Quantum Chemical Calculations of Amine-Catalyzed Polymerization of Silanol

Hongyu Gu¹, Wenbin Xu², Jinlin Zhang¹, Zhenyi Qi¹, Tao Zhang¹,* and Lixin Song¹,*

¹Key Laboratory of Inorganic Coating Materials CAS, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
²Aerospace System Engineering Shanghai, Shanghai 201108, China

*Corresponding author e-mail: lxsong@mail.sic.ac.cn and tzhang@mail.sic.ac.cn

Abstract. Because of the technical importance of organosilicon materials, insight into the related synthetic processes is significantly essential. In this paper, the amine-catalyzed polymerization of silanol has been investigated by the density functional theory (DFT) method. Our data have shown that amines can catalytically promote the hydrogen transfer process by substantially reducing the energy barrier. The activation barrier via hydrogen transfer with catalysis is 38.32 kJ/mol, much lower than that of catalysis-free process (120.88 kJ/mol). The lower energy barrier is in agreement with the much more intense polymerization of silanols with amine catalysts. Based on the above results, amines and other catalysts capable of assisting hydrogen transfer are expected to be used as catalysts for silanol polymerization.

1. Introduction
The organosilicon materials have been used extensively in a wide variety of applications such as in aerospace and microelectronics, owing to their unique physical and chemical properties including excellent thermal stability and chemical resistance [1-3]. Polymerization of silanol related molecules is of practical importance in the manufacture of organosilicon compounds such as inorganic polymers, siloxane backbone polymers, coatings, glasses, gels, adsorbents and catalysts [4-6]. In these processes, various silanol species including mono-, di-, tri-, and tetrafunctional are used extensively to obtain specific products. On the catalytic polymerization of silanol, many experimental studies of silanol polymerization have made significant progress. Secondary and tertiary amines (piperidine, triethylamine, tri-n-butylamine) based catalytic polymerization has been previously reported by professor Chojnowski and Chrzczonowicz to polymerize series of dialkyl- or diarylsilanediols in aqueous dioxane [7]. Accurate comparison of the reaction mechanism and rate data with or without catalysts would greatly help to understand the processes in solutions of reacting silanols, and thus guide the control of sol-gel processes, treatment of mineral/glss fillers and other techniques.

However, few theoretical works focus on the reaction mechanism despite the practical importance of these reactions. Most interpret primary chemistry based on the analyses of corresponding condensed products. The experimental data alone are insufficient to lay down the unambiguous mechanism of the polymerization. It is generally difficult to obtain accurate rate data of silanol polymerization due to the massive parallel or consecutive reactions involved. In this regard, the quantum chemical
calculation should become more fruitful in investigating the reaction mechanism with the increase of calculation precision and velocity [8-9].

Herein, the polymerization mechanism of silanols, especially the amine-catalyzed polymerization mechanism has been investigated by means of density functional theory (DFT). Reaction kinetics is explored within the framework of transition state theory. In detail, using the B3LYP exchange and correlation functionals, we calculate and determine the minimum energy reaction paths (MERPs) together with the transition states (TSs) during polymerization and amine-catalyzed polymerization of dimethylsilanediol.

2. Theory

2.1. Transition state theory
A reaction, as described by transition state theory, is a movement on the potential energy surface from the valley or minimum of the reactants to that of the products. The path, marked by many intermediates and transition states, describe the specific reaction mechanism. The highest point along the MERPs connecting reactants and products are TSs, while the transition structures correspond to the geometric configurations of the first-order saddle point.

2.2. Computational methods
To determine the MERPs and TSs, we used the GEDIIS method as implemented in Gaussian 09 version. The geometry optimization and vibrational frequency calculations were performed exploiting the B3LYP exchange and correlation functionals with the B3LYP/6-31G(d,p) basis set. Vibrational frequencies are obtained by firstly determining the second derivatives of the energy regarding the Cartesian nuclear coordinates and then transforming them to mass-weighted coordinates. Frequency values represent the property of the stable point. Frequencies at local minima are often positive while transition states are featured by imaginary frequencies. Corrections of zero-point energy on the potential energy surfaces are also obtained during the frequency calculation. Then, charge distribution is further calculated using natural bond orbital (NBO) analysis with the optimized geometrical configuration. Dynamic reaction path (DRP) based on the intrinsic reaction coordinate (IRC) or MERP is followed in one or both directions from the transition state at the same level.

3. Results and discussion

3.1. Characteristics of the reactants and catalysts
This work select one of the simplest possible alkylsilanediols, i.e., dimethylsilanediol to represent the typical configuration of silanols. Dimethylamine was used to represent the simplified computational model of amines. Energy minimization was carried out for all reactants, products and the catalysts. Reaction process is based on the characteristics of the reactants and catalysts. Thus, structural optimization of the dimethylsilanediol and dimethylamine was analyzed first.

Figure 1. The optimized geometrical configuration of dimethylsilanediol (a) and dimethylamine (b).
The optimized geometrical configuration of dimethylsilanediol and dimethylamine are shown in Figure 1. The electronegativity of the elements contained in reactants and catalysts is shown in Table 1. The electronegativities of oxygen and nitrogen are relatively high, and the electronegativities of silicon and hydrogen are relatively low. The calculated NBO charge of important atoms in stationary points (minimum) of the reactant and catalyst is shown in Table 2 and Table 3, respectively. The charge distribution is consistent with the element electronegativity drawn from the table. The Si-O, O-H, N-H bonds are partially ionized due to the differences in electronegativity and charge distribution of the bonding atoms, which could be reactive in electrophilic and nucleophilic reactions.

### Table 1. Electronegativity of the elements contained in reactants and catalysts.

| Atoms | Si  | O   | N   | C   | H   |
|-------|-----|-----|-----|-----|-----|
| Reactant | 1.90 | 3.44 | 3.04 | 2.55 | 2.20 |

### Table 2. NBO charge of important atoms in stationary points (minimum) of the reactants.

| Atoms | Si  | O1  | O2  | H1  | H2  | C1  | C2  |
|-------|-----|-----|-----|-----|-----|-----|-----|
| Reactant | 2.127 | -1.138 | -1.138 | 0.523 | 0.523 | -1.253 | -1.253 |

### Table 3. NBO charge of important atoms in stationary points (minimum) of the catalysts.

| Atoms | N  | H3  | C3  | C4  |
|-------|----|-----|-----|-----|
| Catalyst | -0.726 | 0.391 | -0.493 | -0.493 |

3.2. Minimum energy reaction path without catalysis

The dimethylsilanediol would form siloxane and water through intermolecular polymerization. The dehydration polymerization should be expected to run via the transfer of the hydrogen in Si-OH to the oxygen in Si-OH of other molecules. Meanwhile, the reformation of the Si-O bond would generate siloxane and water. The first step of polymerization could be described as shown in Figure 2 [10]. In this work, we would take the first-step polymerization process as the research object to study the catalytic effect of amines on the polymerization process.

![Figure 2](image)

Figure 2. The first step of polymerization of dimethylsilanediol.

Figure 3 is the calculated structure of transition state during the polymerization. As shown in Figure 1 and Figure 3, during the polymerization process, the bond lengths of H1 and O1 increased from 0.96 angstroms to 1.38 angstroms, while H1 and O2 gradually approached 1.08 angstroms. The bond length of Si2 and O2 increased from 1.68 angstroms to 1.92 angstroms, while Si2 and O1 gradually approached 1.99 angstroms. Figure 4 presents the relative energy of stationary points during the catalysis-free polymerization. The activation barrier is 120.88 kJ/mol, and the energy of the free product molecules is -13.85 kJ/mol lower than the free reactant molecules. The results show that the reaction is exothermic and heating would contribute to the reaction.
3.3. Minimum energy reaction path with catalysis

Amines were found to have a catalytic effect on the polymerization of silanols. The catalysis should be supposed to help the transfer of hydrogen in Si-OH to oxygen in Si-OH of other molecules. Figure 4 is the calculated structure of transition state during the polymerization catalyzed by dimethylamine. As shown in Figure 1 and Figure 5, during the polymerization process, the hydrogen in Si-OH would not transfer to the oxygen in Si-OH of other molecules directly. The H1 in Si-OH would transfer to the N in dimethylamine while the H3 bonded to the N in dimethylamine would transfer to the O2 in Si-OH of other molecules. Dimethylamine served as the carrier of H transfer. Meanwhile, the Si-O bond reformed to generate siloxane and water. Specifically, in the transition state, the bond length of H1 and O1 increased from 0.96 angstroms to 2.49 angstroms, while H1 and N gradually approached 1.02 angstroms. The bond length of H3 and N increased from 1.01 angstroms to 1.36 angstroms, while H3 and O2 gradually approached 1.14 angstroms. The bond length of Si2 and O2 increased from 1.68 angstroms to 1.85 angstroms, while Si2 and O1 gradually approached 1.81 angstroms. Relative energy of stationary points during the polymerization catalyzed by dimethylamine is shown in Figure 6. The activation barrier via the catalyzed path is 38.32 kJ/mol, much lower than the path without catalysis (82.56 kJ/mol). The results show that the reaction could proceed smoothly at room temperature.
After passing the transition states as shown in Figure 3 and Figure 5, the siloxane and water were obtained by the formation of Si-O-Si bonds. We have confirmed that the reactant (dimethylsilanediol) and product (tetramethyldisiloxanediol and water) can both be obtained from the transition states based on IRC or MERP.

As a result of B3LYP calculations of transition states, the energy barrier according to the catalyzed path is much lower. Due to the much lower energy barrier, dimethylsilanediol is extremely sensitive to amine catalysts. Amines would promote the rapid polymerization of silanols, resulting in intense polymerization of silanols with amine catalysts. Moreover, amines reduce the energy barrier of the hydrogen transfer process to promote catalysis. Based on the above results, amines and other catalysts capable of assisting hydrogen transfer are expected to be used as catalysts for silanol polymerization.
4. Conclusion
The polymerization mechanism of silanols, especially the amine-catalyzed polymerization mechanism has been studied in the current work. As a result of the calculations, the energy barrier according to the catalyzed path is much lower. The hydrogen transfer related activation barrier with catalysis is 38.32 kJ/mol, which is much lower than activation barrier (120.88 kJ/mol) in the case of catalysis-free hydrogen transfer. Amines promote the hydrogen transfer process by reducing the energy barrier. Amines would enable the rapid polymerization of silanols, resulting in intense polymerization of silanols with amine catalysts. Based on the above results, amines and other catalysts capable of assisting hydrogen transfer are expected to be used as catalysts for silanol polymerization.

Acknowledgments
The current work was supported by the Laboratory foundation of Chinese Academy of Sciences (Grant No. 16S085) and the innovation fund of Computational Materials Center from SICCAS (Grant No. Y75ZC2120G).

References
[1] G. Chandra, Organosilicon materials, Springer, Berlin, 1997.
[2] G. Linti, Organosilicon chemistry VI: from molecules to materials, Wiley, Weinheim, 2005.
[3] Y. Sugiyama, H. Okamoto, T. Mitsuoka, T. Morikawa, K. Nakanishi, T. Ohta and H. Nakano,
Synthesis and optical properties of monolayer organosilicon nanosheets, J. Am. Chem. Soc. 132 (2010) 5946-5947.
[4] P. R. Ortega, M. Montejo, A. M. Ingrain, F. Márquez and J. L. González, Dimethylsilanediol: Structure and vibrational spectra by IR and Raman spectrosopies and quantum chemical calculations, Vib. Spectrosc. 58 (2012) 79-86.
[5] I. S. Ignatyev, F. Partal and J. L. González, Polymerization reactions in silanol–water clusters, Chem. Phys. Lett. 368 (2003) 616-624.
[6] A. S. Lee, S. S. Choi, K. Y. Baek and S. S. Hwang, Hydrolysis kinetics of a sol-gel equilibrium yielding ladder-like polysilsesquioxanes, Inorg. Chem. Commun. 73 (2016) 7-11.
[7] F. D. Osterholtz and E. R. Pohl, Kinetics of the hydrolysis and polymerization of organofunctional alkoxysilanes: a review, J. Adhes. Sci. Technol. 6 (1992) 127-149.
[8] O. Böhm, R. Leitsmann, P. Plänitz, C. Radehaus, M. Schallerc and M. Schreiberb,
Silylation of silicon bonded hydroxyl groups by silazanes and siloxanes containing an acetoxy group. N-trimethylsilylimidazole vs. dimethylidacetoxy silane, Comput. Theor. 991 (2012) 44-47.
[9] O. Böhm, R. Leitsmann, P. Plänitz, C. Radehaus, M. Schreiber and M. Schaller, k-
Restoring processes at carbon depleted ultralow-k surfaces, J. Phys. Chem. A 115 (2011) 8282-8287.
[10] Z. Lasocki and S. Chrzczonowicz, Kinetics of the polypolymerization of dimethylsilanediol, J. Polym. Sci. Pol. Chem. 59 (1962) 259-269.