# Ru and Ag promoted $Co/Al_2O_3$ catalysts for the gas-phase amination of aliphatic alcohols with ammonia

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# Supporting Information

## FIGURE CAPTIONS

Figure S1. Results of the band deconvolution for $H_2$-TPR profiles of 5Co and $5Co_{98.5}$-$NM_{1.5}$ catalysts.

Figure S2. Results of the band deconvolution for $H_2$-TPR profiles of 1.5% a/a Ag promoted Co catalysts as a function of the impregnation sequence (i.e. $Ag_{1.5}$-$5Co_{98.5}$, $5Co_{98.5}(Ag_{1.5})$ and $5Co_{98.5}$- $Ag_{1.5}$).

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Figure S5. Results of the band deconvolution for $H_2$-TPR profiles of 5Co(Ru) catalysts at variable Ru loading [i.e. $5Co_{99.97}(Ru_{0.03})$, $5Co_{99.9}(Ru_{0.1})$, $5Co_{99.7}(Ru_{0.3})$, $5Co_{99.25}(Ru_{0.75})$, $5Co_{98.5}(Ru_{1.5})$ and $5Co_{97}(Ru_3)$].

Figure S6. Co 2p XPS spectra of calcined (a) 5Co, (b) $5Co_{99.7}(Ru_{0.3})$ and (c) $Ag_3$-$5Co_{97}$.

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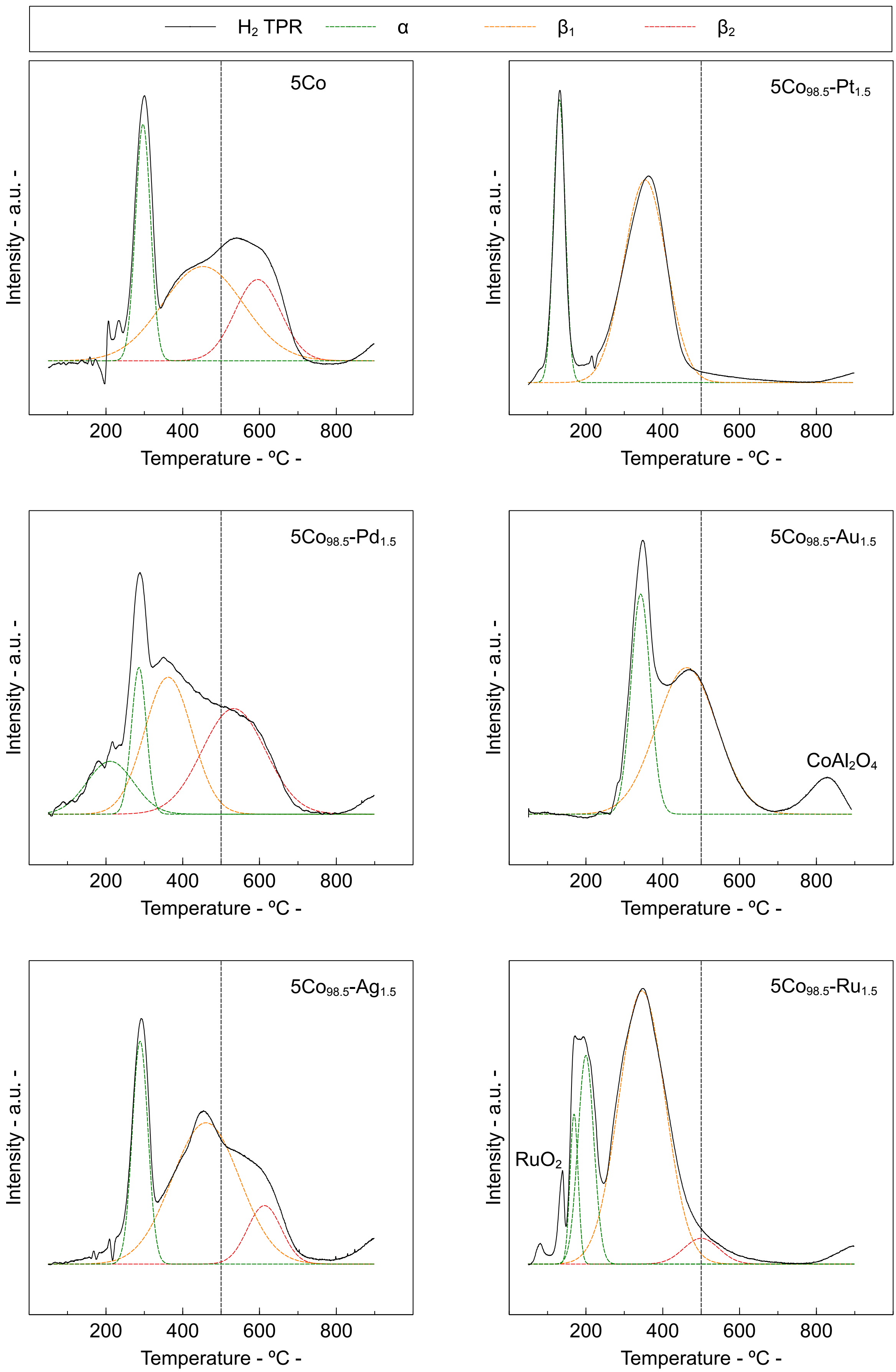



Figure S1. Results of the band deconvolution for $H_2$-TPR profiles of 5Co and $5Co_{98.5}$-$NM_{1.5}$ catalysts.

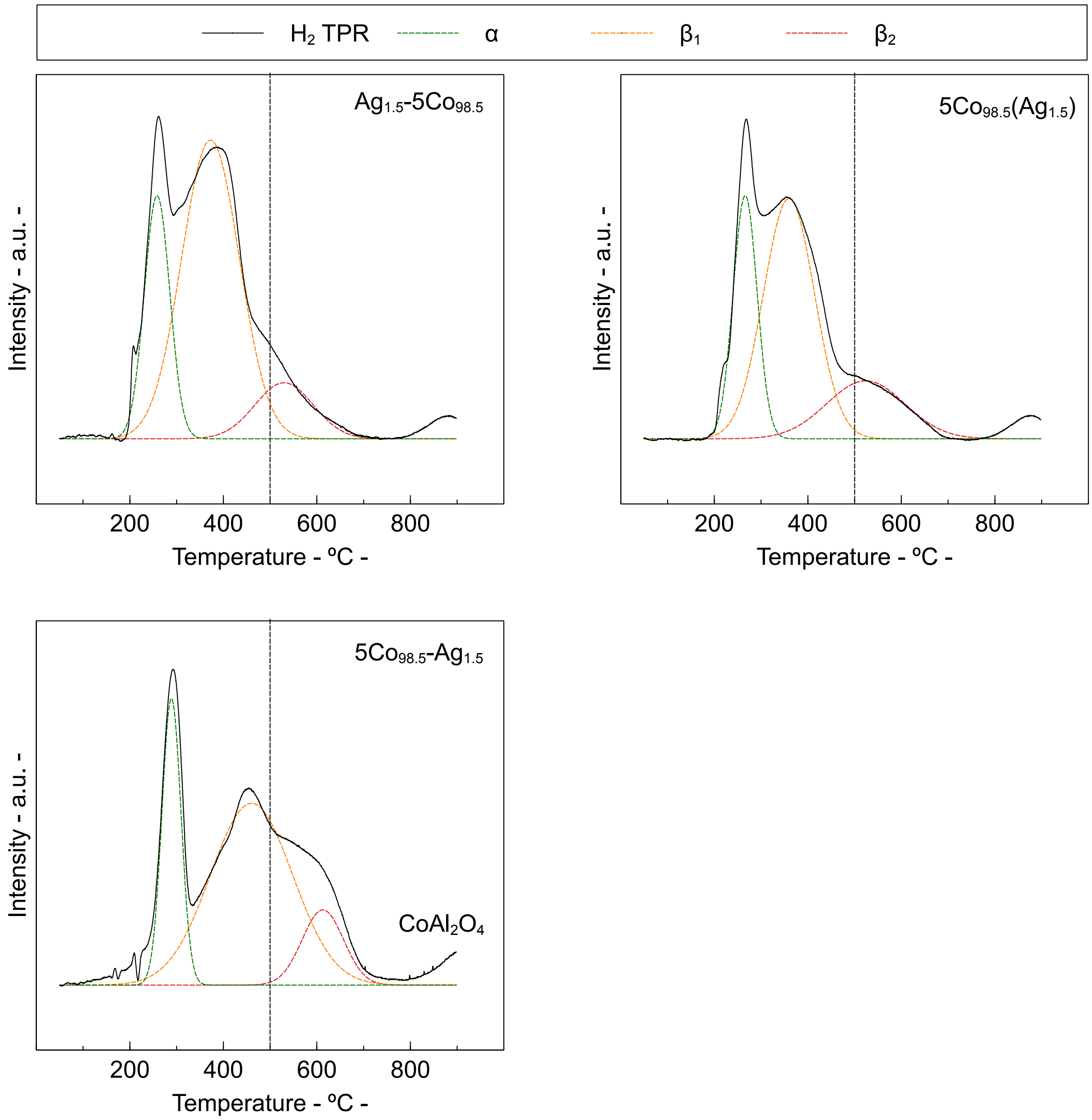



Figure S2. Results of the band deconvolution for $H_2$-TPR profiles of 1.5% a/a Ag promoted Co catalysts as a function of the impregnation sequence (i.e. $Ag_{1.5}$-$5Co_{98.5}$, $5Co_{98.5}(Ag_{1.5})$ and $5Co_{98.5}$- $Ag_{1.5}$).

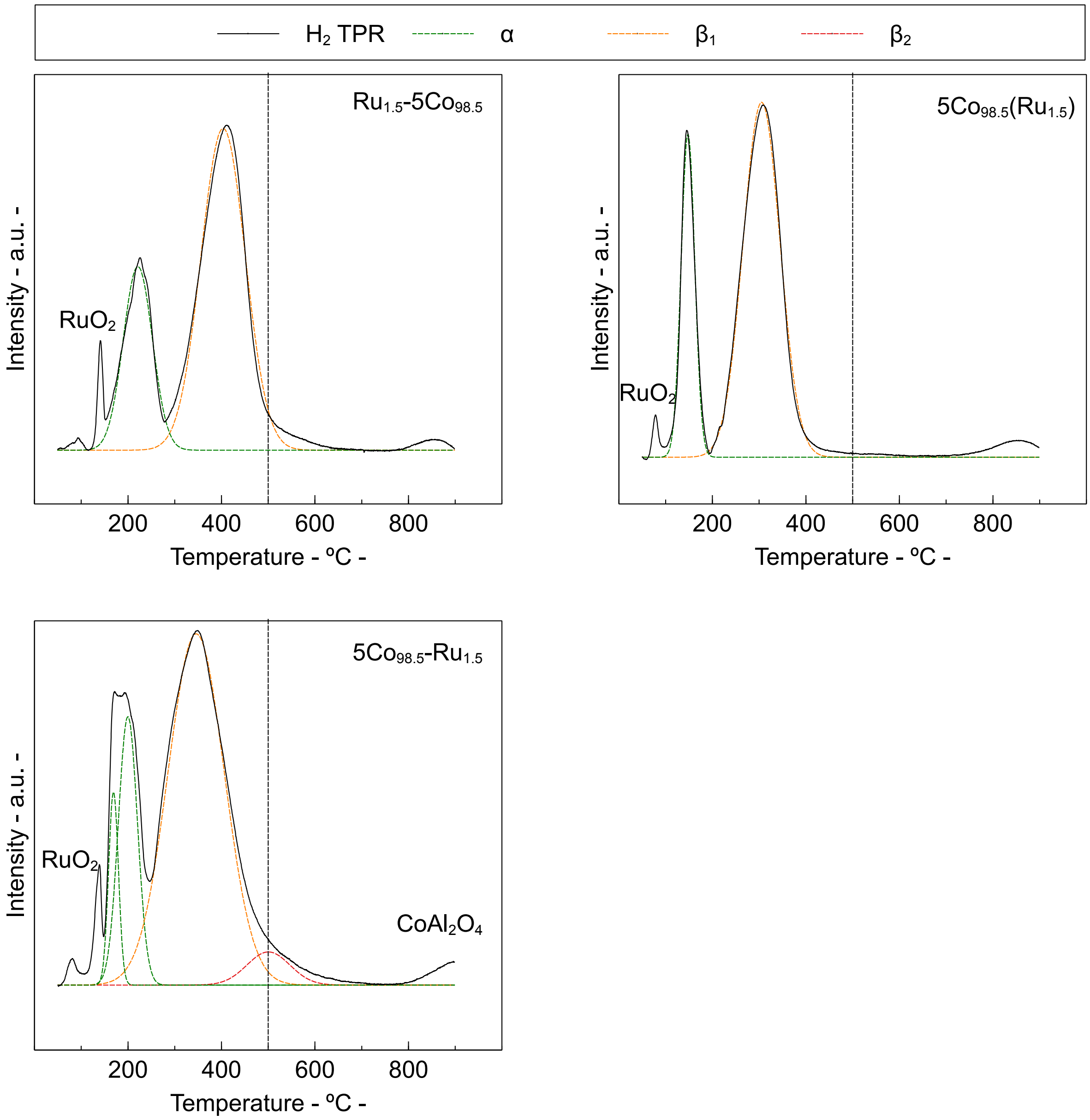
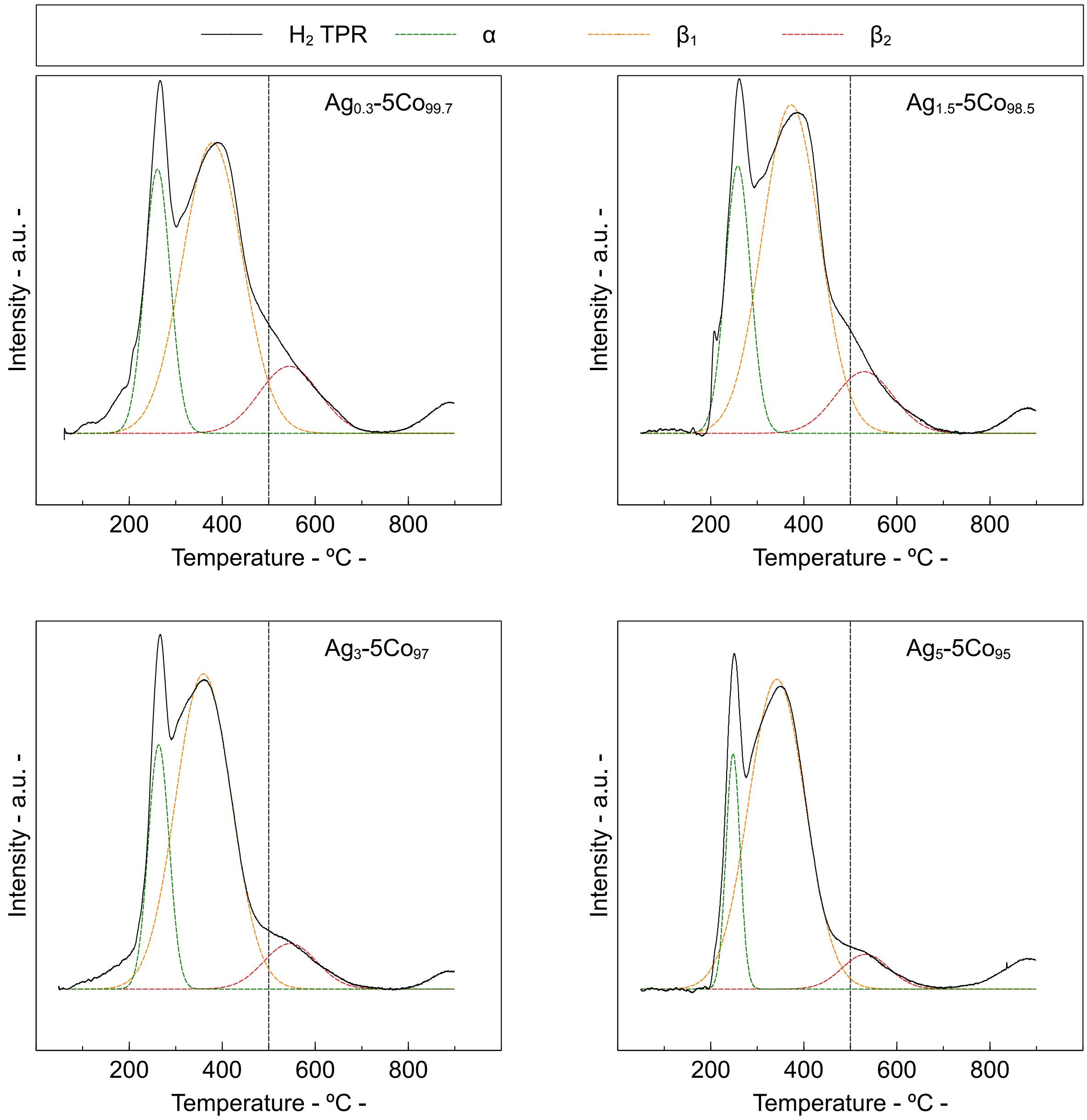



Figure S3. Results of the band deconvolution for $H_2$-TPR profiles of 1.5% a/a Ru promoted Co catalysts as a function of the impregnation sequence (i.e. $Ru_{1.5}$-$5Co_{98.5}$, $5Co_{98.5}(Ru_{1.5})$ and $5Co_{98.5}$- $Ru_{1.5}$).

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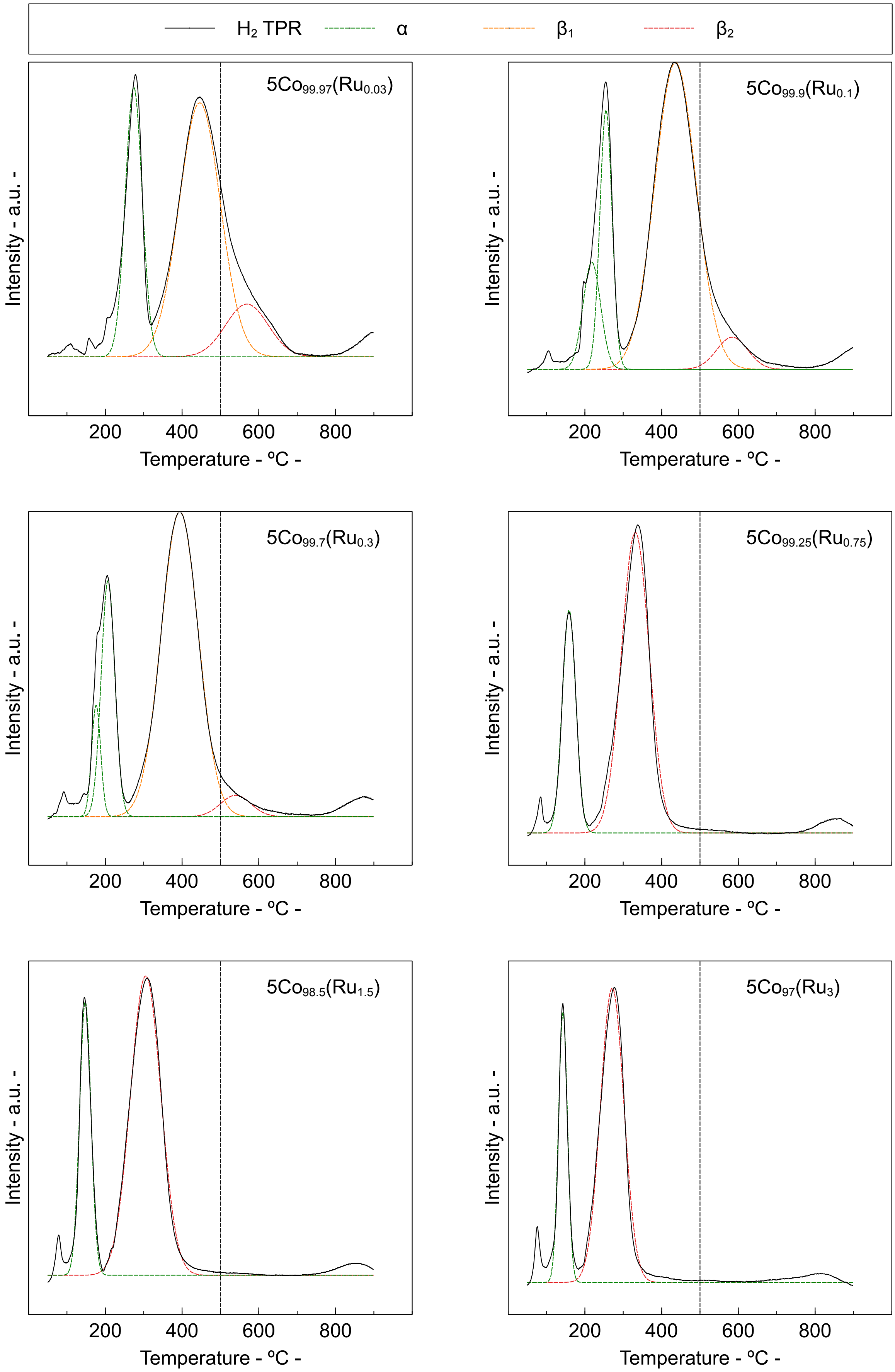


Figure S5. Results of the band deconvolution for $H_2$-TPR profiles of 5Co(Ru) catalysts at variable Ru loading [i.e. $5Co_{99.97}(Ru_{0.03})$, $5Co_{99.9}(Ru_{0.1})$, $5Co_{99.7}(Ru_{0.3})$, $5Co_{99.25}(Ru_{0.75})$, $5Co_{98.5}(Ru_{1.5})$ and $5Co_{97}(Ru_{3})$].

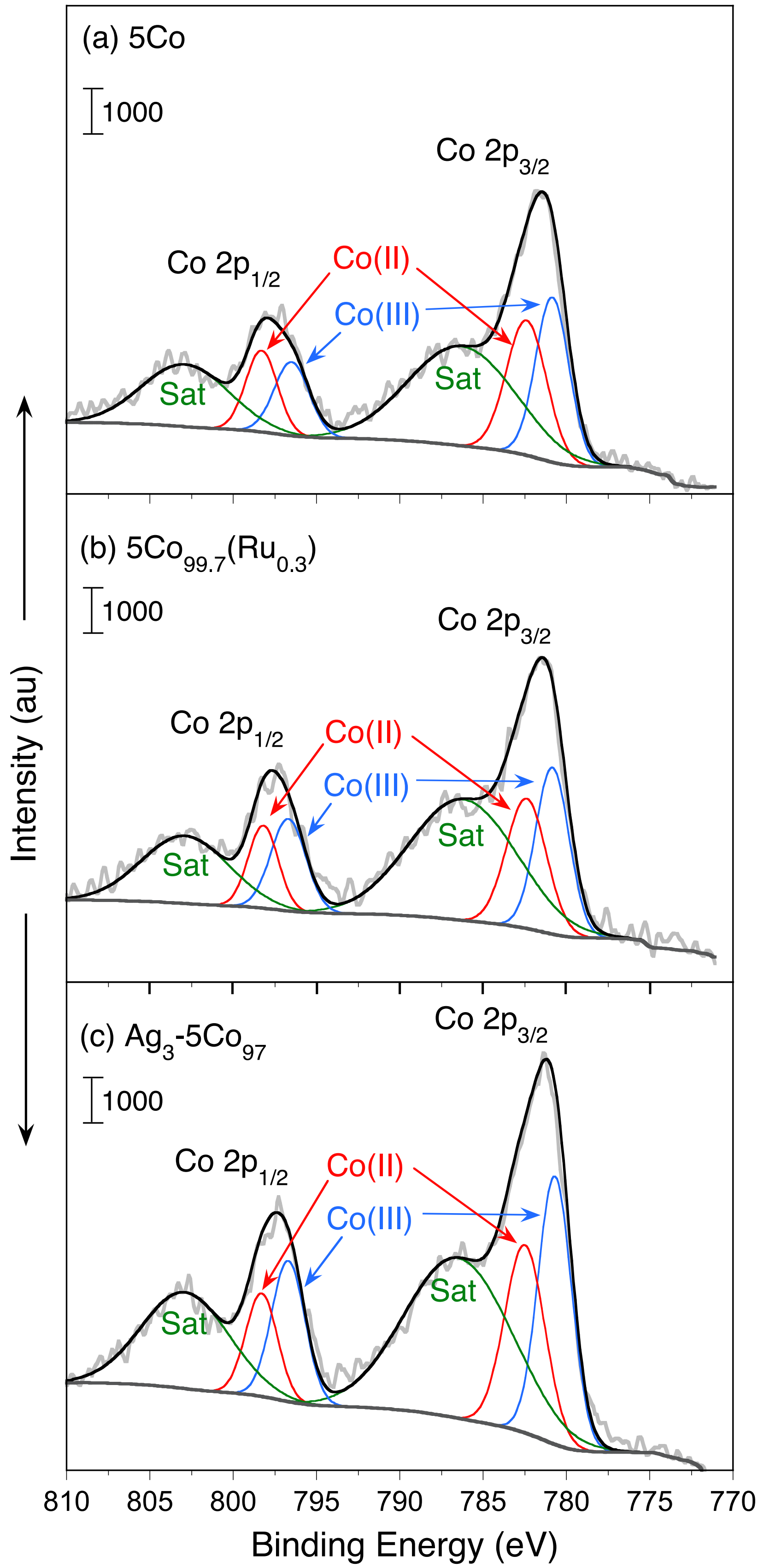


Figure S6. Co 2p XPS spectra of calcined (a) 5Co, (b) $5Co_{99.7}(Ru_{0.3})$ and (c) $Ag_3$-$5Co_{97}$.

Table S1. List of the catalysts prepared in this study

| Catalyst[a] | Promoter | Promoter content (a/a%) | Impregnation method[b] |
|---|---|---|---|
| 12Co | - | - | - |
| 5Co | - | - | - |
| $5Co_{98.5}$-$Pt_{1.5}$ | Pt | | |
| $5Co_{98.5}$-$Pd_{1.5}$ | Pd | | |
| $5Co_{98.5}$-$Ru_{1.5}$ | Ru | 1.50% | S – 1$^{st}$ Co, 2$^{nd}$ NM |
| $5Co_{98.5}$-$Ag_{1.5}$ | Ag | | |
| $5Co_{98.5}$-$Au_{1.5}$ | Au | | |
| $5Co_{98.5}$-$Ru_{1.5}$ | | | S – 1$^{st}$ Co, 2$^{nd}$ Ru |
| $Ru_{1.5}$-$5Co_{98.5}$ | | 1.50% | S – 1$^{st}$ Ru, 2$^{nd}$ Co |
| $5Co_{98.5}(Ru_{1.5})$ | | | Co-impregnation |
| $5Co_{99.97}(Ru_{0.03})$ | | 0.03% | |
| $5Co_{99.9}(Ru_{0.1})$ | Ru | 0.10% | |
| $5Co_{99.7}(Ru_{0.3})$ | | 0.30% | |
| $5Co_{99.25}(Ru_{0.75})$ | | 0.75% | Co-impregnation |
| $5Co_{98.5}(Ru_{1.5})$ | | 1.50% | |
| $5Co_{97}(Ru_{3})$ | | 3.00% | |
| $5Co_{98.5}$-$Ag_{1.5}$ | | | S – 1$^{st}$ Co, 2$^{nd}$ Ag |
| $5Co_{98.5}(Ag_{1.5})$ | | 1.50% | Co-impregnation |
| $Ag_{1.5}$-$5Co_{98.5}$ | Ag | | S – 1$^{st}$ Ag, 2$^{nd}$ Co |
| $Ag_{0.75}$-$5Co_{99.25}$ | | 0.75% | |
| $Ag_{3}$-$5Co_{97}$ | | 3.00% | S – 1$^{st}$ Ag, 2$^{nd}$ Co |
| $Ag_{5}$-$5Co_{95}$ | | 5.00% | |

(a) All catalysts are supported over $\gamma$-$Al_2O_3$. (b) S stands for sequential impregnation.

Table S2. List of catalytic results of all Co and Co bimetallic catalysts developed in this study.

| # | Catalyst | Reaction Conditions[(a),(b)] | OL Conv (%) | Selectivity (%) | | | | | OA Yield (%) | Carbon balance |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | ON | OA | DOA | TOA | DOI | | |
| 1 | 5Co | RC-1 | 25 | 27 | 60 | 0.8 | - | 0.4 | 15 | 97 |
| 2 | $5Co_{98.5}$-$Pt_{1.5}$ | RC-1 | 44 | 15 | 45 | 26 | - | 0.4 | 20 | 95 |
| 3 | $5Co_{98.5}$-$Pd_{1.5}$ | RC-1 | 32 | 14 | 40 | 34 | 4.3 | 0.3 | 13 | 97 |
| 4 | $5Co_{98.5}$-$Ru_{1.5}$ | RC-1 | 29 | 22 | 60 | 0.8 | - | 0.8 | 17 | 95 |
| 5 | $5Co_{98.5}$-$Ag_{1.5}$ | RC-1 | 28 | 20 | 63 | 1.3 | - | 0.5 | 18 | 96 |
| 6 | $5Co_{98.5}$-$Au_{1.5}$ | RC-1 | 15 | 31 | 62 | - | - | - | 9.5 | 99 |
| 7 | $Ru_{1.5}$-$5Co_{98.5}$ | RC-1 | 31 | 24 | 65 | 1.1 | 1.3 | 1.0 | 20 | 98 |
| 8 | $5Co_{98.5}(Ru_{1.5})$ | RC-1 | 34 | 22 | 65 | 1.7 | 0.3 | 1.0 | 22 | 97 |
| 9 | $5Co_{98.5}(Ag_{1.5})$ | RC-1 | 31 | 19 | 63 | 1.6 | 0.4 | 0.9 | 19 | 96 |
| 10 | $Ag_{1.5}$-$5Co_{98.5}$ | RC-1 | 33 | 20 | 75 | 2.4 | 0.5 | 1.2 | 25 | 100 |
| 11 | 12Co | RC-2 | 52 | 8.4 | 79 | 7.0 | 1.3 | 1.0 | 41 | 98 |
| 12 | 5Co | RC-2 | 36 | 14 | 80 | 3.3 | 0.7 | 1.1 | 28 | 99 |
| 13 | $5Co_{99.97}(Ru_{0.03})$ | RC-2 | 38 | 13 | 79 | 2.9 | 0.4 | 1.1 | 30 | 99 |
| 14 | $5Co_{99.9}(Ru_{0.1})$ | RC-2 | 46 | 10 | 76 | 3.7 | 0.4 | 1.0 | 35 | 96 |
| 15 | $5Co_{99.7}(Ru_{0.3})$ | RC-2 | 50 | 10 | 81 | 4.8 | 0.3 | 1.1 | 40 | 99 |
| 16 | $5Co_{99.25}(Ru_{0.75})$ | RC-2 | 49 | 9.4 | 79 | 4.5 | - | 0.9 | 39 | 97 |
| 17 | $5Co_{98.5}(Ru_{1.5})$ | RC-2 | 41 | 13 | 81 | 1.8 | - | 1.1 | 33 | 99 |
| 18 | $5Co_{97}(Ru_{3})$ | RC-2 | 45 | 12 | 82 | 4.0 | 0.7 | 1 | 34 | 100 |
| 19 | $Ag_{0.75}$-$5Co_{99.25}$ | RC-2 | 46 | 10 | 81 | 4.5 | 0.5 | 0.9 | 37 | 99 |
| 20 | $Ag_{1.5}$-$5Co_{98.5}$ | RC-1 | 44 | 11 | 83 | 3.9 | - | 0.9 | 37 | 99 |
| 21 | $Ag_{3}$-$5Co_{97}$ | RC-2 | 51 | 9.5 | 83 | 6.0 | 0.8 | 1.2 | 42 | 100 |
| 22 | $Ag_{5}$-$5Co_{95}$ | RC-2 | 39 | 10 | 79 | 4.7 | 1.2 | 0.7 | 31 | 99 |

(a) Reaction conditions RC-1: T = 180 ºC, P = 101 kPa, OL : $NH_3$ : $H_2$ : $N_2$ (mol%) = 1 : 9 : 2.5 : 0.9, 1.8 $mL.h^{-1}$ OL, 510 mg catalyst, $WHSV_{OL}$ = 2.9 $h^{-1}$. The catalysts were pre-reduced at 500 $^oC$ for 1 h before the reaction.

(b) Reaction conditions RC-2: T = 180 ºC, P = 101 kPa, OL : $NH_3$ : $H_2$ : $N_2$ (mol%) = 1 : 9 : 3.4 : 0, 1.2 $mL.h^{-1}$ OL, 510 mg catalyst, $WHSV_{OL}$ = 1.9 $h^{-1}$. The catalysts were pre-reduced at 500 $^oC$ for 1 h before the reaction.

Table S3. Main bands observed in the $H_2$-TPR profiles of 5Co-NM bimetallic catalysts promoted by Pt, Pd, Ag, Au and Ru (1.5% a/a) using the sequential impregnation protocol

| Catalyst[(a)] | Band | $Co_3O_4 \rightarrow$ CoO [(b)] ($\alpha$) | | $CoO \rightarrow Co^0$ [(b)] ($\beta_1$) | $CoO \rightarrow Co^0$ [(b)] ($\beta_2$) | Reduction Temperature[(c)] | $CoAl_2O_4$[(b)] | Ratio $\beta / \alpha$ |
|---|---|---|---|---|---|---|---|---|
| 5Co | Position | 297 ºC | | 453 ºC | 595 ºC | < 500ºC | > 750ºC | 3.2 |
| | $H_2$ uptake (mmol·g$^{-1}$) | 0.21 | | 0.45 | 0.22 | 0.52 | 0.02 | |
| $5Co_{98.5}$-$Pt_{1.5}$ | Position | 131 ºC | | 355 ºC | | < 500 ºC | > 750 ºC | 2.6 |
| | $H_2$ uptake (mmol·g$^{-1}$) | 0.30 | | 0.79 | | 1.12 | 0.01 | |
| $5Co_{98.5}$-$Pd_{1.5}$ | Position | 211 ºC | 286 ºC | 362 ºC | 533 ºC | < 500 ºC | > 750 ºC | 2.8 |
| | $H_2$ uptake (mmol·g$^{-1}$) | 0.15 | 0.14 | 0.40 | 0.41 | 0.83 | 0.02 | |
| $5Co_{98.5}$-$Ru_{1.5}$ | Position | 169 ºC | 200 ºC | 346 ºC | 500 ºC | < 500 ºC | > 750 ºC | 3.0 |
| | $H_2$ uptake (mmol·g$^{-1}$) | 0.07 | 0.20 | 0.75 | 0.05 | 1.04 | 0.02 | |
| $5Co_{98.5}$-$Ag_{1.5}$ | Position | 289 ºC | | 460 ºC | 612 ºC | < 500ºC | > 750ºC | 3.3 |
| | $H_2$ uptake (mmol·g$^{-1}$) | 0.21 | | 0.57 | 0.12 | 0.56 | 0.02 | |
| $5Co_{98.5}$-$Au_{1.5}$ | Position | 342 ºC | | 462 ºC | | < 500ºC | > 750ºC | 2.4 |
| | $H_2$ uptake (mmol·g$^{-1}$) | 0.26 | | 0.54 | | 0.62 | 0.06 | |

(a) Supported over $\gamma$-$Al_2O_3$. (b) $H_2$ consumption calculated after curve deconvolution using Gaussian distributions. (c) $H_2$ consumption calculated by integrating the $H_2$-TPR profiles using trapezoidal numerical integration.

Table S4. Main bands observed in the $H_2$-TPR profiles of 5Co catalysts promoted by Ag and Ru (1.5% a/a) as a function of the impregnation sequence

| Catalyst[(a)] | Band | $Co_3O_4 \rightarrow CoO$ [(b)] | $CoO \rightarrow Co^0$ [(b)] | | Reduction Temperature[(c)] | $CoAl_2O_4$[(b)] | Ratio $\beta / \alpha$ |
|---|---|---|---|---|---|---|---|
| | | ($\alpha$) | ($\beta_1$) | ($\beta_2$) | | | |
| $5Co_{1.5}$-$Ru_{98.5}$ | Position | 169 ºC 200 ºC | 346 ºC | 500 ºC | < 500 ºC | > 750 ºC | 3.0 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.07 0.20 | 0.75 | 0.05 | 1.04 | 0.02 | |
| $Ru_{1.5}$-$5Co_{98.5}$ | Position | 221 ºC | 404 ºC | - | < 500 ºC | > 750 ºC | 2.7 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.26 | 0.69 | - | 0.92 | 0.03 | |
| $5Co_{98.5}(Ru_{1.5})$ | Position | 148 ºC | 305 ºC | - | < 500 ºC | > 750 ºC | 3.0 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.24 | 0.71 | - | 1.02 | 0.03 | |
| $5Co_{98.5}$-$Ag_{1.5}$ | Position | 289 ºC | 460 ºC | 612 ºC | < 500ºC | > 750ºC | 3.3 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.21 | 0.57 | 0.12 | 0.56 | 0.02 | |
| $Ag_{1.5}$-$5Co_{98.5}$ | Position | 258 ºC | 373 ºC | 530 ºC | < 500ºC | > 750ºC | 3.3 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.23 | 0.63 | 0.12 | 0.96 | 0.03 | |
| $5Co_{98.5}(Ag_{1.5})$ | Position | 266 ºC | 360 ºC | 523 ºC | < 500ºC | > 750ºC | 2.9 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.22 | 0.47 | 0.17 | 0.80 | 0.04 | |

(a) Supported over $\gamma$-$Al_2O_3$. (b) $H_2$ consumption calculated after curve deconvolution using Gaussian distributions. (c) $H_2$ consumption calculated by integrating the $H_2$-TPR profiles using trapezoidal numerical integration.

Table S5. Main bands observed in the $H_2$-TPR profiles of $5Co_X(Ru_Y)$ catalysts as a function of the Ru loading.

| Catalyst[(a)] | Band | $Co_3O_4 \rightarrow$ CoO [(b)] (α) | | CoO $\rightarrow Co^0$ [(b)] (β1) | (β2) | Reduction temperature[(b)] | $CoAl_2O_4$[(c)] | Ratio β / α |
|---|---|---|---|---|---|---|---|---|
| $5Co_{99.97}(Ru_{0.03})$ | Position | 274ºC | | 446º | 569ºC | < 500ºC | > 750ºC | 2.8 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.23 | | 0.54 | 0.11 | 0.72 | 0.02 | |
| $5Co_{99.9}(Ru_{0.1})$ | Position | 218ºC | 255ºC | 436ºC | 584 | < 500ºC | > 750ºC | 2.7 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.10 | 0.17 | 0.68 | 0.05 | 0.86 | 0.01 | |
| $5Co_{99.7}(Ru_{0.3})$ | Position | 176ºC | 207ºC | 394ºC | 536 ºC | < 500ºC | > 750ºC | 2.8 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.06 | 0.21 | 0.73 | 0.04 | 1.01 | 0.03 | |
| $5Co_{99.25}(Ru_{0.75})$ | Position | 160ºC | | 337ºC | - | < 500ºC | > 750ºC | 2.8 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.27 | | 0.75 | - | 1.01 | 0.03 | |
| $5Co_{98.5}(Ru_{1.5})$ | Position | 148 ºC | | 305 ºC | - | < 500 ºC | > 750 ºC | 3.0 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.24 | | 0.71 | - | 1.02 | 0.03 | |
| $5Co_{97}(Ru_3)$ | Position | 143ºC | | 271ºC | - | < 500ºC | > 750ºC | 2.8 |
| | $H_2$ uptake ($mmol \cdot g^{-1}$) | 0.26 | | 0.73 | - | 0.98 | 0.02 | |

(a) Supported over $\gamma$-$Al_2O_3$. (b) $H_2$ consumption calculated after curve deconvolution using Gaussian distributions. (c) $H_2$ consumption calculated by integrating the $H_2$-TPR profiles using trapezoidal numerical integration.

Table S6. Main bands observed in the $H_2$-TPR profiles of 5%$Ag_Y$-$Co_X$ catalysts as a function of the Ag loading.

| Catalyst[(a)] | Band | $Co_3O_4 \rightarrow$ CoO [(b)] (α) | $CoO \rightarrow Co^0$ [(b)] (β₁) | (β₂) | Reduction temperature[(b)] | $CoAl_2O_4$[(c)] | Ratio β / α |
|---|---|---|---|---|---|---|---|
| $Ag_{0.75}$-$5Co_{99.25}$ | Position | 261 ºC | 379ºC | 544ºC | < 500ºC | > 750ºC | 3.2 |
| | $H_2$ uptake ($mmol\cdot g^{-1}$) | 0.25 | 0.64 | 0.15 | 0.90 | 0.03 | |
| $Ag_{1.5}$-$5Co_{98.5}$ | Position | 258 ºC | 373 ºC | 530 ºC | < 500ºC | > 750ºC | 3.3 |
| | $H_2$ uptake ($mmol\cdot g^{-1}$) | 0.23 | 0.63 | 0.12 | 0.96 | 0.03 | |
| $Ag_3$-$5Co_{97}$ | Position | 263 ºC | 360 ºC | 546 ºC | < 500ºC | > 750ºC | 3.9[(c)] |
| | $H_2$ uptake ($mmol\cdot g^{-1}$) | 0.21 | 0.73 | 0.10 | 0.99 | 0.02 | |
| $Ag_5$-$5Co_{95}$ | Position | 248 ºC | 342 ºC | 533 ºC | < 500ºC | > 750ºC | 5.8[(c)] |
| | $H_2$ uptake ($mmol\cdot g^{-1}$) | 0.14 | 0.72 | 0.06 | 0.96 | 0.02 | |

(a) Supported over γ-$Al_2O_3$. (b) $H_2$ consumption calculated after curve deconvolution using Gaussian distributions. (c) $H_2$ consumption calculated by integrating the $H_2$-TPR profiles using trapezoidal numerical integration. (c) Highly overlapping bands, difficult to deconvolute.

Table S7. Results for band deconvolution for the Co 2p XPS spectra measured on the 5Co, $5Co_{99.7}(Ru_{0.3})$ and $Ag_3$-$5Co_{97}$ catalysts.

| Catalyst | | Co $2p_{3/2}$ | | | Co $2p_{1/2}$ | | |
|---|---|---|---|---|---|---|---|
| | | Band I [Co(III)] | Band II [Co(II)] | Band III Satellite | Band I [Co(III)] | Band II [Co(II)] | Band III Satellite |
| 5Co | BE (eV) | 780.8 (1.0) | 782.4 (1.2) | 786.3 (3.2) | 796.5 (1.0) | 798.3 (1.0) | 802.9 (2.6) |
| | % | 26% | 25% | 49% | 24% | 24% | 52% |
| $5Co_{99.7}(Ru_{0.3})$ | BE (eV) | 780.8 (1.0) | 782.4 (1.2) | 786.3 (3.0) | 796.7 (1.0) | 798.2 (0.9) | 802.9 (2.6) |
| | % | 24% | 22% | 54% | 28% | 21% | 51% |
| $Ag_3$-$5Co_{97}$ | BE (eV) | 780.7 (1.0) | 782.5 (1.2) | 786.5 (3.2) | 796.7 (1.0) | 798.3 (1.0) | 802.9 (2.6) |
| | % | 27% | 22% | 51% | 29% | 20% | 51% |

Table S8. Results for band deconvolution for the Ru 3d XPS spectra measured on the $5Co_{99.7}(Ru_{0.3})$ and 0.026Ru catalysts.

| Catalyst | | Ru $3d_{5/2}$ | | | |
|---|---|---|---|---|---|
| | | Band I $[Ru(0)_{I}]$ | Band II $[Ru(0)_{II}]$ | Band III $[Ru(0)_{III}]$ | Band IV $(RuO_2)$ |
| $5Co_{99.7}(Ru_{0.3})$ | BE (eV) | 277.1 (0.3) | 278.2 (0.2) | 279.2 (0.2) | - |
| | % | 50% | 21% | 28% | - |
| 0.026Ru | BE (eV) | - | 278.0 (0.1) | 279.6 (0.4) | 280.6 (0.2) |
| | % | - | 20% | 54% | 26% |

Table S9. Results for band deconvolution for the Ag 3d XPS spectra measured on the $Ag_3$-$5Co_{97}$ and 0.27Ag catalysts.

| Catalyst | | Ag $3d_{5/2}$ | | | Ag $3d_{3/2}$ | | |
|---|---|---|---|---|---|---|---|
| | | Band I [$Ag(0)_I$] | Band II [$Ag(0)_{II}$] | Band III Ag(I) | Band I [$Ag(0)_I$] | Band II [$Ag(0)_{II}$] | Band III Ag(I) |
| $Ag_3$-$5Co_{97}$ | BE (eV) | 365.8 (1.0) | 368.0 (0.5) | 368.9 (0.7) | 372.2 (1.0) | 374.2 (0.6) | 375.8 (0.5) |
| | % | 25% | 46% | 29% | 29% | 42% | 29% |
| 0.27Ag | BE (eV) | 365.8 (1.0) | 368.0 (0.5) | 368.7 (0.7) | 372.2 (0.8) | 374.2 (0.4) | 374.6 (0.8) |
| | % | 11% | 48% | 40% | 12% | 43% | 45% |