

고정화된 이산화탄소의 환원

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Condensation and Reduction of CO₂

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1. Introduction

Carbon and silicon belong to the same group in the periodic table and it can be expected that the two elements should exhibit the similar behavior. But two elements have different sizes and make different bond strengths when participate in the chemical bonds. So they cannot behave in exactly the same way. Even if quartzlike form and other crystalline forms of carbon dioxide are already identified, those forms are only stable in somewhat extreme conditions [1]. Silicon can make more stable form when it is oxidized than carbon and it cannot make double bond with oxygen it cannot exist in single monomeric form. Carbon, on the other hand, makes rather weak bond with oxygen but the double bond between carbon and oxygen helps in stabilizing monomeric CO₂. These facts have another meaning that carbon is more stable than silicon in pure elemental form and this is why natural pure carbon (e.g., graphite and diamond) can exist while natural pure silicon cannot be found. And then another consequence will follow so that CO₂ can be reduced rather easily to pure carbon, namely to graphite. If this is the case, where do the difficulties of reduction of CO₂ come from? This is because the vaporized CO₂ has less Gibb's free energy than the solid form due to its vaporization entropy. This also means that CO₂ can be reduced more easily if we can make stable solid form of CO₂. Recently some attempts were made to find out whether CO₂ molecules can be combined pairwise through condensation reaction on the basis of conjecture that it can make amorphous solid analogous to glass form of silica. The result suggested that CO₂ can exist in a stable form at room temperature and atmospheric pressure [2].

2. Experimental

The reaction was performed in an autoclave by pressurizing CO₂(6Mpa) in to the aqueous solution of HCl(10%). The high purity CO₂ (over99.99%) was used. The amount of reaction solution was 5g. Reaction time was from several hours to several days and after the reaction the solution was dried in the mild condition (around 50°C) and then subjected to the analysis. Several syntheses were tried for various temperature conditions (from -10°Cto20°C) and the yield was very low and the concentration of the harvested material in the solution did not exceed 1%. The original HCl solution left no observable solid residue after drying, and it can be said that the solid residue harvested after experiment is only the consequence of the CO₂ reaction.

The thermal behavior of the synthesized substance (0.25g) was analyzed with the heating rate of 2°C/min and Ar rate of 100cc/min. The TGA equipment was assembled using the Rubotherm magnetic suspension balance and the Rubotherm heating unit. The gases monitored

were CO₂ and O₂ by the quadrupole mass spectrometer IPI GAM 400 model.

Infrared absorption characteristics of the solid residue before and after the thermal treatment was obtained using SensIR Technologies instrument with the number of scans of 64 for the Fourier transform infrared (FT-IR) spectroscopy. And the generation of the graphitic material was detected by observing the Raman shift characteristics with the BRUKER SENTERRA model (wave length 532nm, power 20mW, exposure time 100s).

3. Results and Discussion

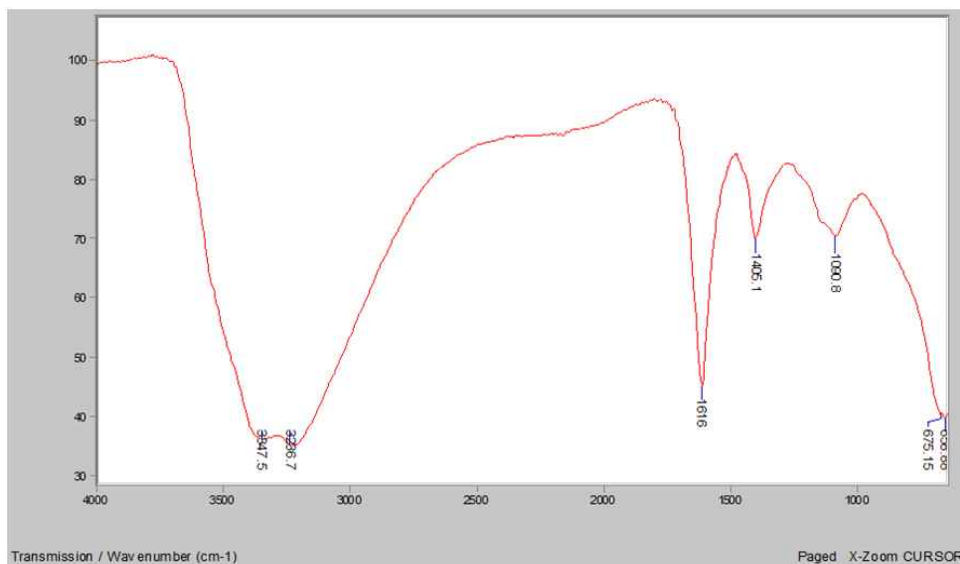
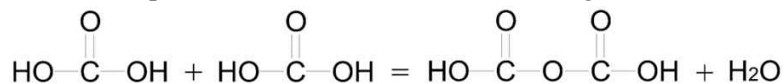
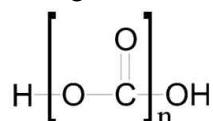


Fig. 1 FT-IR Spectrum for condensed CO₂

The supporting evidences of CO₂ fixation can be observed when we investigate by way of the FT-IR characteristic absorption spectrum. Carbonyl group stretching vibration band and ether group vibration bands can be observed from FT-IR spectrum in some shifted manner. From Fig. 1, we can observe absorption band at 1616 cm⁻¹ that can be assigned to carbonyl group(C=O) stretching vibration. Absorption at 1091 cm⁻¹ can represent ester C—O stretching band. The absorption band at 1405cm⁻¹ appears to be caused by C—O—H bending vibration. The bands in the high frequency region and low frequency region can be interpreted to represent the hydroxyl group and chloride group respectively. The synthesized material of CO₂ fixation has carbonyl and ether groups indicating that there was condensation reaction combining carbonic acids pairwise as shown in the following scheme:



The linear polymer backbone that can be properly named poly(carbondioxide) can also be suggested as the base material resulting from CO₂ fixation:



Abrupt O₂ evolution at about 500°C was observed when the condensed CO₂ was heated in the thermogravimetric analysis. From the first CO₂ evolution was observed and the gas

evolution profile showed that the evolution of CO₂ was switched to the evolution of O₂. As the CO₂ evolves accelerated decrease of mass was observed. The slight acceleration of mass decrease also appears accompanied with the initiation of O₂ evolution. The evolution of O₂ means that the carbon should be left behind as a natural consequence.

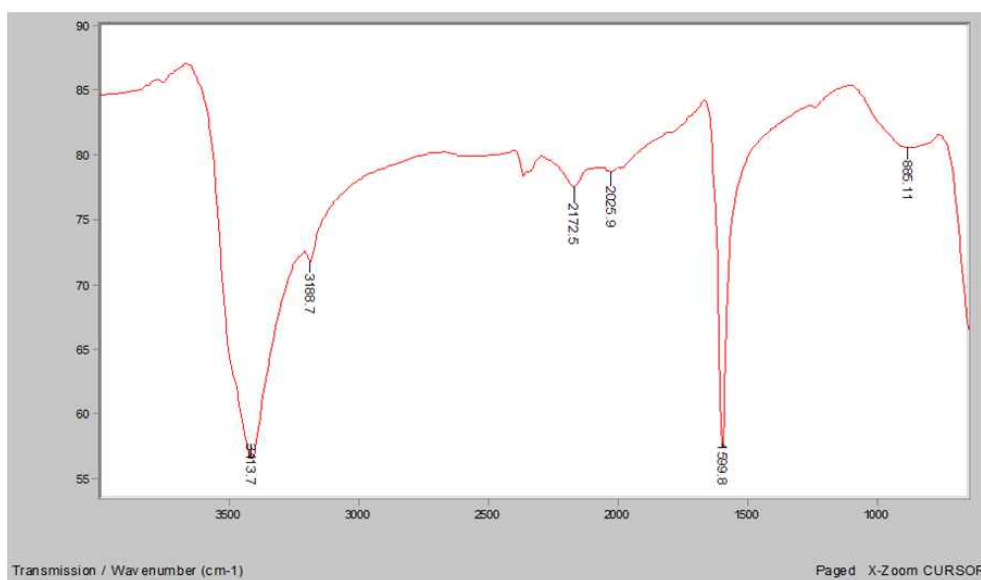


Fig. 2 FT-IR spectrum for the residue after thermal treatment of condensed CO₂

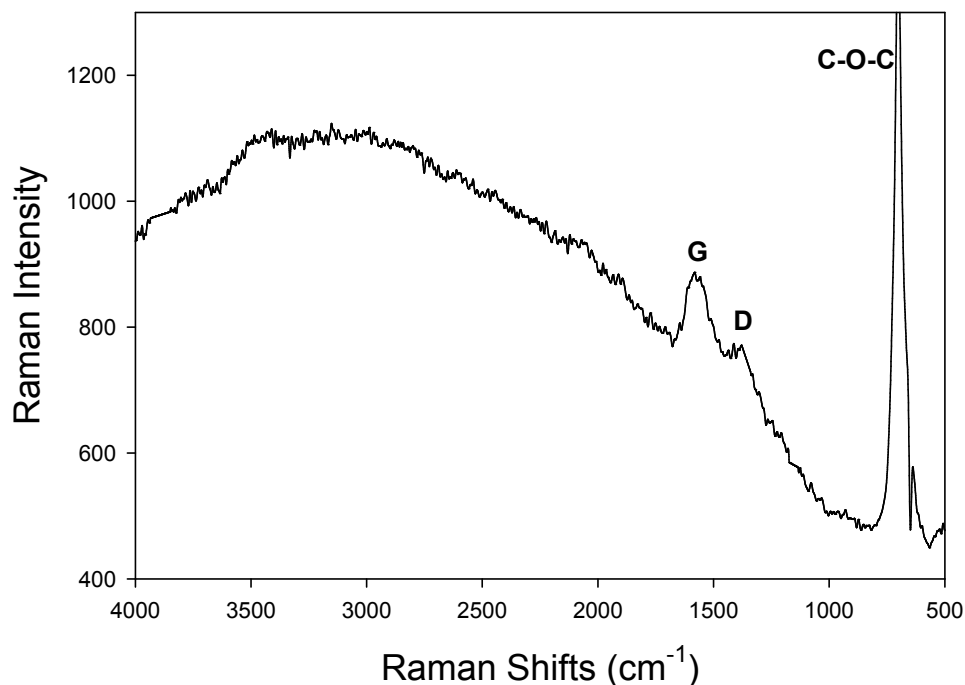


Fig. 3 Raman spectrum for the residue after thermal treatment of condensed CO₂ (G: graphite, D: defect)

The generation of graphite is evidenced from the FT-IR peaks (Fig. 2) that is showing

weakened carbonyl and ether bands and showing other kinds of carbon bonds. The generation of the graphite can be further affirmed with the Raman shift characteristics (Fig. 3). The Raman shift spectrum also shows the defect band and C-O-C group band, and the defect is thought to be caused by C-O-C bonds.

Together with the FT-IR results, the Raman shift spectrum showing the existence of C-O-C bonds supports the generation of the ester which originated from the pairwise combination of the carbonic acids and can be the core part of CO₂ fixation in HCl solution.

The elimination of oxygen from the condensed CO₂ 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. These are thought to be the reasons for the existence of the stable form pure carbon, graphite and diamond. From the condensed form of CO₂, the stable carbon bonds can be derived more readily because of the proximity of the carbon atoms.

4. Conclusions

Some evidence has been obtained to show that CO₂ can exist as a stable condensed form at room temperature and atmospheric pressure. This fact is supported partly because the synthesis was done in a hydrochloric solution without the addition of any other substance, and partly because the product evolves CO₂ and O₂ as it decomposes. The FT-IR results also indicate chemical bonds consistent with a chain molecule. Furthermore, the results obtained supports the conjecture that the oxygen atoms become unstable in the condensed form of CO₂ and can be eliminated when thermally activated. This result confirms that the condensed CO₂ has higher Gibb's free energy that shifts the equilibrium to the decomposition of the molecule and increases the ease of the CO₂ reduction so that O₂ evolution begins from 500°C.

References

1. Iota, V., Yoo, C. S., Cynn, H. 1999, Science, 283, 1510-1513.
2. Kim, J. G. 2011, Korean Patent, 20-2011-0135234, December 15.