Direct Methane Reforming Process and its Applications

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The direct methane reforming (DMR) process which forms hydrogen and carbon nanotubes (CNTs) was studied. The CNTs were first applied to electromagnetic shielding and absorbing materials and then to other functional materials.

Key words: direct methane reforming, catalyst, hydrogen, carbon nanotubes

1. INTRODUCTION

The complete combustion of fossil fuels yields carbon dioxide along with water. Carbon dioxide is, however, a greenhouse effect gas, and the emission of carbon dioxide is one of the most crucial topics today.

The relative amount of carbon dioxide produced from a fuel per unit amount of heat of combustion is known to be 100 for coal, 71 for oil and 51 for methane. In order to reduce the emission of carbon dioxide, we had better use methane as a second best fuel. There are various sources of methane such as natural gas, biogas, coal-bed methane and methane hydrate. The biogas, which mainly consists of methane and carbon dioxide, is produced by the fermentation of biomass attracting recently much attention from a viewpoint of 'carbon neutral'.

The methane (called bio-methane) has been used as a gas fuel directly or as a hydrogen resource. Hydrogen is necessary for fuel-cell vehicles and cogeneration systems. An ideal source of hydrogen is methane, CH_4, because of its large abundance and the highest H/C ratio among saturated hydrocarbons. Hydrogen is usually produced by the so-called steam methane reforming (SMR), $CH_4 + 2H_2O = CO_2 + 4H_2$. This process consists of two reactions, $CH_4 + H_2O = CO + 3H_2$ (steam reforming reaction) and $CO + H_2O = CO_2 + H_2$ (shift reaction). Thus, the SMR inevitably emits carbon dioxide.

Recently, carbon dioxide capture and storage (CCS) is being watched as a promising option for mitigation of climate change. If continuous leakage of CO_2 occurs, it could offset the benefits of the CCS for mitigating climate change. Although the CCS could be the only option for a coal-fired power station, another option except the CCS is likely available for a natural gas-fired power station.

Carbon dioxide produced by the SMR can be reduced with hydrogen to carbons if we combine it with Bosch reaction, $CO_2 + 2H_2 = C + 2H_2O$. The combination eventually results in direct methane reforming (DMR) process, $CH_4 = C + 2H_2$. This process has several advantages: It is fundamentally free from CO_2 emission, solving the drawback of the SMR. The resulting hydrogen is theoretically free from CO which severely damages a polymer electrolyte fuel cell. The resulting carbons are mostly carbon nanofibers (CNFs) involving carbon nanotubes (CNTs).[1-3]

A combination of the DMR with a methane fermentation process producing bio-methane could accomplish 'carbon minus' system, because the bio-methane originates from CO_2 in the air. The DMR process would overcome several difficulties of the CCS, because the carbons (solid) seem to be more suitable for geological storage than CO_2 (gas).

2. DIRECT METHANE REFORMING REACTION

2.1 Subjects for investigation

Subjects for the investigation of the DMR are catalysts, optimum reaction conditions, reactors, the uses of the resulting carbons, etc.

2.2 Catalysts and reaction conditions

For the DMR, iron, cobalt and nickel catalysts supported on hard-reduced metal oxides such as SiO_2, Al_2O_3 and MgO have been used.[4] Percentage conversions of methane depended on the catalyst materials as well as the preparation methods of those catalysts.

The reaction conditions affecting methane conversion were reaction temperature, feed rate, time on stream, etc.

2.3 Fixed-bed reactor

First we used a fixed-bed reactor (Fig. 1). The most active catalyst metal was nickel at 650 °C or less, while iron was more active at 700 °C or more.

Methane conversions over those catalysts strongly depended on the catalyst metal loadings too.

Unfortunately, the catalysts were unable to keep their activity for a long time due to the carbons formed by the DMR. The co-feed of a few percent of a reducing agent or an oxidizing agent successfully solved the deactivation of the catalysts. However, the existence of the oxidizing agent such as carbon dioxide or steam resulted in the formation of a few percent of CO and CO_2.

During the DMR, the carbons went on increasing in the pores of the catalyst pellets and soon crushed those into

pieces, filled up the reactor and finally forced us to stop the DMR immediately. This experience taught us a lesson that the fixed-bed type reactor is not suitable for the long time continuation of the DMR without interruption for taking the reactor contents out.
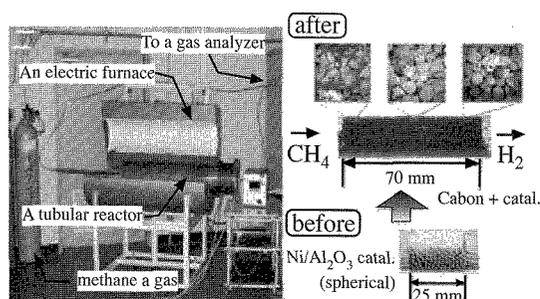
Fig. 1 A fixed-bed reactor for direct methane reforming.

2.4 Moving-bed reactor

Therefore, we newly developed a moving-bed reactor[5] (Fig. 2): This reaction system consists of a catalyst feeder, a reactor having a screw built-in, a gear set for moving the screw, a carbon collecting vessel and gas lines. When the gear rotates, the screw carries a mixture of powdered catalyst and the resulting carbons from one side to the other side, and drops those down into the collecting vessel. This moving-bed type reactor enabled us to carry out the DMR continuously; it can process 40 Nm^3-biogas, giving 30 Nm^3-H_2 and 8 kg-carbons in a day. Although a screw feeder had been frequently used to feed various materials, it was hardly used in a reactor so far. To our knowledge, this apparatus is the first to be developed and seems to be one of the key technologies for making the DMR process practicable.
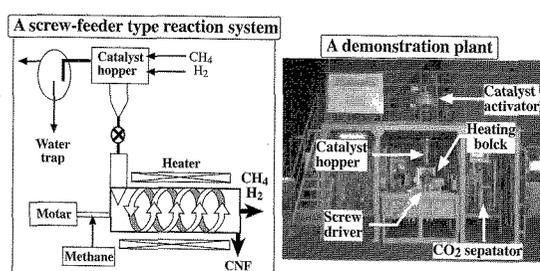
Fig. 2 A screw-feeder type moving-bed ractor for direct methane reforming.

3. CHARACTERIZATION OF CARBON PRODUCTS

The SEM images (Fig. 3a) showed that the carbons formed over Ni/Al_2O_3 and Fe/Al_2O_3 were mostly CNFs. Raman spectra showed that these carbon products consisted of both graphite-like carbons and amorphous carbons. X-ray diffraction analyses indicated that the graphite-like carbons were turbostratic. The TEM image (Fig. 3b) showed that the CNFs produced over Fe/Al_2O_3 at 750 °C were mainly CNTs.

Those as-prepared CNFs showed electric conductivity similar to that of a commercial carbon black and had the specific surface areas of 60-130 m^2/g.
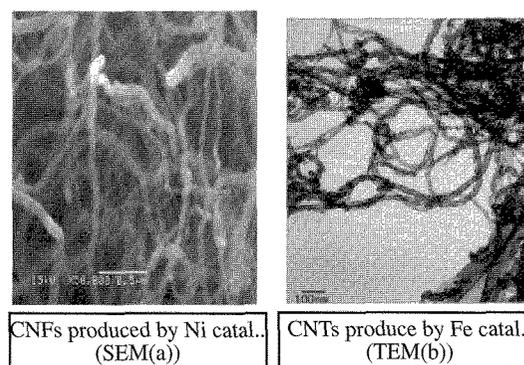
Fig. 3 Characterization of CNTs and CNTs by SEM(a) and TEM(b).
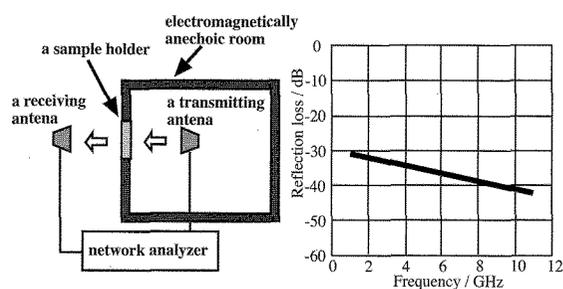
Fig. 4 Characterization of CNFs: electromagnetic property.
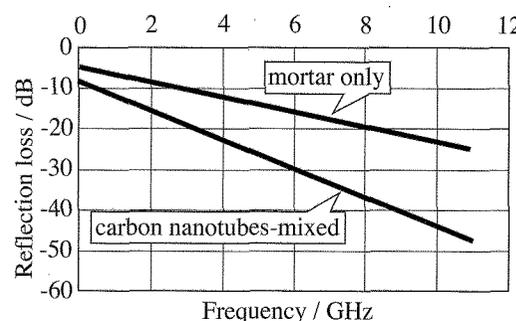
Fig. 5 An electromagnetic shielding mortar slab containing CNTs.

4. INDUSTRIAL APPLICATIONS OF CARBON NANOFIBERS

4.1 As-prepared carbon nanofibers

4.1.1 *Electromagnetic wave shield*:

Electromagnetic wave (EMW) would ruin our health especially when we are exposed to it everyday. In this case an EMW shield produced using the CNFs could reduce the bad effect. As-prepared CNFs were closely packed into an acrylic resin-made sample cell (inner thickness of 6 mm), and the EMW with different frequencies was transmitted towards the sample cell from the antenna in an electromagnetically anechoic room (Fig. 4). The EMW that permeated through the sample layer was received by the other antenna which was set outside of the room. The difference in power between the incoming EMW and the outgoing EMW was expressed as a reflection loss in the following equation, reflection loss = 10log(Po/Pi). For example, a reflection loss of -30 dB means that 99.9% of the incoming EMW was unable to penetrate the sample layer. The reflection loss increased
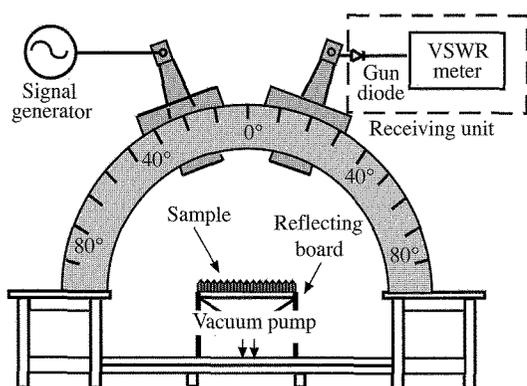
Fig. 6 A free-space method for measuring electromagnetic wave adsorption performance.

with an increase in the thickness of the CNFs layer. An as-prepared CNFs-mixed mortar slab also successfully shielded an object from the EMW of wide frequency region (Fig. 5). These results indicate that the as-prepared CNFs can be a good candidate material for EMW-shielding materials.

4.1.2 *Electromagnetic wave absorber.*

As-prepared CNFs were roughly packed into a polypropylene film bag (300 mm length, 300 mm width and inner thickness 3, 5 or 10 mm), and the EMW absorbing performance was measured by the free space method (Fig. 6). The EMW with different frequencies was transmitted towards the bag from the antenna, and the wave that permeated through the sample layer, reached to the bag-supporting metal stage and then reflected by the metal surface was received by the other antenna that was set on the same side of the transmitting antenna. The difference in power between the incident and reflected wave was expressed as a reflection loss, as a measure of EMW-absorbing performance. It was found that as-prepared CNFs were effective as an EMW-loss material. As the frequency of EMW increased, the reflection loss increased, suggesting that the reflection loss was due to the dielectric loss of the CNFs.

The inner walls of an electromagnetically anechoic chamber (Fig. 7) are fully covered with a number of pyramid-shaped absorbers. Generally an EMW absorber consists of an EMW-loss material (electric conductor, dielectrics or magnetic substance) and its substrate with a specified shape.

Such a piece of absorber is usually prepared by soaking a polyurethane foam in a solution of electric conductive carbon powder, followed by squeezing and drying. However, the polyurethane foam-based absorber can not apply for high-power EMW, because of low heat-resistance; it could emit fumes and sometimes burn when it absorbs high power EMW. Therefore, incombustible EMW absorbers are necessary. Up to now, a commercial inorganic-matrix based absorber has been prepared by solidifying a mixture of cement and carbon-fiber chips. This production method needs much manpower, and its reproducibility of the products was not well. Therefore, we developed an alternative way of the production of incombustible absorbers[6] (Fig. 8): Since the CNFs have electric conductivity and dielectricity as described above,
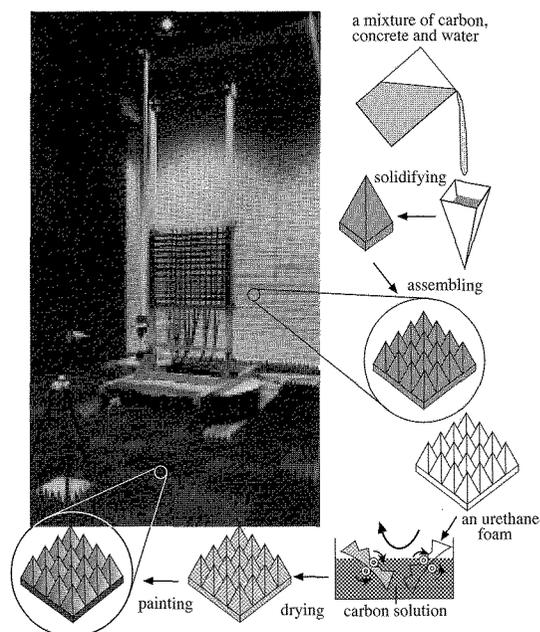
Fig. 7 Pyramid-type electromagnetic wave absorbers used for an anechoic chamber.
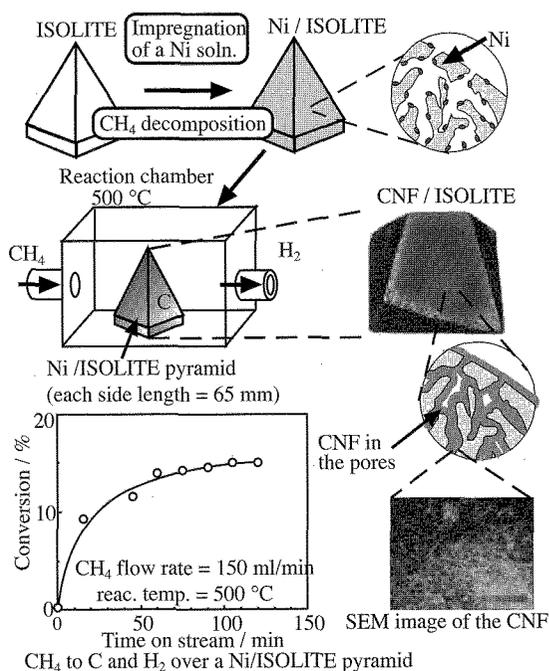
Fig. 8 Carbon deposition on the outer and inner surfaces.

such CNFs could be used as an EMW-loss material. A pyramid-shaped porous ceramic block (ISOLITE) with each side length of 65 mm (designated as a Ni-containing ISOLITE pyramid) was prepared, followed by impregnating with a nickel solution, drying and finally using as a catalyst for the DMR at 800 °C. When the DMR occured on the catalyst-metal particles supported on an inorganic porous matrix, in situ carbon formation took place in the pores of the Ni-containing ISOLITE pyramid, resulting in an EMW absorber.

A module in which 25 pieces of Ni-containing ISOLITE pyramids were arranged in five rows and five lines was

set on a sample stage made of stainless steel, and its EMW absorbing performance was evaluated by the so-called arch method. As a result, the reflection loss was about -20 dB for EMW of more than 5 GHz. The reflection loss depended on the height of the Ni-containing ISOLITE pyramid when the frequency of EMW was fixed: When the height was 115 mm, the reflection loss was -25 dB at 3.0 GHz. The reflection loss was comparable with that (nearly -25 dB) of a commercial incombustible pyramid-shaped EMW-absorber, HP-3 (each side length = 75 mm), which was prepared by E & C Engineering Co.

In addition, our production method was very effective for other-shaped absorbers for the EMW of more than 30 GHz; the reflection loss of the module exceeded -30 dB, even though its height was much lower; that is about 10 mm.

4.2 Dispersed-purified carbon nanofibers

As-prepared CNFs are generally bundled, and a special surface-treatment technique enables to unbundle and disperse those in a solution. Using such a CNFs sol enables us to disperse CNFs uniformly in a sheet of paper (Fig. 9). The sheet was found to absorb the EMW ranging from 1 to 6 GHz. The reflection loss was nearly -15 dB, being independent of the EMW frequency.

A paper-based friction disk was also prepared by using a sheet of paper coated with the CNFs sol. This disc showed a good performance from viewpoint of tribology; it seems to be useful as the wet-type friction parts for automatic transmissions, transfers for both four-wheel drive vehicles and motorcycles.

5. AN ENVIRONMENTAL APPLICATION OF DIRECT METHANE REFORMING

The utilization of the bio-methane as an energy resource is not believed to increase the net CO_2 concentration in the air on the basis of 'carbon neutral'. However, in order to reduce CO_2 in the air effectively, 'carbon-minus' system is essential. The direct reforming of the bio-methane can shift carbon-neutral system to carbon-minus system, because the bio-methane is produced by the fermentation of biomass together with CO_2 and this bio-methane can be converted into CNFs and hydrogen gas by the DMR process (Fig. 10). This hybrid process[7], thus, provides a novel way, 'carbon minus', in reducing CO_2 in the air effectively (Fig. 11).

6. CONCLUSION

The DMR is a safe and best way to produce CNFs and hydrogen gas without releasing CO_2 into the air.

The CNFs alone as well as a CNFs-containing porous ceramic block with a specified shape effectively shielded and absorbed the EMW of a wide frequency.

The DMR process has great potential for the solution of global warming; the direct reforming of every methane resource will solve some problems of the CCS; particularly the direct reforming of bio-methane will make 'carbon minus system' possible.

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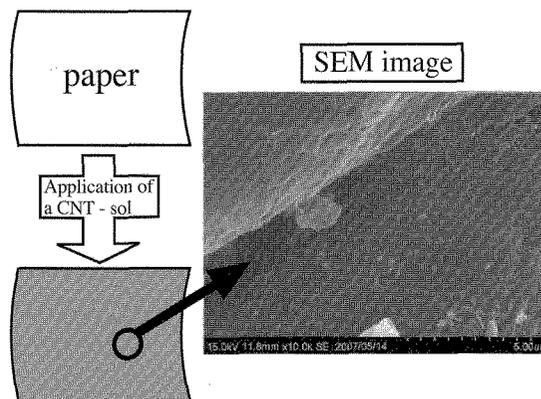
Electricity conductive (about 3MΩ), dustless
⟶ an antistatic paper

Fig. 9 Application of a CNT-sol to a paper.
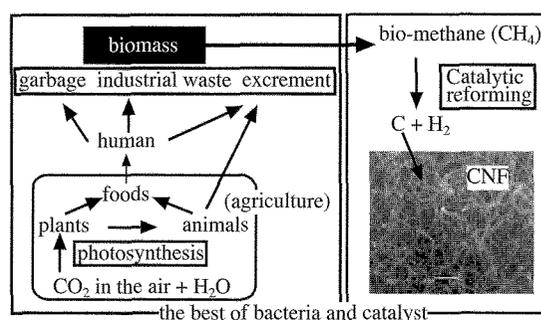
Fig. 10 Conversion of bio-methane to carbon nanofibers and hydrogen.

From carbon-neutral to carbon-minus system!
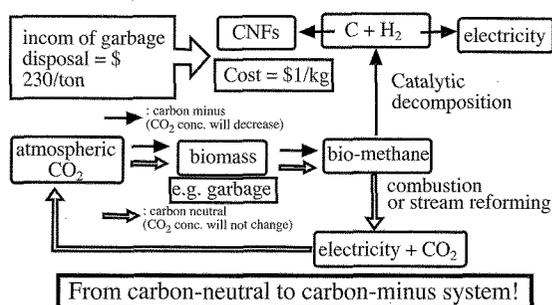
Fig. 11 Direct reforming of bio-methane: key thechnology for carbon-minus system.

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