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STUDY OF STRUCTURES AND PROPERTIES OF SILICA-BASED CLUSTERS AND ITS APPLICATION TO MODELING OF NANOSTRUCTURES OF CEMENT PASTE BY DFT METHODS

PRIYANKA A. BHAT

Department of Physics, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai-400 019, Maharashtra, India

N C DEBNATH

Department of Physics, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai-400 019, Maharashtra, India

Abstract. In order to understand the structure and properties of silicate species in aqueous media and also in various silicate materials with diverse conformations and properties, several silicate clusters viz; monomer, dimer, and trimers (linear and cyclic) have been studied theoretically by DFT-BLYP computational technique. The structural data and IR spectra were computed in details and are reported in this paper. Further, this work was extended to study the nanostructures of C-S-H gel which is a very important component of cement paste. The basic structural unit of the nanostructure of the C-S-H phase has been identified by comparing the computed structural and IR data with the experimental data.

1. Introduction

The importance of developing a basic understanding of the structures, properties and mechanism of formation of different silicate materials need not be over emphasized as silicates in various conformations form the basic structural unit in many important materials like quartz, cristobalite, glass, ceramics, cement etc. In order to understand the structure and properties of diverse silicate materials it is convenient to study the simple silicate clusters that play a key role in the formation of various silicate compounds. In this work, we report the results of ab-initio DFT calculations of structures, energies and also vibrational frequencies of different silicate clusters viz: monomer, dimer and trimer (linear and cyclic) which are good representative models of different species formed during the polymerization of silicates in aqueous media[1-4]. The comparison of computed structures and the corresponding vibrational frequencies of the different silicate clusters with the experimental IR spectra of known as well as unknown compounds of silicates could throw a lot of light in understanding and predicting the structures and properties of these materials. Cement is a highly complex, multi-component and multi-phase silicate compound. When cement powder is mixed with water, it undergoes hydration process which results in the setting and hardening of the cement paste. Calcium silicate hydrate (C-S-H) gel and calcium hydroxide (Portlandite) are the two major cement hydration products. Study of structures and properties of C-S-H gel is very important as it is primarily responsible for the binding property in cement paste. Therefore, as an example we provide a comparative analysis of structure and properties of computed nanostructures of calcium silicate hydrate gel(C-S-H gel) with the crystalline analogues of C-S-H viz: Tobermorite[Ca₅Si₆O₁₆(OH)₂.4H₂O][5-8]. This gel is an important component of cement paste and it consists predominantly of the silicate dimer species (Q^1, Q^2) and is responsible for binding properties in cementitious materials. By comparing the computed structural and IR data of C-S-H cluster [with Ca/Si=1.125] with the experimental data of Tobermorite [9,10] [Table 1,2] it was possible to identify the basic unit of nanostructures of C-S-H phases formed during the early stage of cement hydration.

2. Methods and Materials

In order to prepare samples of cement paste;10 g of cement powder was mixed with 5 g of distilled water in a plastic beaker. The reaction mixture was stirred for approximately 1 min using a glass rod. The beaker was then covered with a watch glass and kept undisturbed at normal room temperature for the desired time period for hydration to take place during which the cement paste hardens and sets to form a cement block. After the desired hydration time was over, the cement block was taken out and first dipped in acetone for half an hour and then dipped in diethyl ether for additional half an hour to terminate the hydration reaction. The cement block was then dried in oven for 3 h at 105°. After drying, the block was ground into fine powder using mortar and pestle. The resulting fine powder of paste samples was used for characterization by FTIR and Solid State ²⁹Si NMR spectroscopy.

3. Results and Discussion

Characterization of cement powder and cement paste was carried out by FTIR spectroscopy and solid state ²⁹Si NMR spectroscopy and the results are shown in Figure 1.The characterization of the nanostructure of cement paste by transmission electron microscopy was also carried out, the results of which are reported in our earlier publication[8]. The three major bands of dry cement

observed in this experiment are centered around 929.6 cm⁻¹ (Si–O asymmetric stretching (v₃) vibration), 522.2 cm⁻¹ (Si–O out-of-plane bending (v₄) vibration) and 461.1 cm⁻¹ (Si–O in-plane bending (v₂) vibration). The band at 1153.6 cm⁻¹ and the two shoulders at 1114.2 and1097 cm⁻¹ are due to S–O stretching (v₃) vibration of SO₄²⁻ and the medium strong bands at 603.7 and 659.7 cm⁻¹ are due to bending vibrations (v₂) of SO₄²⁻. These bands arise from the sulphate (SO₄²⁻) component (gypsum) that is present in cement. The bands at 1433.7 and 1464.2 cm⁻¹ are due to asymmetric stretching vibration (v₃) of CO₃²⁻ and the band at 883.7 cm⁻¹ is due to out-of-plane bending vibration (v₂) of CO₃²⁻. The weak bands at 3658.8 and 1622 cm⁻¹may be attributed to trace amount of water that is present in dry cement. The band assignments are in good agreement with those reported in the literature [11,12,13]. Upon hydration the main peak at 929.6 cm⁻¹, shifts to 974.17 cm⁻¹ indicating polymerization of silicate species and formation of calcium silicate hydrate gel. The Si-O bending peaks also undergo change in profile. The carbonate peaks increase in intensity, since carbonation is inevitable during the hydration process.



(a)





Figure 1. Characterization of cement powder and cement paste by FTIR and solid state ²⁹Si NMR spectroscopy (a) FTIR spectrum of cement powder (b) FTIR spectrum of cement paste after 7 days of hydration (c) NMR spectrum of cement powder (d) NMR spectrum of cement paste after 7 days of hydration.

Solid state ²⁹Si NMR spectrum of cement powder shows a broad peak centered around -71 pm. Comparison with the literature data on ²⁹Si NMR study of pure cement phases indicates that the broad peak can be deconvoluted into contributions from the alite and belite phases. This peak is a combination of a broad peak due to alite phase (C₃S) and a narrow peak due to belite phase (β – C₂S) centered around -71 ppm[14]. This peak can be attributed to the Q⁰ state of the silicate species. Upon hydration the area under the peak at -71 ppm reduces, with the simultaneous appearance of resonance peaks in the range of -75 to -90 ppm. These resonance peaks in the range of -75 to -90 ppm can be attributed to the Q¹ and Q² states of the hydration products. An important conclusion drawn from this study is that during the initial hydration process only the alite phase contributes to the strength development and belite phase remains almost unreacted.

Calcium silicate hydrate (C-S-H) gel has a complex and highly variable structure since the Ca/Si ratio in C-S-H gels may vary from 0.7 to 2.3 with a mean around 1.7.Hence isolation and characterization of this phase from other components of cement paste is difficult. Therefore, we undertook theoretical study of silicate clusters by DFT method to gain more insight into the structure of

cementitious C-S-H gels. The structural models of silicate clusters and their corresponding computed IR spectra are shown in Figure 2. The structural parameters of the silicate clusters are also shown in the respective figures. The polymerization of monomer to dimer results in the appearance of a Si-O-Si bending peak (~670 cm⁻¹) which is observed in the computed spectrum of dimer. The peaks due to Si-O stretching vibration (900-1000 cm⁻¹) remain essentially unchanged due to polymerization. The bending peaks around 400 to 500 cm⁻¹ undergo a change from a singlet peak in monomer to a doublet in dimer. The profile of the IR spectra also undergoes some change from linear trimer to cyclic trimer although the main Si-O stretching peak remains essentially unchanged. This study of silicate clusters was then extended to optimize the structure and compute the corresponding IR spectrum of a C-S-H model [P-Ca-P] which is given in Figure 3.The computed structural data and IR data of C-S-H model is given in Table 1 along with the experimental structural data of Tobermorite. Comparison of IR data of C-S-H cluster with experimental data of Tobermorite, synthesized C-S-H and cement paste is shown in Table 2.





Figure 2.Optimized structures of silicate clusters and their corresponding IR spectra computed by DFT method (a) Monomer (b) Dimer (c) Linear Trimer (d) Cyclic Trimer



Figure 3. (a) Optimized structure of [P-Ca-P] model of nanostructure of C-S-H phase (b) corresponding computed IR spectrum.

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Structural Parameters	GGA /BLYP	Experimental structural data -11Å tobermorite	Assignment of the IR Bands	Wavenumber (cm-1)	Intensity (km/mol)
Si-O _b (Å)	1.750ª,1.665	Si-O bond lengths(Å)			
	1.662,1.675	1.60, 1.61, 1.62, 1.63, 1.64, 1.65, 1.67, 1.68, 1.69	Si-O in-plane bending vibration	396.9	875.37
			-	443.4	234.61
Si-O _t (Å)	1.608 ^a , 1.677 1.677, 1.675			464.4	749.47
				485.4	274.31
				493.1	197.95
Cat-Oca(Å)	2.288, 2.311	Ca-O bond lengths(Å)	Si-O out-of-plane bending	551.7	409.52
	2.290, 2.293	2.24, 2.32, 2.35, 2.36, 2.38, 2.39, 2.40, 2.41,	vibration		
	2.302, 2.297	2.42, 2.44, 2.53, 2.54, 2.57, 2.62.			
	2.298, 2.283		Si-O _b -Si bending vibration	661.3	381.74
			bending violation	761.6	212.94
Ca _m -O _{ca}	2.328, 2.334			779.1	238.29
(Å)	2.337, 2.306				
	2.330, 2.301		Si-O stretching vibration (O1)	814.6	160.94
	2.329, 2.349		stretening violation (Q1)	833.9	110.13
				846.8	138.93
Si-O _b -Si	123.024 ^a			848.4	144.79
(°)	121.715			855.7	752.55
				859.7	1309.26
				877.2	408.55
O _b -Si-O _{ca}	111.698			892.9	382.9
(°)	114.725		Si-O asymmetric stretching vibration	903	651.13
	112.001		Ũ	935.4	908.13
	114.265			951.3	809.99
	114.008			956.7	1642.65
	111.706			971.5	534.78
	110.676 ^a			1008	951.59
	109.006 ^a		SiO-H stretching in SiOH group	3741	177.86
				3747.8	181.91
Interlayer Ca-Ca Distance (Å)	11.162	Experimental value of d002 (Å) - 11.3			

 Distance (Å)
 Of 0002 (A) = 11.5

 Table 1.Structural data and IR frequencies of C-S-H model compared with experimental data.

Assignment of Bands	FTIR data of 1.1nm and 1.4nm tobermorite(cm- 1)	FTIR data of C-S-H	FTIR frequencies of OPC cement paste (cm-1)	Theoretical frequencies of [P-Ca-P] cluster (cm- 1)
Si-O in-plane Bending	~ 450	~ 440- 450	~460-465	443.4, 464.4, 485.4
Si-O out-of-plane Bending	~ 500	~ 500	518- 532	551.7
Si-O-Si bending	~ 670	~ 670	-	661.3
Si-O stretching	-	811 (Q1)	-	814.6, 833.9, 855.7
		(810-830)		859.7
out-of-plane bending of CO32-	875	875	874- 878	-
Si-O stretching	Band with strong peak at ~ 980 (1.1nm T) Broad band at ~ 969 (1.4nm T)	~ 970 (Q2)	973-985	935.4, 951.3, 956.7, 971.5 1008
Si-O stretching	~1060, ~900 (Q2)(shoulders) ~1200 (Q3) (1.1nm T) ~ 1120 (1.4 nm T)	-	-	903
asymmetric stretching of CO32-	1400-1500	1400-1500	1420-1485	-
H-O-H bending Interlayer water	1640 3300, 3600 2800-3700	1640 3300-3600	1650-1670 3400-3500	-
O-H stretching in Ca(OH)2	-	~3600	~3640	-
SiO-H stretching in SiOH group	-	-	-	3741.0, 3747.8

Table 2. Comparison of computed IR data of C-S-H model [P-Ca-P] with different experimental data.

Table 1 shows that the structural data computed for our [P-Ca-P] model accurately agrees well with the experimental data of Tobermorite. The Ca-Ca interlayer distance computed for our model (11.162Å) is in excellent agreement with the reported experimental value of 11.3Å for Tobermorite. Comparison of the IR data of [P-Ca-P] model with the reported experimental data of Tobermorite, synthesized C-S-H and OPC cement paste indicates that our model quite accurately predicts the characteristic frequencies of C-S-H gel.

Conclusions

- 1. The key FTIR peaks of OPC cement samples observed at 929, 522, 461 cm⁻¹ are due to Si-O stretching and Si-O bending vibration respectively.
- 2. As the hydration progresses, the main peak at 929 cm⁻¹ shifts to higher frequency 970- 980 cm⁻¹ due to silicate polymerization and formation of calcium silicate hydrate (C-S-H) gel.
- 3. The peak at 670 cm⁻¹(Si-O-Si bending) is absent in hydrated cement but is observed in both crystalline C-S-H and also has been observed in synthesized C-S-H gels. Our theoretical IR spectra of silicate clusters and C-S-H models also predicts this band with good accuracy.
- 4. ²⁹Si NMR data clearly shows that (i) the cement sample consists of alite and beta C_2S phases(ii) silicate dimers predominate along with monomers in cement paste (iii) the initial hydration reaction is due to the alite phase of cement.
- 5. Theoretical study of the structure and properties of silicate clusters was carried out by *ab-initio* DFT method with BLYP functional. The computed results of Si-O bond length and Si-O-Si bond angle of the clusters agree quite well with the experimental data of the silicate materials.
- 6. The structural parameters of C-S-H cluster; [P-Ca-P] computed by DFT-GGA method with BLYP functional are in good agreement with reported experimental structural data of 1.1nm Tobermorite.
- 7. Computed Infra-red spectra of C-S-H cluster by DFT-GGA (BLYP) functional compares reasonably well with the reported experimental FTIR vibrational frequencies of synthesized C-S-H, 1.1nm and 1.4nm Tobermorite.
- 8. The strong similarity of both structural data and IR spectrum of [P-Ca-P] cluster with 1.1nm Tobermorite, synthesized C-S-H and cement paste indicates that the optimized [P-Ca-P] cluster is probably the most likely basic unit of C-S-H phases which are formed in the early stage of cement hydration.

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