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Regulation of Ni-CNT Interaction on Mn Promoted Nickel
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nanotube; methanation

ABSTRACT: Mn promoted Ni nanoparticles (NPs) supported on oxygen-functionalized carbon nanotubes (CNTs) was synthesized for CO₂ hydrogenation to methane. This novel metal-carbon catalytic system was characterized by both experimental and computational studies. An anomalous metal-support interaction mode (*i.e.* a higher temperature would lead to a weakened Ni-CNT interaction) was observed. Deep investigation confirmed that surface oxygen groups (SOGs) on CNTs played a key role in tuning the Ni-CNT interaction. We proposed that high calcination temperature would firstly lead to the decomposition of SOGs (> 400 °C), then causing a loss of anchoring sites and the anchoring effect of SOGs on Ni NPs, thus cutting off the connection between interfacial Ni atoms and CNT body, so resulting in the migration and coalescence of fine flat Ni NPs into larger sphere ones at 550 °C (geometric effect). Density functional calculation (DFT) study clarified this kind of anchoring effect stemmed from the formation of covalent bonding between interfacial Ni atom and C or O elements of SOGs, causing electrons transferred from Ni atoms to CNT support because of the intrinsic electronegativity of -COOH (electronic effect). Besides, Mn promotion notably boost the activity compared with unpromoted catalysts, which was irrelevant with the size effect but the enhanced CO₂ adsorption and conversion according to the result of CO₂-TPD and transient response experiment. The optimized NiMn350 catalyst endowed with Mn promotion and robust Ni-CNT interaction, showed both high activity and sintering resistance more than 140-hour. Our findings paved the way to reasonably design the metal-carbon catalyst with both high activity and stability.

1. INTRODUCTION

Greenhouse effect caused by the ever-growing atmospheric CO₂ concentration has posed a serious threat to our human life. Great effort has been made on reducing the atmospheric CO₂ concentration through the strategy of physical capture/storage or chemical conversion of CO₂. Obviously, it is more attractive to convert CO₂ as the free carbon source into the valuable product like methane, methanol and olefins.¹⁻³ Among various reactions, the catalytic conversion of CO₂ into methane (CH₄) is regarded as an alternative and potential application to realize the efficient chemical utilization of CO₂ in virtue of its favorable thermodynamics and mild reaction condition.^{4,5}

Numerous previous studies concentrated on the traditional metal-metal oxide (M-M_xO_y, M = Ni,⁶ Ru,⁷ M_xO_y = Al₂O₃,⁸ SiO₂,⁹) catalytic system for CO₂ selective hydrogenation to CH₄ because metal oxide support basically possess good mechanical performance and thermal stability. However, it is still a great challenge that NPs always tend to sinter due to the inferior interaction between NPs and the metal oxide surface. Thereby, some researchers synthesized core-shell structure to solve this problem. Nevertheless, it increased the metal loading or sacrificed the activity due to the coverage of active sites.^{10,11} Moreover, some typical M-M_xO_y catalysts like Ni-Al₂O₃ could readily form the spinel structure during calcination process, which dramatically decreased the activity.¹² While, as a matter of fact, little attention has been paid to develop a novel metal-nonmetal oxide catalytic system to handle this issue. CNTs, a kind of one dimensional carbon support, have been proved to be excellent catalyst supports with respect to traditional metal oxide supports, such as dual loading sites at inner and outer space, high specific surface area (SSA), excellent electrical and thermal conductivity, and porous

structure, which has raised a study upsurge and witnessed a huge development regarding the metal-carbon catalytic system¹³⁻¹⁵ since Bao and coworkers found that NPs confined into the CNT channel would display unique electronic properties and showed superior activity.¹⁶ After that, Su et al. developed the carbon catalyst via surface modification and applied it directly in the oxidative dehydrogenation of n-butane.¹⁷ Another interesting property of carbon support is that its surface can be modified by heteroatoms (O, N, B, P) or functional groups (-COOH, -OH, -NH₂), which bridges the carbon support and active metal, and intensify the in-between interaction and further modulate the activity.¹⁸⁻²⁰ Of late, several investigations focused on the interaction between small noble metal (Pt) NPs and functionalized nanocarbon (CNT or graphene). For example, Xin et al. observed the strength of the Pt-graphene interaction followed the trend of Pt/p-phenyl NH₂-graphene > Pt/p-phenyl SO₃H-graphene > Pt/graphene.¹⁸ Tian et al. found the nitrogen/oxygen modified CNTs exhibited a great promotion in particle dispersion and the selective hydrogenation of cinnamaldehyde.²¹ In order to investigate the interaction between Pt NPs and carbon supports, some specific characterizations like identical location transmission electron microscopy, X-ray photoelectron spectroscopy, and NEXAFS have also been employed recently.^{22,23} And several researchers investigated the metal-CNT interaction via DFT calculation.²⁴⁻²⁶ Wang and Sun found the stronger interaction was observed on the defective CNTs than defect free CNTs,^{26,27} which should be responsible for the higher NPs dispersion. Yet, up to now, the understanding of causal relationship between metal-carbon interaction and physicochemical properties, such as electronic state, particle size distribution (PSD), catalytic activity as well as stability, is still phenomenal and ambiguous, and moreover, rare work has been dedicated to effectively adjust the metal-carbon

(especially for non-noble metal) interaction, which is essential to have a fundamental recognition for the metal-carbon catalytic system.

Herein, Ni-CNT system promoted by Mn was fabricated and applied to CO₂ hydrogenation to CH₄. Based on experimental studies, DFT calculation and our previous work,^{5,27-29} we expounded the nature that the Ni-CNT interaction resulted from the anchoring effect of SOGs through the strong covalent interface bonding between Ni atom and C or O element in SOGs. Meanwhile, the Ni-CNT interaction can be successfully varied just by simply modulating the thermal treatment temperature, consequently, effectively tuning the binding energy/electronic state, dispersion, activity and stability. What's more, the additive, Mn promoter, efficiently improved the activity and selectivity. We believe that this study will broaden the range to develop metal-carbon catalytic system for CO₂ methanation or other hydrogenation reactions and shed light on some fundamental understanding on Ni-CNT interaction to rationally design the metal-carbon catalyst with both high activity and stability.

2. EXPERIMENTAL

2.1. Catalysts synthesis

The pretreatment of CNTs (i.d. = 4-8 nm, o.d. = 10-20 nm, Chengdu Organic Institute) was conducted by refluxing in concentrated HNO₃ at 140 °C for 14 h to remove the metallic catalyst impurities and functionalize the surface of the CNTs. Figure S1 showed the purified CNTs.

Mn promoted Ni-CNT catalysts were prepared by a one-pot ultrasonic co-impregnation method. Typically, 1.835 g Ni(NO₃)₂•6H₂O and 0.643 g of 50 wt.%

Mn(NO₃)₂ aqueous solution were dissolved in 140 mL ethanol. The mixture was stirred for 10 min to form the homogeneous solution. And then, 2 g purified carbon nanotubes were added into the solution and impregnated in an ultrasonic bath for 2 h. Afterward, the as-obtained slurry was placed in a water bath and vaped at 85 °C with continuously stirring until no ethanol was observed. Finally, the precursor was dried at 110 °C for 12 h followed by calcination in N₂ for 4 h at various temperature (350, 450, 550 °C) to get the final catalysts. The content of Ni and Mn in catalyst was fixed at 15 wt% and 4 wt%, respectively. The as-obtained catalysts were donated as NiT and NiMnT (T = 350, 450, 550) as displayed in Table S1.

2.2. Catalytic tests and Characterization

The catalytic tests were conducted under atmospheric condition by using a continuous-flow 6 mm i.d. quartz micro-reactor at 0.1 MPa. Prior to reaction, 100 mg of the catalyst was reduced in the pure H₂ stream at 350 °C for 1 h with a gas flow rate of 30 mL/min. After cooling down to the specific temperature, the catalytic performance was carried out in the range of 210 to 360 °C. The feeding gases of H₂ and CO₂ were introduced at a flow rate of 40 mL/min and 10 mL/min, respectively. The gas hourly space velocity (GHSV) was calculated to be 30,000 mL/(g_{cat}•h). The reaction products from the reactor were analyzed online by a GC-1690A gas chromatograph with a thermal conductivity detector (TCD). CO₂ conversion and CH₄ selectivity were marked as X_{CO2} and S_{CH4}, respectively.

CO₂ conversion and CH₄ selectivity were calculated based on the conservation law of carbon element and defined as below:

$$X_{\text{CO}_2} = \left(\frac{C_{\text{CO}, \text{out}} + C_{\text{CH}_4, \text{out}}}{C_{\text{CO}_2, \text{out}} + C_{\text{CO}, \text{out}} + C_{\text{CH}_4, \text{out}}} \right) \times 100\%$$

$$S_{\text{CH}_4} = \left(\frac{C_{\text{CH}_4, \text{out}}}{C_{\text{CO}, \text{out}} + C_{\text{CH}_4, \text{out}}} \right) \times 100\%$$

where $C_{i, \text{out}}$ is the calibrated concentration of each component in outlet gas. The quantification of all the effluent gas (H_2 , CO , CH_4 , CO_2) were calibrated by standard gas in advance. In detail, for the calibration process, the standard gas was injected into the GC-1690A gas chromatograph with a thermal conductivity detector (TCD), then the signals with a peak order H_2 , CO , CH_4 , CO_2 on the screen were recorded. Calculating the area of each peak and normalizing the concentration of each component, that is a calibration factor (f), $f = C_i/A_i$, where C_i and A_i are the concentration and peak area of each component in standard gas. Therefore, the concentration of the effluent gas after reaction can be quantified by multiplying detected peak area with f . Specifically, the thermodynamic equilibrium conversion data was obtained via Aspen plus software by applying a CO_2/H_2 ratio of 4 in the calculation for CO_2 methanation, accompanying with a side reaction of reverse water gas shift (RWGS) reaction.

Thermogravimetry (TG) was conducted on a microcomputer differential thermal balance (HTC-2, Hengjiu, Beijing) at a heating ramp of $10\text{ }^\circ\text{C}/\text{min}$ in the N_2 flow. FT-IR spectra were recorded with a FT-IR spectrometer (Bruker, Tensor, Germany) in the range of $400\text{--}4000\text{ cm}^{-1}$. H_2 -TPR test was performed on a fixed-bed reactor. 50 mg catalyst was loaded in a quartz reactor inside a vertical furnace with a gas flow rate of $30\text{ mL}/\text{min}$ of 5% H_2/N_2 mixture gas. The signal was recorded by a SC-200 gas chromatograph from 100 to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The H_2 consumption was calibrated by CuO . Inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS intrepid II XSP,

ThermoFisher) was conducted to measure the metallic content (Ni and Mn) of the catalysts. CO₂-TPD experiments were conducted on a mass spectrometer (MS). Prior to CO₂-TPD, 50 mg of catalyst was *in-situ* reduced by H₂ flow (30 mL/min) at 350 °C for 1 h. Then, the sample was cooled to the room temperature with Ar and saturated by CO₂. After flushing with Ar for 2 h, the sample was heated to 800 °C by ramping at 5 °C/min in Ar flow. The detected signals for CO₂ was $m/z = 44$. X-ray diffraction (XRD) patterns of the catalysts after calcination and reduction were measured by a DX-2700 diffractometer (Haoyuan, China) with Cu K α irradiation at 30 mA and 40 kV. The scanning rate was 0.03 °/s ranging from 10 to 85 °. The Brunauer-Emmett-Teller (BET) surface area was measured by N₂ adsorption method using an automated surface area & pore size analyzer (Quantachrome NOVA 1000e apparatus). XPS were measured on a spectrometer (AXIS Ultra DLD) and corrected by the C 1s line at 284.6 eV. The spectrum decomposition was performed using the XPS PEAK 41 software with Gaussian functions after deduction of a Shirley background. Quasi *in-situ* XPS was carried out on a spectrometer equipped with both heating zone and testing zone from 300 to 600 °C under N₂ atmosphere. The sample was transferred to the testing zone once reaching the specified temperature. Raman spectra were recorded by a Raman spectrometer (Horiba-Jobin-Yvon LabRAM HR800) with He-Ne laser excitation at 633 nm. The morphology and metal dispersion was characterized by transmission electron microscope (TEM, JEOL Ltd., Tokyo, Japan) operated at 120.0 kV. HRTEM, HAADF-STEM, and STEM-mapping were conducted to further have a clear insight of the microscope of the catalyst operated at 200.0 kV.

In-situ temperature programmed surface reaction (TPSR) experiment was carried out on a mass spectrometer using Ar as the carrier gas. The main detected signals for each gas

were $m/z = 44$ (CO_2), 2 (H_2), 28 (CO), 16 (CH_4) and 40 (Ar). The flow rate were corrected to be 40, 4, and 1 mL/min for Ar , H_2 and CO_2 , respectively. Prior to the experiment, the catalyst was reduced by H_2 at 350 °C for 1 h. The temperature cooled down to 150 °C and kept for 1 h until the baseline was stable. The desorbed gases from the reactor were monitored until the temperature increased to 750 °C at a rate of 10 °C/min. The transient response for reactants and products after the sudden removal of CO_2 from feeding gas was also performed on MS with the flow rate of 40, 4, and 1 mL/min for Ar , of H_2 and CO_2 , respectively. After the methanation reaction reached a steady state at 350 °C, CO_2 was cut off suddenly and the signals were recorded at the same time.

The DFT calculations were performed using Dmol3 module implemented within the Materials Studio³⁰ of Accelrys, Inc. To keep the balance between the computational accuracy and the cost, a structure of (6, 6) armchairs CNTs were established. What's more, to remove the edge effect, we use hydrogen atoms to saturate the terminal hanging bonds of CNTs models. The generalized gradient approximation (GGA)³¹ with the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the electron exchange and correlation interactions³². During the computation, the double numerical plus polarization functions (DNP) was used as the basis set.³³ The density functional semicore pseudopotential (DSPP) was used for the relativistic effects of Ni atoms, in which the core electrons are replaced by a single effective potential and some degree of relativistic corrections are introduced into the core.³⁴ The thermal smearing level was set as 0.005 Hartree. All of the atoms were fully optimized without any constraints. The double-numeric quality basis set with polarization functions (DNP) was used for Ni, and the double numerical basis set d-polarization function (DND) was used for C, O and H.³³ The binding

energy (BE) of the Ni atom adsorbed on the CNTs was calculated as follows:

$$E_{BE} = - [E_{Ni+CNT} - E_{CNT} - E_{Ni}]$$

Where E_{Ni+CNT} is the total energy of Ni-CNTs system, E_{CNT} is the total energy of CNT model, E_{Ni} is that of isolated Ni atom. The higher is the E_{BE} , the stronger is the Ni-CNTs interaction.

3. RESULTS AND DISCUSSION

3.1. Characterization of the tunable metal-support interaction

The metal-support interaction and the reducibility of the NPs could be reflected from the peak location and peak area in H_2 -TPR. Generally, a higher peak temperature means a stronger interaction between active metal and support or promoter. As revealed in Figure 1a, the peak location negatively shifted in the range of 200-400 °C. From that, one can know catalysts obtained at 550 °C were readily to be reduced than those calcined at 350 °C, *i.e.* a higher thermal treatment temperature gave rise to a weakened Ni-CNT interaction. This interesting phenomenon was rarely reported in Ni-CNT catalytic system. The result was also opposite to that in the $M-M_xO_y$ system because the formation of mixed compounds generally led to the enhanced $M-M_xO_y$ interaction when the calcination temperature rise. Probably due to the formation of solid solution, we could also found the addition of Mn promoter made NiO harder to be reduced, and thus led to a positive shift of the reduction peak.³⁵ Another, for Ni350 and NiMn350, there was a H_2 consumption peak at around 530 °C, which might be assigned to the catalytic reaction of CNT with NiO and the further reaction of released CO hydrogenation to methane.³⁶ This result was in good accordance with the further characterization of *in-situ* TPSR experiment in H_2 stream for

NiMn350 catalyst in Figure S2. Signals for both H₂ and CH₄ reached their minimum and maximum at around 530 °C, agreeing well with the TPR result. The generation of CH₄ came from the hydrogenation of CO/CO₂ that originated from the autocatalytic reactions. The detailed mechanism about autocatalytic reactions was presented in Figure S3 and Figure S4. Additionally, the quantified actual H₂ consumption in TPR experiment was much higher than the theoretical value (Table S2). This strongly demonstrated that H₂ consumption not only resulted from the reduction of NiO but also the hydrogenation reaction of other species including the methane production.

To further determine the electronic interaction between Ni NPs and CNT supports, XPS was conducted. For two-component catalyst, the binding energy of active metal can reflect its interaction with support. The electron transfer inferred from the binding energy can imply the strong metal-support interaction.³⁷ In Figure 1b, there were two obvious peaks in the range of 858~850 eV that were assigned to Ni²⁺ (or NiO) and Ni⁰, respectively. The detected Ni²⁺ species could be probably attributed to the air oxidation of Ni NPs because the nanoscaled particles was quite active.⁵ Another probable reason was that intense Ni-CNT interaction could result in the hard reduction of NiO NPs. For example, cobalt reducibility was to some extent decreased with a higher dispersion and enhanced Co-support interaction.³⁸ Notably, peaks for both Ni²⁺ and Ni⁰ displayed apparent migration. For Ni⁰ species, the binding energy of metallic Ni⁰ showed remarkable shift toward lower BE (853.0, 852.7, and 852.6 for Ni350, Ni450, and Ni550, respectively), demonstrating the Ni-CNT interaction was weakened as temperature elevated. The charge transferred from Ni atoms to CNT support in Ni-CNT system. While for Ni²⁺ species, the BE shifted from 855.3 (Ni350) to 854.9 eV (Ni550) (Table S3). The electrons transfer

phenomenon was further demonstrated by the quasi *in-situ* XPS measurement on the precursor of Ni350 shown in Figure 1c. The peak of NiO phase gradually vanished and shifted to the lower BE side (from 855.5 eV to 854.6 eV), further improving the weakened interaction between NPs and CNT support.

The TPR and XPS revealed the Ni-CNT interaction could be successfully modulated by the simple thermal treatment, *i.e.*, elevating calcination temperature led to the weakened Ni-CNT interaction. Yet, the result was totally opposite to the accepted conclusion in M-M_xO_y system that metal-support interaction should be enhanced with the increasing calcination temperature.³⁹⁻⁴¹ Normally, the host-guest interaction contains several types, like van der Waals force, π - π interaction, hydrogen bond, covalent bond, ionic bond, and metallic bond. The generally observed enhanced interaction in M-M_xO_y system could be assigned to the formation of strong M₁-O-M₂ bonds in the contacted interface. However, the inert carbon surface of CNT decides metal-carbon system must follow an absolutely different bonding mechanism. Hence, the surface properties of CNTs, such as defect, functional groups or heteroatom doping, should be responsible for this unusual interface bonding mode.²⁰

3.2. Toward understanding the tunable metal-support interaction in Ni-CNT system

3.2.1. Surface property of oxygen functionalized CNT supports

The surface chemistry and the thermal stability of oxygen modified CNTs were characterized by EDS-mapping, FTIR, and TPD-MS. As observed in Figure 2a and b, the acidic treatment CNTs successfully introduced SOGs mainly from carboxyl (-COOH).⁴² The thermal stability of SOGs was determined by TPD-MS experiment under pure Ar, *in-*

situ monitoring the decomposition product of oxygen modified CNTs, in order to better understand the modulation role of SOGs in physicochemical properties and Ni-CNT interaction. As displayed in Figure 2c, CO and CO₂ could be detected when temperature exceeded 400 °C. The signal indicated SOGs over CNTs surface started to decompose at around 400 °C via the reaction, $\text{SOGs} \rightarrow \text{CO} + \text{CO}_2$.⁴³ Noteworthiness, the possibility that the released CO/CO₂ gas was derived from CNT pyrolyzation could be ruled out because CNT started to decompose at 525 °C according to TG result (Figure S4), which was much higher than 400 °C via SOGs decomposition. In this case, the amount of SOGs would be gradually reduced as temperature continuously elevated, hence decreasing the anchoring sites for Ni NPs. The reduction of carboxyl on CNTs surface was also supported by the semi-quantitative analysis of C1s XPS data in Figure 2d, where the area proportion of COO⁻ gradually decreased from 11.8 to 7.5 %.

Raman was carried out to further characterize the defect degree of CNTs. As depicted in Figure 2e, all the samples presented typical D and G band at 1350 cm⁻¹ and 1580 cm⁻¹ for carbon nanotubes, respectively.^{44,45} The defect degree inferred from the I_D/I_G ratio became larger for samples at 550 °C than those at 350 °C. The increased defect in CNTs could be related to the following two reasons. Firstly, the metallic NPs can be served as the catalyst to corrode the CNT surface during heat treatment.⁴⁶ Secondly, SOGs were mostly grafted on the defect sites over the CNT graphitic surface.⁴⁷ The defect sites still left after the decomposition of SOGs at high temperature.

Combining EDS mapping, FTIR, TPD-MS, XPS with Raman, we could draw a conclusion that thermal treatment affected the stability of SOGs. Higher temperature promoted the decomposition of SOGs and the formation of more defects. While how these

surface properties tune the Ni-CNT interaction and what is the nature of this kind of Ni-CNT interaction?

3.2.2. DFT calculation

We used DFT calculation to further recognize the nature of the anchoring effect of SOGs and the tunable Ni-CNT interaction at a molecular or atom scope in this work. The SOGs on CNTs surface presented the decreasing trend as calcination temperature increased from 350 to 550 °C. To monitor this situation, five CNTs models were established. They were perfect CNTs (P-CNT), defect CNTs (D-CNT), one carboxyl group grafted CNTs (F-CNT), two carboxyl groups grafted CNTs (S-CNT), and three carboxyl groups grafted CNTs (T-CNT) (Figure S5a-e). Molecular electrostatic potential (MEP) were calculated on different CNTs. MEP can enable one to visualize the variably charged region of a molecule, and allow us to better illustrate the interaction mechanism.⁴⁸ As shown in Figure S5f-j, the CNTs basal are stronger electron accepters because of their large π -systems. The highest occupied molecular orbitals (HOMOs) of CNTs models were displayed in Figure S6. We found that the electron delocalization was slightly reinforced by the carbonyl group.

In order to investigate the interaction between Ni atoms and these five CNTs models, the binding energies for the possible atoms adsorption sites of each model were studied systematically. We considered three possible adsorption sites (top, bridge, and center) for Ni atoms bind with P-CNT, and three possible center sites around vacancy for Ni atoms bind with D-CNT. We found that, Ni atoms preferred to adsorb on the C-C bridge site of P-CNT; while, Ni atoms preferred to adsorb on the defective center sites of D-CNT. Moreover, considering the charge enrichment around the vacancy systems (F-CNT, S-CNT,

T-CNT), we just considered the more possible adsorption center sites of the vacancy for Ni atoms on these systems. Figure 3a-e showed the more energetically favorable optimized geometry structures of Ni adsorbed on different CNTs models studied in this work. For the most stable adsorption site of Ni atom that adsorbs on the perfect CNTs, the E_{BE} was 2.7 eV, and the distance between the nearest carbon atom and the doped Ni atom was 1.88 Å, which was consistent with the results of reported studies.⁴⁹ The distance decreased to 1.81 Å when the defect was introduced. Simultaneously, the covalent bond (Ni-O) formed when SOGs grafted on the defect sites. Ni atoms interacted with the O atom (Ni-O), and even with C atom (Ni-C) if the amount of the SOGs further increased, thus the anchoring was greatly strengthened (Figure 3k). The calculated E_{BE} of individual Ni atom adsorbs on D-CNT, F-CNT, S-CNT, and T-CNT were 4.2, 4.6, 5.5, and 6.1 eV, respectively. The positive association between the BE and the amount of the carboxyl functional groups was completely in line with the experimental result.

To illustrate the adsorption behavior of Ni, the Mulliken atomic charges and MEP were calculated on different CNTs. Mulliken atomic charge analysis of Ni atom binds with CNTs system indicates that the charges on the doped Ni atoms were all positive (+0.364e for Ni-P-CNT system, +0.409e for Ni-D-CNT system, +0.466e for Ni-F-CNT system, +0.517e for Ni-S-CNT system, +0.561e for Ni-T-CNT system), demonstrating that the charge was transferred from Ni atom to the CNTs. This conclusion was in good accordance with the previous XPS result. As further confirmed by the MEP for the Ni atoms bind with CNTs systems in Figure 3f-j, Ni atoms preferred to be adsorbed around the carbonyl group due to the charge enrichment around the carbonyl group, which was consistent with the Mulliken atomic charge results. Additionally, the higher electron density surrounding the

carbonyl group (that is referred to the number of the carbonyl group on CNTs systems) could improve the adsorption of Ni atoms, which was consistent with the binding energy results displayed in Figure 3k.

3.2.3. Proposed Ni-CNT interfacial bonding mechanism

Some physical properties of the calcined catalysts were presented in Figure S7 and Table S4, the specific surface area of all catalysts remained around $160 \text{ m}^2 \text{ g}^{-1}$. Calcination at higher temperature led to the increase of pore volume, average pore diameter, and significantly, influenced the particle size as depicted in Figure 4a-f. The average particle size (APS) became larger from 350 to 550 °C. The catalyst calcined at 550 °C was strongly sintered compared with those of 350 °C. The XRD patterns also exhibited the similar regularity. The peak intensity of metallic Ni (111) plane at 2θ value of 44.4° turned to sharper when temperature increased, and the peak FWHM decreased, accordingly (Figure 4g-h), implying a larger particle size. However, the addition of Mn did not affected the APS efficiently. The deep analysis of detail microstructure of the catalysts was further characterized by HRTEM and HAADF-STEM. As can be seen from Figure 5a-c, many fine NPs (1-3 nm) that were invisible in TEM could be detected in Ni350 under the dark field and HRTEM. Specifically, the small NPs were tightly bonded onto the CNT surface (Fig 5c), and presented flat shape, which indicated a strong interplay with CNT support.^{50,51} However, the small NPs can hardly be observed in Ni450 (Figure 5d-f) and Ni550 (Figure 5g-i). Besides, the observed NPs reveled not flat shape but spherical ones, suggesting the decrease of the contacted surface and the proportion of interfacial Ni atoms. The transformation from flat tiny grains to large spherical NPs, named as geometric

effect,⁵² was mainly due to the SOGs decomposition and the weakened conjunction because defect sites and perfect sites could only weakly constrain the interfacial Ni atoms as demonstrated by the DFT results (Figure 3k). The shape change of NPs was also evidenced in Willinger's recent work, where they found metal-support interaction could be tuned by carbon structure.⁵³ Interestingly, in Ni550, we could clearly find that a large NPs was formed from the smaller aggregated ones; in addition, the grain boundary and defect sites were also detected, suggesting a coalescence process at the high calcination temperature (Figure S8).

Not surprisingly, elevating temperature would cause the particle growth and sintering phenomenon. The as-accepted viewpoint believed that the input energy firstly promoted the increase of surface energy of NPs, and then drove the NPs growth. Nevertheless, prior to sintering, the internal bond must be destroyed or rearranged. The sintering process thus was not only related to the input energy from environment but also the metal-support interaction of the system. Therefore, thermal treatment is just a tool rather than the origin to tune the particle size. For $M-M_xO_y$ system, bulk M_1 phase that weakly interplayed with M_2O support self-aggregated accompanying with the interaction with M_2O to form the firm $M-M_xO_y$ interaction due to the enlarged interfacial contact area and the formation of intermetallic phase at high temperature.^{54,55} The strong interface M_1-O-M_2 bond or formed solid solution in $M-M_xO_y$ system was the main power to prevent the metal sintering.^{12,56,57} Especially, in our control sample of $Ni-Al_2O_3$, the system formed the $NiAl_2O_4$ structure (Figure S9), indicating the strengthened Ni-support interaction.

However, the above mechanism was hard to explain the phenomenon that calcination at higher temperature decreased the metal-support interaction in Ni-CNT system.

Therefore, we proposed a new interface bonding mechanism to understand this phenomenon from two aspects, electronic effect and geometric effect.⁵² The illustration, according to the evidences in experimental and computational result, was presented in Figure 6 and Fig. S10. In Ni350, CNT support was grafted with rich SOGs. SOGs acted as the anchoring sites and bridges to connect NPs and CNT body. The tiny NPs were tightly bonded by the SOGs at the interface between NPs and CNT. DFT illuminated that the covalent bonding interaction between interfacial Ni atoms and C or O atoms in SOGs was the origin of this kind of strong metal-support interaction. Due to the high electronegativity and strong electron-withdrawing property of $-\text{COOH}$,⁵⁸ electrons transferred from NPs to CNT supports. It should be emphasized that the charge transfer direction was also opposite to those observed in classical strong metal-support interaction (SMSI), where electrons always transferred from supports to NPs.^{41,55} The classical SMSI tended to form $\text{M}^{\delta-}$ rather than $\text{M}^{\delta+}$ ($\text{Au}^{\delta+}$) reported by Xu and coworkers, in which they called such new finding oxidative SMSI.⁵⁹ This reverse electronic flow also explained why Ni^0 phase presented $\text{Ni}^{\delta+}$ state in Ni350 compared with Ni550 as analyzed in XPS result. The charge transfer phenomenon here could be called electronic effect.⁵²

As temperature rise up to the critical temperature of about 400 °C, SOGs were broken and the host-guest interaction was impaired. Afterwards, the flat tiny NPs self-aggregated together and grew into larger spherical ones (geometric effect). Although the defect/perfect carbon sites still could be served as anchoring sites for NPs, their binding force was much lower than SOGs. Shortly, the sintering phenomenon in Ni-CNT system, as a matter of fact, was determined by two factors. External cause: calcination temperature, and internal cause: thermal stability of SOGs. As has been proved by DFT calculation,

the Ni-CNT interaction was highly dependent on the amount of SOGs. The more SOGs grafted at defect sites, the stronger was Ni-CNT interaction, and thus the harder was sintering at low input energy/calcination temperature. So the severe sintering at 550 °C and deteriorated NPs dispersion could be attributed to the weakened interaction caused by the SOGs decomposition. This can be further demonstrated by using CNT supports without SOGs as a comparative sample to Ni350 (Figure S11). We found that the CNTs surface were very smooth and could hardly load the NPs (Figure S12). NiO NPs aggregated together severely due to the natural inert surface. Therefore, NPs were more prone to migrate and self-aggregate without the constraint of SOGs.

Overall, the robust Ni-CNT interaction was obtained through the interface bonding by way of CNT-SOGs-Ni and the tunable Ni-CNT interaction could be achieved via controlling the amount of SOGs/calcination temperature.

3.3. Catalytic performance

3.3.1. CO₂ conversion & CH₄ selectivity

Figure 7a-b presented the catalytic activity and selectivity for CO₂ selective hydrogenation to CH₄, respectively. In Figure 7c, the histogram of CH₄ yield gave a direct insight of the effect of thermal treatment temperature and Mn promoter. The CO₂ conversion and CH₄ selectivity gradually decreased as the heat treatment temperature increased from 350 to 550 °C. A higher calcination temperature went against the catalytic performance, but activity did not decline a lot under a large particle size/decreased dispersion. This was rationalized by the existence of rich defect sites (corner, edge or terrace) in Ni550 (Figure S8b-d), because these sites could also contribute to the activity

and only produced above a certain size.^{60,61} As for Mn promotion effect, Mn promoted catalysts showed much more active at low reaction temperature than those unprompted ones and kept nearly 100% CH₄ selectively in all the range of studied temperature. Taking NiMn350 for example, the temperature point when CO₂ conversion reached 50% (T_{50}) sharply decreased from 355 to 262 °C with respect to Ni350, greatly enhancing the low temperature activity for CO₂ conversion. Furthermore, the CO₂ conversion was only 8% for Ni350 while 71.6% for NiMn350 catalyst at the reaction temperature of 300 °C, indicating the remarkable promotion effect of Mn.

3.3.2. Role of Mn promoter

For the catalytic performance, *in-situ* TPSR experiment in Figure 8a demonstrated that NiMn350 catalyst lit off at a very low temperature of about 154 °C, nearly 50 °C lower than Ni350 catalyst, indicating that Mn promoter effectively facilitated the activation of the reactant at low temperature. Moreover, NiMn350 catalyst kept a high CO₂ conversion in a broader temperature region (150 - 400 °C) than Ni350 catalyst, which made NiMn350 catalyst quite flexible in wide operation conditions.

According to the TEM result, the promotion effect of Mn should not be ascribed to the particle size effect because the APS did not change significantly after the addition of Mn, which was in line with Johnson's report⁶¹ but opposite with Zhao's conclusion that Mn could reduce the particle size and prevent the growth of Ni NPs.⁶² However, Mn promoted catalysts showed poorer crystallinity than unprompted ones as indicated from the weaker peak intensity in XRD patterns, suggesting more disorder.⁶³ According to the STEM-mapping of NiMn350 in Figure 8b, Mn evenly mixed with Ni element, which would

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3 increase the prevalence of particles composed of several smaller domains and induce more
4 defects than unpromoted Ni NPs⁶¹ Though the addition of Mn did not decrease the particle
5 size (or promoted the dispersion), they evenly segmented the Ni NPs into small domains,
6 which might increase more defects or extra active sites than Ni350.
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12 In an attempt to have a deeper insight toward the effect of Mn promoter, the transient
13 response experiment was designed and conducted.⁶⁴ When the reaction reached a steady
14 state at 350 °C, CO₂ was suddenly cut off from the reactant, and the signal changes were
15 recorded by MS. In Figure 8c, for both Ni350 and NiMn350 catalysts, it could be found
16 that the detected CO₂ concentration immediately reduced after CO₂ was switched off.
17 Meanwhile, the signal for product of CH₄ also declined due to the consumption of the
18 intermediate species. It was worthy to note that CO, which should derive from CO₂ via
19 reverse water gas shift reaction (RWGS, CO₂ + H₂ → CO + H₂O),⁶⁴⁻⁶⁶ exhibited different
20 response behavior in NiMn350 and Ni350. For Ni350, CO signal did not decay sharply
21 until reached 10 min. While for the NiMn350 catalyst, the signal of CO rise remarkably
22 nearly at the same time when CO₂ was cut off. CO accumulated in large quantities and had
23 no time to further convert to the final product, CH₄, suggesting that the CO consumption
24 rate was slower than its formation rate. But whether CO was directly desorbed from
25 adsorbed CO_{ad} via redox mechanism or transformed from other intermediates via
26 associative mechanism (carbonyl, carbonate, formate) needed to be further identified. The
27 mechanism was quite complex and flexible.⁶⁷ For example, Roldan et al. claimed that
28 NCNF-supported catalysts can store CO_{ad} intermediates due to the Lewis basicity of
29 pyridinic nitrogen.⁶⁸ By changing the supports, CO₂ methanation underwent formate route
30 over Ru/CeO₂ catalyst but CO route over Ru surface in Ru/ α -Al₂O₃.⁶⁹ Besides, from Figure
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8c, we could observe that the baselines of CO for Ni350 and NiMn350 were different. For Ni350, the intensity of the initial baseline for CO was much higher than the terminal (a position where the amount of detected species closed to zero), while there was only nuance for NiMn350. This indicated that at initial stage, the amount of initially produced CO in NiMn350 was smaller than Ni350, *i.e.* NiMn350 showed a higher selectivity toward CH₄. The result was in line with the selectivity data.

Beyond the above, as observed from the peak intensity of CO in these two catalysts, the NiMn350 catalyst displayed the higher CO intensity, thus adsorbing more CO₂ than Ni350 catalyst since the detected CO radically originated from the adsorbed CO₂ via RWGS reaction, which was further demonstrated by the CO₂-TPD result shown in Figure 8d, where peaks in the region of 100-200 °C were assigned to the physisorbed CO₂ and weaker chemisorbed CO₂, and peaks in the range of 400-600 °C could be attributed to the stronger chemisorbed CO₂.⁶⁸ Peaks around 700 °C was due to the CNT gasification,⁴³ which could be also proved by the TG results in Figure S13. The enhanced CO₂ adsorption might also be responsible for the higher activity of Mn promoted catalyst.⁷⁰

3.3.3. Stability performance

140-hour stability tests under 350 °C were employed on Ni350, NiMn350, and NiMn550 catalysts. As displayed in Figure 9a, catalysts calcined in the lower temperature of 350 °C (Ni350 and NiMn350) kept a steady state during the time-on-stream (TOS) test while a decrease of CO₂ conversion could be observed for NiMn550, which suggested it was metal-support interaction rather than Mn promoter that affected the stability. Significantly, no deactivation was observed for NiMn 350 catalyst owing to the robust

metal-support interaction anchored by SOGs as well as the enhance activity promoted by Mn, which was superior to most reported CO₂ methanation catalytic system (Table S5).

Because metal-support interaction played a key role on the aggregation behavior of NPs, TEM was carried out to observe the variation of the APS after TOS tests. In Figure 9b-d, APS had little increase from 8.41 to 8.54 nm for Ni350 and 7.09 to 8.86 nm for NiMn350 by virtue of the strong anchoring effect of SOGs. The HRTEM image of NiMn350 after TOS test presented that the fine particle still tightly attached to the outer wall of CNT (Figure 9e). Besides, XRD result also indicated that the (111) peak still presented diffuse state compared with the fresh catalyst (Figure 9f), implying the good dispersion. Yet, for NiMn550, the particle grew dramatically from 18.16 to 28.62 nm due to the weak metal-support interaction, thus the severe sintering deteriorated the stability performance (Table 1). In one word, thermal treatment at high temperature would cause the decomposition of SOGs, weakening the metal-support interaction, leading to the easy sintering of nanoparticles, which would not benefit for the long-term stability.

4. CONCLUSIONS

At present work, the newly Mn promoted Ni-CNT catalytic system was designed for CO₂ hydrogenation to CH₄ which endowed with both high activity and stability. The tunable Ni-CNT interaction was achieved by thermal treatment. Experimental and computational result illuminated the nature of Ni-CNT interaction, which greatly influenced the particle size, dispersion, electronic state, activity and stability. Some main conclusions were summarized below:

1. The tunable Ni-CNT interaction was evidenced by XPS, quasi *in-situ* XPS, and H₂-

TPR. Higher thermal treatment temperature led to weaker Ni-CNT interaction. The electrons transferred from Ni to CNT, strengthening the Ni-CNT interaction at the calcination temperature of 350 °C, which was further demonstrated by computational result.

2. SOGs over the CNTs started to decompose at about 400 °C following the reaction: $\text{SOGs} \rightarrow \text{CO} + \text{CO}_2$, which was proved by XPS spectra of C1s and TPD-MS results.
3. SOGs acted as the bridge to connect Ni NPs and CNT. The formation of interface covalent bonding between Ni atom and C/O element over SOGs was the origin of the Ni-CNT interaction. Electrons transferred from Ni NPs to CNT support (electronic effect). The anchoring effect on Ni atoms followed the decreasing order: SOGs (rich) grafted CNTs > SOGs (deficient) grafted CNTs > defect CNTs > perfect CNTs as demonstrated by DFT.
4. Elevating calcination temperature from 350 to 550 °C, the average particle size increased from 7.09 to 21.32 nm according to the TEM result. Deep detection by HRTEM and HAADF-STEM confirmed that tiny flat NPs in Ni350 transformed into the large spheric NPs in Ni550 (geometric effect). The particle sintering observed in Ni450 and Ni550 could be attributed to the SOGs decomposition and weakened Ni-CNT interaction.
5. Mn promotion greatly enhanced the low-temperature activity proved by the *in-situ* TPSR, which was not due to the particle size effect but likely the enhanced CO₂ adsorption and dissociation according to transient response experiment and CO₂-TPD.
6. After 140-hour TOS test, no deactivation was observed in Ni350 and NiMn350 catalyst, with a Ni NPs size (ca. 8nm) nearly unchanged, which was assigned to the strong Ni-

CNT interface bonding, while for NiMn550, obvious sintering was detected.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

List of the as-prepared catalysts, purified CNT, TPSR of NiMn350 under H₂ stream, XRD patterns of calcined catalysts, TG and DTA, quantified H₂ consumption, XPS fitting parameters, DFT, optimized geometries of five CNT models, highest occupied molecular orbitals, N₂ adsorption-desorption isotherms, pore size distribution, physicochemical properties, TEM images of rich defects on Ni550, XRD of control sample for Ni/Al₂O₃, logical relationship in regulated Ni-CNT interaction, XPS spectrum of CNT without SOGs, TEM images of comparative catalyst using CNT support without SOGs, comparison data of catalytic performance, TG of Ni350 and NiMn350.

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Notes

The authors declare no competing financial interest.

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Table Captions

Table 1 Avarage particle size and activity change after 140 h TOS test.

Catalysts	Average particle size (nm)		Activity (%)	
	initial	after 140 h TOS	initial	after 140 h TOS
Ni350	8.41	8.54	30.4	36.8
NiMn350	7.09	8.86	81.7	81.3
NiMn550	18.16	28.62	73.1	66.3

Figure 1. (a) H₂-TPR profiles of calcined catalysts, and (b) XPS results of Ni 2p_{3/2} for the catalysts after reduction at 350 °C, and (c) quasi *in-situ* XPS spectra of Ni350 precursor with ramping rate of 5 °C/min from 300 to 600 °C under N₂.

Figure 2. (a) EDS-mapping for surface elementary analysis of oxygen functionalized CNT without heat treatment, (b) FTIR spectra of oxygen functionalized CNT, (c) TPD-MS result of CNT support under pure Ar gas, (d) XPS spectra of C1s for CNT support (1: without heat treatment, 2: treated at 350 °C, 3: 450 °C, and 4: 550 °C), and (e) Raman spectra of the samples.

Figure 3. Optimized geometry structures for the more favorable site of Ni adsorbed on (a) P-CNT, (b) D-CNT, (c) F-CNT, (d) S-CNT, and (e) T-CNT; Electrostatic potential surfaces for Ni atom binds with (f) P-CNT, (g) D-CNT, (h) F-CNT, (i) S-CNT, and (j) T-CNT. The blue region indicates negative charge, while the red area represents positive charge. The isosurfaces are constructed at 0.05 e^{-1} ; (k) Binding energy and Mulliken atomic charge for Ni atoms binding with different CNTs (inset shows the covalent bond length between Ni atom and C/O). Black, grey, red, and blue balls represent the carbon, hydrogen, oxygen, and nickel atoms, respectively.

Figure 4. (a-f) TEM images for the reduced catalysts (the right figure is the distribution of the particle size), (g) XRD patterns of reduced catalysts, and (h) enlarged XRD patterns of Ni (111) plane.

Figure 5. HAADF-STEM and HRTEM images for (a-c) Ni350, (d-f) Ni450, (g-i) Ni550 after calcination.

Figure 6. Proposed interface bonding mechanism in Ni-CNT catalytic system.

Figure 7. (a) CO₂ conversion, (b) CH₄ selectivity, and (c) CH₄ yield for Ni catalysts and Mn promoted Ni catalysts. Reaction conditions: atmospheric pressure, 100 mg catalysts, H₂/CO₂ molar ratio = 4/1, GHSV = 30,000 mL/(g_{cat}·h).

Figure 8. (a) TPSR experiments of for Ni350 and NiMn350 catalysts, (b) STEM-mapping of NiMn350, (c) transient response behavior of reactant and product after CO₂ was cut off from reactant (Experiment condition: Ar: 40 mL/min, CO₂: 1 mL/min, H₂: 4 mL/min, 350 °C), and (d) CO₂-TPD results for Ni350 and NiMn350.

Figure 9. (a) The stability test of Ni350, NiMn350, and NiMn550 catalysts for 140 h at 350 °C. Reaction condition: atmospheric pressure, 100 mg catalysts, H₂/CO₂ molar ratio = 4/1, GHSV = 30,000 mL/(g_{cat}·h). TEM images of catalysts after 140-h stability test for (b) Ni350, (c) NiMn350, and (d) NiMn550, respectively, (e) TEM image showing Ni nanoparticles anchored on CNT support after 140-hour stability test for NiMn350 catalyst, and (f) XRD patterns of fresh, reduced, and used NiMn350 catalyst.

TOC graphic