

Direct Conversion Biogas to Multiwall Carbon Nanotubes and Syngas over Starch Derived Ni@C Nanoparticles.

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Biogas is mainly composed of CH₄ and CO₂ [1]. The primary usage of biogas is as an internal combustion engine (ICE) fuel. Biogas is also studied to produce hydrogen as fuel cell feedstocks. An exciting alternative is to catalytic convert biogas to syngas which can be further upgraded to liquid fuels and chemicals through Fischer–Tropsch process. During CH₄-CO₂ dry reforming process, the most challenging problem is the catalyst deactivation by carbon deposition. This concern is even significant if using biogas directly, since the higher CH₄/CO₂ ratio (up to 1.5~1.6 for biogas) will end with higher and faster carbon formation over the catalyst that rapidly deactivates it. A new approach has been proposed to overcome this catalyst deactivation by converting the deposited carbon to a value-added product while avoiding the catalyst deactivation. The key issue of this procedure is to find a suitable catalyst to implement both the reforming reaction and the nano carbon structure formation since nano-carbons have been widely applied in material, electronic, energy storage, biomedical and environmental area. Nickel-based catalysts are widely used for both methane reforming and nano carbon formation processes. They promote the methane reforming reaction and effectively convert methane into highly valued products like carbon nanotubes, graphene and carbon nanofibers. This reactivity makes nickel-based catalysts an excellent choice to convert biogas into hydrogen-rich syngas and carbon nanostructures since biogas have relatively high CH₄:CO₂ ratios. The principal objective of this work was to produce and characterize multiwall carbon nanotubes (MWCNTs) and hydrogen-rich syngas from biogas over a highly efficient carbon-encapsulated metal nanoparticle catalyst.

Carbon-encapsulated nickel-core nanoparticles were synthesized hydrothermally by the reduction of Ni²⁺ from a starch solution. Six grams of Ni(NO₃)₂•6H₂O, 30 g starch and 250 ml DI water were stirred for 30 min then transferred into a 500-mL Parr reactor; the reactor was heated up to 180 °C and kept for 8 h. After reaction the resulting black product was collected and washed three times with DI water and ethanol. The final product was oven-dried at 110 °C overnight. The dried carbon-encapsulated nickel nanoparticles were calcined at 900 °C under a continuous nitrogen flow (100mL/min) for one hour. Catalytic conversion of biogas was carried out in a stainless steel tubular reactor (0.0127 m O.D.) with 3g of calcined nickel nanoparticles. The catalyst was first reduced at 400 °C under H₂/N₂ (1:1) gas flow for 3 h, then increasing the temperature to 850 °C feeding with CH₄/CO₂ gases (100 mL/min) at a ratio of 3/2 for one hour. The solid sample was collected and boiling in 0.1M HNO₃ solution for one hour. The prepared samples were characterized using microscopy to investigate the morphology, particle size and fine crystal structures. Samples for SEM were prepared by sprinkling the dried material on to double sided carbon tape affixed to AL stubs and coating with 10 nm PT (EMS 150 T coater). Samples were examined using a JEOL JSM 6500F microscope at 10 kv. For TEM the dried samples were mixed with 100 % ETOH and sonicated for 20 min. A drop of the liquid was placed on a formvar/carbon 300 mesh copper grid for one hour then gently removed with filter paper. Grids were examined with a JEOL JSM 2100 microscope at 200kv. X-ray powder diffraction (XRD) patterns of the synthesized samples were obtained using a Rigaku Ultima III X-ray Diffraction.

SEM shows that the fresh nickel catalyst sample is spherical in shape with particle size between 1 and 2 μm (Fig.1a) whereas the micro-sphere calcined at 900 $^{\circ}\text{C}$ exhibits a porous structure (Fig.1b). After catalytic conversion biogas at 850 $^{\circ}\text{C}$ for 1 hour Fig.1c shows a large amount of MWCNTs formed in the spheres. The purified sample (Fig.1d) clearly shows the MWCNTs with much higher purity with diameters ranging from ~ 30 to 100 nm. TEM shows MWCNT with a nickel particle (arrow) on its top (Fig. 2a). The diameter of the nickel particle was about 30 nm. TEM image of MWCNTs indicates 50 to 100 carbon planes with the inter-layer spacing of 0.34 nm which corresponds to its graphite structure (Fig. 2b). MWCNTs formation is also confirmed by XRD ,with the typical peaks for MWCNTs at 26.22 $^{\circ}$ and 53.97 $^{\circ}$ 2θ which corresponds to the (002) and (004) planes of graphite 2H. SEM, TEM and XRD results showed that biogas (CH_4/CO_2 mixture) can be efficiently converted to MWCNTs and syngas over starch derived Ni@C nanoparticles.

References:

[1] S Rasi *et al*, Energy, 32 (8) (2007), p. 1375.

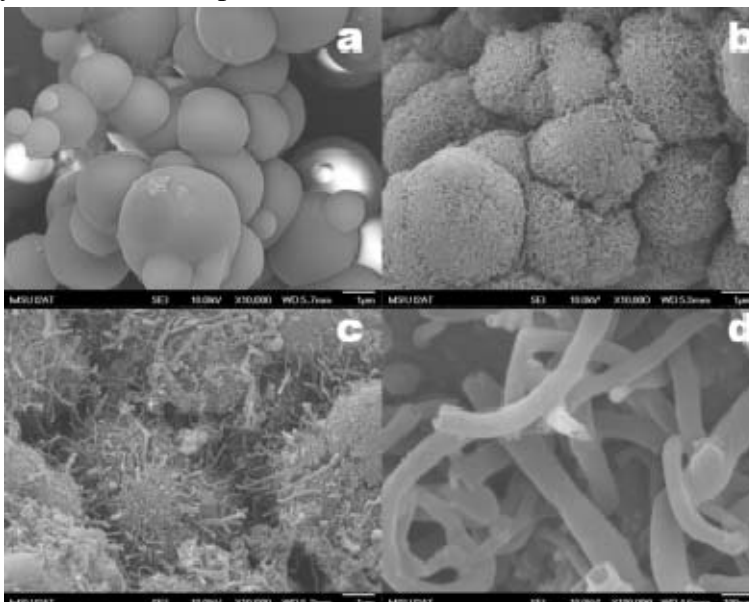


Figure 1. SEM images of the carbon-encapsulated nickel nanoparticles. a: the dried sample; b: the calcined sample; c: the catalytic conversion sample; d: purified sample.

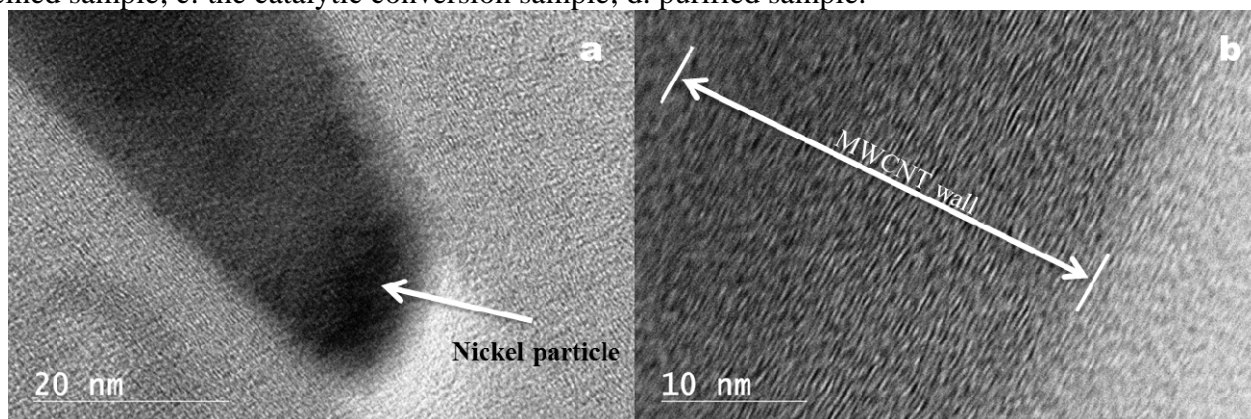


Figure 2. TEM images of MWCNTs formed during biogas conversion. a: MWCNTs with nickel nanoparticle on the top (arrow); b: the graphite plane structure of the MWCNT wall.