Disproportionation mechanism of methylchlorosilanes catalyzed by different clusters $\text{AlCl}_3/\text{ZSM-5}$

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Abstract. Organosilicon material is widely used because of its dual structure. Dimethyldichlorosilane is the largest and most versatile of organic silicon monomer. In this article, MP2/6-311 + + G (3df, 2pd) basis set has been used to calculate the reaction mechanism of disproportionation for producing dimethyldichlorosilane by catalysts $\text{AlCl}_3/\text{ZSM-5}$ (3T, 4T, 6T). The results show that the activation energies (3T, 4T, 6T) of the rate-determining step of the main reaction are: 100.3, 110.6 and 113.1 kJ mol^{-1} , respectively. The structure analysis, activation energy analysis and LOL analysis for different catalysts all show that the catalytic effect of 4T cluster $\text{AlCl}_3/\text{ZSM-5}$ is the best.

Keywords. $\text{AlCl}_3/\text{ZSM-5}$; disproportionation; dimethyldichlorosilane; organosilicon.

1. Introduction

Organosilicon material^{1,2} has many excellent properties such as high and low-temperature resistance, corrosion resistance and physiological inertia. It is widely used in electronics, building materials, transportation, and other fields.³⁻⁵ The level of industrial silicon is determined by the production of its monomer, in which dichlorodimethylsilane ($(\text{CH}_3)_2\text{SiCl}_2$, M_2) is the largest and most versatile organic silicon monomer.^{6,7} At present, the dichlorodimethylsilane is prepared from direct synthesis method.⁸ But this method will accumulate a lot of waste, such as methyltrichlorosilane (CH_3SiCl_3 , M_1) and trimethylchlorosilane ($(\text{CH}_3)_3\text{SiCl}$, M_3). Some experts use disproportionation method⁹ to prepare the M_2 , this method not only solves the problem of waste accumulation but it can also improve the economic efficiency. In the disproportionation reaction for producing dimethyldichlorosilane, the choice of catalyst is very important. Bin Ku *et al.*,¹⁰ studied the disproportionation for producing dichlorodimethylsilane by using AlCl_3 as catalysts under the conditions of high temperature and high pressure. They found

that the yield of dimethyldichlorosilane was 70.3%. B. Pachaly *et al.*,¹¹ used organic amine as catalyst, and found that the yield of dimethyldichlorosilane was 27%. W. Kalchauer *et al.*,¹² used transition metals (more expensive) as catalysts and found that the yield of dimethyldichlorosilane was 67%. When AlCl_3 is used as a catalyst, the yield of dimethyldichlorosilane is the highest. But it requires the reaction environments of high temperature and high pressure. Because its sublimation temperature (178 °C) is low,¹³ it is easy to cause a loss when reacting at atmospheric pressure. Therefore, AlCl_3 is loaded on the carrier to improve its sublimation temperature.^{14,15} As a solid acid catalyst, AlCl_3 ¹⁶ has demonstrated the good catalytic effect in the scission reaction between high-boiling and low-boiling components of silicone.¹⁷ The reaction mechanism was studied for disproportionation of dimethyldichlorosilane catalyzed by 5T cluster $\text{AlCl}_3/\text{ZSM-5}$,¹⁸ 24T and 7T clusters ZSM-5 in our laboratory. The preliminary work showed that the 5T cluster $\text{AlCl}_3/\text{ZSM-5}$ catalyst not only improved the stability, but also increased the yield of dimethyldichlorosilane. The macroporous 24T cluster ZSM-5 has weaker activity in its interior, and the small pore 7T cluster ZSM-5 has no catalytic activity. Experiment¹⁹ indicates that $\text{AlCl}_3/\text{ZSM-5}$ has

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Figure 1. The formation process of 3T, 4T, and 6T clusters $\text{AlCl}_3/\text{ZSM-5}$ catalysts and the numbers of key atoms.

a good catalytic effect. Therefore, the catalytic activity is mainly provided by its surface. At present, the 5T cluster $\text{AlCl}_3/\text{ZSM-5}$ catalyst²⁰ is a relatively popular research area in the preparation of dimethyldichlorosilane. In order to determine the active clusters on the surface of ZSM-5, it is necessary to discuss other small clusters (3T, 4T and 6T) in depth. Finally, the catalytic properties of small clusters model catalysts are explained from a microscopic perspective.

2. Computational

In this paper, Density Functional Theory (DFT) method^{21–23} of quantum chemistry is used to calculate the structures of the reactants, transition states, intermediates, and products at the B3LYP/6-31G level. For structural optimization calculations, the structures are constructed and adjusted by using the Gaussian view.²⁴ Then the input files are written and the structures are optimized for calculation with Gaussian 09^{25,26} (Gaussian Inc., Wallingford CT). The transition states are searched by utilizing TS²⁷ method in this paper. We perform vibration analysis and frequency calculations for all structures (reactants, intermediates, transition states, products). The results of calculations show that the frequencies of all the reactants, intermediates, and products are positive and all the transition states have only one negative frequency, indicating that the transition states are the saddle points on the potential energy surface. Therefore the transition state structures are credible. In order to further confirm the authenticity of the transition states and the reaction paths, we have carried out IRC/Path calculation. The second-order Moller-Plesset perturbation theory²⁸ (at MP2/6-311++G (3df, 2pd) level) is used to calculate the energy of each step and the Zero Point

Energy (ZPE)²⁹ correction is considered. Finally, we perform LOL (localized-orbital locator)^{30,31} and bond order analysis on the three catalysts to compare their catalytic activity. The localized-orbital locator can not only analyze the problems of localization and delocalization but also characterize the chemical bonds. In the paper, all the calculations are completed through Gaussian 09 program.

3. Results and Discussion

The formation process of 3T (Cat.3T), 4T (Cat.4T) and 6T (Cat.6T) clusters $\text{AlCl}_3/\text{ZSM-5}$ catalysts is shown in Figure 1. The stable structure of $\text{AlCl}_3/\text{ZSM-5}$ catalyst (taking Cat.3T as an example) is mainly composed of Al-O-Al-O four-membered ring and four O atoms are bonded to two Al atoms, respectively. During the formation of $\text{AlCl}_3/\text{ZSM-5}$ catalyst, AlCl_3 and ZSM-5 are close to each other, one of Cl atom in AlCl_3 is removed, and it combines with the active site H atom in ZSM-5 to form HCl. The important geometric parameters of the stable structures are shown in Table 1. From Table 1, the order of the bond angle is: Cat.4T > Cat.3T > Cat.6T. The bond angle ($\angle \text{O}^1\text{-Al}^1\text{-O}^2$) of the active site of Cat.4T is increased. It shows that the pore of the catalyst is enlarged, which is conducive for large trimethylchlorosilane to participate in reaction into the channel. It is found that the order of bond length is: Cat.4T > Cat.3T > Cat.6T by comparing the bond length of $\text{Al}^1\text{-Cl}^1$ of the active site. The longer bond length indicates that the $\text{Al}^1\text{-Cl}^1$ bond is more easily

Table 1. Optimized geometric parameters of 3T, 4T, and 6T clusters of $\text{AlCl}_3/\text{ZSM-5}$ catalysts.

		Cat.3T	Cat.4T	Cat.6T
Bond length/nm	$\text{Al}^1\text{-Cl}^1$	0.2192	0.2195	0.2189
	$\text{Al}^1\text{-Cl}^2$	0.2118	0.2189	0.2190
	$\text{Al}^1\text{-O}^1$	0.1814	0.1809	0.1811
	$\text{Al}^1\text{-O}^2$	0.1809	0.1810	0.1812
	$\text{Al}^2\text{-O}^1$	0.1839	0.1843	0.1843
	$\text{Al}^2\text{-O}^2$	0.1856	0.1838	0.1849
	$\text{O}^1\text{-Si}^1$	0.1731	0.1731	0.1734
	$\text{O}^2\text{-H}^1$	0.0979	-	-
	$\text{O}^2\text{-Si}^2$	-	0.1340	0.1728
Bond angle/ $^\circ$	$\angle \text{O}^1\text{-Al}^1\text{-O}^2$	84.4982	84.7504	82.5858
	$\angle \text{O}^1\text{-Al}^2\text{-O}^2$	82.7476	82.7869	80.9239

Figure 2. The reaction equations of the catalytic process.

broken and Cl is more likely to be involved in the reaction. All in all, they show that the catalytic activity of 4T cluster $\text{AlCl}_3/\text{ZSM-5}$ is the best.

The reaction equations of disproportionation for CH_3SiCl_3 and $(\text{CH}_3)_3\text{SiCl}$ catalyzed by Cat.3T (Cat.4T and Cat.6T are same as Cat.3T) are shown in Figure 2. The reaction is divided into two channels. In channel 1, the Cat.3T reacts with $(\text{CH}_3)_3\text{SiCl}$ to produce $(\text{CH}_3)_2\text{SiCl}_2$ and intermediate (I) via the transition state TS1. Then, CH_3SiCl_3 reacts with I to produce $(\text{CH}_3)_2\text{SiCl}_2$ and Cat.3T via the transition state TS2. This is the main reaction. In channel 2, I and by-product of SiCl_4 are gained through CH_3SiCl_3 and Cat.3T reaction, via transition state TS3. Next, $(\text{CH}_3)_3\text{SiCl}$ reacts with I to produce $(\text{CH}_3)_4\text{Si}$ and Cat.3T via the transition state TS4. This is the side reaction. The flow chart of reaction by the 3T cluster $\text{AlCl}_3/\text{ZSM-5}$ is shown in Figure 3.

The vibrational modes of the transition states and the numbers of key atoms in the reaction system are shown in Figure 4. The figure shows that the atomic vibration of the transition state in each step of the reaction system mainly comes from the stretching movement between Al^1 , C^1 , Si^2 and Cl^1 . Take the case of TS1, Cl^1 atom gradually closes to the Si^2 atom, and bonds with it. The

$\text{Si}^2\text{-C}^1$ bond and $\text{Al}^1\text{-Cl}^1$ bond are broken gradually. C^1 atom and Al^1 atom gradually approach and bond. These processes produce the product P1. C^1 atom gradually moves to the Si^2 atom, and bonds with it. Meanwhile, the $\text{Al}^1\text{-C}^1$ bond and the $\text{Si}^2\text{-Cl}^1$ bond stay away from each other and break. Cl^1 atom and Al^1 atom gradually approach and bond. These processes produce the reactant R1. Finally, the reactant and the product are found, which confirms the reliability of the transition state.

The transition states are tracked during calculation in Forward and Reverse using the IRC method. The spacing trend of key atoms along the IRC of 3T, 4T, and 6T clusters $\text{AlCl}_3/\text{ZSM-5}$ catalysts are shown in Figure 5. The spacing of critical atoms has gradually stretched or shortened from the reactants to the products via transition states. Thus, the authenticity of the transition state structures is further proved, and the mechanism mentioned above is believable.

The reaction heat and activation energy of each reaction step are calculated by using second-order Moller-Plesset perturbation theory (at MP2/6-311++G (3df, 2pd) level) and the Zero Point Energy (ZPE) correction is considered. The reaction enthalpies and activation energies are shown in Table 2. Figure 6 shows the activation energies of different clusters catalysts. The energy values of all transition states and products are calculated at zero point of their corresponding products. From Figure 6, we can obtain that the activation energy of the rate-determining step (RDS) in the main reaction is: 111.6, 100.3 and 113.1 kJ mol^{-1} , respectively. Comparing with the 24T and 7T clusters in the channel, it is shown that the catalytic activity of these three clusters surface and 5T cluster¹⁸ is better. Indicating that the main activity of the disproportionation reaction is on the surface of the catalyst, which is consistent with our expectation. The activation energy of RDS in channel 1 is lower than channel 2, indicating that channel 1 is

Figure 3. The flow chart of reaction catalyzed by the 3T cluster $\text{AlCl}_3/\text{ZSM-5}$.

Figure 4. The vibrational modes of the transition states and the numbers of key atoms.

the main reaction. This is consistent with the previous mechanism derivation and experimental results.¹⁹ The activation energy of the rate determining step of side reaction is: 155.6, 279.5, and 150.2 kJ mol^{-1} , respectively. By comparing the activation energy of RDS, it

is found that the activation energy of Cat.4T is low and the reaction is easy to proceed. In the side reaction, the activation energy of Cat.4T is large. It indicates that side reaction is difficult to occur. This situation is advantageous for the production of the main product

Figure 5. The spacing trend of key atoms along the IRC in the system (—Cat.3T, ---Cat.4T,.....Cat.6T).

Table 2. Reaction heat and activation energy in each reaction step.

		Cat.3T	Cat.4T	Cat.6T
Reaction enthalpies/kJ mol ⁻¹	ΔH_1	68.1	54.0	71.8
	ΔH_2	107.7	96.6	110.0
	ΔH_3	152.2	148.0	143.6
	ΔH_4	11.3	24.0	15.5
Activation energies/kJ mol ⁻¹	E_{a1}	70.5	65.4	85.5
	E_{a2}	111.6	100.3	113.1
	E_{a3}	155.6	279.5	150.2
	E_{a4}	23.8	24.8	18.9

(CH₃)₂SiCl₂. The order of the activation energy of RDS in the main reaction is: Cat.4T < Cat.3T < Cat.6T, indicating that the order of the catalyst activity is: Cat.4T > Cat.3T > Cat.6T. In summary, the catalytic effect of 4T cluster AlCl₃/ZSM-5 catalyst is the best. The results of energy analysis correspond to stable structure analysis of the catalyst.

To further explore the activity of the catalyst, the LOL and bond orders are combined to analyze the catalyst. It is shown in Figure 7 and Table 3. From the

LOL, the active position of Al-Cl bond (circled by the black line) where the region is basically blue. It indicates that the localization index is low, and the ability of electronic delocalization is strong. By comparing the color of the active region of each catalyst, we find that the Cl atom of Cat.4T in the deep blue region and the area's color of the Al-Cl bond is deeper, indicating that its delocalization is stronger and it is easier to participate in the reaction. So the electronic delocalization of active site from the strong to the weak is:

Figure 6. The activation energies in catalytic system of 3T, 4T and 6T clusters of $\text{AlCl}_3/\text{ZSM-5}$.

Figure 7. LOL analysis of 3T, 4T, and 6T clusters $\text{AlCl}_3/\text{ZSM-5}$ catalyst.

Table 3. The bond order analysis of 3T, 4T, and 6T clusters of $\text{AlCl}_3/\text{ZSM-5}$ catalyst.

Bond order	Cat.3T	Cat.4T	Cat.6T
Al-Cl Mayer bond order	0.849417	0.809099	0.858440
Al-Cl-O-O bond order	0.0011404	0.0011610	0.0011300

Cat.4T > Cat.3T > Cat.6T. The larger the four center bond order of Al-Cl-O-O is, the more stable the molecular skeleton is, so the stability order of the catalyst skeleton is: Cat.4T > Cat.3T > Cat.6T. The smaller the Mayer bond order (Al-Cl bond) is, the easier the Al-Cl bond is to break, so that the electron delocalization is stronger. The Cl of Al-Cl of Cat.4T is easy to give delocalized electrons, and the skeleton of the structure is strong. Therefore, the order of catalytic activity is: Cat.4T > Cat.3T > Cat.6T. The results of LOL analysis are consistent with the results of activation energy analysis and catalyst structure analysis.

4. Conclusions

In this paper, the mechanism of disproportionation for producing dimethyldichlorosilane catalyzed by $\text{AlCl}_3/\text{ZSM-5}$ in 3T, 4T, and 6T clusters is studied by using MP2/6-311 + + G (3df, 2pd) basis set. The following conclusions are obtained. The activation energy of the rate-determining step in the main reaction is: 111.6 (Cat.3T), 100.3 (Cat.4T), and 113.1 (Cat.6T) kJ mol^{-1} , respectively. The Mayer bond order of active position (Al-Cl) is: 0.849417 (Cat.3T), 0.809099 (Cat.4T), and 0.858440 (Cat.6T), respectively. The four-center bond

order of Al-Cl-O-O is: 0.0011404 (Cat.3T), 0.0011610 (Cat.4T), and 0.0011300 (Cat.6T), respectively. The structural parameters analysis, energy analysis, Mayer bond order analysis, four-center bond order analysis and LOL analysis indicate that the order of catalytic activity is: Cat.4T > Cat.3T > Cat.6T.

Supplementary Information (SI)

The coordinates of optimized geometries of three different clusters catalysts are presented in Supplementary Information, available at www.ias.ac.in/chemsci.

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