Mass Carbon Nanofiber Production from CO_2 using Fluidized-bed Looping DBD: Application to Energy Storage Devices

X. Chen[1], Y. Nishina[2], W. Zhang[1], T. Nozaki[1]

[1]*Department of Mechanical Engineering, Tokyo Institute of Technology, Tokyo, Japan*
[2]*Research Core for Interdisciplinary Sciences, Okayama University, Okayama, Japan*

Abstract:
A loop strategy involving CO_2-to-CO process and Boudouard reaction ($2CO = C + CO_2$) was proposed for a green and mass carbon nanofiber synthesis from CO_2. Fluidized-bed dielectric barrier discharge (FB-DBD) reactor was devised to maximize the plasma-catalytic CO_2 conversion and CO/CO_2 ratio in gas products, thermodynamically enhancing the subsequent Boudouard reaction for continuous carbon deposition and separation. Moreover, the potential application of carbon fiber to the secondary battery or supercapacitor electrodes is introduced.

Keywords: Boudouard reaction, Fluidized bed, DBD, Plasma catalysis, Carbon nanofiber.

1. Introduction

Cost-effective CO_2 conversion to solid carbon is of great significance for carbon neutrality and carbon-based industries. Direct CO_2 splitting ($CO_2 = C + O_2$) is promising but is hardly feasible because of strong C=O bond (804 kJ/mol). Instead, cracking of hydrocarbons, particularly CH_4 ($CH_4 = C + H_2$), is mostly preferred, as C-H bond is relatively weak (413 kJ/mol), and H_2 is co-produced without CO_2 emission. Nonetheless, as an endothermic process, high reaction temperature (>800 °C) and energy cost are still required; meanwhile, swift catalyst deactivation and reactor clogging can be caused by generated carbon, which are the key obstacles for scale-up. Plasma catalysis offers a solution: efficient CO_2/CH_4 activation is available through electron-molecule collisions, thus decoupling the temperature. Meantime, renewable energy, i.e., solar, can be utilized for plasma generation, as has been verified on a laboratory scale. Unfortunately, the conductive carbon can restrain the plasma-catalyst interaction or even plasma generation. Herein, we proposed a plasma-enhanced loop strategy (Fig. 1) to convert CO_2 to carbon nanofiber: a) FB-DBD catalysis focuses on enhancing CO_2-to-CO conversion at relatively low temperature without carbon interference; b) plasma-free Boudouard reaction, potentially self-sustained via exothermic nature, is used for CO-to-carbon deposition. In this sense, maximizing plasma catalysis in Fig. 1a is the key, as it determines the CO/CO_2 ratio of gas products and affects subsequent Boudouard reaction in thermodynamics.

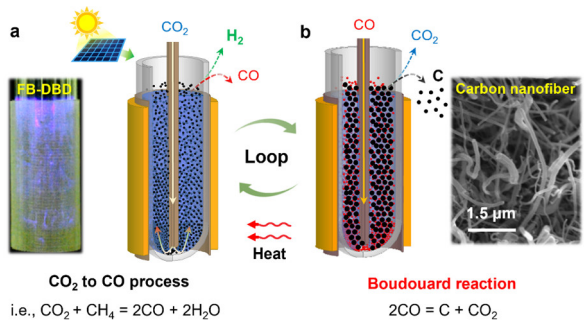

Fig. 1. CO_2 fixation as carbon nanofiber: (a) CO_2-to-CO process and (b) Boudouard reaction loop strategy

2. Experimental

In CO_2 to CO process, newly developed FB-DBD reactor (Fig. 1a) was applied with CO_2-CH_4 reforming as a model. Detailed results have been reported in Ref. [1-2]. Briefly, in FB-DBD, the feed gas was flowed inside the hollow high-voltage electrode, forming a gas jet via the pinhole at the tip and blowing off the La-Ni/Al_2O_3 for self-sustained fluidization and plasma catalysis.

The key superiority of FB-DBD over the conventional packed-bed DBD is: the catalyst powders, as fluidized media, can be drastically decreased in size with minimum pressure drop, while forming more uniform gap and electric field for plasma generation, yielding an enhanced plasma-catalyst coupling and transfer flux of mass and heat.

Consequently, FB-DBD yielded CO_2 conversion of 85% and CO/CO_2 concentration ratio of 11.1 (in gas products) at 600 °C (reached the thermal equilibrium), significantly higher than those in PB-DBD (47% and $CO/CO_2 = 1.7$) and thermal catalysis (38% and $CO/CO_2 = 1.1$).

Therefore, Boudouard reaction for mass CO-to-carbon production is currently the top priority. Parametric studies were conducted first in fixed-bed reactor (quartz tube, i.d. 20 mm, with a boat) over 0.23 g Fe/MgO (1 wt%, 180–300 μm). The redox properties of catalyst were investigated by temperature programmed reduction (TPR) (1 g Fe/MgO, H_2: 50 cm^3/min, Ar: 20 cm^3/min, 55 kPa) and XRD. Furthermore, plasma-free FB configuration (Fig. 1b) was used for continuous carbon nanofiber deposition (1 g Fe/MgO, CO: 50 cm^3/min, H_2: 20 cm^3/min, 90 kPa) and *in situ* separation (Ar: 600 cm^3/min, 15 kPa) at fixed 600 °C.

3. Results and discussion

Fig. 2 a–c shows that, in all cases, CO conversion is about 2 times more than CO_2 yield, implying Boudouard reaction dominates the reaction path. 600 °C and 90 kPa were determined preferred for carbon deposition; both before (Fig. 2d, 2e) and after (Fig. 2h) the process, Fe_3O_4, not Fe, was identified the most stable status. CO conversion was multiplied up to nearly 6 folds by introducing H_2 (Fig. 2c); the *in situ* removal of O* from Fe_3O_4, instead of CO hydrogenation ($CO + H_2 = C + H_2O$), is considered important as the H_2 consumption is too small.

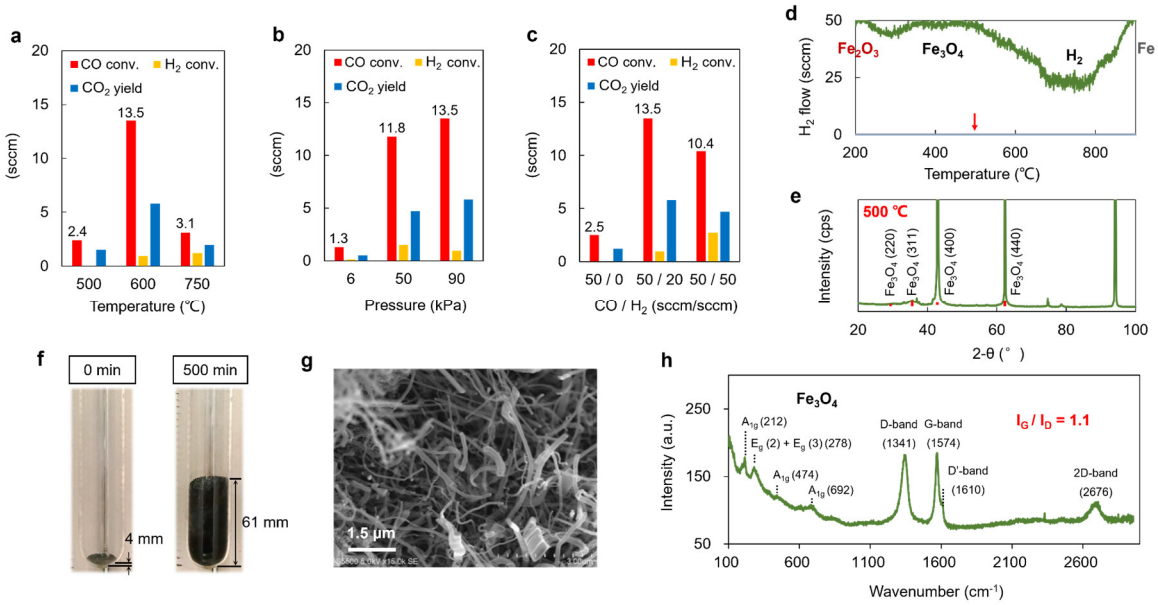

Fig. 2. Boudouard reaction over Fe/MgO. (a–c) parametric studies: effect of temperature, pressure, and H_2, (d) H_2 consumption spectrum during TPR, (e) XRD of catalyst reduced at 500 °C, (f) snapshots of fluidized bed before and after carbon deposition, (g) SEM image of carbon fiber, and (h) Raman spectrum of carbon-Fe/MgO mixtures

Thermodynamic calculations were conducted to draw Fe-C-O-H phase diagram, showing the effect of H_2 on iron status and carbon formation behavior (Fig. 3). Fe_3O_4, FeO and Fe are sequentially distributed as temperature increase; H_2 played the key role in iron reduction. Both Boudouard reaction and CO hydrogenation are feasible for carbon deposition, particularly at low temperatures (<650 °C) and low H_2 concentrations (< 65%); Fe_3O_4 is the most stable, which is consistent with the experimental observations. Importantly, Fe_3O_4 is feasible to be reduced directly to Fe by H_2 at identically low temperatures. Indeed, the Fe_3O_4-to-Fe reduction occurs only in H_2 rich environment, as H_2 is preferred to be consumed by CO in thermodynamics; whereas, in experiment, CO hydrogenation is kinetically inhibited, as discussed previously, thus: 1) Fe_3O_4-to-Fe reduction by trace amount of H_2 is available to enhance Boudouard reaction, and 2) most H_2 produced by CO_2-CH_4 reforming (Fig. 1a) can be utilized as clean energy.

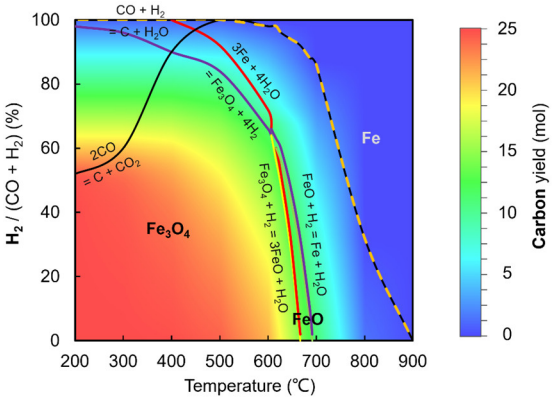

Fig. 3. Thermodynamic phase diagram: distribution of iron status and carbon (by Gem program + MALT)

In addition, in Fig. 2f (FB reactor), carbon is synthesized up to 80 gram_C/gram_Fe with CO conversion of 50% without catalyst deactivation and reactor clogging, and can be *in situ* separated from the catalyst bed. The generated carbon shows filamentous shape, clear 2D peak and satisfactory I_G/I_D ratio of 1.1 (0.74 for commercial carbon nanofiber) (Fig. 2g, 2h). The application of carbon fiber to Li-ion battery electrodes or supercapacitor is being considered, which is important to improve the economic value of the gas-to-solid process via renewable energy.

4. Conclusions

Plasma-enhanced CO_2-to-CO process and Boudouard reaction loop strategy is proposed for mass CO_2 conversion to carbon fiber. FB-DBD plasma catalysis was developed; sufficient CO_2 conversion (85%) and gas products with high CO/CO_2 ratio (11.1) were obtained at 600 °C. Plasma-free Boudouard reaction over Fe/MgO was established; mass carbon nanofiber deposition (≥ 80 gram_C/gram_Fe, CO conversion: 50%, I_G/I_D ratio: 1.1) and separation were achieved without catalyst deactivation and reactor clogging. Heat self-sustaining of Boudouard reaction and integrating two processes in a single reactor is underway.

5. Acknowledgments

This project is supported financially by JST CREST (JPMJCR19R3). X. Chen is supported by MEXT Scholarship (201807090002).

6. References

[1] X. Chen, Z. Sheng, S. Zen, H.-H. Kim, T. Nozaki, *J. CO_2 Util.*, **54**, 101771 (2021).
[2] X. Chen, H.-H. Kim, T. Nozaki, *Plasm Process. Polym.*, to be published, (2023).