

Effect of Sm Addition on Ni–MgO Catalysts for the Synthesis of Carbon Nanotubes via Methane Decomposition

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Carbon nanotubes (CNTs) have been synthesized over Ni–MgO and Ni–Sm–Mg catalysts by decomposition of CH₄ at 923 K. The addition of Sm into Ni–MgO catalyst promotes its catalytic activity and lifetime. The yield of CNTs obtained over the optimized Ni–Sm–Mg catalyst reaches 1260 wt% relative to the weight of the catalyst, which is more than 4 times that of the Ni–MgO catalyst. The possible interaction between Sm and Ni species is discussed.

Catalytic chemical vapor deposition (CCVD) method is regarded as a promising method to synthesize carbon nanotubes (CNTs) because it is of benefit to achieve high yield of CNTs and easily scale-up the production of CNTs at a relatively low cost.¹ In the CCVD approach, both the support and catalyst metals play an important role in CNTs growth.² To enhance the catalytic activity and lifetime of catalyst is an efficient route to increase the yield of CNTs. It has been reported that bimetallic supported catalysts, such as Co–Mo/SiO₂,³ Fe–Co/MgO,⁴ Fe–La/Al₂O₃,⁵ Ni–V/ZSM-5,⁶ are superior to those monometallic supported catalysts, in terms of catalytic activity, selectivity, lifetime, and the yield of CNTs. Among various supports, MgO can be easily removed by acidic treatment. However, as far as we know, few studies on the performance of modified Ni–MgO catalyst for methane decomposition to CNTs were reported. In the present work, we found that the addition of Sm can promote the catalytic activity and the lifetime of the Ni–MgO catalyst.

All catalysts were prepared by combustion synthesis, with citric acid as a foaming and combustion additive. A mixture of citric acid, Ni(NO₃)₂, Mg(NO₃)₂, and Sm(NO₃)₃, with the desired molar ratio was dissolved in distilled water, and then, evaporated at 393 K until a viscous syrup was formed. It was directly burned in air at 773 K and subsequently calcined at 973 K for 5 h, and finally ground to a fine power. According to the molar ratio of Ni:Sm:Mg, the catalysts were defined as Ni–MgO (45Ni–55Mg), 45Ni–5Sm–50Mg, 45Ni–10Sm–45Mg, 45Ni–15Sm–40Mg, 45Ni–55Sm, and 45Sm–55Mg, respectively. 100 mg of catalysts was placed in a horizontal tubular reactor and was first reduced in a flow of purified H₂ from room temperature to 923 K and was kept at the same temperature for 10 min, then the feed was switched to the mixture gas of methane/nitrogen (1:1) at a total flow rate of 80 mL/min. When methane conversion decreased to about 10%, the reaction was stopped, and the sample was cooled to room temperature in N₂ atmosphere. The product mixtures were analyzed on a gas chromatography using high purity Ar (99.99%) as the carrier gas. For purification, about 100 mg of raw products were sonicated in 80 mL 3 M HNO₃ for 20 min at room temperature, then washed with distilled water and dried at 393 K. Temperature programmed reduction

(TPR) of the sample was conducted in a fixed-bed continuous flow reactor-TCDC system. The sample (30 mg) was reduced in a 5% H₂–Ar stream of 40 mL/min, with a heating rate of 10 K/min from room temperature up to 1023 K. The X-ray diffraction (XRD) patterns of the samples were recorded on a PANalytical X'Pert PRO XRD with Cu radiation at a scanning rate of 4°/min. TEM images of samples were obtained on a JEOL-1200EX TEM operating at 80 kV.

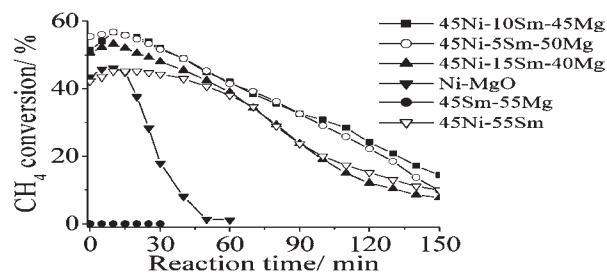


Figure 1. CH₄ conversion as a function of time on stream at 923 K over various Ni–Sm–Mg catalysts. (BET surface area of various Ni containing catalysts: (▼) 25.8 m² g⁻¹, (○) 23.5 m² g⁻¹, (■) 20.0 m² g⁻¹, (▲) 27.1 m² g⁻¹, and (▽) 26.3 m² g⁻¹.)

Figure 1 shows methane conversions with time over the Ni–MgO, Ni–Sm and Ni–Sm–Mg catalysts at 923 K. From Figure 1, we can see that the addition of Sm to the Ni–MgO catalyst increases the catalytic activity, and in particularly the catalytic lifetime, which is about 5 times longer than that of the Ni–MgO catalyst, which indicates the addition of Sm can favor the growth of CNTs, although Sm has no catalytic activity. In addition, the catalytic lifetime of the 45Ni–55Sm catalyst is much longer than that of the Ni–MgO catalyst. The 45Ni–10Sm–45Mg catalyst shows the highest catalytic activity and lifetime, and the yield of carbon nanotubes reaches 1260 wt% (150 min reaction) which is more than 4 times higher than that of the Ni–MgO catalyst, and also higher than that previous reported data.^{7–9} The catalytic activity and lifetime of the 45Ni–5Sm–50Mg catalyst are just a little lower than that of the 45Ni–10Sm–Mg catalyst,

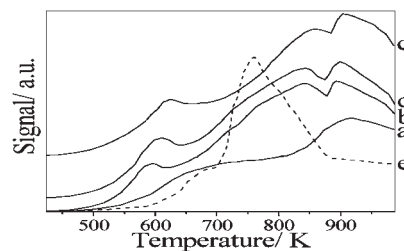


Figure 2. TPR profiles of Ni–MgO (a), 45Ni–5Sm–50Mg (b), 45Ni–10Sm–45Mg (c), 45Ni–15Sm–40Mg (d), 45Ni–55Sm (e).

but higher than that of the 45Ni–55Sm, and 45Ni–15Sm–40Mg catalysts.

Figure 2 shows the TPR profiles of the Ni–MgO, Ni–Sm and Ni–Sm–Mg catalysts. The Ni–MgO catalyst shows a main hydrogen consumption at about 918 K that can be ascribed to the reduction of NiO strongly interacted with MgO (formed Ni–MgO solid solution⁷) and a broad hydrogen consumption between 623 and 823 K due to the reduction of NiO in weak interaction with MgO. The 45Ni–55Sm catalyst shows a main hydrogen consumption peak at about 760 K, which is much lower than that of the Ni–MgO catalyst. Comparing with the Ni–MgO catalyst, the TPR profiles of the Ni–Sm–Mg catalysts showed significant changes. There are two new reduction peaks at about 613 and 853 K except the main peak at about 898 K, which indicates that there is a remarkable interaction of Ni with Sm species. At the same time, the TPR profiles of the Ni–Sm–Mg catalysts present lower temperature peaks with higher hydrogen consumptions than that of the Ni–MgO catalyst. These results clearly reveal that the addition of Sm facilitates the reduction of nickel. Because the presence of Ni metal particles on the supports is essential for the methane decomposition,¹⁰ the Ni–Sm–Mg catalysts show higher catalytic activity than the Ni–MgO catalyst. Furthermore, the TPR profiles of the Ni–Sm–Mg catalysts with different Sm amounts are similar, only small changes in the reduction temperature are observed. The 45Ni–10Sm–45Mg shows the highest temperature peaks (623, 858, 903 K) among the three Ni–Sm–Mg catalysts, while the 45Ni–55Sm–50Mg shows the lowest temperature (597, 842, 893 K). It evidences the complex interactions between Ni species and the support. We suppose a stronger interaction between nickel and Sm species in the 45Ni–10Sm–45Mg, which results in a higher catalytic activity and lifetime.

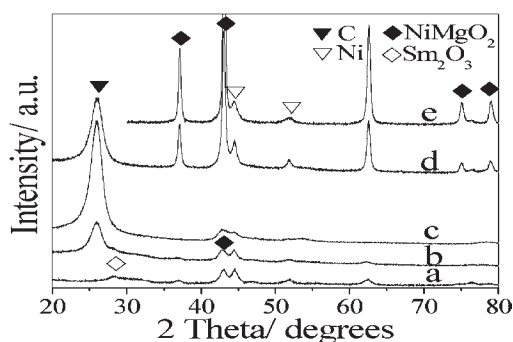


Figure 3. XRD patterns of reduced 45Ni–10Sm–45Mg (a), raw CNTs 30-min reaction over 45Ni–10Sm–45Mg (b), purified CNTs 150-min reaction over 45Ni–10Sm–45Mg (c), raw CNTs 30-min reaction over Ni–MgO (d), and reduced Ni–MgO (e).

Figure 3 shows the XRD of the reduced Ni–MgO and 45Ni–10Sm–45Mg catalysts, the raw CNTs obtained over the above-mentioned catalysts for 30-min reaction, and the purified CNTs over the 45Ni–10Sm–45Mg catalyst for 150-min reaction. The relative intensity of Ni (111) of the Ni–Sm–MgO catalyst (Figure 3a) is much higher than that of the Ni–MgO catalyst (Figure 3e), indicating that a higher fraction of nickel in Ni–Sm–MgO catalyst reduced than that in Ni–MgO catalyst, which is consistent with the TPR results. On the other hand, Figures 3b and 3d show that the average sizes of the Ni particles remained about 22 nm after 30 min reaction for the Ni–Sm–MgO catalyst,

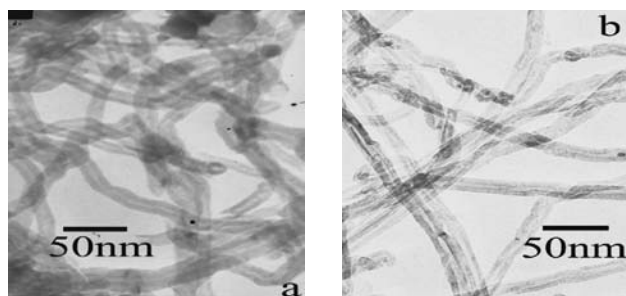


Figure 4. TEM images of raw CNTs 30-min reaction over Ni–MgO (a), raw CNTs 150-min reaction over 45Ni–10Sm–45Mg (b).

while for the Ni–MgO catalyst it increased to about 86 nm according to Scherrer’s equation, which indicates that Sm species can prevent the Ni particles from agglomerating because of the strong interaction between Ni and Sm species. The main reason for the deactivity of Ni–MgO may be the agglomeration of Ni. Therefore, the introduction of Sm into the Ni–MgO catalyst can favor the growth of carbon nanotubes. The XRD pattern of purified CNTs (Figure 3c) shows that characteristic graphitic peaks at 2θ values of 26.03° (002) along with other planes (100) at 42.90° , and (101) at 44.42° . The result shows no significant difference from the diffraction pattern of normal CNTs.¹¹

Figure 4 shows all the carbon nanotubes observed are multi-walled carbon nanotubes, the outer diameters of CNTs obtained from the Ni–MgO catalyst and the Ni–Sm–MgO catalyst are in the range 15–40 nm and 15–25 nm, respectively. The purity of the both CNTs is above 95% by TG analysis (not shown). Because the carbon nanotubes diameter is dictated by the catalyst particle size,¹ it indicates that the agglomeration of Ni particles in the 45Ni–10Sm–45Mg catalyst was suppressed owing to the interaction between Sm and Ni species, which is in agreement with the XRD results. Our results indicate that the introduction of Sm into Ni–MgO catalysts is suitable for the carbon nanotube growth. Nevertheless, further studies will be taken to clear the promoting effect of Sm addition to Ni–MgO catalyst. We suggest that catalytic decomposition of methane on Ni–Sm–MgO catalysts can be a promising a large-scale and low-cost production of CNTs.

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