



Hydrogen and Carbon Nanotubes Production by Catalytic of Ethanol Over the Co–Mo Catalysts

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A series of Cobalt–Carbon, Cobalt–Molybdenum–Carbon catalysts were prepared by impregnation. The molar ratios of Co:Mo were 9:1, 8:2 and 7:3 and the total metal weights of them in the supported catalysts were 5 wt%. Moreover, the effects of reaction temperature and the Co:Mo molar ratios on the produce hydrogen and carbon nanotubes were investigated systematically. Of all the catalysts, Co–Mo (5 wt%, Co:Mo = 9:1)/C was the most effective one on the basis of hydrogen yield (84%), ethanol conversion (95%) and the quality of carbon nanotubes at 600 °C. A small amount of Mo added into the Co/C catalysts resulted in increasing in the yield of hydrogen and improving on quality of carbon nanotubes from ethanol decomposition over the Co–Mo catalysts.

Keywords: Carbon Nanotubes, Co-Mo/C Catalyst, Hydrogen, Chemical Vapor Deposition, Ethanol Decomposition.

1. INTRODUCTION

Carbon nanotubes (CNTs) have been paid increasing attention due to their extraordinary mechanical, electrical and thermal properties,¹ since discovered by Iijima.² The potential applications of CNTs in areas such as carbon nanotubes composite materials, catalyst support and hydrogen storage have been reported.^{3–8} In order to fulfill the potential application, large-scale production of CNTs was crucial. Recently, many methods have been developed for CNTs preparation, such as arc discharge,⁹ laser vaporization,¹⁰ and chemical vapor deposition (CVD).^{11, 12} Among these methods, CVD shows best advantages of low cost and mass production of CNTs. The most used catalysts for CVD technique are transition metals Co, Fe, Ni or their alloy and as co-catalysts Mo, Cr, Ru, Pt.¹³⁻¹⁶ Co-Mo catalysts are very effective for single-wall carbon nanotubes17-19 and multi-wall carbon nanotubes (MWCNTs).²⁰⁻²² Fewer studies have dealt with the production of hydrogen and CNTs over Co-Mo catalysts from ethanol decomposition.

Hydrogen, recently recognized as an important raw material and energy carrier, is widely used in the

industry.²³ There exist four traditional methods of hydrogen production: Water electrolysis, gasification reaction, partial oxidation reaction of heavy oil and hydrocarbon steam reforming reaction.²⁴⁻²⁷ The method of hydrogen production by the ethanol reforming attracted great interest in the application, which is due to the characteristics of renewable source, relativity high hydrogen content, non-toxicity, safe storage, handing and realizing in large industrial.^{28, 29} Many groups reported that hydrogen production over the Co-based catalysts and MoC₂/C for ethanol steaming reforming.^{30–32} In addition, our group has recently reported that co-production hydrogen and CNTs by ethanol decomposition over the Co/C catalysts.33 In order to improve the active of Co-based catalysts performance, massive Co catalysts doped with different Mo loadings were prepared using C as the support.

In the present work, the co-production of H_2 and CNTs from ethanol decomposition over C-supported Co–Mo catalysts was investigated systematically in the range of temperature of 500–700 °C. The effects of the temperature and the molar ratio of Co:Mo on the performance of Co–Mo/C catalysts in co-producing H_2 and CNTs by catalytic decomposition of ethanol was discussed in detail.

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The optimal growth conditions of CNTs were presented. The role of molybdenum in Co–Mo/C for the production of CNTs and hydrogen was proposed.

2. EXPERIMENTAL DETAILS

Co-Mo catalysts supported on graphite with different molar ratio of Co:Mo were prepared by impregnation as described as follow. Co $(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6MO_7O_{24} \cdot$ 4H₂O was dissolved in distilled water, and then 3 g C was added into the aqueous solution. The reaction was further stirred at room temperature for 8 h to achieve a homogeneous impregnation of salts in support. The homogeneous mixture was dried in oven at 80 °C for 12 h and the material was grounded in mortar to break the chunks into fine powder. The prepared of catalysts were denoted as Co–Mo (Co:Mo = X)/C, total metal amount was 5 wt% ((Co+Mo)/(Mo+Co+C) = 5 wt%) in the supported catalyst and the molar ratio of Co:Mo in the catalysts was adjusted to be 9:1, 8:2 and 7:3. The experimental was carried out in a conventional gas flow system with a vertical fixed bed at the center of a quartz tubular reactor (inner diameter 5 mm) as the reaction chamber. The temperature of the bed was monitored with a thermocouple touching the outside wall of the reactor in close proximity to the sample bed. Prior to ethanol decomposition, the catalyst (150 mg) was reduced by hydrogen at 500 °C for 1 h and subsequently purged under Ar at the same temperature for 40 min. Then the decomposition of ethanol was performed on Co-Mo/C at the temperature of 500, 600 and 700 °C. Ethanol was injected through a microinjector into a vaporizing chamber (100 °C) at a flow rate of 0.3 ml/h and switched to the tubular reactor using Ar (40 ml/min) as the carrier gas. During ethanol decomposition, the gaseous products in the exit gases from the tubular reactor were analyzed at 12 min intervals by a gas chromatography (GC). After 60 min, the injection of ethanol was stopped and the solid products were collected from the tubular reactor. The gas products were analyzed using on-line gas chromatograph (SP-9890, SP-6890). The morphologies of the CNTs were characterized by the scanning electron microscopy (SEM) performed on FEI Quanta 400 ESEM-FEG, Raman scattering studies of the CNTs were performed at room temperature using a dispersive Raman spectrometer (Nicolet, ALMEGA) with the excitation wavelength of 523 nm. Composition analyses of solid products were carried out by X-ray diffraction (XRD, D/max-3c, Cu K α , 50 kV, 300 mA, at the room temperature in air). The quality and microstructures of the CNTs were investigated with transmission electron microscopy (TEM) performed on a JEOL JEM-3010 high-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 300 kV.

The catalytic behaviors of the Co–Mo/C catalysts for ethanol decomposition were evaluated by H_2 yield, ethanol conversion and the selectivity of

various gas products (S_i) ,³⁴ which were defined as follows:

$$H_2$$
 yield (%)

 $= \frac{\text{mole of H atom converted to H}_2}{\text{theoretical mole of H atomcontained in ethanol feed} \times 100 (1)}$ Ethanol conversion (%) $= \frac{\text{mol (ethanol) in - mol (ethanol) out}}{\text{mol (ethanol) in}} \times 100 (2)$

$$S_i = \frac{n_i}{n_{i+1}} \times 100 \tag{3}$$

Where n_i is the molar of *i* gas product ($i = H_2$, CO, CH₄ or CO₂), and n_{total} the total molar of all the gas products ($H_2 + \text{CO} + \text{CH}_4 + \text{CO}_2$).

3. RESULTS AND DISCUSSION

Figure 1 showed the effects of reaction temperature and the molar ratio of Co:Mo on the H₂ yield in the ethanol decomposition over the Co-Mo/C catalysts at the temperature of 500 °C, 600 °C and 700 °C. Figures 1(a)–(c) showed the changes of H₂ yield as a function of reaction time. It was significant from Figure 1(a) that the H_2 yield reduced as the molar ratios of Co:Mo decreases from 9:1 to 7:3 at 500 °C. The H_2 yield reduced from 78% to 68%. From Figure 1(b), the average H₂ yield at 600 °C for Co:Mo ratio of 9:1, 8:2, and 7:3 was calculated to be 84%, 73% and 63%. H₂ yield was 50% over the Co (5 wt%)/C at 600 °C within 60 min. The increment of the average of H₂ yield was 32%. At 700 °C, the change of H_2 yield was not various and the H_2 yield was 55% in Figure 1(c). It was determined that the optimal reaction temperature was 600 °C and that the optimal molar ratio of Co:Mo was 9:1 for H₂ yield from ethanol decomposition over Co-Mo/C catalysts. For this situation, the H₂ yield was 84%. It could be concluded that molybdenum addition in small amount (Co:Mo = 9:1) to the Co/C catalyst increased H₂ yield at relatively high temperature of 600 °C. It was reported that the H₂ yield of 52% through auto-thermal reforming of bio-ethanol over Co-based catalysts at 600 °C.35 Our experimental result indicated that H₂ yield for the Co–Mo (5 wt%, Co:Mo = 9:1)/C catalyst at 600 °C reached 84%, which was much higher than reported.

Figure 2 showed the effects of reaction temperature on gas selectivity within 60 min. In addition to hydrogen in gas products, as shown in Figures 2(a)–(d), carbon monoxide, methane and carbon dioxide are also detected from ethanol decomposition over Co (5 wt%)/C and Co–Mo (Co:Mo = X)/C catalysts in the temperature range of 500–700 °C, with their selectivities (S_i) changing in the order of H₂ > CO > CH₄ > CO₂. Figure 2(a) showed that the H₂ selectivity over the Co–Mo/C on the basis of reaction temperature. At 500 °C, H₂ selectivity was higher over the Co (5 wt%)/C than Co–Mo/C. Hydrogen selectivity

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Co:Mo =8:2

Co:Mo =7:3



Figure 1. Change of H_2 yield as a function of the reaction time in ethanol decomposition over Co/C (5 wt%)/C and Co–Mo/C with different moral ratio of Co:Mo 9:1, 8:2 and 7:3 at different temperature: (a) 500, (b) 600 and (c) 700 °C.

reached highest on the Co–Mo (Co:Mo = 9:1)/C (80%) at 600 °C and the change of hydrogen selectivity was not obvious at 700 °C. Meanwhile, Figure 2(b) CO selectivity was least on the Co–Mo (Co:Mo = 9:1) (14%). The addition of Mo to the Co/C catalyst made the CH₄ increased obviously at higher temperature (700 °C) (in Fig. 2(c)). The CO₂ selectivity did not change significantly with the temperature and the ratio of Co:Mo varying. Figure 3 showed the effect of reaction temperature on ethanol conversion from the ethanol decomposition over the Co–Mo/C catalysts. With the ratio of Co:Mo rising from 7:3 to 9:1, ethanol conversion was decreased at 500 °C and firstly

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Figure 2. Change of selectivity of gas products as a function of the reaction temperature in ethanol decomposition over Co (5 wt%)/C and Co–Mo/C with different moral ratio of Co:Mo (9:1, 8:2 and 7:3) at different temperature: 500, 600 and 700 °C.

increased and then decreased at 600 °C and 700 °C. When the ratio of Co:Mo was 9:1, ethanol decomposition highest (95%), which was corresponding with the H_2 yield.



Figure 3. Ethanol conversion over Co (5 wt%)/C and Co–Mo/C catalysts with different moral ratio of Co:Mo 9:1, 8:2 and 7:3 at 500, 600 and 700 $^{\circ}$ C within 60 min.

Solid products deposited on the Co–Mo/C catalysts were characterized by SEM. Figures 4(a)–(c) presented that the SEM images of CNTs over Co–Mo (Co:Mo = 9:1)/C at 500 °C, 600 °C and 700 °C, and the temperature was essential to produce CNTs. The SEM images indicated that CNTs were formed rarely at 500 °C. However, Figure 4(b) showed the length of CNTs with few metals and a little amorphous carbon formed over Co–Mo (Co:Mo = 9:1)/C



Figure 5. XRD pattern of MWCNTs formed by ethanol decomposition over Co–Mo (Co:Mo = 1:9)/C catalyst at 600 °C.

at 600 °C. Figure 4(c) showed carbon nanofibers (CNFs) with width diameter are formed at 700 °C, accompanied with the sintering of catalysts. It presented that the Co–Mo (Co:Mo = 9:1)/C catalyst at temperature of 600 °C was more effective than that at temperatures of 500 and 700 °C, in terms of CNTs production from ethanol decomposition. The reason was that Mo is considered as a role in dispersing metallic Co at temperature of 600 °C. The Co–Mo/C catalysts were sintered and reunited at relatively higher temperature of 700 °C, which leads to larger Co metal particles. The larger metal particles favored the carbon fiber



Figure 4. SEM images of MWCNTs formed by the ethanol over the Co–Mo (Co:Mo = 9:1)/C catalysts at different temperatures: (a) 500, (b) 600 and (c) 700 °C and over the Co–Mo/C with the different ratio of Co:Mo (e) 8:2 and (f) 7:3 at 600 °C. SEM image of MWCNTs formed by the ethanol over the Co (5 wt%)/C at 600 °C (d).



Figure 6. (a) Raman of MWCNTs formed by the ethanol decomposition over the Co–Mo (Co:Mo = 9:1)/C catalysts at different with temperatures: 500, 600 and 700 °C and (b) Raman of MWCNTs formed by the ethanol decomposition over the Co–Mo/C catalysts with the different ratio of Co:Mo (9:1, 8:2 and 7:3) at 600 °C.

formation.³⁶ At 600 °C, with the ratio of Co:Mo decreasing from 9:1 to 7:3, the density of CNTs declined over the Co–Mo/C catalyst in the Figures 4(e) and (f). High concentration of Mo resulted in increasing the CoO crystallites had a negative effect on the quality of CNTs.³⁸ Therefore, the Co–Mo/C catalyst was the most effective for producing CNTs at 600 °C and the optimal molar ratio of Co:Mo was 9:1.

Based on the diffraction angles of the X-ray scattered, X-ray crystallography determines the crystal phases of the catalyst due to different arrangement of atoms in the crystals. The XRD profiles of CNTs was observed grown over the Co–Mo (Co:Mo = 9:1)/C catalysts for 60 min at 600 °C in the Figure 5. It could be seen that the peak appears at $2\theta = 26^{\circ}$ and 54.4° , corresponding to the (002) and (100) reflection of the graphite.³⁹ In addition, the peak appears at $2\theta = 44.7^{\circ}$ attributed to the Co₃O₄.⁴⁰ The characteristic pattern of the MoO₃ was 29.1° and $34.5^{\circ}.^{41}$ The reason may be that the addition of Mo to Co forms MoO₃, which prevented the extensive agglomeration of Co species during the narrow diameter of CNTs synthesis.³⁸

Figure 6 illustrates Raman spectra of CNTs were formed by ethanol decomposition over the Co–Mo/C catalysts. For all the Raman spectra, two bands were observed at 1590 (G band) and 1350 (D band) cm⁻¹. The structure of CNTs



Figure 7. TEM of MWCNTs formed by the ethanol decomposition over the Co–Mo (Co:Mo = 9:1)/C catalysts at different with temperatures: (a) 600 °C and (b) 700 °C.

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could be evaluated via the intensity ratio of G and D band. A larger $I_{\rm G}/I_{\rm D}$ ratio conformed to high purity and less defects in sidewall of CNTs.42,43 Figure 6(a) showed the Raman spectra of CNTs were synthesized over Co-Mo (Co:Mo = 9:1)/C at 500, 600 and 700 °C. It was significant that the $I_{\rm G}/I_{\rm D}$ ratio of CNTs in the temperature order 600 °C $(I_{\rm G}/I_{\rm D} = 4.5) > 500$ °C $(I_{\rm G}/I_{\rm D} = 4) > 700$ °C $(I_{\rm G}/I_{\rm D}=2.5)$, indicating the optimal reaction temperature was 600 °C. Figure 6(b) showed Raman spectra of CNTs were produced by ethanol decomposition over Co-Mo/C catalysts with the Co:Mo ratio of 9:1, 8:2 and 7:3 at 600 °C. CNTs with Co–Mo/C (Co:Mo = 9:1) $(I_G/I_D = 4.5)$ and Co-Mo/C (Co:Mo = 8:2) $(I_G/I_D = 2.5)$ loading had higher G peak and I_G/I_D than Co–Mo/C (Co:Mo = 7:3) $(I_{\rm G}/I_{\rm D} = 2)$. The result demonstrated Co–Mo (Co:Mo = 9:1)/C catalyst was the most effective catalyst for CNTs growth from ethanol decomposition, with higher graphitization and lower defects of CNTs deposited over Co-Mo (Co:Mo = 9:1)/C catalysts.

Figure 7 represented in the TEM images, the CNTs synthesized were MWCNTs with the use of ethanol as a carbon source and Co–Mo (Co:Mo = 9:1)/C as catalysts. From Figure 7(a), TEM studies showed metallic Co nanoparticles were obvious at the tips of the CNTs and the catalyst particles on a long CNTs tip were almost encapsulated by the grapheme layers.⁴⁴ CNTs were observed formed at 600 °C with an inner diameter of 15–20 nm and outer diameter of 25–30 nm. The amorphous carbon deposited over the Co–Mo/C catalysts at 700 °C in the Figure 7(b). Considering the quality of CNTs, the optimal reaction temperature was 600 °C.

4. CONCLUSIONS

In the present work, ethanol decomposition over Co–Mo/C catalysts with different Co:Mo molar ratios were investigated in the temperature range of 500–700 °C. The effects of temperature and the molar ratio of Co:Mo on the hydrogen production, as well as CNTs growth has been discussed systematically. The optimal experiment conditions for hydrogen production and the growth of

CNTs were also obtained. The Co-Mo (Co:Mo = 9:1)/Ccatalysts was the most effective catalyst based on the hydrogen yield (84%) and the high quality of CNTs at 600 °C. The resulted also suggested that a small amount of Mo helps in dispersing active metal precursor at higher temperature of 600 °C, which were active for CNTs growth and H₂ yield.

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