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Governance of the porosity and of the methane decomposition activity sustainability of NiO/SiO_2 nanocatalysts by changing the synthesis parameters in the modified Stöber method

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ABSTRACT

Nanoscience and nanotechnology present ubiquitous possibilities in almost any scientific field because of property enhancement occurring in nanoparticles with unique size and shape. The physicochemical characteristics of nanoparticles play an imperative role in their prospective applications. This article reports an in-depth study on the variance of the physicochemical characteristics, the methane decomposition activity, and the sustainability of nano-NiO/SiO_2 (n-NiO/SiO_2) catalysts with different preparation parameters. The influence of nickel/silicate ratio, octadecyltrimethoxysilane (C18TMS)/tetraethylorthosilicate (TEOS) ratio, and of different solvents was investigated. The characteristic features of the prepared catalysts were inspected using N_2 adsorption–desorption measurements, X-ray diffraction, hydrogen temperature-programmed reduction, field-emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, and methane cracking catalytic activity in a fixed bed reactor. Methane decomposition activity was evaluated by measuring the instantaneous hydrogen production (vol %) and carbon yield (%) at the end of the examination. The results showed that C18TMS has extensively improved the microporosity of the material, hence resulting in the improvement of the catalytic performance. The microporosity of the n-NiO/SiO_2 catalyst has increased from 10.7% to 26.8% when the quantity of C18TMS was increased from 0 to 1.2 mL in the synthesis mixture. Catalysts prepared with a maximum quantity of C18TMS and a minimum quantity of tetraethylorthosilicate exhibited a minimum activity loss of 17.46%.

1. Introduction

Nanoscience and nanotechnology have attracted numerous research interests in the past few decades because nanostructured materials were noted to exhibit exclusive properties as compared with their bulk counterparts [1–3]. Nanostructured materials show novel optical, electronic, and magnetic properties because of the finite surface effect, size effect, and macroscopic quantum tunneling effect at nanodimension. Hence, nanostructured materials unveil an extensive sort of applications in the development of catalysts, fuel cells, gas sensors, photoelectronic devices, energy storage devices, super capacitors, and lithium-ion batteries [4–7]. At present, production of fine nanopowders with superior quality in terms of size, morphology, and structure is a research title of great interest. Different methodologies to fabricate nanosized

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materials were proposed such as solvothermal synthesis [8,9], carbonyl and pulsed laser ablation, microwave irradiation [10], microemulsion [11,12], sonochemistry [13], ultrasonic radiation [14], anodic arc plasma method [15,16], coprecipitation [17], and sol–gel methods [18–20].

An important advantage of the coprecipitation method is the capability to control the physicochemical properties of nanopowders by varying the synthesis parameters without using any sophisticated equipment or expensive chemical reagents. Nanostructured nickel based materials were commonly studied in catalysis because of their relatively low cost, low toxicity, superior activity, stability, and environmentally friendly characteristics [17,21,22]. Furthermore, nickel-based nanomaterials were also used in the development of numerous materials other than catalysts such as electrochromic materials [23], p–n heterojunctions [24], gas sensors [25–27], magnetic materials [28], optical materials [29], fuel cell electrodes [30], batteries [31], electrochemical capacitors [32], and solar cells [33,34]. Coprecipitation cum modified Stöber method was adopted in the present study to produce nano-nickel catalysts with crystal sizes of ~30 nm supported on silicate [17]. The synthesized silicate-supported nickel catalysts were used in methane decomposition in which methane conversion activity and stability were subsequently evaluated. Methane decomposition results in the simultaneous production of two desired products, which are hydrogen and nanocarbons as shown in Eq. 1. Hydrogen and nanocarbons are among the most emergent products in the field of ecofriendly energy and material science, respectively.

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298K} = 74.52 \ kJ \ mol^{-1} \tag{1}$$

Hydrogen can be considered as a potential energy carrier in the current scenario of substantial depletion of fossil fuel resources and deterioration of ecological environment because of high greenhouse gas emission [35]. Hydrogen performs a vital function in addressing the current energy crisis mainly because of its zero greenhouse gas emission during combustion, as shown in Eq. 2 [36]:

$$H_2 + ½O_2 \rightarrow H_2O \quad \Delta H_{298K} = -285.83 \ kJ \ mol^{-1} \tag{2}$$

Furthermore, hydrogen can be produced from renewable raw materials such as water, biomass, and biogas [37,38]. The fully green methane decomposition technology can be considered as a sustainable approach for the production of hydrogen, because methane is the major component of biomass and large methane reserves are accessible in the deep ocean bed and in industrialized countries [21,39]. Hence, automobile industries, science laboratories, and governments have focused more on the application of hydrogen as a possible alternative fuel to simplify both widespread production and distribution.

The implementation of catalysts in methane decomposition is essential because of the high temperature requirement such as 1200 °C for the scission of strong C–H bond to achieve a rational hydrogen and carbon yield [40]. Hence, CH_4 molecule is highly stable with tetrahedral geometrical structure supported with four extremely strong C–H bonds with bond energy of 434 kJ mol^{-1}. The effectiveness of a catalyst is not only constrained to higher methane decomposition rate and conversion at low temperature but also the capability to produce large amounts of nanocarbon while preserving the thermochemical stability of the catalyst. Accordingly, various metal and carbon-based catalysts were introduced [41,42]. Literature survey revealed that metal catalysts exhibited high catalytic activity and high initial methane decomposition rate but deactivate drastically over time [21,41]. On the other hand, carbon-based catalysts and metal-doped carbon catalysts preserved superior stability with a lower deactivation rate than that of metal catalysts. Nevertheless, these catalysts exhibited poor methane conversion in spite of their higher stability. Our previous studies showed that the performance of the Ni/SiO_2 nanocatalyst in terms of its stability and activity for methane decomposition is superior to that of Co/SiO_2 and Fe/SiO_2 nanocatalysts [43,44].

The activity, stability, and selectivity of the catalyst are evidently dependent on the material composition, production parameters, synthesis method, and methane decomposition operating conditions. The introduction of a highly stable catalyst that exhibits higher methane conversion at lower temperature amid huge carbon deposition is obligatory for the establishment of hydrogen production technology from a methane source at the industrial scale. The characteristics of the catalyst and experimental parameters directly influence the stability and activity. For instance, the electronic state of the metal particles (which depends on metal and support interaction), crystallinity, crystalline size, dispersion of metal particles, textural properties and pore geometry [45], catalyst composition [46], calcination and reduction temperature [47,48], catalyst preparation method [49], and catalyst rinsing solvent [50] are some of the major factors which affect the catalyst stability.

The precise structural and functional control for both metal and silicate support were achieved by changing the precursor ratios. Porosity of the catalyst support directly influences the total surface area and catalyst dispersion, resulting in distinctive catalytic properties. In general, catalyst porosity management is accomplished by changing surfactants, soft templates, additives, and reaction conditions [51,52]. However, we have accomplished porous regulation by changing the quantity of octadecyltrimethoxysilane (C18TMS) porogen with respect to silica precursor (tetraethylorthosilicate, TEOS). C18TMS produces heterogeneous domains and leads to the development of large quantity of pores inside the silica structure on thermal treatment [53]. Furthermore, we studied the influence of the concentration of a raw material solution and the type of a solvent on the characteristic properties of the produced nanocatalyst. To the best of the authors' knowledge, this study is the first to deal with the governance of characteristic and catalytic properties of the nano-NiO/SiO_2 (*n*-NiO/SiO_2) nanocatalyst by varying the synthesis parameters in the coprecipitation cum modified Stöber method. Regardless of traditional approaches, coprecipitation cum modified Stöber method offers numerous advantages such as easy scale-up to gram quantities, usage of environmentally friendly precursors and solvents, usage of cost effective chemicals, formation of smaller crystalline