Molecular Aspects of Silica Gel Formation

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Introduction

Silica gels are widely used catalyst supports, adsorbents, and also important intermediates in the synthesis of zeolites and structured mesoporous silicates. The transition of sub-nano sized, dissolved silicate molecules into a desired solid is poorly understood. Even less is known about the molecular constitution of gels which are commonly treated as molecularly indistinguishable homogeneous materials composed of a random mix of smaller and bigger siloxane rings [1]. We have demonstrated in a few papers that FTIR and especially Raman spectroscopy can detect distinct differences between the molecular constitutions of silica gels prepared at different conditions [2-4]. It was found among others that the structures of acid and base set gels substantially differ when prepared from aqueous solutions of a K/Si ~ 0.53 ratio K-silicate but not when made from a K/Si ~ 0.76 silicate solution at otherwise identical conditions.

Here we report comparative structural tests with Na-silicate solutions. Since these relatively cheap, quick, non-invasive molecular spectroscopic techniques can also differentiate between the molecular constitutions of dissolved silicates [5-8] we also conduct in situ syntheses to explore their related potential. To overcome problems due to conflicting band assignments in the literature [5, 9] we also performed model calculations for the vibrational spectra of the small dissolved silicate molecules with known or assumed structures. Some relevant modeling results are also reported in this presentation.

Materials and Methods

The starting aqueous alkaline silicate solutions are commercial products of PQ Corporation. Pertinent properties can be found on the company's web site [10] and in references [5, 8, 9]. Other materials were obtained from Sigma-Aldrich. Our laser Raman and FTIR ATR instrumentation and techniques have also been published [5, 9, 11]. Ab initio and semi-empirical calculations were carried out at different levels and data sets using the DMol^3 and Vamp modules of the Materials Studio program from Accelrys [12].

Results and Discussion

Fig. 1 shows structural differences in two dilute Star^{TM} sodium silicate solutions used for gelling. Fig. 2 demonstrates that the acid set gels from these ingredients have different structures in contrast to comparable K/Si ~ 0.76 ratio Kasil-1624 [4]. The computed Raman spectrum in Fig. 3 became realistic only when H_2O molecules hydrating the silicate ions were explicitly involved similar to our earlier finding for IR models [13]. Fig. 4 illustrates that FTIR, which is more sensitive for this material than Raman, can clearly distinguish between the D4R structured product (framed band assignments) and its ingredients.

Significance

Molecular level understanding of silica gel structures and the process of silica solidification from solutions is desirable. FTIR and Raman spectroscopy can uniquely help in this task.

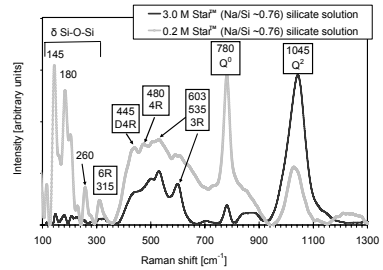

Fig. 1 Raman spectra of Star^{TM} solutions

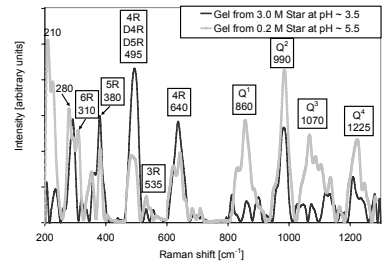

Fig. 2 Raman spectra of acid set gels

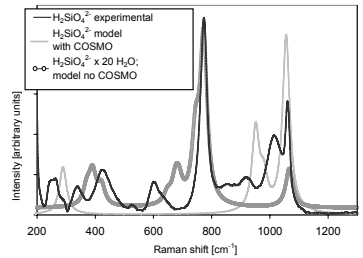

Fig. 3 Experimental and model Raman of dissociated $Na_2H_2SiO_4$ monomer

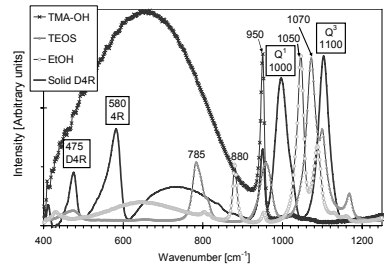

Fig. 4 FTIR ATR spectra of ingredients for synthesis of $[(Me_4N)_8Si_8O_{20} \times 65H_2O$

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