

Progressive Loading Effect of Co over SiO₂/Al₂O₃ Catalyst for CO_x Free Hydrogen and Carbon Nanotubes Production via Catalytic Decomposition of Methane

Sushil Kumar Saraswat, K. K. Pant

Abstract—Co metal supported on SiO₂ and Al₂O₃ catalysts with a metal loading varied from 30 to 70 wt.% were evaluated for decomposition of methane to CO_x free hydrogen and carbon nanomaterials. The catalytic runs were carried out from 550-800°C under atmospheric pressure using fixed bed vertical flow reactor. The fresh and spent catalysts were characterized by BET surface area analyzer, XRD, SEM, TEM and TG analysis. The data showed that 50% Co/Al₂O₃ catalyst exhibited remarkable higher activity at 800°C with respect to H₂ production compared to rest of the catalysts. However, the catalytic activity and durability was greatly declined at higher temperature. The main reason for the catalytic inhibition of Co containing SiO₂ catalysts is the higher reduction temperature of Co₂SiO₄. TEM images illustrate that the carbon materials with various morphologies, carbon nanofibers (CNFs), helical-shaped CNFs and branched CNFs depending on the catalyst composition and reaction temperature were obtained.

Keywords—Carbon nanotubes, Cobalt, Hydrogen Production, Methane decomposition.

I. INTRODUCTION

HYDROGEN has been considered as the ideal energy carrier for the future because it is environmentally clean energy source since pollutants are not generated and combustion product is H₂O. Hydrogen also becomes an attractive alternative since it is a powerful vector of clean energy when used either directly or as a fuel in hydrogen-air fuel cells [1], [2]. In the 21st century hydrogen is expected to be a primary energy source for generating electricity, fuel, and other applications. For automobile applications hydrogen can either be stored in pressurized tanks or generated on-board using a liquid hydrogen carrier such as methanol or gasoline. The use of solid hydrogen carriers such as metal hydrides has also been proposed as an alternate storage form for hydrogen in automobile applications. The use of pure hydrogen also eliminates the need for a clean-up unit required to remove by-products. Natural gas (methane) steam reforming (SRM) is the most common process for industrial hydrogen production, which is mainly based on steam reforming and partial oxidation of hydrocarbons and carbonaceous feed stocks, such as natural gas and petroleum fractions and whose H/C atomic

ratio is the highest (H/C 4) among the hydrocarbons [3]-[6]. However, both the growing restrictions in the legislation about CO₂ emissions (the SRM produces as by-product at least ca. 6t CO₂/t H₂), and the low CO concentration levels in hydrogen stream, required alternate route for hydrogen production process.

Thermocatalytic decomposition of methane (TCD) reaction is moderately endothermic process and a topic of great interest for a long time [7]-[10]. Li et al. [11] proposed a hypothesis to produce CO_x-free hydrogen and carbon nanomaterials simultaneously via TCD reaction. Now, the reaction has become an attractive alternative route both for clean hydrogen and for value-added carbon material due to its simplicity in process and high efficiency. An additional advantage of this process is that, in principle, it does not produce CO_x. Therefore, it is extremely environmentally attractive due to the concern of the global warming problems associated with the excess emission of carbon dioxide into the air-sphere of the earth. Many researchers studied the catalytic activities on transition metals, *i.e.*, Fe, Co, Cu, Mo & Ni and revealed that Co and Ni showed high catalytic activity compare to other metals due to their unique 3d-orbital properties [12]-[16]. Takenaka et al. [17] studied the methane decomposition reaction over Co-based catalysts supported on various supports, *i.e.* MgO, Al₂O₃, SiO₂ and TiO₂, where the results showed that Co/Al₂O₃ and Co/MgO catalysts have higher activities than Co/TiO₂ and Co/SiO₂. Awadallah et al. [18], [19] examined the catalytic performance of Co and Ni supported on a novel aluminosilicate hollow sphere and observed that the superior activity of Co based catalyst compared to the Ni based catalyst, due to the formation of nickel silicates (Ni₂SiO₄) in the catalyst structure. The difficult reducibility of Ni₂SiO₄ species was the main reason for inhibiting the catalytic activity of Ni containing catalyst. However metal catalysts which are usually deposited on supports such as SiO₂ or Al₂O₃ and the performance of the catalyst depends on the combination of metal and support [20], [21].

The present work aims is to evaluate the loading effect of Co on Al₂O₃ and SiO₂ bases catalyst for catalytic decomposition of methane gas to hydrogen & CNT and to determine the optimum metal loading conditions to obtain high yield of these two valuable products (hydrogen and carbon nanotubes).

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II. EXPERIMENTAL

A. Catalyst Preparation and Experimental Setup

Co/Al₂O₃ and Co/SiO₂ catalysts with different loading amounts of Co were prepared using wet impregnation method. The loading amount of Co in the Co/Al₂O₃ catalysts was adjusted to 30-70 wt%. The requisite amounts of SiO₂ or Al₂O₃ support were added to the solution yield the desired Co mass percentages. This slurry was processed at 90°C in a rotary vacuum evaporator and washed with deionized water 5 times, followed by drying at 110°C and calcination for 5 h at 550°C. The prepared catalysts or catalyst precursors were denoted as Co (X wt%)/Al₂O₃/SiO₂, where X wt% is the wt% loading in terms of Co.

In this study, the catalytic experiments were carried out in a fixed bed flow vertical reactor made of quartz glass (19 mm diameter and 600 cm long) packed with 1.0 g of the synthesis catalyst. The effect of reaction temperature was studied within the range 550–800°C. The catalyst was reduced at 550°C under a hydrogen gas flow rate of 30 mL/min and kept at this temperature for 4 h to deoxidize the catalyst. Mixture of methane and nitrogen gases was passed on the catalyst with a flow rate of 30 mL/min at the desired reaction temperature. The gaseous product was analyzed by online gas chromatograph (Nucon series-5700).

B. Catalyst Characterization

The BET surface area of the calcined and spent catalyst was determined using surface area analyzer (Micromeritics ASAP 2010, USA) at 77 K. X-ray diffraction (XRD, Philips X'pert Pro PW3040 diffractometer CuK α , 50 kV, 300 mA, at room temperature in air) was used to characterize the compositions of the catalyst after reduction with hydrogen at 550°C and of the catalyst with solid products after methane decomposition. Scanning electron microscopy equipped with energy dispersive analysis (SEM-EDX) was used to determine crystal composition and surface structure with ZEISS EVO-50 instrument. The transmission electron microscope (TEM) images of CNTs were recorded with a Philips CM12, at an accelerating voltage of 300 kV.

III. RESULTS AND DISCUSSION

A. Activity of Co/SiO₂ and Co/Al₂O₃ Catalysts

Catalytic activity of the Co/SiO₂ and Co/Al₂O₃ catalysts for the methane decomposition reaction was compared under the identical conditions. Fig. 1 shows the catalytic behavior at different metal loadings as a function of the reaction temperature. The decomposition of methane accelerated as the reaction temperature increased due to endothermic nature of the reaction. It can be seen that the catalysts show a significant variation in methane conversion as the temperature increased from 550 to 800°C. Over 50% Co/SiO₂ catalyst methane conversion increased from 20 to 57% as the temperature was increased from 550-800°C. On the other hand, the methane decomposition over 50% Co/Al₂O₃ catalysts was higher than Co/SiO₂ catalyst where more than 62% conversion was achieved at 800°C and GHSV of CH₄ 1800 mL/h.g_{cat}.

Investigations revealed that lower metal loading of Co did not provide enough active sites for methane decomposition reaction. However, Co loading at more than 50 wt%, metal oxide starts to agglomerate, thereby hindering the active catalyst sites and reducing the CH₄ conversion.

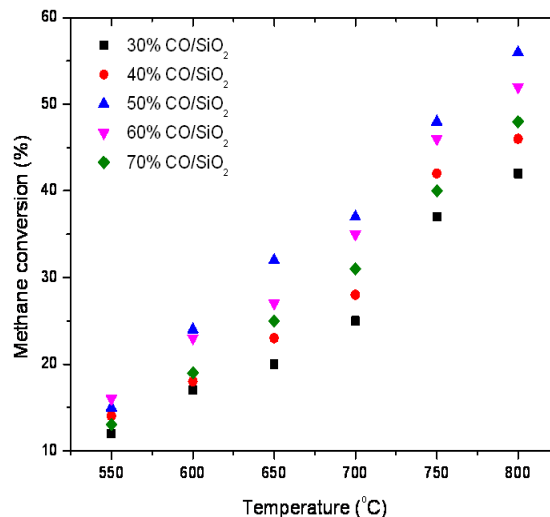


Fig. 1 (a) Effect of Metal Loading on Methane Conversion at Different Temperature (Catalyst Co/SiO₂, GHSV 1800 mL/h.g_{cat})

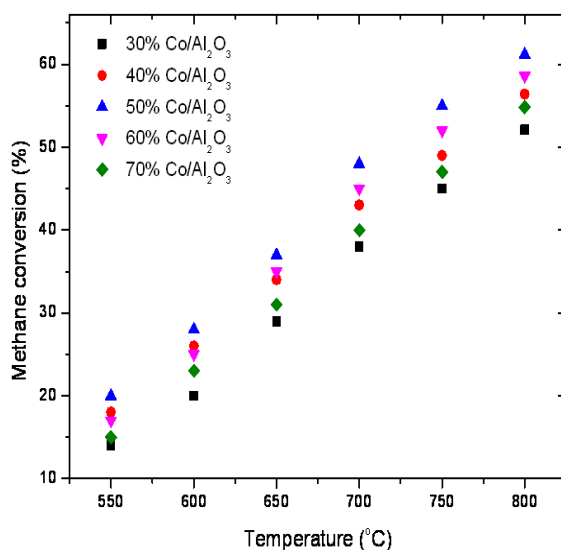


Fig. 1 (b) Effect of Metal Loading on Methane Conversion at Different Temperature (Catalyst Co/Al₂O₃, GHSV 1800 mL/h.g_{cat})

B. Characterization of Co/SiO₂ and Co/Al₂O₃ Catalysts

1. BET Surface Area

It has been revealed that particle size, surface area and nature of interaction between the metal species and support affect the catalyst activity. Tables I and II present physicochemical properties of the Co/SiO₂ and Co/Al₂O₃ catalysts. The results indicate that the surface area of the calcined catalysts decreased with increasing Co loading and loss of surface area is attributed to the partial coverage of

pores upon introducing Co metal. Li et al. reported that for Co/SiO₂ catalyst the loss of surface area is due to the formation of the Co_xSi_{1-x}O solid solution which might have promoted sintering leading to a larger Co particles in the Co/SiO₂ catalyst whereas cobalt oxides (Co₃O₄) was formed on Co/Al₂O₃ catalyst which is finely disperse on the catalyst and resulted higher surface area than Co/SiO₂ catalyst [22]. The surface areas of the spent catalysts further reduced due to the deposition of carbonaceous material in the pores of the catalyst. Another reason for decrease in surface area is probably due to sintering of Co particles at higher temperature.

TABLE I
PHYSICOCHEMICAL PROPERTIES OF THE WET IMPREGNATED Co/SiO₂ CATALYSTS

Catalyst	S_{BET} (m ² /g) Calcined	V_g (cm ³ /g)	Avg. pore size D_p (Å)
30% Co/SiO ₂	107.4	0.45	168.0
40% Co/SiO ₂	86.7	0.31	145.6
50% Co/SiO ₂	69.1	0.22	130.3
60% Co/SiO ₂	54.2	0.20	148.7
70% Co/SiO ₂	39.3	0.13	140.2

TABLE II
PHYSICOCHEMICAL PROPERTIES OF THE WET IMPREGNATED Co/Al₂O₃ CATALYSTS

Catalyst	S_{BET} (m ² /g) Calcined	V_g (cm ³ /g)	Avg. pore size D_p (Å)
30% Co/Al ₂ O ₃	123.4	0.33	107.1
40% Co/Al ₂ O ₃	104.8	0.27	104.6
50% Co/Al ₂ O ₃	95.6	0.24	103.9
60% Co/Al ₂ O ₃	72.1	0.19	105.8
70% Co/Al ₂ O ₃	47.8	0.13	110.9

2. X-Ray Diffraction (XRD)

XRD measurement of the calcined catalysts was carried out, in order to identify the different phases and the crystalline structure of the metal species and the results are shown in Fig. 2 (a). The presence of the diffraction peaks centered at $2\theta = 31.3, 36.8, 45.1, 65.2^\circ$ is due to the formation of Co₃O₄ phase during the calcination step. The other intensive diffraction peaks at $2\theta = 19.1, 38.6, 61.4, 77.3^\circ$, were assigned to CoO phase with cubical structure present in Co/Al₂O₃ catalysts compared to Co/SiO₂ catalysts. Over Co/Al₂O₃ catalyst the diffraction peaks of Co₃O₄ are very close to that of CoAl₂O₄ ($2\theta = 31, 37, 65^\circ$). However, relatively low intensity peak at 45° over Co/SiO₂ catalyst was observed compared to Co/Al₂O₃ indicating the lower crystalline nature of the catalyst. XRD patterns of spent catalysts (Fig. 2 (b)) revealed the diffraction peaks at 2θ values of 26.2° which were ascribed to (0,0,2) reflection of graphite with hexagonal structure. A small diffraction line was also observed at $44.3, 51.6$ and 76.1° due to the presence of pure Co metal. According to Scherrer's formula the crystal size is inversely proportional to peak width. Thus, it is likely that an average crystallite size of Co metal (d_s) was smaller on Co/Al₂O₃ than that on Co/SiO₂. As described above, the catalytic performance (the activity) of Co/Al₂O₃ for the methane decomposition was superior to that of Co/SiO₂.

These results implied that Co metals with smaller crystallite sizes showed higher activity and longer life for the methane decomposition from 550-800°C.

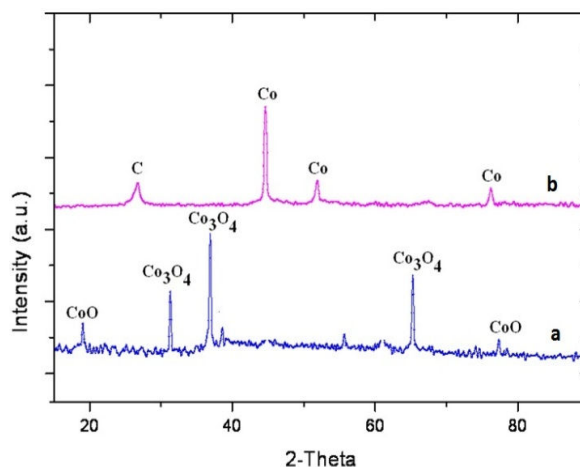


Fig. 2 XRD Patterns of (a) 50% Co/Al₂O₃ Calcined, (b) 50% Co/Al₂O₃ Spent catalyst

3. Morphology of the Catalysts

Fig. 3 shows SEM images of carbon species deposited on the catalysts after methane decomposition at 750°C. It was found that carbon deposited on all the catalysts grew with a filamentous structure over Co catalysts. Fig. 3 (a) depicted that small length of non-uniform diameter carbon nanofibers was observed over 50% Co/SiO₂ catalyst while in the case of 50% Co/Al₂O₃ catalyst (Fig. 3 (b)) these nanofibers were of relatively uniform in diameter. It is worthwhile to note that the Co particles are present in the agglomerated form in the Co/SiO₂ catalyst while in the case of Co/Al₂O₃ catalyst these Co particles are finely dispersed on the catalyst. This was further confirmed by the TEM analysis (Fig. 4). It was observed that cobalt metal particles are present at the tip of carbon nanofibers and the diameter of Co metal particles present at the tip of carbon nanofibers was nearly equal to that of the fiber. The exposed surface of Co metal particles which were at the tip of the fibers continued the decomposition of methane into carbon and hydrogen. It was also found that the Co metal particles observed in the TEM images were wrapped with thick layer of deposited carbons irrespective of their size. The average diameter of the carbon nanofibers produced as observed from the TEM images was in the range (10-30 nm) of the dispersed catalysts particle, although XRD studies implied that average crystallite sizes of Co metal changed by the types of catalytic supports. It has been observed that Co particle size between 10 and 30 nm yielded high quality carbon nanofibers compared to larger (>50 nm) and smaller (<10 nm) catalysts. During TCD reaction Co particle grew in size and this caused the deactivation of the catalyst.

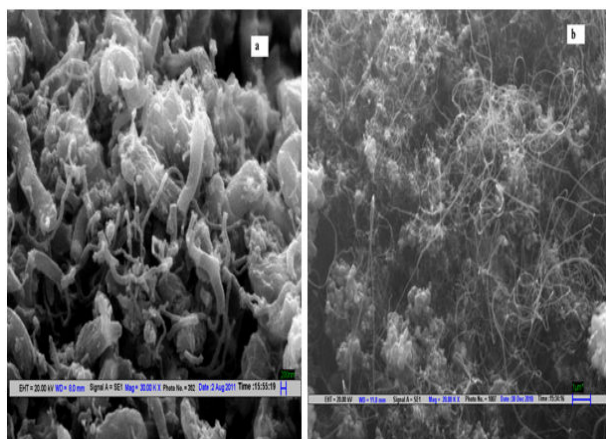


Fig. 3 SEM Micrographs of Carbon Nanofibers Deposited on (a) 50% Co/SiO₂ and (b) 50% Co/Al₂O₃ Catalysts at 750°C

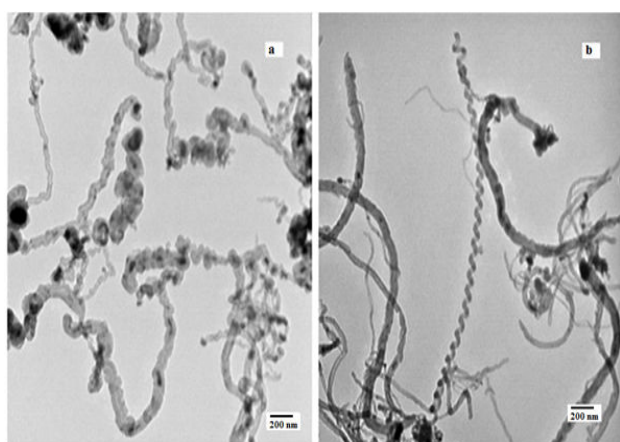


Fig. 4 TEM Images of Carbons Nanofibers Deposited on (A) 50% Co/SiO₂ and (B) 50% Co/Al₂O₃ Catalysts By Methane Decomposition at 750°C

IV. CONCLUSIONS

Simultaneous production of hydrogen and multiwalled carbon nanotubes by catalytic decomposition of methane in a tubular reactor has been carried out using Co catalysts dispersed on SiO₂ & Al₂O₃ supports. The catalysts with different Co loadings were investigated in the temperature range of 500–800°C. The influence of the temperature and the loading amounts of Co/Al₂O₃ catalysts on the hydrogen production and the MWCNT growth was discussed systematically. The higher temperature (800°C) favored the hydrogen production over the catalysts up to 50% Co metal loadings based on the methane conversion/H₂ yield. The product COx free hydrogen produce in this work could be potentially utilized in the fuel cell to help reduce the pollution emission. The carbon products were investigated and different morphologies of CNTs can be found. The CNTs grown on SiO₂ support catalyst are short in size while the CNTs on Al₂O₃ support were complex with various morphs and wide range of size; they were longer and catalyst particles were carried at the CNTs tips.

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