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Synthesis Chemistry and Properties of Ni Catalysts Fabricated on SiC@Al₂O₃ Core-Shell Microstructure for Methane Steam Reforming

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Abstract: Heat and mass transport properties of heterogeneous catalysts have significant effects on their overall performance in many industrial chemical reaction processes. In this work, a new catalyst micro-architecture consisting of a highly thermally conductive SiC core with a high-surface-area metal-oxide shell is prepared through a charge-interaction-induced heterogeneous hydrothermal construction of SiC@NiAl-LDH core-shell microstructures. Calcination and reduction of the SiC@NiAl-LDH core-shell results in the formation of Ni nanoparticles (NPs) dispersed on SiC@Al₂O₃, referred to as Ni/SiC@Al₂O₃ core-shell catalyst. The Ni/SiC@Al₂O₃ exhibit petal-like shell morphology consisting of a number of Al₂O₃ platelets with their planes oriented perpendicular to the surface, which is beneficial for improved mass transfer. For an extended period of methane-stream-reforming reaction, the Ni/SiC@Al₂O₃ core-shell structure remained stable without any significant degradation at the core/shell interface. However, the catalyst suffered from coking and sintering likely associated with the relatively large Ni particle sizes and the low Al₂O₃ content. The synthesis procedure and chemistry for construction of supported Ni catalyst on the core-shell microstructure of the highly thermal conductive SiC core, and the morphology-controlled metal-oxide shell, could provide new opportunities for various catalytic reaction processes that require high heat flux and enhanced mass transport.

Keywords: methane steam reforming; Ni catalysts; silicon carbide; layered double hydroxides; core-shell catalysts

1. Introduction

Heterogeneous catalytic reactions often occur, coupled with the intrinsic reaction kinetics on catalyst surfaces and the mass and heat transport via the inter- and intra- structures of the solid catalysts [1]. In regards to supported metal catalysts, the dispersion and structure of active metal particles on the support surface have significant effects on the intrinsic reaction rates, however, the heat and mass flux through the catalysts is largely determined by support properties, such as thermal conductivity, porosity and pore sizes. The significant effects of heat and mass transport on catalytic chemical reaction processes have been reported in various theoretical and experimental studies [2–5]. For industrial reaction processes that require intensive heat and mass flux with rapid load-follow-up performance, metal foams are utilized for catalyst preparation in order to improve thermal conductivity [6]. In such a scheme, non-active high-surface-area metal oxides, such as alumina, are initially deposited on the metal foam surface, followed by immobilization of the desired active metals or metal oxides on the surface. However, this approach is difficult to apply for the preparation of small catalyst particles or pellets that are commonly utilized in industrial heterogeneous catalytic processes.

In our previous work, we presented a new design and synthesis approach for supported metal catalysts based on hydrothermal oxidation of aluminum (Al) metal particles in order to construct a core-shell microarchitecture including a highly heat-conductive Al metal core and high surface area metal oxide shell [7]. For instance, simple hydrothermal reaction of Al metal particles in water at an elevated temperature can result in a core-shell microstructure consisting of an Al core and a high-surface-area γ - Al_2O_3 shell with various surface morphologies [8]. The shell composition and structure can be modulated by the hydrothermal reaction of Al particles in an aqueous solution of various metal salts [9]. The constructive effects of the enhanced heat and mass transport due to Al@metal-oxide core-shell structures are verified through various catalytic reactions, including methane-steam reforming [10], glycerol-steam reforming [11], and preferential CO oxidation [12]. The basic concept for design of the catalyst structures and the thermal conductivities of various materials [13] are illustrated in Scheme 1. The high thermal conductivity of the Al@metal-oxide core-shell is ascribed to the one-to-two orders of magnitude greater thermal conductivity of Al compared to the common metal oxides, such as Al_2O_3 and SiO_2 , which are used as supports for heterogeneous catalysts.

Scheme 1. (a) Thermal conductivity of various metals and ceramics; (b) schematic of the core-shell catalyst microstructure.

Herein, we report the direct synthesis of Ni catalysts supported on a $\text{SiC@Al}_2\text{O}_3$ core-shell via construction of bimetallic Ni-Al layered double hydroxides (LDHs) on silicon carbide (SiC) particles via charge-interaction-induced heterogeneous hydrothermal reactions. Crystalline SiC exhibits significantly high thermal conductivity ($360\text{--}490 \text{ W m}^{-1} \text{K}^{-1}$ [14]), with even higher values than the common metals, and extraordinary thermochemical stability. In this work, we attempt to fabricate NiAl-LDH on SiC crystalline particles by hydrothermal reaction for construction of a SiC@NiAl-LDH core-shell, which requires studies on the interfacial chemistry and synthesis approach due to the low compatibility of SiC with metal oxides. LDHs represent a class of layered anionic clays with a general formula of $[\text{M}^{2+}_{1-x} \text{M}^{3+}_x (\text{OH})_2]^{x+} (\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and trivalent metal cations, A^{n-} are interlayer anions, and x is the surface charge based on the ratio of two metal cations, $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ [15]. LDHs have been utilized as catalysts and catalyst precursors for various reactions, such as selective oxidation of alcohols, methanol steam reforming, and NO_x reduction [16,17]. As will be shown, calcination and reduction of SiC@NiAl-LDHs results in formation of Ni nanoparticles (NPs) dispersed on a $\text{SiC@Al}_2\text{O}_3$ core-shell, which can afford high catalytic activity in addition to enhanced heat and mass transport properties. The Ni/ $\text{SiC@Al}_2\text{O}_3$ core-shell catalyst is applied for methane steam reforming, and its catalytic performance is investigated.

2. Results and Discussion

2.1. Synthesis Chemistry and Mechanism of Ni/SiC@Al₂O₃ Core-Shell Microstructures

Scheme 2 illustrates the procedure for the preparation of Ni catalysts supported on a SiC@Al₂O₃ core-shell microarchitecture, referred to as Ni/SiC@Al₂O₃ hereafter. The synthesis chemistry of the catalysts depends on the heterogeneous hydrothermal construction of a bimetal Ni and Al layered double hydroxide (NiAl-LDH) shell selectively on the surface of SiC particles. The initial structure formed via hydrothermal reaction of a LDH precursor solution with a suspension of SiC particles at controlled initial pH condition is the SiC@NiAl-LDH core-shell, and its subsequent calcination and reduction results in the formation of finely dispersed Ni NPs on the SiC@Al₂O₃, which will be referred to as Ni/SiC@Al₂O₃ core-shell catalysts.

Scheme 2. Direct synthesis of SiC@NiAl-LDH and Ni/SiC@Al₂O₃ core-shell catalysts.

Figure 1 presents SEM images of the samples obtained after the hydrothermal reactions of the precursor mixture solution of Ni(NO₃)₂ and Al(NO₃)₃ with urea at different initial pH conditions (2, 5, and 8), with SiC particles suspended in the solution. The initial and final pH of the solution are shown in Figure 1. Since the urea was co-added in the precursor solution, the pH of the solution during the hydrothermal reaction rose steadily due to decomposition of the urea [18]. The sample prepared at a low initial pH condition (Figure 1a, pH = 2.0) clearly shows the formation of a NiAl-LDH shell with a petal-like surface morphology consisting of densely distributed platelets grown on the SiC particles. The coverage of the LDH crystallites on the surface of SiC particles was uniform. The LDH platelets were developed with a unidirectional spatial orientation of their *ab* dimension, perpendicular to the SiC particle surface. The typical platelet morphology of LDH crystallites is known to have *ab*-faces of the platelets that are much larger than the dimension along the *c*-axis (thickness) of the platelets [19]. The thickness of the platelets was in the range 10–70 nm, while the width was in the range 500 nm–1.2 μm. Notably, the heterogeneous formation of NiAl-LDH on the surface of SiC particles could only be achieved when the initial pH of the precursor solution was very low. Figure 1b, and 1c shows the resulting samples obtained after the hydrothermal reaction under similar synthesis conditions but using different initial pH of the solutions of 5 (Figure 1b) and 8 (Figure 1c), respectively. Clearly, these samples only exhibit the SiC particles without any indication of the developed LDHs having been attached on the surface. In these conditions, LDH particles were homogeneously formed in the solution, without having a preferential growth on the SiC particles. The results suggest the critical importance of the initial pH of the synthesis solution for the heterogeneous growth of NiAl-LDH crystallites on SiC surfaces, as will be discussed shortly.

Figure 1. SEM images of the samples prepared by the hydrothermal reaction of the Ni and Al precursor solutions at various initial pH conditions with suspended SiC powder: (a) initial pH of 2; (b) pH of 5; (c) pH of 8. The number in parenthesis is the final pH of the solution after completion of the reaction.

The composition and uniformity of the NiAl-LDH shell of the SiC@NiAl-LDH (Figure 1a) obtained at the low initial pH of 2 was characterized by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) and the energy dispersive x-ray spectroscopy (EDS) with elemental mapping. The results are shown in Figure 2. The NiAl-LDH shell formed on the SiC surface had Ni and Al atomic content of 13.1% and 4.8%, respectively. The Ni and Al atomic ratio ($\text{Ni}/\text{Al} = 2.7$) of the sample was nearly identical to the Ni/Al ratio of the initial precursor solution (3.0), indicating that both Ni and Al species had similar reaction kinetics during the formation of NiAl-LDH. The EDS mapping results show a homogeneous distribution of Ni and Al species throughout the LDH structure. The results suggest that the Ni and Al composition of the SiC@NiAl-LDH can be modulated by varying the initial atomic ratio of the constituent metal elements. It also has been reported that stable MeAl-LDH ($\text{Me} = \text{Zn}, \text{Cu}, \text{Mg}, \text{Co}, \text{Ni}$) crystallites can be prepared at various Me/Al atomic ratios typically in the range of 2–4 [20].

Figure 2. (a) Elemental content of Ni and Al in the NiAl-LDH shell of the SiC@NiAl-LDH core-shell characterized by inductively coupled plasma–atomic emission spectroscopy (ICP-AES); (b) energy dispersive x-ray spectroscopy (EDS) atomic mapping for Ni, Al, and O on the NiAl-LDH shell.

The critical dependence of NiAl-LDH development on the SiC particles with the initial pH of the synthesis solution reflects the marked importance of the surface charge of the SiC particles and its physicochemical interactions with the constituent metal complex moieties in the synthesis solution. Figure 3 shows the zeta potential of SiC particles dispersed in water, which is measured at various solution pH values in the range of 2–8. The results suggest that the SiC particles reach the point of zero charge (PZC) when the pH of the solution is at approximately 3.2. Therefore, below a pH of 3.2, the surface of the SiC particles is positively charged, whereas above this value it is negatively charged in the solution. A similar trend in the variation of surface charges with pH of the solution was reported for SiC materials in the literature [21]. Notably, the SiC@NiAl-LDH core-shell could be obtained only for the samples prepared in the initial pH of the solution of 2 (Figure 1a) as discussed above. At low initial pH levels of below 3.2, the surface of SiC particles in the synthesis solution is positively charged, hence, the basic metal hydroxides and nitrate anions formed in the solution by hydrolysis of the Ni and Al precursors with urea are likely to be under a supersaturated state on the surface of SiC particles. The nucleation of NiAl-LDH seeds can then be performed selectively on the SiC surface followed by the growth of NiAl-LDH platelets, which constructs the SiC@NiAl-LDH core-shell microstructures. The highly oriented growth of LDH platelets can be described by the evolutionary selection mechanism first proposed by van der Drift for vapor phase deposition of a PbO layer. [22] The NiAl-LDH seeds formed in the supersaturated region can grow initially in all possible directions. However, their probability of survival is determined by the various crystallographic growth rates of the individual crystals. The vertical growth of the individual NiAl-LDH platelets avoids collisions between the growing crystals and is favored by a faster growth rate in the *ab* crystallographic direction and a great probability of survival. The vertical orientation of the NiAl-LDH platelets is also favorable for diffusion of precursor species through the thickening NiAl-LDH shell. Collectively, the SiC@NiAl-LDH core-shell microstructures with petal-like surface morphology, comprising a number of NiAl-LDH platelets, may be formed. The SEM images of the samples, which were obtained at various hydrothermal synthesis times, strongly backs the proposed mechanism of SiC@NiAl-LDH core-shell structure formation. Figure 4 presents the SEM images of the samples obtained at various hydrothermal synthesis times: (a) fresh SiC powder, (b) 2.5 h, (c) 3 h, and (d) 5 h, respectively. The results revealed that the small NiAl-LDH crystal nuclei with domain sizes in the range 50–300 nm were densely developed on the surface of the SiC particles (Figure 4b). The size of the NiAl-LDH crystals grew as the hydrothermal reaction time increased and large LDH platelets of width in the range 500 nm–1.2 μm could be observed clearly (Figure 4c,d).

Figure 3. Zeta potential of the SiC particles measured in aqueous solution at various pH conditions.

Figure 4. SEM images of the SiC@NiAl-LDH obtained at various hydrothermal synthesis times: (a) fresh SiC particle, (b) 2.5 h, (c) 3 h, (d) 5 h of the reaction.

2.2. Properties of Ni/SiC@Al₂O₃ Core-Shell Catalysts

The Ni catalysts supported on SiC@Al₂O₃ (Ni/SiC@Al₂O₃) were obtained through calcination and reduction of the SiC@NiAl-LDH core-shell. Figure 5 shows the temperature-programmed-reduction (TPR) pattern of the calcined SiC@NiAl-LDH (1023 K in air) in a H₂ stream (ramp = 10 K min^{−1}). The TPR pattern of the sample exhibited two deconvoluted reduction peaks at 752 and 928 K. The major H₂-TPR peak occurred at 752 K and was attributed to the reduction of NiO to metallic Ni, which is consistent with the results reported on Al₂O₃-supported Ni catalysts [23,24]. The high-temperature reduction peak at 928 K was ascribed to the reduction of nickel aluminates [25]. The total amount of H₂ consumption calculated from the H₂-TPR peaks for the reduction of NiO to metallic Ni agreed well with the total Ni content of the sample measured by ICP-AES (18.8 wt.%). Figure 6 shows SEM images of (a) the SiC@NiAl-oxide obtained by the calcination of SiC@NiAl-LDH and (b) the Ni/SiC@Al₂O₃ catalysts obtained by the subsequent reduction in H₂. The SEM images of the SiC@NiAl-oxide revealed that the core-shell structure was stable despite the high-temperature calcination at 1023 K. The typical petal-like surface morphology of the SiC@NiAl-LDH core-shell remained unchanged, without any significant morphological destruction. The core-shell structure was also sustained indicating a strong interfacial bond between the SiC core and NiAl-oxides shell. The reduced Ni/SiC@Al₂O₃ catalysts also did not exhibit morphological changes and preserved the core-shell microstructure. However, the x-ray diffraction (XRD) patterns showed transformation of crystalline structure of the samples through calcination and reduction.

Figure 5. H₂ temperature-programmed reduction (H₂-TPR) profile of the SiC@NiAl-oxide obtained by calcination of the SiC@NiAl-LDH.

Figure 6. SEM images of (a) SiC@NiAl-oxide obtained by calcination of SiC@NiAl-LDH in air at 1023 K; (b) Ni/SiC@Al₂O₃ catalyst prepared by reduction of the SiC@NiAl-oxide in H₂ at 1023 K.

Figure 7 shows XRD patterns of (a) SiC@NiAl-LDH, (b) SiC@NiAl-oxides, (c) Ni/SiC@Al₂O₃, and (d) the pristine SiC particles. The XRD of SiC particles shows the typical diffraction pattern of α -SiC crystals. The SiC@NiAl-LDH core-shell exhibited the sharp characteristic peaks of a typical LDH structure, which can be indexed into a hexagonal lattice with $R3m$ rhombohedral symmetry [26]. Together with the SEM results that reveal the uniform coverage of the NiAl-LDH shell on the SiC particles, the superposition of the typical XRD patterns of NiAl-LDH and SiC verifies the formation of SiC@NiAl-LDH core-shell microstructure via the hydrothermal reaction. The XRD results of the calcined SiC@NiAl-oxides indicated that the typical LDH crystal structure vanished when the calcination was conducted at 1023 K, and a crystalline phase of NiO ($2\theta = 37.3, 43.3,$ and 62.9° , ICDD#01-075-0269) appeared. The XRD pattern of the Ni/SiC@Al₂O₃ catalysts (Figure 7c) showed the sharp characteristic diffraction of metallic Ni particles developed on the sample. The average particle size of Ni NPs calculated using the Scherrer equation was 26 nm. The typical diffraction pattern of Al₂O₃ was not observed after the reduction, apparently due to its low degree of crystallization.

Figure 7. X-ray diffraction (XRD) patterns of (a) SiC@NiAl-LDH, (b) SiC@NiAl-oxide, (c) Ni/SiC@Al₂O₃ catalyst, and (d) SiC particles.

The structure of SiC@NiAl-LDH and Ni/SiC@Al₂O₃ catalysts was further characterized by transmission electron microscopy (TEM). These results are presented in Figure 8. The TEM image of the NiAl-LDH platelets of the SiC@NiAl-LDH core-shell (Figure 8a) indicates that Ni atoms were homogeneously incorporated into the LDH structure without any noticeable phase segregation. The Ni/SiC@Al₂O₃ catalyst (Figure 8b) shows the Ni NPs formed on the surface of the platelets after the reduction treatment. The sizes of these NPs obtained from the TEM analysis are in the range of 10–30 nm with a moderate size distribution (Figure 8b inset). The average size of Ni NPs was about 21 nm which is consistent with the value obtained by the XRD analysis (26 nm).

Figure 8. TEM images of (a) SiC@NiAl-LDH core-shell; (b) Ni/SiC@Al₂O₃ catalyst (inset = Ni particle size distribution).

The pore size and surface area of the samples were characterized from N₂ adsorption-desorption isotherms obtained by volumetric analysis. Figure 9 shows (a) N₂ adsorption-desorption isotherms and (b) Barrett-Joyner-Halenda (BJH) pore size distribution of the SiC@NiAl-LDH, SiC@NiAl-oxides, and Ni/SiC@Al₂O₃ core-shell catalyst. All these samples exhibit the type IV isotherm, which is typical for mesoporous materials with the characteristics of H3-type hysteresis, proving the presence of parallel slit-shaped pores ascribed to the layered structure of the NiAl-LDH platelets. The isotherms of SiC@NiAl-oxide and Ni/SiC@Al₂O₃ catalyst show greater surface areas and pore volumes compared to the SiC@NiAl-LDH due to the removal of nitrate anions and water from the inter-laminar region of the NiAl-LDH via calcination and reduction at elevated temperatures. Table 1 shows the surface area of the samples obtained by the Brunauer-Emmett-Teller (BET) method. For the purposes of comparison, the BET surface area of NiAl-oxide obtained after calcination of the NiAl-LDH (Ni/Al atomic ratio = 3.0, prepared by homogeneous hydrothermal reaction) is also displayed. The morphology and crystallographic structures of the sample characterized by SEM and XRD analysis are presented in the supporting information (Figure S1). As shown, the surface area of SiC@NiAl-oxide is smaller than that of the NiAl-oxide prepared through the homogenous hydrothermal reaction. This is due to the presence of the SiC core in the SiC@NiAl-oxide. By comparing the differences in the surface area and pore volume of these samples, the weight ratio of the SiC core to the NiAl-oxides shell in the SiC@NiAl-oxide could be deduced to be approximately 2.4. The BJH pore-size distribution on the samples are shown in Figure 9b. The SiC@NiAl-LDH core-shell showed a very sharp pore size distribution located at about 3.9 nm. After calcination, the SiC@NiAl-oxide showed a broadening of the pore size distribution with a peak located approximately at 20 nm, due to collapse of the layered pore structure of the NiAl-LDH. The average pore size and pore volume of the samples are summarized in Table 1. The results showed that the average pore size and BET surface area was increased after the calcination and reduction of the SiC@NiAl-LDH core-shell.

Figure 9. (a) N₂ adsorption-desorption isotherm and (b) Barrett-Joyner-Halenda (BJH) pore size distribution of SiC@NiAl-LDH, SiC@NiAl-oxide, and Ni/SiC@Al₂O₃ catalyst.

Table 1. BET surface area, average pore size, and pore volume of the samples.

Catalyst	BET Surface Area (m ² g ⁻¹)	Average Pore Size (nm)	Total Pore Volume (cm ³ g ⁻¹)
SiC@NiAl-LDH	15	11	0.11
SiC@NiAl-oxide	31	21	0.18
Ni/SiC@Al ₂ O ₃	25	21	0.13
NiAl-oxide ^[a]	105	7	0.22

^[a] Prepared by calcination of NiAl-LDH obtained by the homogeneous hydrothermal method.

2.3. Methane Steam Reforming on Ni/SiC@Al₂O₃ Catalyst

The catalytic properties of the Ni/SiC@Al₂O₃ core-shell catalyst were investigated for methane steam reforming (MSR, CH₄ + H₂O ↔ CO + 3H₂, ΔH° = 225.4 kJ mol⁻¹). The MSR reaction is followed by the subsequent water-gas shift reaction (WGS, CO + H₂O ↔ CO₂ + H₂, ΔH° = −42 kJ mol⁻¹), where the CO produced through the MSR further reacts with H₂O to produce additional H₂ and CO₂. The MSR is highly endothermic, hence, facile heat flux through the catalyst bed in a reactor is highly favored. Previous studies have demonstrated the significant effects of enhanced heat transport through the Ru and Rh catalysts supported on metal-ceramic Al@Al₂O₃ and Al@MgAl₂O₄ core-shell microstructures for the endothermic MSR [10] and glycerol steam reforming [7,9] in addition to the exothermic selective CO oxidation reaction [12]. In the hydrothermal construction of Al@Al₂O₃ and Al@MeAl₂O₄ (Me = Mg, Co, Mn, Ni, Zn) core-shell microstructures, Al particles were utilized as a precursor source for the Al₂O₃ shell and a heat-conducting metal-core, and therefore the strong interfacial bonding between the Al core and Al₂O₃ shell was established. For the Ni/SiC@Al₂O₃ core-shell catalysts, the structural stability coupled with interfacial compatibility between the SiC core and the Al₂O₃ shell is of particular importance. In this work, an attempt is not made to demonstrate the effects of enhanced heat and mass transport properties of the Ni/SiC@Al₂O₃ catalysts in comparison to the conventional catalysts, which have been extensively researched in our previous work. In addition, MSR is reported to be structure sensitive [27], hence, a fine control of the dispersion and structure of Ni NPs also bears significant effects on the kinetics of the reactions. The aim of this work is to investigate the chemistry and synthesis methodology for production of Ni/SiC@Al₂O₃ catalysts, and their stability and performance under the practical reaction conditions.

Figure 10a shows time-on-stream methane conversion by steam reforming over the Ni/SiC@Al₂O₃ catalyst. The results show an initial CH₄ conversion of 78% over the catalyst but a gradual decrease of the conversion with reaction time due to the decrease in the catalytic activity of the Ni/SiC@Al₂O₃. After 100 h of the reaction on the stream, the CH₄ conversion dropped by about 17% from the initial conversion level. Figure 10b shows time-on-stream selectivity of the products in terms of H₂/CO and CO/CO₂ mole ratio. The results show that H₂/CO selectivity increased with reaction time concurrently with a decrease of CO/CO₂ selectivity. The results suggest a relatively increasing contribution of water-gas shift reaction to the product selectivity in accordance with the decrease of CH₄ conversion by the MSR. It is noteworthy that a significant amount of carbon deposits were observed in the reactor after the MSR reaction of 100 h. The spent catalyst was characterized by SEM and XRD analysis as shown in Figure 11. The SEM results revealed that the overall core-shell structure and petal-like morphology of the Ni/SiC@Al₂O₃ catalyst was stable during the reaction. The interfacial bond between SiC and Al₂O₃ by the in-situ hydrothermal synthesis and subsequent treatment process appears to be strong, and no peeling-off of the shell from the SiC core was observed throughout the extensive SEM analysis. However, the SEM results revealed a significant formation of carbon deposits on the catalyst surface. The size of Ni NPs on the spent catalyst characterized by XRD results was ~36 nm, which is about twice the size of Ni NPs on the fresh Ni/SiC@Al₂O₃ catalyst. The limited stability of the catalyst against sintering is likely due to the high Ni/Al ratio (2.7) of the catalyst derived from the NiAl-LDH. The size of Ni NPs on the catalyst was large, which is unfavorable for both the catalytic activity and carbon formation. The MSR is structure sensitive, favoring small Ni particle sizes, while carbon formation is reported to increase with increasing particle size [27]. The precise control of Ni particle size and modulation of surface properties against sintering and coking is not covered in the scope of this work. Herein, we present the synthesis chemistry and methodology of heat- and mass-transfer-enhanced core-shell micro-structured catalysts with a highly thermal-conductive SiC core through charge-interaction induced heterogeneous hydrothermal formation of NiAl-LDH shell on SiC particles. The concept and methodology adopted for the preparation of Ni/SiC@Al₂O₃ catalyst derived from the SiC@NiAl-LDH core-shell with enhanced heat and mass transport properties presents new opportunities for various high temperature chemical reaction processes that requires facile heat and mass flux.

Figure 10. (a) Time-on-stream CH₄ conversion and (b) product H₂/CO selectivity (Δ) and CO/CO₂ selectivity ($\square$) by methane steam reforming at 873 K on the Ni/SiC@Al₂O₃ catalyst (S/C = 3.5, F/W = 137,000 mL h⁻¹ g_{cat}⁻¹).

Figure 11. (a) SEM image of the spent Ni/SiC@Al₂O₃ catalyst; (b) XRD spectra of the fresh and the spent Ni/SiC@Al₂O₃ catalysts.

3. Materials and Methods

3.1. Catalyst Preparation

The Ni/SiC@Al₂O₃ core-shell catalysts were prepared by hydrothermal reaction of precursor solution followed by calcination and reduction treatment. First, NiAl-LDH was formed on the SiC particles by hydrothermal reaction in an aqueous Ni and Al solution to construct the SiC@NiAl-LDH core-shell. Typically, 2.0 g of SiC powder (APS 9.3 μm, Alfa Aesar, Ward Hill, MA, USA) and 4.8 mL of polyethylene glycol 600 (Alfa Aesar) was added to 40 mL of deionized water, and the suspension was mixed in an ultrasonic bath. Then, 24 mmol of Ni(NO₃)₂·6H₂O (Alfa Aesar), 8 mmol of Al(NO₃)₃·9H₂O (Alfa Aesar), and 80 mmol of urea (Alfa Aesar) was dissolved in the solution, and the initial pH of the precursor solution was adjusted to a pH of 2 by adding diluted nitric acid (Junsei Chem. Tokyo, Japan). The hydrothermal synthesis with a teflon-lined autoclave (100 mL in volume) was conducted at 363 K for 10 h, steadily maintaining the temperature by proportional-integral-derivative (PID) control. The resulting powder was centrifuged (3000 rpm), washed with copious amount of water, filtered, and dried at 393 K for 12 h. The hydrothermal reaction was conducted at various initial pH solutions of 2, 5, and 8. Second, the resulting SiC@NiAl-LDH core-shell was calcined in air at 1023 K for 4 h and reduced in H₂ at 1023 K for 1 h to obtain the Ni/SiC@Al₂O₃ core-shell catalyst.

3.2. Characterization

The zeta potential of SiC was measured via suspension of the particles in water at various pH values ranging from 2 to 8 (Nanozetasizer, Malvern Panalytical, Malvern, United Kingdom). The pH of the suspension was adjusted by addition of diluted nitric acid (Junsei) and ammonium hydroxide (Alfa Aesar). The surface morphology and elemental composition of the samples were characterized using a field emission scanning electron microscope (FE-SEM, SU8010, Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS). The structure and composition of the catalysts were characterized using a field emission transmission electron microscope (TEM, Jeol, Tokyo, Japan) operated at 300 kV and equipped with an EDS. The size distribution of Ni NPs on the catalyst was characterized by image-analysis software (Image-pro-plus, Media Cybernetics, Rockville, MD, USA). The X-ray diffraction (XRD) pattern of the samples was obtained using a spectrometer (Smartlab, Rigaku, Tokyo, Japan) with monochromic Cu-Kα radiation operated at 45 kV and 200 mA (scan rate = 0.05° s⁻¹).

The overall elemental composition of the samples was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300 DV, Perkin Elmer). The N_2 adsorption-desorption isotherm of the samples was obtained in a volumetric unit (TriStar II, Micromeritics) after drying the samples in vacuum at 473 K for 4 h. The Brunauer-Emmett-Teller (BET) method was used to obtain the surface area from the isotherms. The micropore volume and mesopore size distributions were estimated by t-plot and Barrett-Joyner-Halenda (BJH) methods, respectively. The temperature-programmed reduction (TPR) of the samples was conducted in an automated volumetric analysis unit (AutoChem-II 2920, Micromeritics, Norcross, GA, USA), by raising the temperature of the sample from 298 K to 1100 K (ramp = 10 K min⁻¹) flowing 10 vol.% H_2 (50 mL min⁻¹, Ar balance).

3.3. Methane Steam Reforming

Methane steam reforming was conducted in a fixed-bed tubular quartz-glass reactor (OD = 10, ID = 8, L = 450 mm). The catalysts were pelletized (180–250 μ m), and 50 mg of catalyst was packed in the reactor using a fritted disk and a quartz wool. The reactor was placed vertically in a PID-controlled electric tubular furnace. The reactor temperature was measured using a K-type thermocouple attached to the outside wall of the reactor at the catalyst-bed zone. The catalysts were reduced by flowing 30 vol.%- H_2/N_2 (100 mL min⁻¹) at 1023 K for 1 h. The methane steam reforming reaction was conducted at atmospheric pressure by introducing 125 mL min⁻¹ of CH_4 and H_2O (steam/methane mole ratio = 3.5) using a HPLC pump (Series II, LabAlliance, New York, NY, USA). Nitrogen was fed together with the reactants as an internal standard. The effluent was passed through a condenser maintained at 273.4 K and analyzed online using a gas chromatograph (7890A, Agilent, Santa Clara, CA, USA) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

4. Conclusions

Supported Ni catalysts with significantly enhanced heat and mass transport properties can be prepared through hydrothermal reaction of metal salt precursors with highly thermal-conductive SiC particles, which results in the formation of SiC@NiAl-LDH core-shell microstructures. It was established that the interfacial charge interactions between the basic metal hydroxide complexes of NiAl-LDH and the SiC particle surface has significant effects on the formation of SiC@NiAl-LDH core-shell structure. The core-shell microstructure can be obtained only when the initial pH of solution is low enough to cause the surface charge of SiC particles to become positive. The calcination and reduction of SiC@NiAl-LDH leads to the formation of Ni/SiC@ Al_2O_3 catalysts with Ni NPs dispersed on the SiC@ Al_2O_3 core-shell support. The core-shell structure could provide an enhanced thermal conductivity ascribed to the SiC core and high mass-transport properties as a result of the petal-like shell morphology of the Al_2O_3 shell. The Ni/SiC@ Al_2O_3 catalyst was adopted for the methane steam reforming reaction and exhibited high catalytic activity for an extended reaction time. However, the catalyst suffered from considerable carbon deposition and sintering, which requires further studies regarding the modulation of Ni particle sizes, composition, and support properties for suitability in practical applications. Nevertheless, the methodology and chemistry of using highly thermally conductive and chemically stable SiC particles as a substrate for new core-shell microstructured catalyst are unprecedented and present new opportunities for catalytic reactions that require high heat flux and enhanced mass transport, in addition to high intrinsic catalytic activities.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/4/391/s1>, Figure S1: SEM and XRD analysis results of the NiAl-LDH prepared by the conventional homogeneous hydrothermal method.

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