

Table S1. XPS fit parameters.

| <i>Species</i> | <i>Peak</i> | <i>Binding energy</i> | <i>FWHM</i> | <i>Fitting parameters</i> |
|------------------|-----------------------------|-----------------------|-------------|---------------------------|
| Ru | 3d _{5/2} | 279.9 | 0.93 | LF(0.8,1.25,500,180) |
| | 3d _{3/2} | 284.1 | 0.93 | LF(1.01,1.25,500,50) |
| RuO ₂ | 3d _{5/2} | 280.6 | 0.9 | LF(0.4,1,45,280) |
| | 3d _{3/2} | 285.4 | 1.2 | LF(0.4,1,45,280) |
| | 3d _{5/2} satellite | 282.4 | 2.15 | LF(0.6,1,45,280) |
| | 3d _{3/2} satellite | 286.6 | 2.20 | LF(0.4,1,45,280) |
| | | | | |
| C | 1s | 285.1 | 1.36 | GL(30) |
| C-oxid | 1s | 288.8 | 1.00 | GL(30) |

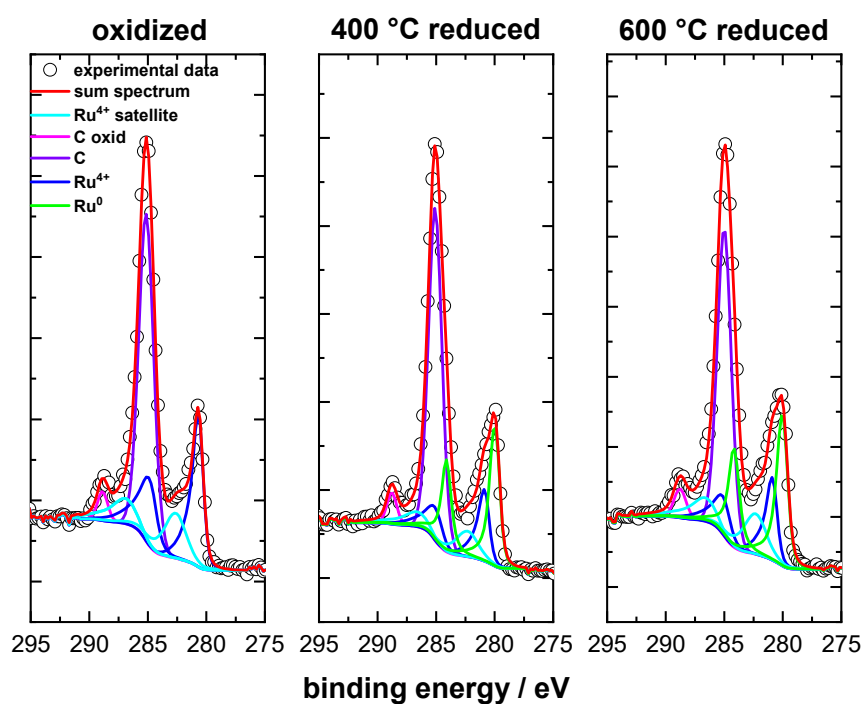


Figure S1. Ru 3d XP spectra of oxidized and reduced RuO₂. The reduction was carried out under 4% H₂ in Ar for 12 h at the stated temperatures.

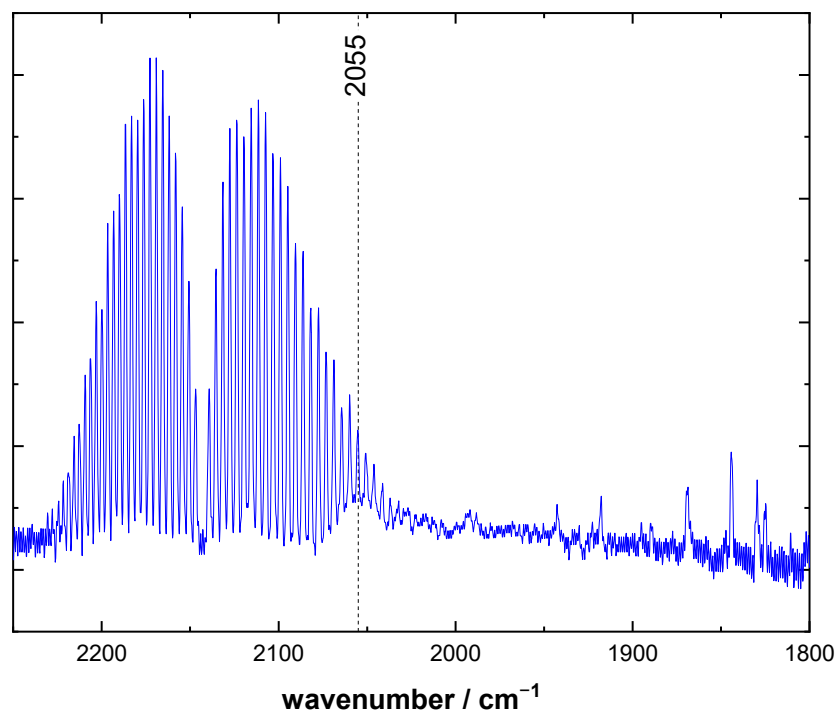


Figure S2. DRIFTS spectrum of CO adsorption on $\text{Ru}^0\text{-TiO}_2$, which has after oxidative pretreatment under 4% O_2 at 300 °C for 12h. As previously shown for $\text{RuO}_2\text{-TiO}_2$ only one band without shoulder is observed.

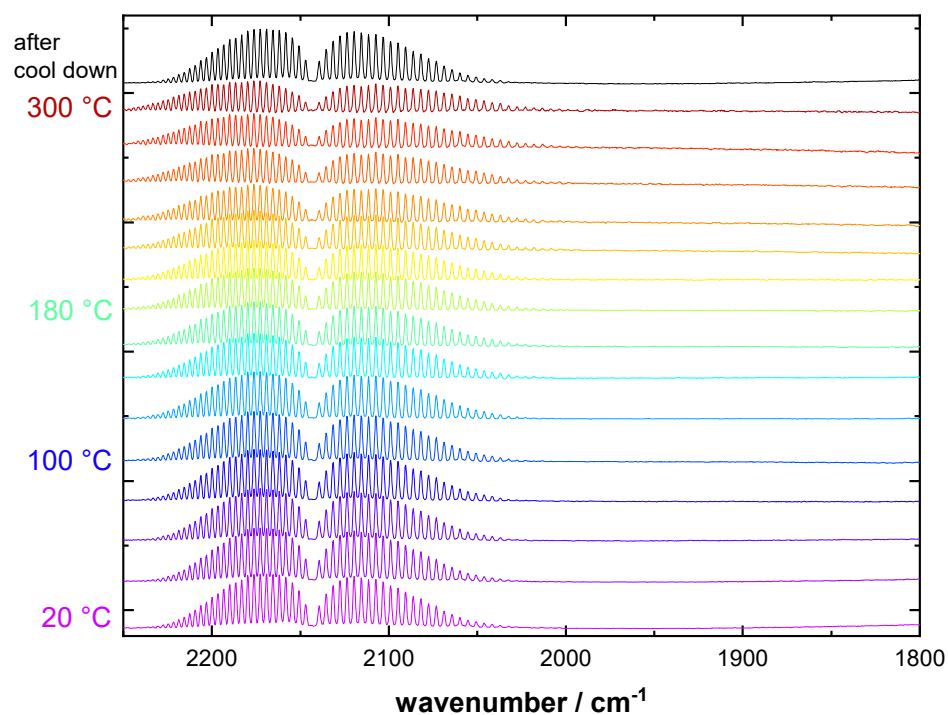


Figure S3. IR spectra of pre-oxidized TiO_2 heated in a CO atmosphere. CO adsorption bands are not observed, while the RoVi finr structure of CO gas appears between 2100-2200 cm^{-1} .

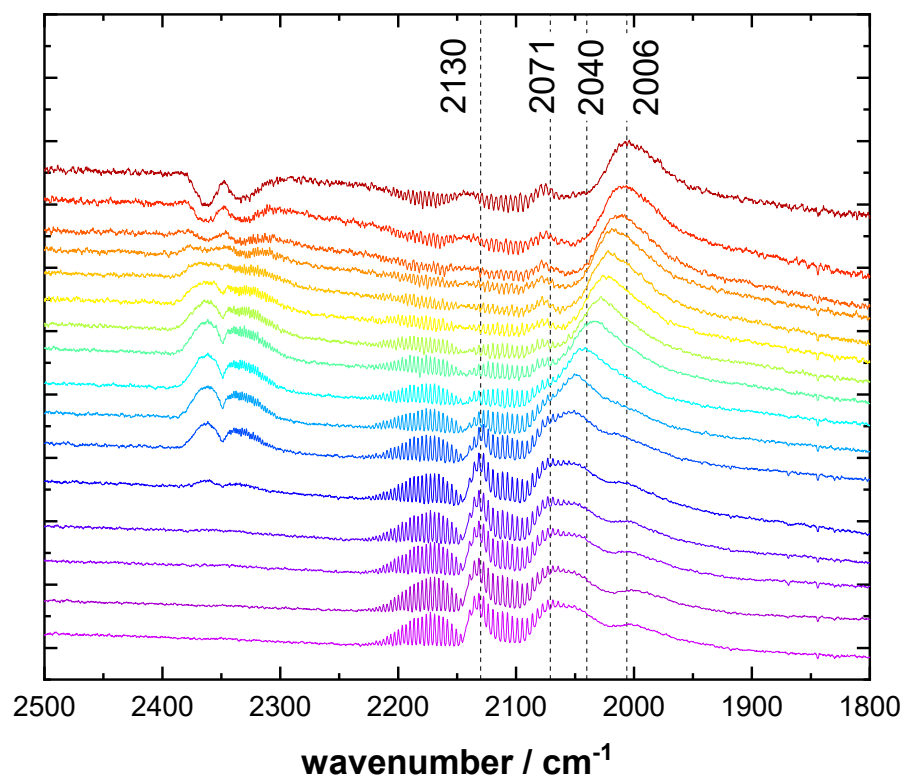


Figure S4. Operando DRIFT spectra of reduced-RuO₂@TiO₂ during cool down under reducing (1% O₂/4% CO/95% Ar) reaction feed composition. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

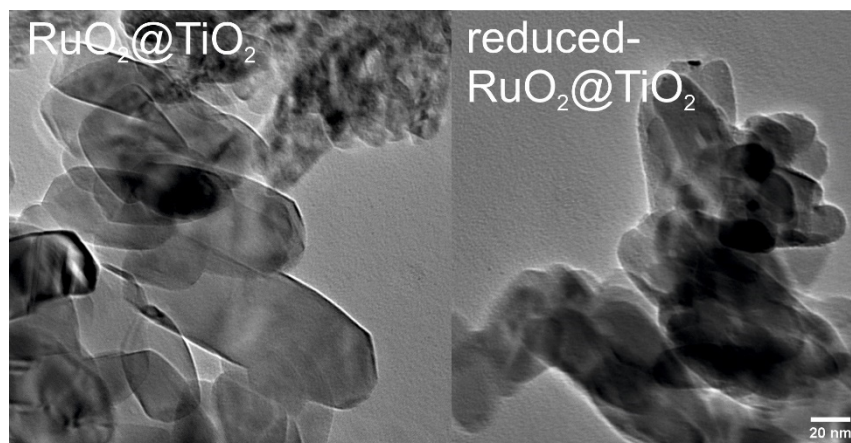


Figure S5. TEM micrographs of RuO₂@TiO₂ (left) before and (right) after reduction. The particles seen correspond to TiO₂ with the RuO₂ not being clearly visible. No morphological changes can be identified after reduction.