Direct Synthesis of Tetraalkoxysilanes from Silica by Reaction with Dialkyl Carbonates

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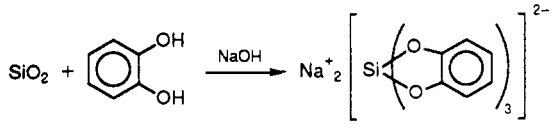
Silica gel reacts with dimethyl carbonate (DMC) to give tetramethoxysilane at 500–600 K in the presence of a catalyst loaded on the silica, the catalyst being an alkali hydroxide or alkali halide. Silica gel loaded with the catalyst was packed in a fixed-bed flow reactor, and DMC was fed in at a constant rate. The complete conversion of silica gel was attained in 30 min at 600 K by using potassium hydroxide as the catalyst. The effects of the reaction variables such as the type of catalyst, amount of catalyst, reaction temperature, and DMC partial pressure were examined. From a change in the DMC partial pressure or reaction temperature during the course of the reaction, the kinetic parameters were obtained. The order of the reaction rate with respect to DMC was 0.68, the activation energy being 89 kJ mol^{-1} for the reaction using potassium hydroxide as the catalyst. Silica gel also reacts with diethyl carbonate to give tetraethoxysilane, sodium chloride being the best catalyst. A complete conversion of silica gel to tetraethoxysilane was attained in 4 h at 700 K. Reaction mechanisms for the gas–solid reactions are proposed.

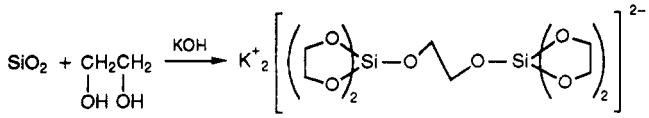
Introduction

Silica is a very stable oxide and therefore the reactions of silica to afford useful chemicals are very limited. In 1931, Rosenheim et al. reported the transformation of silica into hexacoordinated dianionic complexes using catechol as a complexing agent under basic conditions:[1]



Recently, Boudin et al. reported the synthesis of the dianionic complexes in methanol and their reactions with nucleophiles such as Grignard and organolithium reagents. These reactions offer a possible route for the transformation of silica into organosilanes.[2,3]

Recently, Laine et al. reported a method of synthesizing pentacoordinate silicates from silica, ethylene glycol, and base:[4]



We have reported in a recent communication that silica gel reacts with gaseous dimethyl carbonate (DMC) at 500–600 K to yield tetramethoxysilane in the presence of a catalyst, which is supported on the silica:[5]

$$SiO_2 + 2CH_3OC(=O)OCH_3 \rightarrow Si(OCH_3)_4 + 2CO_2 \quad (1)$$

Alkoxysilanes are very important in the production of ceramics by the sol–gel process in which metal alkoxides are polycondensed and the resulting sol is calcined to afford a gel.[6-8] They are also used as starting material for pure silica. Alkoxysilanes are usually prepared from alcohols and silicon chlorides,[9-11] which are, in turn, prepared via metallic silicon from silica. Thus, it is an intriguing proposition to prepare silicon compounds without going through metallic silicon.

The gas–solid reaction we found offers a simple new route for the synthesis of tetramethoxysilane. We have also shown that tetramethoxysilane is obtained from the impure silica, rice hull ash.[12] Besides the reaction with DMC, the reaction of silica gel with diethyl carbonate (DEC) also gives complete conversion of silica gel. In this report, we describe the details of the gas–solid reactions. The effects of the catalyst and the reaction variables on the reaction rates, and the kinetics of the reaction are described. The mechanism of the reaction will also be discussed.

Experimental Section

Silica gel with surface area of 120 m^2 g^{-1} and average pore diameter of 31 nm was obtained from Fuji-Davison Chemical

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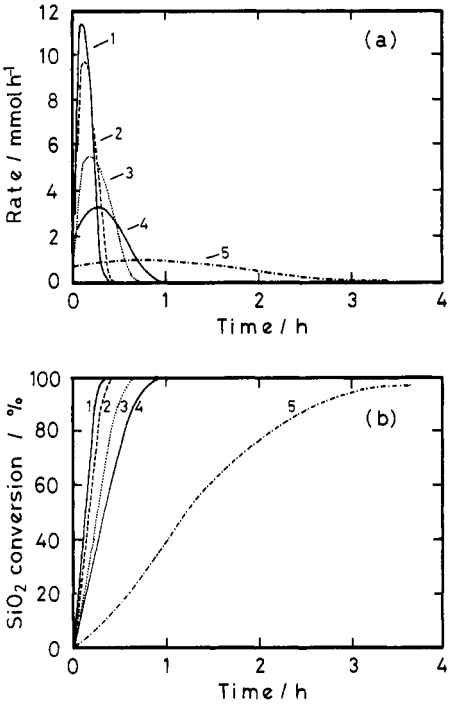


Figure 1. Change in the rate of tetramethoxysilane formation and the conversion of silica gel. (a) Rate of tetramethoxysilane formation. (b) Silica conversion. Catalyst: KOH (5 wt %). Reaction temperature: 600 (1), 575 (2), 550 (3), 525 (4), 500 K (5). DMC: 96 kPa (43 mmol h^{-1}).

Ltd. The size of silica gel particles was 250–545 μm. The silica gel was stirred in an aqueous solution of the catalytic material, e.g., potassium hydroxide. The suspended solution was then heated to dryness and the solid obtained was further dried at 353 K.

The reaction was carried out with a fixed-bed flow reactor placed in a vertical furnace. For the temperature jump experiments, an infrared image furnace (ULVAC RHL-E25N) was used. This furnace enabled us to shift the reaction temperature within 1 min. The silica gel (2.18 mmol) loaded with the catalyst was packed in a quartz reactor (10-mm i.d. and 400-mm length) and kept in a helium stream at the reaction temperature before starting the reaction. By this treatment, practically all adsorbed water was removed from the silica gel.

DMC (or DEC) was fed with a motor-driven syringe into a preheating zone of the reactor. The partial pressure of the alkyl carbonate was controlled by adjusting the flow rate of cofeeding helium. The products were analyzed automatically every 3.5 min by a gas chromatograph equipped with a 2-m-long SE-30 column (338 K) and a thermal conduction detector. As an internal standard, a small amount of heptane was also fed into the reactor.

Results and Discussion

Reaction of Silica Gel with Dimethyl Carbonate. *Time Course of the Reaction.* Figure 1a shows the change in the rate of tetramethoxysilane formation with reaction time at various temperatures. The catalyst was potassium hydroxide, the supported amount being 5 wt % of the silica gel. At each temperature, the rate first increased rapidly and then decreased gradually to zero. Figure 1b shows the conversion of silica as calculated from the rate curve shown in Figure 1a. It is clear that silica gel is completely transformed into tetramethoxysilane. The time required for complete conversion depends on the reaction temperature. At 600 K, complete conversion was attained within 30 min. The rapid increase of the rate at the beginning suggests that the activation of the silica surface occurs at the first stage of the reaction.

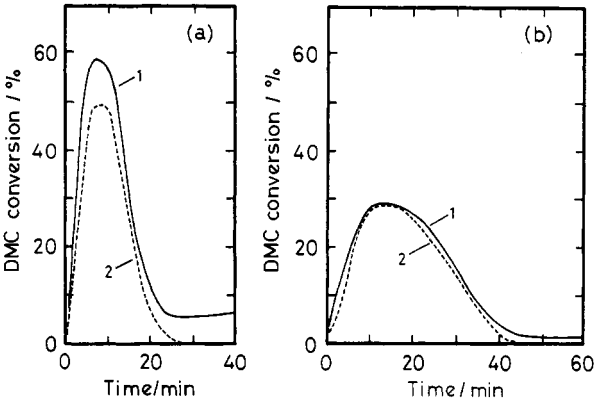


Figure 2. Change in the fraction of DMC consumed and that of DMC converted into tetramethoxysilane with reaction time at (a) 600 K and (b) 550 K. Catalyst: KOH (5 wt %). DMC: 96 kPa (43 mmol h^{-1}). DMC consumption (1) and DMC conversion into tetramethoxysilane (2).

Figure 2 shows the percentage conversion of DMC consumed and the yield of DMC transformed into tetramethoxysilane based on DMC fed into the reactor at 550 and 600 K. At 600 K, the rate of DMC consumption was always greater than that of DMC estimated from the rate of tetramethoxysilane formation according to reaction 1, and the consumption of DMC continued even after the formation of tetramethoxysilane ceased. The analysis of the effluent gas showed that dimethyl ether was produced in addition to tetramethoxysilane and carbon dioxide. Dimethyl ether was produced even in the absence of silica gel. These results indicate that the ether was a product of thermal decomposition of DMC in the gas phase:

$$CH_3OC(=O)OCH_3 \rightarrow CH_3OCH_3 + CO_2$$

The conversion of DMC into tetramethoxysilane was about 50% at the maximum at 600 K. At 550 K, the rate of DMC consumed and that of DMC transformation into tetramethoxysilane were almost equal, indicating that the gas-phase decomposition of DMC was negligible at 550 K. The conversion of DMC transformed into tetramethoxysilane was about 30% at the maximum at 550 K.

Effect of the Catalyst. Alkali hydroxides other than potassium hydroxide were also used as the catalyst. The results at 550 K are shown in Figure 3. Every hydroxide was active and gave complete conversion of the silica gel. As for the rate of the conversion, cesium hydroxide was most active, sodium hydroxide being least active.

Figure 4 shows the effect of the amount of supported potassium hydroxide as the catalyst on the reaction rate. Without a catalyst, no reaction of the silica gel proceeded. The rate increases by increasing the catalyst amount from 1 to 2 wt %. Further increase to 10 wt % did not give an appreciable change in the reaction rate. Increasing the amount of the catalyst to 20 wt % results in a decrease of the rate. The overloading of the catalyst may cause blockage of the silica gel pores. The final conversion of the silica gel was 80% when the loaded amount of the catalyst was 1 wt %, while it was 100% when the catalyst amount was 2 wt % or more. Barium hydroxide was much less effective as the catalyst than the alkali metal hydroxides.

Alkali metal halides were also examined. The results at 575 K are shown in Figure 5. Cesium fluoride is most active, being as active as potassium hydroxide. The activity order for the potassium salts is KOH > KF > KCl.

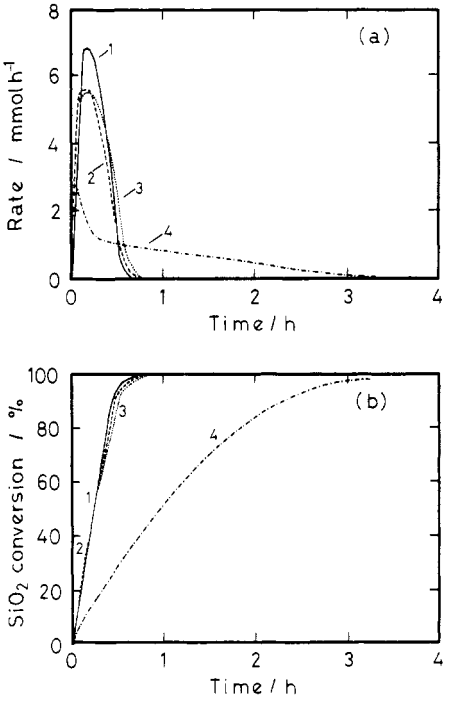


Figure 3. Change in the rate of tetramethoxysilane formation and in the conversion of silica gel with reaction time. (a) Rate of tetramethoxysilane formation. (b) Silica conversion. Catalyst: CsOH (1), RbOH (2), KOH (3), NaOH (4). Catalyst loading: 5 wt %. Reaction temperature: 550 K. DMC: 96 kPa (43 mmol h^{-1}).

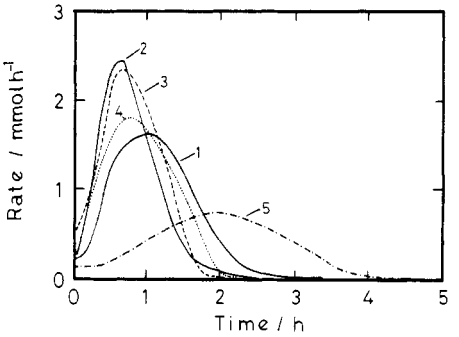


Figure 4. Dependence of the silica conversion on the amount of KOH loaded on silica gel. Reaction temperature: 525 K. DMC: 96 kPa (43 $mmol^{-1}$). KOH: 20 (1), 10 (2), 3 (3), 2 (4), 1 wt % (5).

Even sodium chloride is active for the reaction. The reactions using an alkali halide as the catalyst had a clear induction period except for the case of cesium fluoride. This indicates that the catalysts participate in activating the silica surface.

Sodium carbonate was also active as the catalyst, the complete conversion of silica gel being attained in 210 min at 600 K.

Effect of Heat Treatment of Silica Gel Loaded with a Catalyst. To determine if the interaction occurs between the catalyst and the silica surface, the influence of heat treatment of the silica loaded with a catalyst on the reaction rate was examined. The heat treatment was carried out for 1 h in a helium stream just before feeding DMC.

Figure 6a shows the change in the rate of tetramethoxysilane formation with reaction time for the reaction at 525 K of silica gel loaded with KOH, while Figure 6b shows the change in the rate as a function of the conversion of the silica. As seen in Figure 6, the high-temperature

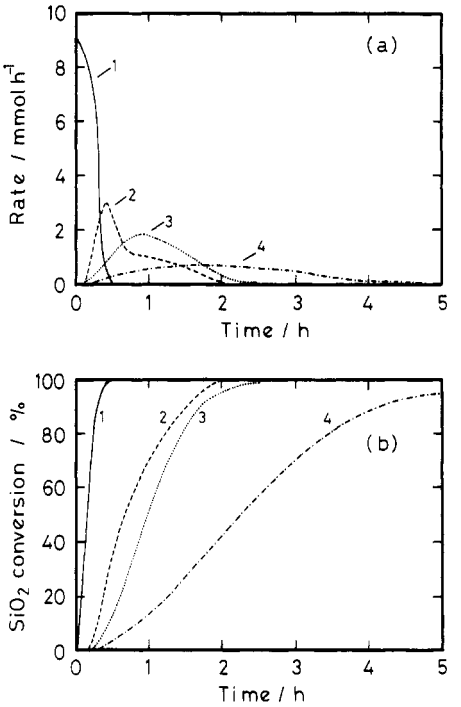


Figure 5. Change in the rate of tetramethoxysilane formation and in the conversion of silica gel with reaction time. (a) Rate of tetramethoxysilane formation. (b) Silica conversion. Catalyst: CsF (1), KF (2), KCl (3), NaCl (4). Catalyst loading: 5 wt %. Reaction temperature: 575 K. DMC: 96 kPa (43 mmol h^{-1}).

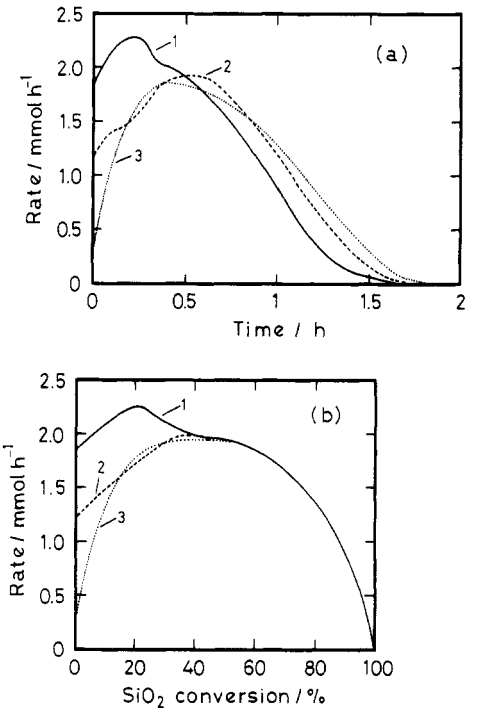


Figure 6. Effect of heat treatment of silica gel loaded with KOH (5 wt %) on the rate of tetramethoxysilane formation. (a) Change in the rate with reaction time. (b) Change in the rate as a function of the conversion of silica gel. Heat treatment was carried out in a helium stream for 1 h at 1025 (1), 775 (2), and 525 K (3). Reaction temperature: 525 K, DMC: 96 kPa (43 mmol h^{-1}).

treatment increases the rate of the reaction especially in the early stage. Thus, higher rates were observed at the start of the reaction by treatment at over 775 K. On the other hand, the rate in the second half of the conversion was not much affected by the heat treatment and the time at the complete conversion of silica was almost independent

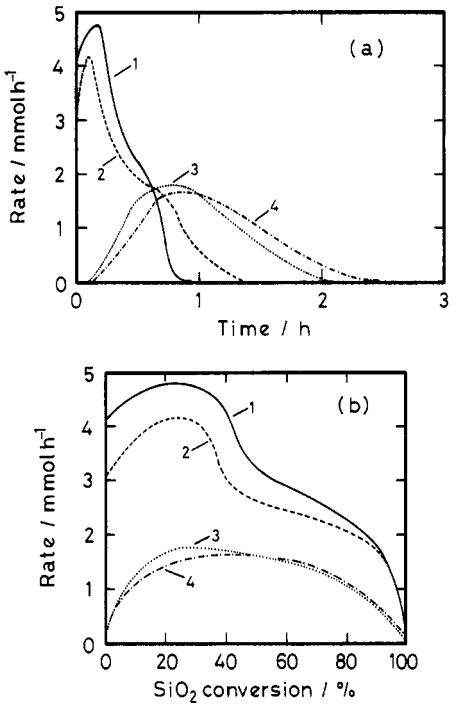


Figure 7. Effect of heat treatment of silica gel loaded with KCl (5 wt %) on the rate of tetramethoxysilane formation. (a) Change in the rate with reaction time. (b) Change in the rate as a function of the conversion of silica gel. Heat treatment was carried out in a helium stream for 1 h at 1025 (1), 900 (2), 775 (3), and 575 K (4). Reaction temperature: 575 K. DMC: 96 kPa (43 mmol h^{-1}).

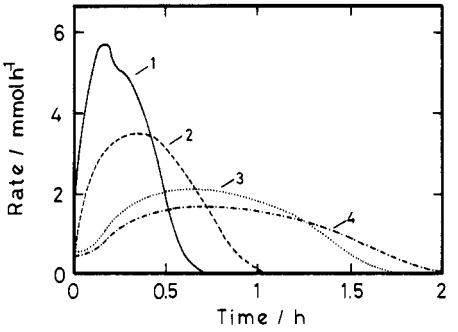


Figure 8. Change in the rate of tetramethoxysilane formation with reaction time at different DMC partial pressures. Catalyst: KOH (5 wt %), Reaction temperature: 550 K. DMC: 96 (1), 48 (2), 21 (3), 15 kPa (4).

of the temperature of the heat treatment.

Figure 7 shows the change in the rate with reaction time and silicon conversion in the case of the reaction at 575 K of the silica loaded with KCl. In this case, heat treatment at 900 and 1025 K eliminated the induction period and the time required for the complete conversion of the silica decreased considerably, though the treatment at 775 K had no appreciable effect on the rate curve. The reaction rate was higher at all conversion levels upon pretreatment at higher temperatures than 775 K.

These results clearly show the interaction between silica and the loaded catalyst is important in activating the silica surface. No new phase was observed by XRD upon the heat treatment of silica gel loaded with KOH.

Kinetics of the Reaction. The effect of the partial pressure of DMC was studied in the reaction of silica gel loaded with KOH. The pressure was changed by adjusting the flow rate of DMC relative to that of helium gas, while keeping the total flow rate constant. As shown in Figure 8, there is a marked effect of the DMC partial pressure, though the final conversion of the silica gel was 100% in every case.

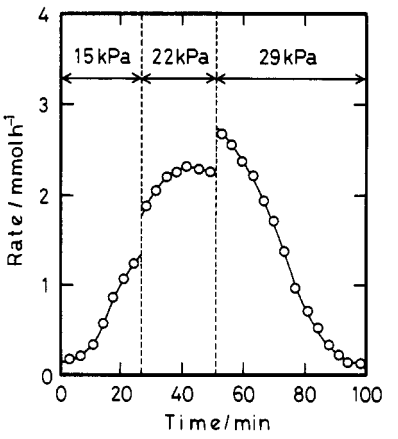


Figure 9. Effect of stepwise change of DMC partial pressure on the rate of tetramethoxysilane formation. Catalyst: KOH (5 wt %). Reaction temperature: 525 K.

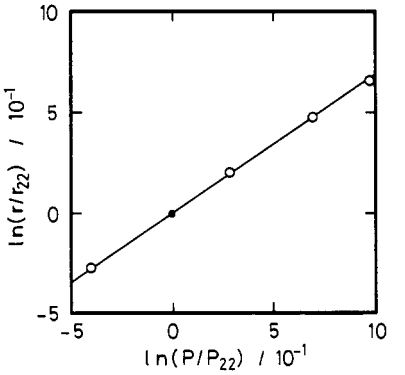


Figure 10. Dependence of the rate of tetramethoxysilane formation on DMC partial pressure. Catalyst: KOH (5 wt %). Reaction temperature: 525 K.

The reaction rate at a specific time depends on two factors, the number of the reactive sites on the surface and the rate per reactive site. Since the surface area changes as the reaction proceeds, the number of the reactive sites changes with time. Therefore, it is difficult to get meaningful information on the reaction mechanism from the overall kinetics. In order to determine the kinetics per reactive site, the number of reactive sites should be fixed. To meet this condition, we used a pressure-jump technique. The change in the reaction rate just before and after the pressure change must be ascribed to the change in the reaction rate per reactive site. The DMC partial pressure was changed stepwise by varying the speed of the syringe travel and the flow rate of helium. The flow rate of DMC and helium shifted to a new steady state within 3 min of the transition. A typical experimental run for silica gel loaded with KOH at 550 K is shown in Figure 9. The pressure was changed from 22 kPa to a new pressure or from a certain pressure to 22 kPa. The rate relative to the rate at 22 kPa was plotted in Figure 10, from which the order of the reaction with respect to DMC is determined to be 0.67. This indicates that DMC molecules interacts with the silica surface before or at the time of the rate-determining step.

In Figure 1 is shown the temperature dependence of the reaction rate for silica gel loaded with KOH. A sharp dependence on the reaction temperature was observed. We also tried to obtain the temperature dependence on

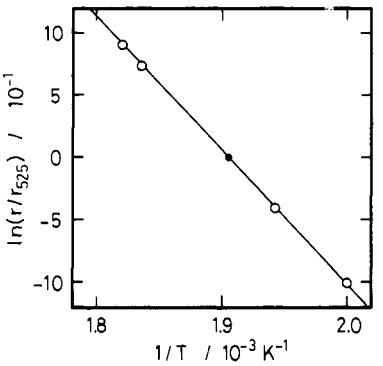


Figure 11. Dependence of the rate of tetramethoxysilane formation on reaction temperature. Catalyst: KOH (5 wt %). DMC partial pressure: 21 kPa (9.5 mmol h^{-1}).

Table I. Kinetic Parameters in Silica Gel–DMC Reaction

catalyst	reaction order for DMC	activation energy/kJ mol^{-1}
NaOH	0.63	93
KOH	0.68	89
CsOH	0.72	86
NaCl	0.79	80
KCl	0.67	73

the reaction rate per reaction site. Thus, the reaction temperature was jumpted from 525 K to another temperature or from a certain temperature to 525 K. The infrared furnace enabled us to shift the reaction temperature within 1 min. The temperature dependence relative to the rate at 525 K is shown in Figure 11, from which the activation energy is determined as 89 kJ mol^{-1}.

The dependence of the reaction rate per reactive site on the DMC pressure and on the reaction temperature was determined for the silica gel loaded with NaOH, KOH, CsOH, NaCl, or KCl. The reaction order with respect to DMC pressure and the activation energy determined are listed in Table I. The reaction order with respect to DMC does not change appreciably with the kind of the catalyst. The activation energy depends slightly on the kind of the catalyst. In every case, the activation energy is far below the bond energy of the Si–O bond (622 kJ mol^{-1}) in SiO_2 (quartz).

Reaction of Silica Gel with Diethyl Carbonate. The reaction of silica gel with DEC was also studied. Figure 12 shows the time courses of the reaction at 700 K with four different catalysts. A higher temperature was necessary for the reaction of silica with DEC compared with its reaction with DMC, reflecting a lower reactivity of DEC. Among the four catalysts, sodium chloride gave the best performance. The complete conversion of silica to tetraethoxysilane was attained in 4 h. The catalysts active for the reaction with DMC, CsF, and KOH, were active in the beginning, but the rate decreased rapidly. This is probably because the use of highly basic catalysts results in the excessive decomposition of DEC on the silica surface at this temperature and the polymerized byproducts block the silica surfaces. Even in the case of NaCl catalyst, DEC decomposes to give diethyl ether and carbon dioxide appreciably.

Figure 13 shows the dependence of the reaction temperature on the rate of the reaction. At 650 K, the reaction proceeds with an induction period and about 5 h was required for the complete conversion of silica. At 675 and 700 K, the reaction rate was much greater. At 675 K, the DEC conversion was about 30% and the selectivity for

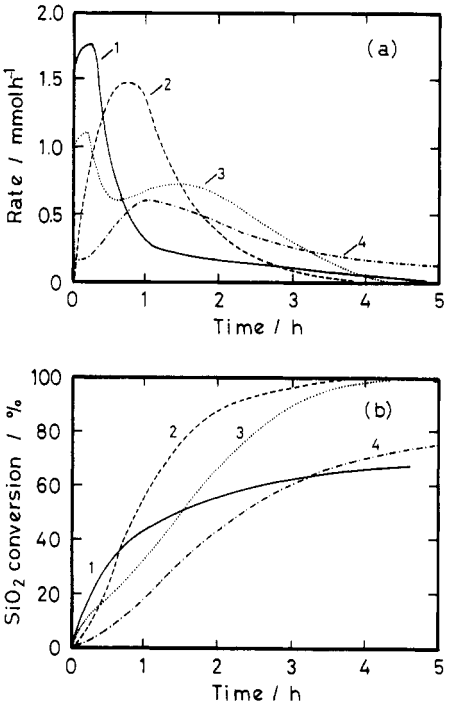


Figure 12. Change in the rate of tetraethoxysilane formation and in the conversion of silica gel. (a) Rate of tetraethoxysilane formation. (b) Silica conversion. Catalyst: CsF (1), NaCl (2), KOH (3), KCl (4). Reaction conditions: 700 K, DEC 94 kPa (41 mmol h^{-1}).

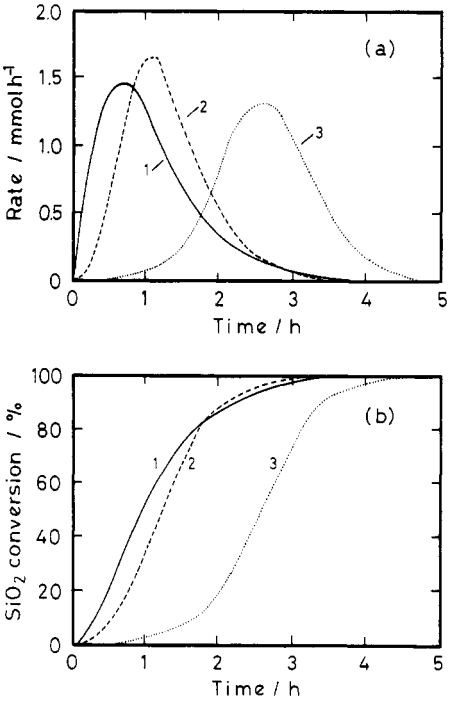
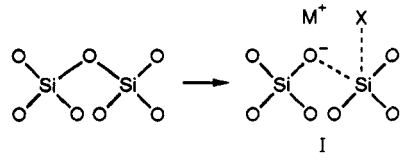


Figure 13. Change in the rate of tetraethoxysilane formation and in the conversion of silica gel. (a) Rate of tetraethoxysilane. (b) Silica conversion. Catalyst: NaCl (5 wt %). Reaction temperature: 700 (1), 675 (2), 650 K (3). DEC: 94 kPa (41 mmol h^{-1}).

tetraethoxysilane was 27% at the time of the maximum DEC yield.

Reaction Mechanism. We propose the following mechanism for the reaction of DMC with silica gel. The surface of silica gel may be activated by two ways. The activation occurs by a cleavage of Si–O–Si bond by its interaction with a catalyst (MX):



(2)

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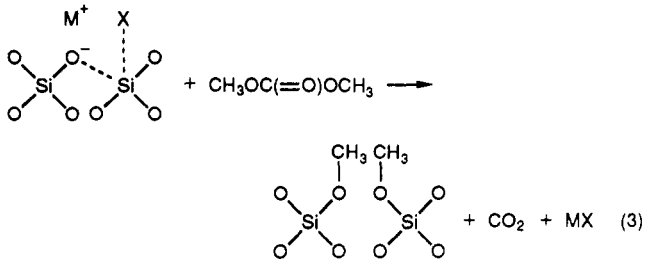
The surface species I may react with DMC to regenerate MX:



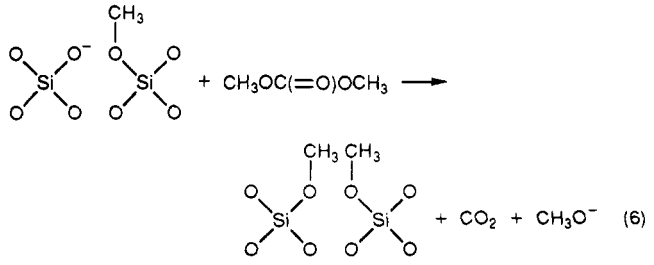
(3)

The activation may also occur through the interaction with DMC. DMC may directly interact with the catalyst to form a reactive species (CH_3O^-), which, in turn, reacts with the silica surface:

(4)

(5)

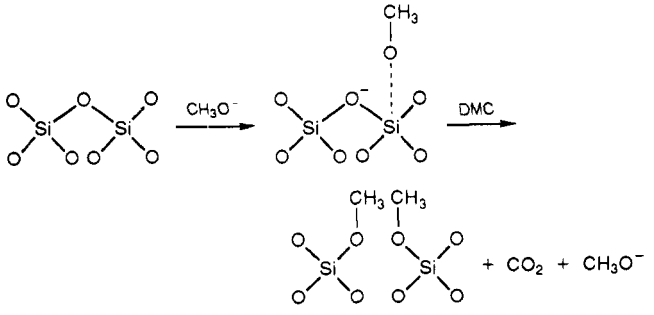
Once a reactive surface site containing SiO^- is formed by reaction 2 or 5, this surface species directly reacts with DMC to afford $SiOCH_3$ and the cleavage of Si–O–Si bond is completed. The presence of $SiOCH_3$ groups on the surface during the reaction was confirmed by infrared spectroscopy:



(6)

Since reaction 6 regenerates CH_3O^-, the cleavage of Si–O–Si bonds can continue by the repetition of reactions 5 and 6.

It is also probable that reactions 5 and 6 simultaneously occur in a concerted manner through a pentacoordinate intermediate:



Heat treatment of silica gel loaded with a catalyst at high temperatures facilitates reaction 1, and this may result in the disappearance of the induction time or the increase in the reaction rate in the beginning of the reaction. Once the several first layers is removed from the silica surface, the surface newly exposed may be somewhat activated and probably more reactive than the original surface. Then, the reaction can proceed simply by the repetition of reactions 5 and 6. This may explain the small dependence of the kinetic parameters on the kind of the catalyst at the later stage.