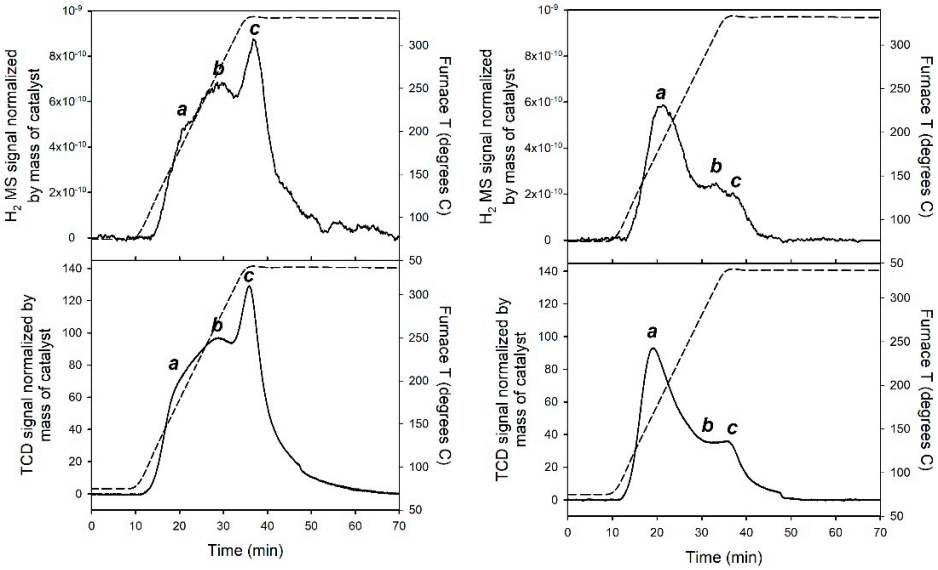
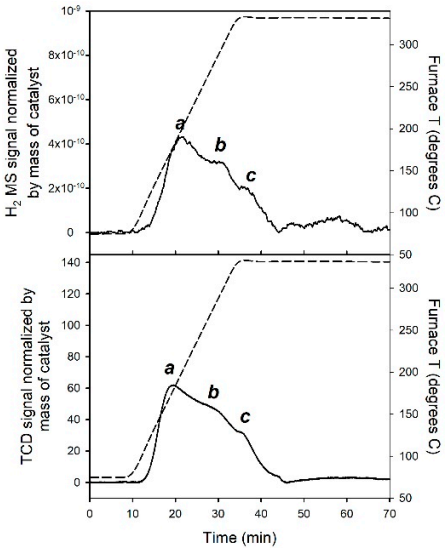
**Table S1**: BET surface area, specific volume, and average pore diameter.

| Sample ID | Measured $A_s$ (BET) ($m^2/g$) | Expected $A_s$ (BET) ($m^2/g$) | $V_p$ (BJH Des) ($cm^3/g$) | $D_p$ (BJH Des) (nm) |
|---|---|---|---|---|
| m-$ZrO_2$ | 95.4 | 95.4 | 0.289 | 9.5 |
| 1%Ru/m-$ZrO_2$ | 90.4 | 94.1 | 0.267 | 9.3 |
| 0.5%Na-1%Ru/m-$ZrO_2$ | 87.5 | 91.2 - 93.0 | 0.255 | 9.2 |
| 1.0%Na-1%Ru/m-$ZrO_2$ | 81.6 | 88.2 - 91.9 | 0.252 | 9.1 |
| 1.8%Na-1%Ru/m-$ZrO_2$ | 73.3 | 83.5 - 90.2 | 0.231 | 9.2 |
| 2.5%Na-1%Ru/m-$ZrO_2$ | 67.0 | 79.3 - 88.6 | 0.211 | 9.3 |
| 5.0%Na-1%Ru/m-$ZrO_2$ | 44.7 | 64.5 - 83.1 | 0.148 | 10.1 |




(a) (b)




(c)

**Figure S1**: Results of hydrogen TPD for (a) 1%Ru/m-zirconia, (b) 2.5%Na-1%Ru/m-zirconia, and (c) 5%Na-1%Ru/m-zirconia. Peaks ***a***, ***b***, and ***c*** represent active sites of increasing chemisorption strength.

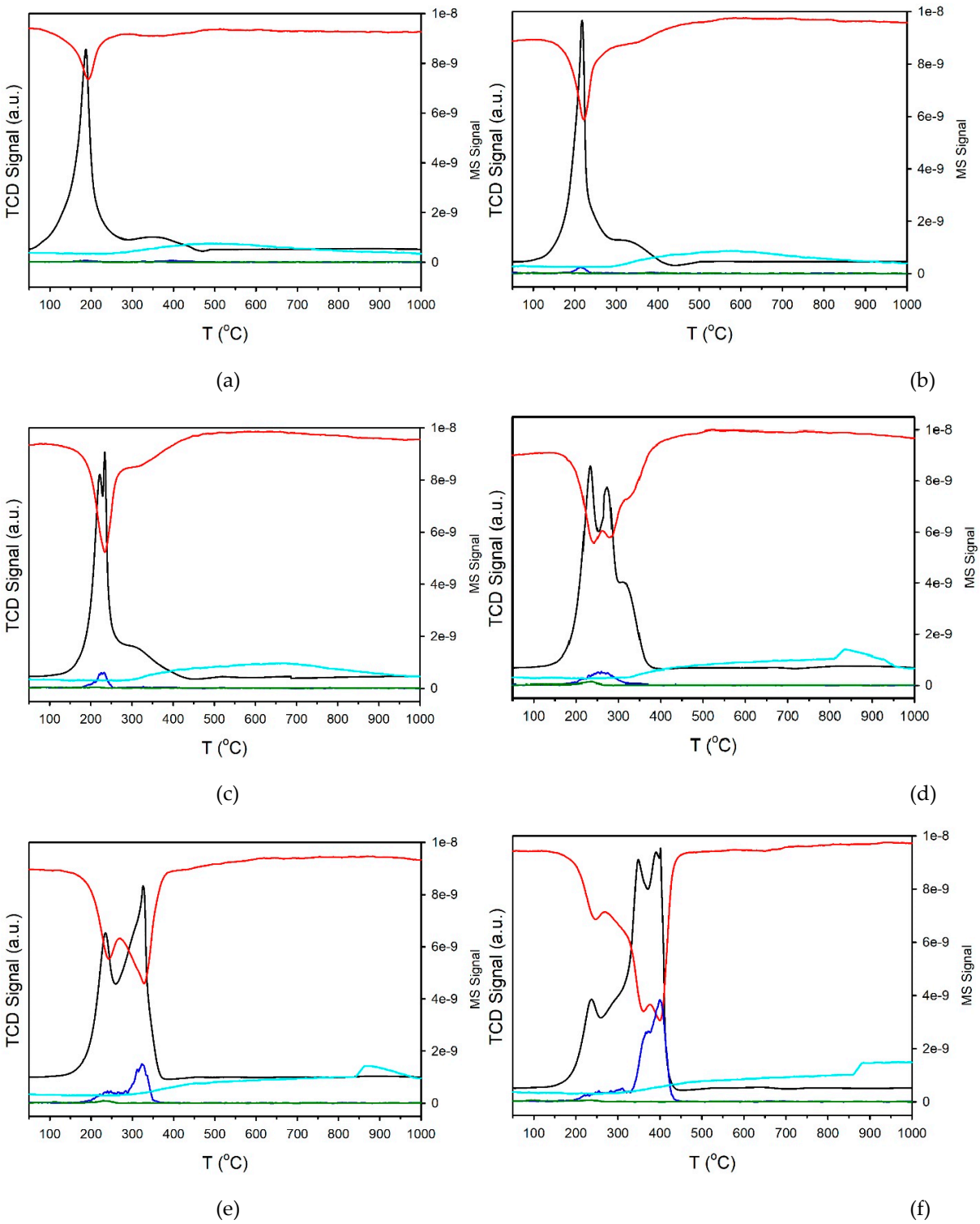



**Figure S2**: Hydrogen-TPR/ TPR-MS for (a) unpromoted 1%Ru/m-zirconia and the promoted catalyst with sodium loadings of (b) 0.5%, (c) 1%, (d) 1.8%, (e) 2.5%, and (f) 5%, including (black) TCD signal, and MS data for (red) hydrogen, (cyan) water, (blue) carbon monoxide, and (green) carbon dioxide.

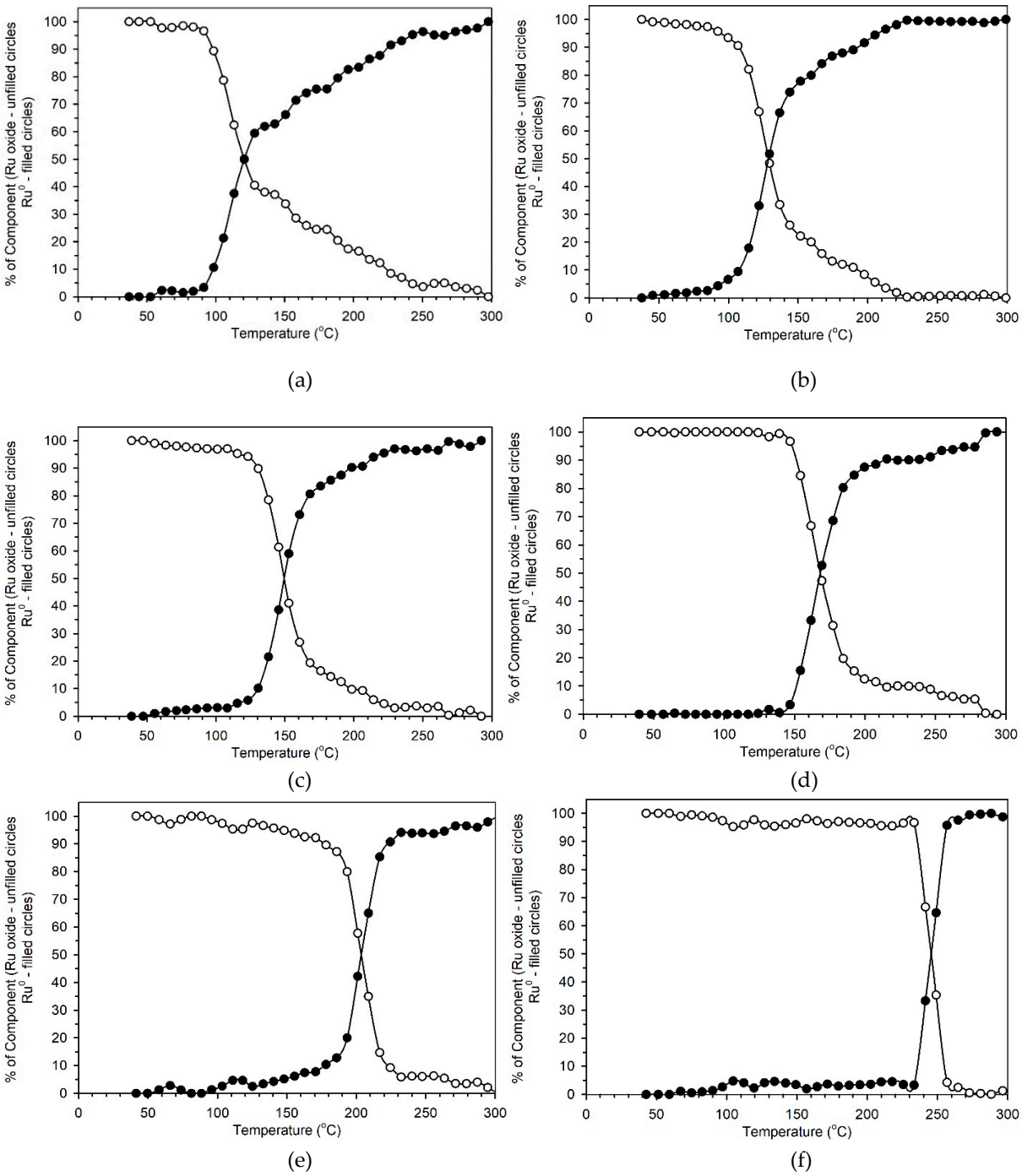



**Figure S3**: Linear combination fittings of TPR-XANES spectra recorded at the Ru K edge as a function of temperature for (a) unpromoted 1%Ru/m-zirconia catalyst and promoted catalysts with Na loadings of (b) 0.5%, (c) 1.0%, (d) 1.8%, (e) 2.5%, and (f) 5%, including (unfilled circles) ruthenium oxide and (filled circles) ruthenium metal. The point of 50% conversion from ruthenium oxide to ruthenium metal occurs at (a) 121°C, (b) 129°C, (c) 149°C, (d) 168°C, (e) 203°C, and (f) 246°C.

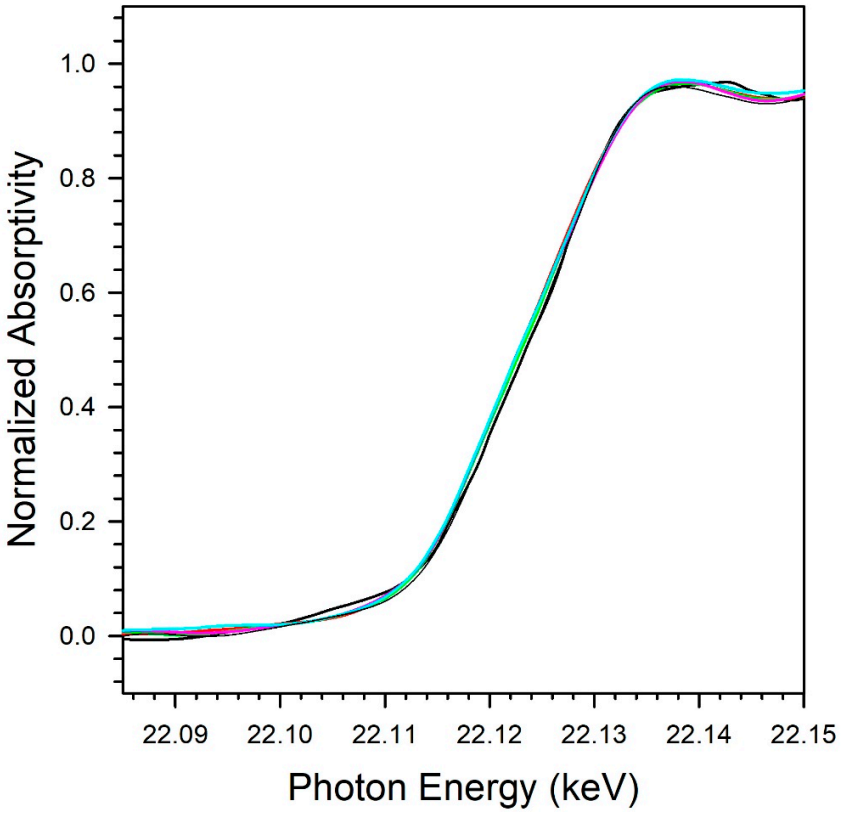



**Figure S4**: XANES overlays following $H_2$-TPR.

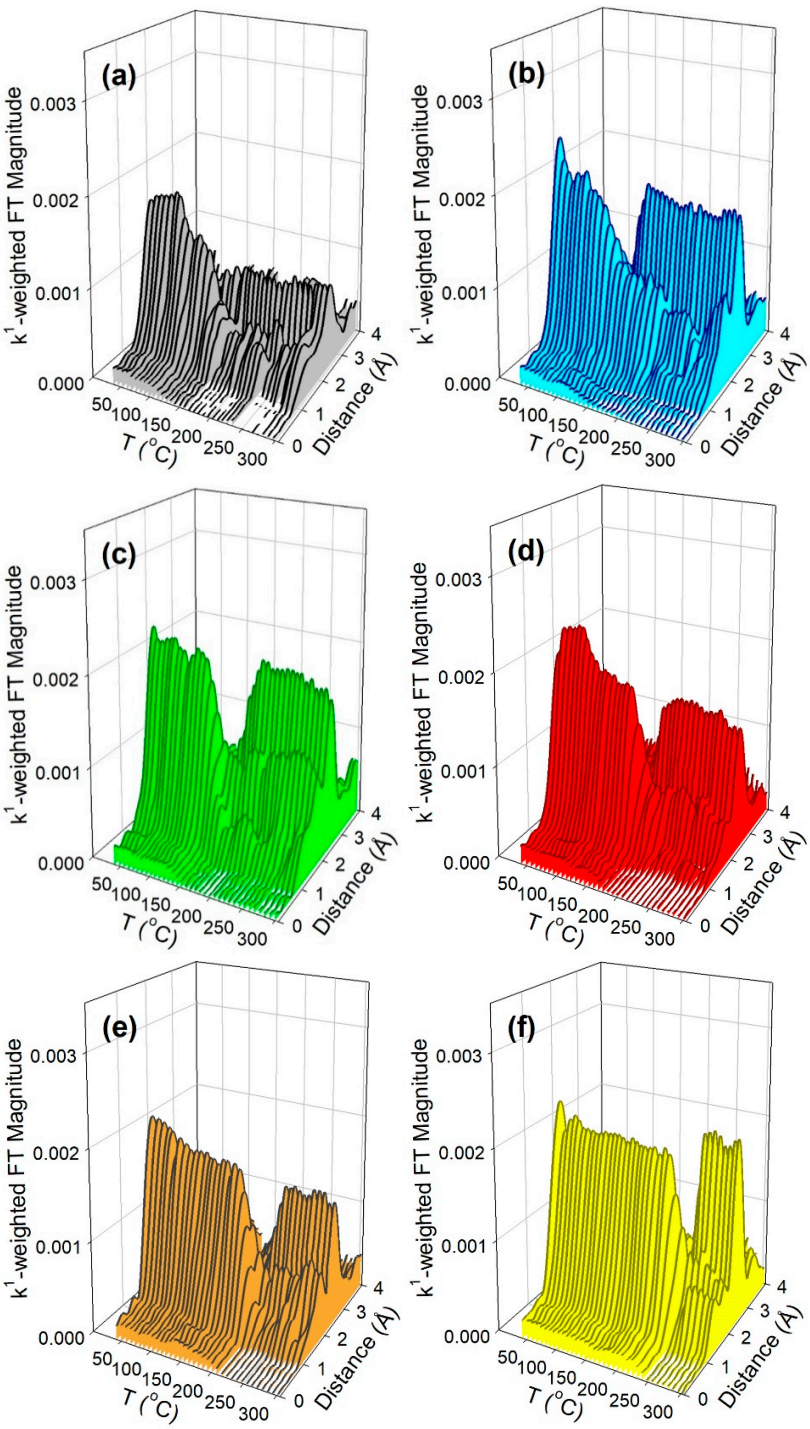



**Figure S5**: TPR-EXAFS Fourier transform magnitude spectra recorded near the Ru K edge as a function of temperature for (a, gray) unpromoted 1%Ru/m-zirconia and promoted catalysts having Na loadings of (b, cyan) 0.5%, (c, green) 1.0%, (d, red) 1.8%, (e, orange) 2.5%, and (f, yellow) 5%.

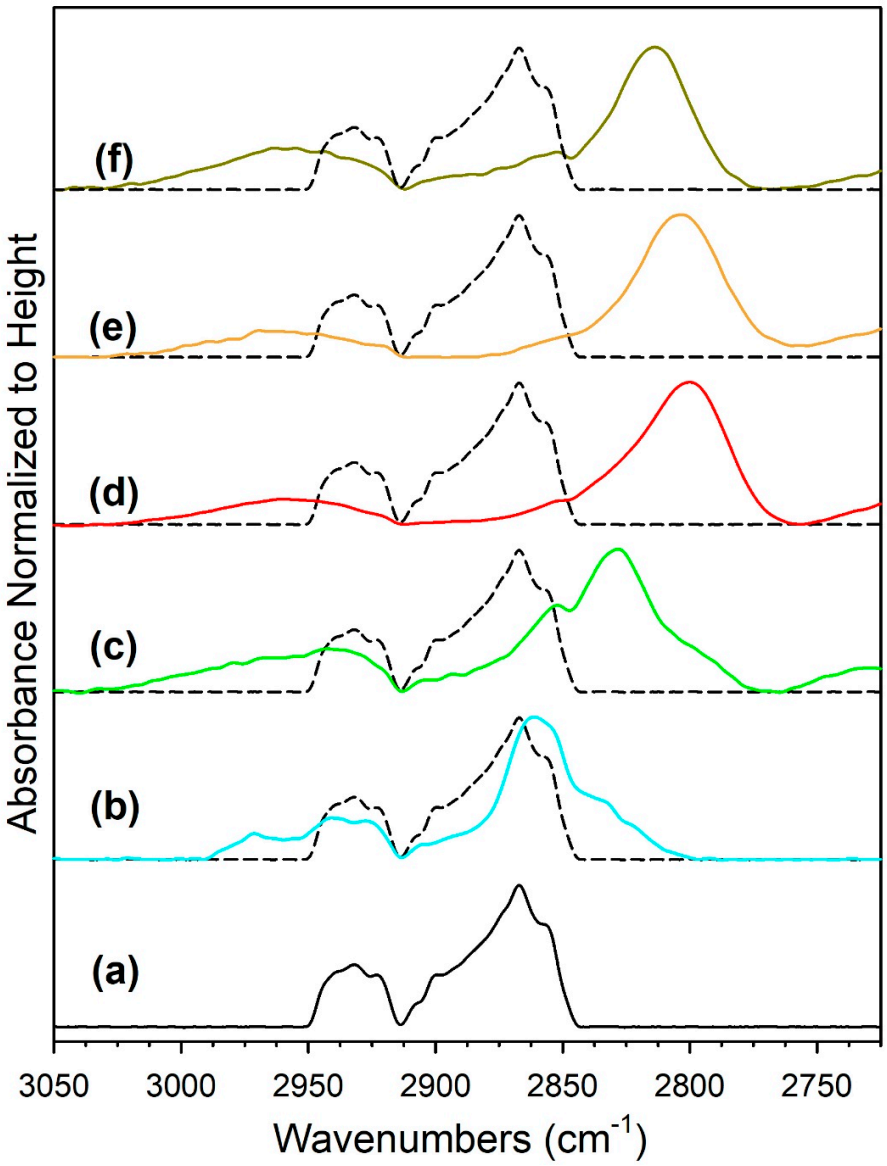



**Figure S6**: DRIFTS of formate ν(CH) band following CO adsorption at 225 °C (and cooling to 130 °C) to react with defect-associated OH groups produced over catalysts reduced at 300°C in $H_2$ and steamed at 225 °C (followed by $H_2$ and He purges at 225 °C), including (a) unpromoted 1%Ru/m-zirconia, and the promoted catalysts having Na loadings of (b) 0.5%, (c) 1%, (d) 1.8%, (e) 2.5%, and (f) 5%.

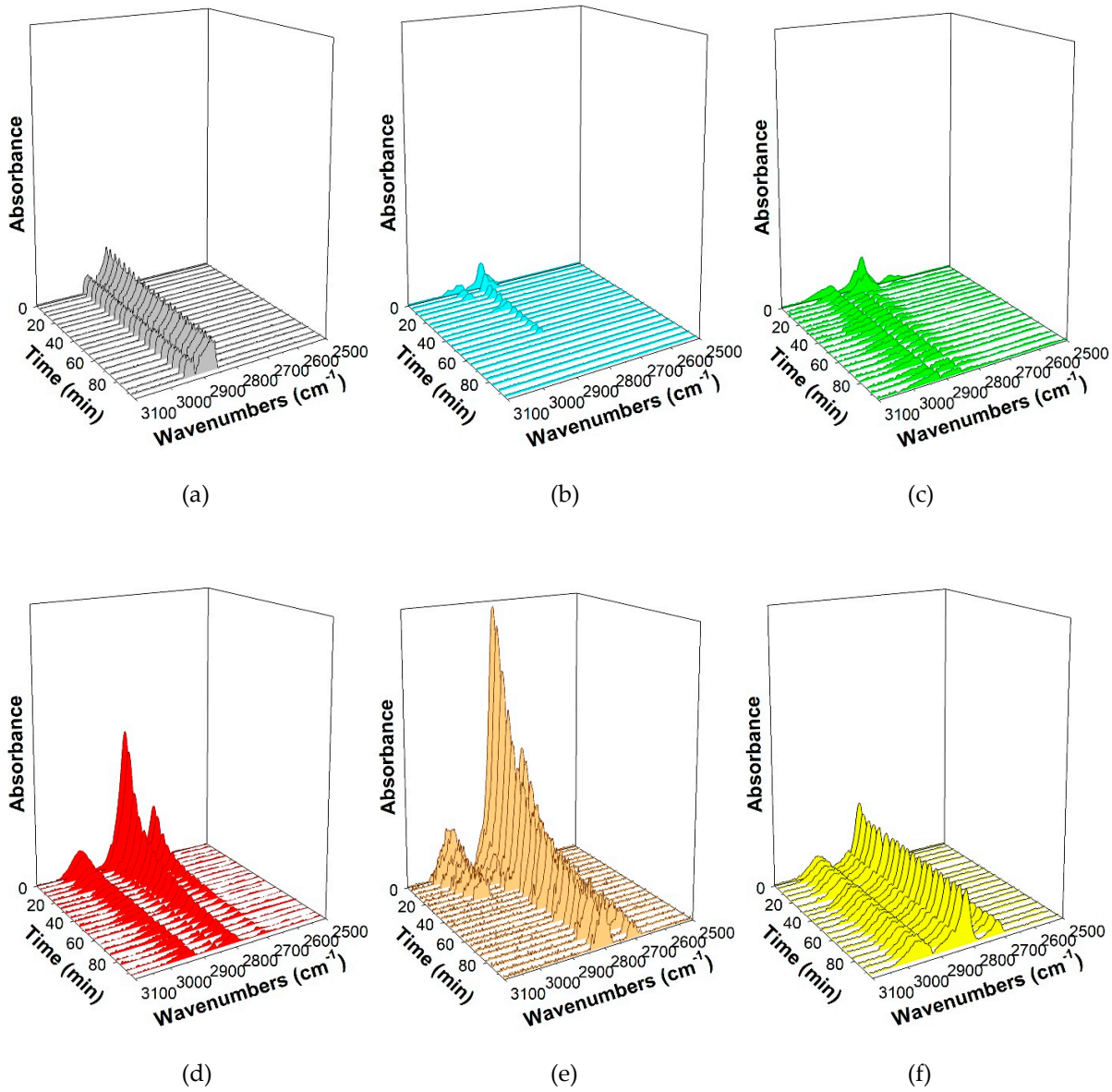



**Figure S7**: Forward formate decomposition in 75 mL/min of 4.4%$H_2O$ in helium at 130°C for (a) unpromoted 1%Ru/m-zirconia, and the promoted catalysts having Na loadings of (b) 0.5%, (c) 1%, (d) 1.8%, (e) 2.5%, and (f) 5%.

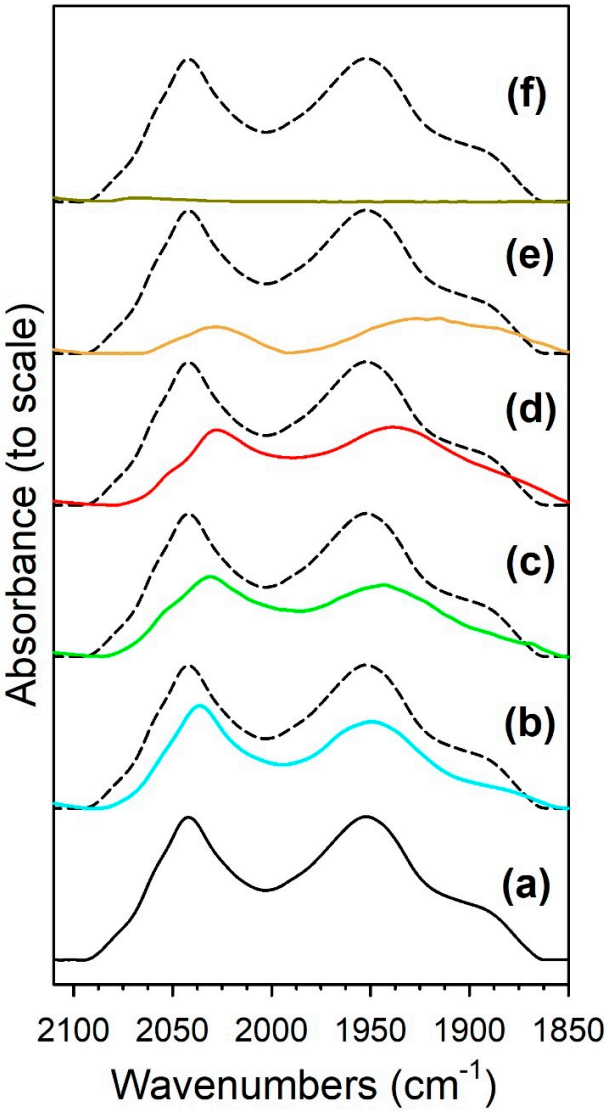



**Figure S8**: Effect of Na on attenuating the Ru carbonyl ν(CO) band intensity following CO adsorption at 225 °C (and cooling to 130 °C) over catalysts reduced at 300°C in $H_2$ and steamed at 225 °C (followed by $H_2$ and He purges at 225 °C), including (a) unpromoted 1%Ru/m-zirconia, and the promoted catalysts having Na loadings of (b) 0.5%, (c) 1%, (d) 1.8%, (e) 2.5%, and (f) 5%.

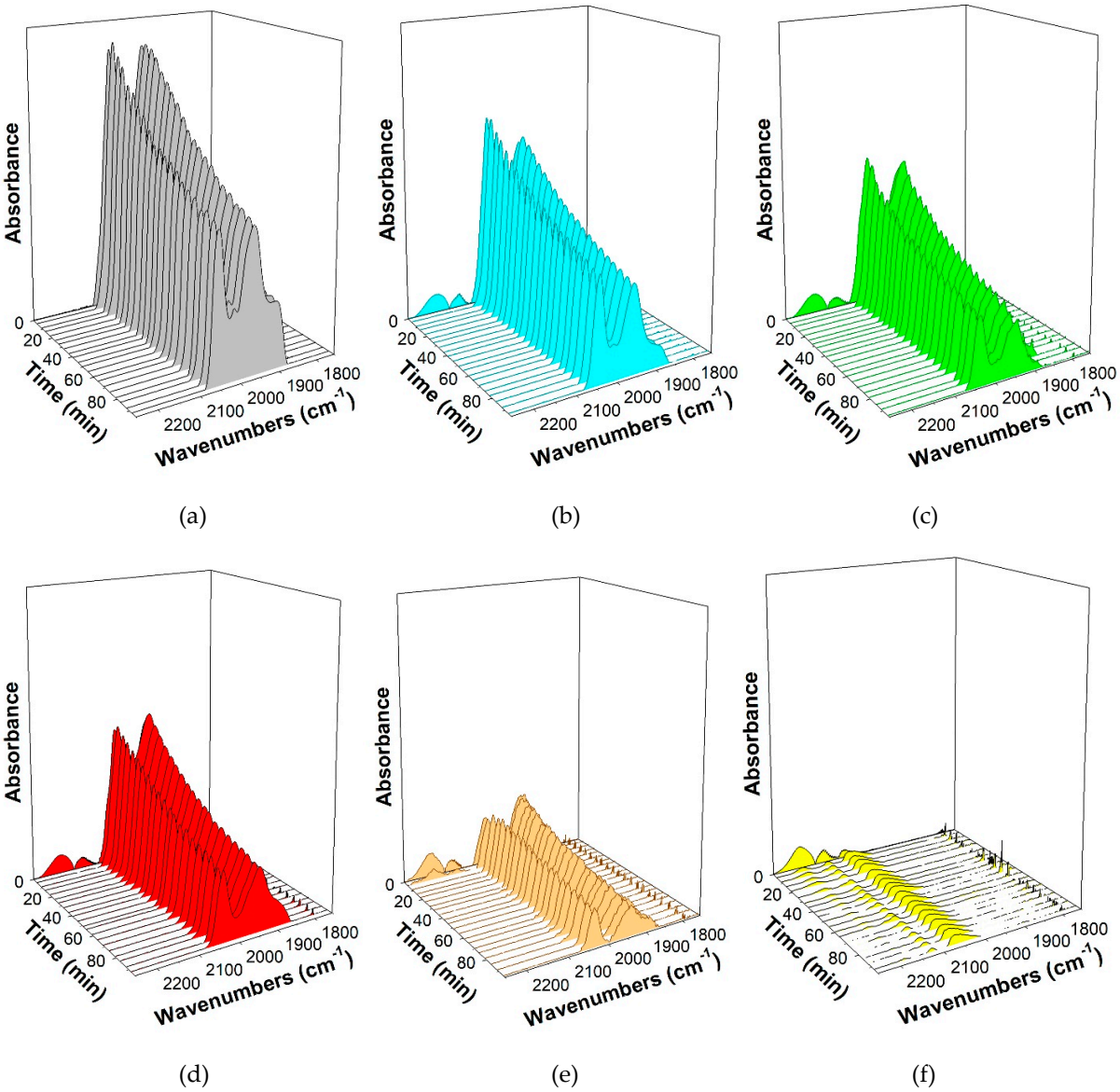



**Figure S9**: Ru-carbonyl decomposition in 75 mL/min of 4.4%$H_2O$ in helium at 130°C for (a) unpromoted 1%Ru/m-zirconia, and the promoted catalysts having Na loadings of (b) 0.5%, (c) 1%, (d) 1.8%, (e) 2.5%, and (f) 5%.

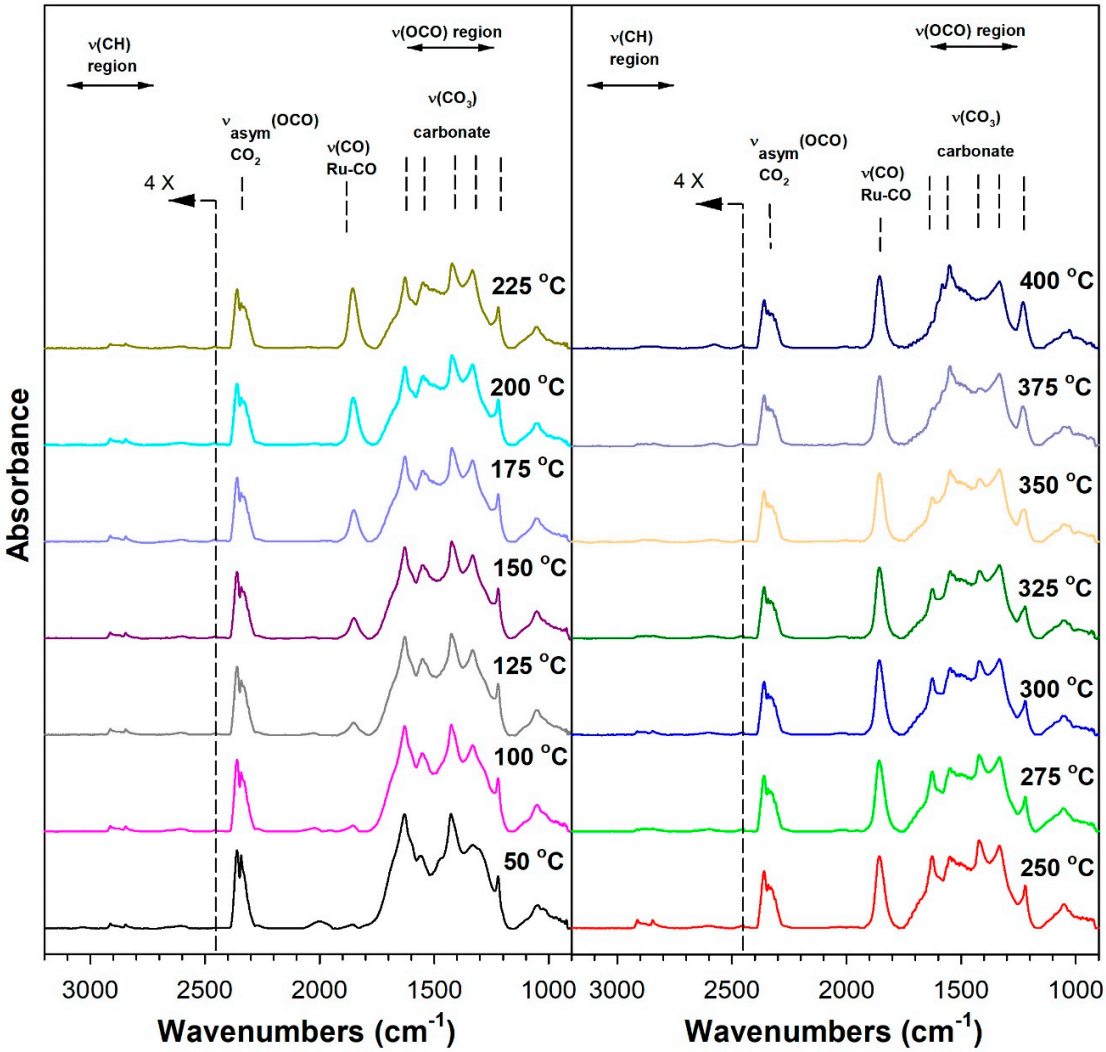



**Figure S10**: DRIFTS of 4%$CO_2$ (balance He) for unpromoted 1%Ru/m-zirconia reduced at 300°C in $H_2$, purged in He, and then cooled to 50 °C prior to $CO_2$ adsorption.

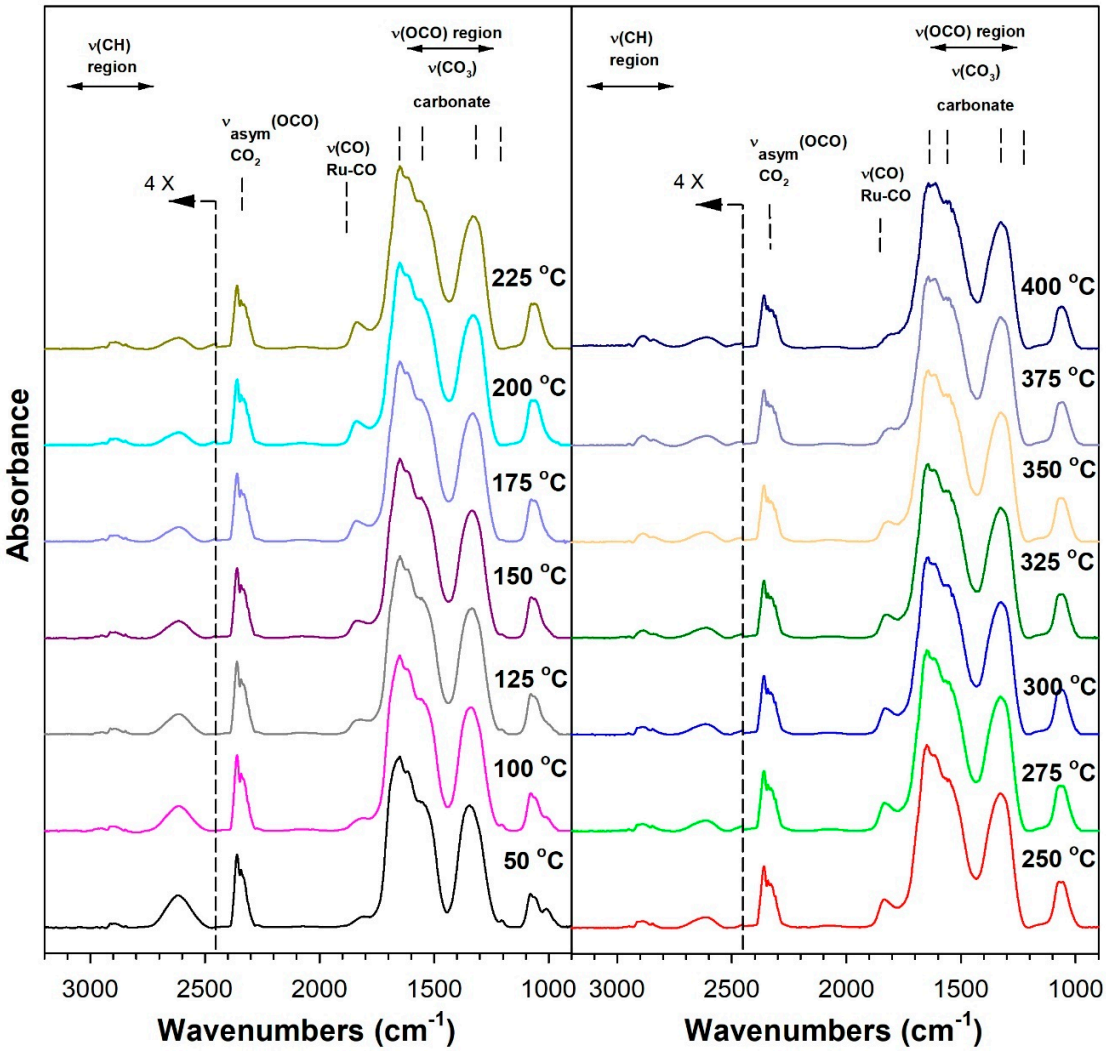



**Figure S11**: DRIFTS of 4%$CO_2$ (balance He) for 2.5%Na-1%Ru/m-zirconia reduced at 300°C in $H_2$, purged in He, and then cooled to 50 °C prior to $CO_2$ adsorption.