Supplementary Materials

Synergy between Sulfonic Functions and Ru Nanoparticles Supported on Activated Carbon for the Valorization of Cellulose into Sorbitol

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Content

S1. S_{2p} peaks from XPS analyses for the SO_3H / AC catalyst without heat-treatment and with heat-treatment at 200 °C, 300 °C and 400 °C

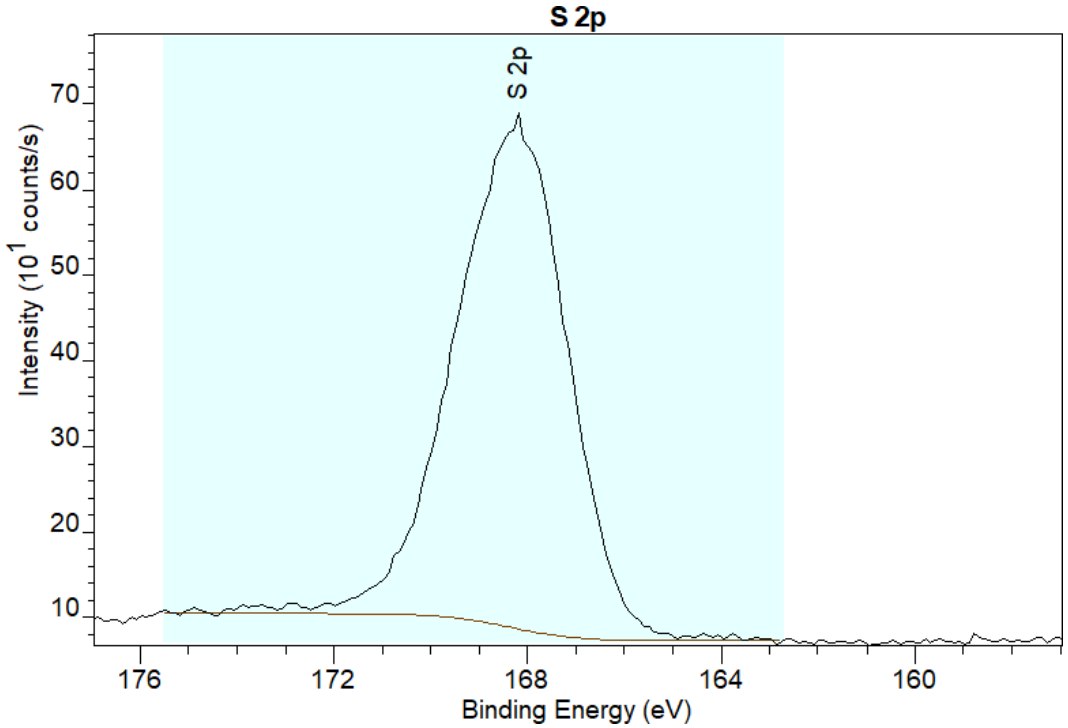

Figure 1: S_{2p} peak from XPS analysis for SO_3H / AC catalyst without heat-treatment

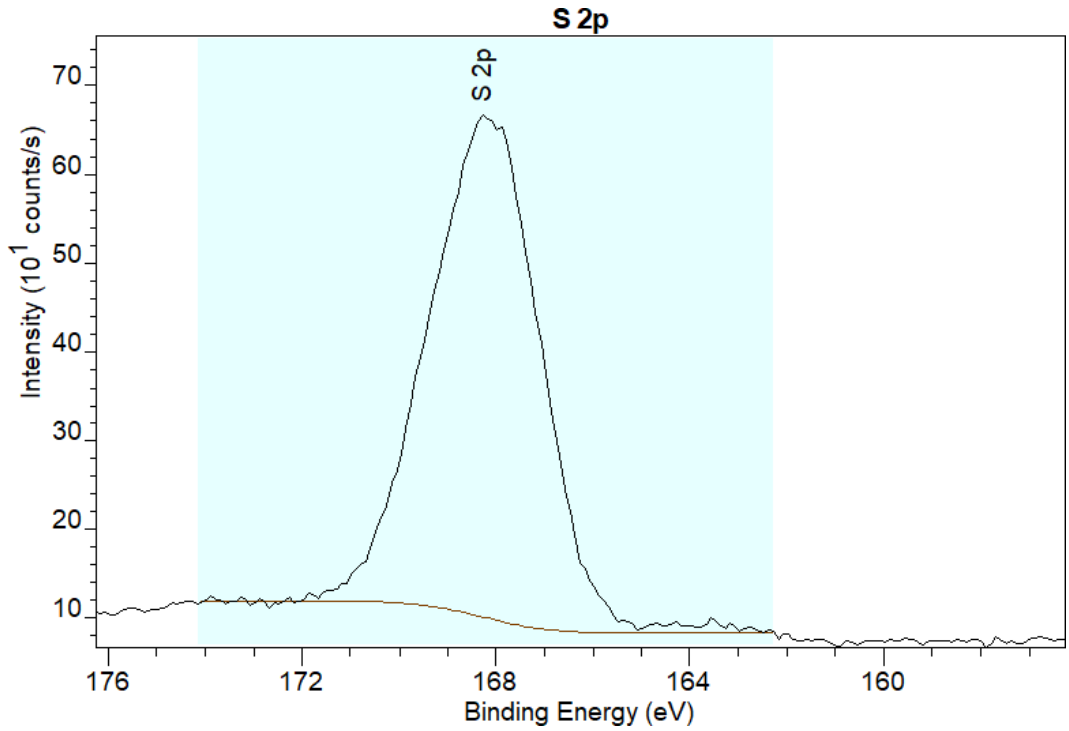

Figure 2: S_{2p} peak from XPS analysis for SO_3H / AC catalyst heat-treated at 200 °C

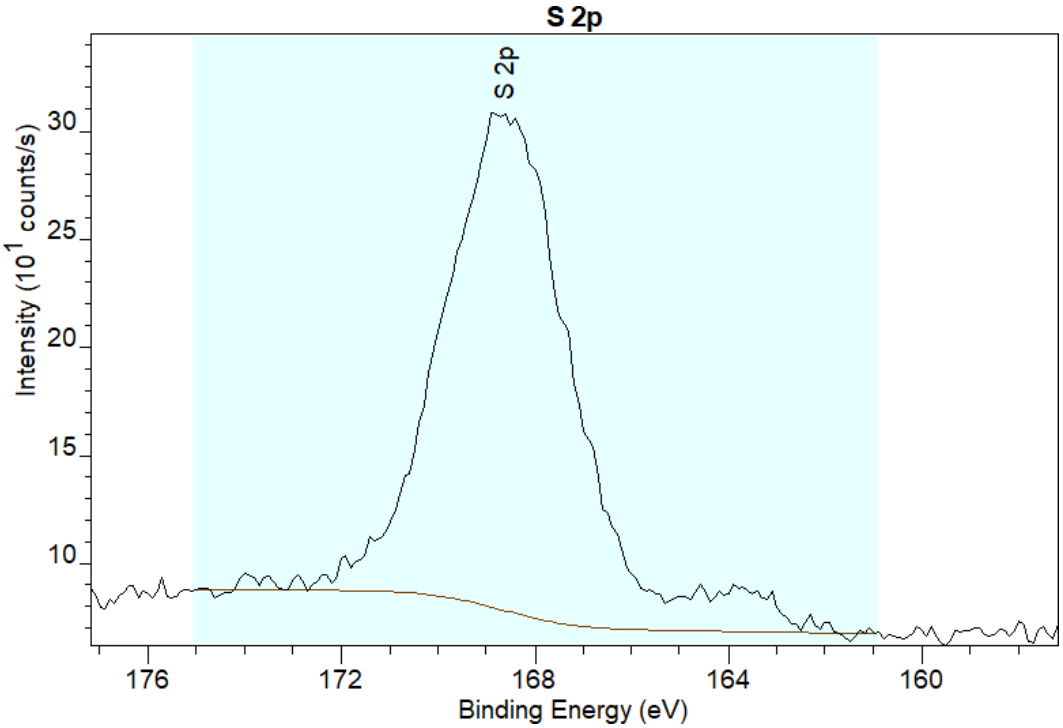

Figure 3: S_{2p} peak from XPS analysis for SO_3H / AC catalyst heat-treated at 300 °C

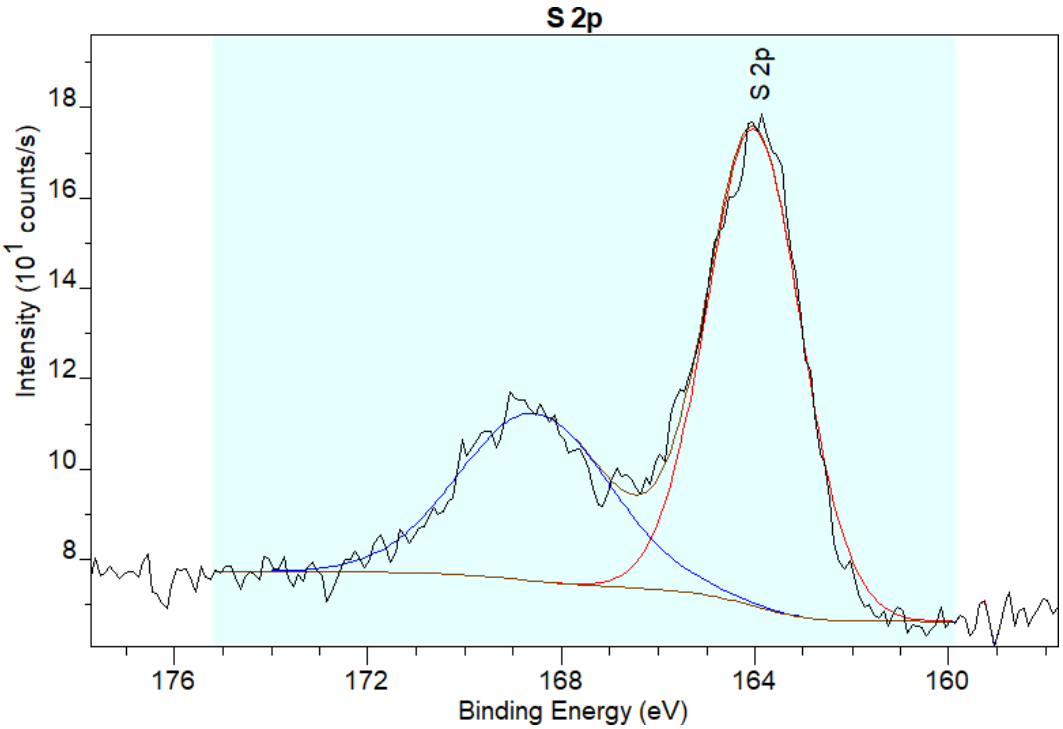

Figure 4: S_{2p} peak from XPS analysis for SO_3H / AC catalyst heat-treated at 400 °C

S2. Kinetic curves for bifunctional catalysts prepared with different SO_3H heat-treatments

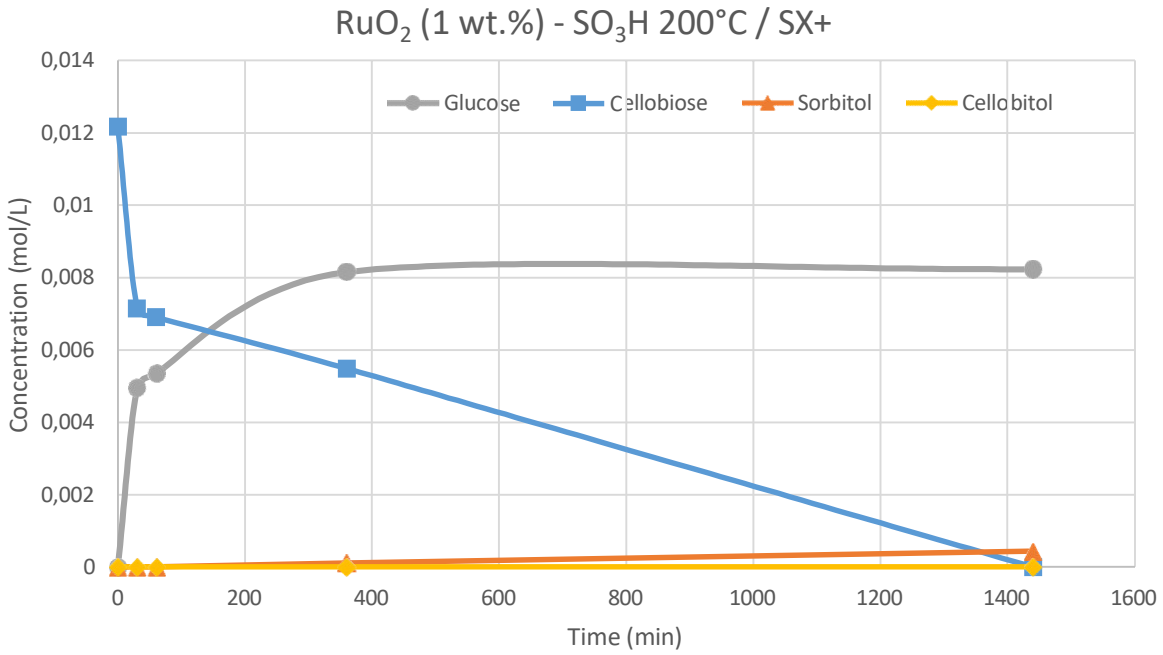

Figure 5: Kinetic curves for the transformation of cellobiose into sorbitol with RuO_2 (1 wt.%) – SO_3H treated at 200°C / SX+ catalyst; the lines connecting experimental points are only a visual aid and do not correspond to any mathematical model

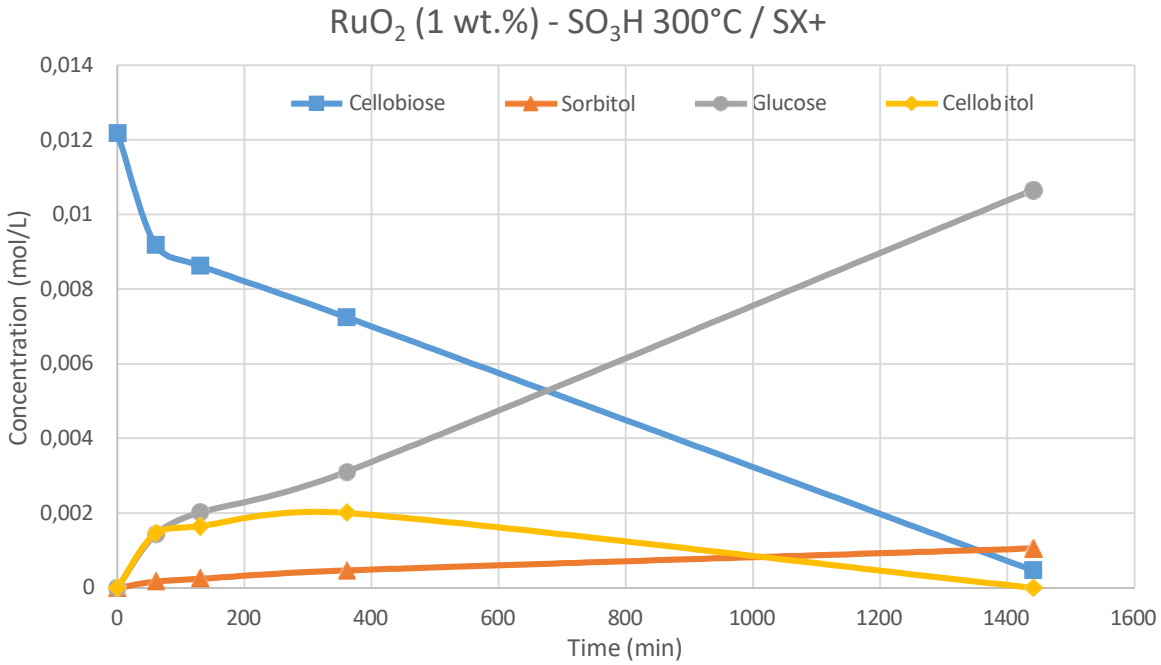

Figure 6: Kinetic curves for the transformation of cellobiose into sorbitol with RuO_2 (1 wt.%) – SO_3H treated at 300°C / SX+ catalyst; the lines connecting experimental points are only a visual aid and do not correspond to any mathematical model

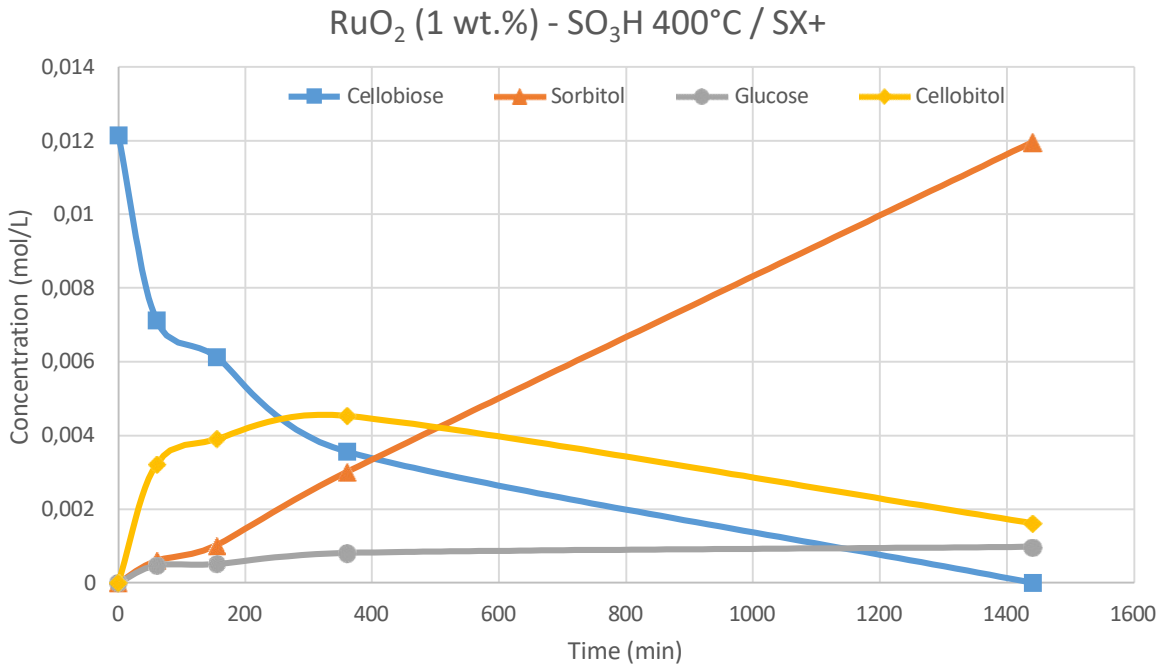

Figure 7: Kinetic curves for the transformation of cellobiose into sorbitol RuO_2 (1 wt.%) – SO_3H treated at 400°C / SX+ catalyst; the lines connecting experimental points are only a visual aid and do not correspond to any mathematical model

S3. S_{2p} peaks and atomic percentages from XPS analyses for the pre-treated SO_3H / AC catalyst

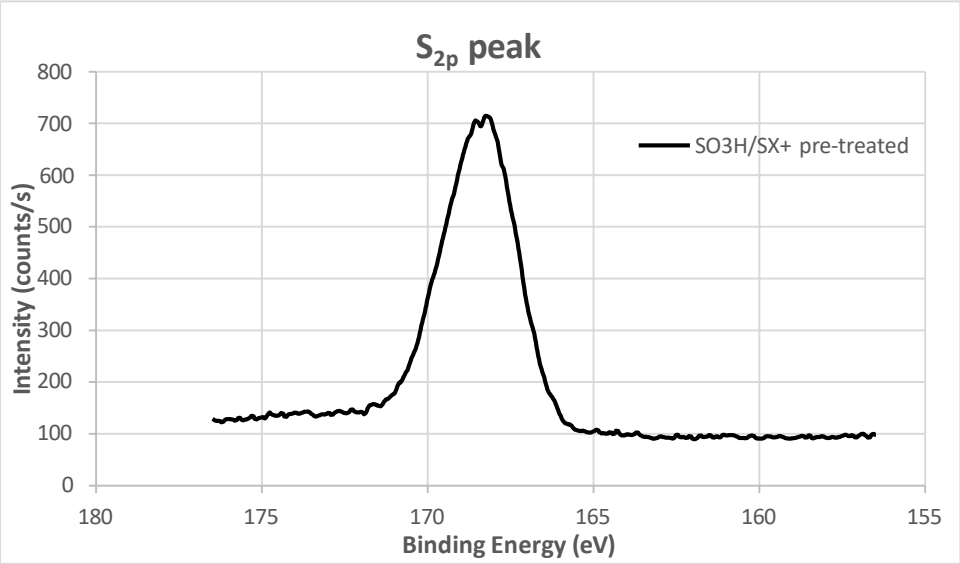

Figure 8: S_{2p} peak from XPS analyses of pre-treated SO_3H / SX+

Table 1: Oxygen and sulfur contents determined by XPS of the acidic catalysts without pre-treatment and with pre-treatment in the same condition as catalytic tests

Catalyst	O (at. %)	S (at. %)
SO_3H / AC	12.95	3.66
Pre-treated SO_3H / AC	13.64	3.10

S4. Conversion of cellobiose, selectivity and yield in sorbitol corresponding to the kinetic curves in main text in Figure 1

Table 2: Results of the kinetic study for the hydrogenolysis of cellobiose with RuO_2 (5 wt.%) / AC; Cellobiose conversion, selectivity in glucose, cellobitol and sorbitol, yield in sorbitol (150°C, 30 bar of H_2, 24h, 150 mg of catalyst)

Time (min)	Cellobiose conversion (%)	Glucose selectivity (%)	Cellobitol selectivity (%)	Sorbitol selectivity (%)	Sorbitol yield (%)
60	100	2	58	16	16
130	100	3	48	22	22
360	100	3	31	28	28
1440	100	0	0	28	28

Table 3: Results of the kinetic study for the hydrogenolysis of cellobiose with RuO_2 (5 wt.%) – pre-treated SO_3H / AC; Cellobiose conversion, selectivity in glucose, cellobitol and sorbitol, yield in sorbitol (150°C, 30 bar of H_2, 24h, 150 mg of catalyst)

Time (min)	Cellobiose conversion (%)	Glucose selectivity (%)	Cellobitol selectivity (%)	Sorbitol selectivity (%)	Sorbitol yield (%)
60	84	6	50	26	22
120	88	6	48	31	27
360	91	6	47	39	35
1440	100	0	5	68	68

S5. List of molecules injected in HPLC

Table 4: List of molecules analyzed by HPLC and observation of their presence or not in catalytic tests

Molecule	Supplier and purity	Observed in catalytic tests
Arabinose	Sigma-Aldrich - ≥ 99 %	**X**
Dulcitol	Sigma-Aldrich - ≥ 99 %	**X**
Erythritol	Sigma-Aldrich - ≥ 99 %	**X**
Fructose	Sigma-Aldrich - ≥ 99 %	✓
Galactose	Sigma-Aldrich - ≥ 99 %	**X**
HMF	Sigma-Aldrich - 99 %	**X**
Lactitol	Sigma-Aldrich - 98 %	**X**
Maltose	Sigma-Aldrich - 99 %	**X**
Mannose	Sigma-Aldrich - ≥ 99 %	**X**
Mannitol	Sigma-Aldrich - ≥ 98 %	✓
Sucrose	Sigma-Aldrich - ≥ 99.5 %	**X**
Xylitol	Sigma-Aldrich - ≥ 99 %	✓

S6. C_{1s} and Ru_{3d} peaks from XPS analyses for different AC supported catalysts

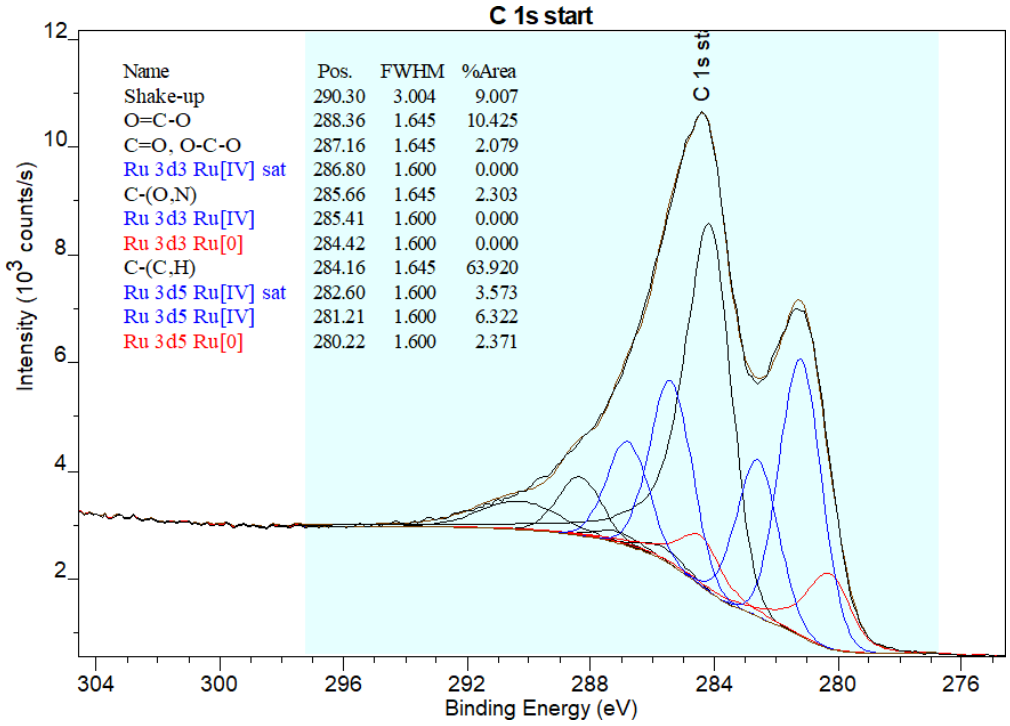

Figure 9: C_{1s} and Ru_{3d} peaks from XPS analyses of RuO_2 (5 wt. %) / AC catalyst

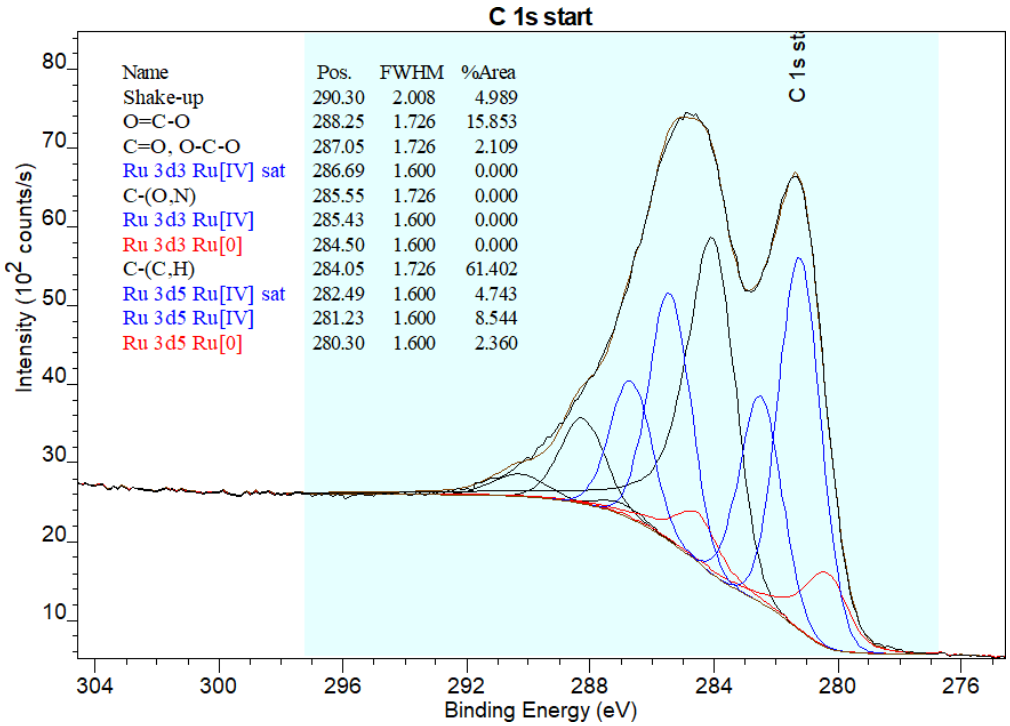

Figure 10: C_{1s} and Ru_{3d} peaks from XPS analyses of RuO_2 (5 wt. %) – pre-treated SO_3H / AC catalyst

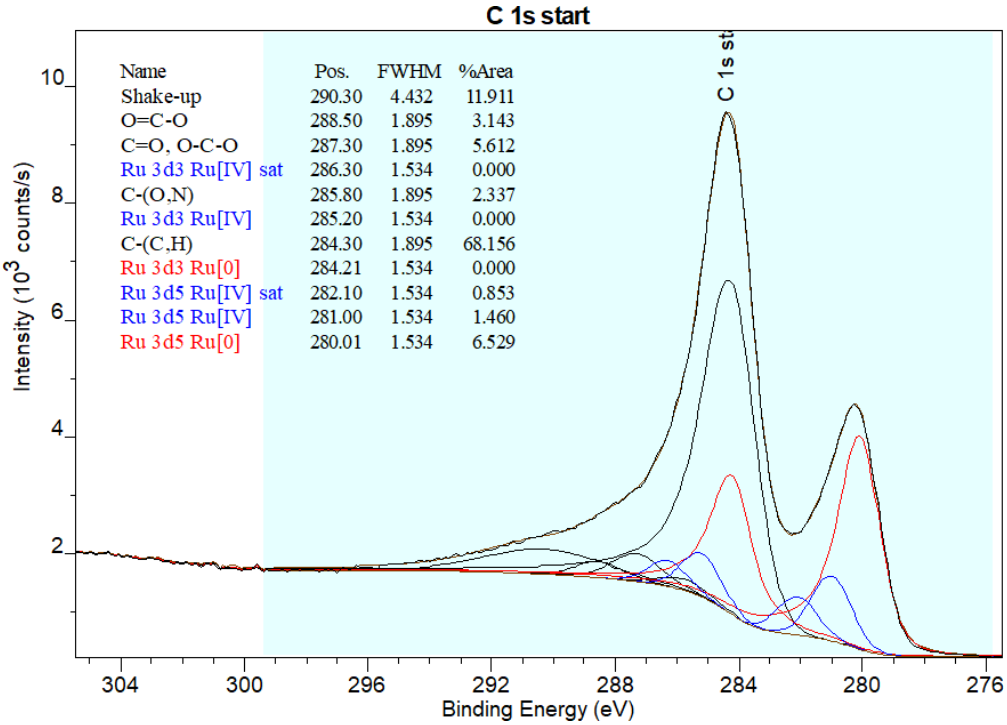

Figure 11: C_{1s} and Ru_{3d} peaks from XPS analyses of RuO_2 (5 wt. %) / AC catalyst after 5 runs

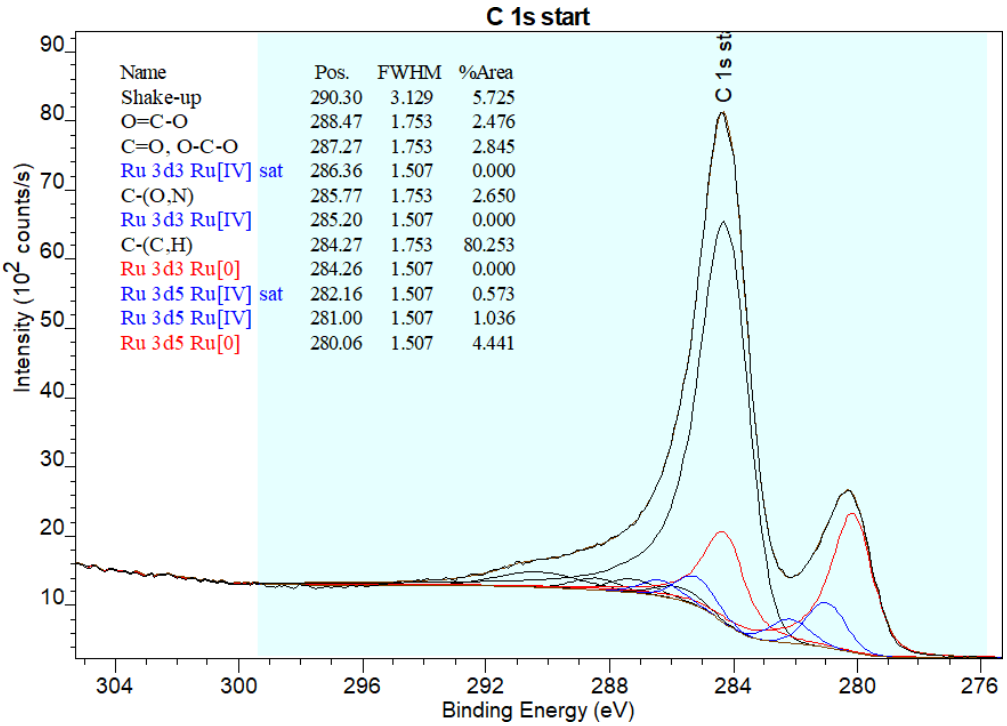

Figure 12: C_{1s} and Ru_{3d} peaks from XPS analyses of RuO_2 (5 wt. %) – pre-treated SO_3H / AC catalyst after 5 runs

S7. Atomic percentage of C_{1s} and Ru_{3d} from XPS analyses of monofunctional and bifunctional catalysts with 3 wt.% of Ru

Table 5: Atomic ratio of C_{1s} and Ru_{3d} for RuO_2 (3 wt.%) / AC and RuO_2 (3 wt.%) – pre-treated SO_3H / AC

Catalyst	C_{1s} (at. %)	Ru_{3d} (IV) (at. %)	Ru_{3d} (0) (at. %)
RuO_2 (3%) / AC	73.4	4.4	0.4
RuO_2 (3%) – pre-treated SO_3H / AC	59.4	5.9	0.6

S8. HR-TEM, STEM and EDX mapping analyses for monofunctional and bifunctional catalysts, before and after catalytic reaction

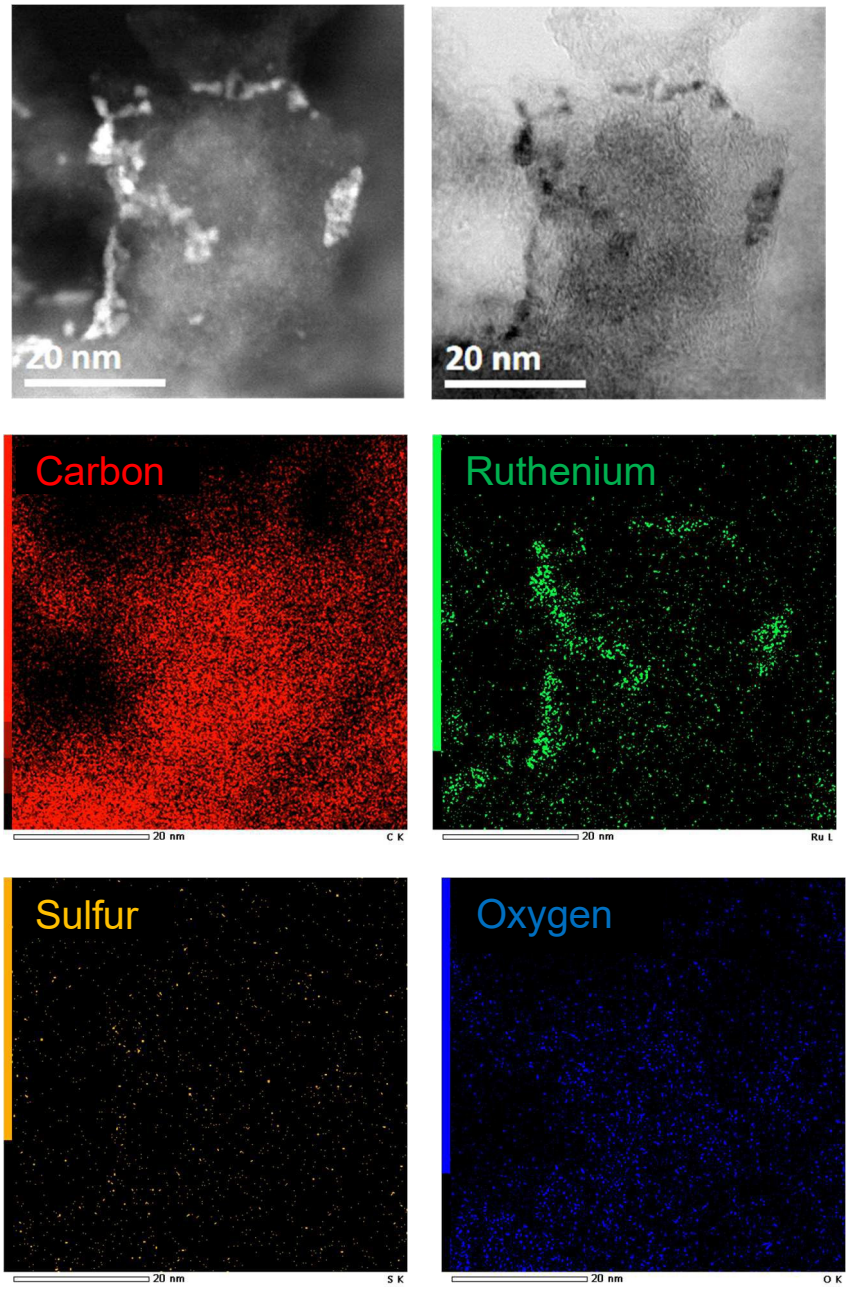

Figure 13: HR-TEM, STEM and EDX mapping analyses for RuO_2 (5%) / AC before catalytic test

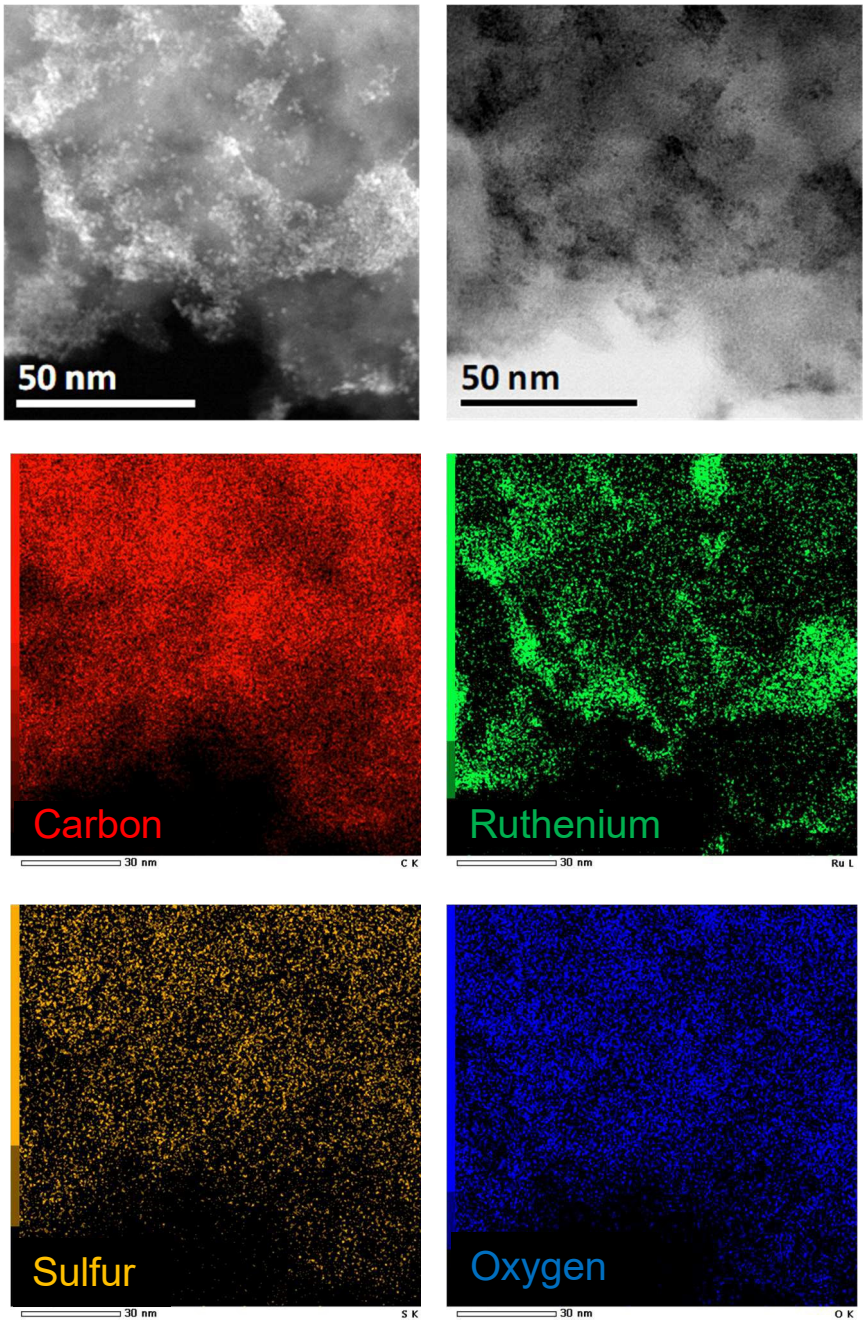

Figure 14: HR-TEM, STEM and EDX mapping analyses for RuO_2 (5%) – pre-treated SO_3H / AC before catalytic test

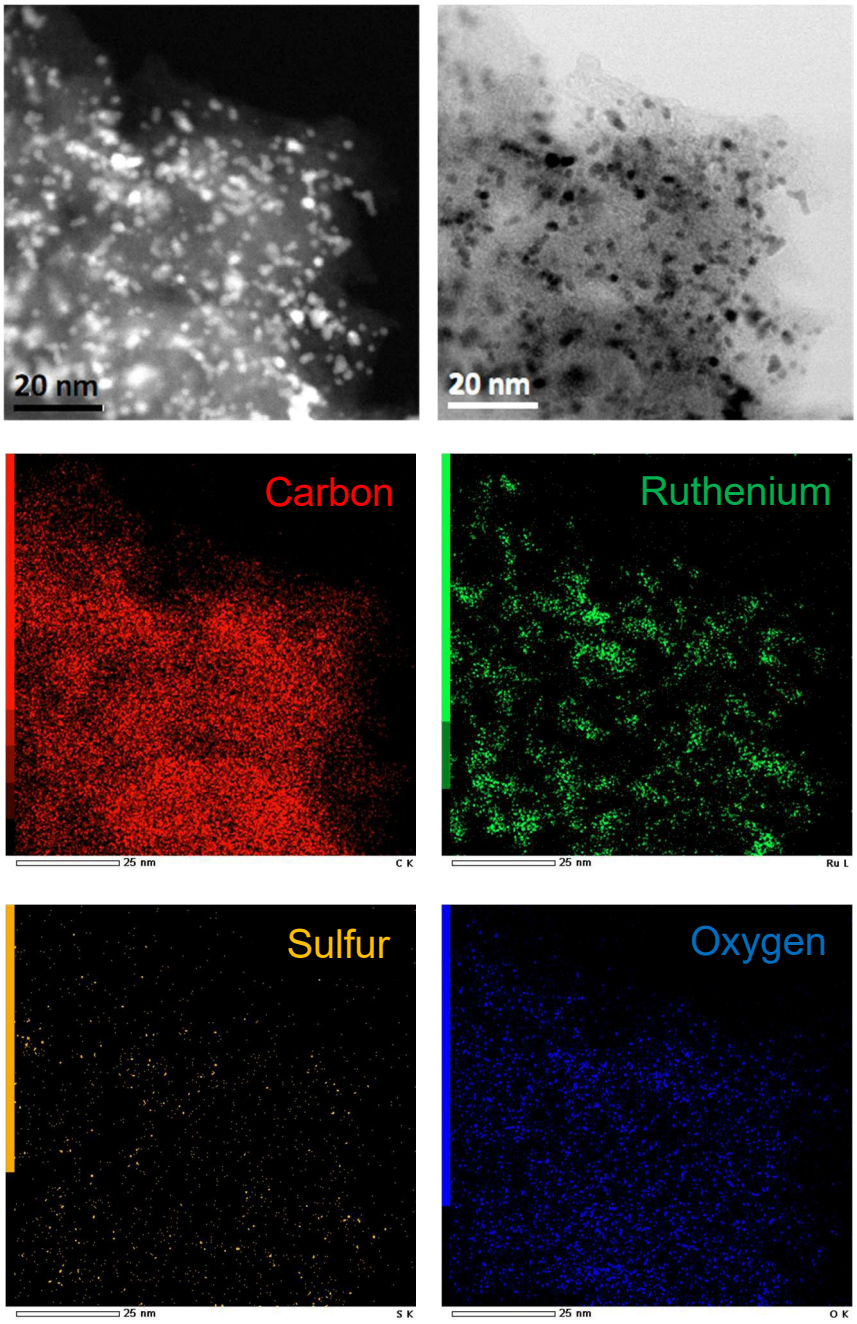

Figure 15: HR-TEM, STEM and EDX mapping analyses for RuO_2 (5%) / AC after 5 runs

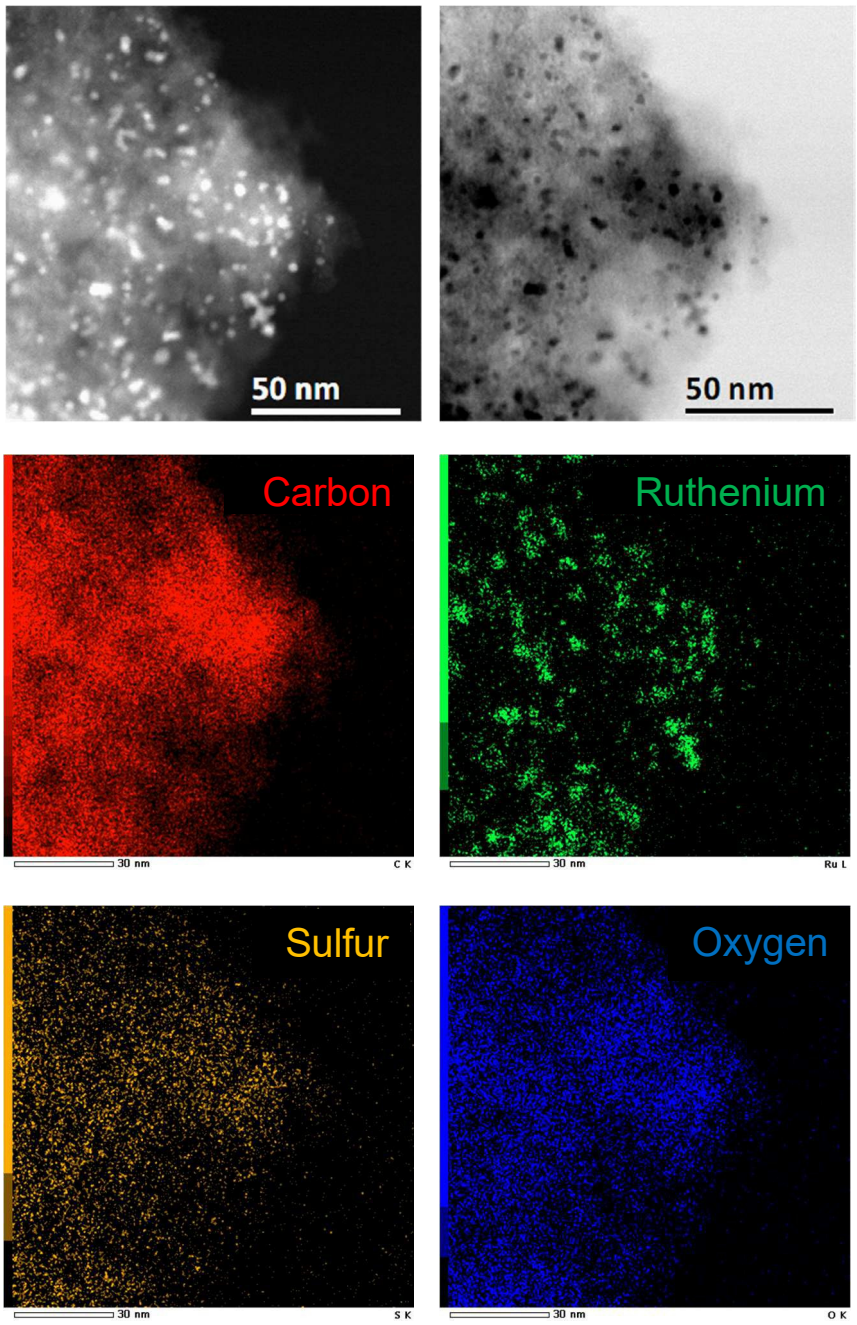

Figure 16: HR-TEM, STEM and EDX mapping analyses for RuO_2 (5%) – pre-treated SO_3H / AC after 5 runs

S9. Comparison of Ru regions from XPS analyses before and after several catalytic runs

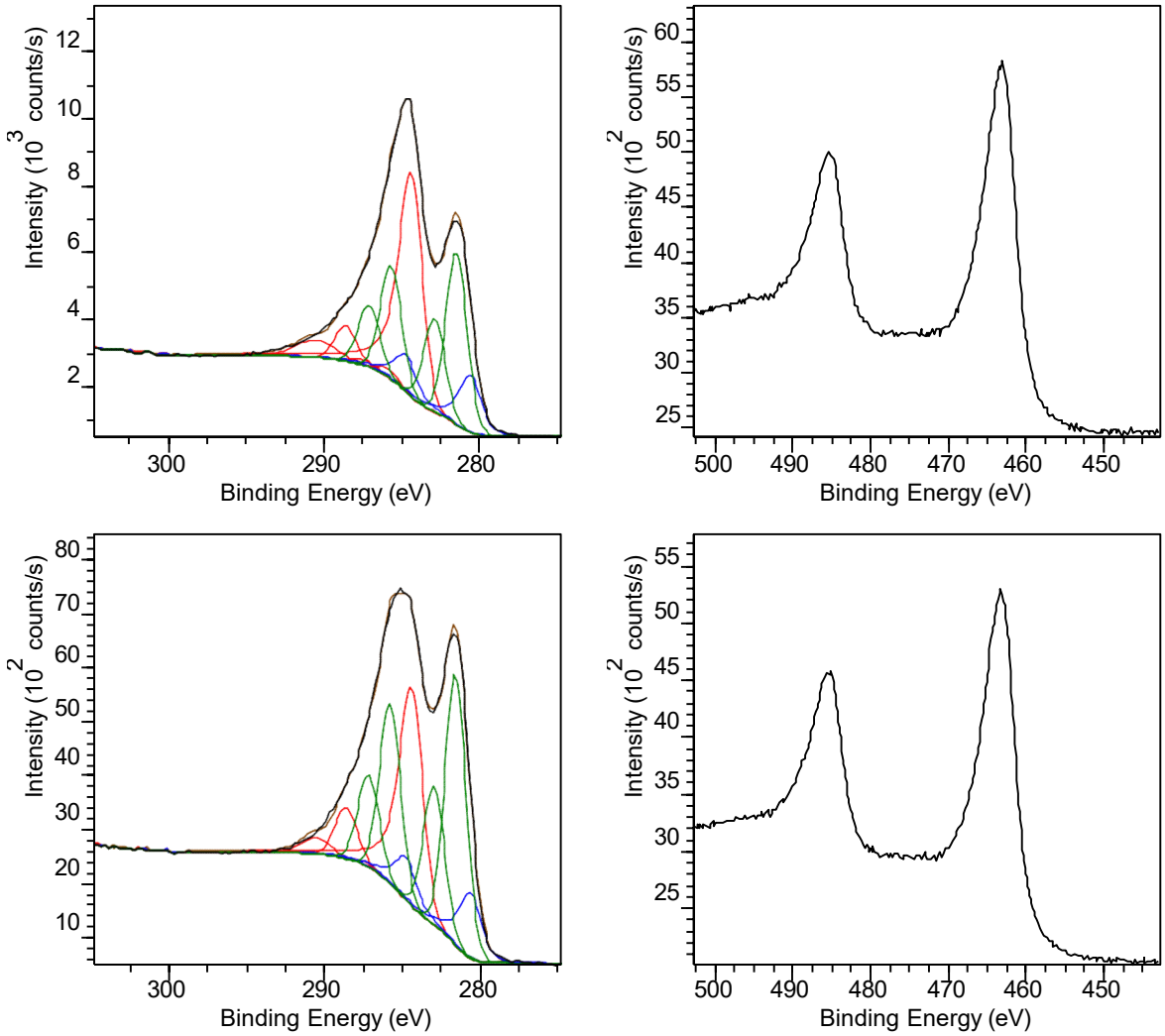

*Figure 17: XPS ruthenium regions for: (TOP) RuO_2 (5%) / AC; (BOTTOM) RuO_2 (5%) – pre-treated SO_3H / AC. Left: Ru 3d doublet + C 1s, blue=Ru[0], green=Ru[IV] (main and satellite peaks), red= carbon species (major asymmetric **C**-(C,H) contribution with oxidized species and aromatic shake-up satellite). Right: Ru 3p doublet*

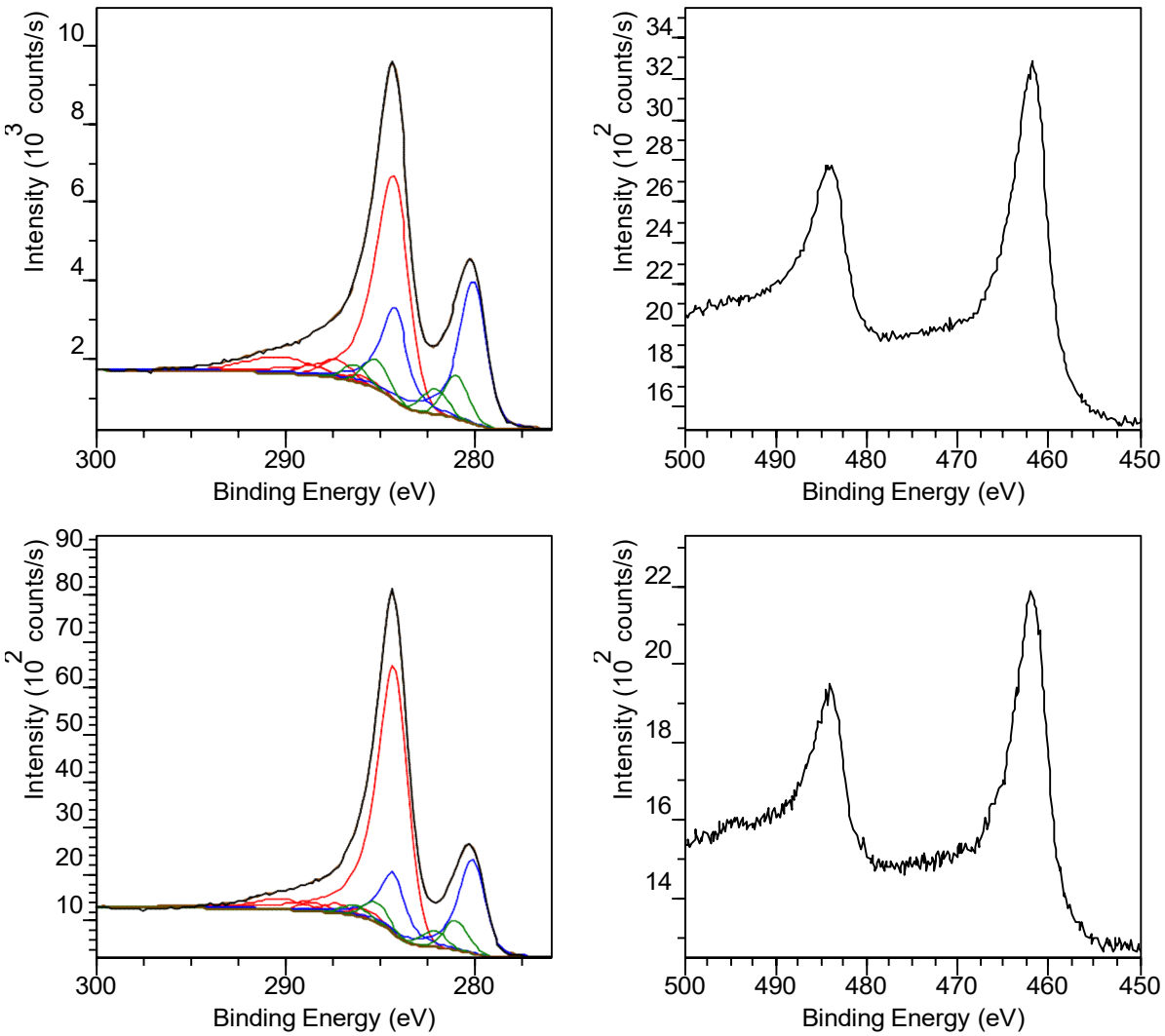

Figure 18: XPS ruthenium regions for: (TOP) RuO_2 (5%) / AC after 4 runs; (BOTTOM) RuO_2 (5%) – pre-treated SO_3H / AC after 5 runs.

*Left: Ru 3d doublet + C 1s, blue=Ru[0], green=Ru[IV] (main and satellite peaks), red= carbon species (major asymmetric **C**-(C,H) contribution with oxidized species and aromatic shake-up satellite). Right: Ru 3p doublet*

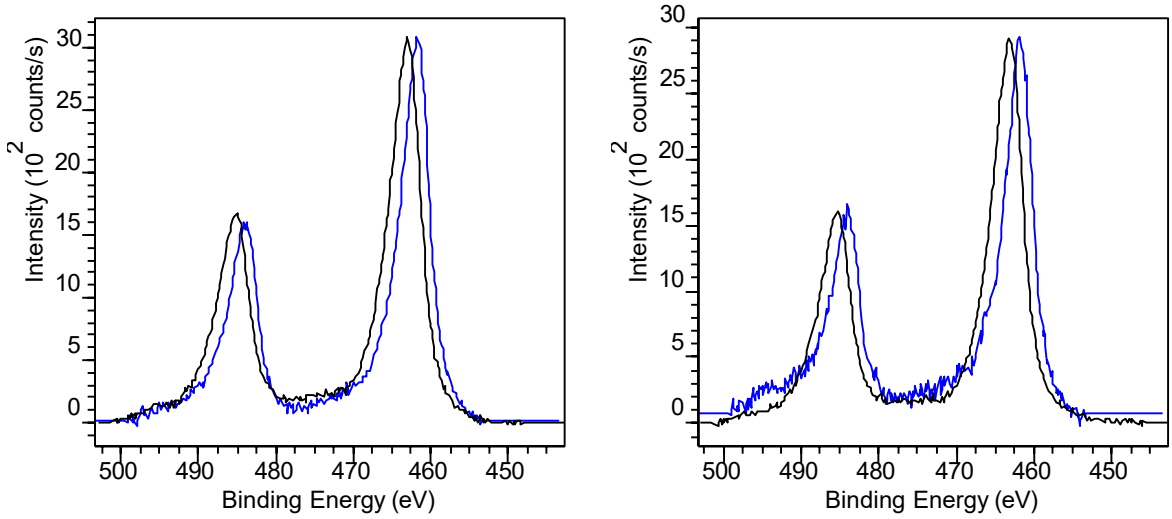

Figure 19: XPS Ru 3p regions for: (LEFT) RuO_2 (5%) / AC before (black) and after 4 runs (blue) ; (RIGHT) RuO_2 (5%) – pre-treated SO_3H / AC before (black) and after 5 runs (blue).