

Supplementary Material

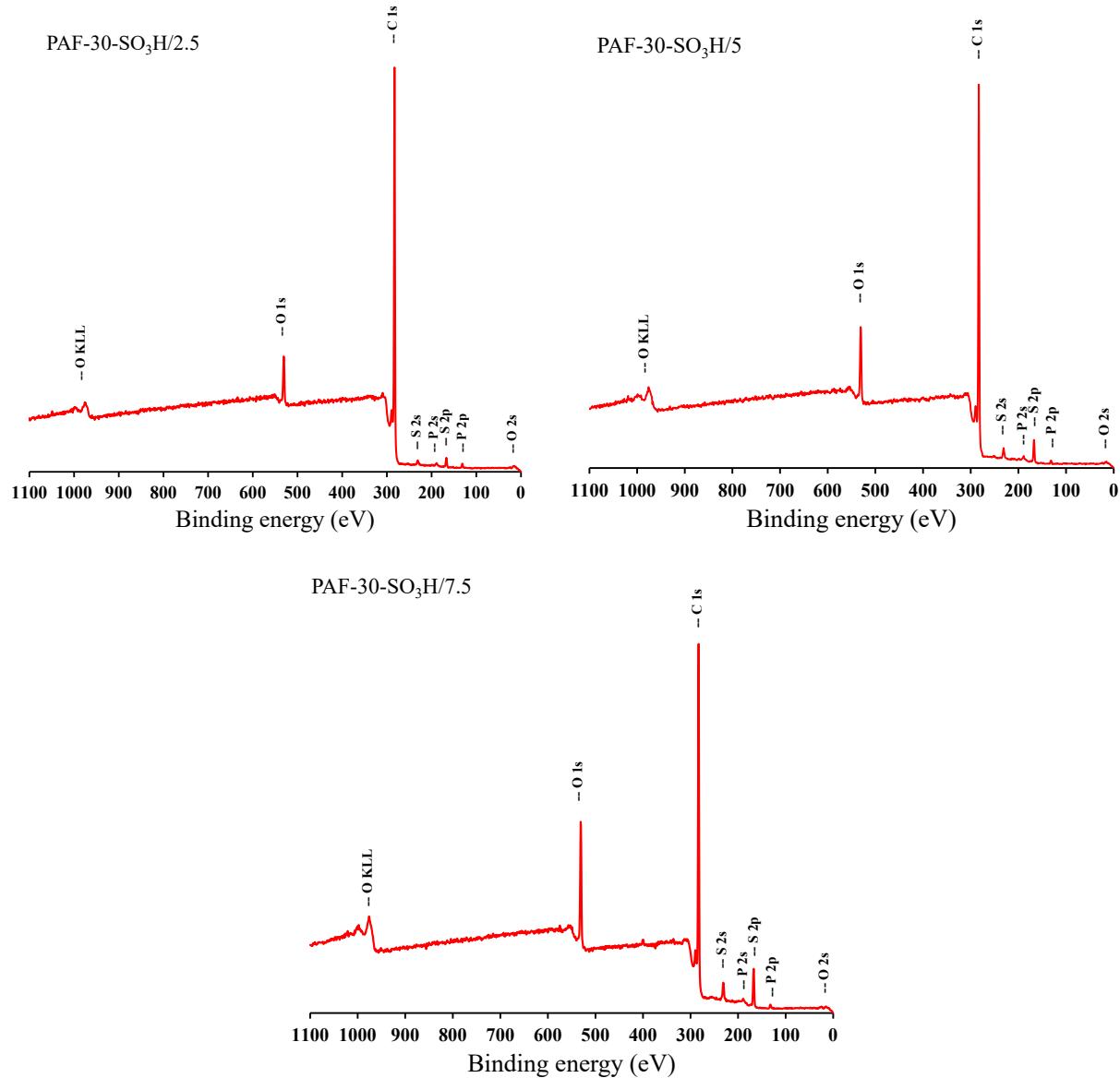


Figure S1. The XPS survey spectra for PAF-30-SO₃H/X (X = 2.5, 5, 7.5).

Table S1. Components of the XPS spectra.

| Materials | Element content, at. % | | | | |
|-------------------------------------|------------------------|------|-----|-----|-----|
| | C | O | P | S | Ru |
| PAF-30-SO ₃ H/2.5 | 92.0 | 6.4 | 0.6 | 1.0 | - |
| PAF-30-SO ₃ H/5 | 87.1 | 10.1 | 0.5 | 2.3 | - |
| PAF-30-SO ₃ H/7.5 | 80.9 | 14.6 | 0.6 | 3.9 | - |
| Ru-PAF-30-SO ₃ H/2.5-COD | 79.8 | 15.3 | 0.2 | 0.6 | 4.1 |
| Ru-PAF-30-SO ₃ H/5-COD | 76.2 | 17.2 | 0.3 | 3.3 | 3.0 |
| Ru-PAF-30-SO ₃ H/7.5-COD | 77.0 | 17.1 | 0.2 | 3.4 | 2.3 |
| Ru-PAF-30-SO ₃ H/2.5 | 79.7 | 15.1 | 0.3 | 0.5 | 4.4 |
| Ru-PAF-30-SO ₃ H/5 | 71.5 | 19.2 | 0.3 | 2.7 | 6.3 |
| Ru-PAF-30-SO ₃ H/7.5 | 76.5 | 16.9 | 0.1 | 3.5 | 3.0 |

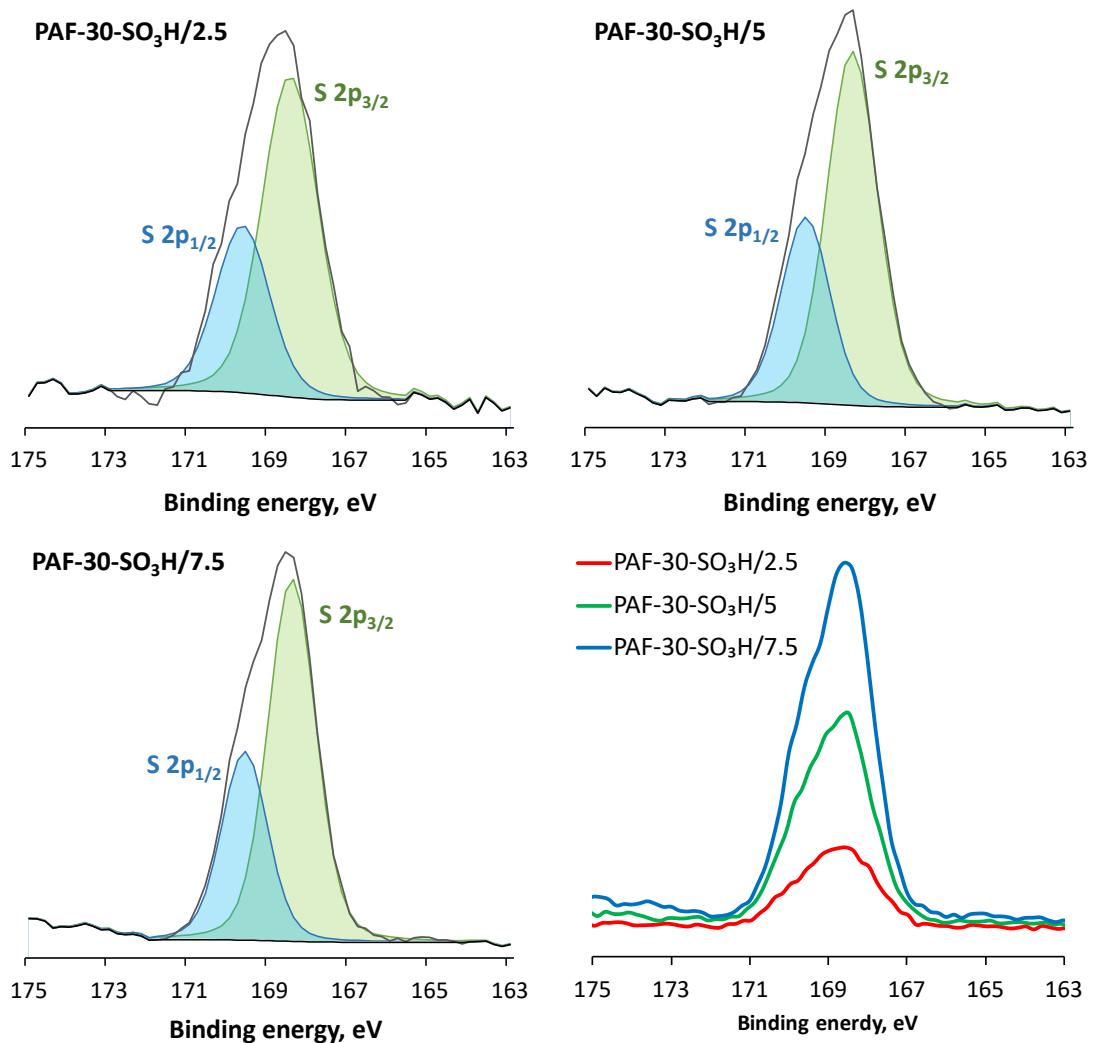


Figure S2. High-resolution XPS spectra of S2p region for PAF-30-SO₃H/X (X = 2.5, 5, 7.5).

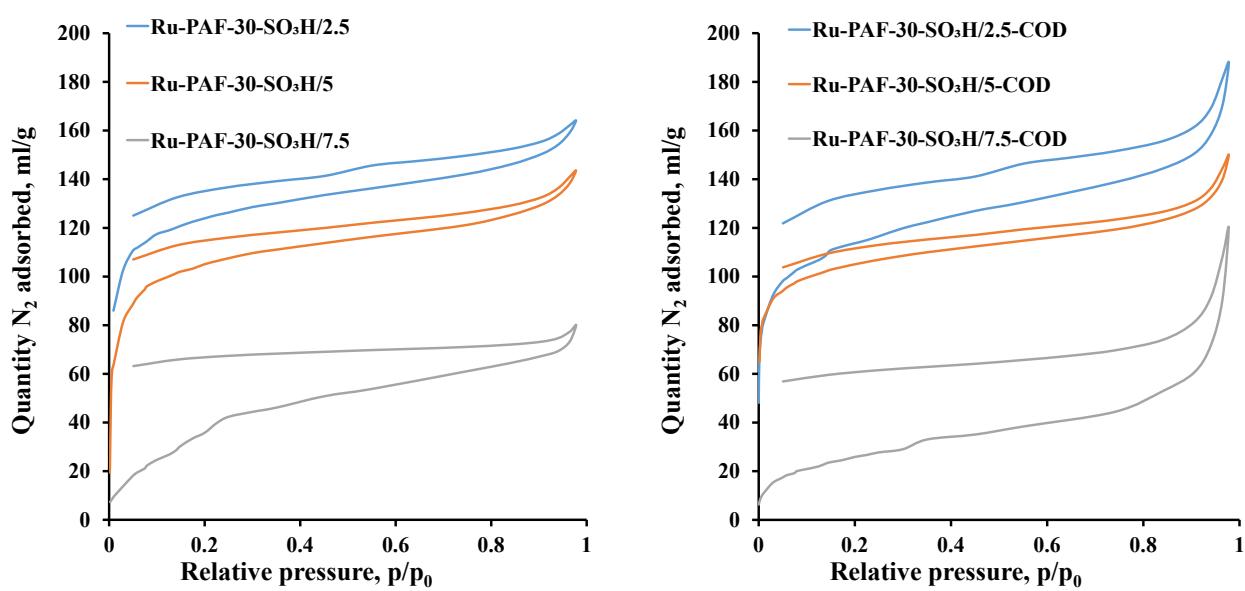
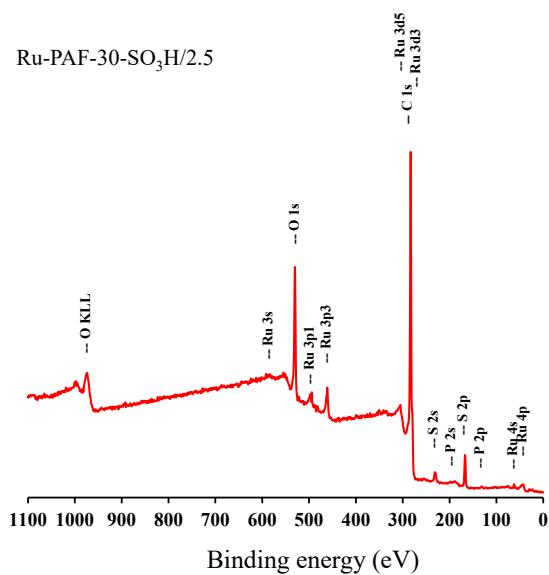
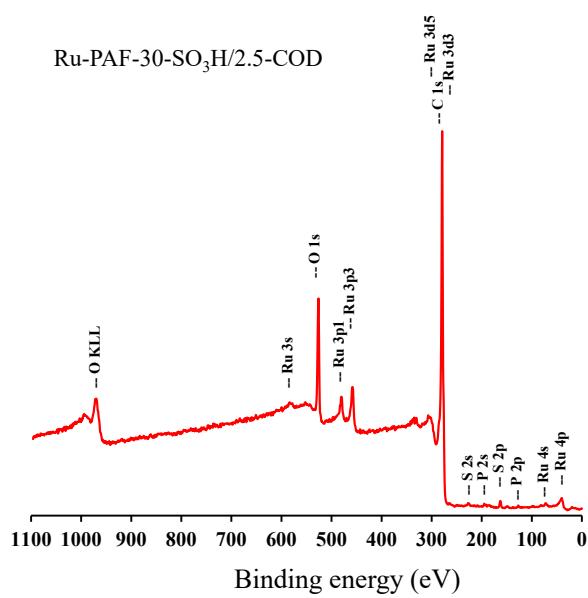


Figure S3. N₂ adsorption isotherms for synthesized catalysts.

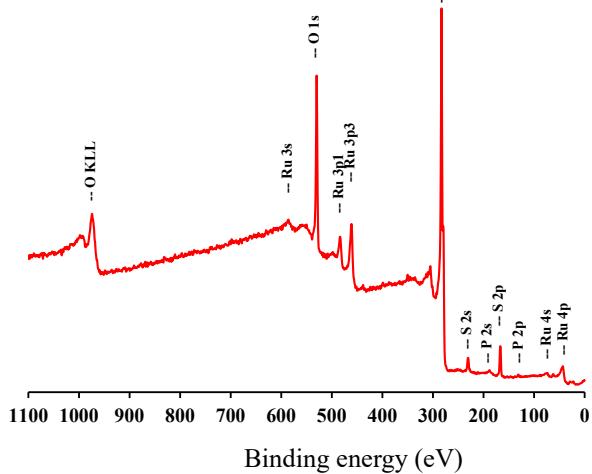
Ru-PAF-30-SO₃H/2.5



Ru-PAF-30-SO₃H/2.5-COD



Ru-PAF-30-SO₃H/5



Ru-PAF-30-SO₃H/5-COD

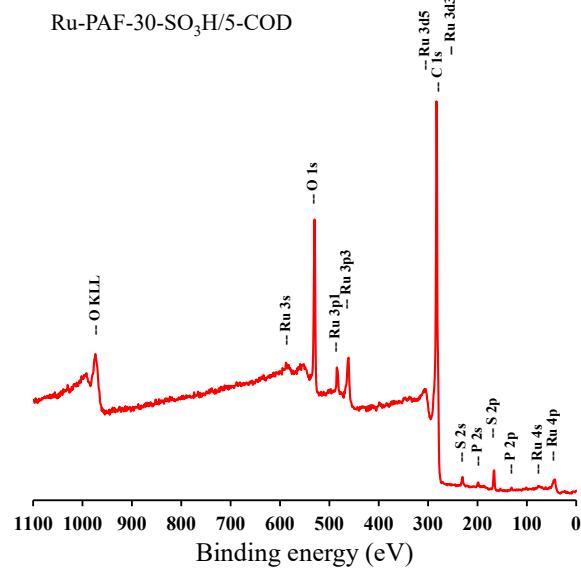
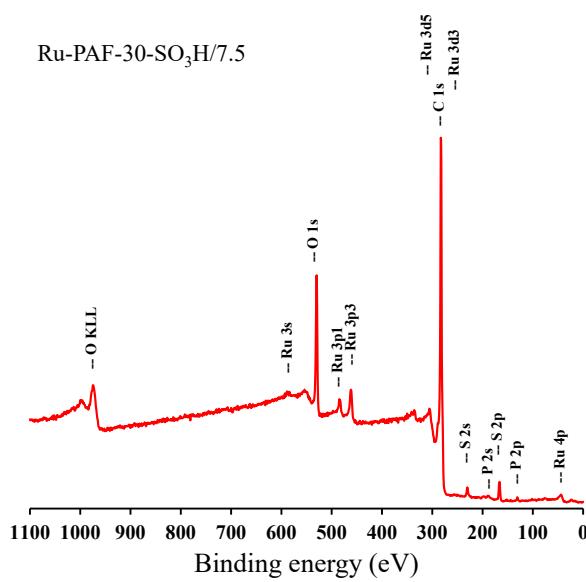


Figure S4. The XPS survey spectra for ruthenium catalysts.

Ru-PAF-30-SO₃H/7.5



Ru-PAF-30-SO₃H/7.5-COD

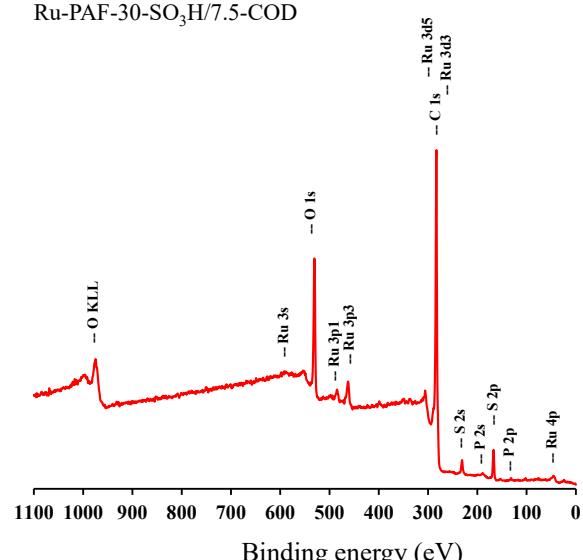


Figure S4. (end) The XPS survey spectra for ruthenium catalysts

Table S2. Peak parameters for XPS spectra of obtained ruthenium catalysts.

| Catalyst | Ru ⁰ 3d _{5/2} | Ru ⁰ 3d _{3/2} | RuO ₂ 3d _{5/2} | RuO ₂ 3d _{3/2} | RuO ₂ × xH ₂ O 3d _{5/2} | RuO ₂ × xH ₂ O 3d _{3/2} | C 1s | π-π 1s |
|---------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---|---|---------|-----------|
| Ru-PAF-30-SO ₃ H / 2.5 | 16.3% | | 62.0% | | 21.7% | | 284.58 | 290.86 |
| Ru-PAF-30-SO ₃ H / 5 | 27.3% | | 59.3% | | 13.4% | | 284.60 | 290.80 |
| Ru-PAF-30-SO ₃ H / 7.5 | — | | 87.0% | | 13.0% | | 284.54 | 290.98 |
| Ru-PAF-30-SO ₃ H / 2.5-COD | — | | 66.1% | | 43.9% | | 284.52 | 290.95 |
| Ru-PAF-30-SO ₃ H / 5-COD | — | | 45.6% | | 54.4% | | 284.50 | 290.80 |
| Ru-PAF-30-SO ₃ H / 7.5-COD | — | | 67.6% | | 32.4% | | 284.54 | 291.00 |

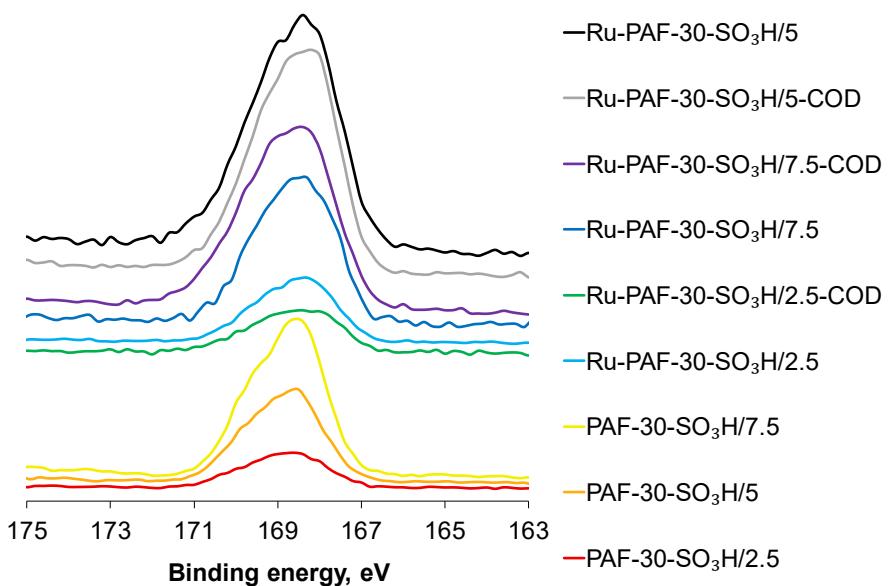


Figure S5. High-resolution XPS spectra of S2p region.

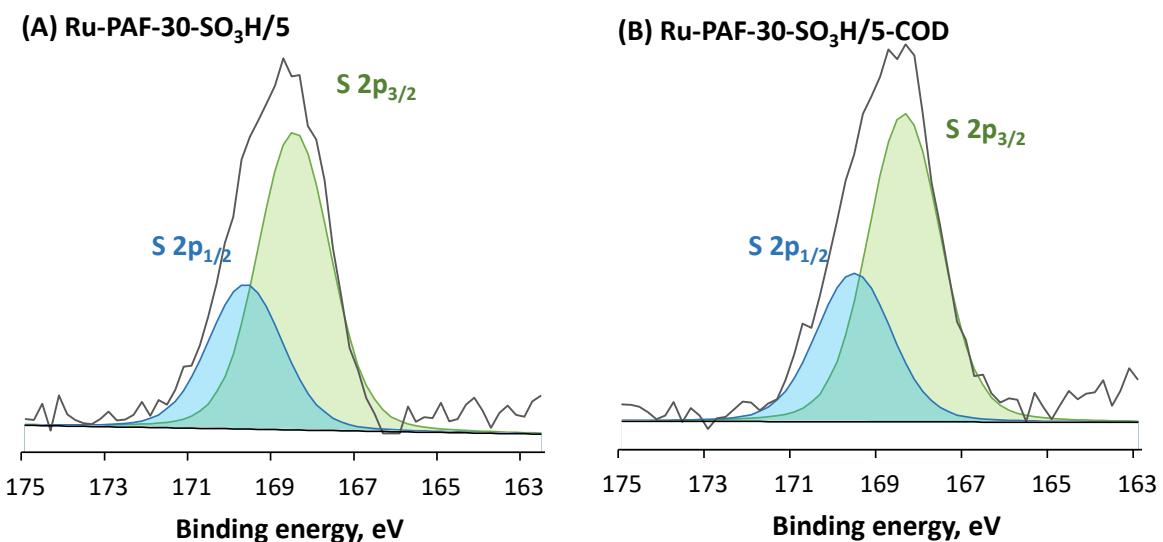


Figure S6. High-resolution XPS spectra of S2p region for Ru-PAF-30-SO₃H/5 (A) and Ru-PAF-30-SO₃H/5 (B) catalysts after the 3rd catalytic run.

Table S3. Guaiacol HDO over different catalysts.

| Catalyst | Sub/Me | Conv., % | Products | Yield, % | Ref. |
|---|--------|----------|---|---|-----------|
| Ru-PAF-30-SO ₃ H/2.5-COD (Ru = 0.79 wt.%) 3 MPa H ₂ ; 250 °C; 500 μL H ₂ O; 0.38 mmol guaiacol; 5 mg of catalyst; 2 h; | 972 | 89 | 2-methoxy-cyclohexanol Cyclohexanol Cyclohexane | 33 40 16 | This work |
| Ru NPs@SILP-1.00 (Ru = 0.32 wt.%) 12 MPa H ₂ ; 175 °C; 1 mL decalin; 2.4 mmol guaiacol; 75 mg of catalyst; 16 h | 1000 | >99% | 2-methoxy-cyclohexanol Methoxycyclohexane Cyclohexanol Cyclohexane | 14 4 1 81 | [1] |
| Ru-MWCNT (Ru = 5 wt.%) 4 MPa H ₂ , 270 °C; 29 mL H ₂ O, 8.96 mmol guaiacol; 20 mg of catalyst; 1h | 906 | 98.1 % | Cyclohexane Methoxycyclohexane Cyclohexanol Cyclohexanone Cyclopentanemethanol 2-methoxy-cyclohexanol 1,2-Cyclohexanediol Catechol | 34.9 0.2 2.2 0.1 2.6 13.6 0.3 0.1 | [2] |
| Ru-AC (Ru = 5 wt.%) 4 MPa H ₂ , 270 °C; 29 mL H ₂ O, 8.96 mmol guaiacol; 20 mg of catalyst; 1h | 906 | 96.1 % | Cyclopentane Cyclohexane Methylcyclohexane Methoxycyclohexane Cyclohexanol Cyclohexanone Cyclopentanemethanol Anisole Phenol 2-methoxy-cyclohexanol 1,2-Cyclohexanediol Catechol | 0.2 24.7 0.3 0.4 10.2 0.8 1.6 0.2 0.3 22.7 1.0 0.1 | [2] |
| Ru-CARF (Ru = 5 wt.%) 4 MPa H ₂ , 270 °C; 29 mL H ₂ O, 8.96 mmol guaiacol; 20 mg of catalyst; 1h | 906 | 81.6 % | Cyclohexane Methylcyclohexane Methoxycyclohexane Cyclohexanol Cyclohexanone Cyclopentanemethanol Anisole Phenol 2-methoxy-cyclohexanol 1,2-Cyclohexanediol Catechol | 5.7 1.1 0.1 24.5 1.9 0.7 0.3 4.2 17.3 0.5 0.1 | [2] |

| | | | | | | |
|---|------|---------|--|--------------------------|------|-----------|
| | | | | Cyclohexane | 11.9 | |
| Ru-Vulcan (Ru = 5 wt.%) | | | | Methylcyclohexane | 1.2 | |
| 4 MPa H ₂ ; 270 °C; 29 mL H ₂ O; 8,96 mmol guaiacol; 20 mg of catalyst; 1h | 906 | 77.0 % | | Methoxycyclohexane | 0.1 | |
| | | | | Cyclohexanol | 12.7 | |
| | | | | Cyclohexanone | 1.1 | |
| | | | | Cyclopentanemethanol | 0.6 | [2] |
| | | | | Anisole | 2.2 | |
| | | | | Phenol | 12.3 | |
| | | | | 2-methoxy-cyclohexanol | 8.8 | |
| | | | | 1,2-Cyclohexanediol | 0.7 | |
| | | | | Catechol | 0.1 | |
| Ru-PAF-30-SO ₃ H/5-COD (Ru = 0.76 wt.%) 3 MPa H ₂ ; 250 °C; 500 μL H ₂ O; 0.38 mmol guaiacol; 5 mg of catalyst; 2 h; | 1010 | 83% | | Cyclohexanone | 44 | |
| | | | | Cyclopentanemethanol | 11 | |
| | | | | Cyclopentanecarbaldehyde | 8 | This work |
| | | | | Cyclohexane | 1 | |
| | | | | Alkylation products | 19 | |
| Ru/HY (Ru = 5 wt.%) 4 MPa H ₂ ; 250 °C; 30 mL H ₂ O; 0.81 mmol guaiacol; 100 mg of catalyst; 2 h; | 16 | 91 | | Cyclohexanone | 27.5 | |
| | | | | Cyclohexane | 18.5 | |
| | | | | Cyclohexanol | 18.1 | |
| | | | | Gases | 10.0 | |
| | | | | Ring-open products | 8.2 | [3] |
| | | | | Cyclopentylmethanol | 7.9 | |
| | | | | Dimers | 6.3 | |
| | | | | Others | 3.5 | |
| Ru-PAF-30-SO ₃ H/5 (Ru = 4.68 wt.%) 3 MPa H ₂ ; 250 °C; 500 μL H ₂ O; 0.38 mmol guaiacol; 5 mg of catalyst; 2 h; | 164 | 100 | | 2-methoxy-cyclohexanol | 35 | |
| | | | | Anisole | 2 | |
| | | | | Cyclohexanol | 8 | |
| | | | | Cyclohexane | 55 | |
| NSMP-Ru (Ru = 3.6 wt.%) 5 MPa H ₂ , 200 °C; 1 mL H ₂ O, 0.4 mmol guaiacol; 5 mg of catalyst, 2h | 225 | >99 % | | Methoxycyclohexanol | 86 | |
| | | | | Cyclohexanol | 13 | |
| | | | | Methylcyclohexanol | <1 | [4] |
| 5%Ru/AMWCNTs (Ru = 5 wt.%) 2MPa H ₂ , 200 °C; 5.4 mL decalin, 10 mmol guaiacol; 100 mg of catalyst, 200 min | 202 | 49.32 % | | Cyclohexanol | 33.2 | |
| | | | | 1,2-Cyclohexanediol | 5.2 | |
| | | | | Cyclohexane | 1.4 | |
| | | | | Cyclohexanone | 1.7 | |
| | | | | Phenol | 1.2 | |
| | | | | Benzene | 1.8 | |
| | | | | Others | 4.9 | |
| Ru/HNT-t (3) (Ru = 2 wt.%) 3 MPa H ₂ ; 180 °C; 2.7 mL H ₂ O; 2.42 mmol guaiacol; 61 mg of catalyst; 3 h; | 200 | 100% | | Cyclohexanol | 35.4 | |
| | | | | 2-methoxycyclohexanol | 25.4 | |
| | | | | 4-methylcyclohexanol | 24.1 | |
| | | | | Cyclohexane | 12.6 | |
| | | | | Phenol | 2.0 | |
| | | | | p-cresol | 0.4 | |
| | | | | Cyclohexanone | 0.1 | |

| | | | | | |
|--|-----|--------|--|--------------------|-----|
| Ru/TiO ₂ –Al ₂ O ₃ (Ru = 1.04 wt.%) 1 MPa Hz; 240 °C; 20 mL octane; 0.81 mmol guaiacol; 50 mg of catalyst; 4 h; | 157 | 91.4 % | Cyclohexane Cyclohexanol 2-methoxycyclohexanol | 89.4 9.0 1.6 | [7] |
|--|-----|--------|--|--------------------|-----|

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