

Direct Transformation of Silica into Alkoxysilanes by Gas–Solid Reactions

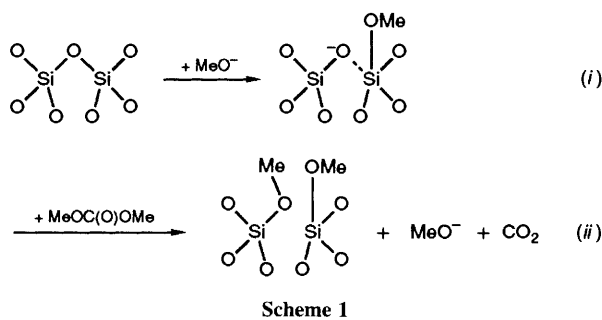
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Silica gel is conveniently and efficiently converted into tetramethoxysilane by treatment with gaseous dimethyl carbonate at 500–600 K in the presence of an alkali hydroxide catalyst supported on the reacting silica.

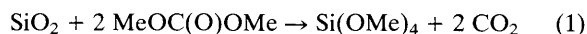
Alkoxysilanes are very important in the production of ceramics by the sol–gel process in which metal alkoxides are polycondensed and the resulting sol is calcined to afford a gel. They are also used as starting materials for pure silica. Alkoxysilanes are usually prepared from alcohols and silicon

chlorides, 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 transformation of silica into hexacoordinated dianionic complexes using catechol as a complexing agent has been known



for a long time.¹ Recently, Boudin *et al.* reported a synthesis of the dianionic complexes in methanol and their reactions with nucleophiles such as Grignard and organolithium reagents.^{2,3} These reactions offer a possible route for the transformation of silica into organosilanes.

Here, we report a simple, new route to alkoxy silanes from silica, see eqn. (1).



A typical experiment was carried out as follows. Silica gel with a particle size of 250–545 μm was stirred in an aqueous solution of a catalytic material and dried at 353 K in an evaporator. The silica (131 mg) loaded with the catalyst was packed in a fixed-bed flow reactor (quartz tubing 10 mm i.d.) and heated to reaction temperature. Dimethyl carbonate was fed with a flow rate of 43 mmol h^{-1} into a preheating zone of the reactor by a motor-driven syringe and the products were analysed automatically every 3.5 min by a gas chromatograph.

Fig. 1(a) 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 increases rapidly and then decreases gradually to zero. Fig. 1(b) shows the cumulative yield of tetramethoxysilane based on silica gel. 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 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, indicating that the ether was a product of thermal decomposition of dimethyl carbonate in the gas phase.

Alkali hydroxides other than potassium hydroxide were also used as the catalyst. In every case, the conversion of silica gel into tetramethoxysilane was complete. As for the rate, hydroxides of rubidium and caesium were as effective as potassium hydroxide. Sodium hydroxide was also useful as the catalyst, but less effective compared with potassium hydroxide. The rate depends on the partial pressure of dimethyl carbonate and also on the supported amount of the catalytic material.

Diethyl carbonate also reacts with silica gel. Thus, a complete conversion of silica, on which 5 wt% of potassium hydroxide was supported, was attained in 270 min at 700 K.

A possible mechanism for the cleavage of Si–O–Si bonds is as follows. The base catalysts (B^-) may act as promoters in the decomposition of dimethyl carbonate to give a reactive intermediate, MeO^- , on the silica surface, eqn. (2). Methoxy anions thus formed may attack and cleave the Si–O–Si bonds of the silica surface. Dimethyl carbonate serves also as a methylating agent. Successive cleavage of Si–O–Si bonds by

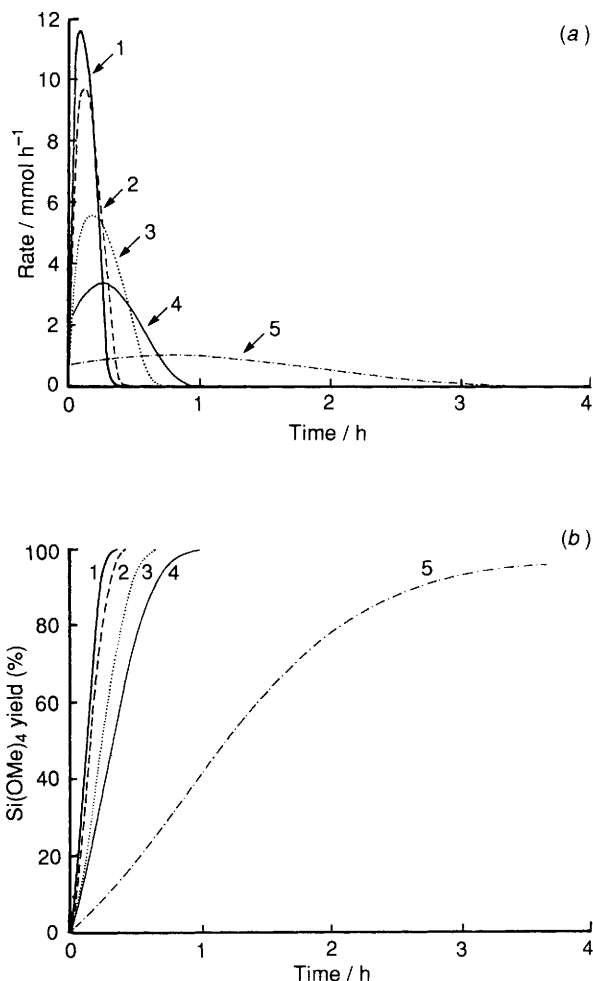


Fig. 1 Changes in the rate of tetramethoxysilane formation and in the cumulative yield of tetramethoxysilane with reaction time. (a) Rate of tetramethoxysilane formation, (b) cumulative yield. Loading amount of potassium hydroxide: 5 wt%. Reaction conditions: Reaction temperature: 600 (1), 575 (2), 550 (3), 525 (4), 500 K (5); dimethyl carbonate: 96 kPa (43 mmol h^{-1}).

the repetition of reactions (i) and (ii) in Scheme 1 leads to the formation of tetramethoxysilane.



Gas–solid reactions of silica gel with alkyl carbonates are a very simple and efficient way to depolymerize silica. The product alkoxydes are easily separable from unchanged silica or impurities in silica. The alkoxydes are also easily separated from the unchanged carbonates and by-products such as ethers and carbon dioxide owing to large differences in their boiling points.

Received, 12th August 1991; Com. 1/04201G

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