Inorganica Chimica Acta, 207 (1993) 259–261

Short Communication

Direct synthesis of tetramethoxysilane from rice hull ash by reaction with dimethyl carbonate

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(Received August 21, 1992; revised January 13, 1993)

Abstract

Rice hull ash (92% SiO_2 purity), when loaded with 5 wt.% of potassium hydroxide, reacts with dimethyl carbonate at 625 K to give almost quantitatively tetramethoxysilane. The ash also reacts with diethyl carbonate to give an 80% yield of tetraethoxysilane at 725 K.

Introduction

The production of chemicals from biomass has attracted increasing attention in recent years. Rice hulls are removed from the grain at a mill and constitute a waste product. Rice hull ash obtained by burning rice hulls is slightly impure silica, which is amorphous and highly reactive [1–4]. Because of its high reactivity, the utilization of silica as raw material for the production of silicon tetrachloride [1, 5], silicon [3, 6] or zeolites [7] has been explored.

We have recently reported that tetraalkoxysilanes are formed by a gas–solid reaction of dialkyl carbonates with silica gel [8]. For example, silica gel reacts quantitatively with dimethyl carbonate to give tetramethoxysilane in the temperature range 500–600 K. The catalysts effective for the reaction are alkali metal hydroxides and alkali metal halides, which are supported on the silica, which is subjected to the reaction.

$$SiO_2 + 2(CH_3O)_2CO \longrightarrow (CH_3O)_4Si + 2CO_2$$

Here, we report the conversion of rice hull ash into tetraalkoxysilanes by its reaction with dialkyl carbonates.

Experimental

Rice hull ash was a kind gift of the National Chemical Laboratory for Industry. It was prepared by calcining rice hull at 723 K for 20 h. The composition of the ash is as follows: SiO_2, 91.7%; K_2O, 4.82%; Na_2O, 0.40%; MgO, 0.32%; CaO, 0.42%, Al_2O_3, 0.66%; others, *c.* 1.7%. The ash was stirred in an aqueous solution of potassium hydroxide and the suspended solution was then heated to dryness under a reduced pressure at 353 K.

Reactions were carried out using a fixed-bed flow-reactor (quartz tubing, 10 mm i.d.). Rice hull ash (147–155 mg) with or without a loaded catalyst was packed in the reactor and heated in a helium stream at the reaction temperature for 1 h. Then, dimethyl carbonate (or diethyl carbonate) was fed with a rate of 43 mmol h^{-1} (41 mmol h^{-1}) at the partial pressure of 96 kPa (95 kPa) together with heptane as an internal standard for gas chromatographic analysis. The effluent gas from the reactor was led to a six-way sampling valve through a stainless steel pipe maintained at 473 K to avoid condensation of the gas. The gas was automatically sampled every 3.5 min and analyzed by a gas chromatograph equipped with a 2 m long SE-30 column operating at 338 K and a thermal conduction detector.

Results and discussion

Figure 1(a) shows the change in the rate of tetramethoxysilane formation with reaction time at various temperatures. The ash was loaded with 5 wt.% of potassium hydroxide. Figure 1(b) shows the cumulative conversion of the SiO_2 component of the ash, which was calculated from the rate–time curves shown in Fig. 1(a). The result of the reaction at 675 K without using a catalyst is also shown in Fig. 1. At every temperature, the rate first increased with reaction time, passed through a maximum and then decreased to zero. At 550 K, SiO_2 conversion was about 75% after 4 h of reaction. As the reaction temperature was raised, not only did the reaction proceed faster, but also the final SiO_2 conversion became higher. At 625 K, SiO_2 conversion reached about 95%, when the reaction ceased at about 1 h. Thus, most of the SiO_2 component in the ash can be extracted as tetramethoxysilane, other metal oxide components being left behind in the reactor.

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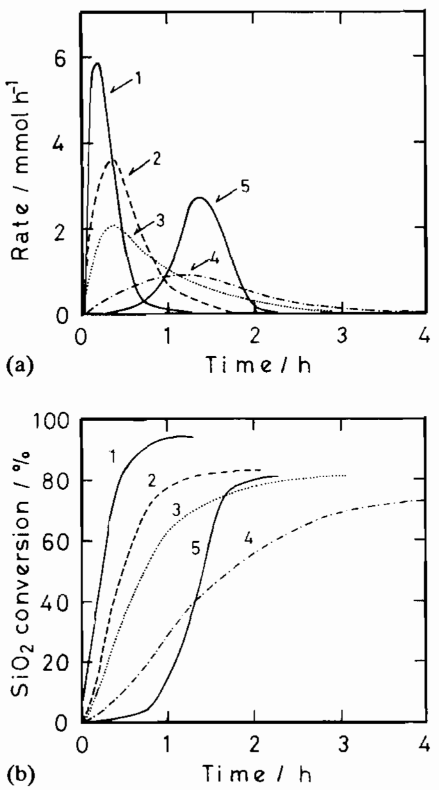

Fig. 1. Reaction of rice hull ash with dimethyl carbonate at various temperatures. (a) Change in the rate of tetramethoxysilane formation with reaction time; (b) change in the cumulative conversion of SiO_2 component with reaction time. Loading amounts of potassium hydroxide = 5 wt.% (1–4) and 0 wt.% (5). Reaction conditions: reaction temperature = 625 (1), 600 (2), 575 (3), 550 (4), 675 (5) K; dimethyl carbonate = 96 kPa (43 mmol h^{-1}).

Besides the reaction with silica, dimethyl carbonate was consumed by decomposition into dimethyl ether and carbon dioxide, the extent being 4 and 25% at 600 and 625 K, respectively.

The reaction proceeded even without a catalyst, though a higher reaction temperature was required. The reaction started with an induction period, and the degree of SiO_2 conversion reached about 80% at 675 K. In the case of the reaction of silica gel with dimethyl carbonate, no reaction takes place without a catalyst. In the case of rice hull ash, the alkaline components such as K_2O and Na_2O in the ash plausibly serve as the catalyst for the reaction. Addition of catalyst ensures both the higher rate of the reaction and the higher final conversion of the SiO_2 component.

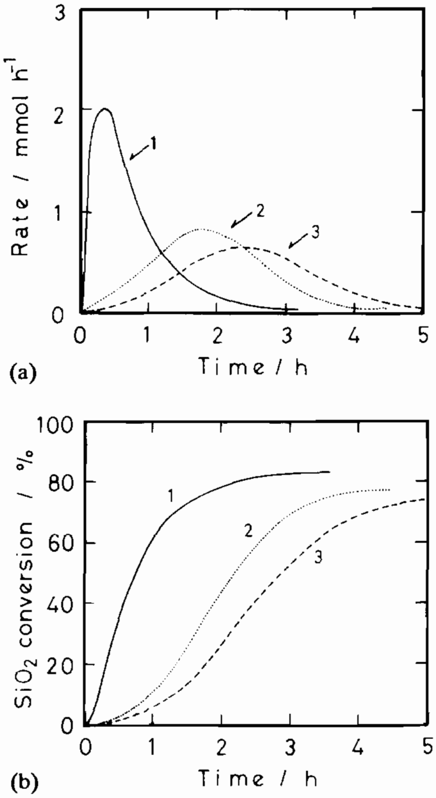

Fig. 2. Reaction of rice hull ash with dimethyl carbonate using various amounts of catalyst (potassium hydroxide). (a) Change in the rate of tetramethoxysilane formation with reaction time; (b) change in the cumulative conversion of SiO_2 component with reaction time. Loading amount of potassium hydroxide = 5 (1), 2 (2), 0.2 (3) wt.%. Reaction conditions: reaction temperature = 575 K; dimethyl carbonate = 96 kPa (43 mmol h^{-1}).

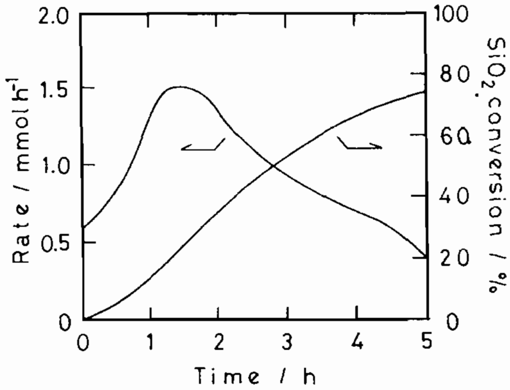

Fig. 3. Changes in the rate of tetraethoxysilane formation and the cumulative conversion of SiO_2 component with reaction time. Loading amount of potassium hydroxide = 5 wt.%. Reaction conditions: reaction temperature = 725 K; diethyl carbonate = 95 kPa (41 mmol h^{-1}).

Figure 2 shows the effect of the loading of potassium hydroxide on the rate of the reaction at 575 K. Without the catalyst, the reaction did not proceed at this temperature. The rate increased with increasing amount of the catalyst. The final yield of tetramethoxysilane was also higher at higher loading of the catalyst. Added potassium hydroxide is more effective as the catalyst than the alkaline component contained in the ash.

The reaction of rice hull ash with diethyl carbonate was also carried out. The loading of potassium hydroxide was 5 wt.%. The reaction of the ash with diethyl carbonate required higher temperatures than with dimethyl carbonate. The result of the reaction at 725 K is shown in Fig. 3. As in the reaction with dimethyl carbonate, the rate first increased and then decreased gradually to zero. The cumulative conversion reached about 80% at the reaction time of 5.5 h.

The results described above clearly show that the SiO_2 component of rice hull ash easily reacts with dialkyl carbonates to form tetraalkoxysilanes. This method provides a convenient way not only to separate the SiO_2 component from the ash, but also to produce tetraalkoxysilanes, which are useful as a raw material for ceramics by the sol–gel method and for pure silica. This method should also be very useful for the production of tetraalkoxysilanes from low-grade silica sources other than rice hull ash.

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