

## PRODUCTION HYDROGEN AND NANOCARBON VIA METHANE DECOMPOSITION USING Ni-BASED CATALYSTS. EFFECT OF ACIDITY AND CATALYST DIAMETER

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### Abstract

Objectives of this research are mainly to study impacts of acidity strength (by varying amount of precipitant and loading Al-Si) and the effect of nickel particle size (by varying calcinations temperature) on decomposition reaction performances. In this research, high-nickel-loaded catalyst is prepared with two methods. Ni-Cu/Al catalysts were prepared with co-precipitation method. While the Ni-Cu/Al-Si catalyst were prepared by combined co-precipitation and sol-gel method. The direct cracking of methane was performed in 8mm quartz fixed bed reactor at atmospheric pressure and 500-700°C. The main results showed that the Al content of catalyst increases with the increasing amount of precipitant. The activity of catalyst increases with the increasing of catalyst's acidity to the best possible point, and then increasing of acidity will reduce the activity of catalyst. Ni-Cu/4Al and Ni-Cu/11Al deactivated in a very short time hence produced fewer amount of nanocarbon, while Ni-Cu/15Al was active in a very long period. The most effective catalyst is Ni-Cu/22Al, which produced the biggest amount of nanocarbon (4.15 g C/g catalyst). Ni catalyst diameter has significant effect on reaction performances mainly methane conversion and product yield. A small Ni crystal size gave a high methane conversion, a fast deactivation and a low carbon yield. Large Ni particle diameter yielded a slow decomposition and low methane conversion. The highest methane conversion was produced by catalyst diameter of 4 nm and maximum yield of carbon of 4.08 g C/ g catalyst was achieved by 15.5 nm diameter of Ni catalyst.

*Keywords:* carbon nanotube, hydrogen, methane decomposition, nickel based catalyst

### 1. Introduction

Natural gas is expected to play an important role in producing hydrogen in the near to medium term future. However, natural gas is also source of anthropogenic CO<sub>2</sub> emissions into the atmosphere and most of reserves of natural gas are categorized as remote or stranded gas, far from the major gas consuming regions. The conventional transportation via pipeline is difficult due to the high capital cost. Direct decomposition (or cracking) of methane is a promising process route for industrial processing of natural gas to produce simultaneously CO/CO<sub>2</sub>-free hydrogen and elemental carbon, eliminates water gas shift and gas separation (CO<sub>2</sub> removal) stages required by the conventional industrial processes of hydrogen production, e.g. steam reforming of methane. This significantly simplifies the process and makes it particularly attractive for fuel cell application in which the presence of CO in hydrogen is often undesirable due to catalyst poisoning in

electrocatalytic cells. Therefore, Carbon nanotubes have particularly attracted the attentions of many scientists due to its advantageous properties such as high Young's modulus, effective capability for the storage of a large amount of hydrogen [1].

The main problem in catalytic decomposition of methane is the low yield of carbon and catalyst deactivation because of the active surface blocking of carbonaceous deposits [2,3]. Effective catalyst which can produce high yield of carbon and hydrogen and deactivated in a long time will be the main key for developing this process.

This paper is to study experimentally impacts of acidity (by varying Al loading) and Ni-Cu/Al catalyst diameter (by varying calcination temperature) on reaction performances mainly quality of products and methane activation.

## 2. Experiment

Catalyst Ni-Cu/Al were synthesized by coprecipitation methods [2] using an aqueous solution of nitrates salts, which are nickel nitrate hexahydrate, copper nitrate trihydrate and aluminum nitrate nonahydrate from Merck. After stirring of 1 h at about 50°C, the solution was dissolved with 25% ammonia solution at the rate of 10ml/min until it reach the desired pH. The thick solution was then stirred for another 1 h at the same temperature and left for aging overnight. The precipitate was filtered out and washed with deionized water in order to remove ammonium nitrate. The washing was repeated for five times. Wetcake was then dried at 120°C for 5 h in a vacuum furnace before calcined at 800°C for 5 h at atmospheric furnace by flowing 20ml/min of nitrogen.

Catalyst of Ni-Cu/Al-Si was prepared with the mixed methods between coprecipitation and sol gel. The same procedure was used for the coprecipitation method, but before the wetcake was dried, it was dissolved with tetraethylorthosilicate (TEOS) 98% of Aldrich, ethanol, and deionized water 1: 4: 6 in molar ratio respectively [4]. Hydrolisis of TEOS took place when the blend was stirred for 2 h at about 50°C. Afterwards, the solution was aged for 24 h, then dried at 120°C for 5 h in a vacuum furnace before calcined at 800°C for 5 h at atmospheric furnace with a flow of nitrogen about 20ml/min.

X-Ray Diffraction (XRD) Phillips measures catalyst crystallinity. Average crystal diameter ( $L$ ) is calculated by Sherrer's equation [5].

$$L = k\lambda / \beta \cos \theta \quad (1)$$

where  $k = 0.94$ ,  $\lambda$  is the wavelength of the radiation used,  $\beta$  is the full width at half maximum of the peak in radians and  $\theta$  is the Bragg angle. Catalyst acidity was tested in the Temperature Programmed Desorption (TPD), ThermoFinnigan 1100. After 0.2 gram catalyst was let to adsorb ammonia at atmospheric temperature and pressure for about half an hour, it was pretreated with 20 cc/min of helium by heating from room temperature to 500°C with heating rate of 15°C/min. Then continue with desorption with the same gas flow rate and heating rates until 650°C and hold for 30 min. Metal composition of samples were analyzed by X-Ray Fluorescence (XRF), JEOL JSX 3211. While nanocarbon products were recorded using Transmission Electron Microscope (TEM), JEOL.

The activity of catalysts were tested using a fixed bed quartz reactor 8 mm in internal diameter. Operating conditions were set at initial methane flow rate of 35-ml/min, 650-700°C and catalyst weight of 0.2 g. Activity test was carried out until catalyst was

deactivated. The outlet gas concentration was determined by GC (Shimadzu). It equipped with activated carbon column and argon as carrier gas. The amount of carbon deposited on the catalyst after the reaction time was determined by weighing unloaded samples.

## 3. Result and Discussion

The properties of the catalyst are shown in Table 1. TPD and XRF analysis showed that the Al content of catalyst increases with increasing the amount of precipitant by means increasing of acidity or amount of ammonia absorbed. This result is in agreement with Mtalsi [6].

Figure 1 shows the methane conversion vs. time on stream for Ni-Cu/Al catalyst. Methane conversion increases with increasing of Ni-Cu content. Ni-Cu/4Al and Ni-Cu/11Al performed the highest conversion of methane ~ 100% at early stage of reaction with poor stability towards carbon deposition due to higher Ni-Cu content and lower acidity. Increasing acidity of catalyst by increasing Al content will improve stability (lifetime), better tolerance on deactivation, but it decrease Ni-Cu content by means decrease methane conversion. Ni-Cu/15Al demonstrated the longest lifetime, but the lower methane conversion (60%) compared to the others. The most effective catalyst is Ni-Cu/15Al, which produced 4.97 g C/g cat for 1460 min.

**Table 1. Influence of pH and catalyst composition on acidity**

Catalyst	pH of solution	Composition Ni:Cu:Al:Si (%) <sup>*</sup>	Acidity (μmol NH <sub>3</sub> /g cat)
Ni-Cu/4Al	5	48:48:4:0	2.59
Ni-Cu/11Al	7	64:25:11:0	1.59
Ni-Cu/15Al	8	62:23:15:0	6.95
Ni-Cu/22Al	9	65:13:22:0	7.50
Ni-Cu/21Si	9	4:25:0:21	61.92**
Ni-Cu/18Al-5Si	9	66:11:18:5	188.92**
Ni-Cu/7Al-8Si	9	74:15:6:5	34.95**

\*Based on XRF analysis; \*\* TPD analysis without degassing (include physical adsorption)

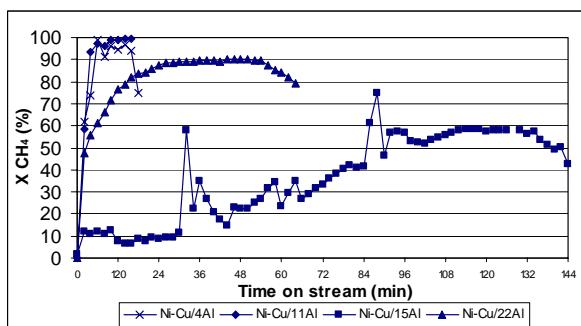


Figure 1. Methane conversion of Ni-Cu/Al catalysts

Table 2. Activity and yield of products catalyst for Ni-Cu/Al

	Ni-Cu/4Al	Ni-Cu/11Al	Ni-Cu/15Al	Ni-Cu/22Al
Acidity ( $\mu\text{mol NH}_3/\text{g cat}$ )	2.59	1.59	6.95	7.50
Lifetime (min)	140	160	1460	635
X CH <sub>4</sub> max. (%)	98	99	60	90
Yield H <sub>2</sub> (mol H <sub>2</sub> /g cat)	0.832	1.390	79.165	19.908
Yield Carbon (g C/g cat)	0.745	1.002	4.976	3.324

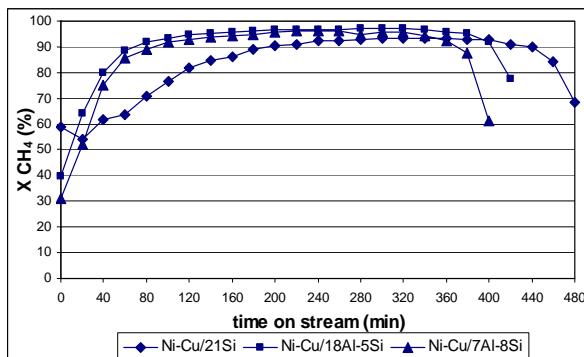


Figure 2. Methane conversion vs. time on stream

The detailed catalyst activity, yield of hydrogen and nanocarbon can be seen in Table 2. For Ni-Cu/Al-Si catalyst tested, the impact of catalyst acidity give almost the same trend as Ni-Cu/Al catalyst (Figure 2). Objective utilization of Al-Si in this work is to study impact of acidity in maintaining Ni-Cu content, however catalyst preparation did not give an expected constant Ni-Cu content. Ni-Cu/21Si performed a better

Table 3. Catalyst activity and yield of products Catalyst for Ni-Cu/Al-Si

	Ni-Cu/21Si	Ni-Cu/18Al-5Si	Ni-Cu/7Al-8Si
Acidity ( $\mu\text{mol NH}_3/\text{g cat}$ )	61.92	188.92	34.95
Lifetime (min)	480	420	400
X CH <sub>4</sub> max	93.5%	97.2%	96.2%
Yield H <sub>2</sub> (mol H <sub>2</sub> /g cat)	12.12	7.85	4.96
Yield Carbon (g C/g cat)	2.811	2.215	1.148

Table 4. Effect of calcination temperature diameter on nickel

Calcination temperature (°C)	Nickel catalyst diameter (nm)
400	4
500	5.5
600	8.5
700	15.5

stability with 60-80 minutes longer than the others and highest yield of carbon (2.81 g C/g catalyst). Comparison Ni-Cu/Al-Si catalyst activity and yield of product is presented in Table 2.

Ni-Cu/Al (58:30:12) was used in this part of experiment. XRD analysis showed that the nickel diameters increase with increasing calcination temperature (Table 4). At high calcination temperature, the catalyst tend agglomerated to form bigger size due to sintering phenomena.

In the case of the impact nickel diameter on methane activation is shown in Figure 3, methane conversion increases with increasing time on stream, and soon after methane conversion drop as a result of catalyst deactivation. The smaller nickel diameter gave higher methane conversion due to higher active site of catalyst but it's deactivated easily. By increasing catalyst diameter lifetime of catalyst was improved.

In addition, as shown in Table 5, the nanocarbon yield depends on methane activation and lifetime of catalyst. In this case, the effect of lifetime is more important comparing to methane conversion. Rapid catalyst deactivation in smaller catalyst is caused by carbon

growth that blocked catalyst pore and minimized methane diffusion through catalyst surface. Calcination temperature may also affect on its promoter structure. At higher temperature, alumina has bigger pore diameter that makes catalyst more stable due to nanocarbon growth is slower. Catalyst diameter of 15.5 nm produced highest carbon yield of 4.08 g C/g cat. Hydrogen purity depends on mainly on methane conversion (un-reacted methane) and small amount of by products such as CO and CO<sub>2</sub>.

Due to limited TEM data, typical textures of nanocarbon products at different calcinations temperatures are shown in Figure 4. Nanocarbon products showed existing of carbon nanotubes with range of diameter is about 25-90 nm.

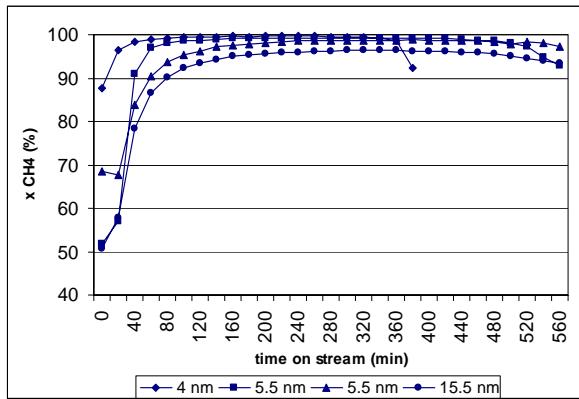


Figure 3. Methane conversion vs. nickel diameter at temperature reaction of 700°C

Table 5. Activity and yield of products for Ni-Cu/Al with varying nickel diameter

Nickel diameter (nm)	4	5.5	8.5	15.5
Lifetime (min)	340	560	560	560
X CH <sub>4</sub> average (%)	98.26	95.13	95.12	91.47
X CH <sub>4</sub> max. (%)	99.60	99.24	98.81	96.42
Yield of H <sub>2</sub> (mol H <sub>2</sub> /g cat)	4.32	4.15	9.40	19.88
H <sub>2</sub> purity (%)	82.81	72.87	81.73	82.22
Yield of Carbon (g C/g cat)	0.80	1.04	4.00	4.08

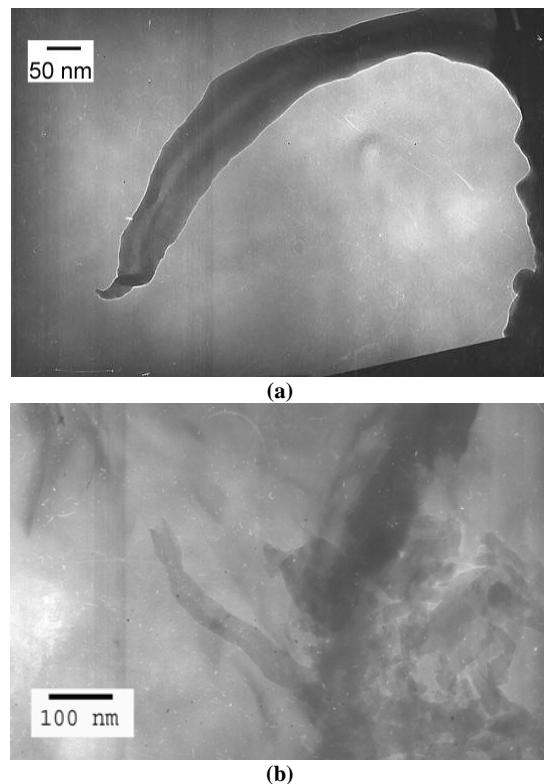


Figure 4. Nanocarbon texture from catalyst Ni-Cu/Al calcined at 800°C (a) and calcined at 500°C (b)

#### 4. Conclusion

Methane conversion increases with increasing of Ni-Cu content. Increasing acidity of catalyst by increasing Al content will improve stability (lifetime), better tolerance on deactivation, but it decrease Ni-Cu content by means decrease methane conversion. Ni-Cu/Al catalyst with lower Al content deactivated in a very short time hence produced fewer amount of nanocarbon with higher conversion close to 99%, while Ni-Cu/Al with higher Al content was active in a very long period with 60% of methane conversion. The most effective catalyst is Ni-Cu/15Al, which produced the biggest amount of nanocarbon, 4.9 g C/g catalyst for life time of 1460 minutes and typical diameters of nanocarbon are 25-90 nm. Catalyst diameter of Ni has significant effect on reaction performances mainly methane conversion and product yield. A small Ni crystal size resulting in a high methane conversion, leading to a fast deactivation and a low carbon yield. Large Ni particle diameter yields a slow decomposition and low methane conversion. The highest methane conversion close to 100% was produced by catalyst diameter of 4 nm and maximum yield of carbon of 4.08 g C/g cat was achieved by 15.5 nm diameter of Ni catalyst.

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