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Full Length Article

Steering catalytic property and reactivity of Ni/SiO₂ by functionalized silica for dry reforming of methane



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ABSTRACT

The dry reforming of methane (DRM) is a promising catalytic reaction for converting greenhouse gases (CH₄ and CO_2) into valuable syngas. Despite the advantages of silica as a catalyst support, its inert nature limits its application in DRM due to reduced binding affinity with nickel. Here, we developed Ni-impregnated silica catalysts exhibiting a bimodal pore system in which silica supports were synthesized by tuning the ratio of aminopropyl triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS). The Ni/silica catalyst prepared by the intermediate concentration of APTES exhibited a unique combination of acidic and basic properties, enhancing DRM activity and catalytic durability. The catalysts displayed a favorable nickel size distribution, with smaller Ni particles in intermediate ratio silica, overcoming the limitations of conventional silica-based catalysts. Our findings demonstrate the suitable catalytic characteristics of Ni/synthesized-SiO₂ for the dry reforming of methane.

1. Introduction

The increasing CO₂ levels, which reached approximately 420 ppm at NOAA's Mauna Loa Observatory in 2023 [1], underscore the urgent need to address carbon emissions. Chemical conversion of CO₂ is a strategic approach to mitigate greenhouse gas emissions by transforming them into valuable chemicals and fuels. Dry reforming of methane (DRM) is a promising method to convert CO₂ and CH₄, major greenhouse gases, into valuable syngas for chemical synthesis and energy production [2]. The active metal components used in catalysts for DRM can be categorized into noble metals and non-noble metals. Numerous studies have demonstrated that noble metal-based catalysts offer exceptional catalytic performance and strong resistance to catalytic deactivation in DRM. However, due to the scarcity and high costs of noble metals, they are less competitive compared to non-noble metal catalysts [3,4]. Consequently, there is growing interest among researchers in non-precious metal catalysts that offer both high performance and cost-effectiveness. Among these, Ni-based catalysts stand out as the only transition metals that can match the catalytic activity of noble metals in DRM [3,4], and are considered a balanced alternative in terms of both economic viability and performance. In addition, Ni-based catalysts are central to this process due to their proficiency in activating C-H bonds and CO_2 [1]. However, the strong endothermic nature of the DRM and its susceptibility to catalyst deactivation through carbon deposition and nickel agglomeration present significant challenges [5].

In the context of DRM reactions, the size and dispersion of nickel are known to affect catalytic activity and stability. Smaller, uniformly dispersed Ni particles are advantageous in inhibiting coke formation [4, 6]. To optimize these parameters, many efforts have been directed towards improving metal-support interactions [7–9], augmenting Ni surface properties [10], and confining Ni within the cavities of micro- and mesoporous materials [2,11–13]. Beyond metal characteristics, surface properties of supports significantly impact resistance to carbon deposition; CH_4 activation typically occurs on Ni surfaces, while CO_2 activation is influenced by the support depending on its type [6]. Support materials possessing strong acidic sites, such as Al_2O_3 , are prone to facilitating carbon buildup through CH_4 decomposition, making them less favorable for DRM applications [6,14].

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Silica emerges as a compelling choice for DRM applications due to its inherent inertness and neutrality, significantly reducing concerns related to coke formation [15]. The inherent cost-effectiveness of silica, coupled with its remarkable thermal and chemical stability, enhances its suitability for this catalytic process. Additionally, imparting basic properties to inert silica could enhance the adsorption-dissociation of CO₂, and mitigate carbon deposition through the reverse Boudouard reaction ($C_{Ads.} + CO_2 \rightarrow 2CO$) [5,6,14]. However, the inert silica nature could compromise its binding affinity with nickel, potentially challenging the achievement of high nickel dispersion [16]. Despite the numerous benefits of silica as catalyst support, strategic modifications are essential to harness its full potential in DRM applications.

To overcome the weak interaction with nickel, many studies have applied ordered mesoporous silica supports such as SBA-15 [17,18], KIT-6 [18], MCM-41 [1,18] and SBA-16 [1,18]. These materials attempt to confine nickel particles within their regularly ordered pore structures to prevent sintering and coking. In particular, Ni supported on MCM-41 catalysts, which stably traps nickel in the pore, have been reported to exhibit high activity and stability [3,4]. The well-controlled silica structures show great potential as supports for Ni-based catalysts in DRM, offering enhanced durability and improved efficiency. However, they often fall short as the resulting materials possess electronically neutral frameworks, which still have weak binding affinity between nickel and silica. This weak interaction allows nickel sintering and reduces catalyst stability, ultimately limiting the long-term effectiveness of the catalysts in DRM applications [1]. Using zeolites as supports, which have acidic pore structures due to the inclusion of aluminum in their framework, can increase the affinity between nickel and the support [19]. However, zeolite structures often collapse under DRM reaction conditions, and the high concentration of acid sites can accelerate coke formation, compromising catalyst stability [19]. Therefore, it is critical to develop modified silica supports to achieve high nickel dispersion, precise control of particle size, and strong interactions between nickel and silica to enhance catalytic performance and stability.

This study aims to design Ni-supported on functionalized silica catalysts by tuning the functionalizing agent (APTES) ratio to the silica backbone agent (TEOS) for the DRM reaction. By meticulously tuning the alkoxysilane composition, we intended to elucidate the intricate relationship between the silica support structure, nickel particle dispersion, catalytic activity, and stability. This approach is expected to uncover the pivotal role of support modification, particularly through APTES-induced surface functionalization, in enhancing CO_2 adsorption and activation, which is a critical step in DRM. Through a combination of temperature-dependent activity assessments, durability tests, and advanced characterization techniques, we identify catalyst formulations that exhibit optimal performance in DRM, thereby contributing to developing more efficient and sustainable catalytic systems for DRM.

2. Experimental

2.1. Synthesis of silica as a function of APTES and TEOS ratio and Nisupported catalysts

In this study, commercial silica (fumed SiO₂, S_{BET}=225 m²/g), tetraethyl orthosilicate (TEOS), aminopropyltriethoxysilane (APTES), oleic acid (OA) and Ni(NO₃)₂•6H₂O (Nickel (II) nitrate hexahydrate) were used. All analytical grade chemicals were obtained from Sigma-Aldrich and used without additional purification.

The proportioned silica was synthesized by the sol-gel method using two alkoxysilanes. Silica precursors were mixed according to the molar ratio (Table S1), and the amine-functionalizing agent (APTES) was increased to 5, 15, 25, 35, 50, 65 and 85 mol.%. The mixture of silica precursors was added in deionized (D.I.) water (57 mL) dispersed with oleic acid (2 mmol) and aging at 80 °C for 12 hours under vigorous stirring. The mixture was dried at 80 °C and calcined at 800 °C (1 °C/min) for 2 h under air. The prepared silica samples were named A/T

(0.1), A/T(0.2), A/T(0.3), A/T(0.5), A/T(1.0), A/T(1.9) and A/T(5.7) according to the molar concentration of the functionalizing agents: APTES to TEOS.

A series of Ni/SiO₂ catalysts with a nickel content of 5 wt.% were prepared using the conventional wet-impregnation method. First, a specific amount of synthesized silica powder was dispersed in 50 mL of deionized water. Subsequently, 50 mL of Ni(NO₃)₂•6H₂O solution was added to the silica dispersion. After thorough mixing, the sample was dried at 80 °C with vigorous stirring and then calcined at 800 °C for 2 hours in a muffle furnace. For comparison to a reference catalyst, Ni impregnated on commercial silica (Ni/com-SiO₂) was prepared using the identical procedure.

2.2. Characterization

The surface area and porosity of fresh and spent catalysts were evaluated using N₂ physisorption at -196 °C by a Micromeritisc ASAP 2020 (MicrotacBEL Corp.) analyzer. The Brunauer-Emmett-Teller (BET) method was employed to calculate specific surface areas and average pore diameters, while pore volumes were determined using the Barrett-Joyner-Halenda (BJH) method.

A high-resolution dual Cs compensated transmission electron microscope (HR-STEM) coupled with an energy dispersive X-ray spectroscope (EDS) (JEOL, JEM-ARM300F2) was utilized to examine particle size, crystal structure, and Ni particle distribution. Samples were prepared by dissolving in ethanol, sonicating overnight, and then depositing on carbon-coated copper grids and dried at 80 °C. The metal particle size of the different catalysts was estimated by measuring the size of 130 particles.

To investigate reduction properties and acid/basic site distribution of catalysts, H₂-temperature program reduction (H₂-TPR), temperature program desorption of CO2 or NH3 (CO2-TPD and NH3-TPD) were performed using BELCAT II (MicrotacBEL Corp.). The H2-TPR analysis was conducted as follows: (a) Ar purging (50 $\text{cm}^3 \text{min}^{-1}$) for 1 hour at 700 °C, (b) cooling down to 30 °C in a pure Ar flow and maintaining the feed for 30 min, (c) introducing 10% H₂/Ar (50 cm³·min⁻¹) into the feed, with temperature ramping from 100 to 800 °C at a rate of 1 °C/min. The CO₂-temperature programmed desorption (CO₂-TPD) was carried out to identify the acidity/basicity of catalysts as follows: (a) pretreatment at 500 °C for 1 hour in a flow of pure He, (b) cooling down to 100 °C in a flow of pure He, (c) CO_2 adsorption with 1% CO_2 /He for 1 hour, (d) purging sample with pure He flow to remove physically adsorbed CO₂ and (e) CO₂ desorption from 100 to 500 °C with pure He flow at a rate of 1 °C/min. The NH₃-temperature programmed desorption (NH₃-TPD) was performed with 5% NH₃/He.

X-ray diffraction (XRD) patterns were analyzed to identify the crystal structure and composition of fresh and reduced samples. The data were obtained using a high-resolution X-diffractometer (SmartLab, Rigaku) equipped with a Cu target K α X-ray source at an accelerating voltage of 40 kV and a current of 30 mA with a scan rate of 8° min⁻¹ over 2 θ ranging from 10° to 80°.

Surface IR analysis of the synthesized material was performed using NICOLER IS50 FT-IR (Thermo Fisher Scientific) equipped with the MCT detector. The spectrum was obtained from 500 cm^{-1} to 4000 cm^{-1} at 35 °C under pure N₂ flow, and the background spectrum was collected using KBr.

X-ray photoelectron spectroscopy (XPS) was performed on a NEXSA (Thermo Fisher Scientific) system with monochromatic Al K α gun (200 eV) radiation as an excitation source to examine the formulation of chemical components and their valence states on the catalyst surface. The binding energy (B.E.) was measured based on carbon contamination utilizing a C1s peak centered at 284.8 eV as a reference.

The pH change of the silica solution as a function of the formulation was measured using a pH meter (Thermo Scientific, ORION STAR A111 pH meter). Before the measurement, the pH was calibrated using a buffer standard solution with pH values of 4, 7, and 10. All pH values

were measured under constant stirring.

The zeta potential (Solid Surface Zeta Potential Measurement System, Photal OTSUKA ELECTRONICS) was measured to confirm the degree of particle dispersion according to the surface properties of silica. Before the measurement, the synthesized silica powder (before and after calcination) was dispersed in DI water (20 mL) and sonicated for 10 min. After that, the surface charge distribution according to the pH of the solution was confirmed.

To evaluate the amount of carbon coking, a thermogravimetric analysis (TGA) was performed employing thermogravimetric analysis and differential scanning calorimetry (TGA-DSC, LABSYS EVO STA). The tested catalysts were placed in a ceramic crucible and subjected to a heat treatment from 20 °C to 900 °C with a ramp rate of 10 °C/min in air (100 mL·min⁻¹). The weight loss (%) detected from 100 °C was considered as the loss of carbon in the tested catalysts.

2.3. Catalytic reactions

Catalytic activities were carried out in a fixed-bed reactor using a quartz tube. The quartz tube was filled with catalyst (20–30 mesh, 0.2 cc) and placed in the center of the reactor. The thermocouple close to the catalyst bed was used to monitor the reaction temperature. For the steady-state test, a feed gas stream consisting of 30 vol.% CH₄, 30 vol.% CO₂, and 40 vol.% Ar balance was introduced with 250 L·g⁻¹_{cat}·h⁻¹ of gas hourly space velocity (GHSV). Prior to the activity test, the catalysts were pretreated with 10 vol.% H₂/Ar at 700 °C (ramp 20 °C/min) for 1

hour, followed by Ar purging at the same temperature. The temperaturedependent activity tests were performed at intervals of 50 °C from 500 to 850 °C (ramp 5 °C/min) while maintaining each temperature for 1.5 hours. The stability tests were performed during 12 hours and 55 hours, respectively, at 800 °C of reaction temperature and 250 Lsg_{cat}^{-1} ·h⁻¹ of GHSV with standard feed composition. The flow rates of the gases were controlled by mass flow controllers (MFC, Brooks), and the composition of outlet gas was analyzed online by a gas chromatography (ChroZen GC system, YOUNG IN) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

3. Results and discussion

3.1. Characteristics of synthesized silica by APTES/TEOS

Depending on the amine concentration (Table S1), the synthesized silica maintained a consistent amorphous SiO₂ phase across all specimens [11,13,20], as evidenced by XRD analysis (Fig. S1). However, their morphologies varied significantly with the base concentration in the sol-gel process, transitioning from characteristic spherical particles to bulk structures as a direct function of the APTES concentration (Fig. 1a). Specifically, in TEOS-dominant conditions (APTES < 50 mol.%), spherical silica was formed, the size of which decreased from *c.a.* 350 nm to *c.a.* 20 nm as the concentration of APTES increased from 5 mol.% to 35 mol.%, accompanied by particle aggregation (Fig. 1a). On the other hand, at functionalization agent (APTES) concentrations equal to



Fig. 1. (a) TEM images of silica as a function of APTES/TEOS ratio, (b) zeta potential of before and after calcination silica, (c) surface IR analysis and (d) BJH plots of silica depending on amine group concentration in sol-gel reaction.

or greater than the backbone agent (TEOS), silica exhibited bulk growth, indicative of a homogeneous phase. Notably, a yolk-shell morphology was exclusively observed in the A/T(0.1) silica (Fig. 1a), synthesized via the microemulsion method, suggesting the completion of TEOS and APTES condensation reactions at the oil-water interface [21,22]. The unique yolk-shell shape observed only in the A/T(0.1) silica underscores the importance of the ratio of the two agents in determining silica morphology.

The pH values (Table S2) and zeta potential (Fig. 1b and Table S3) were investigated to explore the chemical environment and surface charge of silica particles before and after calcination. As the ratio of amine-functionalizer increases, pH and zeta potential of the solution after the sol-gel reaction changed from 7.1 to 9.6 and from -24.22 to -3.26, respectively. This trend is due to the protonated APTES produced by the hydrolysis (APTES + $H^+ \rightarrow APTES-H^+$), and the protonated amine (NH³⁺) distributed on the gel surface. Calcining APTES-dominant silica (APTES > 50 mol.%) in air at 800 °C oxidizes the ammonium ions, leaving behind Si-OH bonds on the surface, thereby rendering a more negative zeta potential. The presence of surface silanol groups in these APTES-dominant samples was confirmed through FT-IR spectroscopy (Fig. 1c). The TEOS-dominant silica (APTES < 50 mol.%) showed stronger bands assigned to Si-O-Si (1200, 1104-1070 and 1058-1038 cm⁻¹) [23–25] compared to APTES-dominant counterparts, suggesting complete condensation of TEOS and APTES (Fig. 1c). The bands at around 936-961 and 856 cm⁻¹, corresponding to Si-OH [22,23,26], were more prominently observed compared to Si-O-Si in APTES-dominant silica. In contrast, those species were not distinct in much higher frequency numbers above 3600 cm^{-1} . This is attributed to abundant protonated amine groups.

The difference in porous structure between the synthesized silica and commercial silica was characterized using N2 adsorption-desorption isotherms (Table S4 and Fig. S2). Commercial silica exhibited a type III isotherm with large pores and weak hysteresis, while the synthesized silica, influenced by the concentration of amine groups, revealed distinctive morphologies. Silica series samples with an equal and predominant proportion of functionalizers (A/T(1.0), A/T(1.9) and A/T (5.7)) exhibited type I isotherm with plateauing at high pressure, indicative of a microporous structure with a uniform pore size of approximately 2 nm, consistent with TEM analyses. Conversely, silica samples with an APTES concentration less than equal mol percent of TEOS displayed type IV isotherm typical of mesoporous structure, accompanied by pronounced hysteresis loops that intensified with increasing backbone agent concentration. Specifically, the A/T(0.1)sample exhibited an H4 hysteresis loop, while both A/T(0.3) and A/T (0.5) displayed H3 hysteresis loops. A/T(0.2) showed hybrid characteristics, with both the sloping hysteresis of H3 and the plateau region of H4 at $0.9 < P/P^0$, suggesting a transitional structure combining characteristics of both H3 and H4 types. This transitional behavior of A/T (0.2) represents an intermediate structural evolution between A/T(0.1)and A/T(0.3), allowing the gradual changes in porous structure to be followed as a function of amine group concentration. Particularly, noteworthy was the bimodal structure (Fig. 1d), which arose from two different formation mechanisms influenced by the concentration of functionalizing agent. The smaller mesopores were generated by controlled general hydrolysis and condensation of the silica precursor. Larger mesopores were voids formed due to the aggregation of these spherical particles, contributing to the larger mesopore size. The formation mechanism and shape of silica, depending on APTES concentration, will be discussed in detail later. Compared to unimodal structures, bimodal structures with increased surface area and pore volume offer significant advantages for catalytic applications by facilitating reactant access to active sites through larger mesopores, thereby enhancing catalytic efficiency [27,28]. The size difference between the two pores became more pronounced as the concentration of APTES increased up to 35 mol.%.

attributed to the behavior of the amine groups in the sol-gel reaction. In the microemulsion system in which all silica samples were in common, amphiphilic APTES precursor, present at the oil-water interface, hydrolyzed to yield APTES-H⁺ (APTES + $H_2O \rightarrow APTES-H^+ + OH^-$) [21]. The resulting OH⁻ ions launch a nucleophilic attack on the most electropositive Si atoms of TEOS [29], initiating the hydrolysis of TEOS $(\equiv$ Si-OEt + OH⁻ $\rightarrow \equiv$ Si-O-Si \equiv + EtOH, where Et represents the ethyl group [21,30,31]). At the oil-water interface, the two hydrolyzed alkoxysilanes (protonated APTES [21,29,30] and deprotonated TEOS [21,30,31]) aggregate by electrostatic attraction and condensation is completed. In TEOS-abundant silica, the hydrophobic TEOS behavior was dominant, with the hydrolysis-condensation occurring mainly in oil droplets (oil in water emulsion) to form spherical silica (Fig. 1a), which grew into agglomerated spheres due to electrical interaction between protonated APTES and deprotonated TEOS. The more constrained ratio of APTES contents (APTES < 5 mol.%), led to the completion of the condensation reaction at the oil-water interface, resulting in the formation of a shell (A/T(0.1)) (Fig. 1a). In contrast, APTES-abundant silica grew in a homogeneous bulk form through the diffusion of protonated APTES into the continuous phase under hydrolysis. A high concentration of APTES is beneficial for achieving a lower zeta potential (Fig. 1b and Table S3), which enhances the binding affinity with nickel. However, for developing a bimodal pore structure with increased surface area and pore volume, a lower concentration of APTES is advantageous. This paradox suggests an optimal concentration of APTES that balances these properties, thereby maximizing nickel dispersion and improving catalyst performance.

3.2. Ni on synthesized silica catalysts

After systematically identifying synthesized silica supports without impregnating Ni, we also examined the characteristics of Ni impregnated on silica catalysts. The XRD patterns revealed the characteristic nickel oxide (NiO) peaks on the silica after nickel impregnation [9], as shown in Fig. S3. The peaks at 37.3°, 43.3°, 62.8°, 75.4° and 79.4° can be assigned to NiO crystalline planes of [111], [200], [220], [311] and [222], respectively (Fig. S3). The broad peak at $2\theta = 21^{\circ}$ was the signal of amorphous silica. The signal of Ni/com-SiO₂ catalyst appears stronger than that of amine-functionalized silica catalysts due to the presence of NiO particles with a highly distinct crystallinity. With an increasing concentration of amine-group, the average crystallite size across all NiO planes increased (Table S5), as calculated by the Scherrer equation. The TEOS-enriched (APTES < 50 mol.%) catalysts had smaller Ni sizes than the APTES-enriched catalysts.

The morphologies of Ni catalysts supported on synthesized silica (A/ T ratio) and commercial silica (Ni/com-SiO₂) are compared in Fig. 2a and S4, respectively. In the Ni/com-SiO2 catalyst, hexagonal nickel particles with distinct crystal planes were placed on silica particles without interacting with the support (Fig. S4). This lack of interaction was due to insufficient dispersion of NiO particles into a macropore structure (Fig. 2d) with collapsed pore structure after nickel loading. On the other hand, the functionalized silica maintained its morphology, changing from a spherical shape to a bulk shape depending on the amine concentration (Fig. 2a), even after Ni loading. Except for the yolk-shell silica, nickel particle size generally decreased with increasing basicity when APTES was equal to or less than the backbone agent, a trend that reversed at higher APTES concentrations (Fig. 2b). The nickel particles loaded on the yolk-shell silica (A/T(0.1)) had the smallest size of 9.3 nm and a narrow range of particle size distribution compared to those on the other silica supports. These nickel particles turned out to be located inside the yolk-shell, evidenced by the EDS line scan profile (Fig. S5).

The comparative surface IR profile of the yolk-shell silica (A/T(0.1)) revealed negligible changes upon nickel loading (Fig. 2c), suggesting minimal interaction between the nickel particles and the silica shell, corroborating their encapsulation within the shell.

The ratio-dependent unique bimodal pore structure of our silica is

Comparing TEM images, nickel particle sizes on TEOS-dominant and



Fig. 2. (a) TEM images of Ni on silica catalysts, (b) nickel particle size distribution, and (c) surface IR and (d) pore size distribution for comparison before (dot line) and after nickel-impregnation on silica (solid line).

APTES-dominant silica supports typically exceeded 50 nm (Fig. 2a and b), respectively. Interestingly, Ni-supported on silica with intermediate APTES concentrations, A/T(0.5) and A/T(1.0), induced two distinct nickel particle sizes: a smaller one (c.a. 14 nm) in the mesopore structure and a larger one (over 40 nm) on the surface of the silica (Fig. 2b). Notably, the small Ni particles in these intermediate ratio silica samples were smaller than those in the TEOS-enriched catalysts, contrasting with the XRD results (Table S5). This paradoxical observation is likely due to XRD calculating the average Ni size (Table S5), where both large and small Ni particles are counted in the intermediate ratio ((A/T(0.5) and A/T(1.0)) (Fig. 2a and b). Thus, the negatively charged surface generated by APTES can increase the dispersion of the supported NiO particles.

The amine concentration in the silica synthetic solution also influenced the nickel particle size distribution. TEOS-dominant silica catalysts exhibited narrower distributions than APTES-dominant silica catalysts, which widened with increasing APTES concentration (Fig. 2b). The presence of nanosized particles (c.a. 1.8 nm) (Fig. 2a and b) on APTES-dominant silica (A/T(5.7)) indicates that the nickel ions (Ni²⁺) were able to penetrate the micropores due to their extremely negative charged surface of silica, as measured by zeta potential (Fig. 1b). However, the contribution of small Ni nanoparticle in TEM images was greatly reduced (Fig. 2a and b) when APTES/TEOS ratio increase over 1 (A/T(1.9) and A/T(5.7)). This is likely due to the significant collapse of pore structure in APTES-dominant silica samples after nickel impregnation. The pore sizes either shrank or enlarged significantly as indicated by Barrett-Joyner-Halenda (BJH) analysis (Fig. 2d), while N2 adsorption-desorption isotherms showed a transition from type I microporous structure to type IV (Fig. S6). The severe decrease in

surface area from 450 to 340 m²·g⁻¹ to ~120 m²·g⁻¹ further supported the collapse of the porous structure (Table S4). In contrast, TEOS-rich silica samples underwent moderate structural alterations, maintaining their type IV isotherms while transitioning from bimodal to unimodal pore configurations post-nickel impregnation (Fig. 2d and S6). A/T(0.2) showed its original hysteresis, A/T(0.1) exhibited a slightly enhanced hysteresis loop (Fig. S6), which could be attributed to the formation of additional mesoporous channels resulting from the interaction between nickel particles and silica framework during the impregnation process. Interestingly, silica with intermediate APTES concentration (A/T(0.5) and A/T(1.0)) had a stable bimodal pore structure with identical N₂ adsorption-desorption patterns even after the nickel loading, accommodating two distinct nickel particle sizes: a smaller one (*c.a.* 14 nm) likely within the mesopore structure and a larger one (over 40 nm) on the surface of the silica (Fig. 2b and S6).

The strong interaction of the Ni cation with APTES-dominant silica can be inferred from the negative zeta potential derived from the hydroxyl group (Table S3). This electrostatic interaction allows the nickel cations to be dispersed uniformly within the silica pores. This led to welldispersing nickel particles, *c.a.* 1.9 nm, particularly in silica with an APTES concentration greater than 35 mol.% (Fig. 2a and 2b). The comparative FTIR before and after nickel impregnation (Fig. 2c) further demonstrated the interaction of nickel with the APTES-enriched silica surface. The consumption of bands at 1104–1070, 1058–1038 and 794 cm⁻¹, corresponding to the Si-O-Si bond and at 960 and 956–936 cm⁻¹ related to the Si-OH band upon Ni addition, suggested the binding of Ni ions to the silica framework. In particular, the consumption of Si-OH bands indicates the possibility of Ni(OH)₂ species formation through the interaction between surface hydroxyl groups (Si-OH) and Ni²⁺ (Ni²⁺ + 20H[−] → Ni(OH)₂). This effect became more pronounced with the increase of concentration of amine groups in the synthesis solution (i.e. APTES). This interaction was particularly distinct for silica samples with amine functional group concentration exceeding 50 mol.%. The minimal consumption of the bands related to OH groups implies that abundant hydroxyl groups still remain on the silica surface even after nickel doping. These OH groups, characteristic of APTES-dominant silica, contribute to the diversity of nickel species on silica, reflecting the complex interplay between nickel incorporation and the silica matrix.

To elucidate the variety of Ni species present within each catalyst, the Ni 2p XPS was collected (Fig. 3a and Table S6). The XPS of the Ni 2p orbital was deconvoluted into three peaks, and the peaks at c.a. 855, 856 and 857 eV correspond to NiO (nickel oxide), Ni(OH)₂ (hydroxylated nickel) and NiOOH (nickel oxide hydroxide), respectively [9,32,33]. The proportion of NiOOH and Ni(OH)2 increased with increasing concentration of APTES (Table S6). The Ni(OH)₂ species distributed with amine group concentration were partially converted to NiOOH by oxidation during calcination at 800 °C in air condition (Ni(OH)₂ \rightarrow $NiOOH + H^+ + e^-$), and the ratio of $Ni(OH)_2$ and NiOOH enriched with increasing APTES concentration. This reflects the zeta potential (Fig. 1b and Table S3) and surface IR (Fig. 2c) results, indicating that the hydroxyl groups increasing with APTES concentration induce and enhance nickel-silica interactions. However, the silica samples with an APTES/-TEOS ratio greater than 1 (A/T(1.9) and A/T(5.7)) did not follow the trend, likely due to the reduced availability of hydroxyl groups originating from a decrease in the BET surface area (Table S4) along with the collapse of the porous structure. The Ni/com-SiO₂ catalyst also contains NiOOH and Ni(OH)₂ species with large negative zeta potential (Table S3). However, the proportion of these species was lower than functionalized silica catalysts. These observations are consistent with TEM images and BET analysis showing weakly interacting NiO particles with collapsed pore structures. The H2-TPR was applied to identify and quantify nickel oxide species (Fig. 3b and Table S7). The TEOS-rich silica catalysts showed a large reduction peak around 300-400 °C, related to NiO species. As the APTES ratio increases, Ni-supported silica samples with APTES > 50 mol.% show reduction peaks from 200 to 300 °C, which are estimated to be NiOOH (Ni³⁺) to hydroxyl Ni (Ni²⁺) reduction. The A/T(5.7) catalyst did not show any reduction around 200 °C because (Fig. 3b), as mentioned above, the reduction of Ni³⁺ species was circumscribed by the collapse of the porous structure of the silica (Fig. 2d). This observation is consistent with the trend in NiOOH and Ni (OH)₂ proportions, calculated from the surface atomic concentrations of nickel species in XPS (Table S6). This trend is concordant with interactions between nickel species and silica interaction by hydroxyl groups. The surface modification of silica by APTES increased an

abundance of hydroxyl groups, leading to a high dispersion of active metals with small size (c.a. 1.9 nm) and strong interaction with silica. Therefore, the basicity of silica could impart properties which are resistant to catalyst deactivation (sintering) in the dry reforming of methane. However, it is noteworthy that excessively high concentrations of APTES can lead to the collapse of the pore structure, resulting in the formation of larger particles.

The basicity of the samples measured by CO₂-TPD is shown in Fig. 3c. The Ni/com-SiO2 catalyst exhibits no peaks across the entire temperature range, indicating neutral acidic/basic surface properties. On the other hand, the functionalized silica catalysts have three distinct categories of basic sites in different temperature ranges: 200 °C < T (Region I), 200 °C < T < 400 °C (Region II) and T < 400 °C (Region III) [34,35]. TEOS-enriched silica clearly distinguishes three types of basic sites. In particular, the strong basic site, which is a metal-oxygen pair and low coordination O⁻ [34], is formed by Ni loading. The samples based on APTES-enriched silica showed a prominent peak at intermediate temperatures with an overlap between the weak and medium basic sites. The prevalence of weakly basic sites is attributed to the prominent surface OH groups observed in FTIR (Fig. 2c). In comparison, the medium basic sites are attributed to the formation of bidentate carbonates on coordinately unsaturated nickel oxides (NiOOH and Ni(OH)₂) confirmed by XPS (Fig. 3a) and H2-TPR (Fig. 3b) [36]. The APTES treatment modified the quantity and distribution of basic sites on Ni-impregnated silica, potentially positively affecting the DRM performance, which will be discussed further.

To further investigate the surface acidity of the Ni-loaded silica catalyst, NH₃-TPD (Fig. 3d) was employed. The Ni/com-SiO₂ catalyst also shows a marginal adsorption profile over the entire temperature range due to its inert properties. All functionalized silica samples exhibited broad desorption peaks at temperatures below 300 °C (Region I), indicating the presence of weakly acidic sites. The weak acid sites are associated with slight acidity of silica supports [37]. Medium acid sites around 300 °C are observed in the intermediate ratio silica catalysts. According to Ni XPS calculations, they are attributed to a higher amount of NiOOH than in the APTES- or TEOS-dominant silica (Fig. 3a and Table S6) [38]. The TEOS-dominant silica displayed large desorption peaks above 300 °C (Region II), indicating the presence of significant medium acidic sites. Conversely, the APTES-dominant silica sample showed relatively low levels of medium acid sites, presumably due to the highly dispersed Ni, which may neutralize Brønsted acid sites. Given that catalyst acidity is often implicated in carbon deposition [39,40], leading to catalyst deactivation, it is expected that TEOS-dominant silica with high acidity would be significantly influenced by coking.



Fig. 3. (a) XPS analysis for Ni 2p, (b) H₂-temperature programmed reduction, and temperature programmed desorption for (c) CO₂ and (d) NH₃ of Ni/SiO₂ catalysts.

3.3. Catalytic activity and stability of dry reforming of methane

Fig. 4a-c shows the temperature-dependent activity of CH₄ and CO₂ conversions and the corresponding product ratio (H₂/CO) during the dry reforming of methane (DRM). Consistent with thermodynamic expectations, both CH₄ and CO₂ conversions increased with increasing temperature, regardless of the type of catalysts. The Ni on A/T controlled catalysts outperform the benchmarking Ni catalyst, Ni on com-SiO₂. At 650 °C, the Ni-supported silica with the A/T(1.0) exhibited the highest CH_4 and CO_2 conversions, while at all other temperatures, the A/T(0.5) catalyst performed better than other catalysts. Contrary to expectations based on the characterizations due to enhanced weak/medium basic sites and facile redox properties by various nickel oxides on APTESdominant silica, these catalysts did not exhibit higher DRM activity than TEOS-dominant silica. This discrepancy can be attributed to the degradation of the high surface area characteristic of APTES-dominant silica, which possesses a microporous structure that was compromised following nickel integration, thereby restricting access to active sites. On the other hand, TEOS-dominant silica catalysts exhibited relatively stable pore structure even after nickel impregnation, despite weak interactions between the large nickel particles and silica. This finding is consistent with a previous report by Mohidem et al. [41] that TEOS contributed more to the structural stability of silica than APTES. The superior DRM activity of the samples with the intermediate APTES concentration can be attributed to its unique pore structure and the high concentration of hydroxyl groups on the silica surface. After adding nickel to silica, the preserved bimodal pore structure maintains a large surface area, providing an improved reactant gas pathway. In the meantime, the surface hydroxyl groups allowed the well-dispersed Ni to interact strongly with silica, facilitating the dissociative adsorption of CO_2 and relieving carbon formation [42,43].

The stability (Fig. 4d-f) for the DRM reaction was also evaluated under conditions at 800 °C for 12 hours. The Ni/com-SiO₂ catalyst exhibited a rapid decrease in CO₂ conversion from 60% to 35%, indicating poor initial conversion and unstable performance. TEOSdominant (A/T(0.2)), intermediate APTES condition (A/T(0.5)), and APTES-dominant (A/T(5.7)) silica-based catalysts showed initial CO₂ conversions of 74%, 96%, and 70%, respectively. This observation is well consistent with the temperature-dependent tests. However, the CO_2 conversion for A/T(0.2) and A/T(5.7) catalysts decreased to 63% and 55%, respectively. In contrast, the catalyst with intermediate ATPES-TEOS silica maintained its activity with a negligible decrease in CO_2 conversion from 94% to 90%.

Thermogravimetric analysis (TGA) was conducted on these catalysts after the stability tests to assess carbon deposition (Fig. S7). The most significant weight reduction was observed in the Ni/com-SiO₂ catalyst at 13.1%, followed by 11.5% for A/T(5.7) and 9.3% for A/T(0.2). A/T(1.0) experienced a weight loss of 7.8%. In contrast, A/T(0.5), which exhibited the most stable DRM activity, showed the smallest weight reduction at just 2.9%. In addition to the 12-hour tests, the A/T(0.5) and A/T(1.0) catalysts were subjected to long-term durability tests over 55 hours (Fig. S8). The A/T(0.5) catalyst initially exhibited a CO₂ conversion of 96%, with only a slight decrease to 94% after 55 hours. Meanwhile, the A/T(1.0) catalyst showed a decrease in the CO_2 conversion from 93% to 85%, a trend consistent with the 12 hours of stability test results. TGA analysis following the long-term durability tests (Fig. S9) revealed weight losses of 7.5% for A/T(0.5) and 13.3% for A/T(1.0). These results further confirm the superior stability and lower carbon deposition of the A/T(0.5) catalyst. This resilience against deactivation is likely due to the facile dissociative adsorption of CO₂ at weak/medium basic sites in the A/T(0.5) catalyst, along with the improved nickel dispersion facilitated by the hydroxyl-rich silica surface, as mentioned above. Furthermore, the stable bimodal structure induced excellent DRM activity and stability by providing a rapid diffusion pathway and ensuring a wide dispersion of active metals, as summarized in Fig. 5.

4. Conclusion

We have synthesized silica supports by adjusting the ratio of two alkoxysilanes (TEOS and APTES) to impart chemical properties (acid/base) to typically inert silica, followed by nickel impregnation. The physicochemical properties of silica were significantly influenced by the protonated APTES (APTES⁺) intermediate during the silica synthesis (sol-gel process). Under APTES-dominant conditions, the silica formed a bulk silica with a bimodal structure, whereas under TEOS-dominant conditions, it formed a spherical silica with a mesoporous structure.



Fig. 4. (a-c) DRM activity of Ni/SiO₂ catalysts under gas flowing of 30 vol.% CH₄, 30 vol.% CO₂ and 40 vol.% Ar. (d-f) Stability tests at 800 °C for 12 hours.



Fig. 5. Characteristics and catalytic activity of Ni on silica catalysts as a function of amine (NH^{3+}) group content in alkoxysilanes, illustrating changes in morphology, surface area, acidity/basicity and nickel species distribution.

Silica synthesized with intermediate ratios of APTES and TEOS showed a bimodal structure characterized by aggregation of spherical silica containing both large and small mesopores. Nickel particle sizes varied significantly depending on the functionalizer concentration. In TEOSenriched silica, nickel particles were generally larger and more uniformly distributed. Conversely, APTES-dominant silica showed a broad distribution of nickel particle sizes, with nanosized particles (approximately 1.8 nm) due to the extremely negatively charged surface, which enhanced nickel dispersion. However, the APTES-dominant silica also experienced significant pore structure collapse after nickel impregnation, leading to larger nickel particles and reduced surface area. Interestingly, silica with intermediate APTES/TEOS ratios combined the benefits of both approaches, maintaining a bimodal pore structure and accommodating both small (approximately 14 nm) and large (over 40 nm) nickel particles.

In APTES-dominant silica, nickel oxides exhibited various states, including NiO, hydroxylated Ni and NiOOH, which showed strong interactions with silica, also producing weak/medium basic sites. In contrast, TEOS-rich silica showed a predominance of strong acidic sites, significantly affecting catalyst deactivation. Silica synthesized at an intermediate ratio incorporated APTES- and TEOS-rich silica characteristics. Nickel oxides interacted strongly with silica through surface hydroxyl groups to promote the weak and medium basic sites, which enhanced CO_2 adsorption-dissociation. Additionally, the presence of dispersed nickel mitigates the impact of strong acidic sites on catalyst deactivation.

Overall, fine-tuning the APTES/TEOS ratio significantly steers the structural and chemical characteristics of porous silica, optimizing the dispersion and interaction of nickel oxides. This approach will provide a promising methodology for preparing highly efficient and stable catalysts using silica as a catalyst support.

CRediT authorship contribution statement

Haehyun Min: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. Ye Jin Ji: Formal analysis, Data curation. Do Yeong Kim: Formal analysis, Data curation. Yangguen Ju: Formal analysis, Data curation. Chang Geun Yoo: Investigation, Data curation. Young Jin Kim: Writing – original draft, Investigation, Funding acquisition, Formal analysis. **Sung Bong Kang:** Writing – original draft, Supervision, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apsadv.2024.100663.

Data availability

Data will be made available on request.

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