Acid Strength Controlled Reaction Pathways for the Catalytic Cracking of 1-Pentene to Propene over ZSM-5

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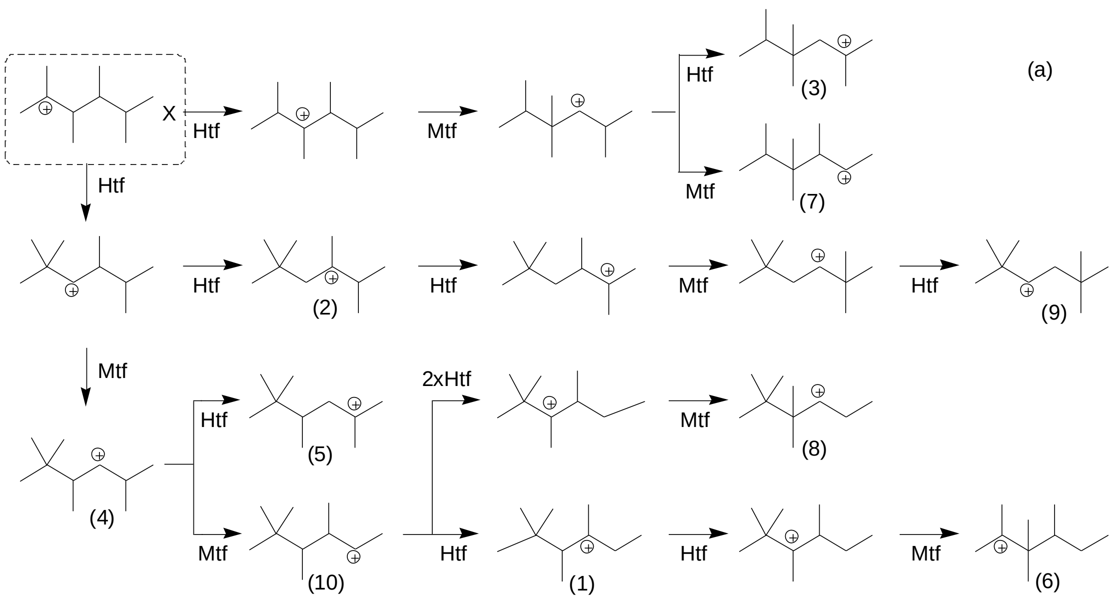
The conservation of mass and carbon atoms

Since in theoretical analysis, the foundation was the law of conservation of carbon atoms, practically, it was necessary to demonstrate the conservation of mass before and after reactions. Figure S1 showed TG curves of five ZSM-5(142) samples after reactions at different temperature. There were two kinds of desorption temperature-dependent weight loss, ranging from 200 to 350 °C and from 500 to 700 °C which were attributed to soft coke and refractory coke respectively [1, 2]. From the TG curves (Figure S1), the amounts of the formed coke on the five samples were all small (< 3%). Therefore coke was neglected when we verified the law of conservation of mass. Table S1 showed carbon atom and the total mass conservation before and after catalytic cracking of 1-pentene over ZSM-5(142) at different temperature. At the reaction temperatures from 450 to 550 °C, the total mass of output was around 7 g h^{-1} which was consistent with the input (7.121 g h^{-1}). In addition, the carbon atom of input was 0.509 mol h^{-1}, while the output from 450 to 550 °C were 0.493, 0.488, 0.502, 0.494 and 0.487 mol h^{-1} respectively, clearly demonstrating the conservation of carbon atom. It was found that the output mass were always a little smaller than the input mass. This missing mass should be caused by a small coke formation. The coke yields were 2.9%, 3.7%, 1.0%, 2.7% and 3.9%, respectively, which were consistent with the results from TG curves (Figure S1).

Before verifying the effect of acid strength, it is also necessary to demonstrate the conservation of mass and carbon atoms. From TG curves (Figure S2), we can see that the amounts of the formed coke on the five samples were all small (< 3%). So we would not take the coke formation into account when demonstrating the conservation of mass and carbon atoms. Table S2 showed carbon atom and the total mass conservation before and after catalytic cracking of 1-pentene over Z-1 – Z-5. The input carbon atoms and input total mass were 0.509 mol h^{-1} and 7.121 g h^{-1} respectively. The output carbon atoms over Z-1 – Z-5 were 0.498, 0.505, 0.481, 0.493 and 0.486 mol h^{-1} respectively, which fitted well with the input value. The output total mass was close to 7.121 g h^{-1}, clearly demonstrating the conservation of mass. A little lower output mass than input mass was also caused by coke formation, and the coke yields were 1.8%, 0.4%, 5.1%, 2.9% and 4.1%, respectively, which were consistent with the results from TG curves (Figure S2).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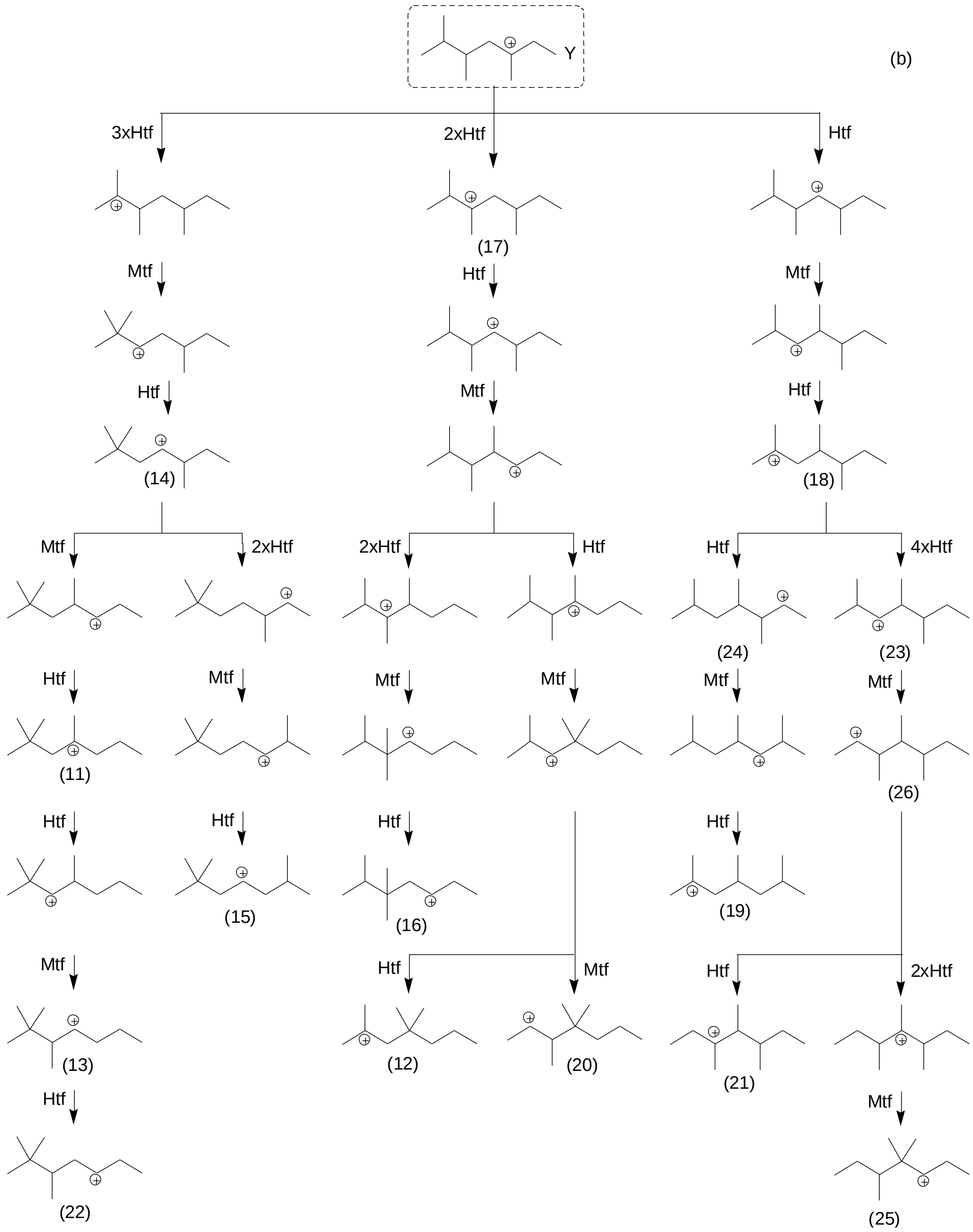

Scheme S1. Reaction Scheme of Formation of Various Decyl Carbenium Ions for the Production of Butenes and Hexenes through Type A, B or C B-Scission over ZSM-5: (a) Isomerization of Decyl Carbenium X, (b) Isomerization of Decyl Carbenium Y[a].

[a]Abbreviations: Htf, hydrogen transfer; Mtf, methyl transfer.

Table S1. Conservation of Carbon Atom and Mass before and after Catalytic Cracking of 1-Pentene over ZSM-5(142) at Different Temperatures[a].

T	carbon atom (mol h^{-1})		mass (g h^{-1})	
(°C)	input	output	input	output
450	0.509	0.493	7.121	6.918
475	0.509	0.488	7.121	6.858
500	0.509	0.502	7.121	7.052
525	0.509	0.494	7.121	6.932
550	0.509	0.487	7.121	6.841

[a]Reaction conditions: cat., 1.0 g; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 7.68 h^{-1}; TOS = 0.5 h.

Table S2. Conservation of Carbon Atom and Mass before and after Catalytic Cracking of 1-Pentene over Z-1 – Z-5[a].

zeolite	carbon atom (mol h^{-1})		mass (g h^{-1})	
	input	output	input	output
Z-1	0.509	0.498	7.121	6.995
Z-2	0.509	0.505	7.121	7.095
Z-3	0.509	0.481	7.121	6.760
Z-4	0.509	0.493	7.121	6.918
Z-5	0.509	0.486	7.121	6.828

[a]Reaction conditions: cat., 1.0 g; temp., 450 °C; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 7.68 h^{-1}; TOS = 0.5 h.

Table S3. Results of Catalytic Cracking of 1-Butene at Different Temperature over Z-1[a].

T (^{o}C)	conv.($C_4^=$) (mol %)	sel. (mol %)								P/E (mol)
		$C_2^=$	$C_3^=$	$C_5^=$	$C_6^=$	$C_1^0 + C_2^0$	$C_3^0 – C_5^0$	H_2	arom	
450	64.7	10.6	59.9	14.7	6.2	0.1	6.8	0.4	1.3	5.7
500	55.7	14.4	60.5	14.2	4.2	0.3	5.2	0.5	0.8	4.2
550	46.5	18.3	59.0	13.7	3.4	0.6	4.0	0.6	0.4	3.2

[a]Reaction conditions: cat., Z-1, 1.0 g; pressure, 0.1 MPa; 1-butene flow rate, 40 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 6.0 h^{-1}; TOS = 1.5 h.

Table S4. Results of Catalytic Cracking of 1-Pentene at Different Temperature over Z-1[a].

T	conv.($C_5^=$)	sel. (mol %)								P/E	P/B
(°C)	(mol %)	$C_2^=$	$C_3^=$	$C_4^=$	$C_6^=$	$C_1^0 + C_2^0$	$C_3^0 - C_5^0$	H_2	arom	(mol)	(mol)
400	78.6	7.5	33.8	34.4	9.7	0.1	10.1	0.5	3.8	4.5	1.0
450	85.2	12.2	41.8	31.3	5.6	0.1	6.9	0.4	1.8	3.4	1.3
500	86.7	27.2	41.0	24.2	2.4	0.3	3.3	0.5	1.2	1.5	1.7

[a]Reaction conditions: cat., Z-1, 1.0 g; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 7.68 h^{-1}; TOS = 0.5 h.

Table S5. Reaction Results of Catalytic Cracking of Different Feedstock over Z-1.

feedstock	conv.($C_4^=$) (mol %)	conv.($C_5^=$) (mol %)	sel. (mol %)									P/E (mol)
			$C_2^=$	$C_3^=$	$C_4^=$	$C_5^=$	$C_6^=$	C_1^0 + C_2^0	$C_3^0 – C_5^0$	H_2	arom.	
Butene[a]	55.7	—	14.4	60.5	—	14.2	4.2	0.3	5.2	0.5	0.9	4.2
Pentene[b]	—	86.7	27.2	41.0	24.2	—	2.4	0.3	3.3	0.5	0.9	1.5

[a]Reaction conditions: cat., Z-1, 1.0 g; temp., 500 °C; pressure, 0.1 MPa; 1-butene flow rate, 40 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; TOS = 1.5 h.

[b]Reaction conditions: cat., Z-1, 1.0 g; temp., 500 °C; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; TOS = 0.5 h.

Table S6. Results of Catalytic Cracking of 1-Butene at Different Temperature over Z-5[a].

T (^{o}C)	conv.($C_4^=$) (mol %)	sel. (mol %)								P/E (mol)
		$C_2^=$	$C_3^=$	$C_5^=$	$C_6^=$	$C_1^0 + C_2^0$	$C_3^0 - C_5^0$	H_2	arom.	
400	77.7	14.8	36.5	9.5	8.9	0.3	23.9	1.0	5.2	2.5
450	80.3	22.8	39.5	5.8	4.9	0.7	19.2	1.7	5.3	1.7
500	81.5	29.5	42.6	3.6	2.9	1.4	12.6	2.8	4.7	1.5
550	85.2	34.6	39.7	1.7	1.4	2.7	9.2	5.1	5.7	1.2

[a]Reaction conditions: cat., Z-5, 1.0 g; pressure, 0.1 MPa; 1-butene flow rate, 40 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 6.0 h^{-1}; TOS = 1.5 h.

Table S7. Results of Catalytic Cracking of 1-Pentene at Different Temperature over Z-5[a].

T	conv.($C_5^=$)	sel. (mol %)								P/E	P/B
(°C)	(mol %)	$C_2^=$	$C_3^=$	$C_4^=$	$C_6^=$	$C_1^0 + C_2^0$	$C_3^0 - C_5^0$	H_2	arom.	(mol)	(mol)
450	94.1	20.5	31.3	17.5	4.3	0.7	18.5	2.1	5.0	1.5	1.8
500	96.1	27.9	30.8	12.4	1.8	1.9	13.7	4.5	7.3	1.1	2.5
550	98.3	37.2	27.7	7.6	0.4	4.6	8.7	8.9	4.9	0.7	3.7

[a]Reaction conditions: cat., Z-5, 1.0 g; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 7.68 h^{-1}; TOS = 0.5 h.

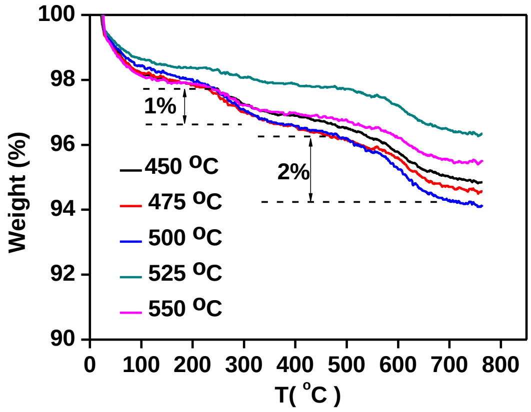

Figure S1. TG Curves of ZSM-5(142) Zeolites Which Have Been Used in the Catalytic Cracking of 1-Pentene for 1.5 h at 450 to 550 °C.

Reaction conditions: cat., 1.0 g; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 7.68 h^{-1}.

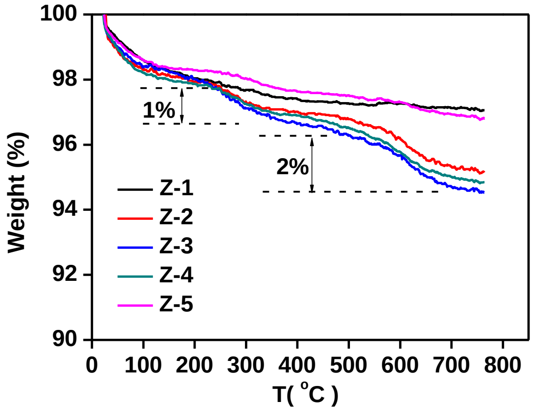

Figure S2. TG Curves of Z-1 – Z-5 Which Have Been Used in the Catalytic Cracking of 1-Pentene for 1.5 h.

Reaction conditions: cat., 1.0 g; temp., 450 °C; pressure, 0.1 MPa; 1-pentene flow rate, 0.2 mL min^{-1}; N_2 flow rate, 320 mL min^{-1}; WHSV, 7.68 h^{-1}.

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[1] Zhang, X. J.; Wang, Y.; Xin, F. *Appl. Catal. A Gen.* **2006**, *307*, 222-230.

[2] Ibáñez, M.; Artetxe, M.; Lopez, G.; Elordi, G.; Bilbao, J.; Olazar, M.; Castaño, P. *Appl. Catal. B: Environ.* **2014**, *148-149*, 436-445.