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In-situ growth of carbon nanotubes on Ni/MgO: A facile preparation of efficient catalysts for the production of synthetic natural gas from syngas

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Ni/MgO-CNTs catalysts are prepared by *in-situ* chemical vapor deposition growth of CNTs on Ni/MgO. These catalysts exhibit an improved performance for synthetic natural gas from syngas, which is attributed to the formation of highly catalytic active interfaces among Ni, CNTs and MgO.

Methanation is one of the key steps to produce synthetic natural gas (SNG) from coal or biomass.[1,2] The methanation of CO or CO_2 to methane is a highly exothermic process.[3] In order to improve the energy efficiency of the overall process, a series of adiabatic reactors with high reaction temperature ($\sim$700 ℃) are generally used in a commercial SNG process.[4] On the other hand, to ignite the reaction and meet the requirement of high methane content in SNG, methanation catalysts should also be active at low reaction temperature (200~300 ℃).[4] Therefore, it is highly desired that methanation catalysts not only have excellent thermostability, but also are active at low reaction temperature. [4]

Carbon nanotubes (CNTs) have been well proven to be excellent catalyst support or catalyst promoter for catalytic hydrogenation, such as ammonia synthesis,[5] higher alcohols synthesis[6] and methanation[7,8] etc. For example, Zhang et al. reported that CNTs supported Ni catalyst exhibited a higher activity for CO methanation than that of Ni/γ-Al_2O_3 due to the existence of a large amount of the delocalized π electrons in CNTs.[7]

Unfortunately, pristine CNTs have insufficient binding sites for anchoring because of their chemical inertness, which significantly limit their applications in catalysis.[9,10] Dispersion of metal and the interaction among catalyst support, metal and promoter have crucial impact on the activity for most supported metal catalysts. In order to introduce more binding sites to

better disperse active metal and provide stronger interaction with other components, surface modifications of CNTs are usually carried out by harsh acid oxidation or covalent functionalization, which, however, typically involve time-consuming and complex chemical processing procedures.[10] The *in-situ* growth of CNTs is another effective and easy way to prepare a catalyst with high dispersion of metal on CNTs and strong interaction between CNTs and metal, which is expected to be more active for catalysis.[11] For example, Ou et al. prepared CNTs-Ni/TiO_2 catalyst by using *in-situ* growth method, which greatly enhanced the activity of photocatalytic hydrogen evolution due to the strong synergetic effect of CNTs with metallic Ni.[11] Ni/MgO is not only a common catalyst for methanation,[12] but also an effective catalyst for CNTs growth by chemical vapor deposition (CVD).[13] In the present study, Ni/MgO-CNTs catalysts for SNG from syngas were synthesized by *in-situ* CVD, in which CNTs were directly *in-situ* grown on the prepared Ni/MgO in the methanation reactor before methanation. This approach is expected to provide a new facile strategy to prepare highly active catalyst for methantion at low reaction temperature.
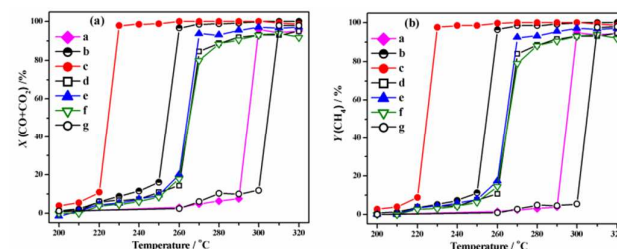

Fig. 1 The performances of syngas methanation over i-Ni/MgO-CNTs-n catalysts: (a) CO conversion; (b) CH_4 yield. (a: i-Ni/MgO-CNTs-5; b: i-Ni/MgO-CNTs-7.5; c: i-Ni/MgO-CNTs-10; d: i-Ni/MgO-CNTs-12.5; e: i-Ni/MgO-CNTs-15; f: i-Ni/MgO-CNTs-20; g: Ni/MgO. Reaction conditions: 0.1 MPa, V(H_2)/V(CO)/V(N_2)/V(CO_2) = 75/15/5/5, GHSV = 40000 mL h^{-1} g^{-1}.)

A series of catalysts were prepared by *in-situ* growth of CNTs on Ni/MgO catalysts *via* CVD with CO as carbon source using different growth times, noted as i-Ni/MgO-CNTs-n (n: growth time, min). As shown in Fig. 1, the CH_4 yield (Y(CH_4)) and

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CO+CO_2 conversion (X(CO+CO_2)) over i-Ni/MgO-CNTs-n catalysts increase with increasing reaction temperature, and eventually reach ~100%. However, in comparison with Ni/MgO catalyst, i-Ni/MgO-CNTs-n catalysts show significantly different catalytic performances for syngas methanation. As can be seen from Fig. 1, the Y(CH_4) and X(CO+CO_2) reach ~100% over i-Ni/MgO-CNTs-5 at 295 °C, while the Y(CH_4) and X(CO+CO_2) could not achieve ~100% until 310 °C over Ni/MgO catalyst. When the growth time increases to 10 min, the Y(CH_4) and X(CO+CO_2) reach ~100% at a much lower reaction temperature of 230 °C. However, as the growth time further increasing to more than 10 min, i-Ni/MgO-CNTs-n (n>10) catalysts show worse "low-temperature superiority" activities than that of i-Ni/MgO-CNTs-10. Nevertheless, all the Ni/MgO catalysts with *in-situ* growth of CNTs show better activity for syngas methanation than the catalysts without CNTs at low reaction temperature. These results indicate that the method of *in-situ* growth CNTs on Ni/MgO is an effective way to improve the low temperature catalytic activity for syngas methanation.
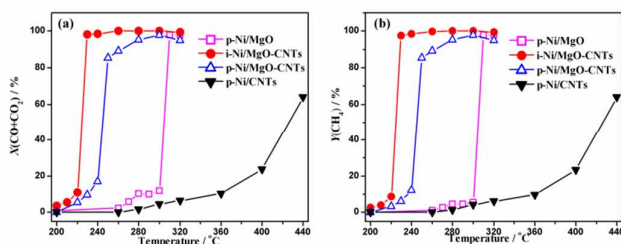

Fig. 2 The performances of syngas methanation over different catalysts: (a) CO conversion; (b) CH_4 yield. (□: p-Ni/MgO; ●: i-Ni/MgO-CNTs; △: p-Ni/MgO-CNTs; ▼: p-Ni/CNTs. Reaction conditions: 0.1 MPa, V(H_2)/V(CO)/V(N_2)/V(CO_2) = 75/15/5/5, GHSV = 40000 mL h^{-1} g^{-1}.)

In order to understand the roles of *in-situ* growth CNTs on Ni/MgO for syngas methanation, three catalysts were prepared for comparison: Ni/CNTs and Ni/MgO were prepared by precipitation method, noted as p-Ni/CNTs and p-Ni/MgO; p-Ni/MgO-CNTs were also prepared by precipitation method, which had the same carbon component as i-Ni/MgO-CNTs-10 (C content of 22.2%, see Tab. S1). As shown in Fig. 2, p-Ni/CNTs catalyst shows the worst catalytic performance for syngas methanation. The catalytic performance for syngas methanation over p-Ni/MgO-CNTs is better than that over p-Ni/MgO, but still worse than that of i-Ni/MgO-CNTs-10, as can be seen from Fig. 2.

XRD and Raman characterizations were carried out to understand how the preparation method and *in-situ* growth CNTs influence the catalytic performances for syngas methanation. XRD patterns of the four as-prepared catalysts before or after reaction were shown in Fig. 3. The diffraction patterns of the catalysts show little change after reaction, except for the impurity carbon at 2θ = 26.5° (JCPDS No. 026-1076) over the used p-Ni/CNTs catalyst. The large Ni particles (~70.9 nm) on p-Ni/CNTs catalyst, calculated by Scherrer equation based on XRD result, suggests that the dispersion of Ni is very poor on CNTs, which is one of possible reasons for poor catalytic performances of syngas methanation over p-Ni/CNTs catalyst. The peaks assigned to metallic Ni are not observed in p-Ni/MgO catalyst, indicating that Ni is uniformly distributed on MgO.

These XRD results indicate that MgO is more beneficial for the dispersion of Ni than CNTs. The i-Ni/MgO-CNTs and p-Ni/MgO-CNTs catalyst have similar Ni particle sizes (9.3 nm and 6.7 nm, respectively), which are smaller than that of p-Ni/CNTs catalyst but larger than that of p-Ni/MgO catalyst. The XRD results and catalytic evaluations suggest that Ni particle size is not the only factor which influences the catalytic performances for syngas methanation.
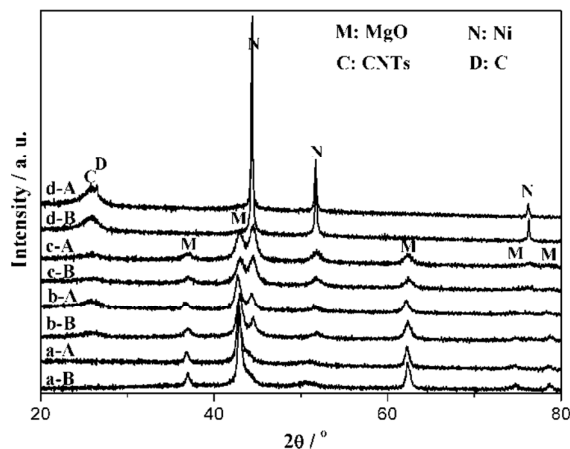

Fig. 3 XRD patterns of Ni catalysts prepared by different method before reaction (noted as –B) and after reaction (noted as –A): a: p-Ni/MgO; b: i-Ni/MgO-CNTs; c: p-Ni/MgO-CNTs; d: p-Ni/CNTs.
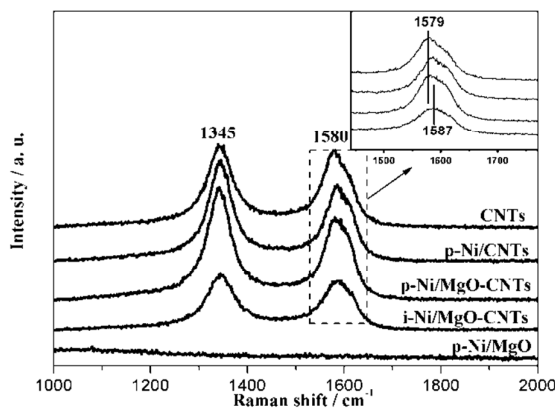

Fig. 4 Raman spectra of CNTs and the Ni catalysts prepared by different methods.

Raman spectroscopy is one of the most effective methods for CNTs characterization. In Raman spectra, CNTs shows a strong peak around 1580 cm^{-1} noted as G band (Graphite band), which is related to the C-C stretching vibration of the sp^2 orbital structure, and a strong peak around 1350 cm^{-1} noted as D band (Disorder band), which is contributed to the disorder-induced vibration of C-C bond.[14] Fig. 4 shows the Raman spectra of i-Ni/MgO-CNTs, p-Ni/MgO-CNTs and p-Ni/CNTs, as well as CNTs. The Raman band at ~1345 cm^{-1} and ~1580 cm^{-1} correspond to

the D band and G band of CNTs. The ratios of I_D/I_G of the catalysts are between 1.0 and 1.2, which are very close to each other, indicating that the graphitization extents of CNTs are relatively uniform in different catalysts. However, it is worth noting that the G band shows up-shift from 1579 to 1587 cm^{-1} for i-Ni/MgO-CNTs catalyst compared with the purified CNTs, p-Ni/MgO-CNTs and p-Ni/CNTs. Guo et al.[15] reported that in comparison with graphene (GR), a G-band up-shift from 1595 to 1604 cm^{-1} was observed for WO_3@GR prepared by ultrasonic method, and demonstrated the charge transfer and a dyadic bonding between GR and WO_3. We speculate that the G band up-shift of i-Ni/MgO-CNTs is attributed to the strong interaction between CNTs and Ni/MgO in i-Ni/MgO-CNTs catalyst prepared by *in-situ* CVD growth of CNTs on Ni/MgO. However, there is no shift of G band observed in the catalysts prepared by precipitation method, indicating weak interaction between CNTs and Ni or Ni/MgO in p-Ni/CNTs and p-Ni/MgO-CNTs. These results indicate that *in-situ* growth CNTs on Ni/MgO by CVD is an effective method to enhance the interaction between CNTs and Ni/MgO.
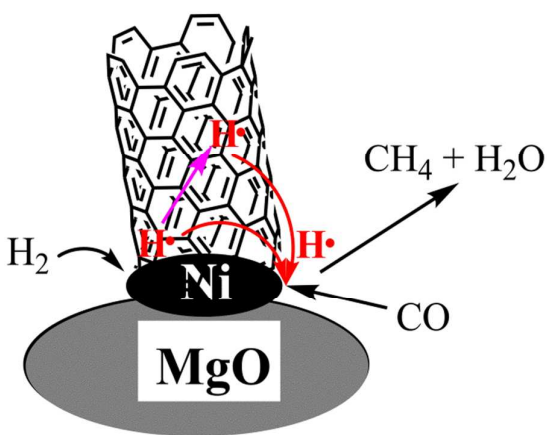

Fig. 5 Interface of Ni, CNTs and MgO with strong interaction in i-Ni/MgO-CNTs catalyst for methanation.

The growth of CNTs using CVD method is believed to occur *via* decomposition of the CO gas molecules on the Ni particle surface, diffusion of the carbon atoms through the particle, and subsequent precipitation at the Ni particle/CNTs interface.[16] Generally, the major growth mechanisms of CNTs using CVD method involve either base growth or tip growth.[17] The adhesion force between the metal particles and the substrate is considered to be the determinant of the growth mode of CNTs using CVD method that a weak interaction favors the tip-growth mode while a strong interaction favors base-growth.[18] The strong interaction between Ni and MgO has been previously reported.[19] It is believed that Ni is sufficiently strong in Ni/MgO catalyst to prohibit Ni particles from moving during the CNTs growth process. Indeed, the hollow tip shown in Fig. S5 (in ESI) implies that the growth of the CNTs on Ni/MgO catalyst using CVD method is attributed to the so-called "base growth" mode in which the Ni particle is located at the base of the growing

CNTs.[16] This growth mode will result in strong interaction between Ni and CNTs in i-Ni/MgO-CNTs catalyst prepared by *in-situ* CVD, which is attributed to the up-shift of G band from 1579 to 1587 cm^{-1} for i-Ni/MgO-CNTs in Raman spectra. Meanwhile, there is a strong interaction between Ni and MgO. Based on the above findings, the model of i-Ni/MgO-CNTs catalyst is suggested as shown in Fig. 5. Fig. 5 illustrates that Ni interacts strongly with both CNTs and MgO, therefore, resulting in the formation of an interface of Ni, CNTs and MgO with strong interaction with each other.

Hydrogenation of CO to methane mainly involves two reaction steps: 1). activation of CO; 2) hydrogenation of C*-adspecies to form CH_x*.[20] It is likely that smaller Ni particles provide more active sites for CO activation and C* hydrogenation, but the chemical environment of Ni may play more important role in these steps as confirmed by above XRD characterizations, catalytic evaluations, which are also supported by literature reports.[21] As mentioned above, *in-situ* CVD method resulted in a strong interaction between Ni/MgO and CNTs, which greatly changed the chemical environment of Ni. On the other hand, the interface formed among Ni, CNTs and MgO in i-Ni/MgO-CNTs with strong interactions among these components had more influence on the chemical environment of Ni. Moreover, the interface of metal and supports is generally believed to have more crucial impact on the activity of catalyst.[22] Therefore, the improved performances for SNG from syngas on i-Ni/MgO-CNTs can be attributed to the highly active interface formed among Ni, CNTs and MgO with strong interaction with each other. It is also worth noting that there are two properties of CNTs which are closely related to the catalytic performances for hydrogenation, one is hydrogen storage,[23] the other is electron-storage capacity (one electron for every 32 carbon) which can serve as electron channels for catalytic reaction.[24] No doubt, the strong interaction between CNTs and Ni/MgO is in favour of the storage of hydrogen, which is dissociated on Ni, and electrons transfer between CNTs and Ni active sites and thus increasing the rate of catalytic reactions. Based on above results, a model of enhanced catalytic performance for syngas methanation over i-Ni/MgO-CNTs catalysts can be proposed which is shown in Fig. 5.

In summary, we presented here a new facile strategy for the preparation of Ni/MgO-CNTs catalyst by *in-situ* CVD growth of CNTs on Ni/MgO in methanation reactor. By introducing CO to the reactor before methanation, the CNTs promoted Ni/MgO catalysts are *in-situ* prepared which exhibit excellent catalytic performances for SNG from syngas at low reaction temperature. This preparation method requires neither a surfactant/ligand nor a CNTs pre-treatment. The improved catalytic activity at low reaction temperature for i-Ni/MgO-CNTs may be attributed to the following aspects from the *in-situ* growth of CNTs on Ni/MgO. First, the highly active interface was formed among Ni, CNTs and MgO with strong interaction with each other. In addition, the strong interaction between CNTs and Ni/MgO is in favour of the storage of hydrogen and electrons transfer between CNTs and Ni active sites and thus increasing the rate of catalytic reactions. It is expected that this simple and environmentally friendly preparation method for *in-situ* preparation of CNTs promoted catalysts presented herein may be further extended to prepare

other CNTs promoted catalysts with excellent catalytic performance.

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