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Formation of bamboo-like nanocarbon and evidence for the quasi-liquid state of nanosized metal particles at moderate temperatures

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Carbon nano-filament formation in hydrocarbon and syngas based catalytic processes is fatal for supported metal catalysts as this leads to deactivation and crushing, and hence limitation of carbon deposition has been a major topic in catalysis.[1–5] Recently, the deliberate preparation of catalytically grown nanocarbons has been investigated because of their specific structure and potential for application in many fields.[6–8] Many nanocarbon conformations have been reported, such as tubular, coiled, helical, branched, octopus, *etc.* and have been found to be sensitive to the reaction conditions and catalyst properties.[9–14] Catalytic hydrocarbon decomposition[9–13] or arc-discharge evaporation of graphite[14–18] have been often used as preparation methods, though in the latter case, the presence of a metal is necessary as catalyst in the form of either vapor or droplets of melt. The selective preparation of a given formation is a challenge to catalysis researchers. Here, several nanocarbon conformations are shown to be formed with high morphological purity from methane on a copper–nickel–alumina catalyst, and some interesting phenomena related to the nanosized metal are reported.

A catalyst with a mol ratio Ni : Cu : Al of 75 : 15 : 10 was prepared by coprecipitation. The precipitate has a Feitknecht compound structure, which in ideal composition has formula $Ni_6Al_2CO_3(OH)_{16}\cdot 4H_2O$, However, here part of the Ni was replaced by Cu, the amount of Al was reduced, and the structure was distorted. After calcination, an NiO like phase is observed but with scattered XRD peaks. During reduction uniformly nanometer sized Ni-Cu alloy was obtained, as shown in Figs. 1 and 2. It is interesting that no structural information of other components except for NiO and Ni appeared in the XRD profiles of the oxidized and reduced state, respectively. Detailed catalyst preparation and reaction conditions have been published elsewhere.[9,10]

When this catalyst is exposed to methane–nitrogen (v/v = 1 : 2), at 773 K, and after the reaction rate reduced to zero, a large amount [93.5 mg C(mg Ni)$^{-1}$] of morphologically pure octopus carbon was formed. As shown in Fig. 3, the metal particles are polyhedral and are the origin of several nanocarbon fibers. When the temperature was 1023 K, and with the same feed, a large amount of hollow nanocarbon tubes are produced as shown in Fig. 4, with rare stick-shaped nanocarbon formed at the same time.

When this catalyst was exposed to methane–hydrogen (1 : 2, v/v) at temperatures of 1003 and 1043 K, a large amount of

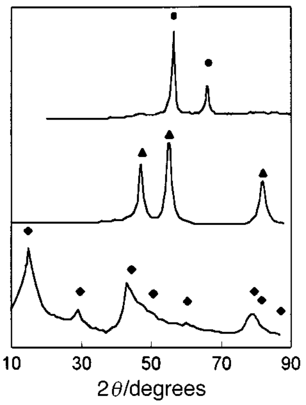

Fig. 1 XRD patterns of the catalyst and precursors: (◆) precipitate precursor, marked points are the position and height of the peaks of $Ni_6Al_2CO_3(OH)_{16}\cdot 4H_2O$; (▲) calcined material, marks are the peaks of NiO; (●) catalyst in reduced state, marks are the peaks of nickel.

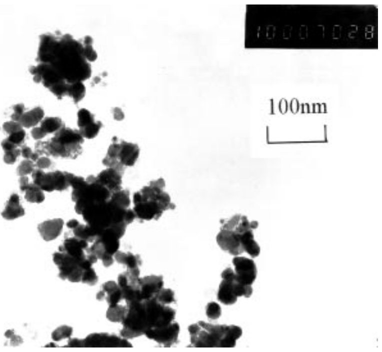

Fig. 2 TEM image of the catalyst in the reduced state.

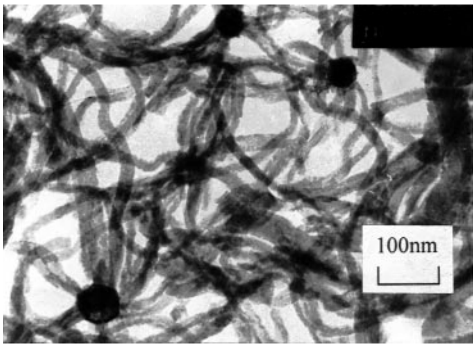

Fig. 3 Octopus carbon grown on the catalyst in methane–nitrogen at 773 K.

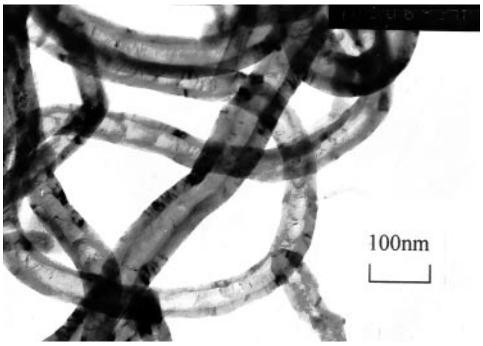

Fig. 4 Carbon nanotubes grown on the catalyst in methane–nitrogen at 1023 K.

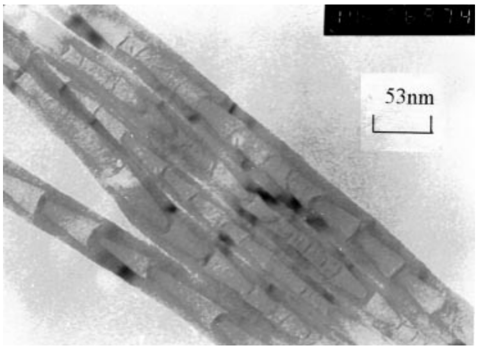

Fig. 5 Bamboo-shaped carbon grown on the catalyst in methane–hydrogen at 1043 K.

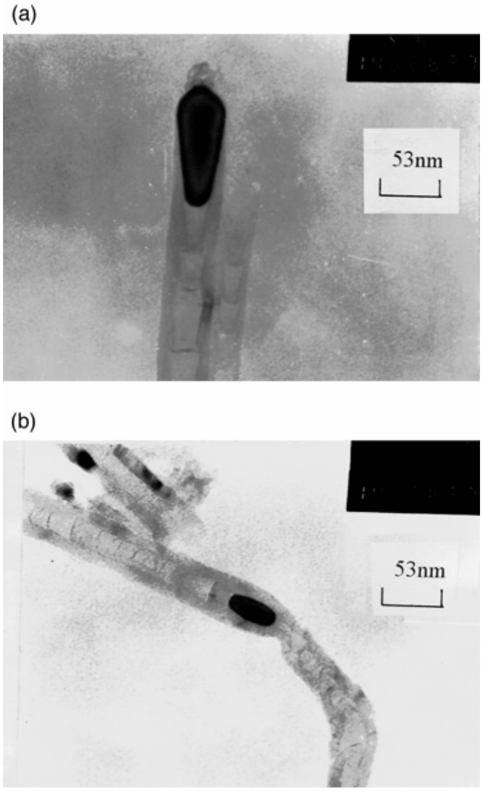

Fig. 6 Bamboo-shaped carbon grown on the catalyst in methane–hydrogen at 1003 K with encapsulated metal.

bamboo-shaped nanocarbon was obtained in a high morphology purity. The bamboo-shaped carbons formed under several conditions are shown in Figs. 5 and 6.

These conformations of carbon have been reported previously, though they were found together with other forms. Adveeva *et al.*[19] has reported octopus-shaped carbon, which was formed under nearly the same conditions as in this work. Saito[14] and Kovalevski and Safronov[20] reported separately bamboo-like carbons formed either from arc-discharge evaporation of graphite or from catalytic pyrolysis of hydrocarbons at 2223–2873 K. They attributed the formation of bamboo-like carbon to the catalytic effect of melted droplets of metal.[14,20]

Inspections of Figs. 2 and 3 show that the metal particles before reaction are irregularly shaped while after reaction at 773 K they are polyhedral, indicating recrystallization during induction of carbon formation. Micrographs in Fig. 6 show clearly that the metal, either at the tip of the carbon fiber or encapsulated inside, resembles a drop of mercury in a glass capillary, indicating that it is in a quasi-liquid state during reaction. Although no metal tip was found in Figs. 4 and 5, due to the crushing of the nanotubes before TEM observation, the carbon shows the same structure growth indicating the catalytic function of the liquid like metal. The shape of the carbon shows that it was formed by jumping of the metal tip at regular time intervals over similar distances. This can only be explained by supposing that the metal is in a quasi-liquid state with high surface energy and poor wetting ability towards graphite carbon. The highest temperature studied for these reactions was 1043 K, which is far below the melting point of the metals either in the pure or alloyed state. The melting point of nickel is 1728 K, while that of copper is 1357.5 K.[21] A Ni–Cu alloy with the same composition as the catalyst here has a melting point of 1423 K.[21] Some literature[22,23] has proposed metal carbide formation in this system, however, the temperature of Ni_3C formation is 1773–2373 K and the lowest melting temperature of a C–Ni alloy (atomic ratio 9 : 91) is 1573 K.[24] The existence of the metal in a quasi-liquid state at *ca*. 1000 K can only be attributed to the size effect of the metal at the nanometer level and the interfacial effect between nanocarbon and nanometal.

Results presented here suggest that (1) The conformation of a nanocarbon is sensitive to the reaction conditions and catalyst, and its morphological purity can be controlled. (2) The Ni–Cu/Al_2O_3 catalyst used here can catalyze nanocarbon formation both in the solid and molten state. (3) The Ni–Cu alloy undergoes recrystallization during induction of carbon formation producing pure octopus carbon in methane–nitrogen at 773 K, while a catalyst prepared under the same conditions but without doping of copper showed different behaviour.[10] (4) Ni–Cu alloy exists in the reaction system at as a quasi-liquid state at moderate temperatures owing to its nanosize and interfacial effects. (5) These phenomena may help to validate reaction mechanisms for nanocarbon formation on metals.

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