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.

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 can be prepared to be double salt NaAlCl₄ of the supported catalyst, we would solve the above problem. Experiment [4] indicated that the catalytic effect of NaAlCl₄-ZSM-5 and AlCl₃/ZSM-5 catalyst was approximate, but the stability of complex catalyst was better than AlCl₃/ZSM-5. In order to explain the result of the experiment, this paper discussed that the reaction mechanism of the disproportionation with complex catalyst. Yu *et al*. [5] studied

acidity and catalytic activity of Mg-ZSM-5 catalyst, finding that the strong Brønsted acid strength of ZSM-5 zeolite gradually weaken and Lewis acid gradually strengthen. Our paper discussed that the disproportionation was just as catalyzed by Lewis acid, so we proposed that adding metal Mg to ZSM-5 zeolite could increase the catalytic activity of ZSM-5 zeolite and the paper also researched the action mechanism of NaAlCl₄/Mg-ZSM-5 catalyst.

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 strucrure. 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
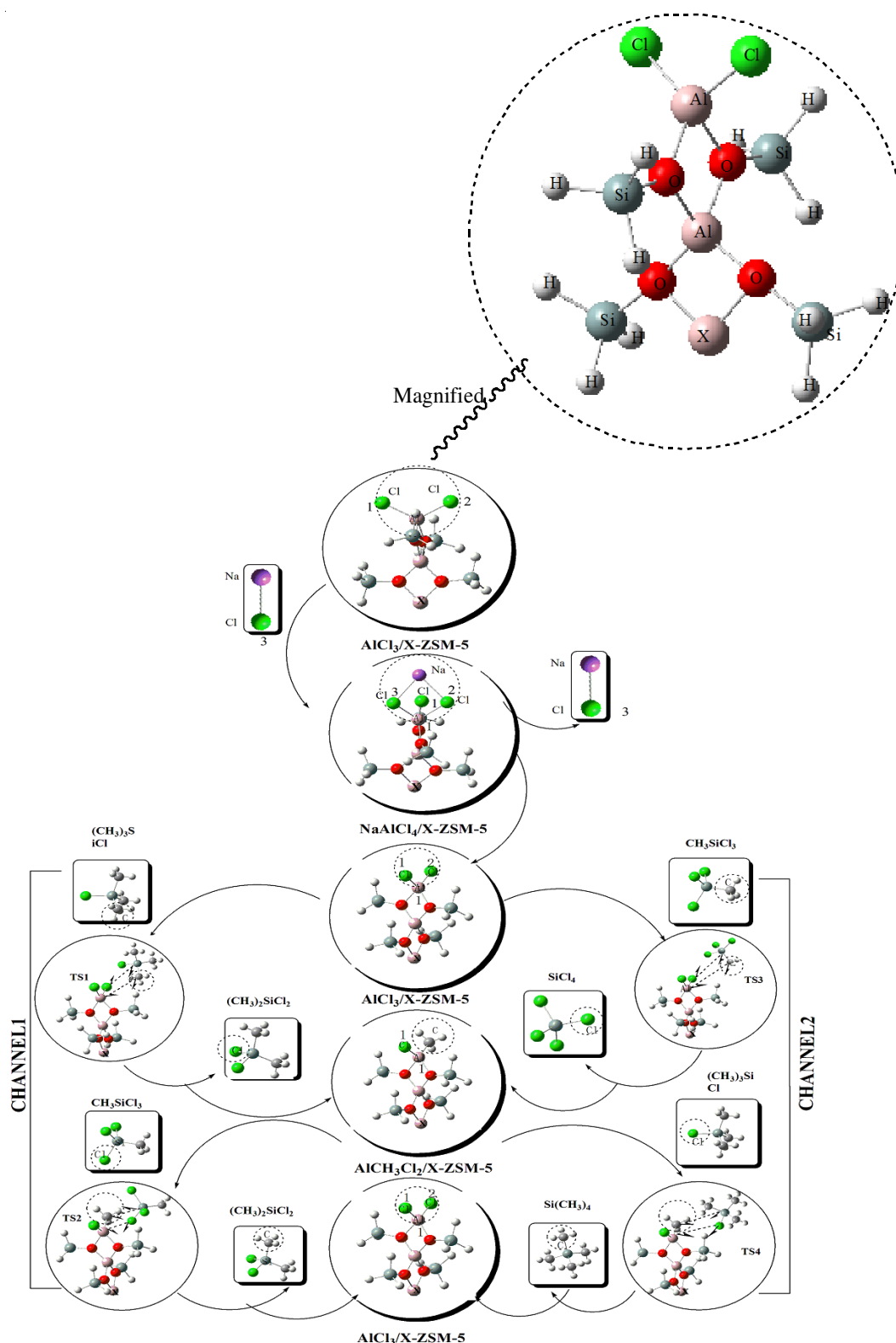

Fig. 1. Molecular structures and reaction process of overall reaction (X is the modified location of ZSM-5)

to $AlCl_3$/ZSM-5 catalyst firstly, going through the transition state TS1, generating intermediate I (CH_3AlCl_2/ZSM-5) and dimethyldichlorosilane. And methyltrichlorosilane reacted to intermediate I though transition state TS2, reducing $AlCl_3$/ZSM-5 catalyst and the main product dimethyldichlorosilane. 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 methyltrichloro-silane reacted to $AlCl_3$/ZSM-5 catalyst by functional group interconversion firstly, yielding the intermediate I (CH_3AlCl_2/ZSM-5) and chemical byproduct silicon tetrachloride, then M3 reacted to I(CH_3AlCl_2/ZSM-5) reducing $AlCl_3$/ZSM-5 catalyst and byproduct tetramethyl silane.

NaAlCl_4/ZSM-5 catalyst: Fig. 2 showed the reaction process of $NaAlCl_4$/ZSM-5 complex catalyst. When NaCl and $AlCl_3$/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_3 gradually elongated to 2.5580 Å from 2.4110 Å, at the same time Cl_3 attacked number Al_1 and they were together gradually each other. Sodium attacked Cl_2 and their distance was continuously shortening, formatting the transition state (TS). Then the bond length of Na and Cl_3 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 $AlCl_3$/ZSM-5 catalyst. We can find clearly that the plane constituting by Al_1-Cl_1 and Al_1-Cl_2 deflected from original verticality to the plane of O_1-Al_1,O_2-Al_2 and the bond length of Al_1-Cl_1 magnified to 2.3030 Å from original 2.2070 Å. The bond length of Al_1-Cl_2 enlarged to 2.3390 Å from original 2.2070 Å, which indicated rechlorination of $AlCl_3$/ZSM-5 catalyst could make the bond for Al-Cl of $AlCl_3$/ZSM-5 catalyst activate, so as to dechlorination easily and disproportionation happened more easily. Moreover angle of Cl_1-Na-Cl_2, Cl_2-Na-Cl_3 and Cl_3-Na-Cl_1 were 79.77°, 76.58°, 77.72°, respectively, there were little difference among these three angles of Cl_1-Na-Cl_2, Cl_2-Na-Cl_3 and Cl_3-Na-Cl_1. 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_2-O_1, Al_2-O_1 decreased to 1.8380 Å, 1.8190 Å from 1.8890 Å, 1.8890 Å separately, which indicated rechlorination of $AlCl_3$/ZSM-5 catalyst can make the structure of $AlCl_3$/ZSM-5 catalyst more stable and lower the risk of dealuminization. After rechlorination the oxygen bridge in ZSM-5 cluster would gathered up slightly, the angle of O_1-Al_1-O_2 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 $NaAlCl_4$ is an ionic crystal which combined with each other by electrostatic interaction, so melting point and boiling point of the $NaAlCl_4$ was higher than $AlCl_3$. There were positive and negative center on ZSM-5 which reacted to the molecular crystals $AlCl_3$ weaker, so the resistance of running off atom aluminum of complex salt catalyst was stronger. In a word, analyses from the configuration of $AlCl_3$/ZSM-5 catalyst and $NaAlCl_4$/ZSM-5 catalyst, we could come to conclusion that rechlorination of $AlCl_3$/ZSM-5 catalyst can enhance the stability of catalyst which was in

agreement with outcomes of previous experimentations. When $NaAlCl_4$/ZSM-5 catalyst reacted, $NaAlCl_4$/ZSM-5 would first reduce to $AlCl_3$/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, afterword $AlCl_3$/ZSM-5 catalyst and NaCl complexed to $NaAlCl_4$/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 $NaAlCl_4$/ZSM-5 catalyst calculated were E_a = 17 kJ mol^{-1}, E_{ar} = 77 kJ mol^{-1}, respectively as shown in Fig. 2.
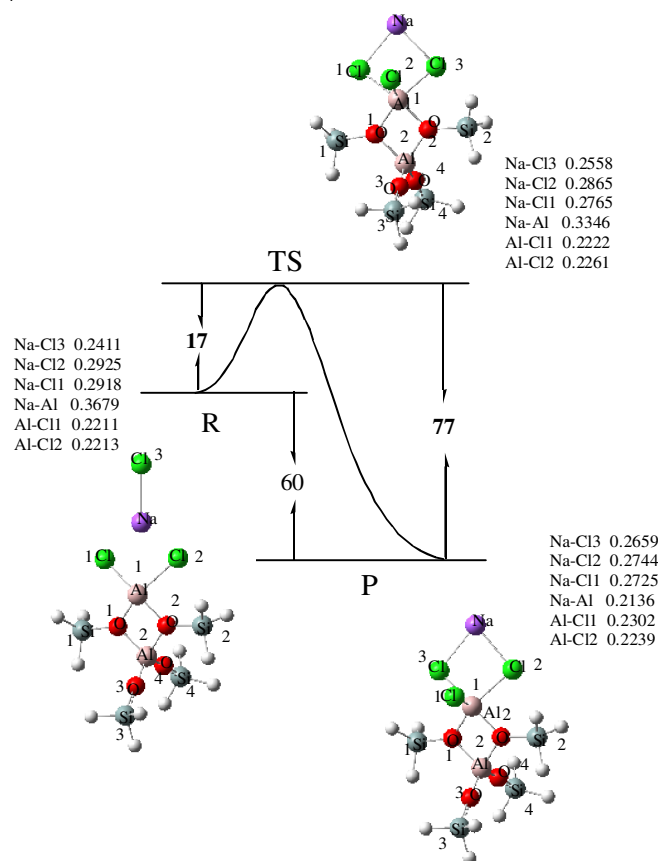

Fig. 2. Reaction process, geometrical parameters and intrinsic reaction curve of $NaAlCl_4$/ZSM-5 [bond lengths (Å) and energies (kJ/mol)]

NaAlCl_4/Mg-ZSM-5 catalyst: Reaction process and procedure of disproportionation in ethyltrichlorosilane and trimethylchlorosilane that $NaAlCl_4$/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 $NaAlCl_4$/Mg-ZSM-5 catalyst was indeed, as shown in Fig. 2. The calculated outcomes were that $NaAlCl_4$/Mg-ZSM-5 catalyst first transform to $AlCl_3$/Mg-ZSM-5 catalyst then reacted to M3 producing intermediate (CH_3AlCl_2/Mg-ZSM-5) and main product M2 and the intermediate (CH_3AlCl_2/Mg-ZSM-5) reacted to M1 generating M2, reducing intermediate (CH_3AlCl_2/Mg-ZSM-5) to $AlCl_3$/Mg-ZSM-5 catalyst, which was the whole catalytic reaction process and also was the main reaction of the disproportionation, the rate-determining step was the first step of the
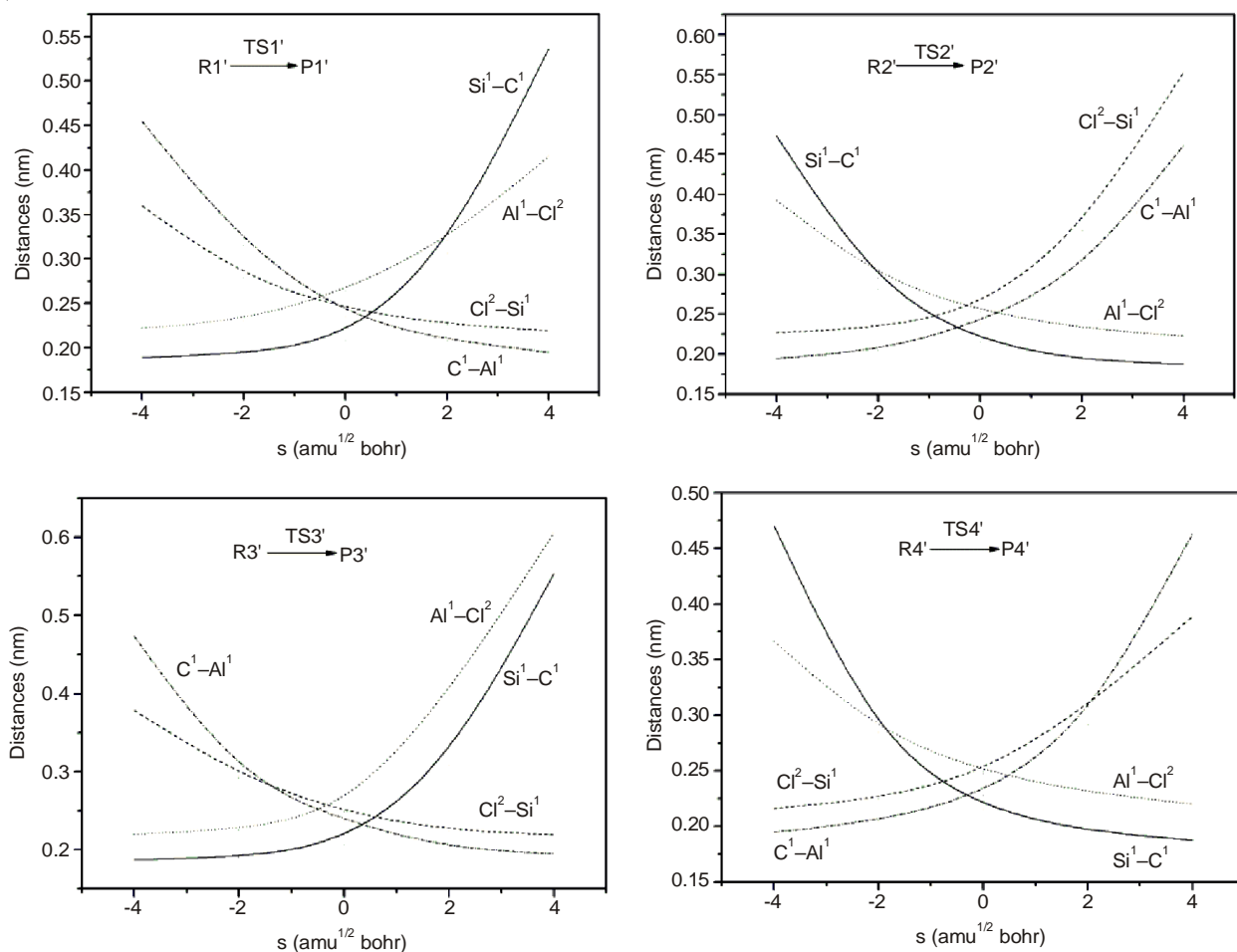
Fig. 3. Spacing trend of key atoms along intrinsic reaction curve

above reaction process of which the active energy was 162.52 kJ mol⁻¹. The intrinsic reaction curve of AlCl₃/Mg-ZSM-5 and AlCl₃/ZSM-5 catalyst participated reaction as shown in Fig. 4. It is clear that the catalytic activity of modified AlCl₃/ZSM-5 catalyst is weaker than the AlCl₃/ZSM-5 catalyst through the active energies. Fig. 4 showed that the AlCl₃/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 AlCl₃/ZSM-5 catalyst was not satisfactory, the frontier molecular orbital analyses of AlCl₃-ZSM-5, AlCl₃/Mg-ZSM-5, (CH₃)₃SiCl, CH₃SiCl₃, CH₃AlCl₂/ZSM-5, CH₃AlCl₂/Mg-ZSM-5 were calculated (Fig. 5).

Frontier molecular orbitals of interactants in the reaction are shown in Fig. 5 and the HOMO and LUMO orbital level values are listed in Table-1. According to the principle of similar energy, reaction mainly happened at the LUMO orbitals of AlCl₃/ZSM-5 catalyst and AlCl₃/Mg-ZSM-5 catalyst and the HOMO orbital of (CH₃)₃SiCl molecule which interacted on each other and the LUMO orbitals of the intermediates CH₃AlCl₂/ZSM-5, CH₃AlCl₂/Mg-ZSM-5 reacted to the HOMO orbital of CH₃SiCl₃ molecule in reaction process. The electronic cloud density of LUMO orbital from AlCl₃/Mg-ZSM-5 catalyst and the intermediate CH₃AlCl₂/Mg-ZSM-5 mostly concentrate on Mg atom around, but the electronic cloud density of the active location-AlCl₂ of the disproportionation decreased
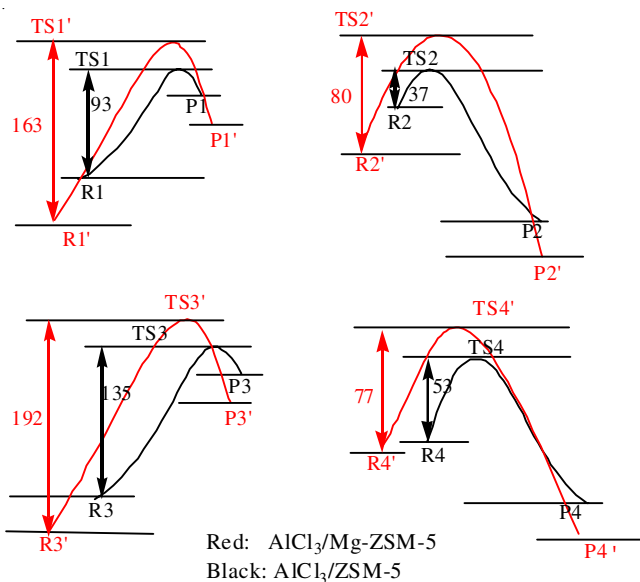
Fig. 4. Intrinsic reaction curve of AlCl₃/Mg-ZSM-5 and AlCl₃/ZSM-5 catalyst participated reaction (kJ/mol)

because the electronic configurations of molecules were changed due to metal Mg addition and decreasing the electronic cloud density of the active location-AlCl₂, 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 Al₁ atom from Lewis
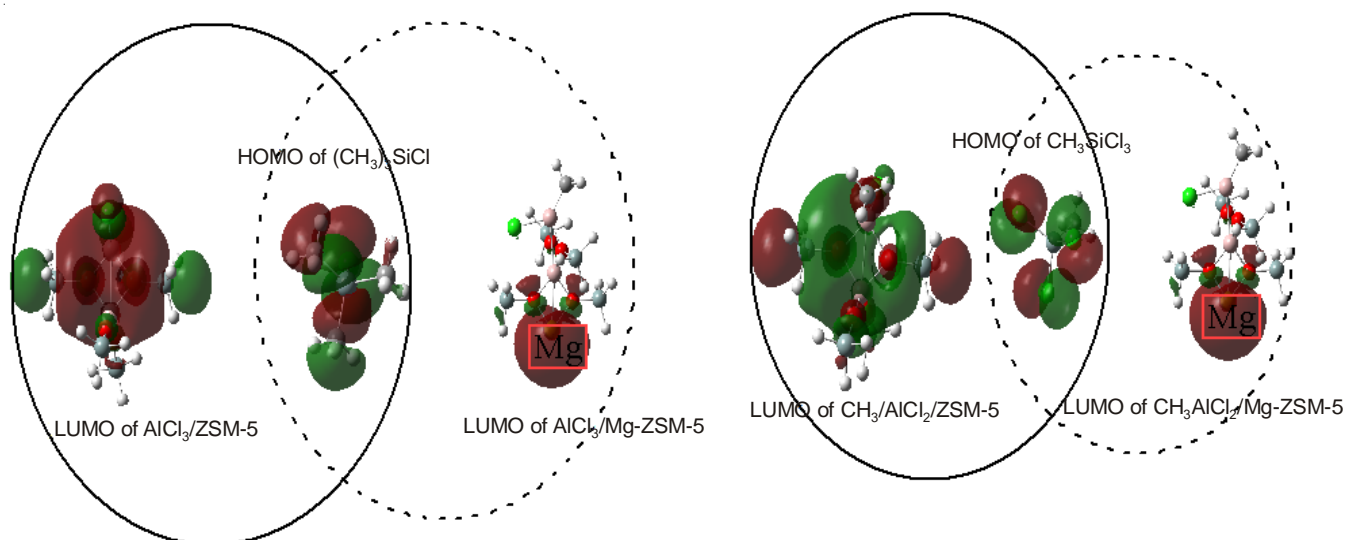
Fig. 5. Frontier molecular orbital

	(CH₃)₃SiCl	AlCl₃/ZSM-5	AlCl₃/Mg-ZSM-5	CH₃SiCl₃	CH₃AlCl₂/ZSM-5	CH₃AlCl₂/Mg-ZSM-5
HOMO (ev)	-0.2917	-0.28780	-0.5170	-0.3371	-0.03516	-0.4203
LUMO (ev)	-0.0223	-0.04963	-0.4333	-0.0834	-0.27980	-0.5137

TABLE-2
CONTRIBUTION RATE OF MOLECULAR LUMO ORBITAL FROM KEY ATOMS CALCULATED BY HIRSHFELD METHOD (%)

Catalyst	AlCl₃/ZSM-5			AlCl₃/Mg-ZSM-5			
Key atom	Al₁	Cl₁	Cl₂	Al₁	Mg	Cl₁	Cl₂
Contribution rate	4.104	0.1440	95.37	0.0370	82.74	0.0031	0.0028

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 disproportionatedly with methyltrichlorosilane and trimethylchlorosilane catalyzed by AlCl₃/ZSM-5, NaAlCl₄/ZSM-5, NaAlCl₄/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) NaAlCl₄/ZSM-5 catalyst would convert to AlCl₃/ZSM-5 catalyst firstly when NaAlCl₄/ZSM-5 catalyst reacted, however the stability of NaAlCl₄/ZSM-5 catalyst is higher than AlCl₃/ZSM-5 catalyst. The activation energies calculated of NaAlCl₄/ZSM-5 catalyst in forward and reverse reactions were E_a = 17kJ mol⁻¹, E_{ar} = 77kJ mol⁻¹, respectively. (3) Catalytic activity of NaAlCl₄/Mg-ZSM-5 catalyst was weaker than AlCl₃/ZSM-5 and NaAlCl₄/ZSM-5 catalysts, the reason was that acid strength of ZSM-5 zeolite decreased because of Mg addition.

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