Preparation and Redistribution Mechanism of Dimethyldichlorosilane Catalyzed by the AlCl₃/ZSM-5(5T)@MIL-53(Al) Core-Shell Catalyst

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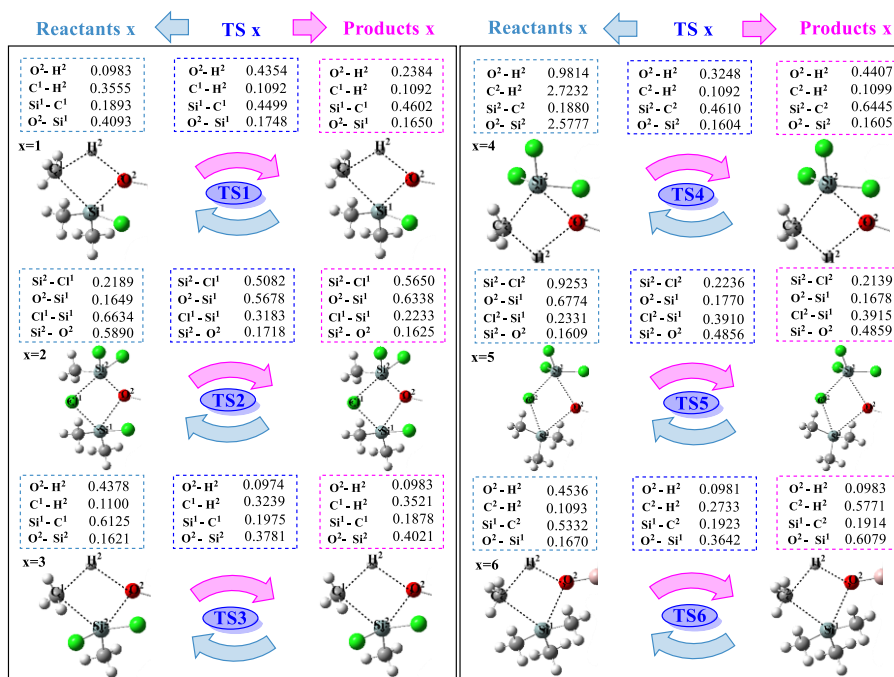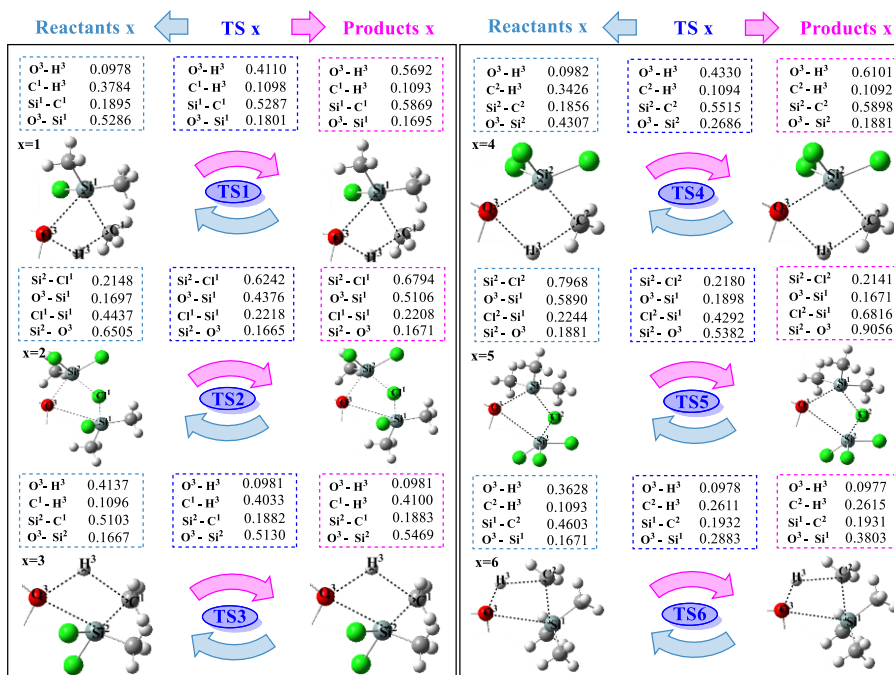
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Abstract: Dimethyldichlorosilane, which is the most important organic silicon monomer, can be prepared by using a novel core-shell catalyst. However, the redistributed mechanism is still a debate. In this research, the redistributed mechanism catalyzed by the ZSM-5(5T)@MIL-53(Al) catalyst was theoretically studied via the density functional theory (DFT) on the level of M06-2X/def2-TZVP. Then, the catalytic performances of different active centers modification with AlCl₃ were evaluated. The results showed that the active center of the former was Brønsted acid, while that of the latter one modified by AlCl₃ was Lewis acid. In addition, the catalytic activity could be improved by Lewis acid in comparison with Brønsted acid. The calculations of activation energy, frequency vibrational analysis, bond order analysis, frontier molecular orbital theory, electronic localization function (ELF) and localized orbital locator (LOL) analyses were well agreed with the said mechanism and results.

3. Results and discussion

3.1. ZSM-5(5T)@MIL-53(Al) Core-shell catalyst

The corresponding reaction transition state structure model of active site 2-4 at each step is shown in Figure. S1-S3. The key atom markers are consistent with active site 1. Also, the reactants in the route, the transition states, and the bond lengths or distances of the products are included. The transition states at each step come mainly from stretching vibrations between key atoms. The transition state TSx was calculated in both Forward and Reverse directions, and finally the reactant Rx and the product Px were found. It is found that the longitudinal length or radial extension vibrations between the key atoms are equivalent which confirms the authenticity of all transition state structures.

Reactants x ← **TS x** → **Products x** (left panel) and **Reactants x** ← **TS x** → **Products x** (right panel)

x=1 (TS1)

Reactants		TS		Products	
O^2-H^2	0.0983	O^2-H^2	0.4354	O^2-H^2	0.2384
C^1-H^2	0.3555	C^1-H^2	0.1092	C^1-H^2	0.1092
Si^1-C^1	0.1893	Si^1-C^1	0.4499	Si^1-C^1	0.4602
O^2-Si^1	0.4093	O^2-Si^1	0.1748	O^2-Si^1	0.1650

x=4 (TS4)

Reactants		TS		Products	
O^2-H^2	0.9814	O^2-H^2	0.3248	O^2-H^2	0.4407
C^2-H^2	2.7232	C^2-H^2	0.1092	C^2-H^2	0.1099
Si^2-C^2	0.1880	Si^2-C^2	0.4610	Si^2-C^2	0.6445
O^2-Si^2	2.5777	O^2-Si^2	0.1604	O^2-Si^2	0.1605

x=2 (TS2)

Reactants		TS		Products	
Si^2-Cl^1	0.2189	Si^2-Cl^1	0.5082	Si^2-Cl^1	0.5650
O^2-Si^1	0.1649	O^2-Si^1	0.5678	O^2-Si^1	0.6338
Cl^1-Si^1	0.6634	Cl^1-Si^1	0.3183	Cl^1-Si^1	0.2233
Si^2-O^2	0.5890	Si^2-O^2	0.1718	Si^2-O^2	0.1625

x=5 (TS5)

Reactants		TS		Products	
Si^2-Cl^2	0.9253	Si^2-Cl^2	0.2236	Si^2-Cl^2	0.2139
O^2-Si^1	0.6774	O^2-Si^1	0.1770	O^2-Si^1	0.1678
Cl^2-Si^1	0.2331	Cl^2-Si^1	0.3910	Cl^2-Si^1	0.3915
Si^2-O^2	0.1609	Si^2-O^2	0.4856	Si^2-O^2	0.4859

x=3 (TS3)

Reactants		TS		Products	
O^2-H^2	0.4378	O^2-H^2	0.0974	O^2-H^2	0.0983
C^1-H^2	0.1100	C^1-H^2	0.3239	C^1-H^2	0.3521
Si^1-C^1	0.6125	Si^1-C^1	0.1975	Si^1-C^1	0.1878
O^2-Si^2	0.1621	O^2-Si^2	0.3781	O^2-Si^2	0.4021

x=6 (TS6)

Reactants		TS		Products	
O^2-H^2	0.4536	O^2-H^2	0.0981	O^2-H^2	0.0983
C^2-H^2	0.1093	C^2-H^2	0.2733	C^2-H^2	0.5771
Si^1-C^2	0.5332	Si^1-C^2	0.1923	Si^1-C^2	0.1914
O^2-Si^1	0.1670	O^2-Si^1	0.3642	O^2-Si^1	0.6079

Figure. S1. The virtual vibrational mode diagrams of the transition states of Cat.* (active site No.2)

Reactants x ← **TS x** → **Products x** (left panel) and **Reactants x** ← **TS x** → **Products x** (right panel)

x=1 (TS1)

Reactants		TS		Products	
O^3-H^3	0.0978	O^3-H^3	0.4110	O^3-H^3	0.5692
C^1-H^3	0.3784	C^1-H^3	0.1098	C^1-H^3	0.1093
Si^1-C^1	0.1895	Si^1-C^1	0.5287	Si^1-C^1	0.5869
O^3-Si^1	0.5286	O^3-Si^1	0.1801	O^3-Si^1	0.1695

x=4 (TS4)

Reactants		TS		Products	
O^3-H^3	0.0982	O^3-H^3	0.4330	O^3-H^3	0.6101
C^2-H^3	0.3426	C^2-H^3	0.1094	C^2-H^3	0.1092
Si^2-C^2	0.1856	Si^2-C^2	0.5515	Si^2-C^2	0.5898
O^3-Si^2	0.4307	O^3-Si^2	0.2686	O^3-Si^2	0.1881

x=2 (TS2)

Reactants		TS		Products	
Si^2-Cl^1	0.2148	Si^2-Cl^1	0.6242	Si^2-Cl^1	0.6794
O^3-Si^1	0.1697	O^3-Si^1	0.4376	O^3-Si^1	0.5106
Cl^1-Si^1	0.4437	Cl^1-Si^1	0.2218	Cl^1-Si^1	0.2208
Si^2-O^3	0.6505	Si^2-O^3	0.1665	Si^2-O^3	0.1671

x=5 (TS5)

Reactants		TS		Products	
Si^2-Cl^2	0.7968	Si^2-Cl^2	0.2180	Si^2-Cl^2	0.2141
O^3-Si^1	0.5890	O^3-Si^1	0.1898	O^3-Si^1	0.1671
Cl^2-Si^1	0.2244	Cl^2-Si^1	0.4292	Cl^2-Si^1	0.6816
Si^2-O^3	0.1881	Si^2-O^3	0.5382	Si^2-O^3	0.9056

x=3 (TS3)

Reactants		TS		Products	
O^3-H^3	0.4137	O^3-H^3	0.0981	O^3-H^3	0.0981
C^1-H^3	0.1096	C^1-H^3	0.4033	C^1-H^3	0.4100
Si^2-C^1	0.5103	Si^2-C^1	0.1882	Si^2-C^1	0.1883
O^3-Si^2	0.1667	O^3-Si^2	0.5130	O^3-Si^2	0.5469

x=6 (TS6)

Reactants		TS		Products	
O^3-H^3	0.3628	O^3-H^3	0.0978	O^3-H^3	0.0977
C^2-H^3	0.1093	C^2-H^3	0.2611	C^2-H^3	0.2615
Si^1-C^2	0.4603	Si^1-C^2	0.1932	Si^1-C^2	0.1931
O^3-Si^1	0.1671	O^3-Si^1	0.2883	O^3-Si^1	0.3803

Figure. S2. The virtual vibrational mode diagrams of the transition states of Cat.* (active site No.3)

Reactants x	TS x	Products x	Reactants x	TS x	Products x

x=1

O^4-H^4	0.0989	O^4-H^4	0.3826	O^4-H^4	0.4944
C^1-H^4	0.3168	C^1-H^4	0.1096	C^1-H^4	0.1096
Si^1-C^1	0.1189	Si^1-C^1	0.4984	Si^1-C^1	0.7244
O^4-Si^1	0.3400	O^4-Si^1	0.1641	O^4-Si^1	0.1641

x=4

O^4-H^4	0.0985	O^4-H^4	0.4212	O^4-H^4	0.5068
C^2-H^4	0.7770	C^2-H^4	0.1096	C^2-H^4	0.1095
Si^2-C^2	0.1880	Si^2-C^2	0.5600	Si^2-C^2	0.7269
O^4-Si^2	0.9411	O^4-Si^2	0.1605	O^4-Si^2	0.1605

x=2

Si^2-Cl^1	0.2194	Si^2-Cl^1	0.3815	Si^2-Cl^1	0.4773
O^4-Si^1	0.1643	O^4-Si^1	0.3935	O^4-Si^1	0.6815
Cl^1-Si^1	0.4804	Cl^1-Si^1	0.2214	Cl^1-Si^1	0.2197
Si^2-O^4	0.5148	Si^2-O^4	0.1625	Si^2-O^4	0.1612

x=5

Si^2-Cl^1	0.6584	Si^2-Cl^1	0.2232	Si^2-Cl^1	0.2137
O^4-Si^1	0.4602	O^4-Si^1	0.1758	O^4-Si^1	0.1659
Cl^2-Si^1	0.2257	Cl^2-Si^1	0.4862	Cl^2-Si^1	0.7027
Si^2-O^4	0.1607	Si^2-O^4	0.5442	Si^2-O^4	0.9049

x=3

O^4-H^4	1.0330	O^4-H^4	0.0987	O^4-H^4	0.0985
C^2-H^4	0.1093	C^1-H^4	0.3374	C^1-H^4	0.4768
Si^2-C^1	0.9675	Si^1-C^1	0.1971	Si^1-C^1	0.1883
O^4-Si^2	0.1614	O^4-Si^2	0.4117	O^4-Si^2	0.7414

x=6

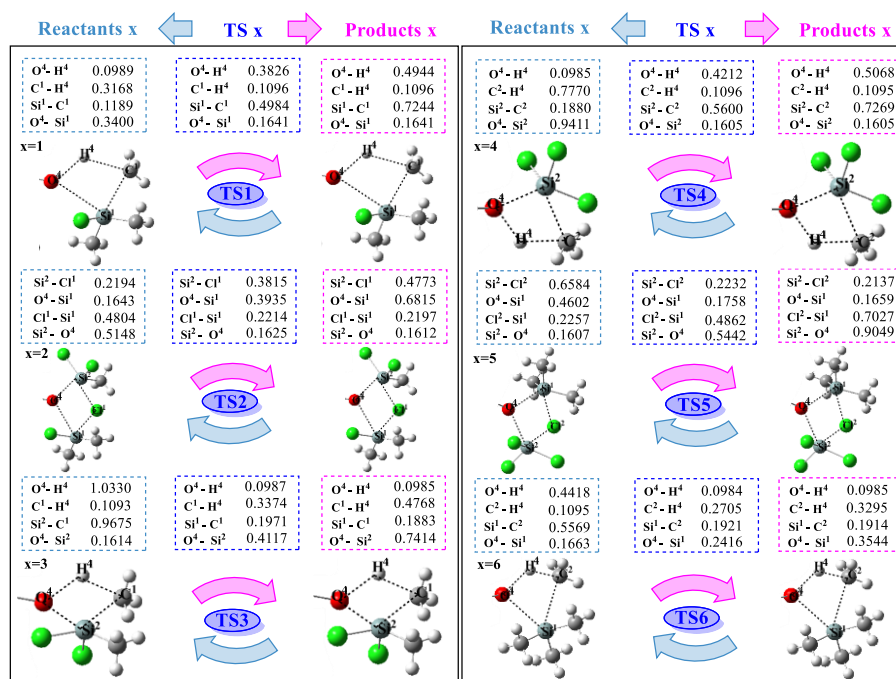| O^4-H^4 | 0.4418 | O^4-H^4 | 0.0984 | O^4-H^4 | 0.0985 |
C^2-H^4	0.1095	C^2-H^4	0.2705	C^2-H^4	0.3295
Si^1-C^2	0.5569	Si^1-C^2	0.1921	Si^1-C^2	0.1914
O^4-Si^1	0.1663	O^4-Si^1	0.2416	O^4-Si^1	0.3544

Figure. S3. The virtual vibrational mode diagrams of the transition states of Cat.[*] (active site No.4)