이산화탄소고정 및 환원에 관한 열화학 속도론적 고찰

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Thermochemical Kinetic Aspects of Solidification and Reduction of CO₂

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1. Introduction

It is well known as a fact that CO_2 cannot exist as a solid in ambient temperature and pressure, which is an obstacle for the free CO_2 to react. Because of this, the recycle of carbon from its spent form to a useful reduced form begins with the fixation of CO_2 inside the photosynthetic cells [1]. Until now it is known that the core part of the carbon cycle is the CO_2 fixation into solid through the photosynthesis resulting in the carbohydrates. When carbon atoms are released into the atmosphere in the form of CO_2, it can be taken up by a plant during photosynthesis and then be incorporated into the tissues. The carbon atom will return to atmosphere through oxidation in the living organism or in furnaces for the production of various forms of energy and a cycle is completed (Fig. 1).
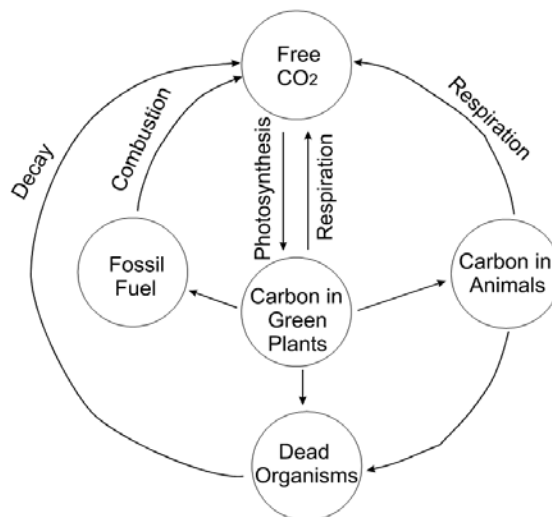

Fig. 1　Representation of CO_2 cycle between biosphere and atmosphere

A recent experimental evidences showed that CO_2 can exist in stable solid form in ambient pressure and temperature and moreover oxygen elimination from this form of CO_2 can also be facilitated [2, 3]. And this fact suggests that another carbon cycle can be completed artificially going through the rather simple CO_2 solidification step.

Generally CO_2 is known to be too unstable to be condensed in atmospheric pressure and temperature. Even if quartzlike form and other crystalline forms of CO_2 are already identified, those forms are only stable in somewhat extreme conditions [4]. 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 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. The stabilization of the solid CO_2 means there exists energy barrier which prevents it from becoming free CO_2 in room temperature.

2. Solidification and Stabilization of CO_2

In real systems, most states are subject to change with large perturbation and are not in the ultimate stability but in the metastable state. In this sense, the extent to which a barrier exists is dictated not by thermodynamic reasoning but by rate or kinetic considerations. If the rate of a possible transition is too slow to be significant within the time span of interest, we consider the barrier as an impenetrable internal restraint. For simple systems, such barriers may be visualized as activation energies that prevent chemical reactions. The solid form of CO_2 can be stabilized in a metastable state if there is energy barrier that hinders it to alter to gaseous form. The present knowledge says that the crystalline quartzlike form of CO_2 barely has this energy in the state it is formed and this means that it can barely be stabilized on its own without the help of some other measures.

The generation of energy barrier and the stabilization of solid CO_2 can be brought about by forming the solid of lower energy state. If the energy state of one form is lower than the other form, the decrease of energy of formation can be realized as the creation of activation energy barrier according to the thermochemical kinetic theory [5]. Because the linear form of the solid CO_2 has double bonds, it has less potential energy than the crystalline form. When the crystalline form is created, one double bond generates two single bonds and the bond energies are 358kJ/mol for single bonds and 799kJ/mol for double bonds [6]. In this case, the energy difference is 166kJ for one mole of CO_2. But for the linear form the existence of double bonds decreases the potential energy and the oxygen ends of the double bonds can be further stabilized by the hydrogen bonds with the interstitial water molecules because the linear molecules are loosely intercalated. The energy decrease means the increase of energy barrier from the product side (Fig. 2).

Another aspect of the production of stabilized solid CO_2 is the reaction condition. The condition described in the literature [4] requires high temperature and the state of the product at that temperature would be so reactive that the product would return to the low energy state of CO_2 quickly even if there is any energy barrier. But the condition for the reaction producing the linear form is not so severe and the reaction occurs even at low temperature

[2]. The energy barrier plays a greater role when the temperature is low and molecules are less activated and this is the case when the linear form becomes the stabilized product.
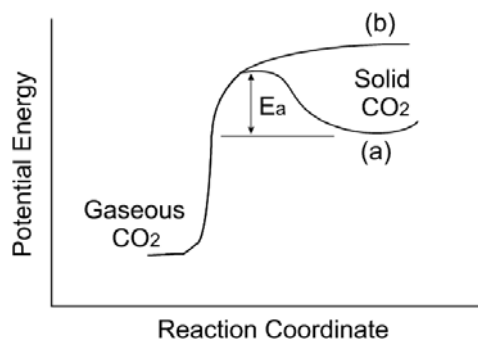

Fig. 2   Acivation energy increase and stabilization of solid CO_2

3. Reduction of CO_2

The solid CO_2 has greater energy and has the entropy minus the translational entropy. This means that it needs less activation energy and the equilibrium is more favorable for the product side when it is transformed to graphite than the gaseous CO_2 (Fig. 3). The elimination of oxygen from the solidified CO_2 can be reasoned based on the physical and chemical principles. The carbon atoms are smaller in size and have more covalent bonds than oxygen atoms, which means that more atoms can be packed into the same volume and more stabilized with more chemical bonds when the solid is composed only of carbon without oxygen. The eliminated oxygen can be easily removed the equilibrium will further shift to the product side with the continual removal of it.
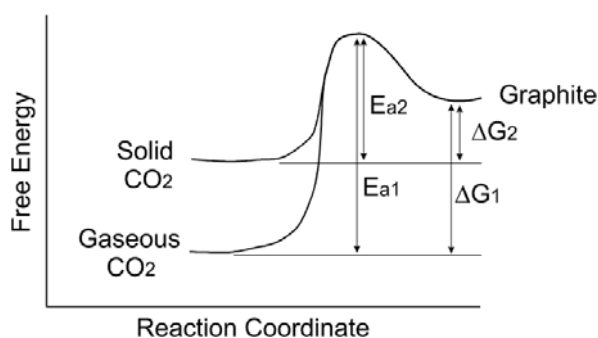

Fig. 3   Comparison of energy difference between gaseous and solid CO_2

Because oxygen can be easily removed from fixed 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. 4. 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.   Without the intermediate solidification step, producing graphite from CO_2 requires high temperature because of high energy barrier.

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.
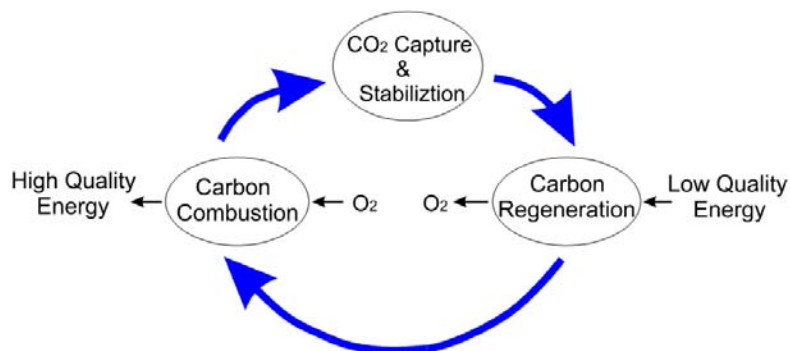

Fig. 4   A suggestion of carbon cycle utilizing CO_2 fixation and reduction steps

4. Conclusions

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.

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 reaction temperature lower and lower, and the range of the useful energy will become broader and broader.

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

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