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Short Communication

Silicon-like behavior of carbon

J. G. Kim*

Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, San 31,
Hyoja-dong, Pohang, 790-784, South Korea

ABSTRACT

We can expect CO_2 and SiO_2 to take analogical forms in nature as carbon and silicon belong to the same group in the periodic table. The macromolecular forms of SiO_2 in nature are very stable. The purpose of the present trial is to find out whether macromolecular forms of CO_2 that are stable can exist in nature. Some evidence and possibilities for this are presented here. If the synthesis routes resulting in those forms are established, we can expect the technology development for the CO_2 fixation to make a breakthrough.

KEYWORDS: crystal, amorphous, chainlike polymer, CO_2, fixation, glasslike

1. INTRODUCTION

Carbon and silicon belong to the same group in the periodic table and it can be expected that the two elements exhibit similar behavior. But the two elements have different sizes and make different bond strengths when forming chemical bonds. So they cannot behave in exactly the same way. The principal oxide of silicon is silica or silicon dioxide, SiO_2. Unlike carbon, however, silicon cannot make stable double bond with oxygen and so silica cannot take the free SiO_2 molecule form that CO_2 takes and conversely it is known that CO_2 cannot take the stable solid form that silica takes. Silicon oxide can easily take macromolecular forms, crystalline and amorphous, that are represented as quartz and glass respectively, but no stable CO_2 solids have been synthesized yet. Even if quartz-like form and other crystalline forms of carbon dioxide are already identified, those forms are only stable in somewhat extreme conditions and cannot be used as usual materials [1]. There is possibility for CO_2 to take an amorphous polymer form analogous to glass and be stable in atmospheric conditions, but there still is possibility that this form would be different from the usual amorphous silica. Ordinary glass, which is obtained by melting silica with lime and sodium carbonate, is a polymeric silicate with chains and networks of Si-O bonds. In this sense, we can imagine chain-like forms of CO_2 polymer analogous to glass. Because of the differences between carbon and silicon, CO_2 polymer doesn’t necessarily have to be of the same form and character as the glass form of silica, and because amorphous form of CO_2 polymer is not yet identified, its property is not yet known. There is still hope that the amorphous nature can have some stabilizing effect on C-O bond chains that can make it possible for CO_2 to be fixed into amorphous solid. With respect to the efforts for the fixation of CO_2, it is worth doing research on this area. Recently some trials were made to obtain evidence on the existence of amorphous CO_2 solid and it was suggested that the successful result and enhancement of the yield can be had by increasing reaction sites [2, 3]. More convincing discussions of the synthesis of the amorphous CO_2 polymer are given here based on the FT-IR results.

2. MATERIALS AND METHODS

Two kinds of trials were made to probe the possibilities of the CO_2 fixation in the form of

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*kim0691@postech.ac.kr

amorphous solid. The experiment was carried out in acidic aqueous solution with and without the addition of methanol. Pressurization was needed to maintain the encounter of the carbonic acid with hydrogen ion sufficiently resulting in the esterification because CO_2 solubility is very low in acidic solution. This experimental design was based on the acid catalyzed transesterification scheme. The transesterification with the help of hydrogen ion is depicted in Scheme 1.

Reaction medium was HCl 10% solution and after 50 g of solution was filled in the autoclave, CO_2 (purity over 99.99%) was pressurized into the autoclave up to 6 MPa. When methanol was used as a promoter, it was added to the solution to be 1% concentration. After the CO_2 was filled, the reaction mixture was kept 3~4 days undisturbed for the pressure to be equilibrated while the temperature was kept at 20°C during the reaction. The trace of solid residue was obtained after the solution was dried at around 50°C from each trial and the weight of the harvested residue never exceeded 0.01 g without methanol addition and 0.05 g with methanol addition.

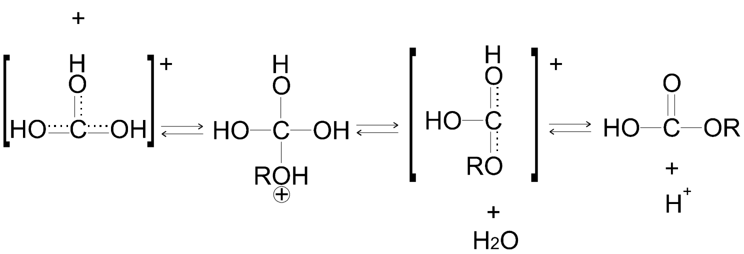
3. RESULTS AND DISCUSSION

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 1405 cm^{-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.

When we compare Fig. 1 and Fig.2, carbonyl group stretching absorption appears at a little higher frequency, and the additional bands arising from terminal methyl group can be observed. The C–H stretching (2973 cm^{-1}) and bending (1263 cm^{-1} and some other bands deemed to be overlapped) vibrations can be observed.

Above results offer some convincing evidences for the existence of the amorphous CO_2 polymer because Fig. 1 and Fig. 2 show good agreement except for the characteristic bands of methyl group showed in Fig. 2, and the agreement can be thought of as showing the fingerprint of CO_2 condensed through esterification. It is suggested here that the characteristic bands shown in Fig. 1 be the property of CO_2 polymer.

The band assigned to carbonyl stretching vibration appears in a way somewhat shifted to lower frequency than usual carbonyl group that appears in aliphatic ketone. An explanation is that it is the effect of neighboring group other than alkyl group. Two effects that can be mentioned in shifting the carbonyl band to lower frequency in this case are resonance effect and hydrogen bonding effect. The resonance effect is caused by the delocalization of the π electrons of the carbonyl group and reduces the double bond character of the C=O bond so that the shift of the absorption band to lower wave numbers can occur. The coplanarity which can be supported by the chain-like conformation of the amorphous CO_2 polymer is thought to be the major cause of the resonance. Another cause for the shift can be considered to be due to the hydrogen bond with the water molecule, which is included because the sample is not completely dried. The hydrogen bonding causes the hindrance for the vibration and



Scheme 1. Transesterification reaction involving CO_2 as reactant.

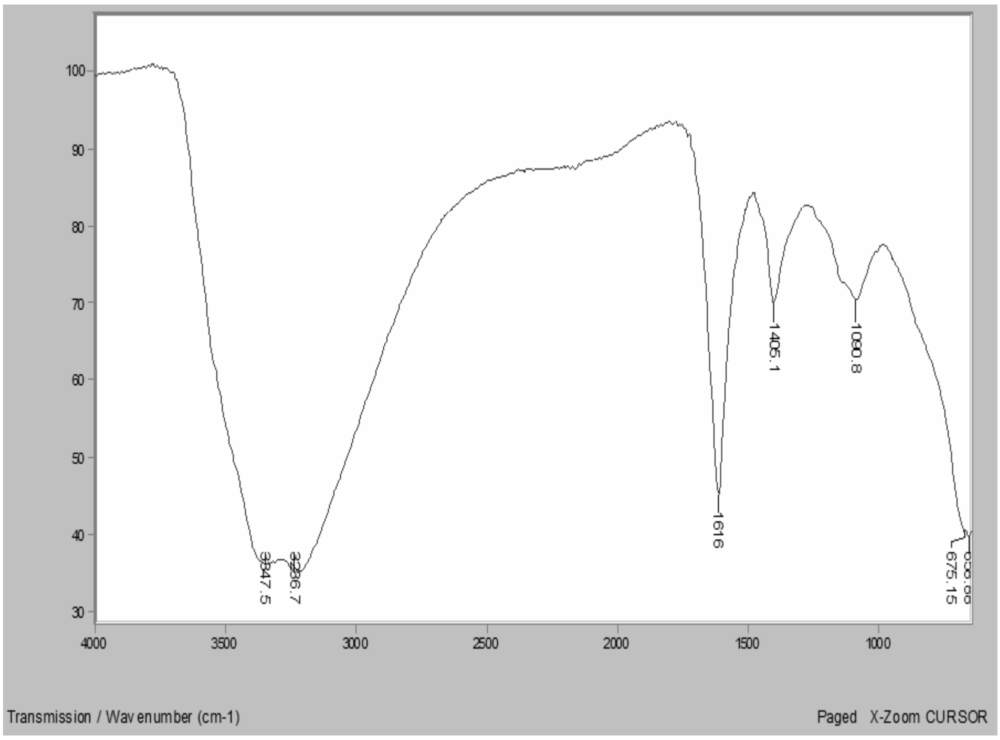


Fig. 1. FT-IR spectrum obtained from condensed CO_2.

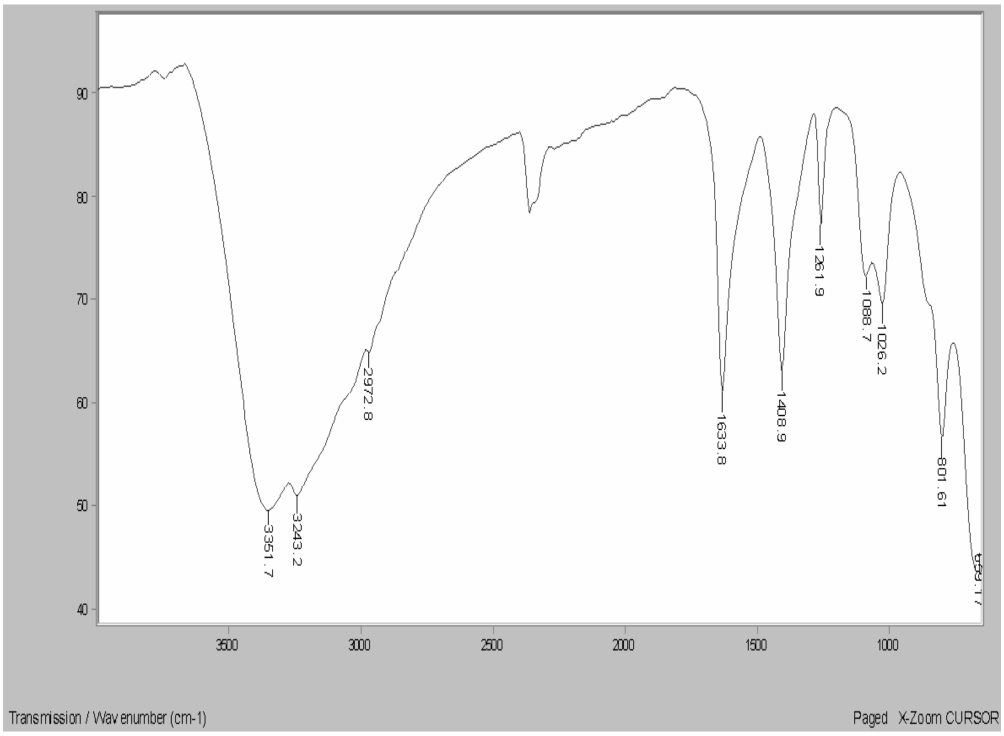


Fig. 2. FT-IR spectrum obtained from condensed CO_2 with the use of methanol.

lowers the frequency of the vibration. In this manner a little higher frequency of the absorption band of the carbonyl group for the case of the methanol addition can be explained in that the hydroxyl band is weaker, indicating the less water molecule existence, and the hydrogen bond has the lesser effect.

The trials to synthesize the amorphous solid of CO_2 have given some evidences of the existence of CO_2 polymer. As a result of the scrutinization of the FT-IR characteristic bands, it can be suggested that the condensation reaction can make CO_2 into chain-like molecules.

4. CONCLUSION

The silicon-like behavior of carbon can be concluded considering former reports and results presented in this communication. Especially the existence of amorphous solid of CO_2 polymer suggested in this report gives another possibility of CO_2 fixation. The difference in size and electronic structure between two atoms can cause the difference of the molecular structure and/or the properties of the synthesized material even if there is analogy between two atoms.

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