Korean J. Chem. Eng., **27**(1), 320-323 (2010)
DOI: 10.1007/s11814-009-0291-7

CO_2 conversion to O_2 by chemical lung in the presence of potassium superoxide in the silicone polymer matrix

Jin Ho Kim*, YoonKook Park*,†, and Soon Kwan Jeong**

*Department of Chemical System Engineering, Hongik University, Yongi-gun 339-701, Korea
**Zero Emission Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea
(*Received 6 April 2009 • accepted 23 May 2009*)

Abstract−This study demonstrates the use of a chemical lung consisting of potassium superoxide and silicone polymer to convert carbon dioxide in air to oxygen. In order to reduce its extremely high reactivity, potassium superoxide was combined at various ratios with polysiloxane. Silicone polymer served as both water repellant and the polymer matrix. In general, the amount of carbon dioxide converted increased as the proportion of potassium superoxide in chemical lung increased. The small surface area of chemical lung and rapid reaction rate illuminated that CO_2 conversion in the presence of chemical lung was predominantly by reaction between CO_2 and potassium superoxide. FTIR spectroscopy revealed that the Si-O bond in potassium superoxide containing chemical lung appeared at 1,050 cm^{-1} and absorbance of chemical lung containing higher amounts of silicone was higher than that of chemical lung containing lower amounts.

Key words: Chemical Lung, Silicone, CO_2, O_2, Potassium Superoxide

INTRODUCTION

Among the many air purifying treatments in general use [1-5], the most widely used method passes polluted air through a column packed with an air purifying agent composed of a strongly alkaline material such as lithium hydroxide, sodium hydroxide, or calcium hydroxide. However, since this column process requires a sophisticated mechanical system and a large space for installation, it is highly desired to develop new materials for use in limited spaces, such as space shuttles and submarines. Although activated carbon and zeolite rapidly adsorb large quantities of toxic compounds, these mesoporous materials are quickly saturated and then begin to slowly release the pollutants back into the air because they rely on reversible adsorption principles. Furthermore, these mesoporous materials only adsorb toxic gases and are not able to generate oxygen, which is one of the requirements for the new materials applicable in limited spaces.

Due to its exceptional oxygen generation properties, potassium superoxide is used in spacecraft life support systems, where it is a vital part of the atmosphere revitalization and control subsystems (ARCS) [6], in self-contained breathing apparatus (SCBA) and closed circuit re-breathers (CCR) in space suits. However, its high reactivity and hygroscopic properties severely limit the use of potassium superoxide as safety considerations are a major issue.

Several attempts have been made to construct a more commercially viable filter by mixing a strongly alkaline air purification material with a polymer resin [2]. Potassium superoxide is a strong candidate for use in such air revitalization materials because it efficiently not only captures CO_2 present in air, but also generates O_2, as depicted in reaction 1 below:

$$2KO_2+CO_2 \rightarrow K_2CO_3+3/2\ O_2 \quad (1)$$

However, owing to its extremely high reactivity, spontaneous ignition is likely to occur when the potassium superoxide is blended with a molten polymer. To overcome this problem, Rho and Jurng [2] suggested the use of silicone as the polymer resin because silicone has much higher gas permeability than any other polymer resin, which allows harmful gases to rapidly and easily pass through the silicone. In addition, since silicone is highly water repellent the superoxide will not readily react with water, even when in direct contact with it; and as silicone is cured at room temperature, a blend with a superoxide offers little danger of spontaneous ignition.

In this study, the chemical lung consisted of potassium superoxide, organopolysiloxane, and a curing agent was used to capture CO_2 and generate O_2. The effect of the amount of potassium superoxide in chemical lung on CO_2 conversion was investigated at room temperature and at various CO_2 initial concentrations. The BET surface area analysis was also carried out to determine texture properties of chemical lung used.

EXPERIMENTAL

1. Materials and Sample Preparation

Potassium superoxide (KO_2, CAS No.: 12030-88-5, Cat. No.: 278904), methyltriacetoxysilane (CAS No.: 4253-34-3372358, Cat. No.: 372358), and dibutyltin dilaurate (CAS No.: 77-58-7291234, Cat. No.: 291234) were purchased from Aldrich. Dimethylpolysiloxane (CAS No.: 9016-00-6) with a viscosity of 1,000 cSt at room temperature, having both terminal ends of the molecular chain blocked by hydroxyl groups, was purchased from Sigma. The SFC grade carbon dioxide supplied by a local gas company (Sebotech Inc., S. Korea) had a reported purity of 99.999%. All chemicals were used as received without further purification. Dimethylpolysiloxane, meth-

†To whom correspondence should be addressed.
E-mail: parky@hongik.ac.kr

Table 1. Chemical lung composition (basis: 5 g sample)

No.	Ratio[a]	Silicon polymer			KO_2
		Dimethyl polysiloxane	Methyltriacetoxy silane	Dibutyl superoxide	
S3K7	3 : 7	1.366	0.143	0.002	3.5
S5K5	5 : 5	2.273	0.227	0.005	2.5
S7K3	7 : 3	3.182	0.318	0.007	1.5

[a]Mass ratio between silicon polymer and KO_2

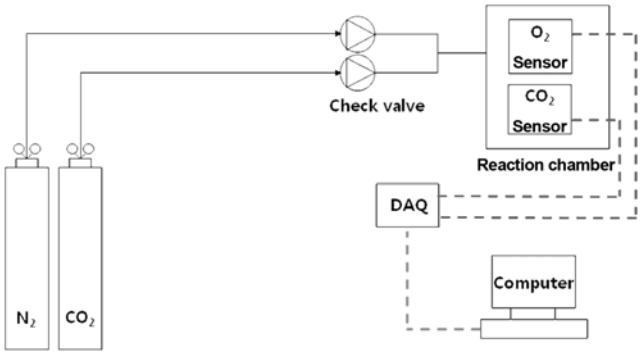

Fig. 1. Experimental setup.

yltriacetoxysilane, dibutyltin dilaurate, and potassium superoxide were then mixed and cured to prepare chemical lungs at different ratios just before each experiment was performed (Table 1). Detailed physical properties of the polysiloxanes can be found in the literature [7].

2. Experimental Setup and Method

A container made of acrylic plate (L×W×H=32 cm×32 cm×42 cm) was used and sealed with a commercially available glue gun to obtain a reliable seal for the container as shown in Fig. 1. A fan was placed inside the container in order to mix the gas in the container efficiently. USB-6008 Multifunction DAQ (12-bit 10-kS (Sample)/s, National Instruments, Seoul, S. Korea) was used for data acquisition (DAQ). CO_2 sensor (Telaire 6004 CO_2 module, GE Sensing, Billerica, MA) and O_2 sensor (AO_3 CiTiceL, City Technology Ltd., Portsmouth, UK) were placed inside the container to monitor the CO_2 and O_2 concentrations over time. Before any experimental data were collected, a blank test in the absence of the chemical lung was carried out to ensure the sensors functioned correctly and were capable of monitoring the changes in the CO_2 and O_2 concentrations. As soon as the chemical lung was synthesized, it was loaded onto the glass plate and placed in the center of the container. The initial CO_2 concentration inside the container was set at 0.2% controlled by using mass flow controllers for CO_2 and nitrogen. CO_2 and N_2 supplied via a 1/8" stainless steel tube were connected to the back of the container. To investigate the effect of CO_2 concentration, initial CO_2 concentrations were varied from 0.2%, 0.3%, and 0.4%. The temperature and moisture in the container were in the ranges of 24±2 ºC and 20±5%, respectively.

3. Analytical Method

Fourier transform infrared (FTIR) spectroscopy (Shimadzu IRPrestige-21) with an attached ATR cell (PIKE, MIRacle™ ATR cell) was used to characterize the chemical lung after the experiment. To determine the texture properties of the chemical lung, a BET surface area analyzer (BELSORP-max, BEL-Japan, Inc.) was used.

RESULTS AND DISCUSSION

1. CO_2 Conversion to O_2 in the Presence of Chemical Lung

Fig. 2 shows that CO_2 is converted into O_2 in the presence of high ratio of potassium superoxide in chemical lung (silicon : KO_2=3 : 7) at 0.2% of CO_2 initial concentration. Almost all CO_2 was converted into O_2 within 3 hrs, while the conversion rate was able to be controlled by varying the amount of potassium superoxide in chemical lung. To investigate the effect of initial CO_2 concentration as well as the amount of superoxide in chemical lung, a series of experiments were carried out, and the results are shown in Figs. 3-5. Before the CO_2 conversion experiments with chemical lung were performed, blank experiments were carried out few times in the absence of chemical lung. In the absence of chemical lung, the concentration of CO_2 remained relatively constant [8] (results are not shown in this study), although a small decrease (<2%) in the CO_2 concentration was observed after 10 hrs. This is probably due to diffusion

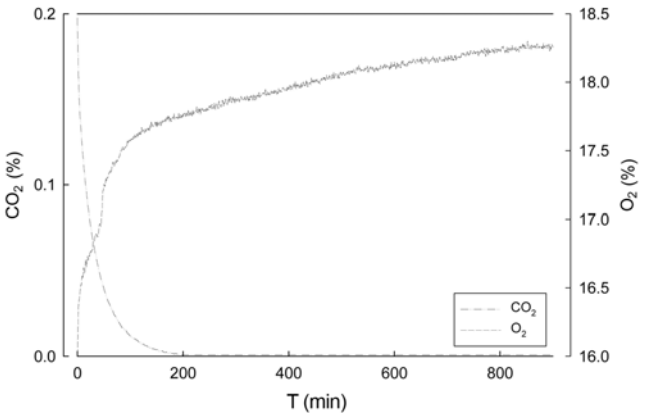

Fig. 2. Conversion of CO_2 to O_2 in the presence of chemical lung composed of silicon : KO_2=3 : 7.

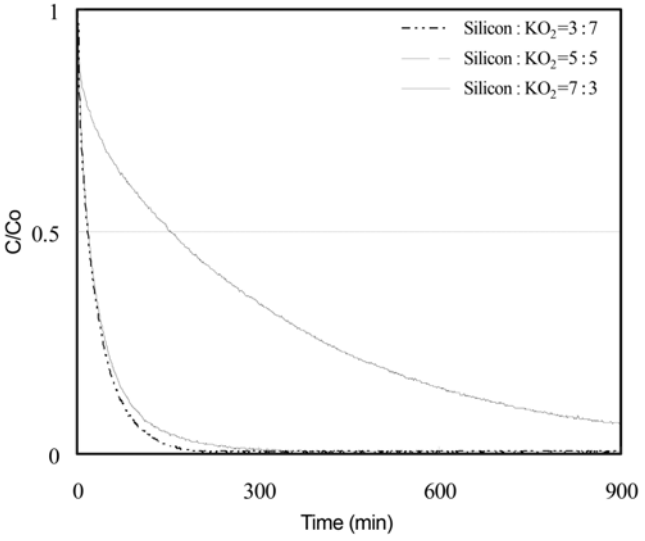

Fig. 3. Conversion of CO_2 in the presence of different amounts of potassium superoxide at 0.2% of CO_2 initial concentration.

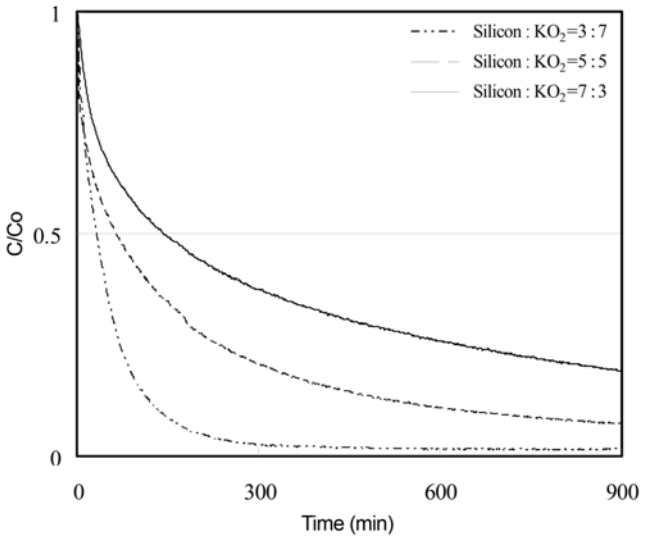

Fig. 4. Conversion of CO_2 in the presence of different amounts of potassium superoxide at 0.3% of CO_2 initial concentration.

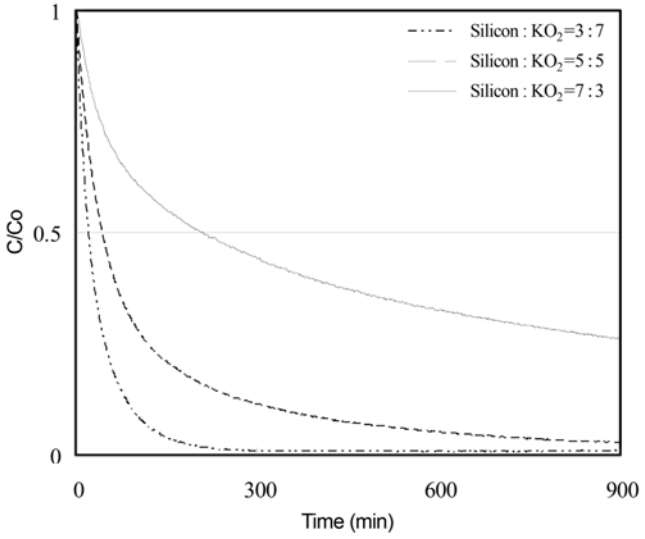

Fig. 5. Conversion of CO_2 in the presence of different amounts of potassium superoxide at 0.4% of CO_2 initial concentration.

of the CO_2 out of the container through the seals.

When a low ratio of potassium superoxide was used (7 : 3, S7K3) at 0.2% CO_2 concentration, more than 90% CO_2 conversion was achieved after 15 hrs as can be seen in Fig. 3. Increasing the potassium superoxide to 50% on a mass basis (5 : 5, S5K5) markedly improved the CO_2 conversion, and for the highest ratio of 70% (3 : 7, S3K7) almost all CO_2 was converted to oxygen. Similar results were obtained with initial CO_2 concentrations of 0.3 and 0.4%, as shown in Figs. 4 and 5, respectively. Based on the stoichiometry in reaction (1), the amount of CO_2 converted increased as the potassium superoxide content increased from 30% to 50% to 70% in chemical lung.

Looking only at the CO_2 conversion rate, clearly the rapid CO_2 conversion to O_2 was obtained for the highest mass ratio of potassium superoxide (S3K7) in chemical lung. However, it is important to note that as the potassium superoxide content increases, safety becomes an issue and great care must be taken to avoid triggering a fire.

2. Estimation of Diffusion Coefficient

Under these experimental conditions, the CO_2 conversion in the presence of chemical lung is expected to primarily be a diffusion controlled process. The propagation of CO_2 into the block geometry (about L×W×H=3 cm×2 cm×1 cm) of chemical lung can be described by the well-known Fick's law of diffusion [9].

$$\frac{c_{A,t}-c_{A,\infty}}{c_{A,0}-c_{A,\infty}} = E_a E_b E_c \tag{2}$$

where $c_{A,t}$, $c_{A,\infty}$, and $c_{A,0}$ are the concentration of CO_2 at time t, that for $t\rightarrow\infty$, and that at t=0, respectively. E_a, E_b, and E_c can be expressed by below.

$$E_a = \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}e^{-\frac{(2m+1)^2\pi^2 Dt}{4a^2}} \tag{3-1}$$

$$E_b = \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}e^{-\frac{(2m+1)^2\pi^2 Dt}{4b^2}} \tag{3-2}$$

$$E_c = \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}e^{-\frac{(2m+1)^2\pi^2 Dt}{4c^2}} \tag{3-3}$$

where D is the diffusion coefficient, a, b, and c are height, width, and length of bar geometry, respectively. The decrease of pressure corresponds to an increase of CO_2 concentration in chemical lung, such that $c_{A,t}$ and $c_{A,0}$ are proportional to $p(t)-p_\infty$ and p_0-p_∞, respectively. This makes it possible to derive the Eq. (4).

$$\frac{p(t)-p_\infty}{p_0-p_\infty} = \frac{\Delta p(t)}{\Delta p_0} = E_a E_b E_c \tag{4}$$

We assume that the first term in Eqs. (3-1) to (3-3) is good enough to approximate the solution of this type of problem, which results in Eq. (5).

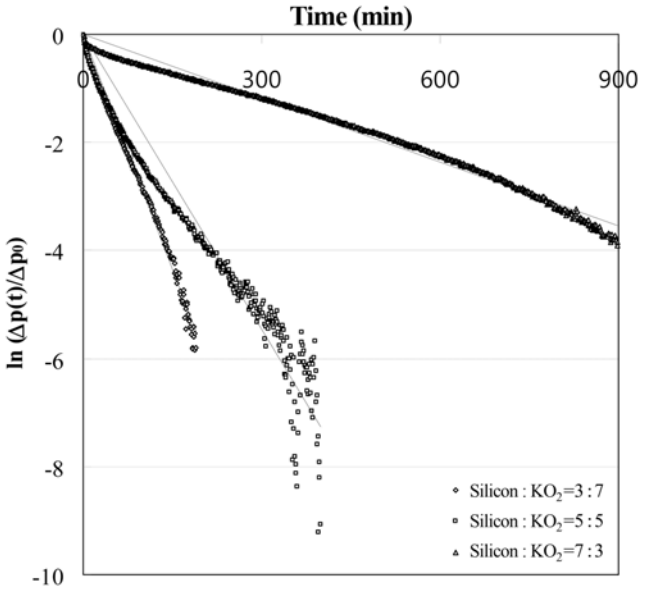

Fig. 6. Determination of diffusion coefficient (D) using Eq. (5) at 0.2% of CO_2 concentration.

Table 2. The diffusion coefficient, D ($10^3 \times cm^2/s$), at 297 K

No.	Initial CO_2 concentration (%)		
	0.2	0.3	0.4
S3K7	0.291	0.276	0.313
S5K5	1.356	0.373	0.469
S7K3	2.161	1.222	1.677

$$\frac{\Delta p(t)}{\Delta p_0} = \frac{8}{\pi^2}\left(e^{-\frac{\pi^2 D}{4a^2}t} + e^{-\frac{\pi^2 D}{4b^2}t} + e^{-\frac{\pi^2 D}{4c^2}t}\right) \quad (5)$$

Eq. (5) allows to plot of $\ln(\Delta p(t)/\Delta p_0)$ against t to obtain diffusion coefficient D. As can be seen in Fig. 6, the plot of $\ln(\Delta p(t)/\Delta p_0)$ vs. t at 0.2% of CO_2 concentration is well described by straight line fit and similar results were obtained at other CO_2 concentrations of 0.3 and 0.4%. In all cases, the value of p_∞ in Eq. (5) was close to 0. Table 2 shows the diffusion coefficients estimated under various conditions. In general, as potassium superoxide mass ratio was increased, the diffusion coefficient was decreased. For example, the diffusion coefficient was 1.677×10^{-3} [cm^2/s] at 30% of potassium superoxide was used in chemical lung, while that was 0.313×10^{-3} [cm^2/s] at 70% potassium superoxide was used in chemical lung at 0.4% initial CO_2 was used.

It is noteworthy that there is a difference between the data obtained experimentally and the simulated data. This difference may be attributed to the diffusivity's direction insensitivity, consideration of the first term only in Eqs. (3-1) to (3.3).

3. Texture Properties of Chemical Lung

The Brunauer-Emmet-Teller (BET) specific surface area (S_{BET}) and the pore volume (V_{pore}) for chemical lung were determined by using a BET surface area analyzer. The specific surface areas (<30 cm^2/g) of chemical lung investigated in this study are extremely small compared to those of most sorbents. The pore volumes are almost nonexistent. This BET result reveals the fact that the CO_2 conversion to O_2 is predominantly carried out by reaction shown in Eq. (1).

4. FTIR Spectroscopy

Fig. 7 shows the FTIR spectra of chemical lung obtained after the reaction by using the ATR cell. The stretching Si-C bond can be observed at 790 cm^{-1}, and its intensity increases as the amount of silicone polymer increases from 30% (S3K7) to 70% (S7K3). The peaks near 1,000 cm^{-1} and 1,250 cm^{-1} correspond to the CH_2 bonds in $SiCH_2$ and Si-CH_3, respectively [10]. The Si-O bond [11] as a repeating unit in organopolysiloxane appears at 1,050 cm^{-1} and the intensity of this peak for samples with a higher silicone content (S7K3) is much higher than for samples containing less silicone (S3K7).

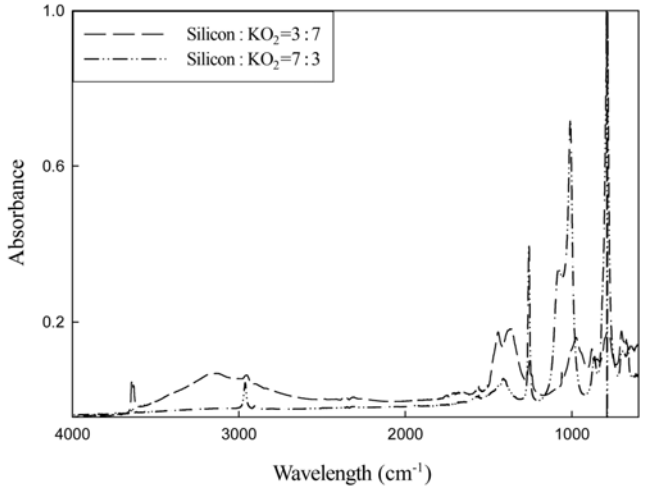

Fig. 7. FTIR spectra of the chemical lung obtained after the conversion reaction.

CONCLUSIONS

A chemical lung consisting of potassium superoxide, methyltriacetoxysilane, dibutyltin dilaurate, and dimethylpolysiloxane provides an excellent result in terms of converting carbon dioxide in air to oxygen. Overall, the greater the proportion of potassium superoxide in the chemical lung, the higher the conversion of carbon dioxide was obtained. The amount of potassium superoxide in chemical lung would be a critical factor to control the CO_2 conversion reaction rate. The BET surface area analysis indicates the CO_2 sorption on the chemical lung is a far less important mechanism than CO_2 conversion reaction.

In addition to potassium superoxide, potassium peroxide, calcium peroxide, lithium peroxide, and sodium superoxide can also be used to convert carbon dioxide contained in air and generate oxygen. The chemical lung composition proposed and tested here may extend the application of potassium superoxide as a capture, enabling it to be used as a safe and effective way to remove acidic gases, such as sulfur oxides and nitrogen oxides, from air.

ACKNOWLEDGMENTS

This work is supported by the 2009 Hongik University Research Fund. We also appreciate the helpful assistance of Dr. Tae H. Jurng at J. C. Technology Inc.

REFERENCES

1. H. Kang, B. Choi, G. Son and D. E. Foster, *JSME Int. J., Ser. B*, **49**, 419 (2006).
2. M. Rho and T. Jurng, WO 085708 (2006).
3. P. Pichat, In *Chemical degradation methods for wastes and pollutants: Environmental and industrial applications*; ed. M. A. Tarr, Marcel Dekker, New York/Basel, 77 (2003).
4. J. Taranto, D. Frochot and P. Pichat, *Ind. Eng. Chem. Res.*, **46**, 7611 (2007).
5. Y. Seo, S. H. Jo, H. J. Ryu, D. H. Bae, C. K. Ryu and C. K. Yi, *Korean J. Chem. Eng.*, **24**, 457 (2007).
6. P. C. Wood, E. V. Ballou, L. A. Spitze and T. Wydeven, NASA Technical Report (SAE PAPER 820873) (1982).
7. *Encyclopedia of polymer science and engineering*, ed. H. F. Mark, Wiley-Interscience, vol. 15, 204 (1989).
8. J. Kim, MS Thesis, Hongik University (2009).
9. R. E. Treybal, *Mass-transfer operations*, 3rd Ed., McGraw-Hill Inc., New York (1981).
10. T. Kaneko, D. Nemoto, A. Horiguchi and N. Miyakawa, *J. Crystal Growth*, **275**, e1097 (2005).
11. F. L. Galeener, *Phys. Rev. B.*, **19**, 4292 (1979).