# Controllable Synthesis of Ir(Rh)-Sn/$SiO_2$ Bimetallic Catalysts via Surface Organometallic Chemistry for the Production of Ethanol from Hydrogenolysis of Ethyl Acetate

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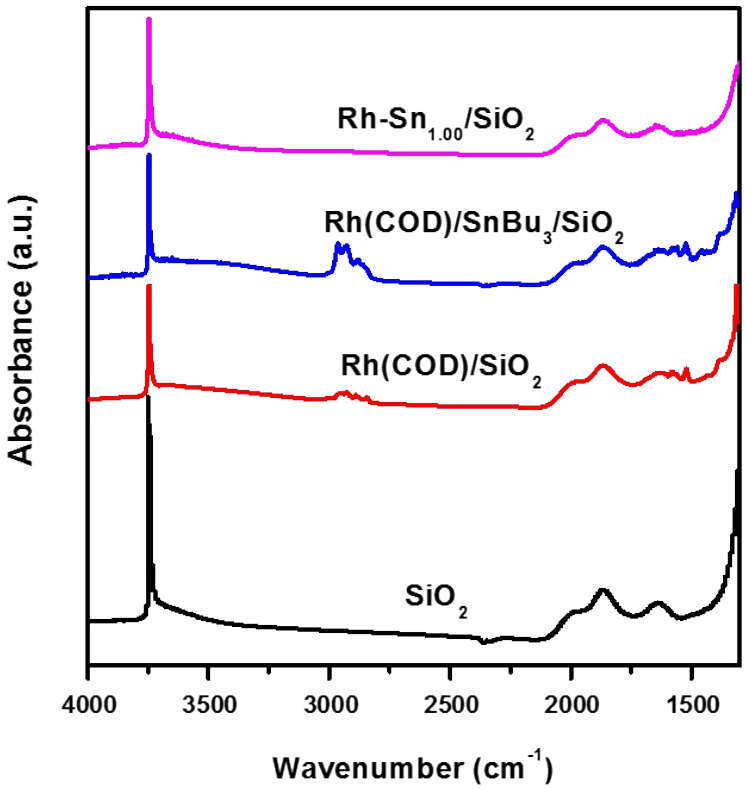


**Figure S1**. IR spectra of dehydroxylated $SiO_2$, Rh(COD)/$SiO_2$, Rh(COD)/$SnBu_3$/$SiO_2$ and Rh-$Sn_{1.00}$/$SiO_2$ obtained from the $H_2$ treatment of Rh(COD)/$SnBu_3$/$SiO_2$ at 400 °C.

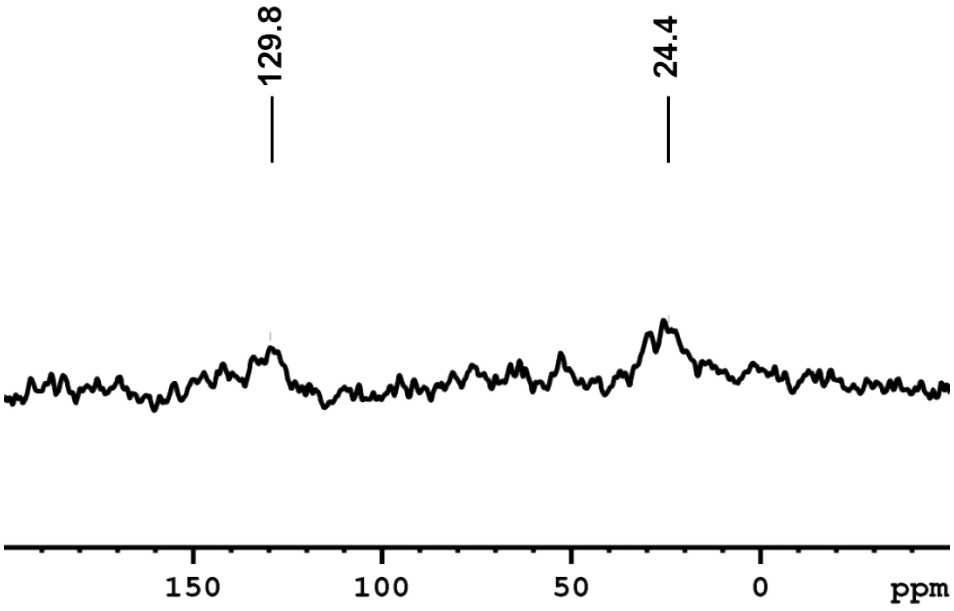


**Figure S2**. $^{13}C$ CP/MAS spectrum of monometallic surface compound Rh(COD)/$SiO_2$.

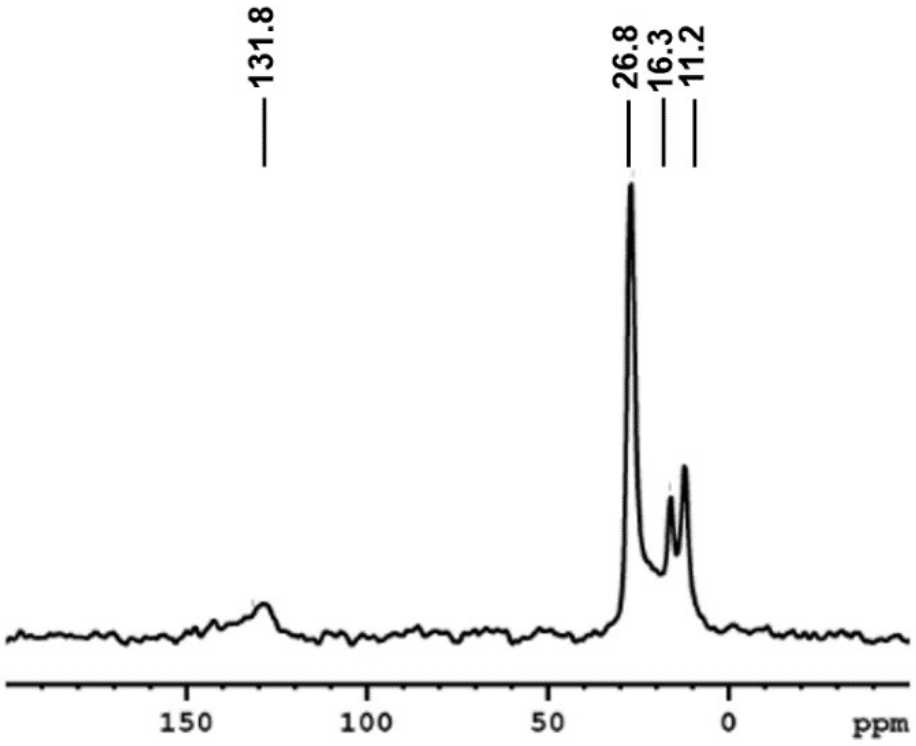


**Figure S3**. $^{13}C$ CP/MAS spectrum of bimetallic surface compound Rh(COD)/$SnBu_3$/$SiO_2$.

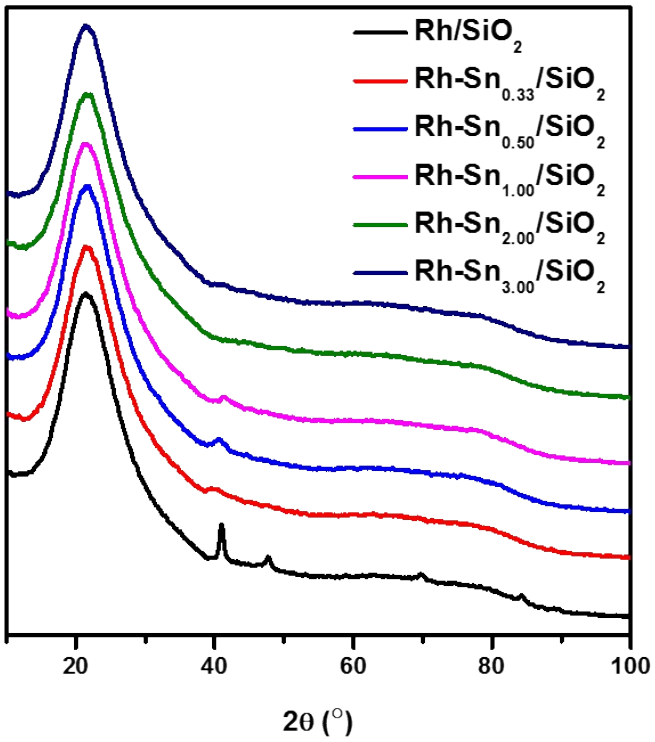


**Figure S4**. XRD patterns of Rh-Sn/$SiO_2$ bimetallic catalysts with different Sn/Rh ratios.

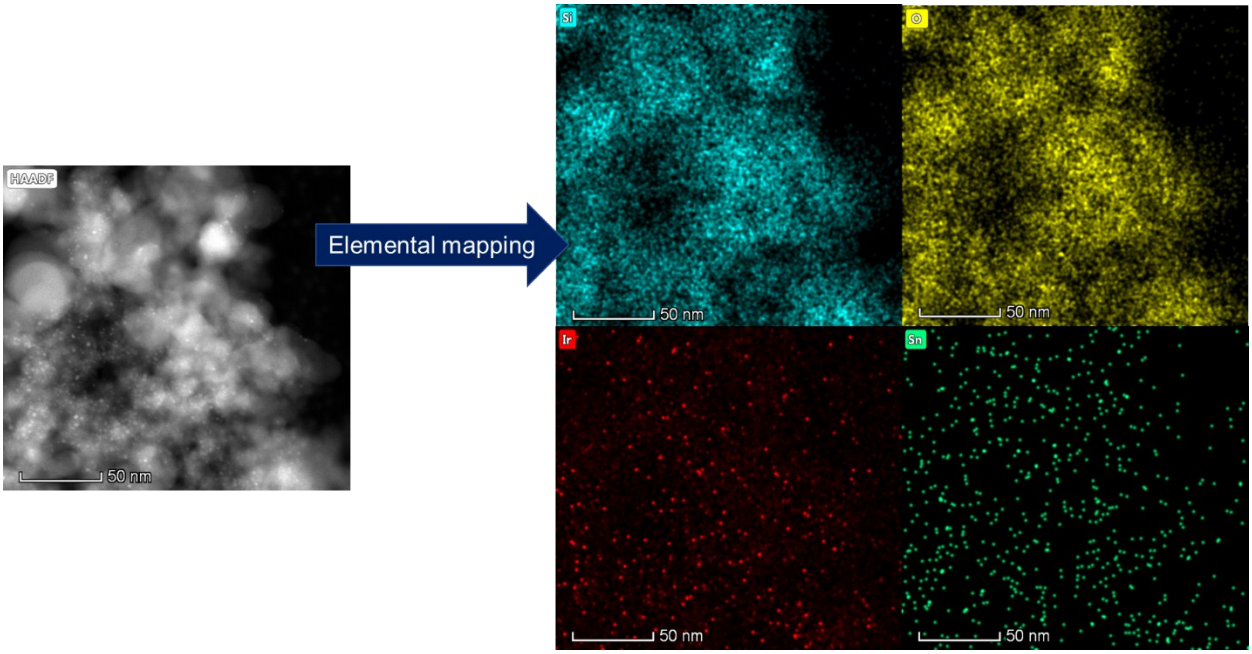


**Figure S5**. STEM-EDS elemental mapping of Ir-Sn/$SiO_2$ bimetallic catalyst.

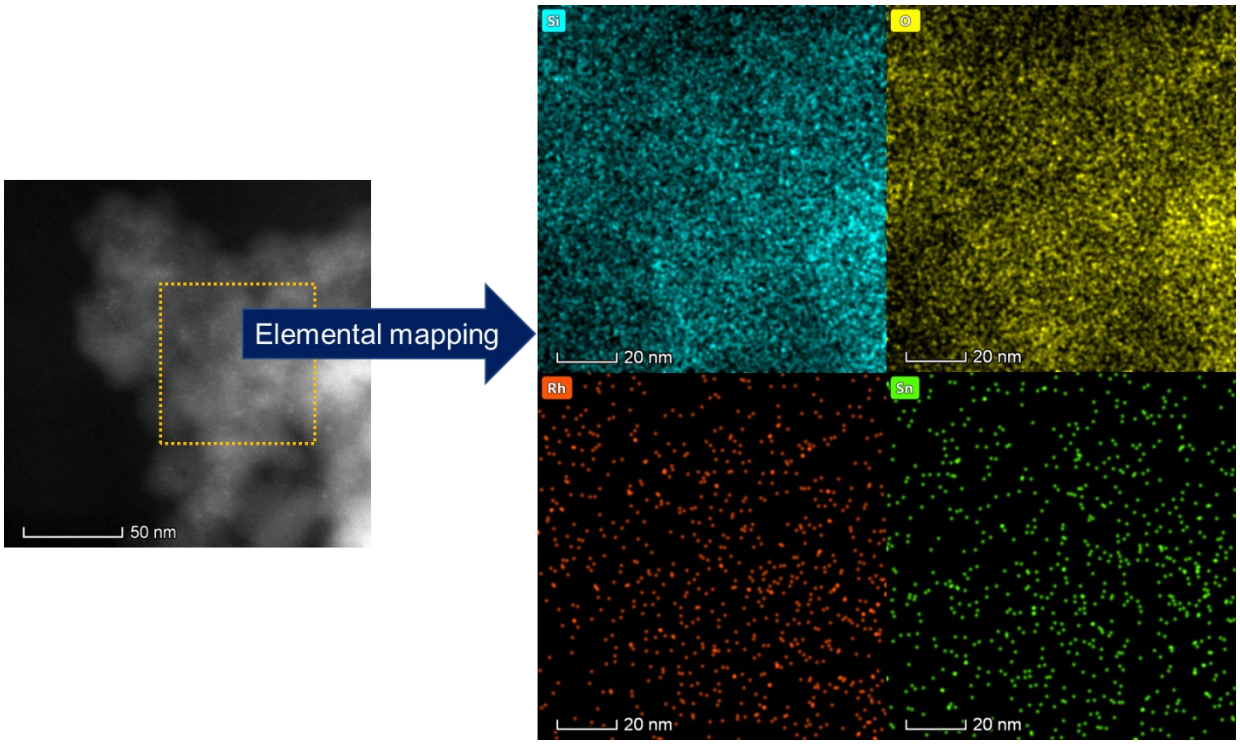


**Figure S6**. STEM-EDS elemental mapping of Rh-Sn/$SiO_2$ bimetallic catalyst.

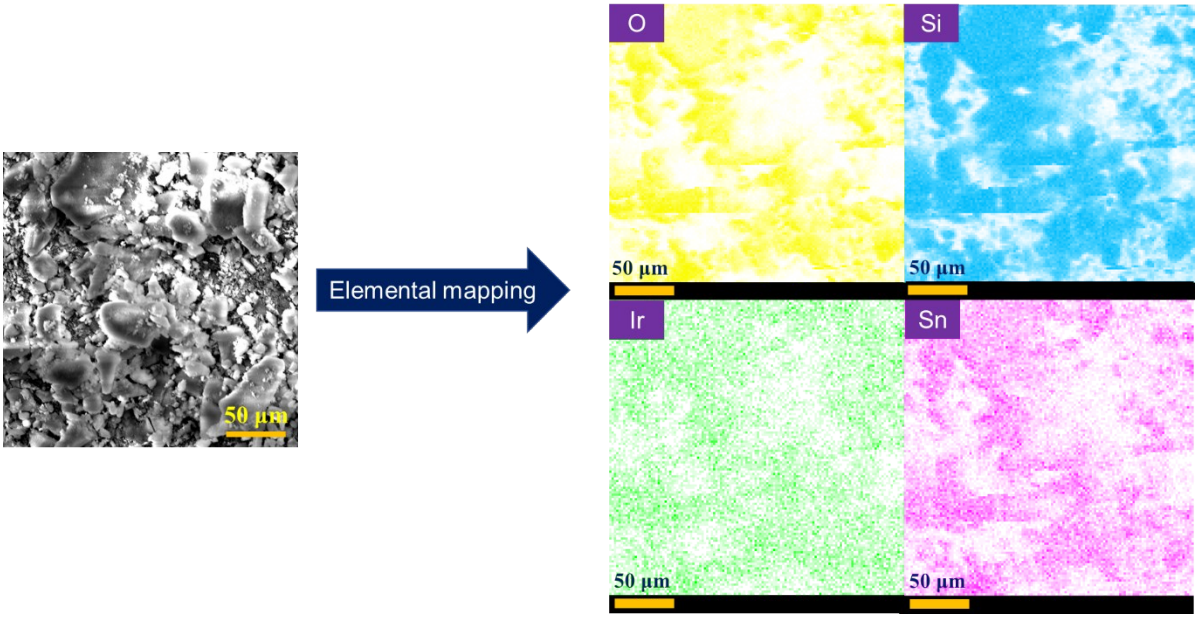


**Figure S7**. SEM-EDS elemental mapping of Ir-Sn/$SiO_2$ bimetallic catalyst.

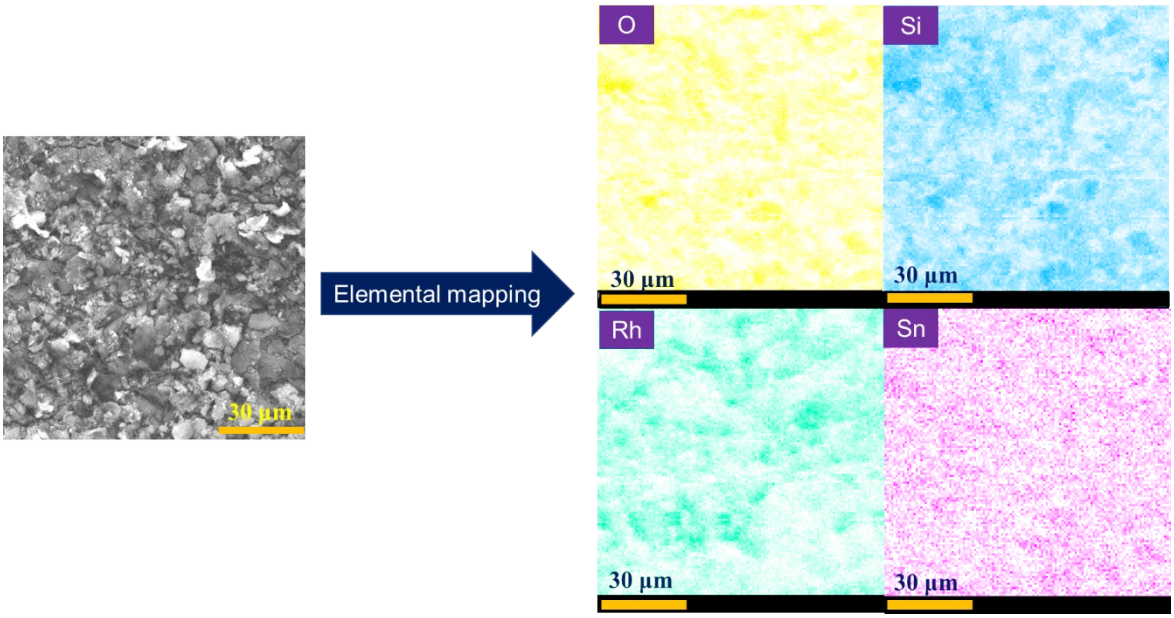


**Figure S8**. SEM-EDS elemental mapping of Rh-Sn/$SiO_2$ bimetallic catalyst.

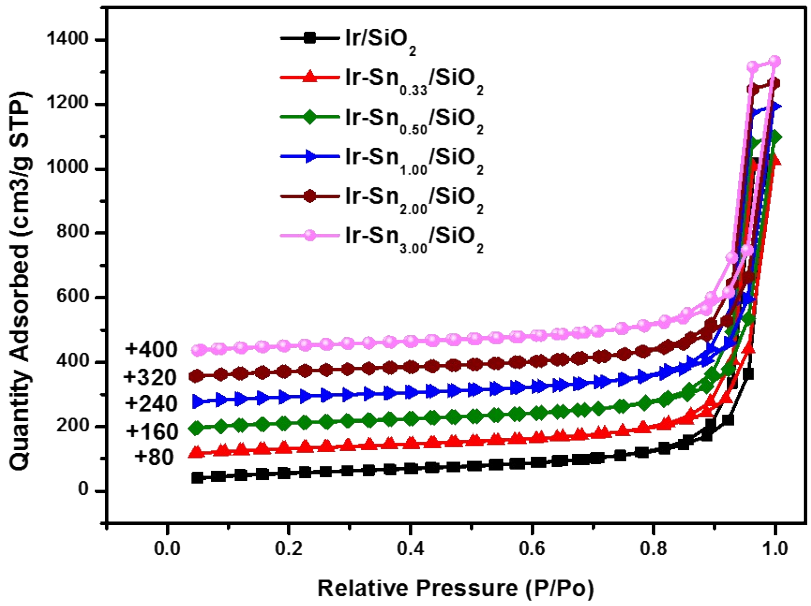


**Figure S9**. Nitrogen adsorption isotherms of Ir-Sn/$SiO_2$ samples with different Sn/Ir ratios.

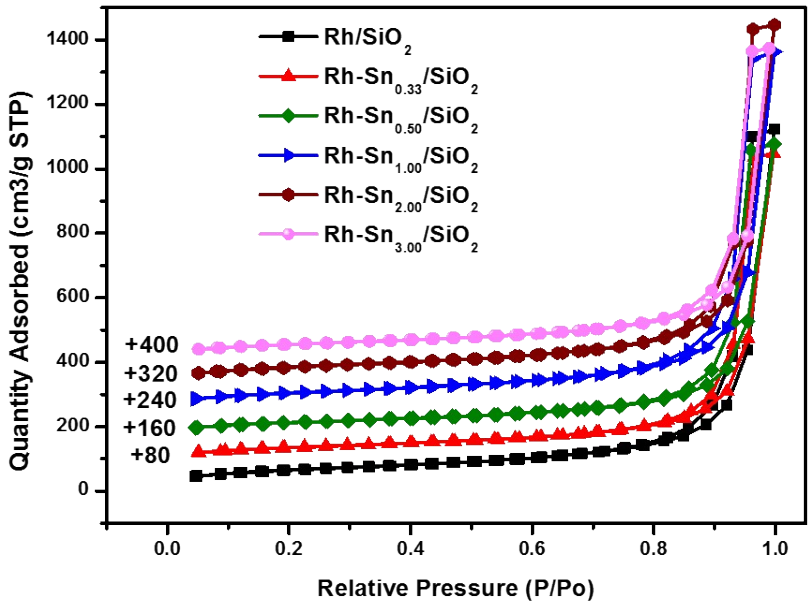


**Figure S10**. Nitrogen adsorption isotherms of Rh-Sn/$SiO_2$ samples with different Sn/Rh ratios.

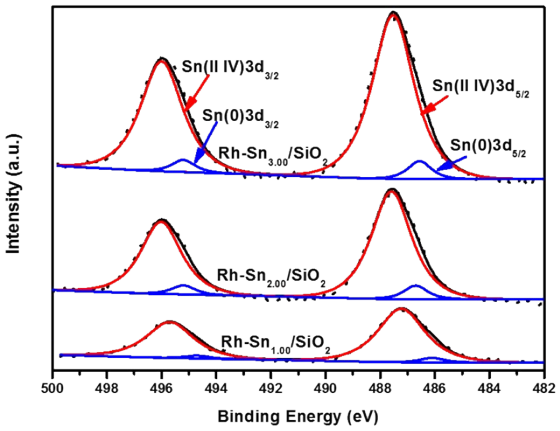


**Figure S11**. XPS of Sn 3d core level of Rh-Sn/$SiO_2$ bimetallic catalysts with Sn/Rh ratios of 1, 2 and 3.

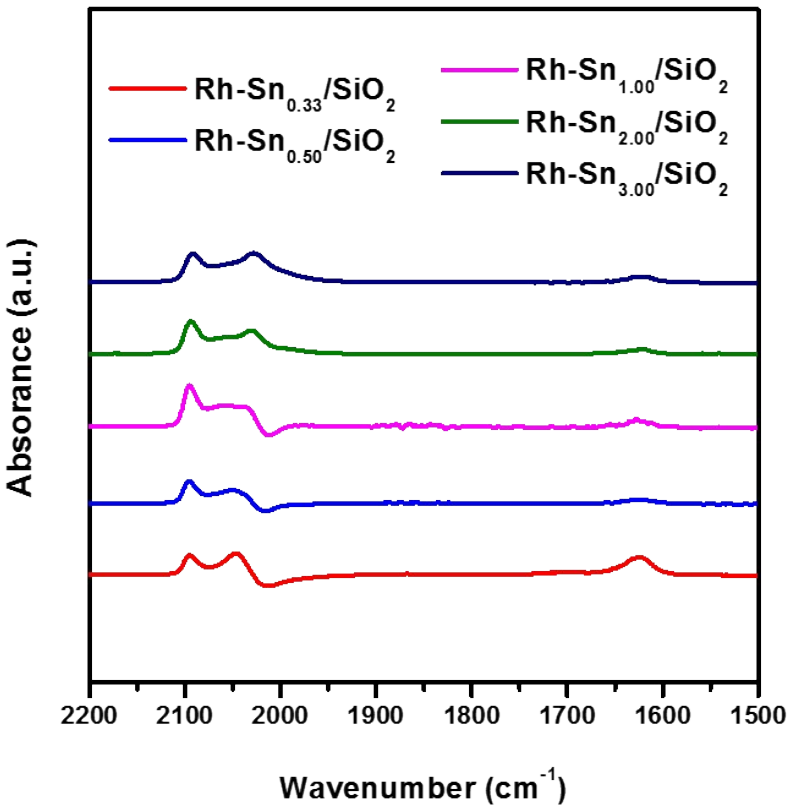


**Figure S12**. Infrared spectra of CO adsorbed on the Rh-Sn/$SiO_2$ bimetallic catalysts at room temperature.

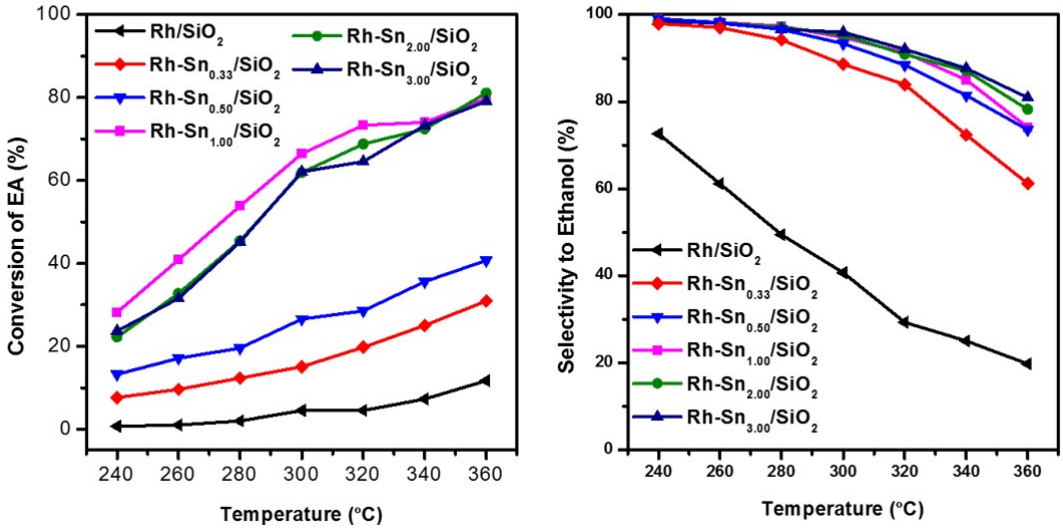


**Figure S13**. Catalytic performance of Rh-Sn/$SiO_2$ catalysts for ethyl acetate hydrogenolysis reaction from 240 to 360 °C. Reaction conditions: pressure=5 MPa, $H_2$/ethyl acetate ratio=5 and WHSV=1.08 $h^{-1}$.

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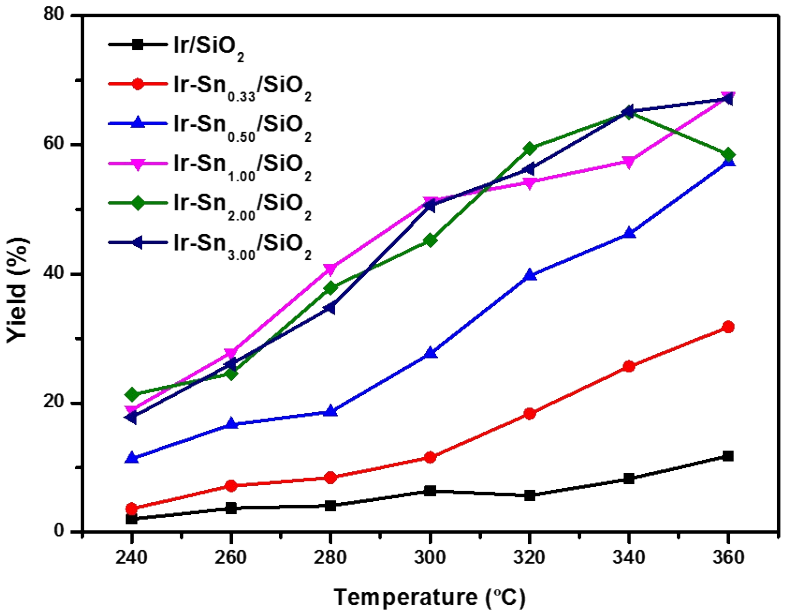


**Figure S14**. Ethanol yield achieved in ethyl acetate hydrogenolysis over Ir-Sn/$SiO_2$ catalysts with different Sn/Ir ratios. Reaction conditions: pressure=5 MPa, $H_2$/ethyl acetate ratio=5 and WHSV=1.08 $h^{-1}$.

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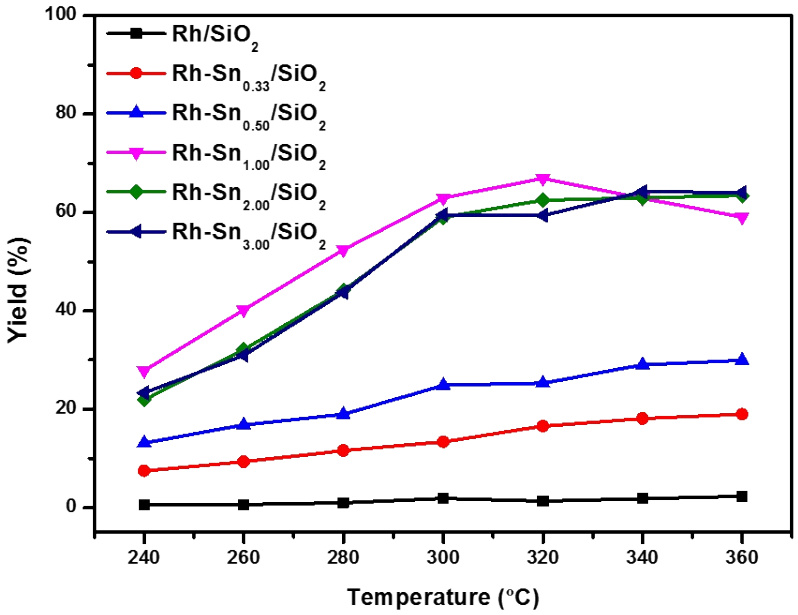


**Figure S15**. Ethanol yield achieved in ethyl acetate hydrogenolysis over Rh-Sn/$SiO_2$ catalysts with different Sn/Rh ratios. Reaction conditions: pressure=5 MPa, $H_2$/ethyl acetate ratio=5 and WHSV=1.08 $h^{-1}$.

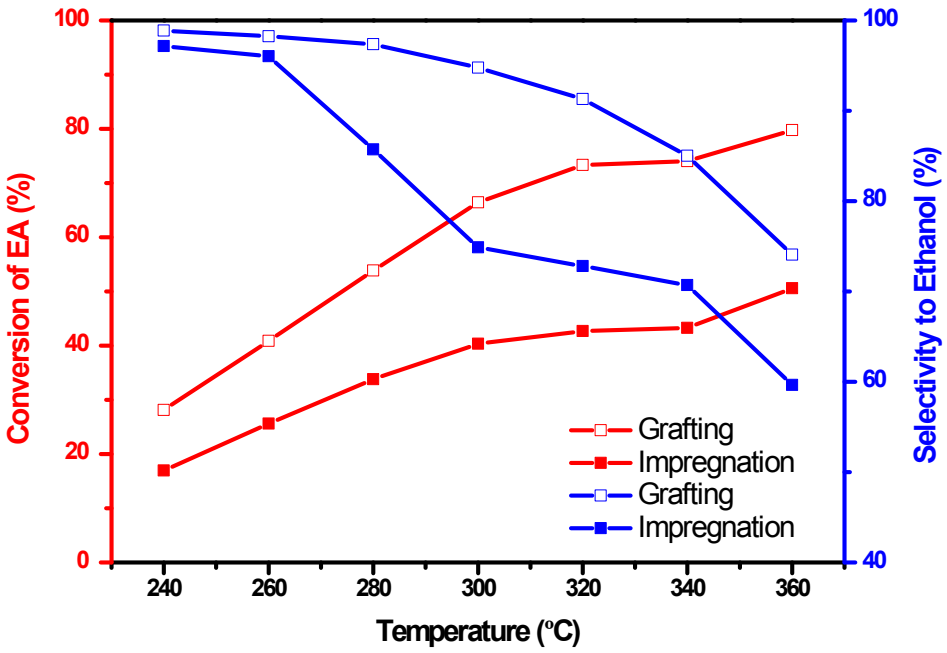


**Figure 16**. Ethyl acetate conversion and ethanol selectivity over Rh-$Sn_{1.00}/SiO_2$ catalysts from grafting and impregnation synthesis. Reaction conditions: pressure=5 MPa, $H_2$/ethyl acetate ratio=5 and WHSV=1.08 $h^{-1}$.

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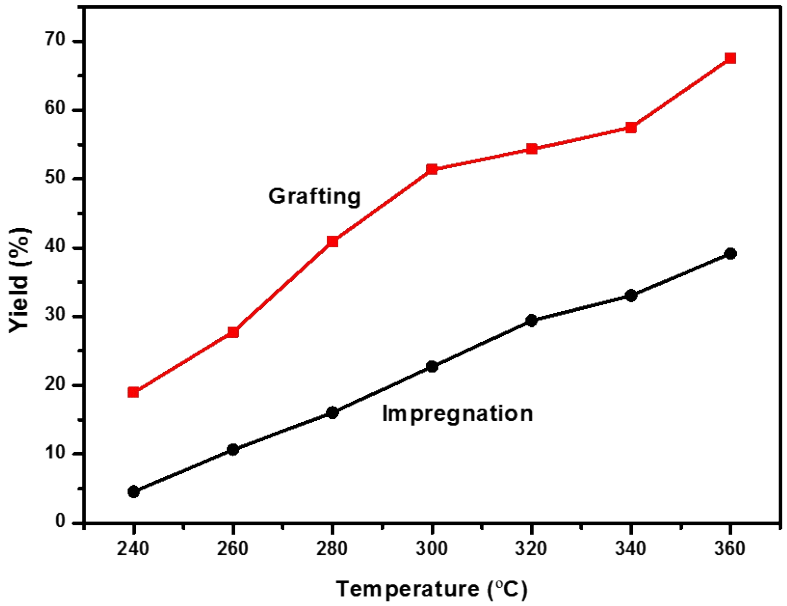


**Figure S17**. Ethanol yield achieved over Ir-$Sn_{1.00}/SiO_2$ catalysts from grafting and impregnation syntheses. Reaction conditions: pressure=5 MPa, $H_2$/ethyl acetate ratio=5 and WHSV=1.08 $h^{-1}$.

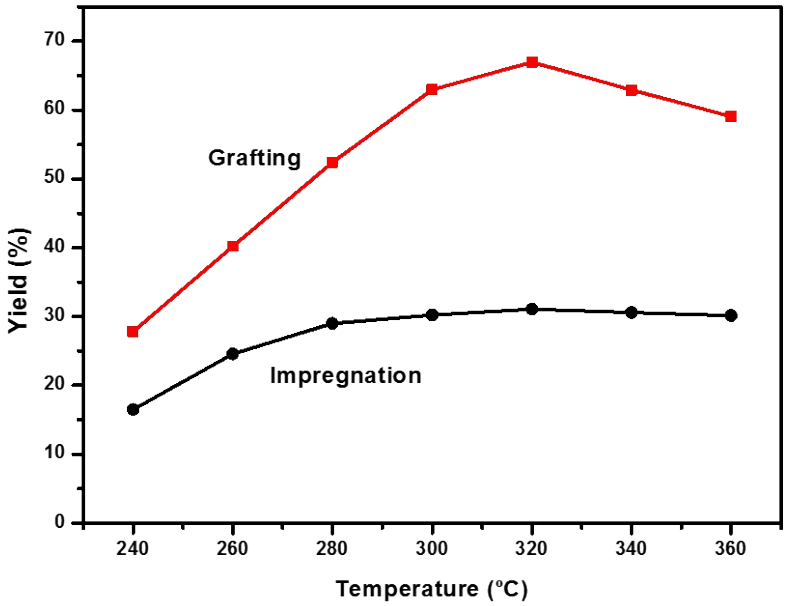


**Figure S18**. Ethanol yield achieved over Rh-$Sn_{1.00}/SiO_2$ catalysts from grafting and impregnation syntheses. Reaction conditions: pressure=5 MPa, $H_2$/ethyl acetate ratio=5 and WHSV=1.08 $h^{-1}$.

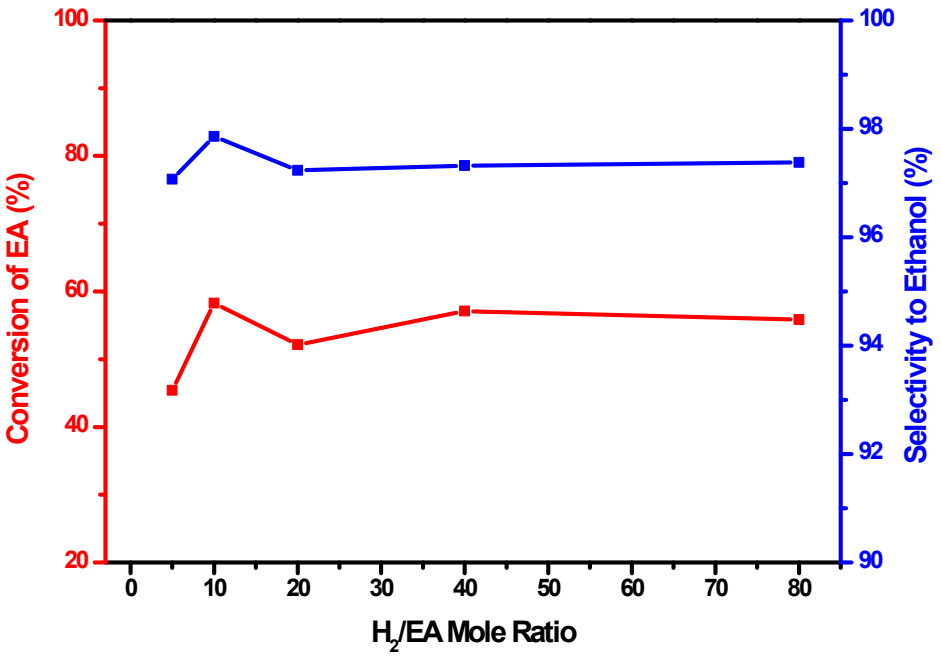


**Figure S19**. The effect of $H_2$/ethyl acetate ratios on the catalytic performance of Rh-$Sn_{1.00}/SiO_2$ catalyst. Reaction conditions: temperature=300 °C, pressure=5 MPa and WHSV= 1.08 $h^{-1}$.

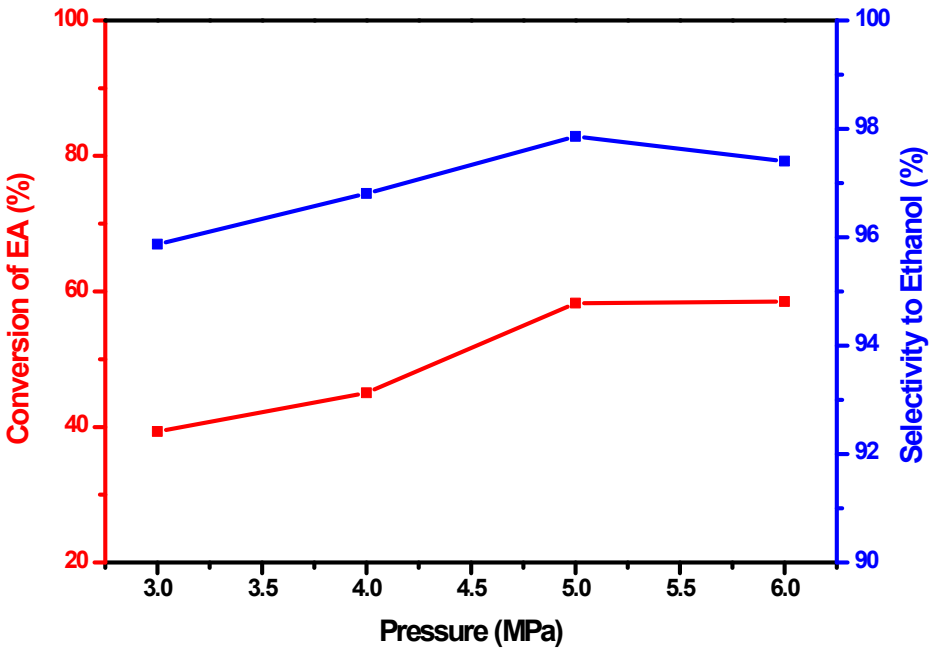


**Figure S20**. The effect of reaction pressure on the catalytic performance of Rh-$Sn_{1.00}/SiO_2$ catalyst. Reaction conditions: temperature=300 °C, $H_2$/ethyl acetate ratio=10 and WHSV=1.08 $h^{-1}$.

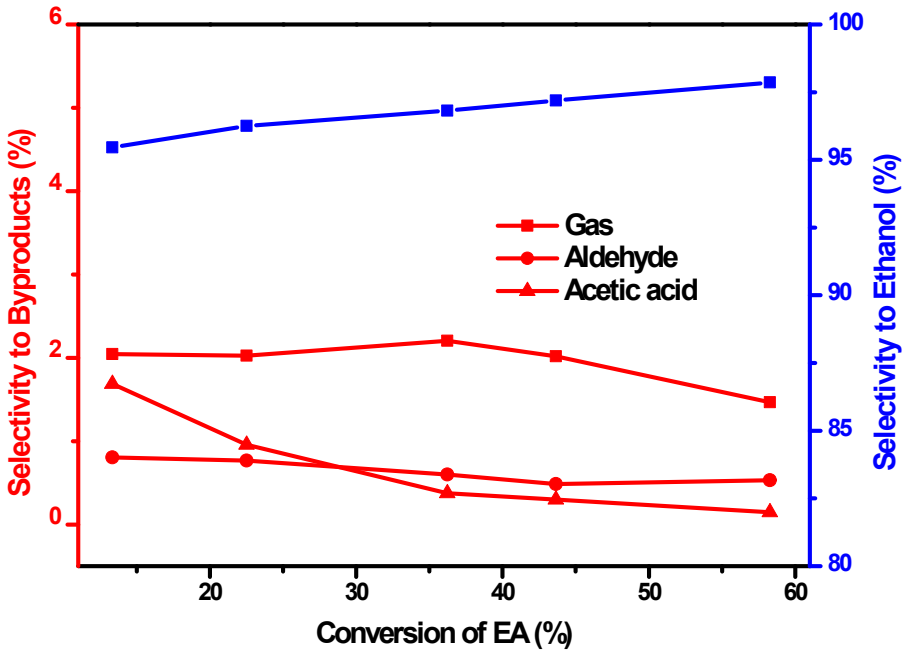


**Figure S21**. Product selectivity versus ethyl acetate conversion over Rh-$Sn_{1.00}/SiO_2$ at 280 °C. Reaction conditions: pressure=5 MPa and $H_2$/ethyl acetate ratio=10.

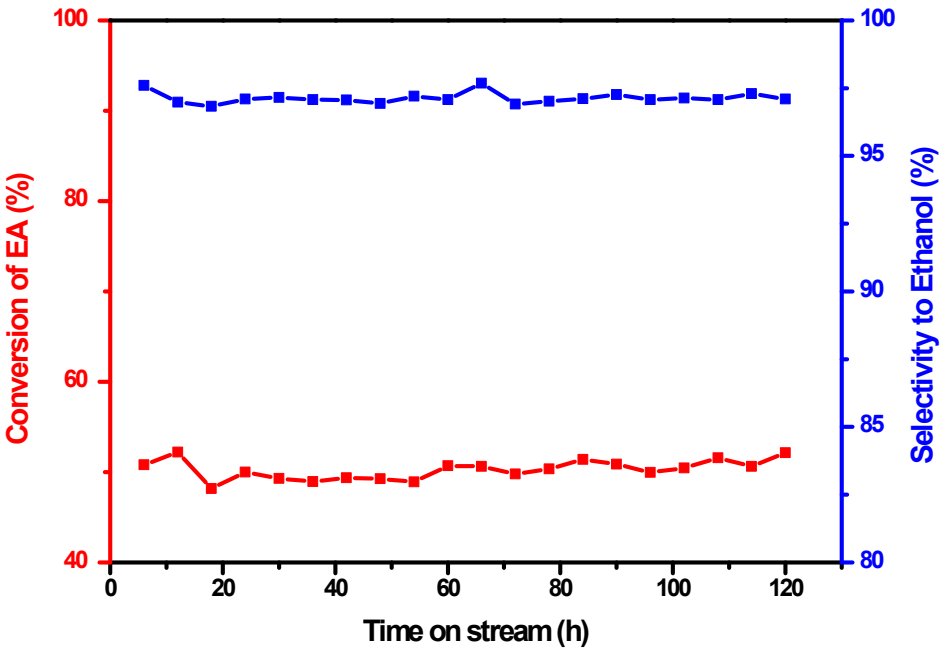


**Figure S22**. Stability of Rh-$Sn_{1.00}/SiO_2$ catalyst in ethyl acetate hydrogenolysis reaction. Reaction conditions: temperature=280 °C, pressure=5 MPa, $H_2$/ethyl acetate ratio=10 and WHSV=1.08 $h^{-1}$.