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Theoretical Study on the Thermolysis Mechanism of Monohydrate Magnesium Chloride

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Abstract

The mechanism of the thermolysis reaction of monohydrate magnesium chloride was studied detailedly by PM3 method. The geometrical parameters, harmonic vibrational frequencies and energies of stationary points on the potential energy surface were obtained. Two reaction paths have been proposed for the subject reaction with the major reactive channel corresponding to the dissociation of the monohydrate magnesium chloride. The calculated results show that the best strategy for controlling the hydrolysis reaction is decreasing the reactivity of magnesium chloride so that preventing the dehydrogen reaction process. Simultaneity, the addition of the Nano-metal catalysis also restrains the hydrolysis reaction.

1. Introduction

Anhydrous magnesium chloride is the excellent source to produce magnesium by electrolysis. Dehydrating crystal water and producing anhydrous $MgCl_2$ from the bischofite of Salt Lake is a key technology for obtaining magnesium or magnesium alloy [1]. With the large-scale development of potash manure in Western Salt Lake, hundreds of thousands of tons of magnesium chloride are unused every year. Numerous loss of magnesium chloride brine not only waste resources, but also increases the difficulty of further development of industrial potassium chloride [2-4]. Consequently, environmental development and rational utilization of magnesium resources of salt lake has been the subject which needs to be solved. However, the difficulty is that the dehydration process of monohydrate magnesium chloride is extremely complex, and the side reaction is difficult to control. In addition, the presence of trace water is undesired for electrolysis of materials. We have proposed that commingling with Salt Lake bischofite ($MgCl_2 \cdot 6H_2O$) and the metal nano powder directly to produce magnesium alloys by high-temperature sintering in combination with nano-catalyst technology [5], and the dehydration kinetics of monohydrate magnesium chloride is crucial in it. Thus, it is significant to research and

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understand of the mechanism of the thermolysis reaction of monohydrate magnesium chloride so as to inhibit the side reaction and obtain the desired anhydrous magnesium chloride and magnesium alloys purposefully. However, scientists are focused on the improvement of dehydration process route during a long time, the study of dehydration mechanism study is only considered in the part of the thermodynamics [6-11]. Obviously, it is imperfect to clarify the mechanism of dehydration by the thermodynamic data.

In this paper, the mechanism of the thermolysis reaction of monohydrate magnesium chloride was investigated by quantum chemical calculation in order to server better the experimenttal study.

2. Computational Methods

The equilibrium geometries and reaction transition state were optimized by the semi-empirical PM3 method, all energy values was corrected by zero-point energy. The authenticity of the transition states are confirmed by vibration frequencies analysis, all the properties of the transition states are identified by the calculations of its response vector(the eigenvectors corresponded by the only negative eigenvalues of second derivative of energy) and intrinsic reaction coordinate (IRC) .

3.Results and Discussion

3.1 Reaction Path

Theoretical calculations shows that the thermolysis reaction of monohydrate magnesium chloride is a complicated multi-channel reaction, according to the optimization of various reaction paths and the calculation verification of the IRC of transition state, and two reaction paths shown in Scheme 1 and 2 were vertified. An intermediate product (INT1a) was produced in reaction path (1) when magnesium chloride and water molecules form a coordination bond. Reaction path (2) produced two intermediate products (INT1a and INT2b). The geometrical parameters and energies of reactant(R) 、intermediates(INT1a ,INT2A and INT2b) 、transition state(TS1、TS2a and TS2b)、products (P1 and P2) are shown in Table 1 and Table 2 , respectively.

3.1.1 Reaction path (1)

According to the dehydration pathway of monohydrate magnesium chloride, 341.83i is the only imaginary frequency in vibration frequency of transition state TS1 by vibration analysis. According to the response vector (the eigenvectors corresponded by the only negative eigenvalues of second derivative of energy) of transition state TS1, this transition state between INTa and P1can be further confirmed by the IRC results of the step length is 0.05amu$^{-1/2}$ • bohr (TS1: -0.2481334 a.u. ← -0.2016474 a.u. → -0.2164818 a.u.) . In Table 2, reaction path (1) consists of two reactions, and the corresponding potential energy surface shown in Fig.1. The bond length of 1.8423 Å between magnesium atom and oxygen atom exhibit the strong covalent bond have been formed between magnesium chloride and water molecule. Monohydrate magnesium chloride transfers to the complex (INT1a) by dehydrated decomposition firstly, and the bond length changed to 2.35 Å. This result show that the interaction of between water and magnesium chloride is weakened and almost closes to their equilibrium geometries (Table 1). Besides, it can directly see that the first step of the reaction just requires to across small energy barrier (5.78 kJ • mol^{-1}). The second step of reaction is a transition from the intermediate product INT1a to a transition state of dehydration, at this point the bond distance between magnesium and oxygen is increased to 3.0546 Å, the interaction of between water and magnesium chloride is further weakened and more closes to their equilibrium

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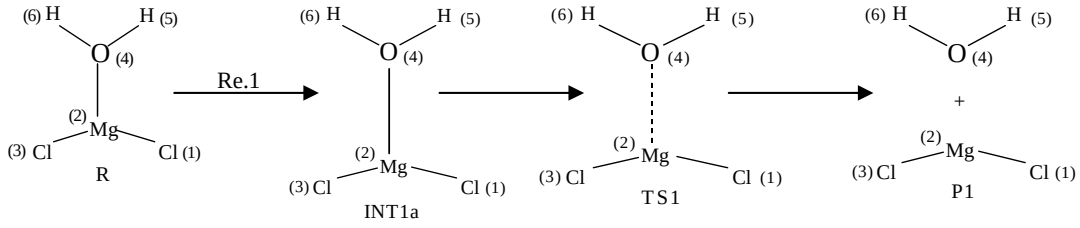


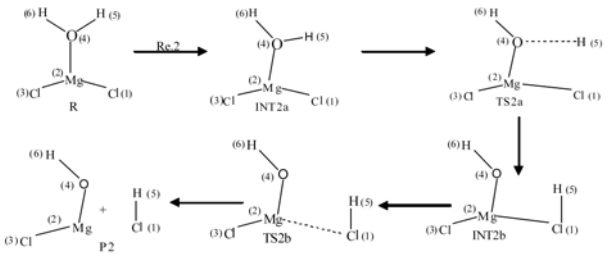
Scheme 1. The reaction process and the atomic numbers for the dehydration reaction

geometries. The potential energy surface shows that this step needs to overcome the larger barrier of 110.30 kJ • mol^{-1}. In contrast to the reactant(R) simultaneously, dehydrate completely needs to overcome 116.08 kJ • mol^{-1} activation energy, which is in accord well with the experimental value of 115 ~ 126 kJ • mol^{-1}.

3.1.2 Reaction path (2)

The reaction path of dehydrochlorination for monohydrate magnesium chloride is very complex, which needs two transition states of dehydrogenation and dechlorination. 1800.44i and 196.36i are the only imaginary frequencies by analyzing the vibrational frequencies of transition state TS2a and TS2b, consequently. Besides, according to the response vector (the eigenvectors corresponded by the only negative eigenvalues of second derivative of energy) of transition states TS2a and TS2b, the TS2a is the transition state betwwen INT2a and INT2b, and the TS2b is the transition state between INT2b and P2. In addition, the IRC results (TS2a : -0.2460585 a.u.←-0.230654 a.u. → -0.2435148 a.u.; TS2b : -0.2435148a.u. ← -0.1825877 a.u. →-0.1887563 a.u.) further confirmed the correction of transition states.

According to Table 2, reaction path (2) consists of three reactions, the potential energy surface is shown in Fig.1, water molecules have a tendency of dissociation during the first reaction under the influence of the magnesium chloride catalyst based on the data of Table 2, the H(5) of intermediate product is close to Cl(1)and the bond distance of magnesium and oxygen almost has no change, but the direction of Cl (1) sloped and the distance of bond O(4) – H(5) has a little protraction, which weakens the interaction force between H (5) and O (4) and increases the attraction force between Cl(1) and H (5). In contrast to the intermediate product INT1a, the difference of activation energy is very small, which indicate that the probability is near between path (1) and path (2). It exists significant differences of activation barrier in the second-step reaction, the potention energy surface of Fig.1 shows the further reaction has two options after R form into intermediate product INT1a and INT2a. The first option is dehydrated directly by INT1a, which needs to across 110.30 kJ • mol^{-1} energy barrier; the other option is dehydrogenated by INT2a, which needs to across 25.53 kJ • mol^{-1} energy barrier. Obviously, dehydrogenation is easily to occur because of the lower barrier. The mechanism for the dehydrogenation step can be explained by the theory of catalysis, since the magnesium chloride is a good activity Ziegler-Nata catalyst component [12], the bond length of O (4)-H (5) in water molecules is stretched to 1.354 Å and the bond length of Cl(1)-H(5) is attracted to 1.5475Å under the catalysis of magnesium chloride。



Scheme 2. The reaction process and the atomic numbers for the hydrolysis reaction

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The above results show that the interaction between H (5)-O (4) H (6) is weakened and easily to be catalyzed and dissociated into the hydroxyl and hydrogen ions, it may also be explained by the changes of charge distribution. From magnesium atom of INT2 with 1.03 positive charge and chlorine with 0.67 negative charge to the magnesium of TS2a with 1.01 positive charge and chlorine with 0.51 negative charge, hydroxyl ions are easily adsorbed on the surface position of the active centre of magnesium, on the contrary, hydrogen ions distant from the magnesium ions and close to the negatively charged chloride ions in order to make the conformation stabilized. The schematic diagram of structural changes consistent with this viewpoint in scheme 2: the magnesium oxygen bond distance of INT2a changes from 1.84 Å to 1.82 Å of TS2a and to 1.79 Å of INT2b, of which indicate the bonding force of hydroxyl ion and magnesium ion gradually increased, at the same time, the bond length of Cl(1)- H(5) of INT2a changes from 1.87 Å to 1.55 Å of TS2a and to 1.32 Å of INT2b, which also indicates the bonding force of hydrion and chloridion gradually increased from non-bonding to bonding. For the third-step dechlorination reaction, with the decrease of O(4)-Mg(2) distance and the increase of Cl(1)-Mg(2) distance, the TS2 dissociated into MgOHCl and HCl. The changes in charge distribution shows that Mg(2) of INT2b changes from 0.948 to 0.95 of TS2b, Cl(1) of INT2b changes from-0.26 to -0.19 of TS2b，O of INT2b changes from-0.61 to -0.58 of TS2b, this shows the bonding ability of Cl (1)-Mg (2) is significantly decreased, which cause the distance of Cl (1)- Mg (2) almost has no effect on the charge of Mg(2), whereas the Cl (1)-Mg (2) bond has a trend of cleavage and the bond length of O(4)-Mg(2) gradually increased. The potential energy surface in Fig.1 shows, dechlorination needs across 149.82 kJ • mol^{-1} energy barrier and the reaction temperature is higher, whereas the reverse reaction, i.e. reaction of MgOHCl and HCl, only needs overcome 20.37 kJ • mol^{-1} activation energy, so the reverse reaction is easy. This shows that the hydrolysis reaction under the atmosphere of hydrogen chloride could be prevented well. However, suppressing the side reaction is not completely under the atmosphere of hydrogen chloride because of turnning INTa to TS2a and last to INTb in the second step.

To sum up, the reaction (2) shows that a dehydrogenation reacton is easy to occur in dehydrochlorination reaction channel, thus lead this reaction channel to be the main reaction channel for decomposition of monohydrate magnesium chloride. Dehydrogenation is not a simple reaction of direct dehydrochlorination as people think, but a complex three-step reaction. The best strategy for controlling the second-step reaction is decreasing the activity of magnesium chloride and preventing the dehydrogenation reaction.

3.2 Catalyse of Nano-Al powder

The geometry optimization of the reaction of single aluminum atom and monohydrate magnesium chloride is shown in Fig. 2. Structural analysis shows that the addition of aluminum atoms has a greater impact to the configuration of monohydrate magnesium chloride. The 2.467Å distance of Al-Mg improves the formation of metal bonding, the angle of Cl-Mg-Cl decreased from 151.48° to 113.50°, the Cl-Mg bond length elongated slightly from 2.3164 to 2.3450, the O-Mg bond length decreased slightly from 1.8423Å to 1.838Å by the attraction of aluminum atom, the Al-Cl bond length is 2.3710Å. These changes show that the strong bond have been formed between aluminum atom and two chlorine atoms, further, blocks the dissociation of chlorine atoms and inhibits the hydrolysis. Moreover, water molecular structure has almost no change, two hydrogen atoms distribute on both sides of the Al-Mg bond evenly, but oxygen atom have a trend of closing to aluminum atom.

According to the structure varietal tendency of monohydrate magnesium chloride after adding nano-metal catalysts, we find that the addition of metal catalysts inhibits the hydrolysis of monohydrate magnesium chloride and forms

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Al-Mg metal bond, thereby reduced the activity of Mg. It indicates that it is possible to mix Salt Lake bischofite ($MgCl_2 \cdot 6H_2O$) with nano-metal powder to produce magnesium alloys by the high-temperature sintering. At the same time, it is possible for aluminum atoms attracting oxygen to forming metal oxide inorganic material.

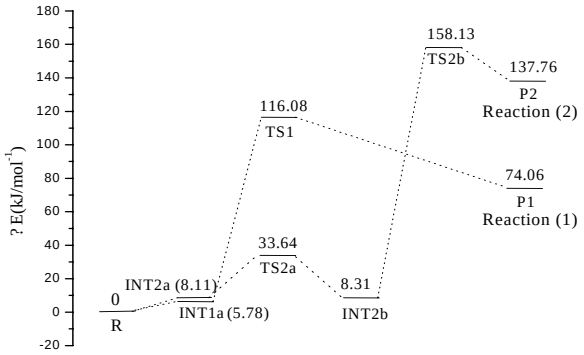

Figure. 1 Potential energy surface for the thermolysis reaction of the monohydrate magnesium chloride at PM3 level.

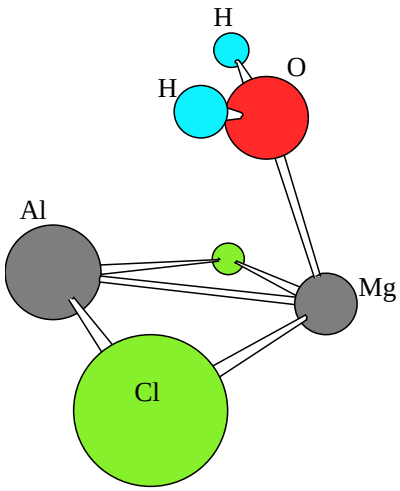

Figure. 2 Reaction structure between aluminum atom andmonohydrate magnesium at PM3 level

Table 1 The geometrical parameters for the stationary points of the thermolysis reaction of the monohydrate magnesium chloride at PM3 level

Species		Structure Parameters*							
P1	$MgCl_2$	Mg-Cl (1.8874)				∠ClMgCl (157.37)			
	H_2O	O-H (0.9510)				∠HOH (107.67)			
P2	HCl	H-Cl(1.2676)							
	MgOHCl	Mg-Cl (2.3006)		Mg-O (1.7744)		O-H (0.9371)	∠ClMgO=124.63		∠MgOH(123.08)
	Cl(1)–Mg(2)		Cl(3)–Mg(2)	O(4)–Mg(2)		O(4)–H(5)	O(4)–H (6)	Cl(1)–H(5)	Cl(3)–H(6)
R	2.3164		2.3163	1.8423		0.9614	0.9614	2.5978	2.5983
INT1a	1.8979		1.8979	2.3500		0.9558	0.9558	2.7608	2.7594
TS1	1.8908		1.8908	3.0546		0.9520	0.9520	4.2883	4.2881
INT2a	2.3662		2.2927	1..8424		1.0065	0.9496	1.8699	3.3256
TS2a	2.4014		2.2931	1.8200		1..3540	0.9385	1.5475	3.6407
INT2b	2.4091		2.3052	1.7904		1.7690	0.9370	1.3233	3.8159
TS2b	3.1634		2.2987	1.7805		2.5747	0.9384	1.2728	3.6747
	A(1,2,3)	A(1,2,4)	A(3,2,4)	A(2,4,5)	A(2,4,6)	A(5,4,6)	D(3,2,4,6)	D(1,2,4,5)	D(1,2,4,6)	D(3,2,4,5)
R	151.48	86.86	86.88	116.47	116.47	111.91	8.30	-8.35	-143.89	143.81
INT1a	138.10	95.98	95.94	91.55	91.55	108.93	40.47	-15.41	-124.40	124.35
TS1	143.24	107.92	107.92	43.90	43..90	107.69	10.08	-10.1	-161.60	161.60
INT2a	152.31	72.61	106.02	103.09	122.55	114.11	18.05	-2.80	-113.13	148.32
TS2a	145.80	72.98	117.16	50.50	123.93	114.26	18.67	2.34	-125.93	-142.08
INT2b	157.28	76.62	125.30	88.67	124.37	146.59	-1.71	0.46	-175.05	-27.50
TS2b	157.00	77.70	121.98	103.77	121.62	134.61	-0.016	0.029	179.98	176.90

*bond length : Å , bond angle: (º C)

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Table 2 The electronic structure energy, zero-point energy，total energy and relative energy for the species of the thermolysis reaction of the monohydrate magnesium chloride at PM3 level

Species	Electronic structure energy/a.u.	Zero-point energy/a.u.	Total energy/a.u.*	Relative energy/(kJ • mol^{-1})
R	-0.2503317	0.031404	-0.2189277	0.00
INT1a	-0.2481334	0.031408	-0.2167254	5.78
TS1	-0.2016474	0.026932	-0.1747154	116.08
P1	-0.2164818	0.025703	-0.1907188	74.06
INT2a	-0.2460585	0.030219	-0.2158395	8.11
INT2b	-0.2435148	0.027753	-0.2157618	8.31
TS2a	-0.230654	0.024823	-0.206115	33.64
TS2b	-0.1825877	0.023888	-0.1586997	158.13
P2	-0.1887563	0.022300	-0.1664563	137.76

*total energy = electronic structure energy + zero-point energy

4. Conclusions

In this paper, the reaction paths and thermolysis mechanism of monohydrate magnesium chloride were studied by PM3 method. The following conclusion can be drawed by the reaction mechanism of monohydrate magnesium chloride and the effect of the addiction of nano-metal aluminium powder.

1. The reaction path (2) dissociated into MgOHCl and HCl is the major reaction channel for dissociation of monohydrate magnesium chloride. However, the reaction of intermediate coordinatine structure (INT1a) dissociated into H_2O and $MgCl_2$ by a transition state TS1 is less likely to occur because of the higher activation barrier (110.30 kJ • mol^{-1}).

2. The best strategy for controlling the hydrolysis reaction is decreasing the activity of magnesium chloride so that preventing dehydrogen reaction process.

3. The addition of the nano-metal catalysis restricts the hydrolysis reaction of monohydrate magnesium chloride. So it is possible to mix Salt Lake bischofite ($MgCl_2$ • $6H_2O$) with the nano-metal powder to produce magnesium alloys by high-temperature sintering in combination with nano-catalyst technologyassumptions on objective function $f(x)$ in (1.1), which have been often used in the literature to analyze the global convergence of nonlinear conjugate gradient methods with inexact line searches for unconstrained optimization problems.

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