

Enhanced Activation and Decomposition of CH₄ by the Addition of C₂H₄ or C₂H₂ for Hydrogen and Carbon Nanotube Production

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The decomposition of CH₄ in the presence of C₂H₄ or C₂H₂ using a nanosized iron or nickel based catalyst with volume ratios of C₂H₄ or C₂H₂ to CH₄ of 1.75:1 to 0.55:1 was investigated. The presence of C₂H₄ or C₂H₂ increased the conversion of CH₄ to 3 to 5 times that with no C₂H₄ or C₂H₂; that is, it significantly increased the production rate of carbon from 20–30 to 45–75 g/gcat/h at 723–873 K. The online detection of the time dependent composition of the product gas and experiments in which the feeding sequence of CH₄ and C₂H₄/C₂H₂ was changed allowed us to propose a mechanism for the enhanced decomposition as follows. First, the facile exothermic adsorption and decomposition of C₂H₄ or C₂H₂ provides the driving force for the in situ endothermic decomposition of CH₄. Subsequently, the thermodynamically favored intermediate products of aromatics or poly aromatics are formed by the insertion of CH₄ into adsorbed C₂H₄ or C₂H₂ fragments. Finally, the intermediate products are rapidly dehydrogenated on the high activity catalyst to form carbon nanotubes (CNTs). The enhancement effect is dependent on the ratio of C₂H₄ to CH₄ but independent of the ratio of C₂H₂ to CH₄, which was explained as being due to the different exothermicities of the C₂H₄ and C₂H₂ reactions. This finding provides a new stimulus for methane activation at low temperature to produce hydrogen and CNTs with high efficiency.

Introduction

There is continuous interest in the activation and decomposition of CH₄ due to its importance in hydrogen production by steam reforming, partial oxidation, CO₂ reforming,^{1,2} and direct catalytic decomposition (to produce H₂ free of carbon oxides (as a fuel for the proton exchange membrane fuel cell) and carbon nanotubes (CNTs) simultaneously).^{2–8} The common feature in the above processes is the high temperature operation due to the stable C–H bond of CH₄ that makes it very difficult to decompose.² For instance, when graphite is the final carbon product in the direct catalytic decomposition of CH₄, a thermodynamics calculation showed that the temperature has to be higher than 973 K to get a conversion of CH₄ higher than 60%.^{5,6,8} However, the actual conversions of CH₄ at 873 and 973 K are only 20% and 30%, respectively, due to the lower thermodynamic stability of other carbon products present besides the assumed graphite.^{2–8} A high temperature operation, however, not only needs high energy consumption, but also presents challenges concerning the reactor material and thermal stability and activity of the catalyst.^{2–8} Also, rapid sintering and carbon encapsulation of the catalyst are often reported in the direct decomposition of CH₄.^{2–8} Thus, it is of significance to find ways

to increase the conversion of CH₄ in low temperatures to overcome these disadvantages.

A previous study reported that the conversion of CH₄ could be increased to 70% at 873–973 K and the yield of carbon increased 4 times when directly using the unreduced nickel or cobalt catalyst to decompose CH₄.⁸ The possible mechanism for this is the reaction equilibrium shift by hydrogen consumption (by the in situ catalyst reduction) and a possible heat coupling effect from the exothermic reaction of catalyst reduction and the endothermic decomposition of CH₄. However, this effect is difficult to maintain in a steady state operation due to the gradual consumption of the oxygen on the catalyst.

Here, we report, for the first time, a simple way to decrease the decomposition temperature of CH₄ as well as maintain its high conversion by the addition of C₂H₄ or C₂H₂ to the feed. Specifically, the conversion of CH₄ can be increased to 80% by the addition of C₂H₄ or C₂H₂ when using a nickel based catalyst at 723 K or an iron based catalyst at 873 K. The production rate of carbon was increased from 30 to 45–75 g/gcat/h. This observed effect existed with many kinds of nanosized catalysts including Ni/Cu/Al₂O₃, Ni/Al₂O₃, and Fe/Mo/Al₂O₃. The stable lifetime of the catalyst was about 2 h when used in a fluidized bed reactor. These results are useful for finding an effective way to decompose CH₄ at low temperatures.

Experimental Section

The Ni/Cu/Al₂O₃ and Fe/Mo/Al₂O₃ catalysts used have been reported elsewhere.^{6,9} Detailed information of the catalysts,

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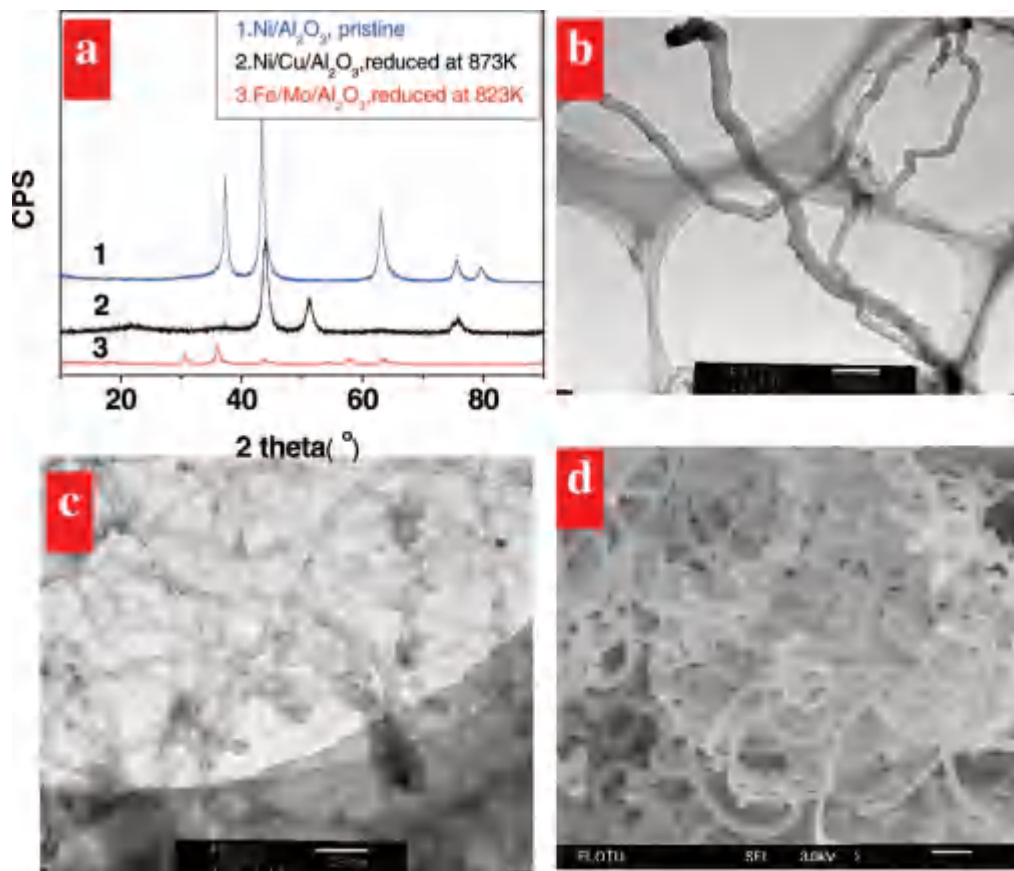


Figure 1. XRD plot of catalysts and TEM/SEM images of as-grown CNTs: (a) XRD plot of catalysts (Ni/Cu/Al₂O₃ and Fe/Mo/Al₂O₃ catalysts are in the noncrystalline state, so XRD is conducted after their reduction under protection by ethanol); (b) TEM image of CNTs grown on a Ni/Cu/Al₂O₃ catalyst (C₂H₄/CH₄ = 0.25, scale bar = 500 nm); (c) TEM image of CNTs grown on a Fe/Mo/Al₂O₃ catalyst (C₂H₄/CH₄ = 0.55, scale bar = 50 nm); and (d) SEM image of CNTs grown on a Ni/Al₂O₃ catalyst (C₂H₄/CH₄ = 0.25, scale bar = 200 nm).

including the Ni/Al₂O₃ catalyst, is shown in section S1 of the Supporting Information. The gases (CH₄, H₂, C₂H₄, and C₂H₂, all 99.99% purity) used were purchased from Beijing Analytic Instrument Company. The experiments were conducted in a quartz fluidized bed with an inner diameter of 20 mm and a height of 600 mm (section S2 in the Supporting Information). Generally, about 0.03–0.1 g of catalyst was put into the fluidized bed reactor and reduced by hydrogen at set temperatures. The reactant gases were then fed into the reactor from the bottom of the fluidized bed and decomposed by catalysts to make CNTs. The product gas was analyzed by using an online gas chromatograph (HP4890 D, TCD detector and TDX-carbon sieve column) and a mass spectrometer (Hiden, QIC20 demo, equipped with a secondary electron multiplier detector and a Faraday detector, respectively). The mass spectrometer has two detectors for the different concentrations of gases and is effective to detect H₂, CH₄, and C₂H₄/C₂H₂ in large amounts and the aromatics in small amounts simultaneously. The method to calculate the conversion of CH₄ and the method to determine the carbon production rate are in the Supporting Information (S3 and S4).

The carbon products over the different catalysts were characterized by transmission electron microscopy (TEM, JEOL12010) and scanning electron microscopy (JSM7401F).

Results and Discussion

Figure 1 presents the X-ray diffraction (XRD) results of different catalysts and the morphologies of typical CNT products. These are metal supported catalysts with metal

crystallite sizes in the range of 8–25 nm (Figure 1a) and are effective to decompose carbon sources and to make CNTs by the chemical vapor deposition method (Figure 1b–d and section S5 in the Supporting Information). Though these catalysts varied in their composition and crystallite size and the CNT products also varied in diameter and straightness, we observed the enhanced effect of C₂H₄ or C₂H₂ on the activation and decomposition of CH₄ using various catalysts, indicating the generality of this method.

As follows, we will mainly discuss the catalysis of such an enhanced effect. First, the conversions of pure CH₄, C₂H₄, and C₂H₂ over the catalysts were obtained. The conversions of CH₄ on the Ni/Cu/Al₂O₃ catalyst at 823 and 873 K were 13.5% and 22%, respectively, in agreement with previous results.⁶ C₂H₄ or C₂H₂ were 100% decomposed on the iron or nickel catalyst at 823–873 K. Figure 2a presents the conversion of CH₄ without and with the addition of C₂H₂ on the Ni/Cu/Al₂O₃ catalyst at 873 K. The conversions of pure CH₄ and pure C₂H₂ were 22% and 100%, respectively. However, the initial conversion of CH₄ in the presence of C₂H₂ significantly increased from 22% to 53% to 70% using different ratios of C₂H₂ to CH₄. With gradual carbon deposition on the catalyst as shown in Tables 1 and 2, the catalyst lost its activity gradually and the stable lifetime for a conversion of CH₄ greater than 40% was about 20–40 min. To the effect of C₂H₄ addition, the initial conversion of CH₄ was a function of the ratio of CH₄ to C₂H₄ (Figure 2b). It is seen that the initial conversion of CH₄ can be higher than 80% over the Ni/Al₂O₃ catalyst at 723 K and over the Fe/Mo/Al₂O₃ catalyst at 873 K. It should be noted here that the conversion

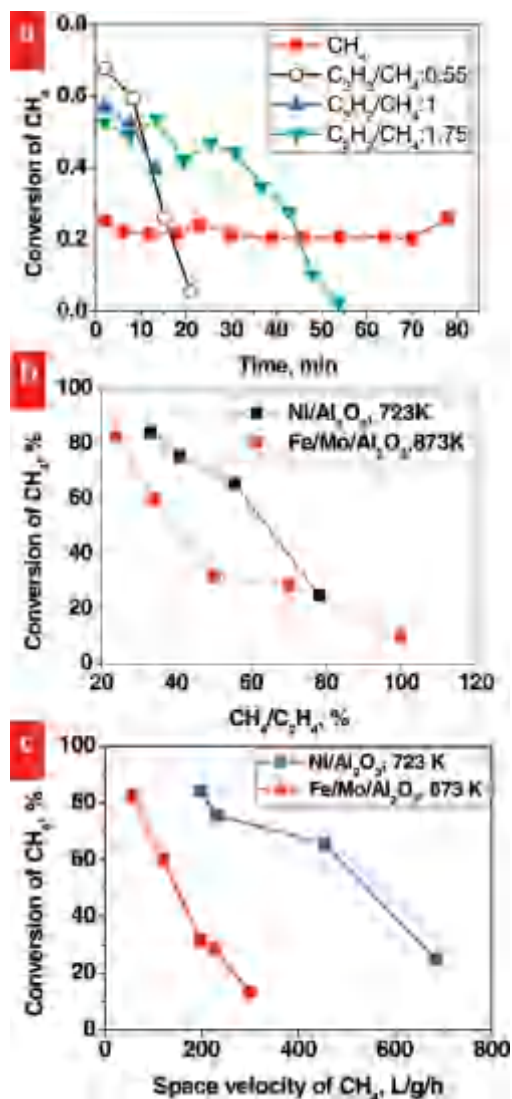


Figure 2. Enhanced effect of C₂H₂ or C₂H₄ on the activation and conversion of CH₄: (a) conversion of CH₄ as a function of the ratio of C₂H₂ to CH₄ on a Ni/Cu/Al₂O₃ catalyst at 873 K; (b) conversion of CH₄ as a function of the ratio of CH₄ to C₂H₄ on a Fe/Mo/Al₂O₃ and a Ni/Al₂O₃ catalyst (at a constant flow rate of C₂H₄); and (c) CH₄ conversion at different space velocities of CH₄, at a constant space velocity of C₂H₄ of 200 L/gcat/h.

of CH₄ in the presence of C₂H₂ or C₂H₄ at 723 and 873 K was far higher than the thermodynamic equilibrium value for the decomposition of pure CH₄ at the same temperature. Moreover, in contrast to Figure 2a, the initial conversion of CH₄ increased almost linearly with the decreased ratio of CH₄ to C₂H₄ (Figure 2b). It appears that C₂H₄ present in a large amount provides a large driving force for the conversion of CH₄, which will be further discussed below. These data were obtained with keeping the flow rate of C₂H₄ unchanged. Thus, the space velocity of CH₄ and C₂H₄ for a high ratio of CH₄ to C₂H₄ (Figure 2c) was nearly twice that of a low ratio of CH₄ to C₂H₄, which caused the catalyst to deactivate rapidly.⁵

We also present the detailed carbon deposition rate and gross weight of carbon product in Tables 1 and 2. Generally, different catalysts deactivated at different rates that vary from 20 to 120 min for total deactivation under different space velocities. For a fair comparison, we mainly use the carbon deposition rate to evaluate the enhancement effect by C₂H₄ or C₂H₂. This reflects the average carbon deposition rate at specified times. Tables 1

and 2 both show that the carbon deposition rate from pure CH₄ or pure C₂H₄ on a particular catalyst both increase with temperature. The effect on the Fe/Mo/Al₂O₃ catalyst is less significant than that on the Ni/Cu/Al₂O₃ catalyst, indicating that the activity of iron is lower than that of nickel. These tendencies are both in agreement with previous results.⁶ Although there is some data fluctuation, most of the data of Table 1 indicate that the carbon production rate is 45–75 g/gcat/h in the presence of C₂H₄, which is higher than the 20–30 g/gcat/h rate from the summed value from pure CH₄ and pure C₂H₄. Similarly, most of the data of Table 2 indicate that the carbon production rate is 40–60 g/gcat/h in the presence of C₂H₂, which is higher than the 35 g/gcat/h rate from the summed value from pure CH₄ and pure C₂H₂. The above results all indicated clearly that the decomposition of CH₄ is significantly enhanced in the presence of C₂H₄ or C₂H₂.

To understand this in more detail, we traced the detailed process of the combined decomposition of CH₄ and C₂H₄ (Figure 3) or CH₄ and C₂H₂ (section S6 in the Supporting Information) by mass spectrometry (MS). Generally, the peak intensities of H₂, CH₄, and C₂H₄ are about 10⁻⁶–10⁻⁷ Torr (Figure 3a and b), and the peak intensity of some aromatics is about 10⁻¹¹ Torr (Figure 3c). The existence of aromatics is independent of the isolated feed of CH₄ and C₂H₄/C₂H₂ or the feed of mixed gases of CH₄ and C₂H₄/C₂H₂, though their peak intensities varied in different operating conditions. The results indicated that aromatics are intermediate products in the process. The existence of aromatic intermediates in the formation of CNTs in the present work is in agreement with the previous UV–Raman characterization of CNT products as decomposing C₂H₂ on an iron catalyst¹⁰ and is similar to those in other reaction systems.^{11–13} The result, we think, is reasonable because our catalysts (Ni/Cu/Al₂O₃, Fe/Mo/Al₂O₃) contain Mo or Cu species and the Al₂O₃ support has some acidic property, which is to some degree similar to the catalyst for the aromatization of CH₄.¹¹ Meanwhile, the intensity of aromatics in the feed of mixed gas is lower than that in the feed of pure CH₄, also indicating the quick dehydrogenation of aromatic intermediates to form the final CNT products.

Furthermore, the time dependent gas composition by MS indicated that there is an obvious induction period at the initiation of the reaction, where the intensity of H₂ is very low as compared with those of CH₄ and C₂H₄ (Figure 3d). The result indicated that C₂H₄ is not first totally decomposed to H₂ and CNTs but simultaneously decomposed with CH₄. Though there was a difference using C₂H₂ and C₂H₄, aromatics were formed as intermediate products and then the subsequent dehydrogenation of aromatics led to the significant increase in the concentration of hydrogen in the MS pattern. This provides clear evidence of the combination of CH₄ and C₂H₄ or C₂H₂ to form aromatics (see also S6 in the Supporting Information). Meanwhile, such results are supported by the calculation of the thermodynamics of the decomposition of CH₄ and C₂H₄/C₂H₂ considering the immediate products or not. In detail, if we assumed the prior total decomposition of C₂H₄ or C₂H₂, the presence of H₂ in large amounts is unfavorable for the subsequent decomposition of CH₄. The conversion of CH₄ will be significantly decreased, a conclusion which apparently differs from the experimental results. However, considering aromatics as immediate products, the conversion of methane in the presence of C₂H₄/C₂H₂ will become favorable in thermodynamics, in agreement with those in the aromatization of CH₄ in the presence of C₃H₈/C₄H₁₀.¹¹ Thus, we propose that the reaction route is first the combination of adsorbed CH₄ with adsorbed

TABLE 1: Data of Methane Decomposition Assisted by Ethylene Based on the Mass Balance

reaction system	catalyst (g)	space velocity (ml/s/g)			carbon g/g(cat)	time (min)	carbon deposition rate (gC/gcat/h)
		CH ₄	C ₂ H ₄	gross			
Ni/Cu/Al ₂ O ₃ 873 K	0.0317	35.05	0	35.05	16.62	78.5	12.7
	0.034	0	16.81	16.81	60.96	77.5	47.2
	0.040	27.78	15.28	43.06	93.61	78.4	71.6
	0.0344	11.63	11.63	23.26	100.16	110	54.6
	0.0464	15.30	26.94	42.24	50.64	48.8	62.3
Ni/Cu/Al ₂ O ₃ 823 K	0.0395	25.32	0	25.32	9.24	89	6.2
	0.0519	0	13.76	13.76	51.85	102.5	30.4
	0.0339	20.06	11.03	31.09	101.60	109	55.9
	0.0437	38.14	38.14	76.28	78.32	73.39	64.0
	0.056	14.29	25.01	39.30	71.35	65.3	65.6
	0.0557	19.75	0	19.75	1.34	101	0.8
Fe/Mo/Al ₂ O ₃ 873 K	0.0618	0	16.18	16.18	35.23	72	29.4
	0.0997	6.88	3.78	10.66	15.81	85	11.2 ^a
	0.0386	12.95	12.95	25.9	30.81	54.5	33.9
	0.0554	7.22	12.27	19.49	25.36	83.8	18.2 ^a
Fe/Mo/Al ₂ O ₃ 823 K	0.0349	28.65	0	28.65	1.71	88.5	1.2
	0.0574	0	19.16	19.16	26.05	118	13.2
	0.0377	18.04	9.92	27.96	36.73	63	35.0
	0.0623	13.38	13.38	26.76	12.84	46	16.7
	0.035	11.43	20.0	31.43	46.12	64.8	42.7

^a These data are low compared with other data, probably because of the fluctuation of the operation.

TABLE 2: Data of Carbon Deposition Rate over Different Catalysts Using the Feed of CH₄ and C₂H₂

reaction system	catalyst (g)	space velocity (ml/s/g)			carbon g/g(cat)	time (min)	carbon deposition rate (gC/gcat/h)
		CH ₄	C ₂ H ₄	gross			
Ni/Cu/Al ₂ O ₃ 873 K	0.0317	35.05	0	35.05	16.62	78.5	12.7
	0.0345	0	33.52	33.52	44.63	75	35.7
	0.0349	20.34	11.17	31.51	30.11	44.3	40.8
	0.0374	13.90	13.90	27.80	44.80	49.3	54.5
	0.0337	11.87	20.77	32.64	97.87	78	75.3
Ni/Cu/Al ₂ O ₃ 823 K	0.0395	27.84	0	27.84	9.24	89	6.2
	0.0412	0	32.14	32.14	70.8	120	35.4
	0.034	20.88	11.47	32.35	85.8	120.2	42.8
	0.0367	14.99	14.99	29.98	112.10	149.2	45.1
	0.0360	11.11	19.44	30.55	83.31	99	50.5
Fe/Mo/Al ₂ O ₃ 873 K	0.0557	19.75	0	19.75	1.34	101	0.8
	0.0339	0	32.45	32.45	58.41	101	34.7
	0.0369	10.57	19.24	29.81	11.14	37.8	17.7 ^a
	0.0390	14.10	14.10	28.20	20.82	31	40.3
	0.0336	11.90	11.90	23.80	43.73	56	46.9
Fe/Mo/Al ₂ O ₃ 823 K	0.0349	28.65	0	28.65	1.71	88.5	1.2
	0.0362	0	27.62	27.62	44.36	75	35.5
	0.0337	11.57	21.07	32.64	6.91	43.5	9.5 ^a
	0.0377	14.59	14.59	29.18	8.24	60.0	8.2 ^a
	0.0327	16.82	16.82	33.64	5.20	46.5	6.7 ^a

^a These data are low compared with other data, probably because of the fluctuation of the operation.

C₂H₄/C₂H₂ into aromatics, similar to that in ref 11. The role of the nanosized metal catalyst in this process lies in that it not only has high activity to decompose CH₄ or the mixed hydrocarbons, but also has excellent ability to form metal carbide, which is the key for the subsequent supersaturation of carbon in the bulk phase of metal and the final precipitation of carbon to form CNTs, via the vapor-liquid-solid model.^{3,5,6,8,10} Comparatively, the catalyst in the aromatization system is unable to endure the deposition of carbon in large amounts and is apt to deactivation.¹¹

To further provide evidence for the activation of CH₄ by C₂H₄/C₂H₂, we compared the operating mode of first feeding C₂H₄ and subsequently feeding CH₄ after 1 min, and first feeding CH₄ and subsequently feeding C₂H₄ after 1 min. In the former operating mode, the initial conversion of CH₄, decomposed by the Fe/Mo/Al₂O₃ catalyst, can be 70–75%, which is higher than the 60–65% observed in the latter operating mode. Similar

results were observed on changing the feeding sequence of CH₄ and C₂H₂. These results are clear evidence that the prior adsorption and decomposition of C₂H₄ or C₂H₂ on the catalyst provides the driving force for the further decomposition of CH₄. The process is probably similar to the formation of C₃H₆ by the reaction of CH₄ and C₂H₄, where the primary pathway involves the reaction of methyl radicals with adsorbed C₂H₄ to produce propyl radicals, which then lose a hydrogen atom to yield C₃H₆.¹³ In the present work, the formation of aromatics from the interaction of CH₄ and C₂H₂/C₂H₄ is very quick, because there are no C₃ hydrocarbons in Figure 3. Thus, we propose a model with C₂H₂ as an example to describe the above process, which is shown in Figure 4. In this model, we stress the prior adsorption of acetylene, the insertion of CH₄ into adsorbed C₂H₂ to form aromatics, and the further dehydrogenation of these intermediates allow the final formation of CNTs following either the tip growth mode or base growth mode. Here,

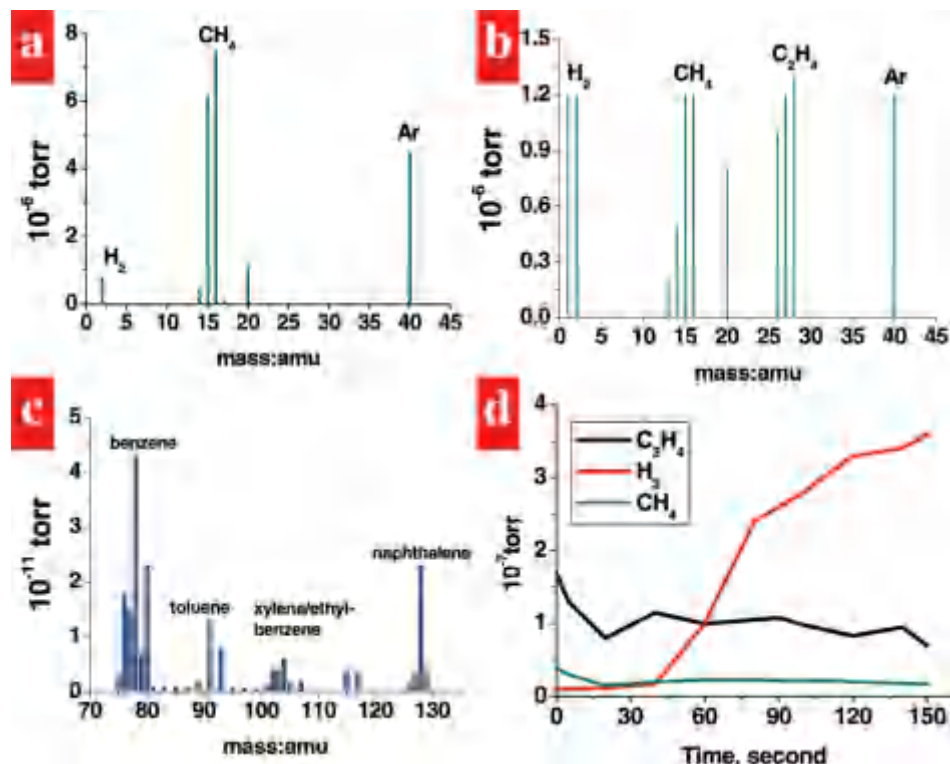


Figure 3. MS pattern of gas compositions in the feed of pure methane or mixed CH_4 and C_2H_4 over $\text{Fe}/\text{Mo}/\text{Al}_2\text{O}_3$ catalyst: (a) gas compositions in the feed of pure CH_4 (Faraday detector); (b) gas compositions in the feed of mixed CH_4 and C_2H_4 (Faraday detector); (c) composition of aromatics in the feed of mixed CH_4 and C_2H_4 (secondary electron multiplier detector); and (d) time dependent gas compositions in the feed of mixed CH_4 and C_2H_4 (Faraday detector).

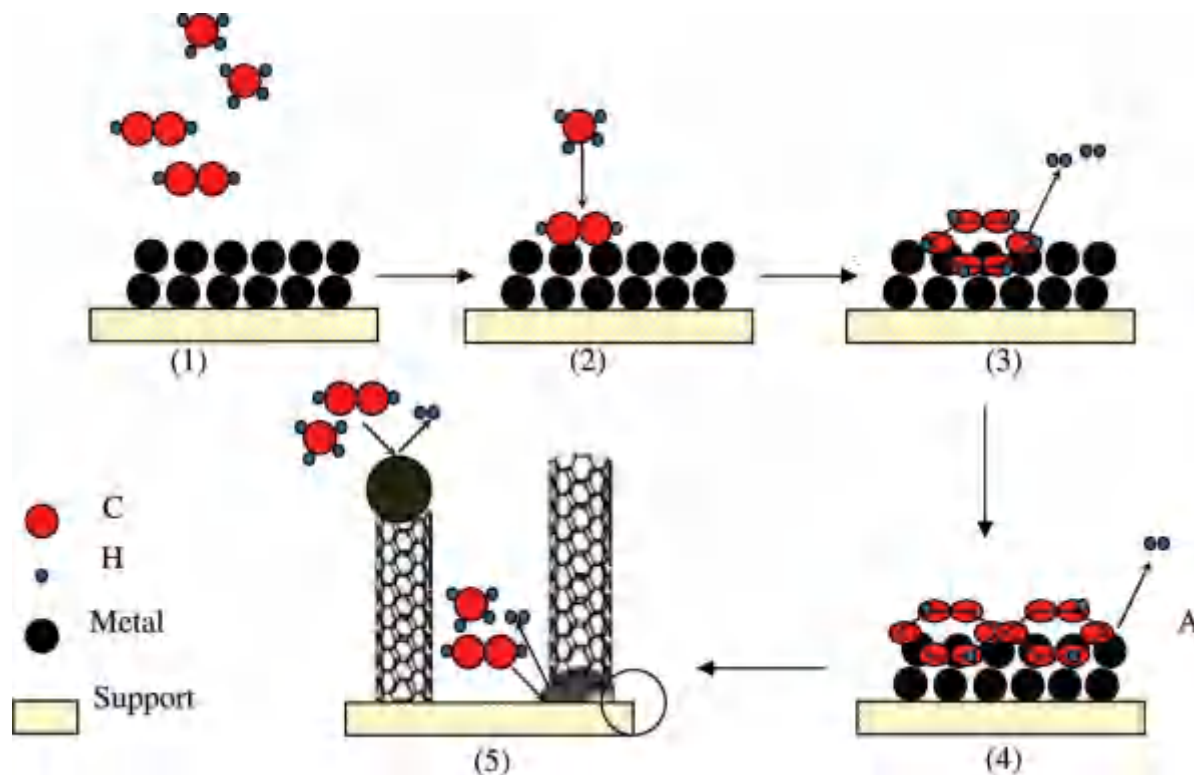


Figure 4. Model of the combined decomposition of CH_4 and C_2H_2 on a catalyst to produce H_2 and CNTs: (1) C_2H_2 in the bulk gas phase to the surface of the catalyst; (2) CH_4 insertion into adsorbed C_2H_2 on the surface of the catalyst; (3) formation of an aromatic intermediate on the surface of the catalyst; (4) formation of a polyaromatic intermediate on the surface of the catalyst; and (5) gradual dehydrogenation of intermediates to form the final CNT product. Note: (4) is the local A region of (5).

we admit the process is complex and the detailed formation route of aromatic intermediates is not considered in this model. Further investigation is needed.

Further, we also demonstrated the difference in the effect of C_2H_4 and C_2H_2 on CH_4 and the catalyst. With C_2H_4 , the initial conversion of CH_4 increased nearly linearly with an increasing

ratio of C₂H₄ to CH₄, while it is nearly independent of the ratio of C₂H₂ to CH₄. We proposed that this can be attributed to the different exothermic reaction heat contribution from C₂H₄ compared to C₂H₂. The decomposition of CH₄ is an endothermic reaction with a reaction heat of 75 kJ/mol.^{6,8,14–16} The decomposition of C₂H₄ and C₂H₂ are exothermic reactions with reaction heats of 52 and 269 kJ/mol,^{17,18} respectively. Previous results confirmed that, on Ni [111], C₂H₂ adsorbs exothermically with an adsorption energy of 2.9 eV,^{17,18} which is far higher than the (endothermic) 0.55–1 eV adsorption energy of CH₄.^{14–16} From this viewpoint, C₂H₂ in a small amount is enough for the activation of CH₄, as compared with the effect of C₂H₄. Moreover, C₂H₂ addition caused a more rapid deactivation of the catalyst as compared with C₂H₄, in agreement with the previous results.¹⁹ Thus, the average carbon deposition rate from C₂H₂ is lower than that from C₂H₄, as shown in Tables 1 and 2.

However, although deactivation of the catalyst is unavoidable, the lifetime of the catalyst in the fluidized bed reactor is much higher than that in a packed bed reactor (data not shown here). We propose here that the fluidized bed reactor has the large space suitable for the rapid volume increase of the CNTs during growth²⁰ and, consequently, can effectively avoid the deactivation of the catalyst by carbon encapsulation in a small growth space.^{6,20} Also, the lifetime of the catalyst using the mixture of CH₄ and C₂H₄/C₂H₂ is longer than that when using the pure carbon source, if the same space velocity is kept (Tables 1 and 2). This may be due to, with the use of the mixture of CH₄ and C₂H₄/C₂H₂, the gross reaction heat being mild (that is, neither highly exothermic nor highly endothermic), which is favorable for the thermal stability of the nanosized metal crystallites, especially for those in the inner pores of the catalyst, which could be adversely affected by a temperature gradient in the porous catalyst. As a further advantage, the combined decomposition of CH₄ and C₂H₄/C₂H₂ has lower gross energy consumption as well as much easier operation or control of the reactor than in the case of the decomposition of pure CH₄.

Our finding has many practical applications. The enhanced decomposition of hydrocarbons or other carbon sources, based on the heat coupling effect to break the equilibrium of an individual carbon source, may be general to increase the conversion of the carbon source, which is originally difficult to decompose. Since there are many kinds of gases containing CH₄ and C₂H₂ or containing both CH₄ and C₂H₄ or C₂H₆ (off gases in yields of up to millions of tons per year in the oil refinery industry), these may be used as a cheap carbon source to produce H₂ and CNTs on a large scale using our method, if they are equipped with the necessary purification steps to remove sulfur and other species poisonous to the catalyst.

Conclusions

We presented evidence that the decomposition of CH₄ can be enhanced by the presence of C₂H₄ or C₂H₂. This enhancement exists with different catalysts. We proposed that the mechanism is the facile prior adsorption of C₂H₄ or C₂H₂, the subsequent insertion of CH₄ into adsorbed C₂H₄ or C₂H₂ to form an aromatic or polyaromatic intermediate product on the catalyst, and the further dehydrogenation of the intermediates to form CNTs. This provides a new alternative for the low temperature activation and decomposition of CH₄ to produce hydrogen and CNTs on a large scale and at low cost.

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Supporting Information Available: XRD plots of Ni/Cu/Al₂O₃, Fe/Mo/Al₂O₃, and Ni/Al₂O₃ catalysts; schematic showing the experimental setup and CNT synthesis; calculation method of the conversion of methane; determination of the carbon deposition rate over different catalysts; TEM images of CNTs prepared by using different catalysts and carbon sources; and MS results of the decomposition of methane and acetylene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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