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Deoligomerization of cyclooligosiloxanes with dimethyl carbonate over solid-base catalysts

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Cyclooligosiloxanes, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane were efficiently deoligomerized with dimethyl carbonate using an alumina-supported potassium fluoride catalyst under a continuous vapor-phase flow condition to form dimethoxydimethylsilane monomer. In the deoligomerization of larger cyclooligosiloxanes, the catalyst was deactivated. The addition of a small amount of methanol suppressed the deactivation. These results strongly suggest a new method for recycling silicone via monomers.

KEY WORDS: silicone; polysiloxane; recycling; dimethyl carbonate; deoligomerization.

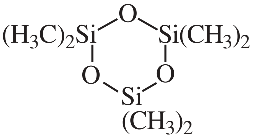
1. Introduction

Silicone polymers are useful as resin, rubber or oil materials due to high chemo-, thermo- and mechano-stability and nontoxicity. Recently, the production of silicone has increased; thus, waste of the polymer has also been on the increase. Considering silicone recycling, one solution is depolymerization of the polymers to form monomers, which can be readily purified and then will give pure polymers again. The backbone of silicone is the silicon–oxygen–silicon linkage; that is, the depolymerization of silicone means cleavage of siloxane bonds.

Many reagents for depolymerizing silicone, such as alcohol [1], hydrogen chloride [2], thionyl chloride [3] and amines [4], have been reported. However, there are the following drawbacks for the depolymerization: the reaction using alcohol is an equilibrium reaction, the chlorides and amines are toxic, and an anticorrosive reactor is required when using the chlorides. Zhurkina *et al.* have reported deoligomerization of octamethylcyclotetrasiloxane with ethyl orthoformate [5]. Dimethyl carbonate also has been reported as a reagent for silicone depolymerization [6]. These reagents are less toxic, and it is not an equilibrium reaction; however, the degree of the deoligomerization was very low using the orthoformate [5], and the disposal of waste of sulfuric acid catalyst is inevitable in both cases.

We have found that the siloxane bond of hexamethyldisiloxane and hexamethylcyclotrisiloxane is efficiently cleaved with dimethyl carbonate (DMC) in the vapor phase over solid-base catalysts to afford methoxytrimethylsilane and dimethoxydimethylsilane respectively [equations (1) and (2)] [7]. These are not equilibrium reactions. Furthermore, the disposal of acid waste is avoidable because of using the solid catalyst.

$$(CH_3)_3SiOSi(CH_3)_3 + (CH_3O)_2CO \longrightarrow (CH_3)_3SiOCH_3 + CO_2 \qquad (1)$$



$$+\ 3\ (CH_3O)_2CO \longrightarrow 3\ (CH_3)_2 \times Si(OCH_3)_2 + 3\ CO_2 \qquad (2)$$

In this work, deoligomerization of larger cyclooligosiloxanes, octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, together with hexamethylcyclo-trisiloxane, was attempted using solid-base catalysts on purpose to recycle silicone, because these cyclosiloxanes are readily formed by thermal degradation of the most general silicone, poly(dimethylsiloxane) [8,9], especially by using potassium hydroxide as a catalyst [9].

2. Experimental

The alumina-supported potassium fluoride catalyst was prepared as follows. Alumina, Neobead GB-26, from Mizusawa Kagaku Co., Ltd was dried in an oven at 130 °C for one night and added to a 0.5 M aqueous solution of potassium fluoride. The mixture was allowed to settle for one night and then dried by a rotary evaporator at 40 °C to give the catalyst. Other supported catalysts were also prepared in the same manner.

The reaction was performed in a fixed-bed flow reactor at atmospheric pressure. The catalyst was placed in a quartz reactor (10 mm i.d.) and pretreated at 400 °C.

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After the pretreatment, the mixture of cyclooligosiloxane and DMC was fed to the reactor heated at 400 °C. The products were identified by GC-MS and quantitatively analyzed by gas chromatography.

The contact time was defined as W/F, the catalyst amount (W: g) divided by the total flow rate (F: mol h^{-1}).

3. Results and discussion

3.1. Deoligomerization of cyclooligosiloxanes

Hexamethylcyclotrisiloxane, which is the simplest cyclooligosiloxane, was used to examine the deoligomerization of cyclooligosiloxanes. In our previous report, alumina-supported potassium salt and hydroxide catalysts were active for the cleavage of the siloxane bond of the simplest linear siloxane, hexamethyldisiloxane [7]. Several alumina-supported alkali metal salts and hydroxides were used as a catalyst for hexamethylcyclotrisiloxane deoligomerization. Table 1 lists dimethoxydimethylsilane yields at 2.5 and 6.5 h of time onstream. All catalysts showed high activities at 2.5 h, especially the potassium fluoride and the cesium hydroxide catalysts, while the cesium hydroxide catalyst was deactivated at 6.5 h. These results indicate that alumina-supported potassium fluoride catalyst is the most active and stable one for cyclooligosiloxane deoligomerization among the catalysts investigated.

Figure 1 shows the effect of the reaction temperature. At 300 °C, the yield decreased with time onstream to 22% at 6.5 h. The yield increased with increasing temperature and was stable at 400 °C. The main product was dimethoxydimethylsilane, and other silanes such as trimethoxymethylsilane were detected at 400 °C. Each yield of these by-products was below 4%. They are most probably formed by disproportionation of dimethoxydimethylsilane or linear siloxanes as reaction intermediates. Below 350 °C, only dimethoxydimethylsilane was formed as a silane monomer. Thus, a temperature higher than 400 °C is not suitable for obtaining dimethoxydimethylsilane solely. The conversions of DMC at 300, 350 and 400 °C were 68, 88 and 100% respectively.

Table 1
Deoligomerization of hexamethylcyclotrisiloxane using various base catalysts

Catalyst	Dimethoxydimethylsilane yield (%)	
	2.5 h	6.5 h
KF/Al_2O_3	52	54
CsF/Al_2O_3	40	42
KOH/Al_2O_3	40	43
$CsOH/Al_2O_3$	55	42

Note: Hexamethylcyclotrisiloxane: 5.7 kPa; DMC: 17.2 kPa (3 equivalents of the siloxane); Reaction temperature: 400 °C; Contact time (W/F): 33 g h mol^{-1}.

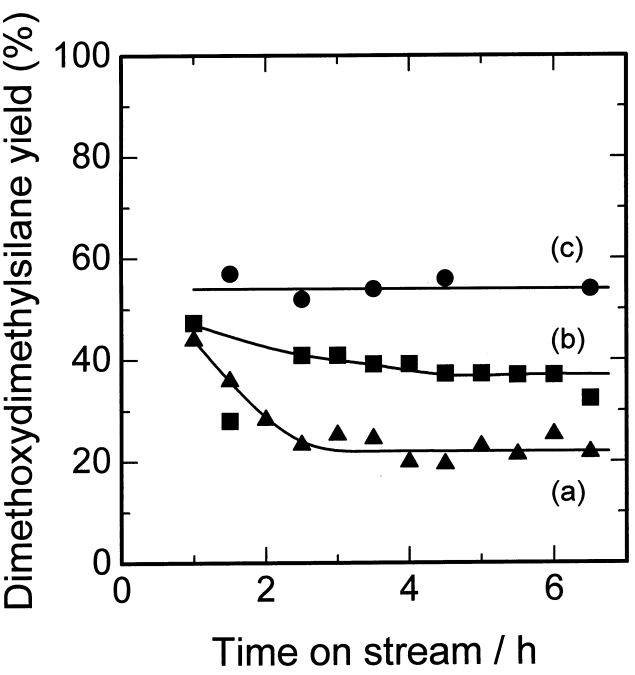


Figure 1. Effect of reaction temperature on the dimethoxydimethylsilane yield in the deoligomerization of hexamethylcyclotrisiloxane. The catalyst was alumina-supported potassium fluoride (500 mg, KF: 5.0 mmol g^{-1}). Hexamethylcyclotrisiloxane: 5.7 kPa, DMC: 17.2 kPa (3 equivalents of the siloxane). Contact time (W/F): 33 g h mol^{-1}. Reaction temperature: (a) 300, (b) 350, and (c) 400 °C.

The deoligomerization of hexamethylcyclotrisiloxane (5.7 kPa) with DMC (34 kPa) was performed at various contact times, 7.3, 9.1 and 33 g h mol^{-1}. At 7.3 and 9.1 g h mol^{-1}, dimethoxydimethylsilane was solely formed with around 92% yield. At higher W/F, 33 g h mol^{-1}, the yield decreased to 71%. Trimethoxymethylsilane and dimethoxytetramethyldisiloxane were formed together with dimethoxydimethylsilane. The percentages of trimethoxymethylsilane and dimethoxytetramethyldisiloxane in the silicon-containing products were 4 and 6% respectively. This indicates the disproportionation of dimethoxydimethylsilane or linear siloxanes at a long contact time. No formation of other silicon-containing products at a lower W/F indicates that only the reaction shown as equation (2) proceeds.

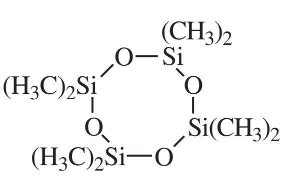
Larger cyclooligosiloxanes, octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane were tested for the deoligomerization with DMC. These cyclooligosiloxanes are mainly formed by poly(dimethylsiloxane) degradation in the presence of potassium hydroxide [9]. The results of deoligomerization of these cyclooligosiloxanes are summarized in table 2. Octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane were also deoligomerized with DMC. The reaction equations of the deoligomerization of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane are equations (3) and (4) respectively. The pressure of DMC was twice the stoichiometric pressure for the deoligomerization. Small amounts of hexamethylcyclotrisiloxane (hexamethyl-

Table 2
Deoligomerization of various cyclosiloxanes with DMC

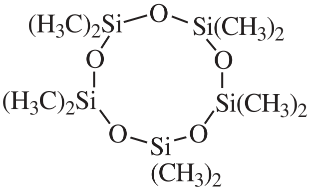
$[Me_2SiO]_n$ n	Dimethoxydimethylsilane yield (%) at 3 h (6 h)	
	Without methanol	With methanol[d]
3[a]	90 (94)	–
4[b]	94 (78)	94 (86)
5[c]	92 (88)	91 (91)

Note: The catalyst was alumina-supported potassium fluoride (500 mg, KF: 5.0 mmol g^{-1}). Cyclosiloxane: [a]5.7, [b]2.9, [c]2.9 kPa; DMC: twice stoichiometric pressure ([a]34, [b]23, [c]29 kPa); [d]Methanol: 1/50th pressure of DMC; Reaction temperature: 400 °C; Contact time W/F): 7.3 g h mol^{-1}

cyclotrisiloxane and octamethylcyclotetrasiloxane in the case of decamethylcyclopentasiloxane deoligomerization) and 1,3-dimethoxytetramethyldisiloxane were formed. The yield of dimethoxydimethylsilane decreased with time onstream in the deoligomerization of larger cyclooligosiloxanes, while the deactivation of the catalyst was not observed in hexamethylcyclotrisiloxane deoligomerization.



$$+ 4\ (CH_3O)_2CO \longrightarrow 4\ (CH_3)_2 \times Si(OCH_3)_2 + 4\ CO_2 \quad (3)$$



$$+ 5\ (CH_3O)_2CO \longrightarrow 5\ (CH_3)_2 \times Si(OCH_3)_2 + 5\ CO_2 \quad (4)$$

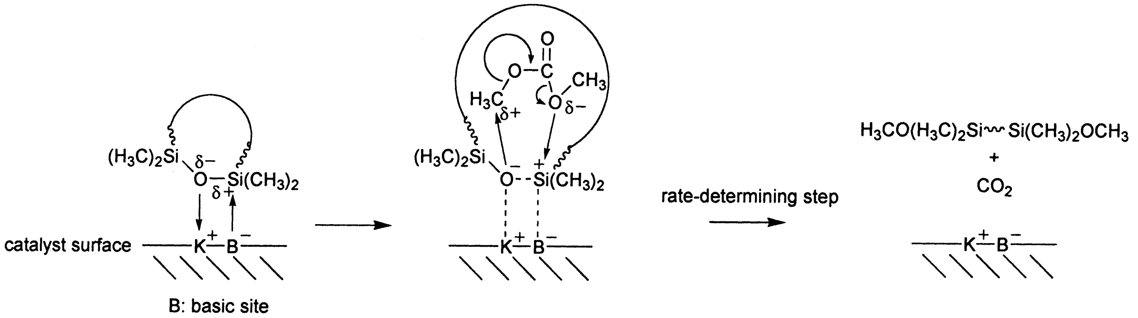
3.2. Effect of methanol addition

As mentioned above, in the deoligomerization of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, the yield of the monomer decreased with time onstream. Methanol at 1/50th pressure of DMC was added to the reaction feed. The results are listed in table 2. In cases of both octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, the yield of dimethoxydimethylsilane at 3 h in the presence of methanol was almost the same as that in the absence of methanol. At 6 h, nonuse of methanol resulted in a decrease in the yield, while the addition of methanol resulted in a high yield. These results indicate that methanol addition inhibits the deactivation of the catalyst. After the reaction without methanol, the catalyst became black. Addition of methanol plausibly prevents coke formation on the catalyst.

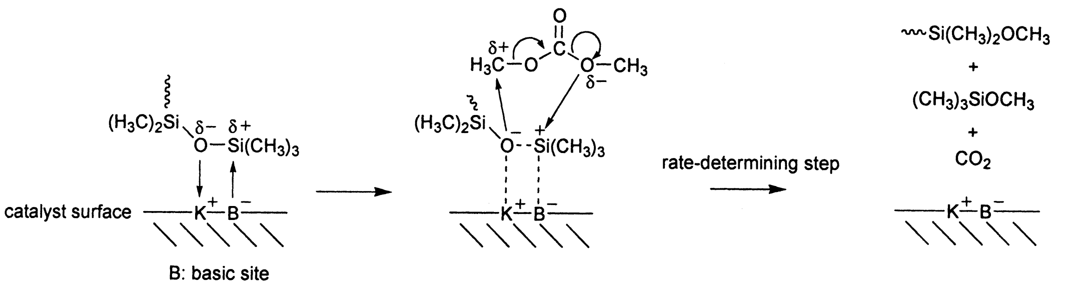
The results of this work suggest that the deoligomerization with DMC is a part of a new recycling system of silicone, since these cyclosiloxanes are readily formed by thermal degradation of the silicone [8,9].

3.3. Reaction mechanism

The following reaction mechanism of the ring opening of methylcyclooligosiloxane with DMC in the absence of methanol was speculated (scheme 1). Methylcyclooligosiloxane is activated on alumina-supported potassium fluoride. The siloxane bond of methylcyclooligosiloxane cleaved partially on the catalyst reacts with DMC to form methoxy-terminated linear siloxane and carbon dioxide. This linear siloxane formed reacts with DMC in accordance with the mechanism (scheme 2) similar to the ring-opening mechanism of cyclooligosiloxane with



Scheme 1. Speculated mechanism for the ring-opening reaction of cyclooligosiloxanes with DMC.



Scheme 2. Speculated mechanism for the deoligomerization of linear oligosiloxane intermediates with DMC.

DMC (scheme 1). Finally, cyclooligosiloxane is converted to dimethoxydimethylsilane monomer. The cleavage of the siloxane bond of cyclooligosiloxane or the linear siloxanes is a rate-determining step.

4. Conclusion

Cyclooligosiloxanes can be deoligomerized with DMC into dimethoxydimethylsilane monomer with a high yield above 80% over a solid-base catalyst, alumina-supported potassium fluoride. At a high temperature or at a long contact time, other silane monomers were formed probably by the disproportionation of dimethoxydimethylsilane or siloxane intermediates. The reaction of larger cyclooligosiloxane resulted in decreasing the monomer yield with time onstream. The use of methanol as an additive inhibited the deactivation of the catalyst. These results strongly suggest that silicone can be recycled via the corresponding monomer by using DMC.

Acknowledgment

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