Promoting Effect of Nb_2O_5 Addition to Ni–Cu Catalysts on Hydrogen Production via Methane Decomposition

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The catalytic decomposition of methane to hydrogen and filamentous carbon was carried out over Ni–Cu–Nb_2O_5 catalysts. The results indicate that the addition of Nb_2O_5 can promote the carbon capacity of Ni–Cu catalysts, and increase the lifetime of the catalysts in methane decomposition at high temperature. The highest yield of carbon is 743 gC/gNi for 65Ni–10Cu–5Nb_2O_5, which is one of the highest values among those for catalysts reported so far.

The catalytic decomposition of methane to hydrogen and carbon is of current interest from the viewpoint of an alternative route of hydrogen production from methane[1] because no CO is contained in the hydrogen formed by this process. Thus, hydrogen produced by this process can be directly introduced to the fuel cells without any CO-removal process. However, it is ineluctable that the catalysts will lose their activity owing to carbon deposition and have to be regenerated with CO_2,[2] oxygen[3] or steam,[4] which makes the avoidance of ppm level CO_x in hydrogen product difficult. For these reasons, it is very important to increase the capacity for methane decomposition to hydrogen.

In the published literatures, Ni–Cu catalysts for hydrocarbon decomposition are more stable than Ni–Al_2O_3 catalysts[5–9] under conditions of carbon segregation. Niobium oxide, owing to its considerable acidity, has been used as a support for bi-functional catalysts, which have both acidic and hydrogenation activities.[10,11] Niobia-supported catalysts have been investigated, mainly in connection with the strong metal-support interaction (SMSI) generated when these catalysts are heated in hydrogen at high temperatures.[12,13] However, few studies on the performance of Nb_2O_5 containing catalyst for methane decomposition to hydrogen were reported. In the present work, we found that the addition of Nb_2O_5 can promote the carbon capacity of Ni–Cu catalysts for methane decomposition, and increase the lifetime of the catalysts for methane decomposition at high temperature. The highest yield of carbon is 743 gC/gNi (grams of carbon accumulated on per gram Ni) for 65Ni–10Cu–5Nb_2O_5 (molar ratio), which is one of the highest values among those for catalysts reported so far.

Ni–Cu–Nb_2O_5 catalysts were prepared by addition of Nb_2O_5 into a solution of $Ni(NO_3)_2$ (0.1 g NiO/mL) and $Cu(NO_3)_2$ (0.1 g CuO/mL). The mixtures were treated ultrasonically for 60 minutes, and then stirred violently for 6 h. The residual water in the mixtures was evaporated in a rotary evaporator at 373 K. Finally, the solids were calcined at 873 K for 4 h, and then ground and sieved to less than 150 meshes.

The reactions were carried out in a fixed-bed quartz reactor (30-mm i.d.) under atmospheric pressure with pure methane. 50 mg of catalyst powder was added for each run. The reactions went on until the methane conversion decreased to about 3%. All samples were reduced in situ with a 25% H_2/N_2 mixture (40 mL/min, v/v) at 923 K for 30 min prior to the reaction. The product mixtures were analyzed on a gas chromatography using high purity Ar (99.99%) as the carrier gas. TEM images of samples were obtained on a JEOL-1200EX transmission electron microscope operating at 80 kV.

Figure 1 depicts the range of methane conversion in the outlet gas during methane decomposition as a function of time on stream at 773–1023 K over 65Ni–25Cu–10Nb_2O_5, at a gas hourly space velocity (GHSV) of 48000 $mLg^{-1}h^{-1}$. The results show that the values of gC/gNi at 773, 873, 923, 973, and 1023 K are 339, 686, 666, 608, and 361, respectively. The catalyst presents a steady carbon capacity for methane decomposition to hydrogen between 873 and 973 K. The value of gC/gNi reaches its maximum of 686 at 873 K.

Figure 2 shows the promoting effect of Nb_2O_5 on methane decomposition over Ni–Cu catalyst at 873 K. From the reactions, we found that pure 65Ni–25Cu alloy has no catalytic activity for methane decomposition at a GHSV of 48000 $mLg^{-1}h^{-1}$, which shows that the Ni–Cu alloy agglomerates greatly after the reduction at 923 K. However, the results show that the maximal methane conversion over the 65Ni–25Cu alloy is about 42% at a GHSV of 24000 $mLg^{-1}h^{-1}$ (hollow symbols), with a gC/gNi value of about 516. The addition of Nb_2O_5 can increase the activity of Ni–Cu catalysts at high GHSV (solid symbols). Further addition of Nb_2O_5 will decrease the activity of the catalyst. Comparing the results of Figures 1 and 2 with those of Ni–Cu/Al_2O_3,[8,9] we can see that the addition of Nb_2O_5 can increase the gC/gNi value of Ni–Cu catalyst, and increase the lifetime and gC/gNi value at high temperature greatly. 65Ni–25Cu–5Nb_2O_5 has the best activity among the four Ni-Cu–Nb_2O_5 catalysts (Figure 2) and the gC/gNi value of 743 is one of the highest values among those for catalysts[5–9] reported so far. Effects of other additives such as TiO_2, SiO_2 are still in progress in our laboratory.

From Figure 2, the conversion of methane can be divided in-

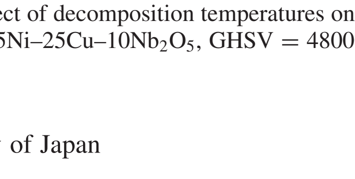

Figure 1. Effect of decomposition temperatures on methane conversion over 65Ni–25Cu–10Nb_2O_5, GHSV = 48000 $mLg^{-1}h^{-1}$.

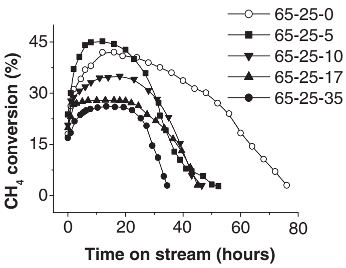

Figure 2. Methane conversion with time on stream over various Ni–Cu–Nb_2O_5 catalysts at 873 K: (○) GHSV = 24000 $mLg^{-1}h^{-1}$; (■), (▼), (▲), and (●) GHSV = 48000 $mLg^{-1}h^{-1}$.

to three stages: (1) the induction period, in which the methane conversion increases, is from the beginning of the reaction to about 8 h; (2) the steady state, in which the methane conversion is constant, is from about 8 h to about 24 h; (3) the deactivation stage, in which the methane conversion decreases to about 3%. TEM images of carbon formed at different stages during methane decomposition over 65Ni–25Cu–10Nb_2O_5 at 873 K are shown in Figure 3. The images show that the induction period and the steady growth of filamentous carbon occur mostly on Ni–Cu alloy particles lager than 60 nm, which are significantly larger than those of the reduced catalyst before methane decomposition (about 25 nm, not shown). Therefore, only coalesced metal particles produce filamentous carbon intensively.[14] It can be seen that the quasi-octahedral particles sizes of Ni–Cu alloy are about 60–170 nm (Figures 3a–3c). In this case, several filaments grow on one particle to form the so-called "octopus" structure. The diameter of the grown filaments is less than that of the metal particle. Several fish-bone-like filaments about 30 to 65 nm in diameter are presented in Figure 3b, they are the branches extended from the backbone of the filaments formed during the reaction. Comparing Figures 3c and 3d with Figures 3a and 3b, we can see that the filaments are very fragile which are easily crushed into filaments of very small sizes in length. Nanocarbon particles are separated from the filaments because the samples have been treated by ultrasonic before the TEM images were taken.

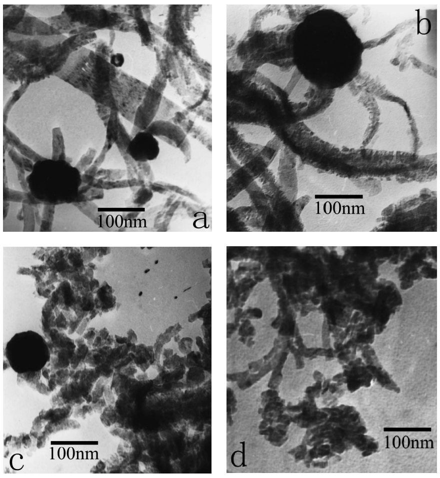

Figure 3. TEM images of carbon formed at different stages during methane decomposition over 65Ni–25Cu–10Nb_2O_5 at 873 K: Methane decomposition for 20 min (a), 120 min (b), and 18 h (c); methane conversion decreased to about 3% (d).

The commonly accepted model of methane decomposition and carbon growth over nickel catalysts includes the stages of activation and decomposition of methane on Ni(100) and Ni(110) planes, carbon dissolution and diffusion through the particle, carbon segregation in the form of graphite-like phase on Ni(111) planes due to crystallographic matching of Ni(111) planes to (002) graphite planes.[8,15] Thus, modifying the particle shape, one increases the number of Ni(100) and Ni(110) planes for methane decomposition and Ni(111) planes for carbon segregation, which in turn, providing an increase in the carbon capacity of the catalysts and decrease of the deactivation rate.[8] Recently, Nb_2O_5 has been used as a promoter in metal catalysts supported on SiO_2 or Al_2O_3.[16] In our studies, we found that the addition of Nb_2O_5 can increase the carbon capacity of Ni–Cu catalyst for methane decomposition. XRD results (not shown) reveal obviously the characteristic peaks of Nb_2O_5 of the samples of Figures 3a and 3b, and no obvious peaks of Nb_2O_5 of the samples of Figures 3c and 3d due to high amounts of filamentous carbon formed. From the XRD results of the three unreduced samples (i.e. 65Ni–25Cu, 65Ni–25Cu–5Nb_2O_5 and 65Ni–25Cu–10Nb_2O_5), we found that addition of Nb_2O_5 can change the morphology of the Ni–Cu catalysts. The reduced 65Ni–25Cu–5Nb_2O_5 sample shows the largest relative intensity of Ni(111) plane among the three samples, that is the intensity ratio between Ni(111) and Ni(200) plane, which may be the reason that the catalyst presents a high carbon capacity for methane decomposition.

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