

Theoretical Study for Disproportionation of Dimethyldichlorosilane Catalyzed by NaAlCl₄/X-ZSM-5

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The most important monomer dimethyldichlorosilane can be prepared by disproportionating trimethylchlorosilane with methyltrichlorosilane. The geometries of product were optimized by density functional theory through B3LYP/LanL2DZ and B3LYP/6-31++G(3df,2pd) approaches. Iron and boron have been added into catalyst in order to rise up the activity of Lewis acid, but not all of them would work. Conclusion are as follows: the rate-determining step of main reaction catalyzed by NaAlCl₄/Fe²⁺-ZSM-5 and NaAlCl₄/(FeCl₂)⁺-ZSM-5 is the reaction of absorbing trimethylchlorosilane. The rate-determining step of main reaction catalyzed by NaAlCl₄/(BCl₂)⁺-ZSM-5 is the reaction that methyltrichlorosilane absorb intermediate (CH₃AlCl₂)/(AlCl₂)⁺-ZSM-5). The activation energies of three reactions are 443.7756, 267.3725 and 175.0666 kJ mol⁻¹ respectively. The introduction of (BCl₂)⁺ is good for reaction running but Fe²⁺ and (FeCl₂)⁺ are not. It matches well with frontier orbital analysis.

Keywords: NaAlCl₄/ZSM-5, Dimethyldichlorosilane, Disproportionation, Density functional theory.

INTRODUCTION

Fregert and Rorsman [1] reported silicone high-performance materials, its mainly inorganic structure chain, with organic groups as side chain. It possesses the advantages of the inorganic and organic compounds [2] and its top priority was to monomer dimethyldichlorosilane [3] (referred to M2). As the demand of the market of M2 was increasing, the direct synthesis method products by-product, namely, more and more methyltrichlorosilane (referred to M1) and trimethylchlorosilane (referred to M3). So it received much concern to how to make wasteful methyltrichlorosilane and trimethylchlorosilane to dimethyldichlorosilane profitable. Previous experiments [4,5] had put AlCl₃ into double salt NaAlCl₄. NaAlCl₄ was first restored to NaCl and AlCl₃ in the reaction. It was equal that the catalytic effect was contributed by AlCl₃. It didn't influence catalytic effect, but also avoid the loss of catalyst active component. ZSM-5 was loaded by AlCl₃ replaced proton H and released HCl, forming -AlCl₂ catalytic activity of Lewis acid site [6]. Previous workers [7,8] indicated that the introduction of Fe and B could strengthen Lewis acid of catalysts. The disproportionated reaction which is main concern of this study was just catalyzed by Lewis acid, so we imagined that the introduction of Fe²⁺, (FeCl₂)⁺ and (BCl₂)⁺ could increase the catalytic activity of NaAlCl₄/ZSM-5 by DFT [9] and MP2 [10].

COMPUTATIONAL METHODS

The geometries for all the reactants, products, intermediates and transition states were fully optimized by density functional theory [11-15] 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 Eigen vector tracking method AM1 firstly and then further optimized by density functional theory (B3LYP/6-31++G**), certified through vibration analysis and were calculated through IRC [16]. Finally, the energies were corrected by secondary perturbation MP2/6-31++G** method again. All the calculations have been done by the GAUSSIAN 09 [17] program (Rev E01) and Gaussian view, ChemBioDraw [18] in computing workstation of East China Jiaotong University, Nan Chang, P.R. China.

RESULTS AND DISCUSSION

The key atoms number and reaction process of disproportionated reaction in M1 and M3 that AlCl₃/ZSM-5 catalyst participated as shown in Fig. 1. First double salt NaAlCl₄/ZSM-5 was reduced to AlCl₃/ZSM-5 and NaCl and Lewis acid active site AlCl₂ was appeared. It marked the beginning of the reaction. Reaction process mainly divided into two channels: in channel 1, M3 reacted to AlCl₃/ZSM-5 catalyst firstly, going through the

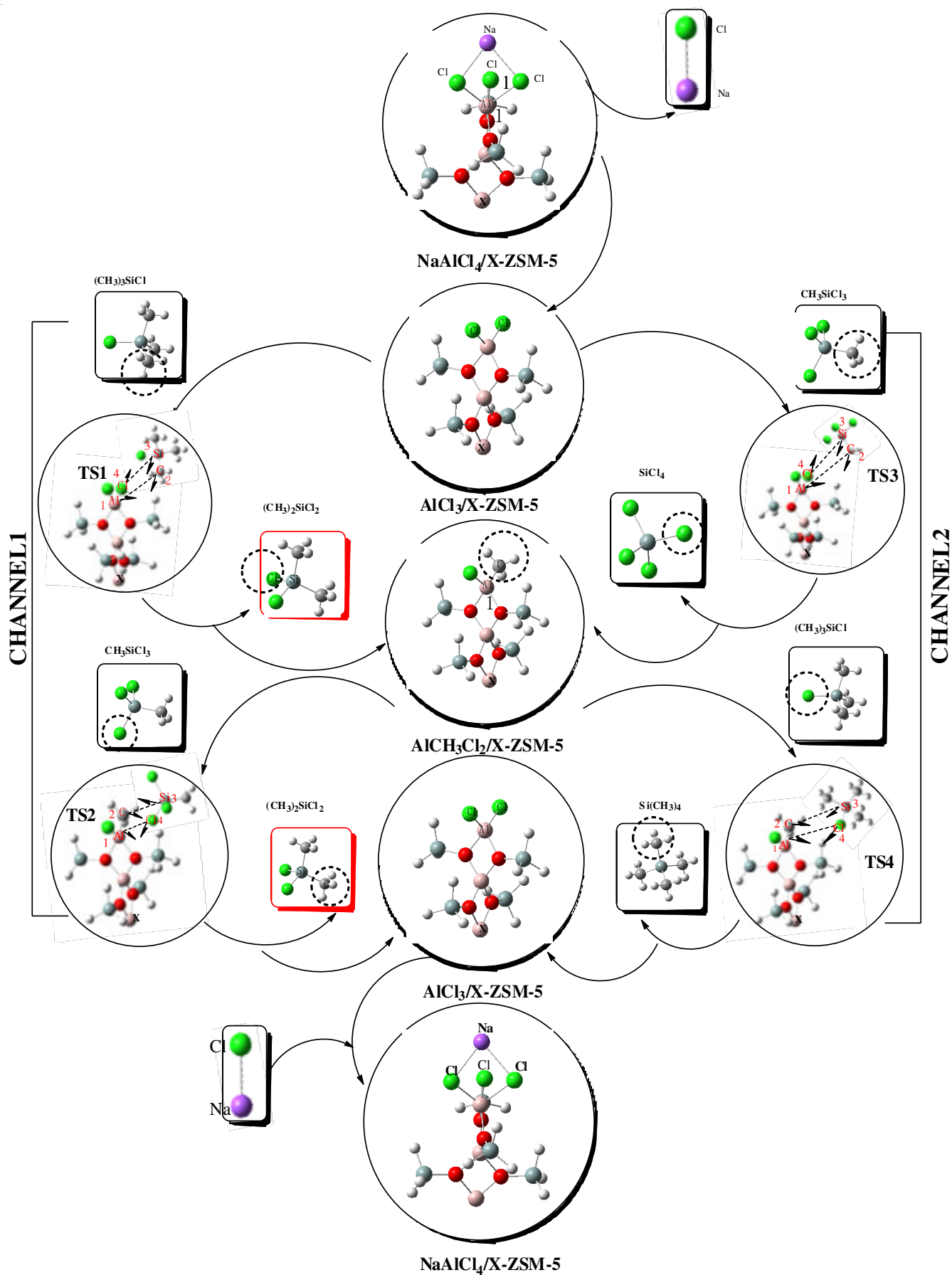


Fig. 1. Key atomic number, imaginary vibration mode of transition state and reaction process [X representatives Fe^{2+} , $(\text{FeCl}_2)^+$ and $(\text{BCl}_2)^+$]

transition state TS1, generating intermediate I ($\text{CH}_3\text{AlCl}_2/\text{ZSM-5}$) and M2. And M1 reacted to intermediate I through transition state TS2, producing $\text{AlCl}_3/\text{ZSM-5}$ catalyst and the main product M2. The channel 1 was the main channel in reaction process; channel 2 was that M1 reacted to $\text{AlCl}_3/\text{ZSM-5}$ catalyst by functional group interconversion firstly, yielding the intermediate I ($\text{CH}_3\text{AlCl}_2/\text{ZSM-5}$) and chemical byproduct silicon tetrachloride, then M3 reacted to I ($\text{CH}_3\text{AlCl}_2/\text{ZSM-5}$) producing $\text{AlCl}_3/\text{ZSM-5}$ catalyst and byproduct tetramethylsilane (referred to M4). Finally, $\text{AlCl}_3/\text{X-ZSM-5}$ can combine with NaCl into double salts, participating the reaction in cycle.

It expressed catalyst Cat.1, Cat.2 and Cat.3 (Cat.1 representatives $\text{NaAlCl}_4/\text{Fe}^{2+}\text{-ZSM-5}$; Cat.2 representatives $\text{NaAlCl}_4/(\text{FeCl}_2)^+\text{-ZSM-5}$; Cat.3 representatives $\text{NaAlCl}_4/(\text{BCl}_2)^+\text{-ZSM-5}$) the spacing trend of key atoms along IRC in Fig. 2. From the reaction beginning to end the distance of key atoms had the trends of shortening or lengthening, which confirmed the right connection of reactants and products. So the transition states we calculated also have been confirmed. Take $\text{R1} \rightarrow \text{P1}$ as example and contrasted with virtual vibration model of TS1 in Fig. 1, bond $\text{C}^2\text{-Si}^3$ in M3 and bond $\text{Al}^1\text{-Cl}^4$ in $\text{NaAlCl}_4/\text{ZSM-5}$ were broken, then the bond distance present trends of lengthening. However, Al^1 , C^2 and Si^3 , Cl^4 gradually closed to form

new keys, then the bond distance present trends of shortening. It also applied similarly to other figure analysis.

According to preliminary study [19,20], activation energy of various reaction steps which $\text{NaAlCl}_4/\text{ZSM-5}$ participated was 243.31 and 271.18 kJ mol^{-1} . Each step of catalyst Cat.1, Cat.2 and Cat.3 modified heat of reaction and activation energy in Fig. 3. As shown in illustration from the Fig. 3, in channel 1 the rate-determining step was M3 reacted to Cat.1 and Cat.2 catalyst separately, going through the transition state TS1 and TS1*, but the transition state TS2** for Cat.3 catalyst. Their activation energy were 443.78, 267.37 and 176.42 kJ mol^{-1} separately. Compared with the rate-determining step of side reaction in channel 2, going through the transition state TS3 (TS3* and TS3**). Their activation energy were 357.29, 322.15 and 292.85 kJ mol^{-1} . The modified Cat.1 catalyst favoured the side reaction, but Cat.2 and Cat.3 catalyst also favoured the happening of side mainly reaction. Compared with the previous data, the activation energy of main reaction increases a little, but it decreased obviously for Cat.3 catalyst. Hence, the catalytic activity of Cat.1 and Cat.2 catalyst was weaker than Cat.3 catalyst, indicating that $\text{NaAlCl}_4/\text{ZSM-5}$ catalyst modified by Fe was not appropriate for disproportionated reaction with M1 and M3 for which the reason was acidity of ZSM-5 zeolite decreased because of Fe addition. To further

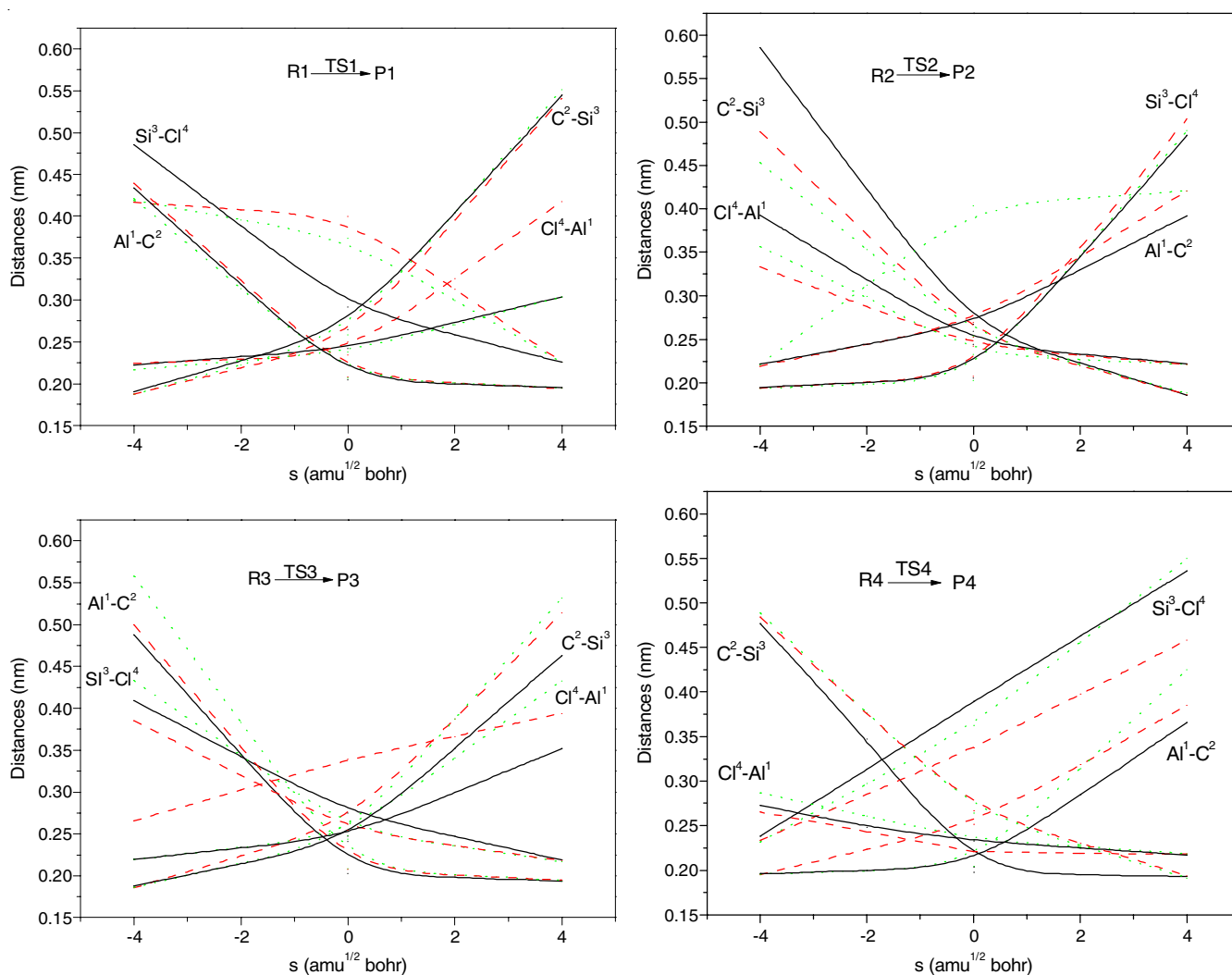


Fig. 2. Spacing trend of key atoms along IRC (----- representatives Cat.¹; representatives Cat.²; representatives Cat.³)

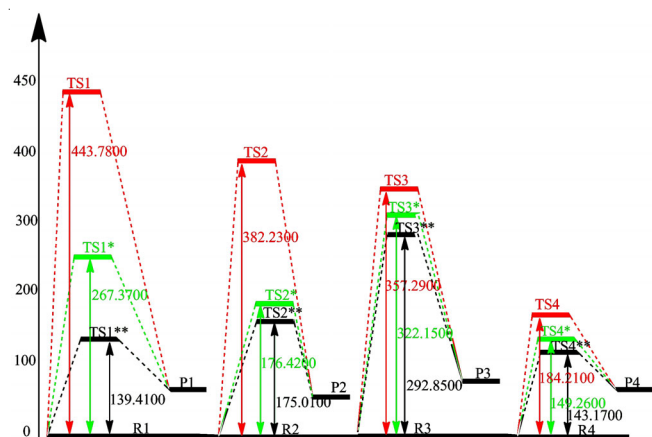


Fig. 3. Energy profiles in catalytic system

validate above presumption, we have analyzed their bond order by LOL contained Mayer bond order of Al-Cl and four center bond order of Al, Cl, O⁴ and O⁵ atom in Fig. 4.

Fig. 4 showed that the mayer bond order in numerical order was Cat.2 > Cat.2 > Cat.3. It illustrated that Mayer bond order of Cat.3 was minimum and so Al-Cl was more fragmented. The four center bond order of Al, Cl, O⁴ and O⁵ in numerical order was Cat.3 > Cat.2 > Cat.1. It illustrated that

four center bond order of Cat.3 was maximum and most stable situation. So the stability of framework of each catalyst in numerical order was Cat.3 > Cat.2 > Cat.1. Hence, it is presumed that Cat.3 catalyst had best catalytic activity and matched with energy analysis. From LOL analysis, compared with Cat.1 and Cat.2 that Al-Cl being within area of baby blue, Cat.3 was within area of dark blue, index of the locality was much more lager and Al-Cl was more easy to fragment. From being within framework area of Al, Cl, O⁴ and O⁵ atoms colour, index of the locality in numerical order was Cat.3 > Cat.2 > Cat.1, the stability of framework of Al, Cl, O⁴ and O⁵ in numerical order was Cat.3 > Cat.2 > Cat.1, matched with Al-Cl Mayer bond order and four center bond order of Al, Cl, O⁴, O⁵. From Al-Cl Mayer bond order, four center bond order of Al, Cl, O⁴ and O⁵, LOL analysis and energy analysis, it demonstrated that Cat.3 had the best catalyst activity.

To further validate above presumption, the frontier molecular orbital analyses of each catalyst were calculated (Fig. 5). The reason may be the introduction of Fe weak Lewis acid of ZSM-5 zeolite, for validation it, the frontier molecular orbital analyses were calculated (Fig. 5).

According to the principle of similar energy, the reaction mainly happened at the LUMO orbitals of Cat.1, Cat.2 and Cat.3 catalyst and the HOMO orbital of (CH₃)₃SiCl molecule

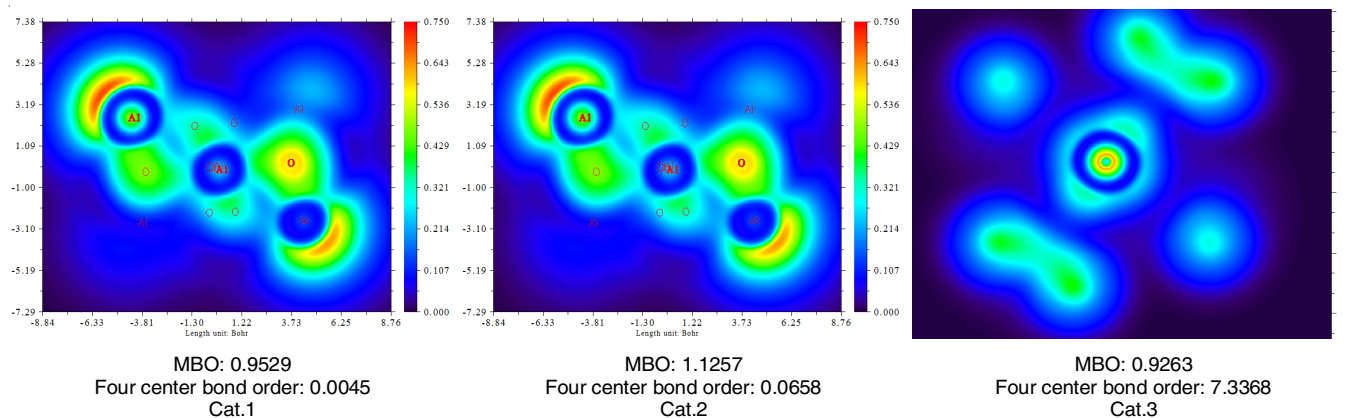
(TS1-TS4representatives Cat.¹, TS1*-TS4*representatives Cat.², TS1**-TS4**representatives Cat.³)

Fig. 4. LOL analysis of catalyst

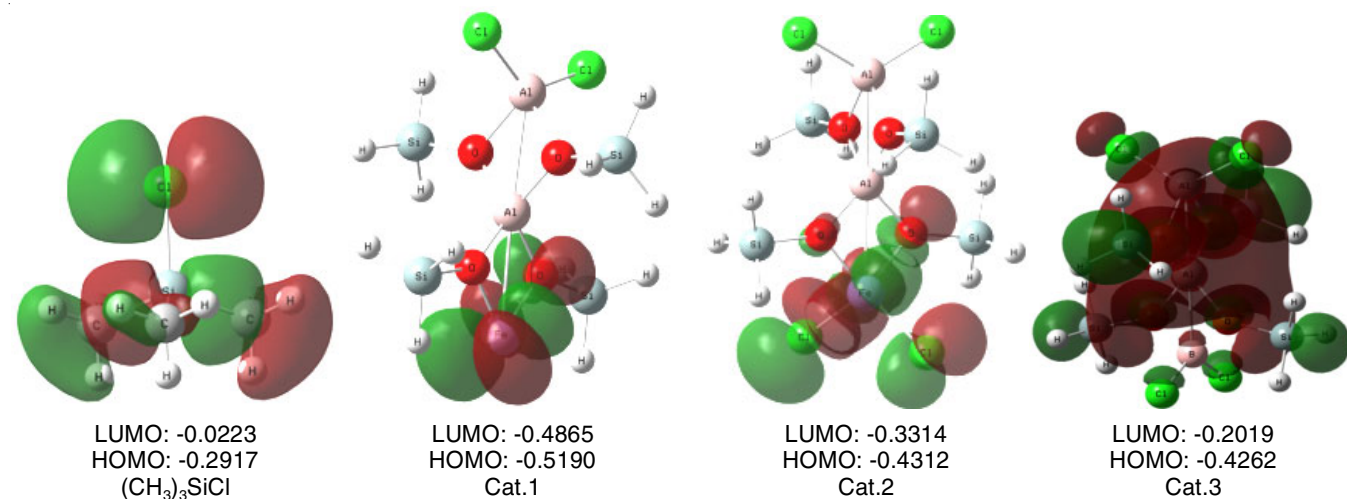
Fig. 5. Configuration of HOMO in (CH₃)₃SiCl and LUMO in Cat.1, Cat.2and Cat.3

TABLE-1
CONTRIBUTION RATE OF MOLECULAR LUMO ORBITAL FROM KEY ATOMS CALCULATED BY HIRSHFELD METHOD (%)

NaAlCl ₄ /ZSM-5			NaAlCl ₄ /Fe ²⁺ -ZSM-5				NaAlCl ₄ /(FeCl ₂) ⁺ -ZSM-5				NaAlCl ₄ /(BCl ₂) ⁺ -ZSM-5			
Al ¹	Cl ¹	Cl ²	Al ¹	Cl ¹	Cl ²	Fe	Al ¹	Cl ¹	Cl ²	Fe	Al ¹	Cl ¹	Cl ²	B
0.21	0.095	0.019	0.019	0.0328	0.0216	89.944	0.0191	0.019	0.0064	57.11	9.47	4.48	4.47	-

which interacted on each other and the LUMO orbitals of the intermediates Cat.1, Cat.2 and Cat.3 reacted to the HOMO orbital of CH₃SiCl₃ molecule in reaction process. The energy level difference that LUMO orbitals of (CH₃)₃SiCl and the HOMO orbital of Cat.1, Cat.2 and Cat.3 was 0.5413, 0.0397 and 0.4535 eV separately. But the electronic cloud density of LUMO orbital from Cat.1 and Cat.2 catalyst mostly concentrate on Fe atom around and the electronic cloud density of the active location-AlCl₂ of the disproportionation decreased due to the addition of Fe atom. This decreased the electronic cloud density of the active location -AlCl₂ and weakened Lewis acid activity of catalyst. However, we can forecast that B will be a good new active site which can be calculated in the follow-up work. The electronic cloud density of LUMO orbital from NaAlCl₄/AlCl₂²⁺-ZSM-5 and CH₃AlCl₂/AlCl₂²⁺-ZSM-5 mostly concentrated on the middle of molecule and distribute evenly on the two -AlCl₂ groups which declare that -AlCl₂ will be a good new active site. The electronic cloud density of LUMO orbital from Cat.3 catalyst and the intermediates CH₃AlCl₂/(BCl₂)⁺-ZSM-5 distributed evenly on -AlCl₂ and (BCl₂)⁺ group. It declared that (BCl₂)⁺ will be a good new active site. The contribution rates of molecular LUMO orbital from key atoms were calculated by Hirshfeld method as shown in Table-1. Because of the addition of Fe²⁺, (FeCl₂)⁺ and (BCl₂)⁺, the contribution rate of Lewis acid activity (-AlCl₂) atoms to LUMO orbital have increased. But the amplitude from Fe²⁺ and (FeCl₂)⁺ is low which can be ignored. On the contrary, the contribution rate concentrate on Fe and reach up to 89.9435%. The addition of Fe atom weaken the Lewis acid activity of catalyst. But the addition of (BCl₂)⁺, the contribution rates of Cl¹, Cl² atoms connected with Al¹ to LUMO orbital increase to 4.48% and 4.47% from original 0.095% and 0.118% respectively. Besides, the contribution rate of new added atom Al¹ to LUMO orbital increases to 9.47% from original 0.210%, which is considerable. It also confirm that the AlCl₂ will be a good new active site.

Conclusions

Reaction process of dimethyldichlorosilane prepared disproportionatedly with methyltrichlorosilane and trimethylchlorosilane catalyzed by NaAlCl₄/Fe²⁺-ZSM-5, NaAlCl₄/(FeCl₂)⁺-ZSM-5 and NaAlCl₄/(BCl₂)⁺-ZSM-5 was investigated by DFT and MP2 methods. The following conclusions were drawn:

- Activation energies of rate-determining step of main reaction catalyzed by NaAlCl₄/Fe²⁺-ZSM-5, NaAlCl₄/(FeCl₂)⁺-ZSM-5 and NaAlCl₄/(BCl₂)⁺-ZSM-5 catalysts were 4443.78, 267.37 and 167.7224 kJ mol⁻¹, respectively. It is obvious that B has better catalytic activity than Fe atom.

- From LOL analysis of catalyst, NaAlCl₄/(BCl₂)⁺-ZSM-5 Mayer bond order was 0.9263 and four center bond order of Al, Cl, O⁴ and O⁵ was 7.3368. It has good catalyst activity.

- From the perspective of frontier orbital, the introduction of (BCl₂)⁺ increases active site -AlCl₂ the contribution rates of frontier orbital and also increased the catalytic activity of Lewis. On the contrary, Fe modified NaAlCl₄/ZSM-5 catalyst had worse catalytic effect, so the results of frontier orbital accord with activation energies.

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