이산화탄소의 축합 반응을 이용한 탄소의 순환

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Artificial Carbon Cycle Utilizing Condensation Reaction of CO_2

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1. Introduction

The natural process of carbon cycle involves photosynthesis as a central part. Carbon in the form of CO_2 appears in the atmosphere and functions as a greenhouse gas. From the time of industrial revolution, human activity disturbed natural carbon cycle, and CO_2 level is showing increasing trend and intensifying greenhouse effect. In order to keep the atmospheric CO_2 level in balance, there should be artificial effort to harness the released CO_2 to be a reduced form. Many artificially implementable measures are suggested since the global warming has been an issue. Until now, CO_2 capture and sequestration is generally advanced as the option to tackle greenhouse gases, but in the sense of the completion of the carbon this option is deficient of the reduction step. Artificial photosynthesis is one of the plausible measures to keep CO_2 in the balanced carbon cycle. But utilizing sunlight in CO_2 conversion reactor in large scale is not successful yet [1]. The natural photosynthesis cannot cope with the human indutrial CO_2 emmission, and artificial photocatalytic conversion of CO_2 is not so adaptable.

There was revealed another possibility to convert CO_2 through low energy route, which involves the pressurization of CO_2 in room temperature producing polymerized CO_2 stable in ambient condition and the subsequent thermal decomposition during which carbon is regenerated [2]. The proposed theory is that CO_2 can be easily reduced to graphite once it is solidified as shown in Fig. 1. If the decomposition or O_2 evolution reaction can be achieved at the temperature level of 100~200°C, natural sunlight can be used for regeneration of carbon to complete the carbon cycle which would supplement the natural carbon cycle.

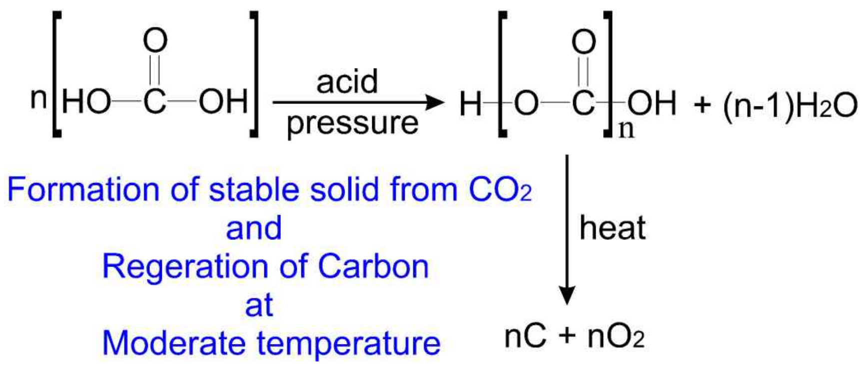

Fig. 1 Representation of CO_2 solidification and reduction

2. Solidification of CO_2

Generally CO_2 is known to be too unstable to be condensed in atmospheric pressure and temperature. It is because carbon can form stable double bond with oxygen and CO_2 can exist as a free molecule while silicon only can exist polymeric form due to its inability to form double bond. The size difference of these two atoms is thought to make this difference. One of the size effect is conjectured that the size difference between silicon and oxygen is quite large and the mismatch causes the difficulties in the formation of the π bond. Another effect is that the existence of oxygen atoms among the large silicon atoms can stabilize the crystalline form because the atoms can be packed more densely while the chemical bonds are too weakened with interference of the larger oxygen atoms for the CO_2 to form crystalline polymer. In this sense the carbon tend to exist as reduced pure carbon solid in nature, namely graphite or diamond. Once CO_2 is solidified its reactivity increases and oxygen is easily eliminated to form more stable pure carbon crystal. Solidifying and stabilizing of CO_2 can benefit in recycling and reducing atmospheric CO_2.

The origin of solidification and stabilization of CO_2 in ambient condition can be explained that the potential energy of the product is lower because it has mixture of single and double bonds and there are hydrogen bonds with interstitial water molecules stabilizing carbonyl groups. Because the linear form of the solid CO_2 has double bonds, it has less potential energy than the crystalline form. Because the bond energies are 358kJ/mol for single bonds and 799kJ/mol for double bonds [3], the linear form has lower energy that the crystalline form due to the existence of double bonds. The stabilization of the solid CO_2 means there exists energy barrier which prevents it from becoming free CO_2 in room temperature. Supporting evidences of this conjecture can seen from the proposed glass-like structure based the FT-IR characteristic bands [4]. Even if the the possibility of solidification of CO2 which is stable at ambient condition, the recovery of solid in large scale is not yet realized, and this is seemingly because the existence of the solid in bulk condition is severely inhibited, and this difficulty raises the development of bulk stabilization additives.

3. Reduction of CO_2

The completion of carbon cycle can be brought about by reducing solid CO_2 to carbon again. And this is done already. The stabilized glass-like structure can be expected to be less stable than gaseous form and it was more easily reduced to result in graphite [5]. The unstabilized structure eliminated the oxygen more readily with thermal treatment, and transformed to graphite with continuous removal of the eliminated oxygen shifting the equilibrium to reduced condition. The elimination of oxygen occurred around 500^{o}C and continued as the temperure was further increased. But this temperature is still too high to utilize dispersed low quality energy.

For the further decrease of temperature of the carbon regeneration, some catalytic effect is needed. Utilization of water glass (Na_2SiO_3) to stabilize solid recovery and lower the reducing temeprature was tried. The aqueous solution of sodium silicate (10%) was filled into the autoclave, and CO_2 was pressurized into the autoclave. The amount of reaction solution was 50g. Reaction time was from 2 hours to 5 days. Reaction temperatures ranged -5~15^{o}C, and pressures 5~10MPa. After the reaction, the solution was dried in the mild condition (around 50^{o}C). But the recovery of solid CO_2 is not so much improved. The content of CO_2 solid was less than 20% of the dried total solid. The recovered solid (1g) was subjected to the thermogravimetric analysis with real time monitoring of the gas evolution. The temperature was raised in maximum rate to 360°C with Ar flow rate of 5cc/min.

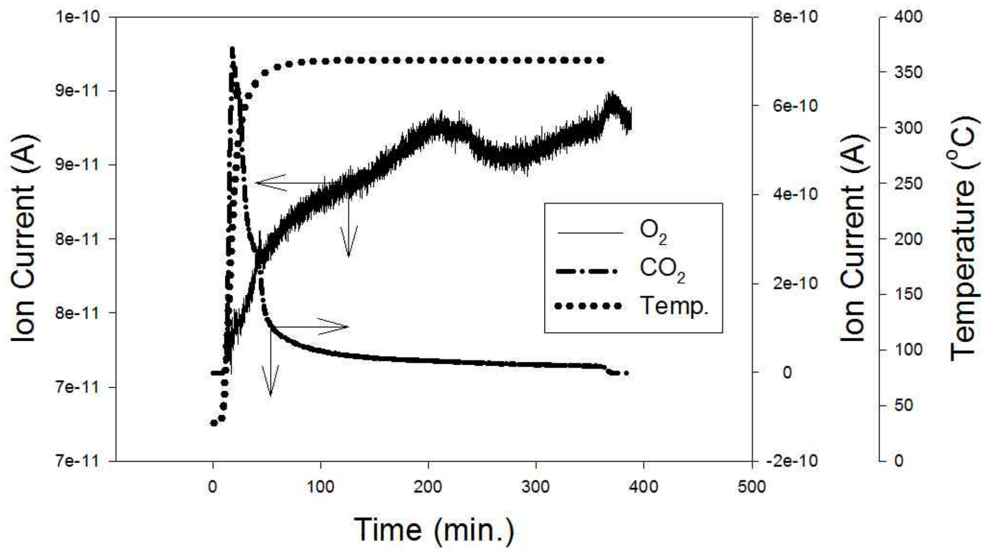

Fig. 2 Gas evolution characteristic of Na_2SiO_3-CO_2 solid under heating

Even though the stabilization CO_2 solid is not significantly improved the temperature of the carbon regeneration was shown quite decreased as can be seen in Fig. 2. This result shows the evolution of CO2 rapidly decreases above 300°C and then O_2 evolution is switched on. This means that the silica compound can stabilize graphite formation, and CO_2 evolution and O_2 evolution has the completely different characteristics. The thermal decomposition of the solid cannot activate both kinds of reaction simultaneously. This result shows the possibility of the activation of O_2 evolution and the carbon regeneration at low temperatures. And this result also has significance that there are still possibilities of the utilization of the natural dispersed low temperature sources in regeneration of the carbon from CO_2. For this purpose further research is needed to find out reagents which has the stabilization effect for CO_2 solid and promote its reduction.

4. Conclusions

Because oxygen can be easily removed from solid CO_2, this phenomena can be exploited in recycling carbon. The carbon plays the role of energy carrier while it is cycling through the biosphere and atmosphere and in similar way it can cycle through simpler route as shown in Fig. 3. The first step is concentrating step and the solidification step follows. The next step is conversion step transforming CO_2 to graphite. The graphite is the energy source and produces CO_2 which completes the cycle. Stabilizing CO_2 by solidification is a great progress in carbon cycle because the stabilization can be achieved by pressurization, which can be achieved with low quality energy, and then easier way of CO_2 reduction can be brought about as a carbon regeneration step. Stabilization of solid CO_2 can be explained that the energy barrier is generated when it took the linear form because it has lower energy than the crystalline form whereas the crystalline form is in such a high energy state that there is no room for the significant activation energy. Decrease of energy can come from the remaining double bonds and interstitial foreign molecules which stabilizes the double bonding carbonyl oxygen.

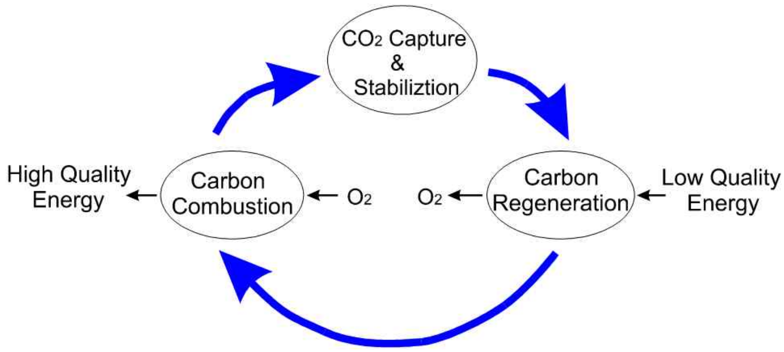

Fig. 3 A suggestion of carbon cycle utilizing CO_2 solidification and reduction

Due to the stabilizing effect of translational entropy let alone the reaction energy, the reaction of CO_2 is not facilitated in mild conditions. But once the free molecule is fixed its Gibb's free energy increases partly due to the entropy decrease and partly due to the enthalpy increase. In this way, the conversion of CO_2 to carbon is made more favorable and carbon regeneration can be done with lower quality (i.e., lower temperature) energy. Starting from this concept, further development can bring down the oxygen evolution temperature lower and lower, and the range of the useful energy will become broader and broader. Even further lowering down decomposition temperature will facilitate the usage of sunlight in the desert area where the sunlight is most intensive and produces highest temperature condition on earth, making the most devastated wilderness into carbon recovery farm.

A new concept of carbon cycle can be suggested in which the carbon regeneration is done with low quality energy after the carbon is oxidized producing high quality energy. If we can get high quality energy by putting in low quality energy, CO_2 emission can be minimized with the development of technology gathering waste energies to be utilized in the suggested cycle or ultimately speaking, carbon can be recycled perpetually if the cycle produces no additional CO_2.

References

1. Mackintosh, S. 2011, Catalyst (Feb), 13-15.
2. Kim, J. G. 2013, Theor. Appl. Chem. Eng., 19 (1), 1000-1003.
3. Ebbing, D. D. and Wrighton, M. S. 1984, *General Chemistry*, Houghton Mifflin Company, Boston.
4. Kim, J. G. 2012, Trends Chem. Eng., 14, 71-74.
5. Kim, J. G. 2014, Korean Patent, 2014-0001421.