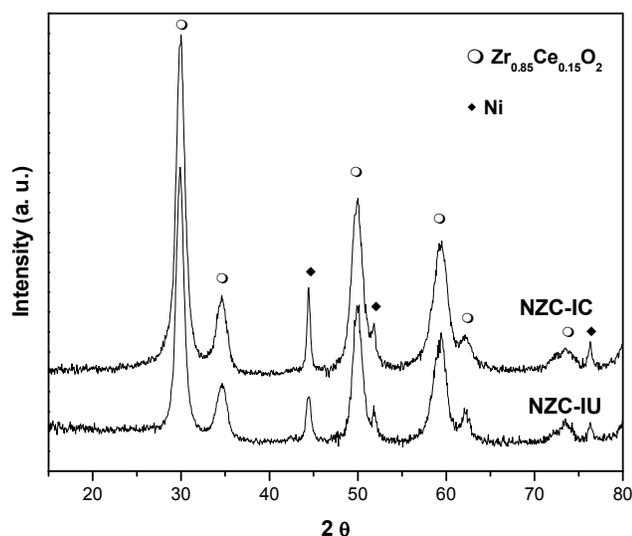


Figure 4. Diffraction patterns of Ni/ZrO₂-CeO₂ catalysts after reaction in CDM at 500 °C.

bands of ZrO₂-CeO₂ oxides at 135, 250, 307, 464 and 632 cm⁻¹ [14], however the presence of amorphous carbon is only obvious in the case of the catalyst synthesized by impregnation-ultrasound (NZC-IU) by the presence of the bands between 1100 and 1800 cm⁻¹ characteristic of amorphous carbon [15]. It is observed the presence of two bands at 1356 (band D) and 1605 (G band) cm⁻¹ attributed to the formation of multi-walled carbon nanotubes; the band D represents the structural imperfection of graphite sheet, while the G band corresponds to the oscillation in the plane of the carbon atoms in sp² graphite sheet of CNTs, indicating the existence of ordered structures of CNTs [16]. The intensity ratio I_D/I_G indicates the structural disorder degree of carbon nanotubes, it has been reported I_D/I_G values of 0.051 for highly oriented graphite layers and 1.15 to 3.56 for CNTs produced by catalytic methods [2]; in our case we obtained an average ratio of 1.08 indicating that in this case multi-walled carbon nanotubes, in partial disarray, are forming. The comparison between both spectra indicates a higher production of CNTs on the ultrasound treated sample, which also indicate higher activity although we did not find any carbon signals by XRD in the samples used in the CDM reaction (Figure 4).

These changes are attributed to the effect of sonication in the liquid near to the Ni/ZrO₂-CeO₂ surface during the preparation method, when liquids are irradiated with ultrasound, the alternating expansive and compressive acoustic waves creates bubbles (cavities) and makes the bubbles oscillate. The oscillating bubbles can accumulate ultrasonic energy effectively while growing to a certain size, under the right conditions, a bubble can overgrow and subsequently collapse, releasing the concentrated energy stored in the bubble within a very short time (>10¹⁰K s⁻¹). This cavitation implosion is very localized and transient with a temperature of 5000 K and a pressure of 1000 bar [13]. In this case, we are supposing that the bubbles that implode near the solids surface can be generating unusual morphological changes on the Ni/ZrO₂-CeO₂ surface such as surface damage and particle fragmentation because of the high-speed interparticle collisions, probably by this action

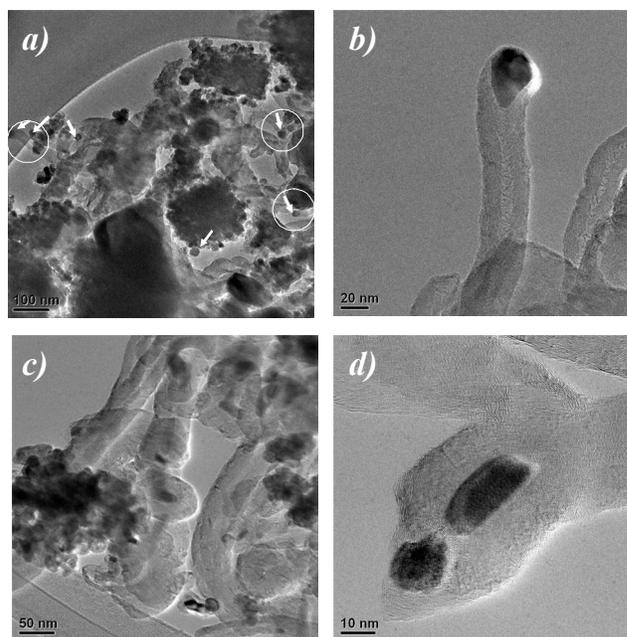


Figure 5. HRTEM micrographs of samples synthesized by impregnation after the reaction in CDM at 500 °C: a) and b) pretreated with ultrasound irradiation (NZC-IU), c) and d) conventional synthesis without pretreatment (NZC-IC).

the surface is disorganized, then local effects as dislocation and vacancies are produced and this generates a positive effect on reactivity by creating a major Ni exposition to the reactants as it was found in the samples prepared by ultrasonic irradiation [17].

It is possible that Ni particles are more dispersed and more exposed in the US irradiated samples, and as a consequence there are a greater number of adsorption/reaction sites that are available to interact with the methane to produce hydrogen and CNT. It has been reported that the advantages of the sonochemical approach over conventional methods in the synthesis of nanostructures include more uniform size distribution, a higher surface area, and improved phase purity [18].

Finally, from the HRTEM analysis of samples synthesized by impregnation (Figure 5), it is possible to observe that after 150 min of reaction, multiwall carbon nanotubes (MWCNTs) of different diameters and lengths are formed from the methane decomposition over Ni/ZrO₂-CeO₂ catalysts. In Fig. 5a some Ni nanoparticles are arrowed and in Fig. 5b a high resolution image of a MWCNT with a Ni particle in the top is shown. It has been reported that in CNTs obtained by catalytic methods, generally the growth of CNTs is given by combined mechanisms, either by nickel growing on the top or in the base of the nanotube [2]. This behavior was observed in both cases; catalysts prepared with ultrasound irradiation (Figs. 5a and 5b) and without irradiation (Figs. 5c and 5d), however, in the case of untreated samples a high concentration of Ni particles encapsulated in carbon was observed. Ni particles are detected because they appear darker than the support and the carbon structures.

According to CNT formation mechanism proposed by Hoogen-

raad [19] methane decomposes into carbon and hydrogen atoms on the nickel surface, then carbon dissolves and forms a metastable nickel carbide which is then decomposed into metallic nickel and graphite, which encapsulates Ni particles. Subsequently the process continues when the Ni particle is compressed out by the graphite walls due to pressure build-up because of the formation of graphite layers. Finally, Ni is pushed toward the tip of the nanotube, exposing fresh Ni surface to the methane again, and thus the activity and growth of CNTs continues. According to the catalytic test results (Figure 1), it can be seen that the ultrasound treatment promotes this behavior, and apparently in those samples without this treatment the mechanism of nucleation and CNTs growth stops due to the encapsulation of the Ni particles. Probably the energy produced by the ultrasound treatment during the support preparation would produce modification in the surface of the support that generate less interaction between the Ni and the ZrO₂-CeO₂, facilitating the Ni separation from the support and therefore the catalytic activity to produce hydrogen and the formation of CNTs.

The overall analysis of the results indicates that despite the structural similarities of the catalysts obtained by different procedures, the impregnation method is more effective to produce active Ni/ZrO₂-CeO₂ catalysts for the methane decomposition, because, although it includes a greater number of stages synthesis, the Ni impregnation after the formation of the ceria-zirconia oxide allows higher exposure of Ni and thus better accessibility of methane to the catalytic active phase. On the other hand, in the coprecipitation technique, the simultaneous precipitation of Ni with the ZrO₂-CeO₂ oxide produces a system where Ni is highly dispersed and during the calcination process, a fraction of NiO nanoparticles are encapsulated by ZrO₂-CeO₂ oxide. Thus NiO cannot be reduced and the catalytic action of metal decreases.

It is also noted that ZrO₂-CeO₂ pretreatment with ultrasound prior to the calcination increases the catalytic activity, probably due to the high pressures and temperatures generated by cavitation (creation, explosion and destruction of small bubbles displayed when a liquid is irradiated by US) can cause changes in the ZrO₂-CeO₂ lattice as vacancies or dislocations, creating a major Ni exposition to the reactants. A further advantage of the US treatment is that it reduces the synthesis time, since the support needs only one hour for the ceria and zirconia interaction, versus 16 h needed to aging in the conventional method.

4. CONCLUSIONS

It was found that the catalytic methane decomposition over Ni/ZrO₂-CeO₂ catalysts to generate hydrogen and carbon is suitable to form MWCNTs by both methods impregnation and coprecipitation; however, the ultrasound-assisted impregnation method increased the catalytic activity and therefore an increased production of hydrogen and carbon nanotubes. Moreover, the conventional aging time is reduced from 16 h to 1 h with US irradiation. It is possible that decomposition of methane and subsequent carbon formation on the catalyst surface is promoted by the ultrasound irradiation pretreatment, probably because the bubbles that implode near the solids surface can be generating unusual morphological changes on the Ni/ZrO₂-CeO₂ surface such as surface damage and particle fragmentation because of the high-speed interparticle collisions, then local effects as dislocation and vacancies are produced and this generates a positive effect on reactivity by creating a major

Ni exposition to the methane, and therefore a greater number of adsorption/reaction Ni sites that are available to interact with the methane to produce hydrogen and CNT.

5. ACKNOWLEDGMENTS

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