Journal of Molecular Liquids 261 (2018) 115–122

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Investigation on the decomposition process of sodium aluminate solution by spectroscopic and theoretical calculation

Wei Liu [a], Ya-ling Huang [a], Zhou-lan Yin [a], Zhi-ying Ding [a,b,*]

[a] School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China
[b] Hunan Provincial Key Laboratory of Efficient and Clean Utilization of Manganese Resources, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:
Received 21 January 2018
Received in revised form 3 March 2018
Accepted 4 April 2018
Available online 05 April 2018

Keywords:
Sodium aluminate solution
Elementary reaction
Raman
UV–Vis
Theoretical calculation

ABSTRACT

This study focused on the determination of intermediate (6AlO-OH) structure and its elementary reaction path design during the decomposition process of sodium aluminate solution by combining experimental and theoretical approach. The molecular structure, Raman spectra, UV–Vis spectra, frontier molecular orbitals and molecular electrostatic potential of $Al(OH)_4^-$,$[(HO)_2-Al-O_2-Al-(OH)_2]^{2-}$, $[(HO)_2-Al-O_2-Al-(HO)_2-Al-O_2-Al-OH)_2]^{2-}$, 6AlO — OH were characterized by density functional theory calculation. The calculated Raman and UV–Vis spectra of 6AlO-OH agreed with experiments results, which showed that the supposed structure of 6AlO — OH was reasonable. Combined with the theoretical calculation results, a possible elementary reaction path of intermediate (6AlO-OH) formation was designed to propose the generation mechanism of intermediate.

1. Introduction

The decomposition of sodium aluminate solutions has played a very important role in alumina production [1]. However, it is very complicated and inherently slow and has been becoming an urgent problem [2,3]. It is a research hotspot to study the decomposition mechanism of sodium aluminate solutions.

Many of previous research was especially focused on the properties of sodium aluminate solutions, such as physicochemical properties, thermodynamics and spectroscopy [4–7]. It indicated that the possible existence of Al-containing species could infer the decomposition mechanism of sodium aluminate solutions. Moreover, numerous researchers have studied the nucleation process of gibbsite from sodium aluminate solutions. Harris et al. [8] used a dynamic light scattering (DLS) method to study the gibbsite particle nucleation and growth. Rossiter et al. [9] applied the multi-angle laser light scattering (MALLS) method together with TEM, XRD, and IFSEM measurements to study the nucleation of gibbsite. Li et al. [10] established an online conductance testing system to study the homogeneous nucleation process of gibbsite. These studies measured the induction period and important nucleation parameters with the classical nucleation theory.

Quantum chemical calculation was also applied to analyze the structure of Al-containing species and the decomposition mechanisms of sodium aluminate solutions. Liu et al. [11] used ab initio calculation method and semi-empirical method to optimize the structure of conjecture for $Al(OH)_4^-$ and $[Al_2O(OH)_6]^{2-}$, and then applied the DVXα method to calculate the UV–Vis spectra of Al-containing species. It was found that the calculated UV–Vis spectra were close to those of the experimental results. Gerson et al. [12] applied a semi-empirical

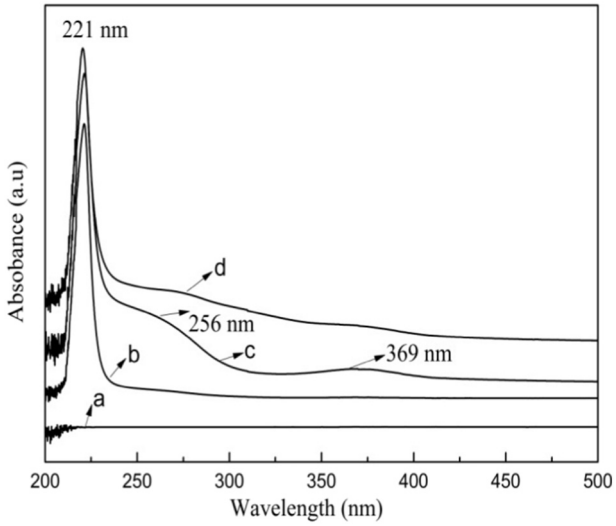

Fig. 1. UV–Vis spectra of the different solutions (a) high purity water (b) sodium hydroxide solution, $c_{NaOH} = 4.52\ mol \cdot L^{-1}$, (c) sodium aluminate solution decomposed for 5 h, $\alpha_K = 1.46$, $c_{NaOH} = 4.52\ mol \cdot L^{-1}$ (d) sodium aluminate solution at the end of decomposition (mother solution).

* Corresponding author.
E-mail address: 312371149@qq.com. (Z. Ding).

https://doi.org/10.1016/j.molliq.2018.04.014
0167-7322/

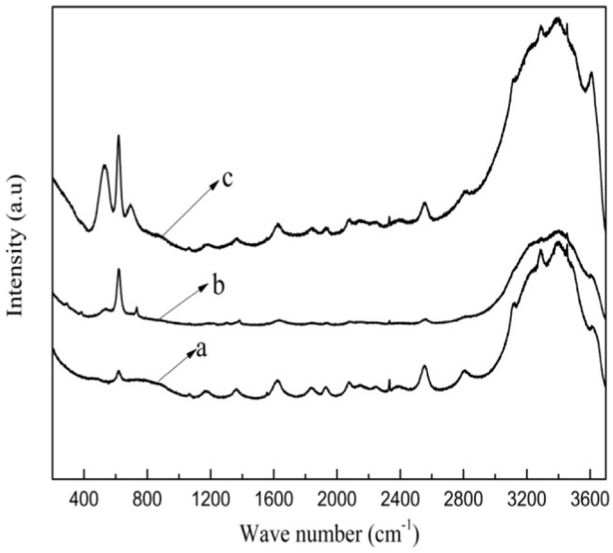

Fig. 2. Raman spectra of sodium aluminate solutions (a) $\alpha_K = 6.06$, $c_{NaOH} = 2.42$ mol·L^{-1} (b) $\alpha_K = 1.52$, $c_{NaOH} = 4.84$ mol·L^{-1}; (c) $\alpha_K = 1.48$, $c_{NaOH} = 11.29$ mol·L^{-1}.

quantum mechanical molecular modeling to analyze the heat formation for a series of Al-containing species, and proposed the gibbsite nucleation mechanism. The calculations suggested that $Al(OH)_3(H_2O)_2$, $Al(OH)_3(H_2O)$ and $Al(OH)_5^{2-}$might be present in low concentration sodium aluminate solutions. Gale et al. [13] used ab initio methods to calculate the possible species in the sodium aluminate solutions with different concentration, and presented the potential transformation way for species. Yin et al. [14] adopted density functional theory to determine the model geometry of Al_3-B cluster and the relevant part of reactivity in sodium aluminate solutions. Then designed the possible paths of cyclization reaction for Al_3-B cluster with·OH radical. Li [15] used transition-state theory calculation method to study the possible generation mechanisms of gibbsite, and proposed the growth unit ($Al_6(OH)_{18}(H_2O)_6$) of favoring precipitation in sodium aluminate solutions. Wu et al. [16] applied quantum chemical calculation to study the growth mechanisms of the favorable growth unit ($Al_6(OH)_{18}(H_2O)_6$) of gibbsite in sodium aluminate solutions, and proposed the combination mechanisms of gibbsite growth unit.

In summary, the decomposition mechanisms of sodium aluminate solutions have been studied using different methods. However, the lack of direct experimental results is important to identify the intermediate of decomposition process of sodium aluminate solutions.

In the previous study, by using UV–Vis spectroscopy, we proposed the existence of an intermediate in the kinetics study of the decomposition process of sodium aluminate solution [17]. In this paper, the result of Raman spectra study of sodium aluminate solution during the decomposition process about detecting the intermediate was reported. A reasonable generation mechanism of the intermediate was proposed, and the structure of Al-containing species in the decomposition process was inferred. The optimized geometry, vibrational frequencies, frontier

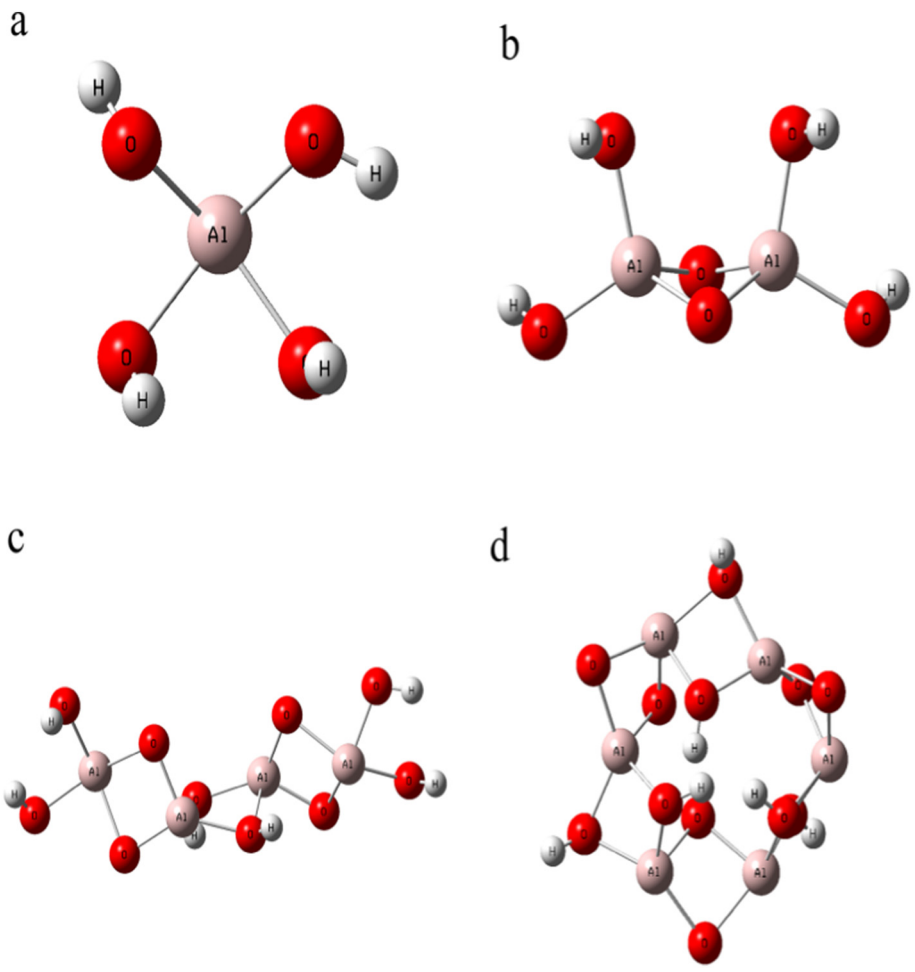

Fig. 3. Space structure of different Al-containing species (a) $Al(OH)_4^-$, (b) $[(HO)_2 - Al - O_2 - Al - (OH)_2]^{2-}$, (c) $[(HO)_2 - Al - O_2 - Al - (HO)_2 - Al - O_2 - Al - (OH)_2]^{2-}$, (d) 6AlO − OH.