Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary information:

Theoretical investigation of the conversion between different C_2H_x species over Pd-Ag/Pd(100) surface alloys: the influence on the selectivity and transformation of carbonaceous

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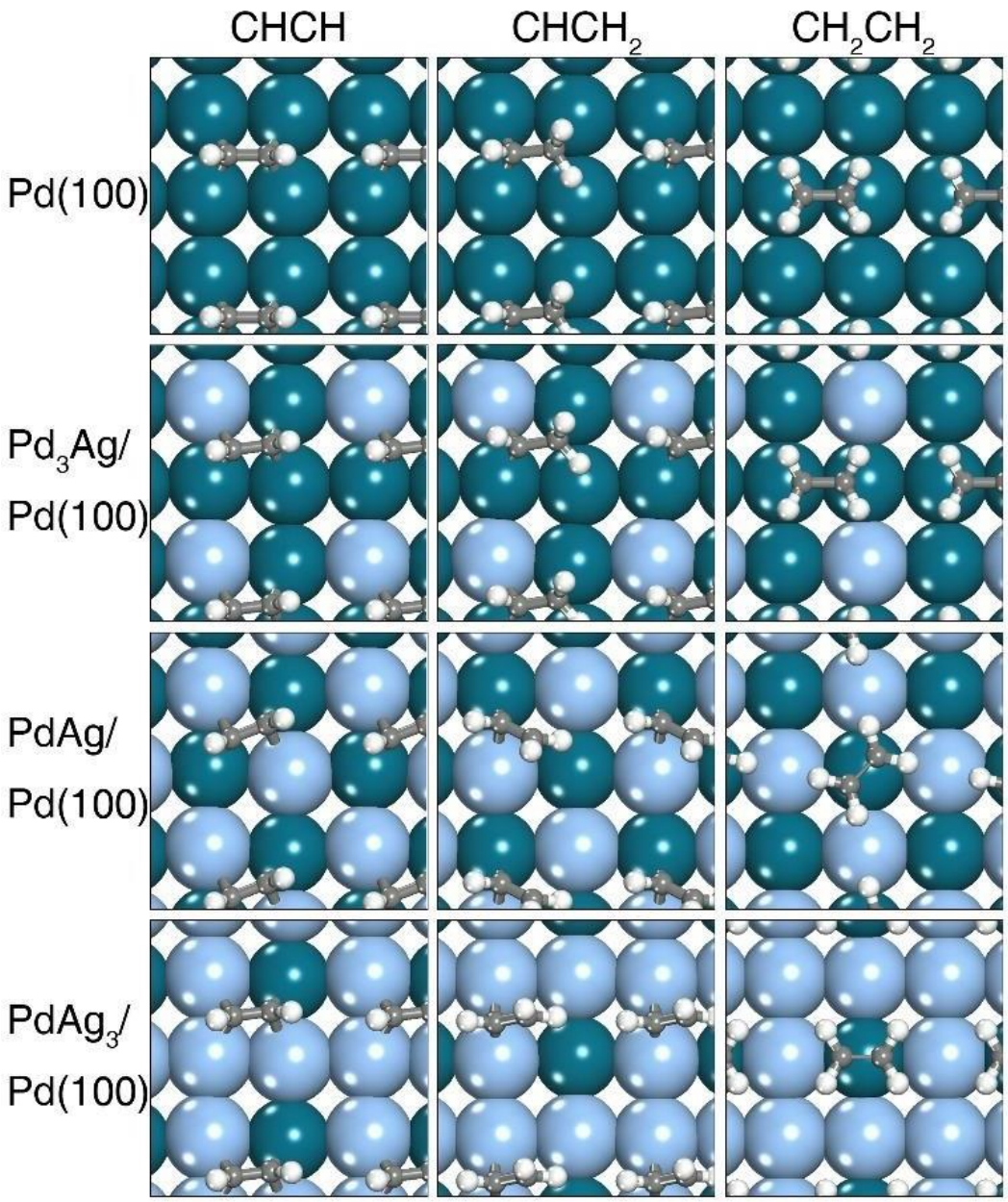

Fig S1. Stable adsorption structures of C_2H_2, C_2H_3, and C_2H_4 on Pd(100), Pd_3Ag/Pd(100), PdAg/Pd(100), and $PdAg_3$/Pd(100) surfaces.

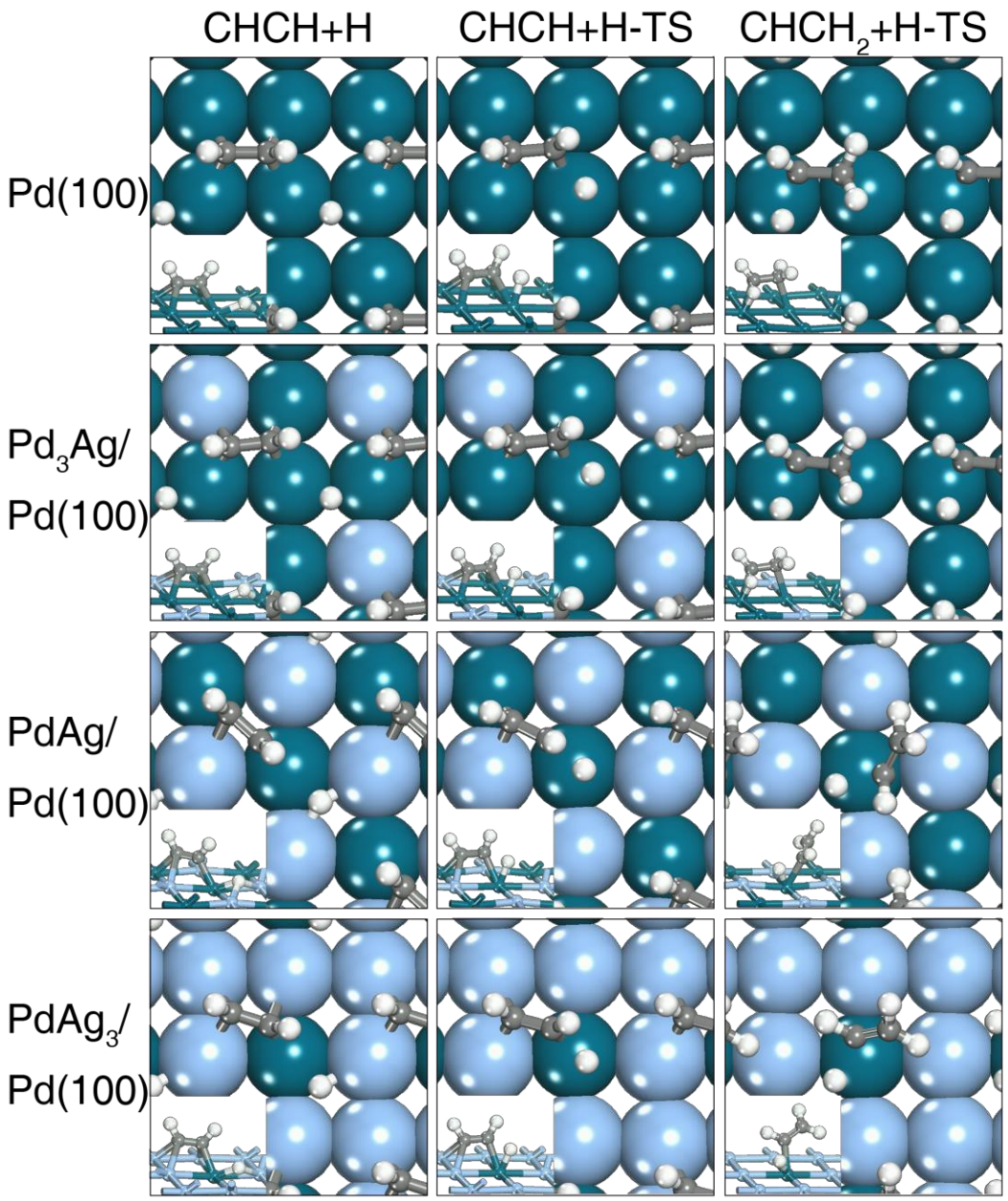

Fig. S2 Co-adsorption structures of C_2H_2 with H atom and Transition-state (TS) structures of C_2H_2 and C_2H_3 hydrogenation on Pd(100), Pd_3Ag/Pd(100), PdAg/Pd(100), and $PdAg_3$/Pd(100) surfaces.

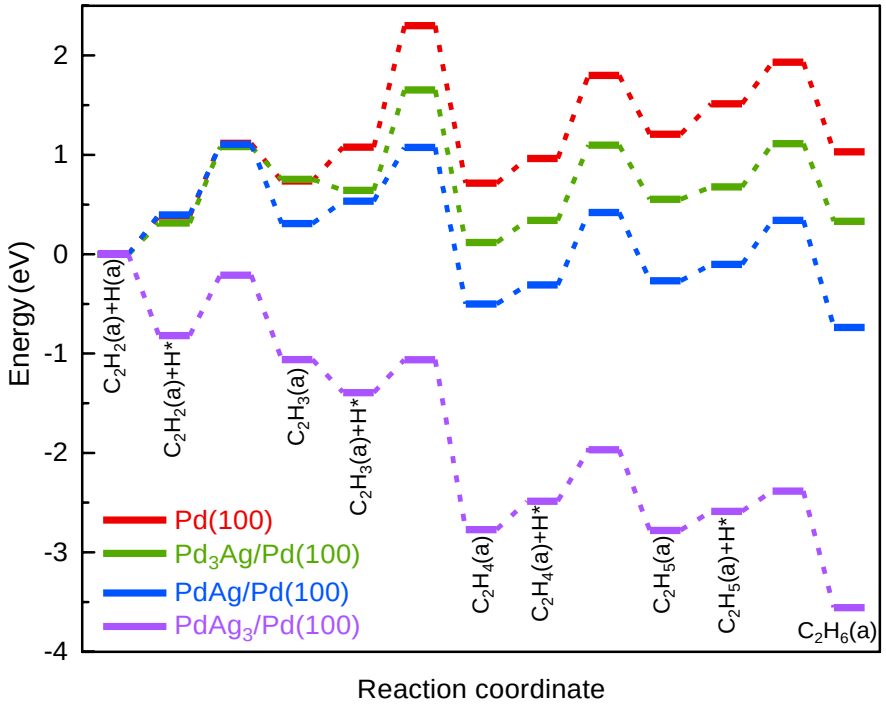

Fig. S3. Energy profiles of the hydrogenation pathways of the acetylene to ethylene on Pd(100) surface and its surface alloys with Ag atoms. Metastable hydrogen diffusion steps are indicated by “H*”. The script “a” signals the adsorbed state of a molecule.

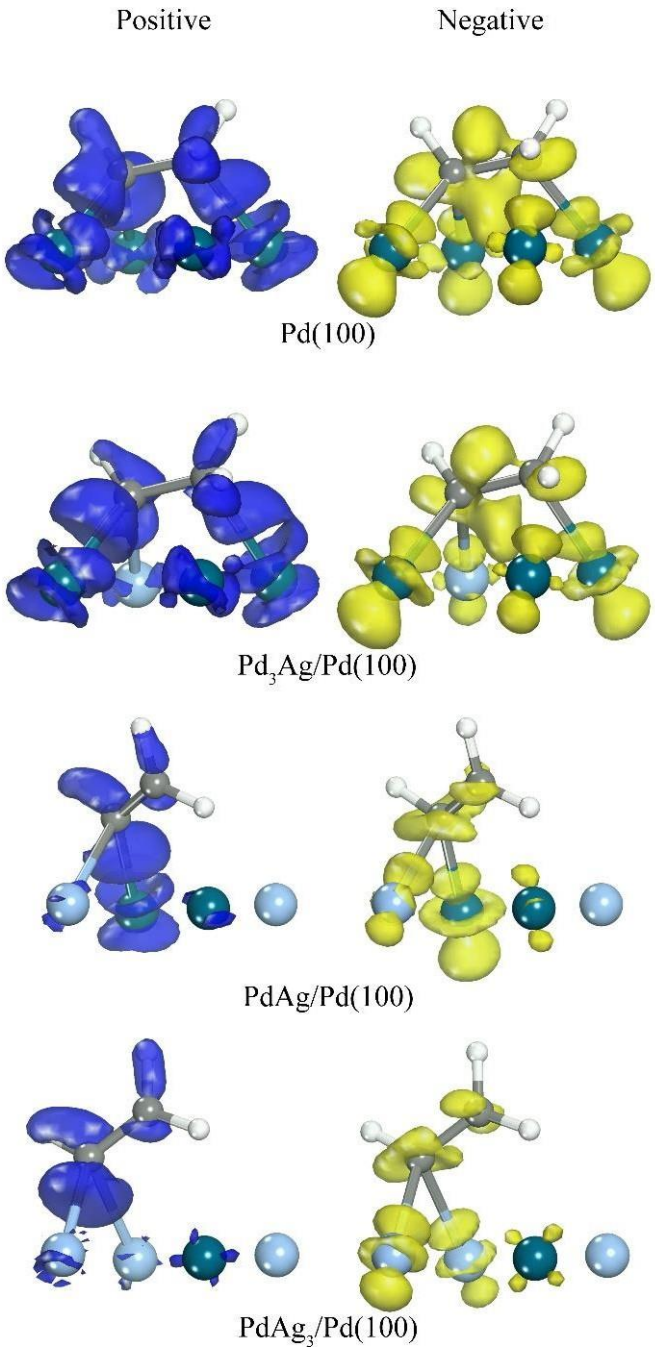

Fig. S4. Electron density difference plots for the adsorption of $CHCH_2$ on the Pd(100) surface and its surface alloys with Ag atoms. The blue contours represent electron accumulations, and the yellow contours denote electron depressions.

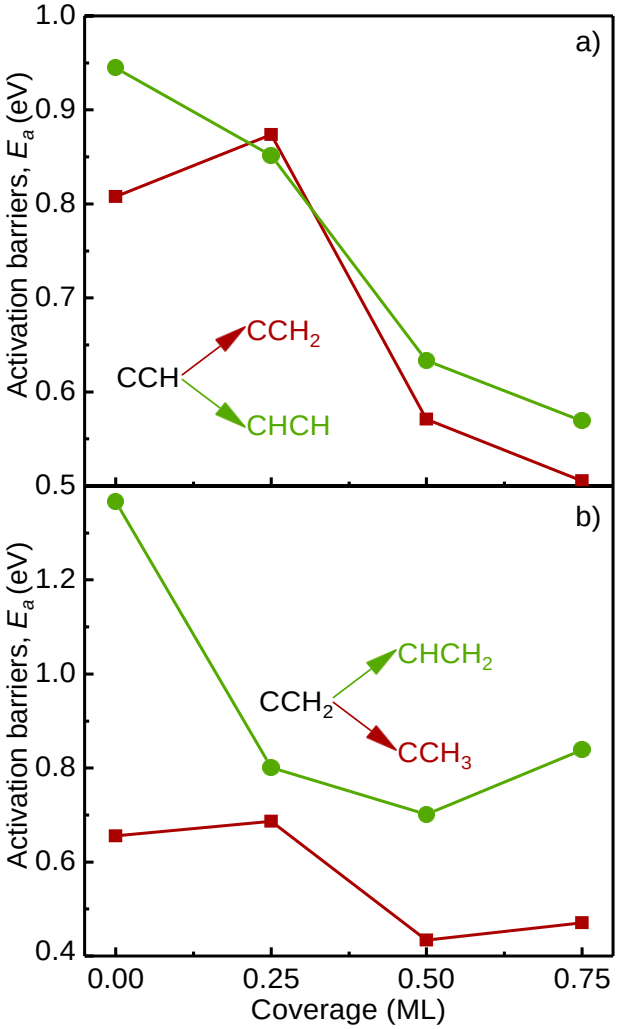

Fig. S5. The trend of activation barriers (E_a) for the hydrogenation of CCH (a) and CCH_2 (b) as a function of the coverage of Ag atoms on Pd-Ag/Pd(100) surface alloys.

Table S1. Miliken charges of adsorbed $CHCH_2$ molecules on the Pd-Ag/Pd(100) surface alloys.

	C1	C2	H1	H2	H3	CH	CH_2
pure	-0.34	-0.63	0.34	0.30	0.33	0	0
Pd(100)	-0.4	-0.62	0.12	0.14	0.04	-0.28	-0.44
Pd_3Ag/Pd(100)	-0.47	-0.61	0.13	0.15	0.04	-0.34	-0.42
PdAg/Pd(100)	-0.48	-0.54	0.14	0.21	0.03	-0.34	-0.30
$PdAg_3$/Pd(100)	-0.61	-0.51	0.15	0.24	0.09	-0.46	-0.18

Table S2. Calculated reaction energies ΔE (eV), barrier energies from both reactant E_a (eV) and product E_a' (eV), and all the slab energies for all initial (E_i), final (E_f), and transition (E_t) states for the elementary steps involved in the conversion of acetylene hydrogenation system on Pd(100) surface.

	E_i	E_f	E_t	E_a	E_a'	ΔE
$CH{\equiv}CH+H\rightarrow CHCH_2$	-16340.0461	-16339.6949	-16339.3157	0.7303	0.3792	0.3512
$CHCH_2+H\rightarrow CH_2CH_2$	-16356.0701	-16356.4344	-16354.8499	1.2202	1.5845	-0.3642
$CH_2CH_2+H\rightarrow CH_2CH_3$	-16372.9044	-16372.6612	-16372.0684	0.8360	0.5929	0.2432
$CH_2CH_3+H\rightarrow CH_3CH_3$	-16389.0733	-16389.5581	-16388.6570	0.4163	0.9011	-0.4848
$CCH+H\rightarrow CHCH$	-16323.2749	-16323.7118	-16322.3304	0.9445	1.3814	-0.4369
$CCH+H\rightarrow CCH_2$	-16323.1495	-16323.4147	-16322.3417	0.8078	1.0730	-0.2652
$CCH_2+H\rightarrow CCH_3$	-16339.8258	-16340.2712	-16339.1702	0.6556	1.1010	-0.4454
$CCH_3+H\rightarrow CHCH_3$	-16356.6977	-16356.0761	-16355.1321	1.5656	0.9441	0.6215
$CCH_2+H\rightarrow CHCH_2$	-16339.9759	-16339.6924	-16338.6089	1.3670	1.0835	0.2835
$CHCH_2+H\rightarrow CHCH_3$	-16356.1725	-16356.0788	-16355.2560	0.9165	0.8227	0.0938
$CHCH_3+H\rightarrow CH_2CH_3$	-16372.4931	-16372.6612	-16371.6949	0.7982	0.9663	-0.1682

Table S3. Calculated reaction energies ΔE (eV), barrier energies from both reactant E_a (eV) and product E_a' (eV), and all the slab energies for all initial (E_i), final (E_f), and transition (E_t) states for the elementary steps involved in the conversion of acetylene hydrogenation system on Pd_3Ag/Pd(100) surface.

	E_i	E_f	E_t	E_a	E_a'	ΔE
$CH{\equiv}CH+H\rightarrow CHCH_2$	-16569.1423	-16568.7037	-16568.3749	0.7675	0.3288	0.4386
$CHCH_2+H\rightarrow CH_2CH_2$	-16585.4750	-16586.0023	-16584.4651	1.0099	1.5372	-0.5272
$CH_2CH_2+H\rightarrow CH_2CH_3$	-16602.4388	-16602.2278	-16601.6826	0.7562	0.5453	0.2109
$CH_2CH_3+H\rightarrow CH_3CH_3$	-16618.7644	-16619.1100	-16618.3274	0.4370	0.7825	-0.3455
$CCH+H\rightarrow CHCH$	-16552.2504	-16552.7973	-16551.3989	0.8515	1.3984	-0.5469
$CCH+H\rightarrow CCH_2$	-16552.2573	-16552.7417	-16551.3835	0.8738	1.3582	-0.4844
$CCH_2+H\rightarrow CCH_3$	-16569.0627	-16569.6530	-16568.3763	0.6864	1.2767	-0.5902
$CCH_3+H\rightarrow CHCH_3$	-16586.0019	-16585.7185	-16584.6355	1.3664	1.0830	0.2834
$CCH_2+H\rightarrow CHCH_2$	-16568.9706	-16569.0740	-16568.1698	0.8009	0.9042	-0.1033
$CHCH_2+H\rightarrow CHCH_3$	-16585.4546	-16585.7185	-16584.8319	0.6227	0.8866	-0.2639
$CHCH_3+H\rightarrow CH_2CH_3$	-16602.1585	-16602.3453	-16601.4115	0.7469	0.9337	-0.1868

Table S4. Calculated reaction energies ΔE (eV), barrier energies from both reactant E_a (eV) and product E_a'(eV), and all the slab energies (eV) for all initial (E_i), final (E_f), and transition (E_t) states for the elementary steps involved in the conversion of acetylene hydrogenation system on PdAg/Pd(100) surface.

	E_i	E_f	E_t	E_a	E_a'	ΔE
CH≡CH+H→$CHCH_2$	-16798.0263	-16798.1156	-16797.3169	0.7094	0.7988	-0.0894
$CHCH_2$+H→CH_2CH_2	-16814.4070	-16815.4426	-16813.8658	0.5411	1.5767	-1.0356
CH_2CH_2+H→CH_2CH_3	-16831.7671	-16831.7260	-16831.0399	0.7272	0.6860	0.0411
CH_2CH_3+H→CH_3CH_3	-16848.0803	-16848.7150	-16847.6356	0.4447	1.0794	-0.6347
CCH+H→CHCH	-16781.1720	-16781.9058	-16780.5385	0.6335	1.3672	-0.7337
CCH+H→CCH_2	-16781.2697	-16781.6946	-16780.6988	0.5709	0.9958	-0.4248
CCH_2+H→CCH_3	-16797.7366	-16798.5727	-16797.3027	0.4339	1.2700	-0.8360
CCH_3+H→$CHCH_3$	-16814.6328	-16814.5136	-16813.6063	1.0265	0.9073	0.1192
CCH_2+H→$CHCH_2$	-16797.7952	-16798.0811	-16797.0940	0.7012	0.9871	-0.2858
$CHCH_2$+H→$CHCH_3$	-16814.4055	-16814.5136	-16813.4999	0.9056	1.0137	-0.1080
$CHCH_3$+H→CH_2CH_3	-16830.8012	-16831.7260	-16830.2532	0.5480	1.4728	-0.9248

Table S5. Calculated reaction energies ΔE (eV), barrier energies from both reactant E_a (eV) and product E_a'(eV), and all the slab energies for all initial (E_i), final (E_f), and transition (E_t) states for the elementary steps involved in the conversion of acetylene hydrogenation system on $PdAg_3$/Pd(100) surface.

	E_i	E_f	E_t	E_a	E_a'	ΔE
CH≡CH+H→$CHCH_2$	-17026.8675	-17027.1088	-17026.2603	0.6072	0.8485	-0.2413
$CHCH_2$+H→CH_2CH_2	-17043.7144	-17045.0933	-17043.3856	0.3288	1.7077	-1.3789
CH_2CH_2+H→CH_2CH_3	-17061.0814	-17061.3756	-17060.5640	0.5174	0.8116	-0.2942
CH_2CH_3+H→CH_3CH_3	-17077.4592	-17078.4273	-17077.2556	0.2036	1.1717	-0.9681
CCH+H→CHCH	-17010.3444	-17010.8357	-17009.7752	0.5692	1.0605	-0.4913
CCH+H→CCH_2	-17010.2092	-17010.6031	-17009.7039	0.5053	0.8992	-0.3940
CCH_2+H→CCH_3	-17026.5794	-17027.3323	-17026.1085	0.4709	1.2238	-0.7529
CCH_3+H→$CHCH_3$	-17043.3056	-17044.0813	-17042.7091	0.5965	1.3722	-0.7758
CCH_2+H→$CHCH_2$	-17026.6809	-17027.7277	-17025.8428	0.8381	1.8850	-1.0468
$CHCH_2$+H→$CHCH_3$	-17043.7969	-17044.0905	-17042.3861	1.4109	1.7045	-0.2936
$CHCH_3$+H→CH_2CH_3	-17060.2648	-17061.3756	-17060.0973	0.1675	1.2783	-1.1108