Production of Hydrogen and Nanocarbon from Direct Decomposition of Undiluted Methane on High-nickeled Ni–Cu–Alumina Catalysts

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Very active and stable high-nickeled Ni–Cu–alumina catalysts were used to produce hydrogen and nanocarbon by direct decomposition of undiluted methane at 773–1013 K. The growth way of nanocarbon depends on reaction temperatures and may be related with the catalyst stability.

Direct catalytic decomposition of methane is regarded as an economical process to produce hydrogen,[1,2] especially to obtain CO_x-free (CO, CO_2) hydrogen for fuel cells.[3] However, the catalysts are deactivated quickly owing to carbon deposition and have to be regenerated with oxygen or steam, which makes it difficult to avoid ppm level CO_x in hydrogen product.[3,4] Ermakova[5] and Li[6] investigated the possibility of production of hydrogen and nanocarbon by direct catalytic decomposition of methane. The equilibrium conversion of methane decomposition under atmospheric pressure is about 32%, 59%, and 81% at 773 K, 873 K, and 973 K, respectively.[6] However, the catalysts are easily deactivated in undiluted methane atmosphere at high temperatures. In the published literatures, to keep the stability of catalyst, the process is carried out by low methane conversion, at low temperature ($\leq$873 K),[3,5,7,8] with diluted methane,[3,4] or on catalysts of low loading active components.[8]

In the present work, high-nickeled Ni–Cu–alumina catalysts will be employed for production of hydrogen and nanocarbon from undiluted methane at high temperatures.

Catalyst precursors with a layered hydrotalcite-like anionic clay structure, were prepared by coprecipitation from a mixed aqueous solution of the nitrates with sodium carbonate. By this method, well-mixed Ni–Cu–alumina catalysts can be obtained. The preparation details and the catalyst structure information can be found in a previous paper.[9] 100 mg of catalysts was placed in a horizontal tubular reactor and was first reduced for 2 h at 973 K in a H_2/N_2 (1/3 vol) flow of 150 mL/min (STP). Then the temperature was adjusted to reaction temperature in nitrogen and the feed was switched to a methane flow of 68 mL/min (STP). All the reactions were carried out under atmospheric pressure. When methane conversion decreased to about 3%, the reaction was stopped. The solid carbon formed was unloaded and was observed with a JEOL JEM 100CXII TEM.

Figure 1 shows methane conversion, hydrogen concentration in the outlet gas with time at 773–1013 K, on a Ni–Cu–alumina catalyst of the atomic ratio, Ni:Cu:Al = 15:3:2 (15Ni–3Cu–2Al). Hydrogen was the only gas product. It can be seen that the highest values of conversion at 773 K, 873 K, 973 K, and 1013 K, are 10%, 22%, 60%, and 65%, respectively. However, with the increase of the reaction temperature, the catalyst stability becomes weak. After the reactions were stopped, the gC/gcat values (grams of carbon accumulated on per gram catalyst) are 167, 380, 280, and 39, respectively at four different temperatures. It can be found that the catalyst is still fairly stable at 873 K and 973 K: 30 vol% hydrogen and 70 vol% hydrogen can be produced steadily at 873 K and 973 K, respectively.

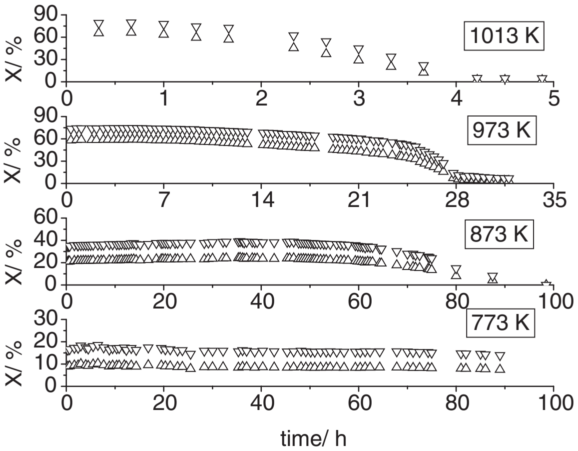

Figure 1. Methane conversion (△) and hydrogen concentration (▽) in the outlet gas during undiluted methane decomposition on 15Ni–3Cu–2Al catalyst at 773–1013 K. Flow rate = 68 mL/min.

Figure 2 shows methane conversion and hydrogen concentration in the outlet gas with time at 1013 K on the other two catalysts, 2Ni–1Cu–1Al and 3Ni–3Cu–2Al. The gC/gcat values are 152 and 42, respectively after the reactions. Methane conversion and hydrogen concentration on 2Ni–1Cu–1Al catalyst

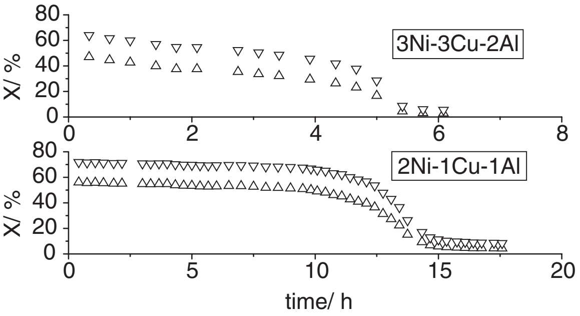

Figure 2. Methane conversion (△) and hydrogen concentration (▽) in the outlet gas during undiluted methane decomposition at 1013 K on the two catalysts, 2Ni–1Cu–1Al and 3Ni–3Cu–2Al. Flow rate = 68 mL/min.

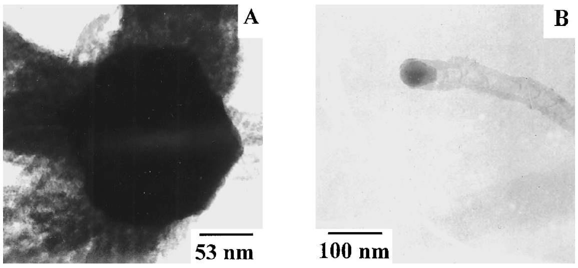

Figure 3. Fibrous nanocarbon formed with catalyst particles on 15Ni–3Cu–2Al catalyst. A, at 773 K; B, at 1013 K.

can steadily retain 60% and 70%, respectively.

The observation with TEM shows that on 15Ni–3Cu–2Al catalyst, at 773 K and 873 K, octopus-shaped solid fibers were formed; at 1013 K, hollow fibers with pear-shaped catalyst particles in their tips were produced; at 973 K, the two growth morphology was found together, seen in Figure 3. However, without copper addition, only the growth morphology like Figure 3B is obtained on Ni–alumina catalysts at these reaction temperatures.[7] Hollow fibers were formed on 2Ni–1Cu–1Al and 3Ni–3Cu–2Al catalysts at 1013 K. Many smooth catalyst particles are found to be encapsulated in the cavities, seen in Figures 4A and 4B. Maybe the Ni–Cu–alumina catalyst particles are in the quasi-liquid state owing to the addition of copper and the wetting of them with carbon layers is improved even when the temperature is much lower than the normal melting point of nickel.[10] For instance, the encapsulation may happen at (a)-(c) in Figure 4C. The catalyst particles are polyhedral in Figure 3A, which implies that they should not be in the quasi-liquid state and the encapsulation of catalyst particles may be not easy. The result above indicates a relation between the stability of the catalyst activity and the catalyst particle state. The addition of copper can influence the state and improve the stability in the reaction.

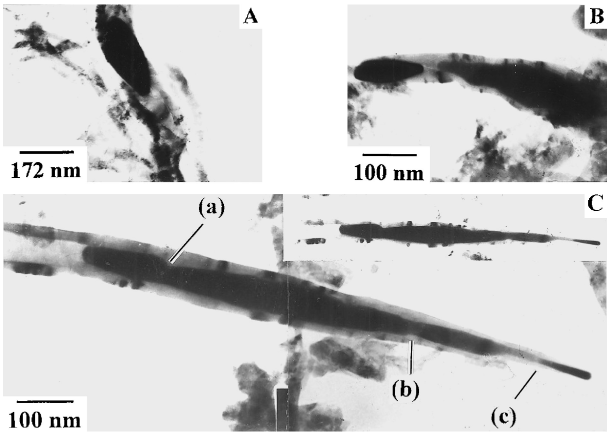

Figure 4. Fibrous nanocarbon formed with catalyst particles on 3Ni–3Cu–2Al catalyst at 1013 K.

Copper can also enhance the hydrogen mobility as the active component of hydrogenation catalysts.[11] The effect was also found in the TPR process of Ni–Cu–alumina.[9] It is advantageous to the gasification of the carbon formed on the surfaces of Ni–Cu–alumina catalyst particles in methane decomposition. It is also proposed that copper has a high affinity with the graphite structure, thereby inhibiting the formation of graphite layers.[12] These effects of copper may reduce the growth rate of carbon on nickel surface and the encapsulation of catalyst particles by carbon layers is retarded because of too fast accumulation of them on nickel surface, which is regarded as the main reason of catalyst deactivation. However, too much copper may make the catalyst particles easily become quasi-liquid and weaken their stability at high temperatures. These effects of copper addition are pronounced because Ni–Cu–alumina is well mixed by the preparation method in this work. So copper is a good component to improve the stability of nickel if employed in an appropriate amount and in a suitable doping way.

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