

# Vibrational Spectra of Silica Gels Made From Different Aqueous Sodium Silicate Solutions Using Various Methods

Istvan Halasz,\* Runbo Li, Mukesh Agarwal, Neil Miller

Research and Development Center, PQ Corporation, 280 Cedar Grove Road, Conshohocken, PA 19428 (USA); \*istvan.halasz@pqcorp.com

## Introduction

Gelling is an important step in many applications of dissolved silicates including the synthesis of zeolites and silica supported catalysts. However, this process has largely remained an empirical art because the composition of dissolved silicate molecules and their transition into polymers are poorly understood [1-3]. Even simple questions like "Can different silicate solutions result in distinct gel structures?" elude firm answers. Maybe yes because some gels appear to release exclusively monomers when leached by water [4, 5] but others mainly release larger particles [6-8]. Moreover an appropriate selection of silicate solution is usually deemed to be important for selective zeolite synthesis [4], but some authors consider almost every silica source equally good for this purpose [5]. It must also have a molecular basis that dried sodium silicates are stronger adhesives than their acid precipitated counterparts [9]. Is it possible that the mode of solidification affects the gel structure? Are these solids identical when made by the same polymerization process from different silicate solutions? These unresolved issues are addressed here by investigating the Raman and IR spectra of various sodium silicate solutions and gels.

## Materials and Methods

The starting crystalline  $\text{Na}_2\text{SiO}_3$  (Metso® bead) and  $\text{N}^\ominus$ -silicate (28.7%  $\text{SiO}_2$ ;  $\text{Si/Na} \sim 1.67$ ) are commercial products of the PQ Corp. [10]. The properties of dissolved silicates including dissociation, average mole weight (AMW), and vibrational spectra have been published in details [10, 11]. Our laser Raman and FTIR ATR techniques have also been published [12].

## Results and Discussion

Fig. 1 illustrates some characteristic differences in the Raman scatterings of  $\text{Na}_2\text{SiO}_3$  and N silicate which contain pure monomers and high AMW ( $\sim 957\text{g/mol}$  assuming only siloxane ring structures) in their 3M solutions, respectively. The 1008, 931, 777, 606, and 454  $\text{cm}^{-1}$  vibrations correspond to the  $\nu_{\text{as}}$  (Na)O-Si-O(H),  $\nu_{\text{s}}$  (Na)O-Si-O(H),  $\delta_{\text{as}}$  (H)O-Si-O(H),  $\delta_{\text{s}}$  (Na)O-Si-O(Na), and  $\delta_{\text{s}}$  (Na)O-Si-O(H) asymmetric (as) and symmetric (s) stretching ( $\nu$ ) and bending ( $\delta$ ) vibrations of monomer  $\text{Na}_2\text{H}_2\text{SiO}_4$  ( $\text{Q}^0$ ) or terminal  $-\text{O-Si-[O(X)]}_3$  ( $\text{Q}^1$ ) units, respectively ( $\text{X} = \text{H, Na}$  or  $\bar{\text{c}}$ harge;  $\text{Q}^n = \text{number of neighboring Si atoms}$ ) [3, 11]. The 1068  $\text{cm}^{-1}$  band probably belongs to  $\text{Na}_2\text{CO}_3$ , the 1043  $\text{cm}^{-1}$  is  $\nu_{\text{as}}$  Si-O-Si vibration and some characteristic bending vibrations of double 6 (D6R) and other rings are marked on the figure. Fig. 2 illustrates that the structure of dried  $\text{Na}_2\text{SiO}_3$  gel is quite different from that of the crystalline  $\text{Na}_2\text{SiO}_3$ . Fig. 3 shows only slight differences between the IR spectra of gels obtained by drying and by adding excess NaOH to the solution of 3M  $\text{Na}_2\text{SiO}_3$  [11]. HCl gels form very slowly ( $>24$  h) from this monosilicate but their IR spectra strongly resemble the spectra of the instantaneously HCl-precipitated gels from N silicate solution (Fig. 4). Excess

NaOH does not gel from the N-silicate solution. When water is evaporated from the N-silicate, the structure of the remaining gel (Fig. 4) resembles that obtained by water evaporation from the  $\text{Na}_2\text{SiO}_3$  solution (Fig. 3), but differs from that of the acid precipitated gel (Fig. 4). Consequently the method of gel fabrication might be more important than the  $\text{Si/Na}$  ratio. A more detailed structural comparison involving both IR and Raman studies will be presented.

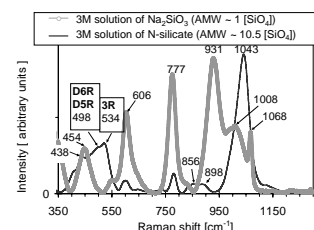


Fig. 1 Raman spectra of dissolved silicates

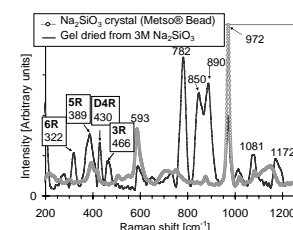


Fig. 2 Raman spectra of  $\text{Na}_2\text{SiO}_3$  solids

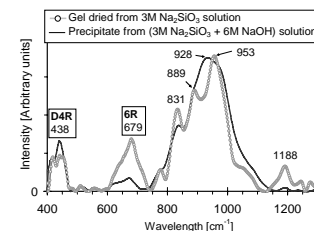


Fig. 3 FTIR ATR spectra of gels from  $\text{Na}_2\text{SiO}_3$

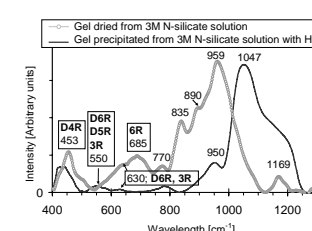


Fig. 4 FTIR ATR spectra of gels from  $\text{N}^\ominus$

## Significance

Raman and FTIR studies have been carried out to understand the effect of sodium silicate selection and method of fabrication on the structure of silica gels for various applications.

## References

- P. W. J. G. Wijnens, T. P. M. Beelen, R. A. van Santen, *Surfact. Sci. Ser.* 131, 597 (2006).
- I. Halasz, M. Agarwal, R. Li, N. Miller, *19<sup>th</sup> NAM, Philadelphia*, P#122 (2005).
- I. Halasz, M. Agarwal, R. Li, N. Miller, *Phys. Chem. Chem. Phys.*, in preparation.
- R. M. Barrer, "Hydrothermal Chemistry of Zeolites", Acad Press, London, NY, 1982.
- J. M. Fedeyko, D. G. Vlachos, R. F. Lobo, *Microp. Mesop. Mater.* 90, 102 (2006).
- C. T. G. Knight, J. Wang, S. D. Kinrade, *Phys. Chem. Chem. Phys.* 8, 3099 (2006).
- M. Haouas, F. Taulelle, *J. Phys. Chem. B* 110, 3007 (2006).
- I. Halasz, M. Agarwal, R. Li, N. Miller, *Catalysis Today*, in press.
- H. H. Weldes, K. R. Lange, *Ind. Eng. Chem.* 61, 29 (1969).
- www.pqcorp.com
- I. Halasz, M. Agarwal, R. Li, N. Miller, *Applied Spectroscopy*, submitted.
- I. Halasz, M. Agarwal, B. Marcus, W. E. Cormier, *Microp. Mesop. Mater.* 84, 318 (2005).

