INTRODUCTION

Organic silicon material is widely used in many aspects [1]. But the commonly adopted direct synthesis approach [2] for preparing dimethyldichlorosilane (M2) would produce a number of chemical byproducts of which methyltrichlorosilane (M1) is in the majority. The disposal of the chemical byproducts refers to the future and destiny of the whole organic silicon industry. Now mostly researching AlCl3 is used as catalyst for the disposal of M1. But AlCl3 dissolves in reaction system easily, which leads to difficulties for subsequent separations and greatly influences the purity of the products. Previous experiments [3] put forward that catalyst of ZSM-5 zeolite supported by AlCl3 catalyzed the disproportionation under atmospheric and low temperature (70 °C, 100 kPa), the yield of M2 was more than 88 %. But AlCl3 sublimated and dissolved in samples. If AlCl3/ZSM-5 catalyst would reduce to AlCl3/ZSM-5 catalyst in reaction process, activation energies of which in forward and reverse reactions were Ea = 17 kJ mol⁻¹, Ear = 77 kJ mol⁻¹, respectively. The stability of NaAlCl4/ZSM-5 catalyst was higher than AlCl3/ZSM-5 catalyst; catalytic effect of NaAlCl4/Mg-ZSM-5 catalyst was not as good as AlCl3/ZSM-5 catalyst, which activation energy of rate-determining step in main reaction was 163 kJ mol⁻¹.

Keywords: NaAlCl4/ZSM-5, DFT, MP2, Dimethyldichlorosilane, Trimethylchlorosilane.

THEORETICAL CALCULATION FOR DISPROPORTIONATION OF METHYLTRICHLOROSILANE AND TRIMETHYLCHLOROSILANE CATALYZED BY NaAlCl4/ZSM-5

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Disproportionation of dimethyldichlorosilane prepared with methyltrichlorosilane and trimethylchlorosilane catalyzed by AlCl3/ZSM-5, NaAlCl4/ZSM-5, NaAlCl4/Mg-ZSM-5 catalysts was calculated through MP2/6-31+G** and B3LYP/6-31+G** approaches. AlCl3/ZSM-5 catalyst performed better catalytic effect for the disproportionation whose activation energy in rate-determining step of its main reaction was 92.68 kJ mol⁻¹. But AlCl3/ZSM-5 catalyst has the disadvantages of subliming and dissolving in samples; NaAlCl4/ZSM-5 catalyst would reduce to AlCl3/ZSM-5 catalyst in reaction process, activation energies of which in forward and reverse reactions were Ea = 17 kJ mol⁻¹, Ear = 77 kJ mol⁻¹, respectively. The stability of NaAlCl4/ZSM-5 catalyst was higher than AlCl3/ZSM-5 catalyst; catalytic effect of NaAlCl4/Mg-ZSM-5 catalyst was not as good as AlCl3/ZSM-5 catalyst, which activation energy of rate-determining step in main reaction was 163 kJ mol⁻¹.

Keywords: NaAlCl4/ZSM-5, DFT, MP2, Dimethyldichlorosilane, Trimethylchlorosilane.

COMPUTATIONAL METHODS

The geometries for all the reactants, products, intermediates and transition states were fully optimized by density functional theory [6-9] at B3LYP/6-31+G** levels of which energies were corrected by the secondary perturbation MP2/6-31+G** method. The geometries for transition states were fully optimized by the eigen vector tracking method AM1 firstly and then further optimized by density functional theory (B3LYP/6-31+G**), certificated through vibration analysis and were calculated through intrinsic reaction curve (IRC), finally the energies were corrected by the secondary perturbation MP2/6-31+G** method again. All the calculations have been done by the GAUSSIAN 03 program in computing workstation of East China Jiaotong University.
RESULTS AND DISCUSSION

**AlCl₃/ZSM-5 catalyst:** Roohi and Jahantab [10] proposed a kind of metal-exchanged M-ZSM-5 modern. Metal atoms were connected with two O atoms. Because of the symmetry structure of ZSM-5, we replaced metal atoms with AlCl₃ and Mg. It is known that the protonic acid H which connected on O atom can combine with Cl atom, so it appeared -AlCl₂ group in the structure. However, -AlCl₂ group has been reported to be an active site by Kelly [11] and Basset [12]. Reaction process and procedure of disproportionation in methyltrichlorosilane and trimethylchlorosilane (M3) that AlCl₃/ZSM-5 catalyst participated as shown in Fig. 1. Reaction process mainly divided into two channels: in channel 1 trimethylchlorosilane reacted...
to AlCl/ZSM-5 catalyst firstly, going through the transition state TS1, generating intermediate I (CH3AlCl/ZSM-5) and dimethylchlorosilane. And methyltrichlorosilane reacted to intermediate I though transition state TS2, reducing AlCl3/ZSM-5 catalyst and the main product dimethylchlorosilane. The channel 1 was the main channel in reaction process the first step of the channel was rate-determining step that activation energy was 93 kJ mol⁻¹; channel 2 was that methyltrichlorosilane reacted to AlCl/ZSM-5 catalyst by functional group interconversion firstly, yielding the intermediate I (CH3AlCl2/ZSM-5) and chemical byproduct silicon tetrachloride, then M3 reacted to I(CH3AlCl/ZSM-5) reducing AlCl3/ZSM-5 catalyst and byproduct tetramethyl silane.

**NaAlCl4/ZSM-5 catalyst:** Fig. 2 showed the reaction process of NaAlCl4/ZSM-5 complex catalyst. When NaCl and AlCl3/ZSM-5 were close to each other in reaction process, they would form supramolecular combination R. As the reaction was going on, the bond length of Na and Cl grew gradually to 2.5580 Å from 2.4110 Å, at the same time Cl attacked number Al, and they were together gradually each other. Sodium attacked Cl and their distance was continuously shortening, formatting the transition state (TS). Then the bond length of Na and Cl2 gradually elongated to 2.6590 Å from original 2.4110 Å and finally break generating product (P). The structure parameter of complex salt P in above equation was different from the structure of AlCl3/ZSM-5 catalyst. We can find clearly that the plane constituting by Al1-Cl1 and Al1-Cl2 deflected from original verticality to the plane of O1-Al1,O2-Al2 and the bond length of Al1-Cl2 enlarged to 2.3390 Å from original 2.0700 Å. The bond length of Al1-Cl enlarged to 2.3390 Å from original 2.0700 Å, which indicated rechlorination of AlCl3/ZSM-5 catalyst could make the bond for Al-Cl of AlCl3/ZSM-5 activate, so as to dechlorination easily and disproportionation happened more easily. Moreover angle of Cl1-Na-Cl2, Cl2-Na-Cl3 and Cl3-Na-Cl1 were 79.77°, 76.58°, 77.72°, respectively, there were little difference among these three angles of Cl1-Na-Cl2, Cl2-Na-Cl3 and Cl3-Na-Cl1. The structure composed of Na and above three chlorines was tetrahedron similarly, which that especial structure can quite increase the stability of catalysts. The bond length of Al-O1, Al1-O2 decreased to 1.8380 Å, 1.8190 Å from 1.8890 Å, 1.8890 Å separately, which indicated rechlorination of AlCl3/ZSM-5 catalyst can make the structure of AlCl3/ZSM-5 catalyst more stable and lower the risk of dealumination. After rechlorination the oxygen bridge in ZSM-5 cluster would gathered up slightly, the angle of O1-Al1-O2 would decreased to 81.07° from original 84.48°, which make activate location of the catalyst react to reaction system and select reactive molecules in reaction process more easily. Baenziger [13] pointed out that NaAlCl4 is an ionic system and select reactive molecules in reaction process more easily. Moreover interaction, so melting point and boiling point of the NaAlCl4 crystal which combined with each other by electrostatic dealuminization. After rechlorination the oxygen bridge in ZSM-5 cluster would gathered up slightly, the angle of O1-Al1-O2 would decreased to 81.07° from original 84.48°, which make activate location of the catalyst react to reaction system and select reactive molecules in reaction process more easily. Baenziger [13] pointed out that NaAlCl4 is an ionic system and select reactive molecules in reaction process more easily. Moreover interaction, so melting point and boiling point of the NaAlCl4 crystal which combined with each other by electrostatic agreement with outcomes of previous experimentations. When NaAlCl/ZSM-5 catalyst reacted, NaAlCl/ZSM-5 would first reduce to AlCl3/ZSM-5 catalyst and NaCl, showing the active location of Lewis acid which reacted to methyl of M1 and M3 and they exchanged with each other, afterward AlCl3/ZSM-5 catalyst and NaCl complexed to NaAlCl4/ZSM-5 catalyst. It was both resistance of running off active components and little influence to catalytic effect. The activation energies for forward and reverse reactions of NaAlCl/ZSM-5 catalyst calculated were $E_a = 17$ kJ mol⁻¹, $E_u = 77$ kJ mol⁻¹, respectively as shown in Fig. 2.

**NaAlCl4/Mg-ZSM-5 catalyst:** Reaction process and procedure of disproportionation in ethyltrichlorosilane and trimethylchlorosilane that NaAlCl4/Mg-ZSM-5 catalyst participated as shown in the Fig. 1. The spacing trend of key atoms along intrinsic reaction curve were calculated as shown in Fig. 3. indicating that the reaction process of NaAlCl/Mg-ZSM-5 catalyst was indeed, as shown in Fig. 2. The calculated outcomes were that NaAlCl/Mg-ZSM-5 catalyst first transform to AlCl3/Mg-ZSM-5 catalyst then reacted to M3 producing intermediate (CH3AlCl/Mg-ZSM-5) and main product M2 and the intermediate (CH3AlCl/Mg-ZSM-5) reacted to M1 generating M2, reducing intermediate (CH3AlCl/Mg-ZSM-5) to AlCl3/Mg-ZSM-5 catalyst, which was the whole catalytical reaction process and also was the main reaction of the disproportionation, the rate-determining step was the first step of the
above reaction process of which the active energy was 162.52 kJ mol\(^{-1}\). The intrinsic reaction curve of AlCl\(_3\)/Mg-ZSM-5 and AlCl\(_3\)/ZSM-5 catalyst participated reaction as shown in Fig. 4. It is clear that the catalytic activity of modified AlCl\(_3\)/ZSM-5 catalyst is weaker than the AlCl\(_3\)/ZSM-5 catalyst through the active energies. Fig. 4 showed that the AlCl\(_3\)/ZSM-5 catalyst modified by metal Mg was not appropriate for disproportionation with M1 and M3 for which the reason was acid strength of ZSM-5 zeolite decreased because of Mg addition.

To further validate the catalytic effect of modified AlCl\(_3\)/ZSM-5 catalyst was not satisfactory, the frontier molecular orbital analyses of AlCl\(_3\)/ZSM-5, AlCl\(_3\)/Mg-ZSM-5, (CH\(_3\))\(_3\)SiCl, CH\(_3\)SiCl\(_3\), CH\(_3\)AlCl\(_2\)/ZSM-5, CH\(_3\)AlCl\(_2\)/Mg-ZSM-5 were calculated (Fig. 5).

Fig. 3. Spacing trend of key atoms along intrinsic reaction curve

Fig. 4. Intrinsic reaction curve of AlCl\(_3\)/Mg-ZSM-5 and AlCl\(_3\)/ZSM-5 catalyst participated reaction (kJ/mol)

because the electronic configurations of molecules were changed due to metal Mg addition and decreasing the electronic cloud density of the active location-AlCl\(_3\), weakening the Lewis acid activity of catalyst. The contribution rates of molecular LUMO orbital from key atoms were calculated by Hirshfeld method as shown in Table-2. The contribution rate of Al\(_1\) atom from Lewis
acid location on ZSM-5 zeolite to LUMO orbital decreased to 0.0191 % from original 4.104 % and the contribution rates of Cl1, Cl2 atoms connected with Al1 atom to LUMO orbital decreased to 0.0031 % and 0.0028 % from original 0.1440 %, 95.37 %, respectively. The constitution of LUMO orbital was high percentage of 82.74 % mainly from Mg atom. The acid strength of catalyst decreased because of Mg addition, comparing to AlCl3/ZSM-5 catalyst.

Conclusion

Reaction process of dimethyldichlorosilane prepared disproportionated with methyltrichlorosilane and trimethylchlorosilane catalyzed by AlCl3/ZSM-5, NaAlCl3/ZSM-5, NaAlCl3/Mg-ZSM-5 catalysts was investigated by MP2/6-31++G** and B3LYP/6-31++G** methods. Following conclusions were drawn: (1) AlCl3/ZSM-5 catalyst had better catalytic effect for the disproportionation but it dissolves in samples easily. (2) NaAlCl3/ZSM-5 catalyst would convert to AlCl3/ZSM-5 catalyst firstly when NaAlCl3/ZSM-5 catalyst reacted, however the stability of NaAlCl3/ZSM-5 catalyst is higher than AlCl3/ZSM-5 catalyst. The activation energies calculated of NaAlCl3/ZSM-5 catalyst in forward and reverse reactions were Ea = 17kJ mol⁻¹, Ear = 77kJ mol⁻¹, respectively. (3) Catalytic activity of NaAlCl3/Mg-ZSM-5 catalyst was weaker than AlCl3/ZSM-5 and NaAlCl3/ZSM-5 catalysts, the reason was that acid strength of ZSM-5 zeolite decreased because of Mg addition.

<table>
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<tr>
<th>Catalyst</th>
<th>AlCl3/ZSM-5</th>
<th>AlCl3/Mg-ZSM-5</th>
<th>CH3SiCl3</th>
<th>CH3AlCl2/ZSM-5</th>
<th>CH3AlCl2/Mg-ZSM-5</th>
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<td>HOMO (eV)</td>
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<td>-0.03516</td>
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<tr>
<td>LUMO (eV)</td>
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<td>-0.04963</td>
<td>-0.4333</td>
<td>-0.0834</td>
<td>-0.27980</td>
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<th>AlCl3/Mg-ZSM-5</th>
<th>CH3SiCl3</th>
<th>CH3AlCl2/ZSM-5</th>
<th>CH3AlCl2/Mg-ZSM-5</th>
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<td>Key atom</td>
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<td>Cl1</td>
<td>Cl2</td>
<td>Al1</td>
<td>Mg</td>
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<tr>
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<td>0.1440</td>
<td>95.37</td>
<td>0.0370</td>
<td>82.74</td>
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TABLE 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>AlCl3/ZSM-5</th>
<th>AlCl3/Mg-ZSM-5</th>
<th>CH3SiCl3</th>
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<td>-0.0834</td>
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</tr>
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</table>

TABLE 2

Acknowledgements

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References