

Polymerization of tetramethylcyclotetra-siloxane monomer by ion-exchanged montmorillonite catalysts

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ABSTRACT: Montmorillonites ion-exchanged with Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Ni^{2+} and acidic clay were used as catalysts for the polymerization of a cyclic siloxane monomer, 2,4,6,8-tetramethylcyclotetrasiloxane. Montmorillonites with Ni^{2+} and Mg^{2+} in the interlayer, and acidic clay exhibit a greater ability for siloxane polymerization in both yield and mean molecular weight of products than those containing Li^+ , Na^+ and K^+ . The difference in catalytic ability of the ion-exchanged montmorillonites is caused by the number of Brønsted acid sites due to the polarization of H_2O . This was confirmed experimentally by FTIR analysis of pyridine-treated samples. Therefore, it may be possible to design a catalyst for controlling siloxane polymerization (i.e. mean molecular weight of product) by changing the number of Brønsted acid sites through exchange of the interlayer cations of montmorillonites.

Phyllosilicates have long been known for their catalytic ability in polymerizing siloxane monomers. For example, acidic clay is utilized as the catalyst to produce polysiloxane oil (Allcock, 1967; Carmichael & Heffel, 1965). In the presence of micas, siloxane monomer cross-links itself and forms polysiloxane rubber (Fukui *et al.*, 1993). Kaolinite also catalyses siloxane polymerization into oil in a similar manner to acidic clay (Fukui *et al.*, 1993).

The polymerization products of siloxane monomer are quite different depending on the phyllosilicate species used as catalyst. Some previous reports paid attention to the interlayer cations of phyllosilicates which may control the synthesis of hydrocarbon compounds (Adams *et al.*, 1982; Pitchumani *et al.*, 1993), but little has been reported concerning siloxane polymerization. To elucidate the role of the exchange cations in phyllosilicates for siloxane polymerization, a systematic study using phyllosilicates with a series of interlayer cations is necessary. Because montmorillonites easily exchange their interlayer

cations compared with other phyllosilicates such as micas and kaolinite, they have been chosen to study the cation effect in the same host (Farmer & Mortland, 1965; Russell, 1965).

In this paper, montmorillonites ion exchanged with some mono- and divalent cations are used as catalysts for siloxane polymerization. The cationic dependence of polymer yield and mean molecular weight of the product may suggest the catalytic mechanism of the ion-exchanged montmorillonites.

EXPERIMENTAL

Materials

The siloxane monomer used was 2,4,6,8-tetramethylcyclotetra-siloxane (hereafter referred to as TMCTS) with low boiling point (409 K). Due to the low vapour pressure of TMCTS, the polymerization was carried out using a chemical vapour deposition (CVD) method (Fukui *et al.*, 1992).

The TMCTS was >99% pure (Shin-Etsu Chemical Co. Ltd.). The montmorillonite used was

natural bentonite from the Tsukinuno mine, Yamagata Pref., Japan (Kunipia F, $\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$, Kunimine Kogyo Co. Ltd.). The reagents used were all analytical grade (Junsei Kagaku Co. Ltd.).

Aqueous solutions (1 M) of each chloride salt were prepared. One gram of montmorillonite was dispersed in 1 l of the exchange solution (montmorillonite/solution = 1 g/1000 ml), stirred for 24 h and separated from the solution by centrifugation. This ion exchange process was repeated three times and the ion-exchanged clays were washed with distilled water five times and then freeze dried. Acidic clay was prepared in the same process using 1 M of HCl.

Polymerization of TMCTS

Ion-exchanged montmorillonites were dried at 393 K for 72 h. After drying, all samples were passed through 100 mesh sieve. The montmorillonite catalysts and TMCTS were separately charged into a closed desiccator. The temperature was maintained at 353 K to ensure vapourization of the TMCTS. After 72 h, siloxane polymer was formed around ion-exchanged montmorillonites.

Characterization

Polymerization products (oil) were dissolved in chloroform (0.1 wt% poly-TMCTS solution), and the mean molecular weight of the poly-TMCTS was determined using gel permeation chromatography (Shodex GPC system-11; Showa Denko Co. Ltd.). Analytical conditions were as follows: the sample and reference columns used were Shodex GPC KF-805L and KF-800R, respectively. The injection volume was 50 μl . The eluent was chloroform flowing at 1 $\text{cm}^3 \text{min}^{-1}$ under a pressure of 25 kg cm^{-2} .

Ion-exchanged montmorillonites passed through the 100 mesh sieve were exposed to pyridine vapour in a closed desiccator at 353 K and 0.1 MPa. After 24 h, they were removed from the desiccator, and dried at 423 K and 1×10^{-4} MPa for 150 h to remove the physisorbed pyridine.

Fourier transform infrared (FTIR) spectra of pyridine-treated samples were recorded using samples mixed with KBr powder in the ratio of sample : KBr = 1 : 9 by weight. The mixture was pelletized using a hydraulic press (600 kg cm^{-2}). The discs were analysed in the range 4000–

400 cm^{-1} with a double-beam FTIR analyser (Digilab FTS-65; Nippon Bio-Rad Laboratories).

RESULTS

Polymerization of TMCTS by ion-exchanged montmorillonite catalysts

The TMCTS was successfully polymerized by some of the ion-exchanged montmorillonites. All products were transparent oils of differing viscosity. The yields of the polysiloxane were strongly dependent on the cationic species in the ion-exchanged montmorillonites (Fig. 1). One group, montmorillonites with Li^+ , Na^+ and K^+ , polymerized siloxane a little, but the other group, those containing Ca^{2+} , Mg^{2+} and Ni^{2+} as interlayer cations, and acidic clay produced significant quantities of polysiloxane. The yield of polymerized siloxane oil increased in the order of $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Ni}^{2+} < \text{acidic clay}$ (Fig. 1).

The mean molecular weight of the polysiloxane also depended on the interlayer cations. There was a linear relationship between the amount of polymerized siloxane and the mean molecular weight, suggesting that the ion-exchanged montmorillonites which produced a higher yield of polymer also tended to produce larger molecules (Fig. 2).

FTIR analysis of the acid character of ion-exchanged montmorillonite

After pyridine adsorption, the Ni^{2+} - and Mg^{2+} -montmorillonites and acidic clay showed strong bands at ~ 1600 , 1540, 1490 and 1450 cm^{-1} in their FTIR spectra (Fig. 3). By contrast, Li^+ -, Na^+ - and K^+ -montmorillonites showed little or no absorbance between 1800 and 1300 cm^{-1} . Pyridine-treated Ca^{2+} -montmorillonite exhibited a spectrum intermediate between those of the two groups above (Fig. 3). The FTIR band near 1540 cm^{-1} is diagnostic of pyridine bound to Brønsted acid sites (Connell & Dumesic, 1987; Breen, 1991a). The bands near 1600 cm^{-1} and 1450 cm^{-1} may be attributed to either a residue of physisorbed pyridine or pyridine bound to a Lewis acid site. Physisorbed and hydrogen-bonded pyridine are, however, known to be removed at temperatures > 423 K, and, thus, the bands at 1600 cm^{-1} and 1450 cm^{-1} are attributed to pyridine bound to a Lewis acid site (Breen, 1991b). The band at

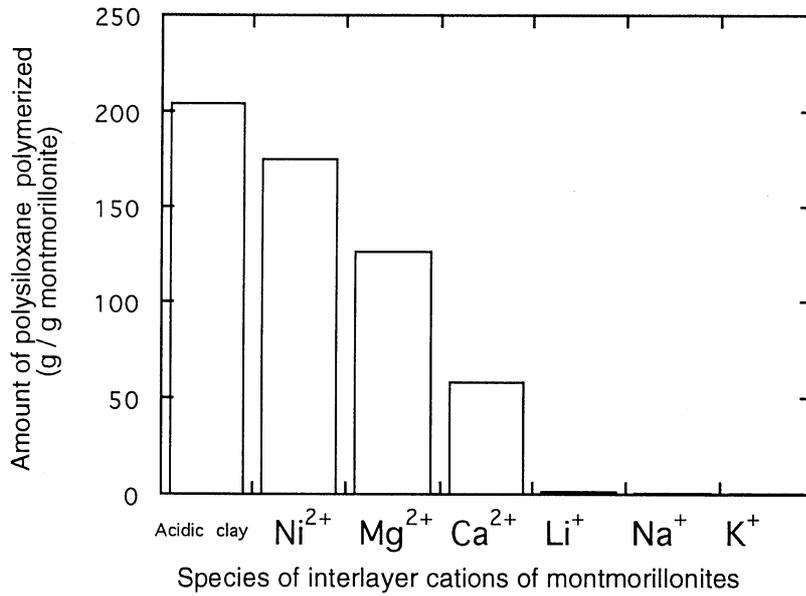


FIG. 1. Amount of TMCTS polymerized by various ion-exchanged montmorillonite.

1450 cm⁻¹ contains contributions from both Lewis- and Brønsted-bound pyridine. The semi-quantitative integrated intensities of the two bands

attributed to Brønsted acid sites exhibited a tentative proportionality to the amounts of polysiloxane (Fig. 4) produced.

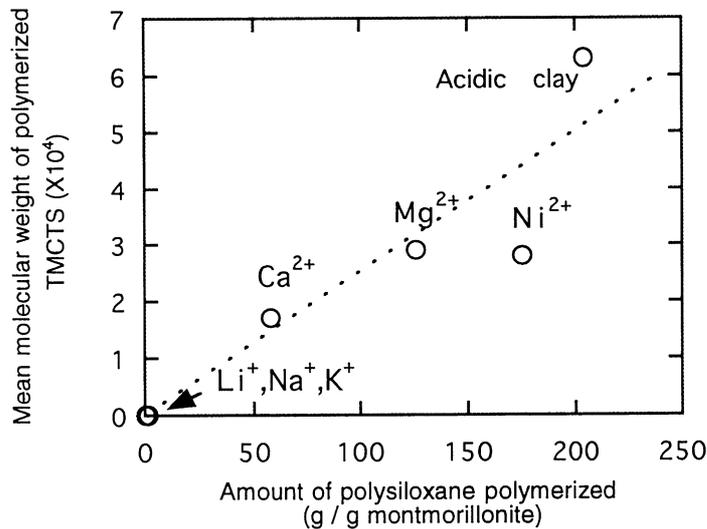


FIG. 2. Relationship between mean molecular weights of polymerized siloxane oil and interlayer cations in the montmorillonite catalysts.

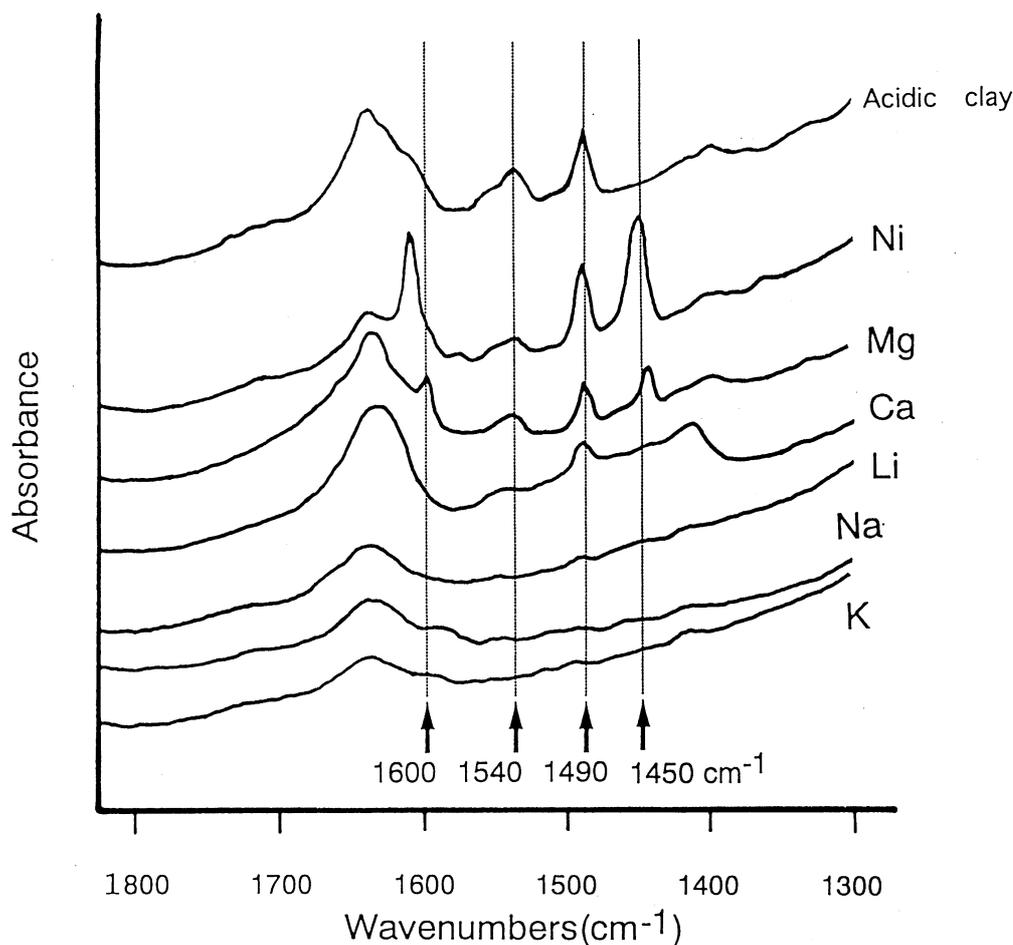


FIG. 3. FTIR spectra of ion-exchanged montmorillonites with absorbed pyridine.

DISCUSSION

TMCTS polymerization mechanism using ion-exchanged montmorillonites as catalysts

In the experiments described, it is obvious that the catalytic capability of montmorillonites for TMCTS polymerization is strongly affected by the nature of the interlayer cations (Figs. 1,2). The amount of polysiloxane produced was approximately proportional to the number of Brønsted acid sites on each ion-exchanged montmorillonite (Fig. 4). These indicate that the TMCTS polymerization is catalysed by the Brønsted acid sites formed on ion-exchanged montmorillonites (Adams *et al.*, 1983). A previous study pointed out that the

dominance of Lewis or Brønsted acidity depends to some extent on the drying temperature used (Breen, 1991b). This is consistent with the present experiment, i.e. the temperatures used for pretreatment (423 K) and siloxane polymerization (353 K) in this study are far lower than 523 K, the temperature at which Lewis sites control the acidity of the clay. The acid sites which dominate siloxane polymerization are probably of the Brønsted type.

The mechanism may be explained as follows (Fig. 5): Brønsted acid sites of ion-exchanged montmorillonites are formed by polarization of H₂O in the interlayer, as discussed previously (Adams *et al.*, 1979; Atkins *et al.*, 1983; Bylina *et al.*, 1980). In the case of acidic clay, leaching of

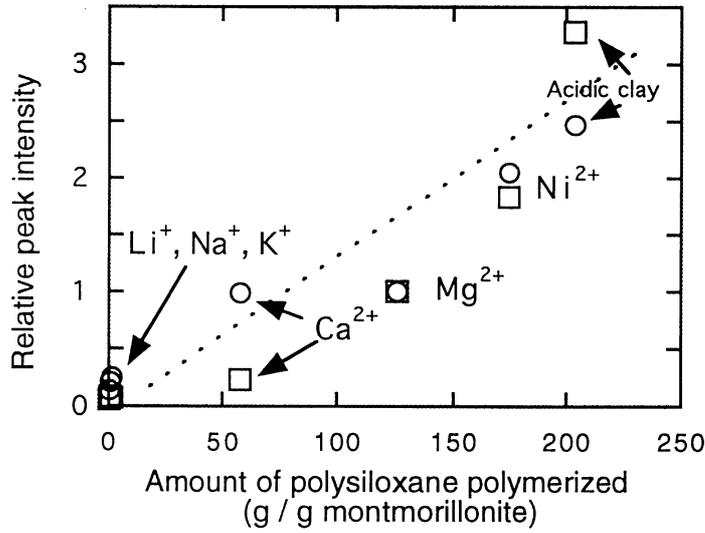


FIG. 4. Relationship between the amount of TMCTS polymerized per 1 g of various ion-exchanged montmorillonite and the relative peak intensity in FTIR spectra for absorbed pyridine. The integrated peak intensity is normalized to that of Mg-montmorillonite as 1. □: integrated peak intensity between 1570 and 1510 cm^{-1} ; ○: integrated peak intensity between 1510 and 1470 cm^{-1} .

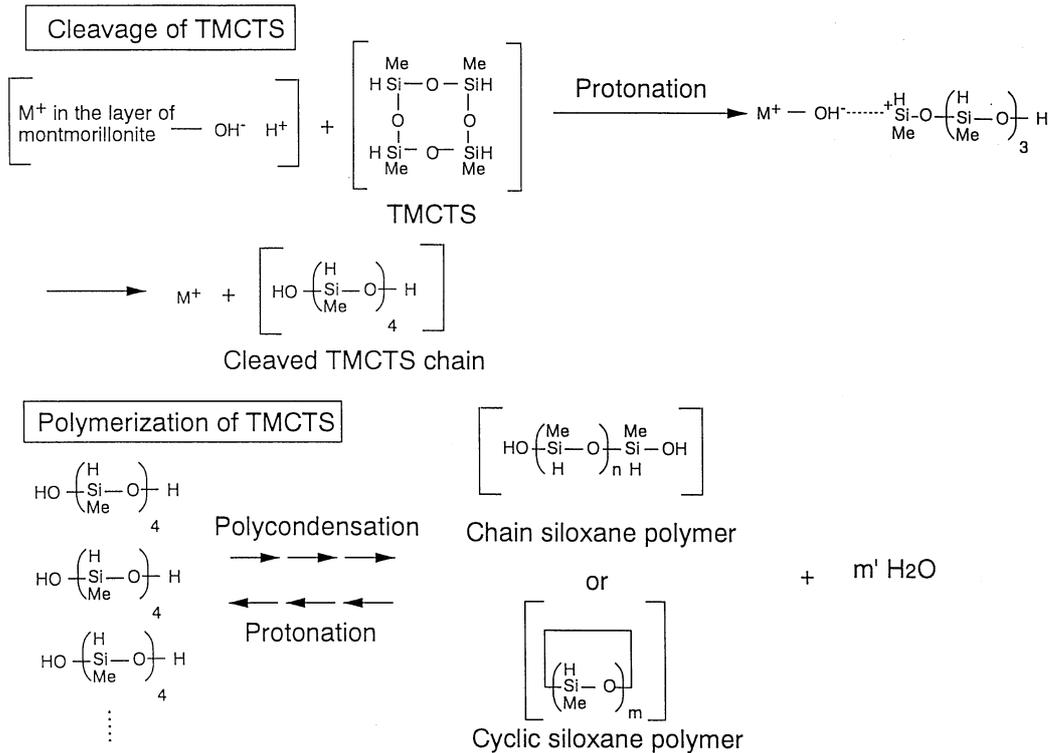


FIG. 5. Schematic view of TMCTS polymerization in the presence of ion-exchanged montmorillonites.

the phyllosilicate structure by HCl has to be considered. Octahedral ions, such as Al^{3+} and Mg^{2+} , are displaced and then occupy the interlayer sites (Brindley & Brown 1984) and form Brønsted acid sites. Acidic clay is thus more active in catalysing siloxane polymerization.

In the presence of H^+ (Brønsted acid), cyclic siloxane monomer is cleaved by protonation (Allcock, 1967). Larger amounts of Brønsted acid site cleave more TMCTS. Cleaved TMCTS is known to have high activity and polymerize by polycondensation due to dehydration of the -OH groups on the cleaved siloxane chains (Allcock, 1967, 1970). This also occurs on the Brønsted acid sites of the ion-exchanged montmorillonites. Freshly cleaved TMCTS chains are added successively to the previously formed chains. Siloxane monomers are eventually converted into polysiloxane oil.

Molecular design of poly-TMCTS using different types of ion-exchanged montmorillonite

Both the amount of polymerized siloxane and its mean molecular weight increase in proportion to the number of Brønsted acid sites. The number of Brønsted acid sites can be controlled by exchanging the interlayer cations in montmorillonite. Therefore, it may be possible to design a catalyst which can produce polysiloxanes of controlled mean molecular weight by use of different types of ion-exchanged montmorillonite. The catalyst to produce polysiloxane of an intermediate molecular weight may require the use of a mixture of montmorillonite.

CONCLUSIONS

Ion-exchanged montmorillonites having larger amounts of Brønsted acid sites have a greater ability to produce active TMCTS chains and to yield polysiloxanes with a greater mean molecular weight. The sites that control the TMCTS polymerization process are Brønsted acid sites arising from the polarization of interlayer H_2O . These acid sites cause cleavage of TMCTS and the cleaved TMCTS chains polymerize into polysiloxane oil. The present study suggests that the mean molecular weight of the oils can be controlled by the use of different types of ion-exchanged montmorillonite.

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