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Supporting Information

Rapid Screening of Gas Catalysts in Methane Activation Using ICP-QQQ-MS

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1. The selectivities of C_2H_4 and C_2H_6 catalyzed by different gas ions catalysts in ICP-QQQ-MS system

The relationship between the MS intensities (at m/z =28 and 30) and the concentrations of C_2H_4 and C_2H_6 in standard mix gas were shown in Fig.S2 and Fig.S3, respectively. According to the linear relationship in Fig.S2 and Fig.S3, the concentrations of C_2H_4 and C_2H_6 formed by CH_4 activation by different gas ions catalysts in ICP-QQQ-MS system could be calculated.

The selectivities of C_2H_4 and C_2H_6 were calculated as follows:

$S(C_2H_4)$ =2Concentration(C_2H_4)/Consumed concentration(CH_4);

$S(C_2H_6)$ =2Concentration(C_2H_6)/Consumed concentration(CH_4).

However, the consumed concentration of CH_4 in ICP-QQQ-MS system could not be precisely calculated. To semi-quantitative estimation of the selectivities of C_2H_4 and C_2H_6, $S1(C_2H_4)$ and $S1(C_2H_6)$ were used, which

$S1(C_2H_4)$ =2Concentration(C_2H_4)/Original concentration(CH_4);

$S1(C_2H_6)$ =2Concentration(C_2H_6)/Original concentration(CH_4).

Compared S and S1, it could be concluded that S should be higher than S1. The $S1(C_2H_4)$ and $S1(C_2H_6)$ catalyzed by different gas ions in ICP-QQQ-MS system were calculated in Table S2."

2. The calculation for conversion and selectivity by Se catalyst in DBD-GC system

According to Table 1, the conversion of methane induced by Se catalyst ($\Delta Conv_{CH4}$) was calculated as:

$\Delta Conv_{CH4}$ = (3925 / 53881) ×100% = 7.3%;

The concentration of CH_4 consumed by Se catalyst (ΔCH_4) was calculated as:

ΔCH_4 = (3925 / 79.19) ×10 = 495 ppm;

The concentration of C_2H_6 produced by Se catalyst (ΔC_2H_6) was calculated as:

ΔC_2H_6 = (132 / 129.97) ×10 = 10.15 ppm;

The concentration of C_2H_4 produced by Se catalyst (ΔC_2H_4) was calculated as:

ΔC_2H_4 = (671/133.53) ×10 = 50.25 ppm;

The selectivity of C_2H_6 induced by Se catalyst (ΔS_{C2H6}) was calculated as:

$\Delta S_{C2H6} = 10.15 \times 2 / 495 = 4.1\%$;

The selectivity of C_2H_4 induced by Se catalyst (ΔS_{C2H4}) was calculated as:

$\Delta S_{C2H4} = 50.25 \times 2 / 495 = 20.3\%$.

Table S1 The parameters used in ICP-QQQ-MS.

Parameters	Values
Scan type	MS/MS
RF power(W)	1550
Extract 1 (V)	0
Q1 bias (V)	1.0
Q1→Q2	x→2~260
Octopole bias (V)	-5.0
Octopole RF (V)	150
Collision He gas speed(mL min^{-1})	1.0
The third gas speed (%)	5
Energy discrimination (V)	-7.0
Extract 2 (V)	-165
Wait time offset (ms)	2
Sweeps / replicate	5
Integration time / mass (s)	0.1
Replicates	3

Table S2 The S1(C_2H_4) and S1(C_2H_6) catalyzed by different gas ions for CH_4 activation in ICP-QQQ-MS system.

Catalysts	S1(C_2H_4, %)	S1(C_2H_6, %)	Catalysts	S1(C_2H_4, %)	S1(C_2H_6, %)
Sc^+	—	—	Cd^+		—
Ti^+	—	—	In^+		—
V^+	1.20E-5	—	Hf^+	4.84E-3	—
Cr^+	8.16E-4	—	Ta^+	8.86E-3	—
Mn^+	2.09E-2	—	W^+	1.29E-2	—
Fe^+	0.499	—	Re^+	6.85E-3	
Co^+	8.16E-4	—	Ir^+	1.21E-5	
Ni^+	8.16E-4	—	Pt^+	1.59E-2	13.0
Cu^+	—	—	Au^+	1.69E-2	0.176
Zn^+	—	—	S^+	1.89E-2	4.41E-2
Ga^+	—	—	As^+	—	—
Y^+		—	Se^+	0.121	—
Zr^+		—	Sn^+	—	—
Nb^+	3.70E-2	—	Sb^+	—	—
Mo^+	4.84E-3	—	Te^+	—	—
Ru^+	4.84E-3	—	Pb^+		—
Rh^+	—	—	Bi^+		—
Pd^+	—	—	Hg^+	3.43E-3	—
Ag^+	—	—			

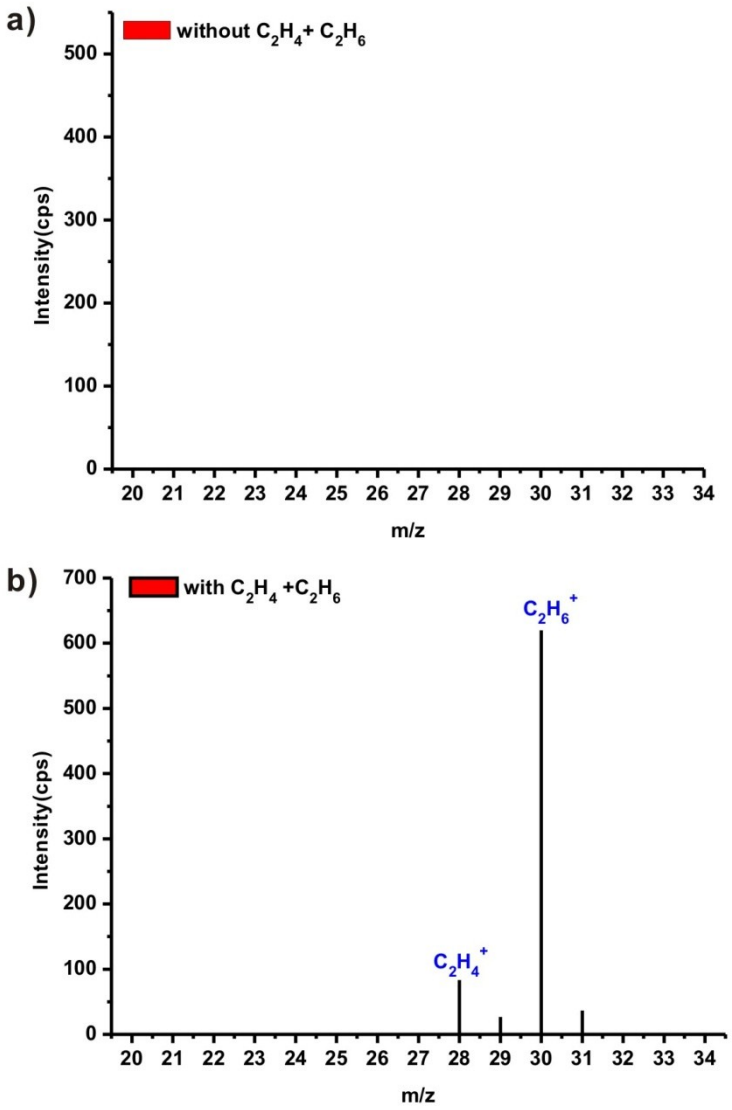

Fig.S1 The mass spectra of the standard mix gas of ethylene and ethane with the same concentration of 10ppm(b) and its blank(a) in our homogeneous system.

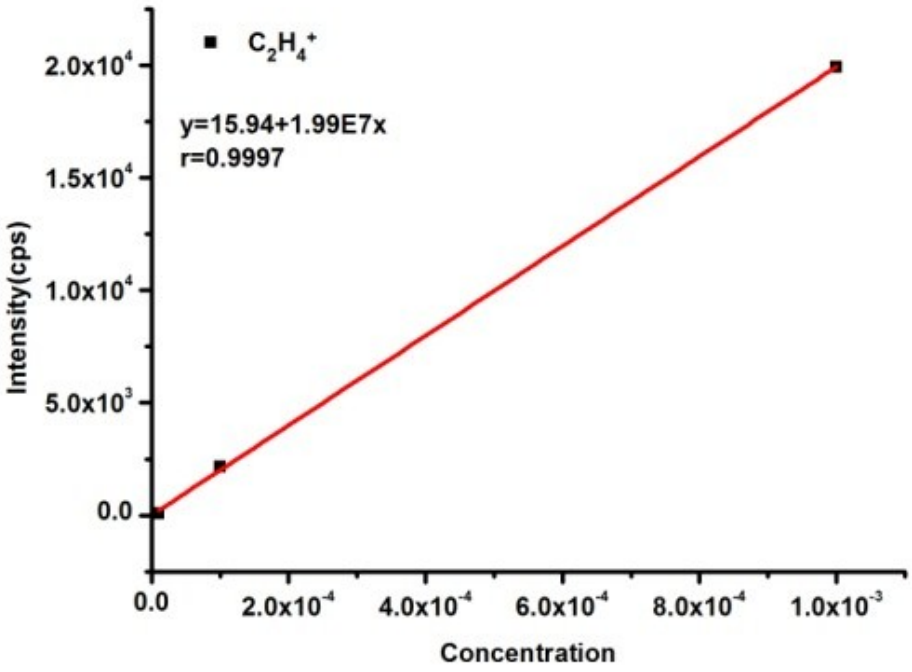

Fig.S2 The relationship between the MS intensities (m/z 28) and the concentrations of C_2H_4 in ICP-QQQ-MS system.

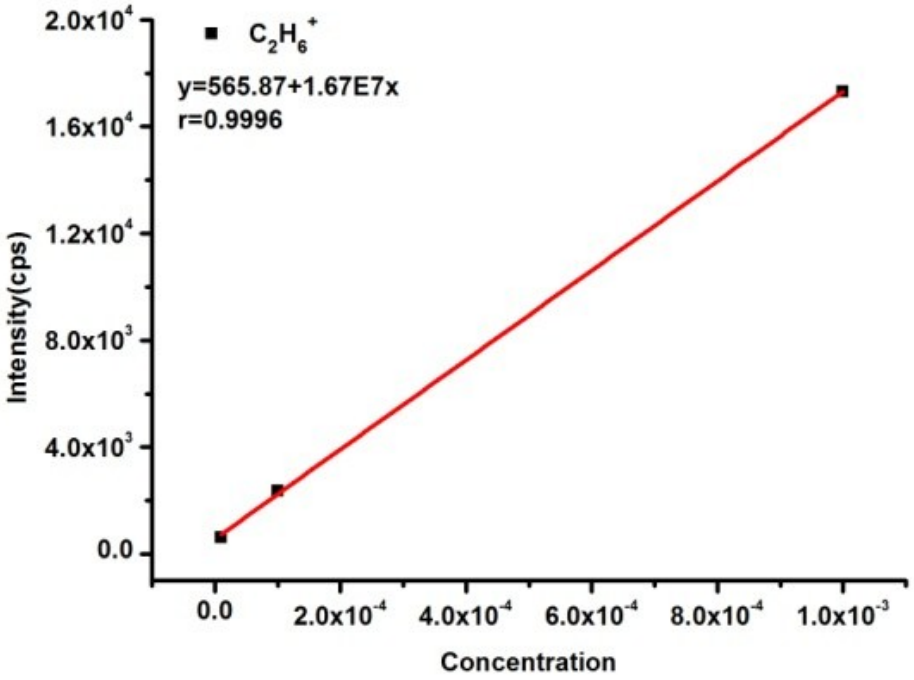

Fig.S3 The relationship between the MS intensities (m/z 30) and the concentrations of C_2H_6 in ICP-QQQ-MS system.

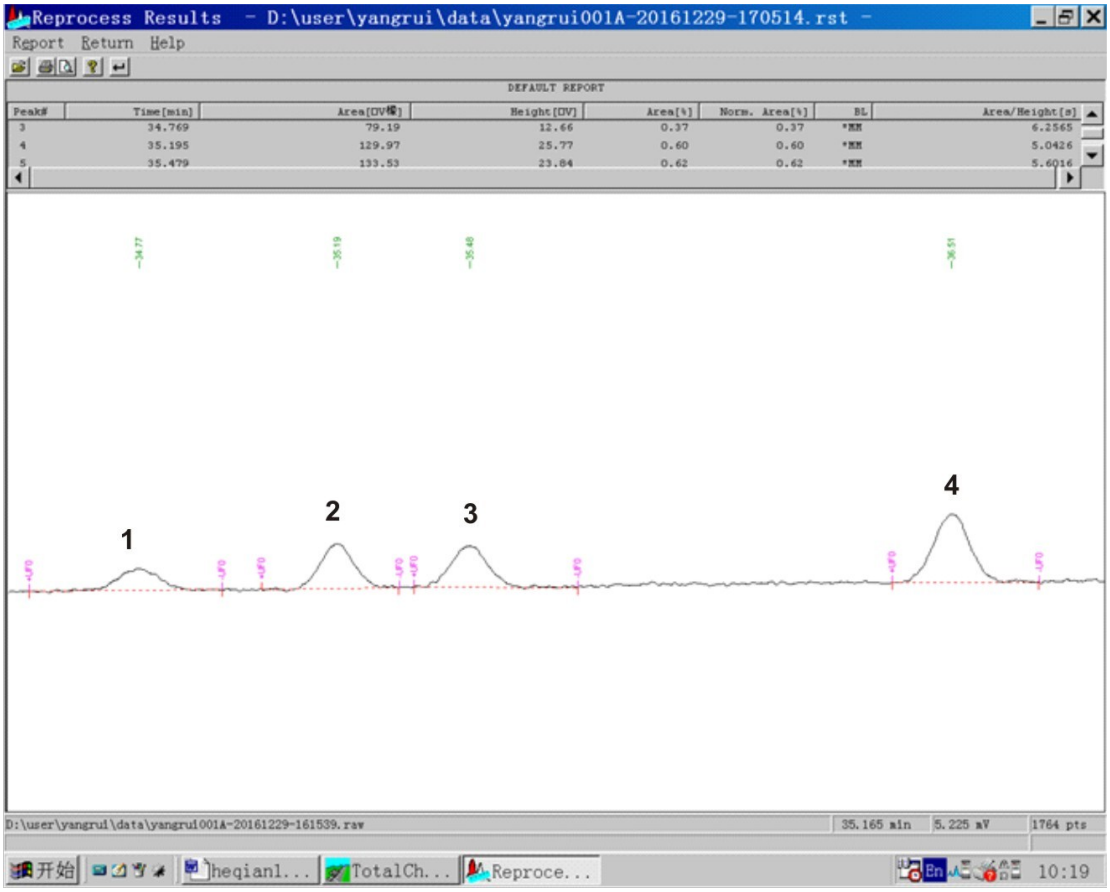

Fig.S4 The GC chromatogram of the standard mix gas of methane, ethylene, ethane and propylene with the same concentration.

Table S3 The values in the GC chromatogram in Fig.S4.

Peak	Species	Relative Retention Time(min)	Concentration (ppm)	Peak Area
1	CH_4	0	10	79.19
2	C_2H_6	0.426	10	129.97
3	C_2H_4	0.71	10	133.53
4	C_3H_6	1.743	10	218.54

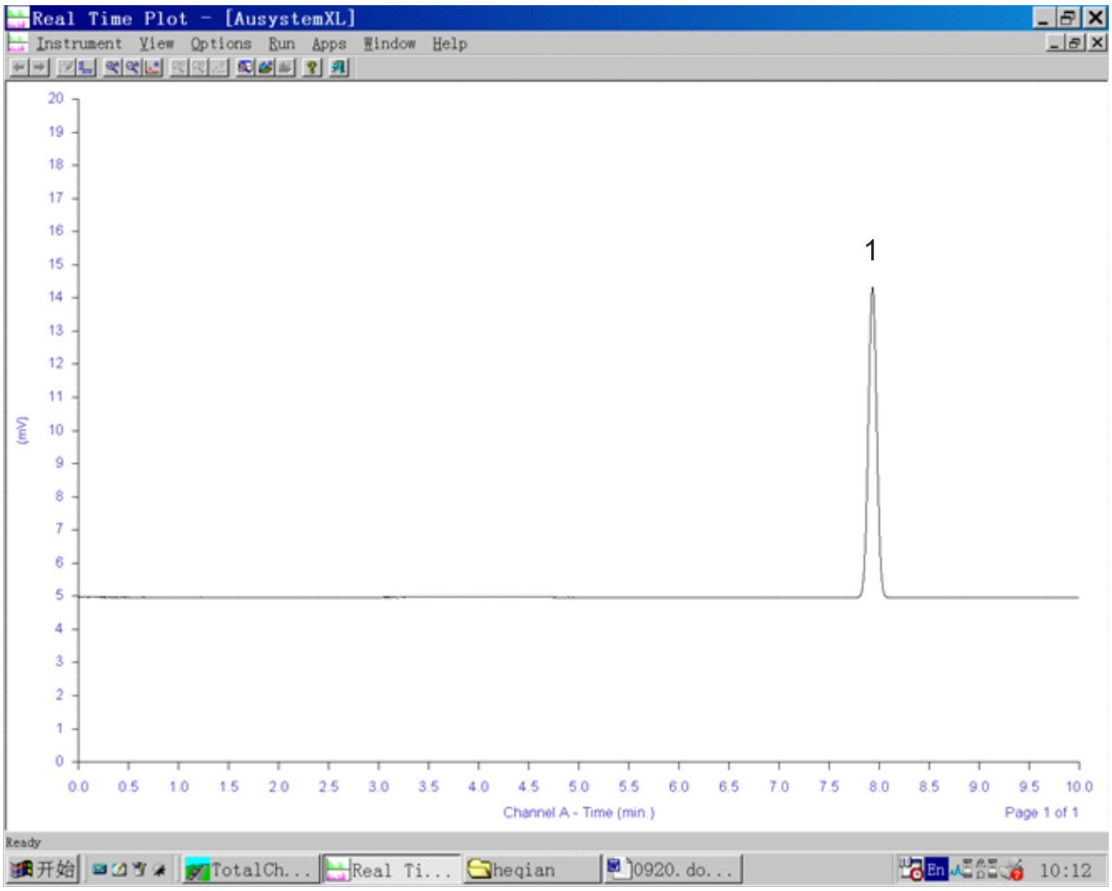

Fig.S5 The GC chromatogram of methane itself.

Table S4 The values in the GC chromatogram in Fig.S5.

Peak	Species	Relative Retention Time(min)	Peak Area
1	CH_4	0	53881

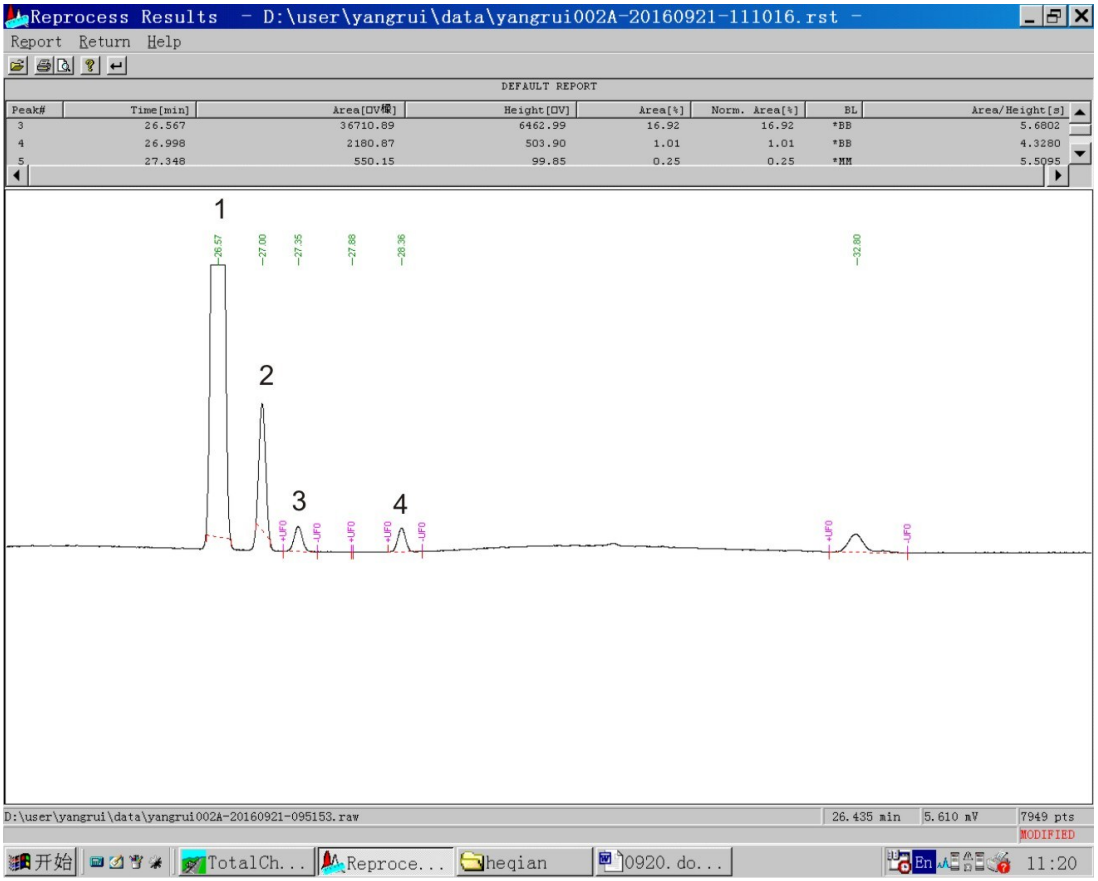

Fig.S6 The GC chromatogram of methane in DBD system.

Table S5 The values in the GC chromatogram in Fig.S6.

Peak	Species	Relative Retention Time(min)	Peak Area
1	CH_4	0	36710
2	C_2H_6	0.43	2180
3	C_2H_4	0.78	550
4	C_3H_6	1.79	485

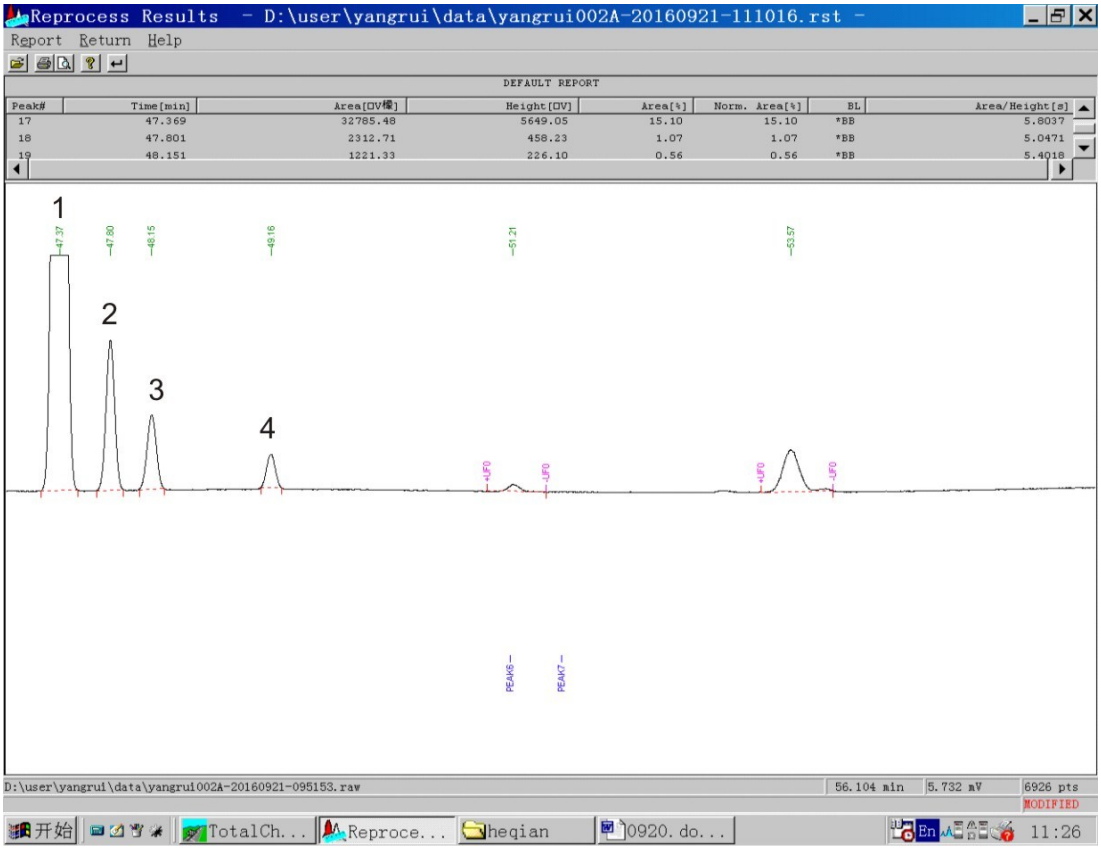

Fig.S7 The GC chromatogram of methane/Se mixture in DBD system.

Table S6 The values in the GC chromatogram in Fig.S7.

Peak	Species	Relative Retention Time(min)	Peak Area
1	CH_4	0	32785
2	C_2H_6	0.43	2312
3	C_2H_4	0.78	1221
4	C_3H_6	1.79	508