# Synthesis of Metal Silicides Using Polyhedral Oligomeric Silsesquioxane as Silicon Source for Semi-Hydrogenation of phenylacetylene

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**Chemicals**

Analytical-grade Pd(CH$_3$COO)$_2$, Ni(acac)$_2$, RuCl$_3$, and PtCl$_4$ were obtained from Tianjin Xiensi Chemical Reagents, China. Tetrahydrofuran, toluene, dimethoxymethylsilane, and phenyltriethoxysilane were purchase from Aladdin. All chemicals were from commercial sources and used without further purification.

**Synthesis of Ni$_2$Si/SiO$_2$, Ru$_x$Si/SiO$_2$ and Pt$_x$Si/SiO$_2$ catalyst**

20 mg nickel Ni(acac)$_2$ was dispersed in 20 mL of tetrahydrofuran, 1 g of the as-prepared phenyl-POSS sample was added. After stirring for 2 h at room temperature. Finally, the mixture

was separated by rotary evaporator, and dried at 70 $^{\circ}$C overnight in the oven. The resulting solid was heated to 1000 $^{\circ}$C at a ramp of 20 $^{\circ}$C/min and kept for 2 h under hydrogen atmosphere. The catalysts were designated as $Ni_2Si/SiO_2$ catalyst. The $Ru_xSi/SiO_2$ and $Pt_xSi/SiO_2$ catalysts were prepared by the same way as $Ni_2Si/SiO_2$ catalyst, except for using 20 mg $RuCl_3$ or $PtCl_4$ in 20 mL ethanol.
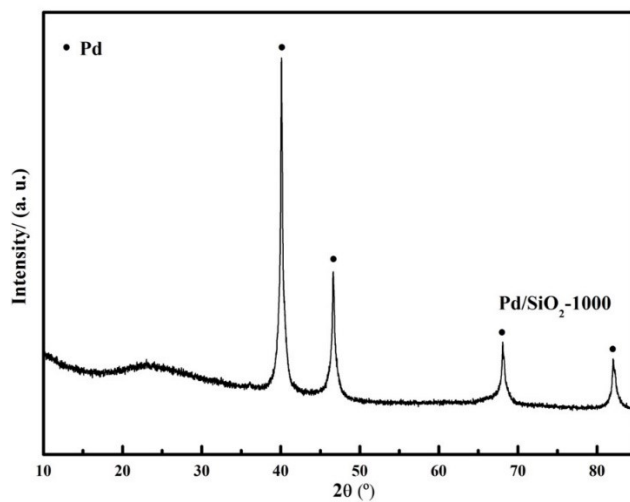
Figure S1. The XRD pattern of Pd/SiO$_2$-1000 catalyst.
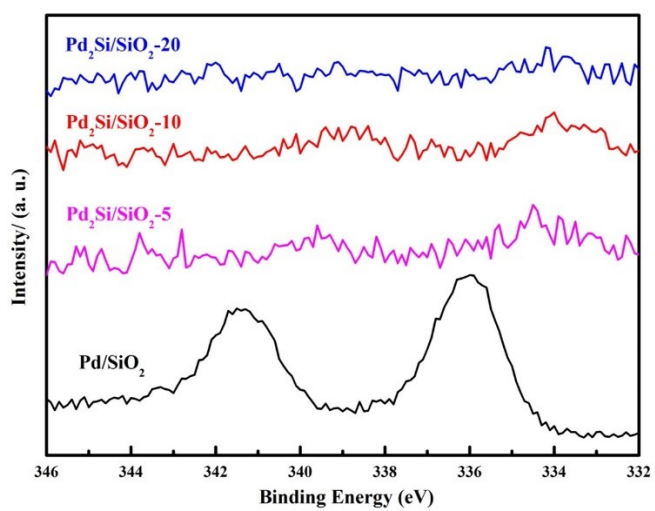


Figure S2. Pd 3d XPS spectra of Pd$_2$Si/SiO$_2$-X and Pd/SiO$_2$ catalysts.
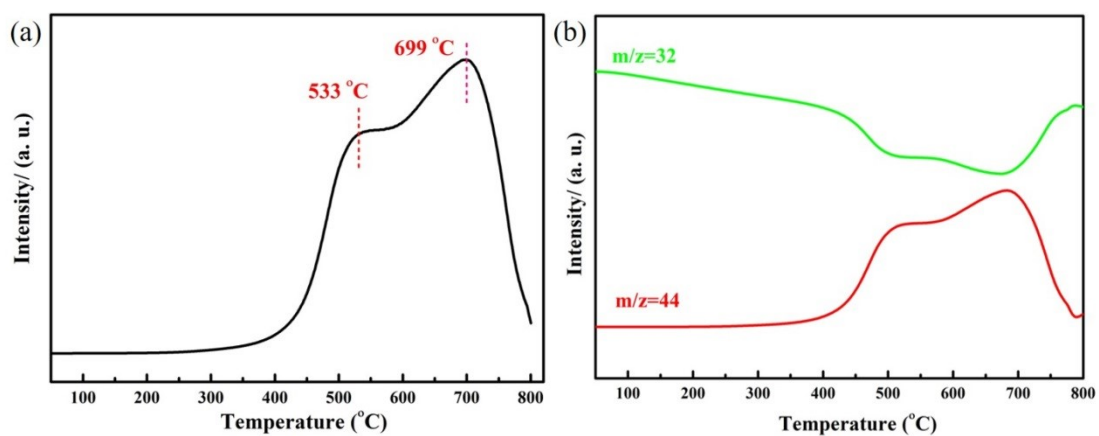
Figure S3. $O_2$-TPO-MS profile of the $Pd_2Si/SiO_2$-1000-$H_2$ catalyst.
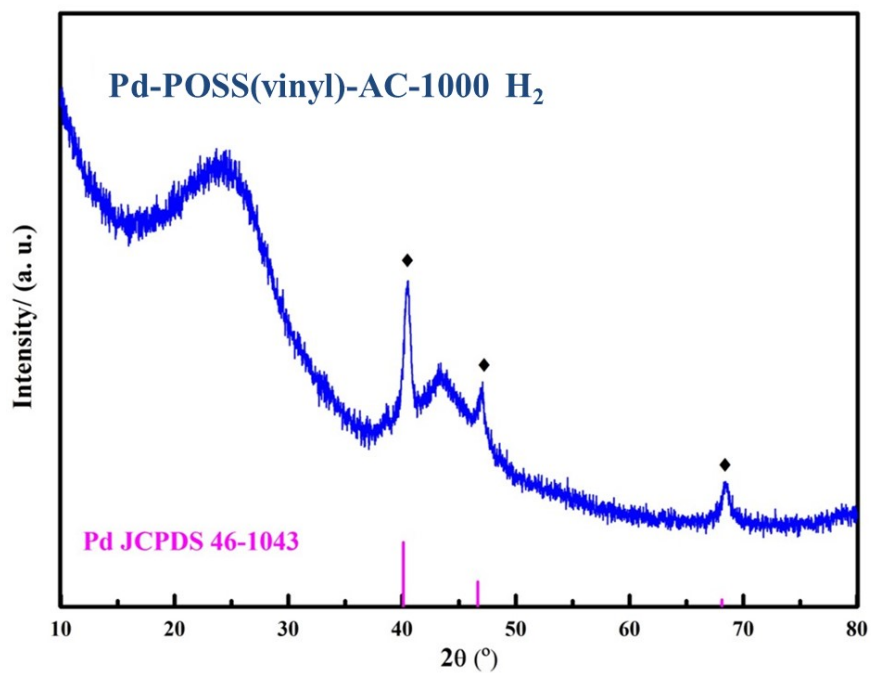


Figure S4. The XRD pattern of Pd-POSS-AC-1000 $H_2$ sample.
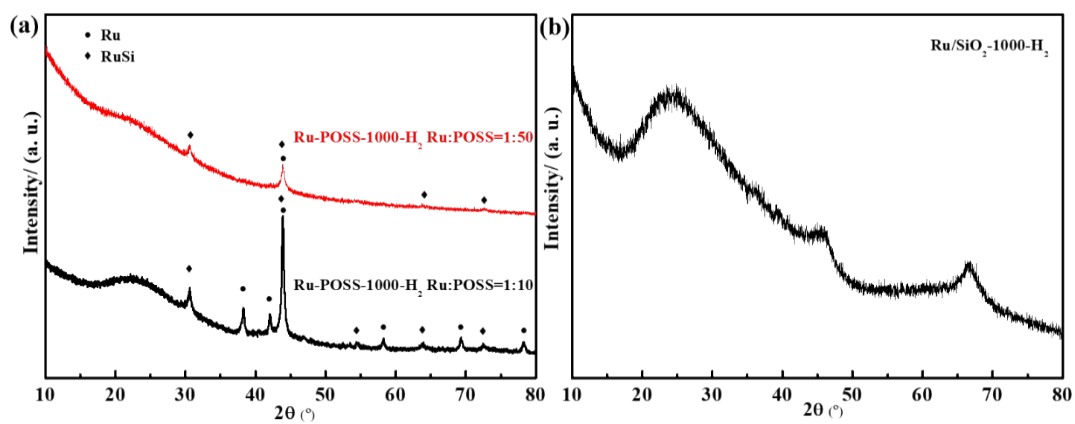
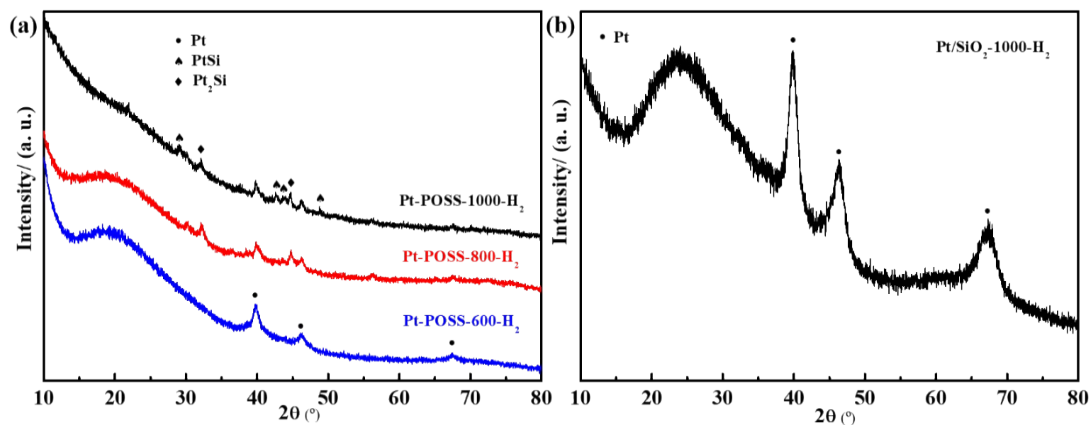Figure S5. XRD patterns of Ru-POSS-1000-$H_2$ and Ru/SiO$_2$-1000-$H_2$ catalysts.



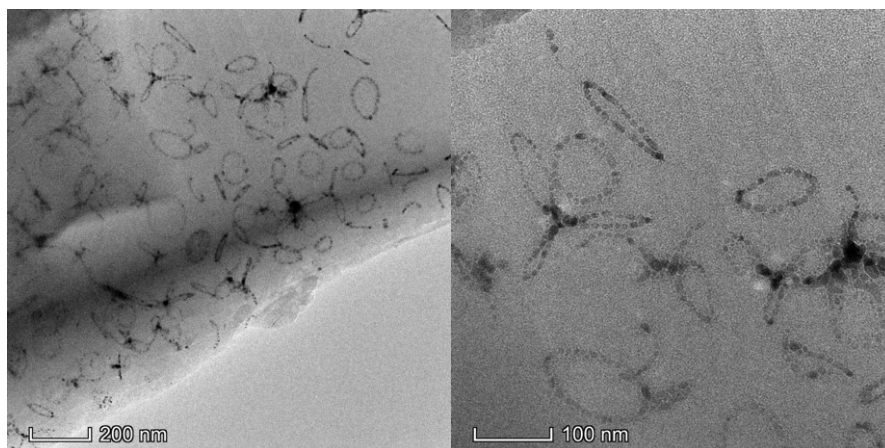Figure S6. XRD patterns of Pt-POSS-600/800/1000-$H_2$ and Pt/SiO$_2$-1000-$H_2$ catalysts.

Figure S7. TEM images of $Ru_xSi/SiO_2$ catalyst.
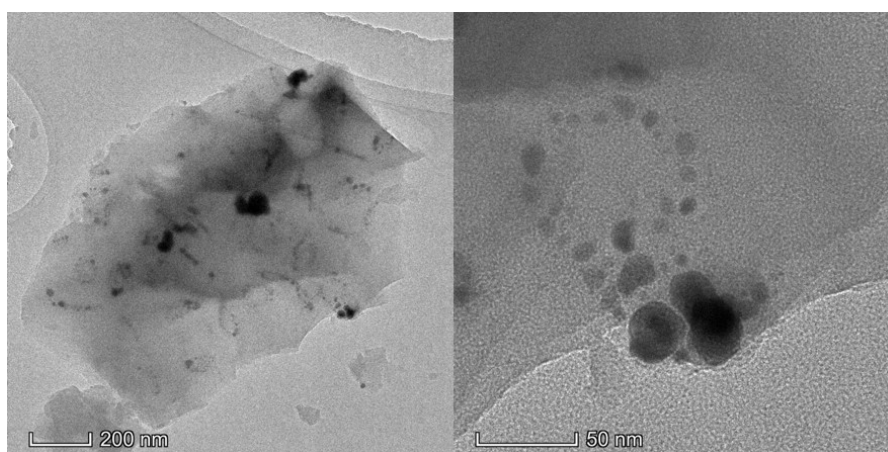


Figure S8. TEM images of $Pt_xSi/SiO_2$ catalyst.
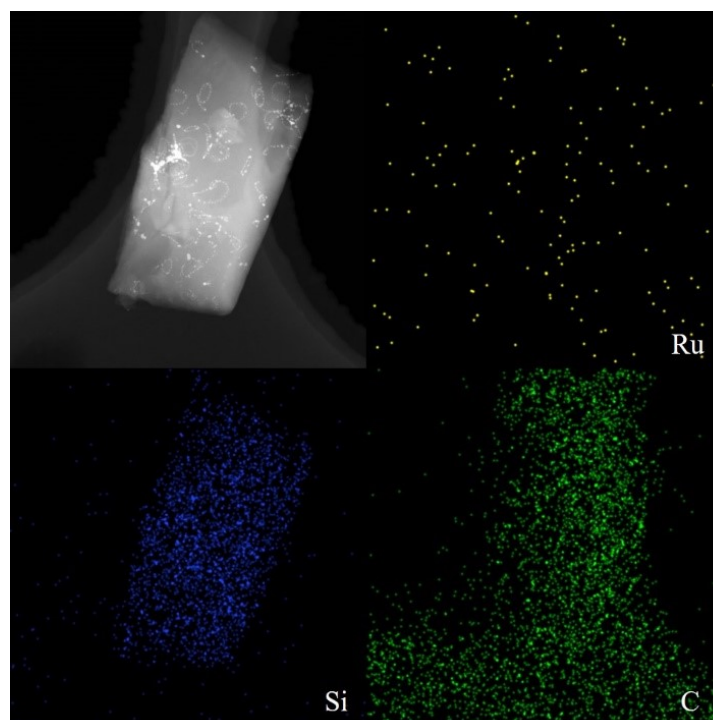
Figure S9. EDX-mapping of Ru, Si and C element in Ru$_x$Si/SiO$_2$ catalyst.
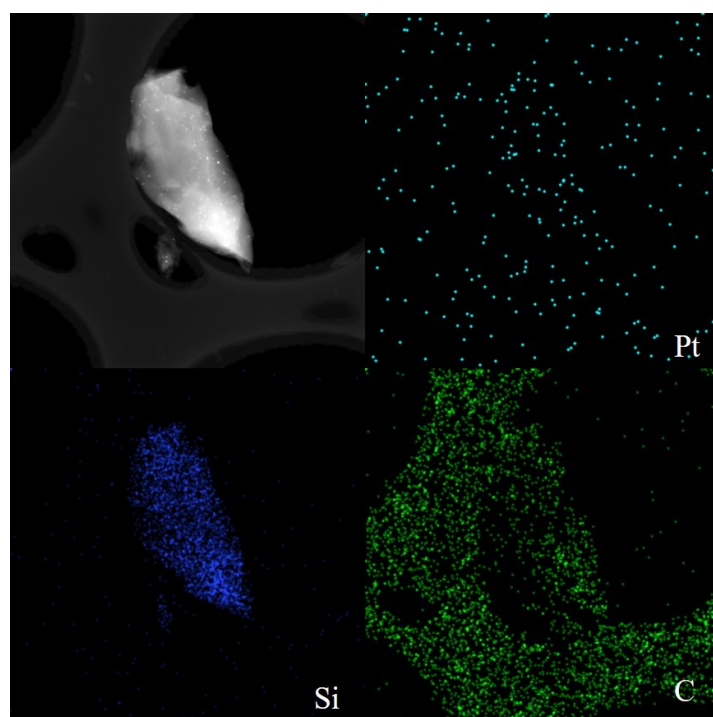


Figure S10. EDX-mapping of Pt, Si and C element in Pt$_x$Si/SiO$_2$ catalyst.
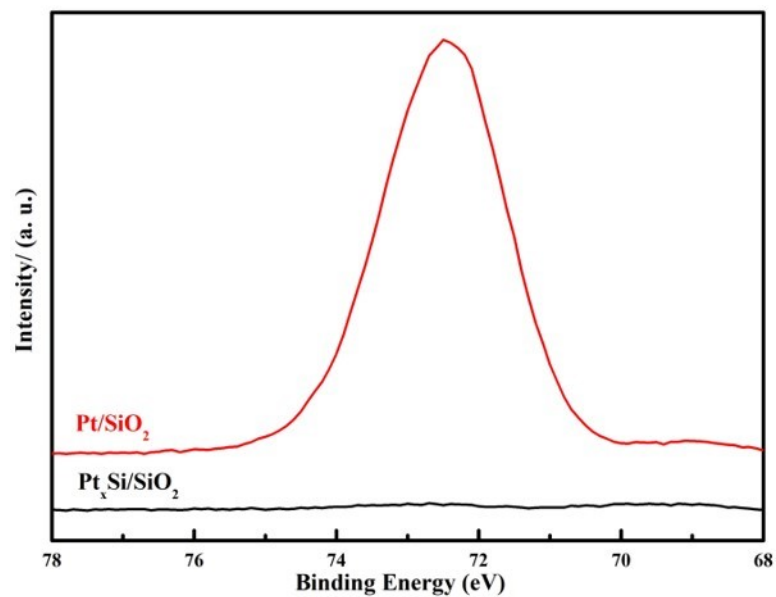
Figure S11. Pt 3d XPS spectrums of Pt$_x$Si/SiO$_2$ and Pt/SiO$_2$ catalysts.



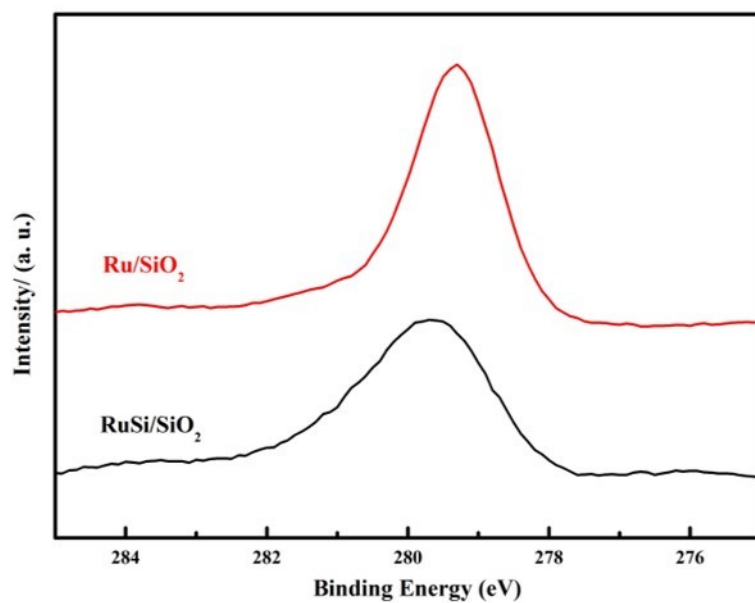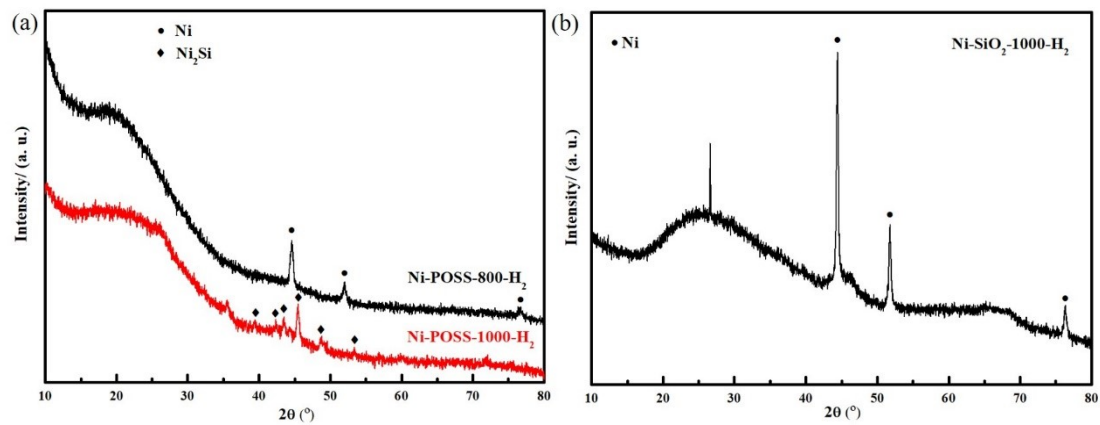Figure S12. Ru 3d XPS spectrums of Ru$_x$Si/SiO$_2$ and Ru/SiO$_2$ catalysts.

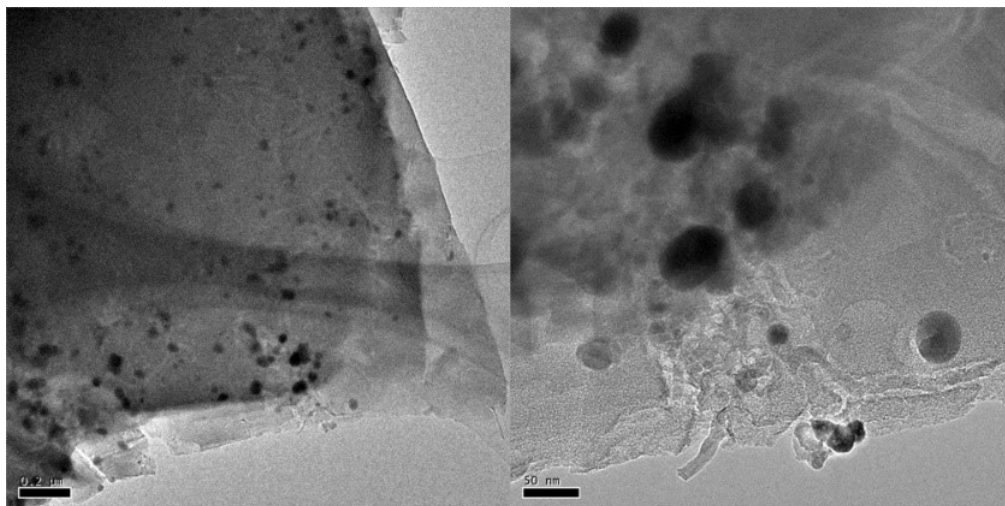Figure S13. The XRD patterns of Ni-POSS-800/1000-$H_2$ and Ni/SiO$_2$-1000-$H_2$ catalysts.



Figure S14. The TEM images of Ni$_2$Si/SiO$_2$ catalyst.
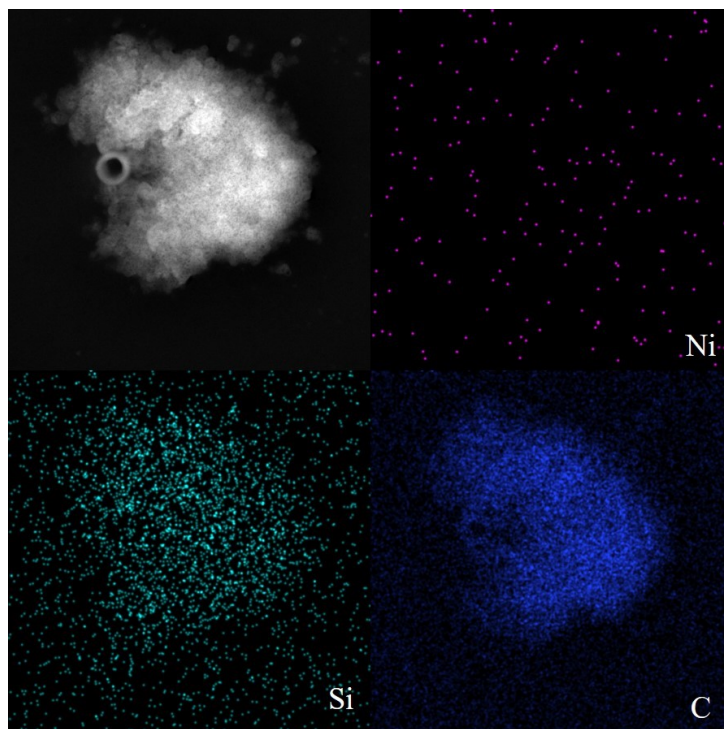
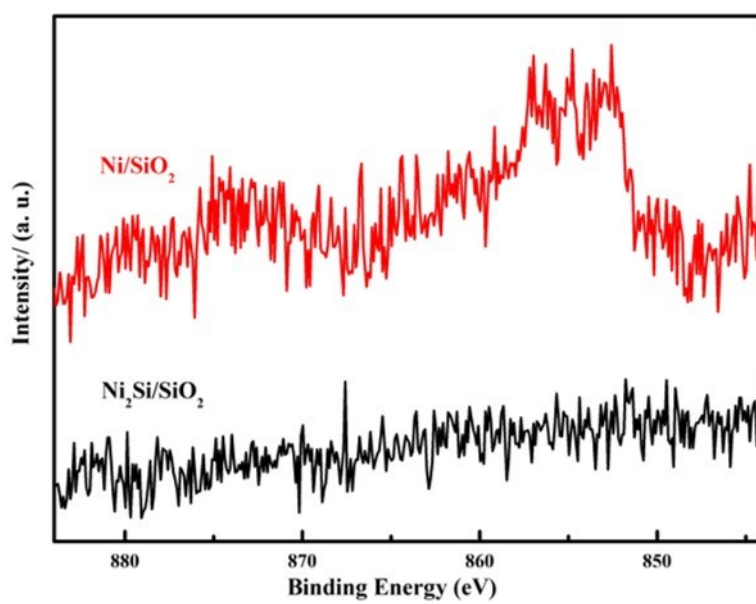Figure S15. EDX-mapping of Ni, Si and C element in $Ni_2Si/SiO_2$ catalyst.



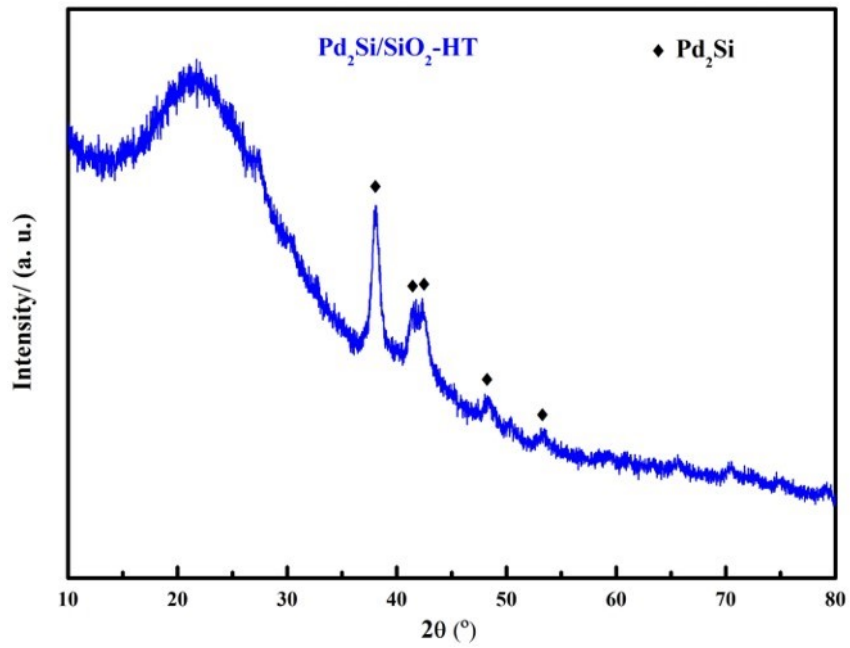Figure S16. Ni 2p XPS spectrums of $Ni_2Si/SiO_2$ and $Ni/SiO_2$ catalysts.
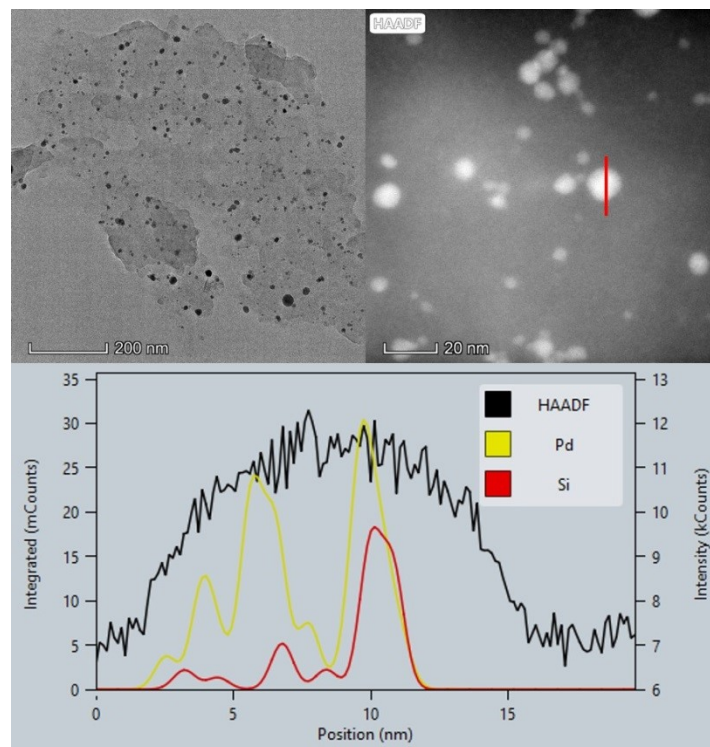
Figure S17. The XRD pattern of Pd$_2$Si/SiO$_2$-HT catalyst.



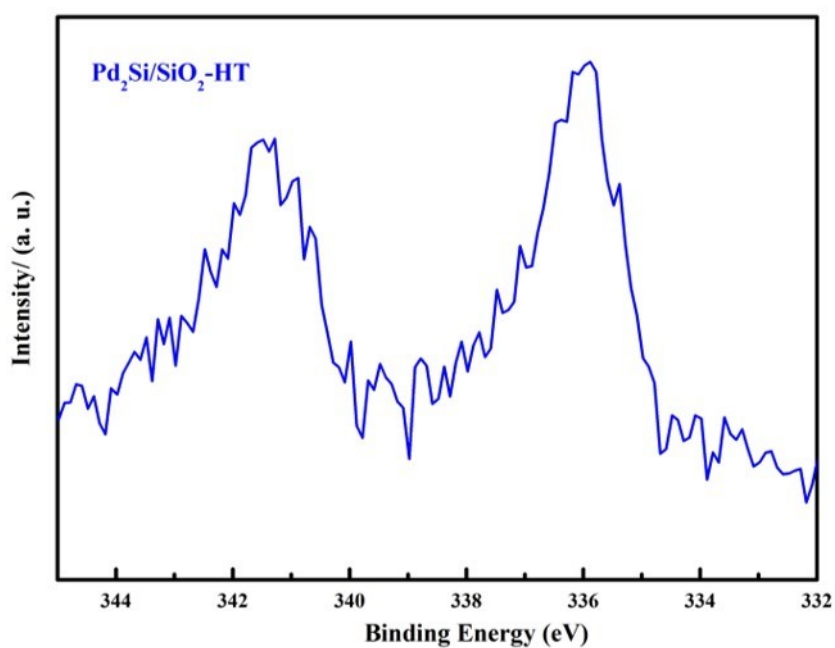Figure S18. The TEM images and element distribution of Pd$_2$Si/SiO$_2$-HT catalyst.
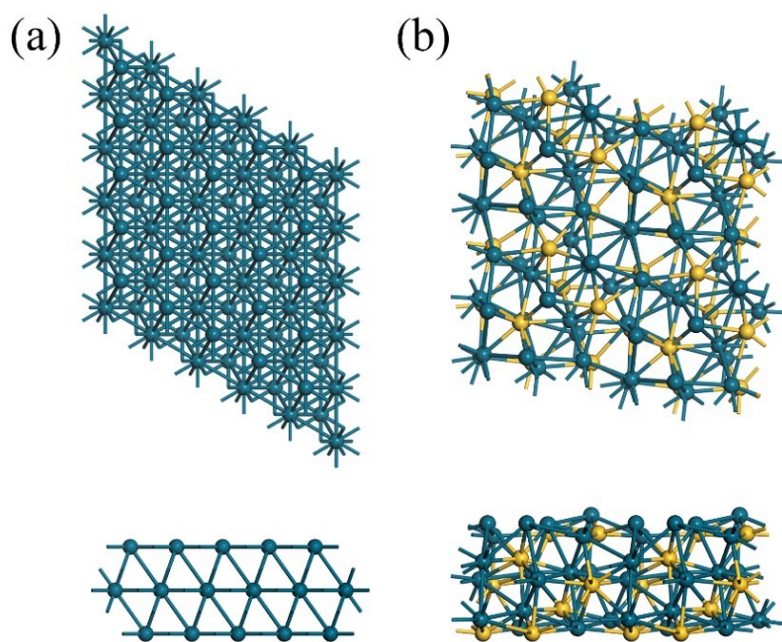
Figure S19. Pd 3d XPS spectrum of Pd$_2$Si/SiO$_2$ catalyst.



Figure S20. Top (upper) and side (lower) view of optimized atomic structures for (a) Pd(111) and (b) Pd$_2$Si(111) surface. The black green and yellow balls represent Pd and Si atoms, respectively.
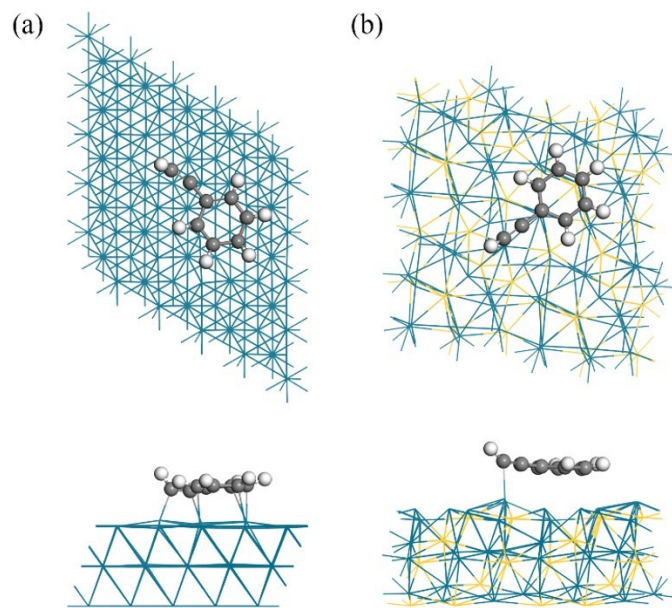
Figure S21. Optimized atomic configurations of phenylacetylene adsorbed on (a) Pd(111) and (b) $Pd_2Si(111)$ surface. The grey and white balls represent carbon and hydrogen atoms, respectively.
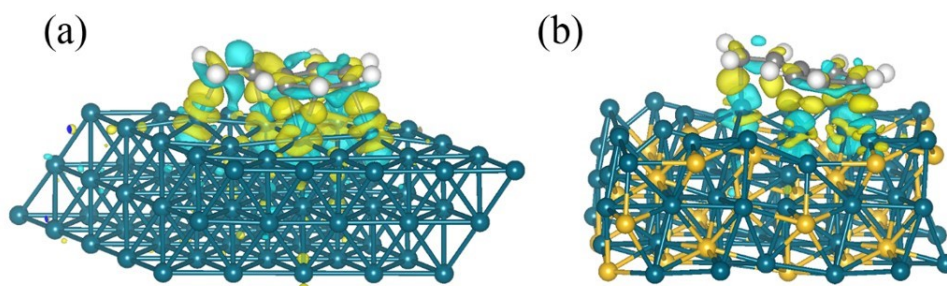


Figure S22. Deformation electronic density of styrene adsorbed on (a) Pd(111) and (b) $Pd_2Si(111)$ surface with an isosurface of $0.003$ e Å$^{-3}$. The yellow and cyan regions represent the accumulation and depletion of electron, respectively.