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Deoligomerization of siloxanes with dimethyl carbonate over solid-base catalysts

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Hexamethyldisiloxane and hexamethylcyclotrisiloxane were almost completely deoligomerized with dimethyl carbonate over alumina-supported potassium fluoride catalyst to form methoxytrimethylsilane (85% yield) and dimethoxydimethylsilane (94% yield), respectively, and moreover the addition of a small amount of methanol to the hexamethyldisiloxane deoligomerization reaction enhanced the methoxytrimethylsilane yield to 98%.

Silicones are widely used as resins, rubbers or oils in various areas, because of their high thermal and mechanical stability and their highly insulating, chemically-inactive and non-toxic nature. The main structures in silicones are siloxane linkages. To decompose silicone materials for recycling, it is necessary to cleave siloxane bonds in the polymer backbone to convert silicones into monomers.

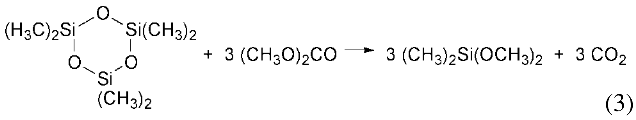
Some methods for cleaving a siloxane bond have been reported. Alcohols are one of the most common reagents,[1] however, water formed as a by-product has to be removed from the reaction system to shift the equilibrium. Hydrogen chloride[2] and thionyl chloride[3] can depolymerize siloxanes. The drawback of these reactions is the requirement of an anticorrosive reactor for chlorine. Amines have been also reported as depolymerization reagents,[4] but their toxicity is unfavorable for recycling. It is desirable to find a new non-halide and non-toxic reagent which does not lead to water formation. Zhurkina *et al.* have found that ethyl orthoformate, a non-halide reagent, can cleave silicon–oxygen bonds in octamethylcyclotetrasiloxane[5] without formation of water using a strong acid catalyst such as sulfuric acid. However, the degree of deoligomerization was low, and a procedure for disposal of waste acid is inevitable.

We have found that silica gel can be decomposed by reaction with dimethyl carbonate using an alkali metal hydroxide or salt as a catalyst to form tetramethoxysilane [eqn. (1)].[6] The significance of this reaction is that silicon–oxygen linkages can be broken by attack of dimethyl carbonate.

$$\mathrm{SiO_2 + 2\,(CH_3O)_2CO \longrightarrow Si(OCH_3)_4 + 2\,CO_2} \qquad (1)$$

Here, we report that dimethyl carbonate can more efficiently deoligomerize siloxanes over solid-base catalysts to form the corresponding methoxysilanes as monomers in high yields. Dimethyl carbonate is a non-halide reagent with a very low toxicity. In this work, hexamethyldisiloxane and hexamethylcyclotrisiloxane were tested for deoligomerization as the shortest linear siloxane and cyclosiloxane, respectively [eqns. (2) and (3)].

$$\mathrm{(CH_3)_3SiOSi(CH_3)_3 + (CH_3O)_2CO \longrightarrow (CH_3)_3Si(OCH_3) + CO_2} \qquad (2)$$



(3)

The reaction was performed in a fixed-bed flow reactor at atmospheric pressure. The catalyst was placed in the quartz reactor (10 mm i.d.) and pretreated at an optimum temperature for each catalyst. After the pretreatment, the mixture of siloxane and dimethyl carbonate was fed into a reactor heated at 400 °C. The effluent gas was identified by GC–MS and quantitatively analyzed by gas chromatography.

The yields of methoxytrimethylsilane as a monomer in the deoligomerization of hexamethyldisiloxane (2.14 kPa) with dimethyl carbonate (6.75 kPa: 3.15 equivalents of the siloxane) are summarized in Table 1. Alumina-supported potassium fluoride, hydroxide and nitrate were active for the deoligomerization. Methoxytrimethylsilane is the sole silicon-containing product, carbon dioxide being formed as a by-product. The hexamethyldisiloxane conversion was equal to the methoxytrimethylsilane yield. These results indicate that hexamethyldisiloxane is converted only to methoxytrimethylsilane [eqn. (2)]. Using the fluoride catalyst, the yield gradually increased with time on stream, while deactivation was observed with the hydroxide or nitrate catalyst. Over other base catalysts, magnesium oxide and calcium oxide, the reaction did not proceed. A solid acid catalyst, HY zeolite, also did not show any activity. For the deoligomerization of the siloxane, a strong base catalyst is necessary, and alumina-supported potassium fluoride was found to be the best catalyst.

The addition of a small amount of methanol to the feed of dimethyl carbonate and hexamethyldisiloxane enhanced the yield of methoxytrimethylsilane to almost 100%. When the reaction of hexamethyldisiloxane (1.75 kPa) with dimethyl carbonate (5.52 kPa: 3.15 equivalents of the siloxane) at 400 °C at 7.4 g h mol^{-1} of contact time was carried out without methanol, the yield of methoxytrimethylsilane was 84%. Adding 0.175 kPa of methanol (one-hundredth the amount of dimethyl carbonate) resulted in a yield of 98%. Almost all methanol remained in the effluent gas, indicating that methanol plays a role as catalyst.

The deoligomerization of hexamethylcyclotrisiloxane with dimethyl carbonate was also carried out. Using an alumina-supported potassium fluoride catalyst at 400 °C at 7.3 g h mol^{-1} contact time, hexamethylcyclotrisiloxane (5.73 kPa) reacted

Table 1 Deoligomerization of hexamethyldisiloxane over various solid catalysts

	Methoxytrimethylsilane yield (%)	
Catalyst	2 h[a]	5 h[a]
KF/Al_2O_3	79	85
KOH/Al_2O_3	83	76
KNO_3/Al_2O_3	76	63
MgO	0	0
CaO	0	0
HY zeolite	0	0

[a] Time on stream. KF/Al_2O_3 was pretreated at 400 °C for 1 h in a helium stream. KOH/Al_2O_3, KNO_3/Al_2O_3 and HY zeolite were pretreated at 500 °C for 1 h in a helium stream. MgO and CaO were prepared from $Mg(OH)_2$ and $Ca(OH)_2$ by heating at 450 and 500 °C, respectively, for 3 h in a helium stream. Catalyst amount: 500 mg (KF, KOH and KNO_3: 5 mmol g^{-1}). Hexamethyldisiloxane: 2.14 kPa, dimethyl carbonate: 6.75 kPa (3.15 equivalents of the siloxane). Reaction temperature: 400 °C. Contact time (*W*/*F*): 9.0 g h mol^{-1}.

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with dimethyl carbonate (34.4 kPa: 6 equivalents of the cyclosiloxane) to give dimethoxydimethylsilane in 94% yield. No formation of other silicon-containing products was observed. This indicates that the reaction proceeds according to eqn. (3).

In conclusion, dimethyl carbonate can deoligomerize siloxanes into the monomers over a solid-base catalyst. This strongly suggests that silicones can be recycled *via* a corresponding monomer with using dimethyl carbonate.

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