**Supporting Information (SI)**

# Oxidative Steam Reforming of Ethanol over $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca) Catalysts: Effect of Alkaline Earth Metal Substitution and Support on Stability and Activity†

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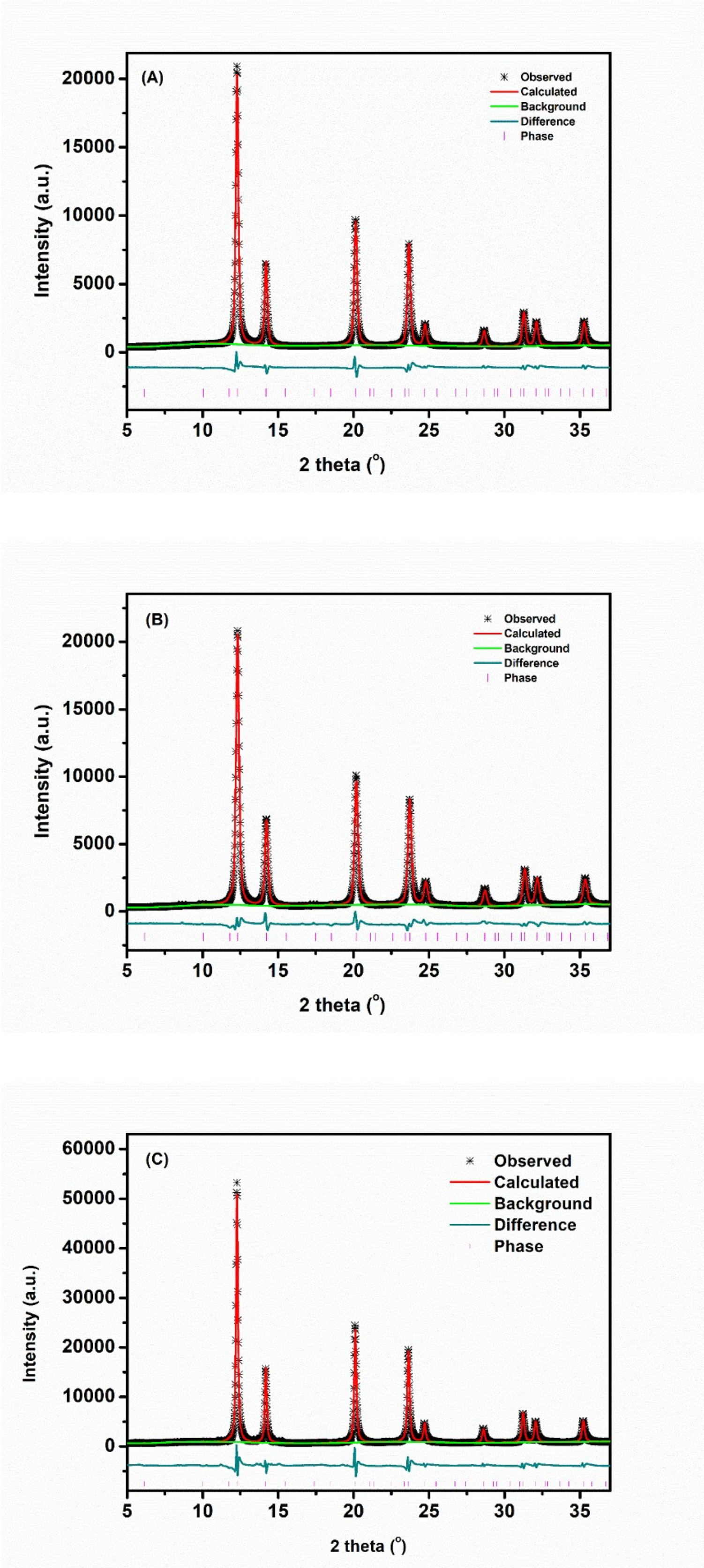
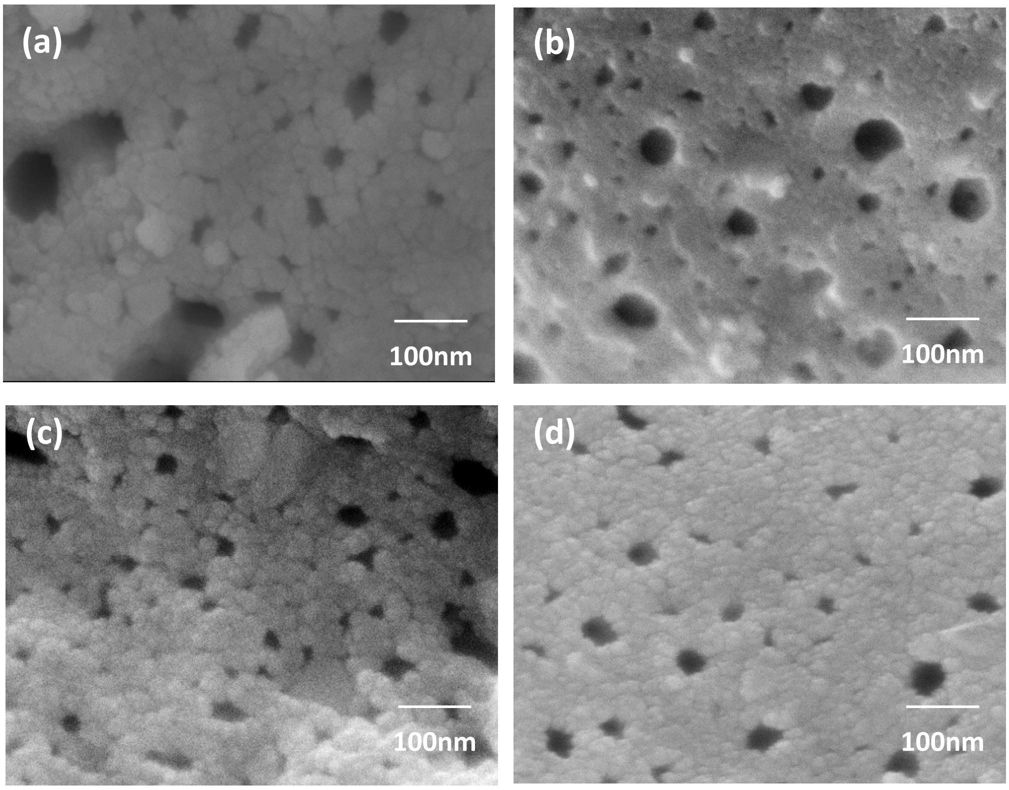
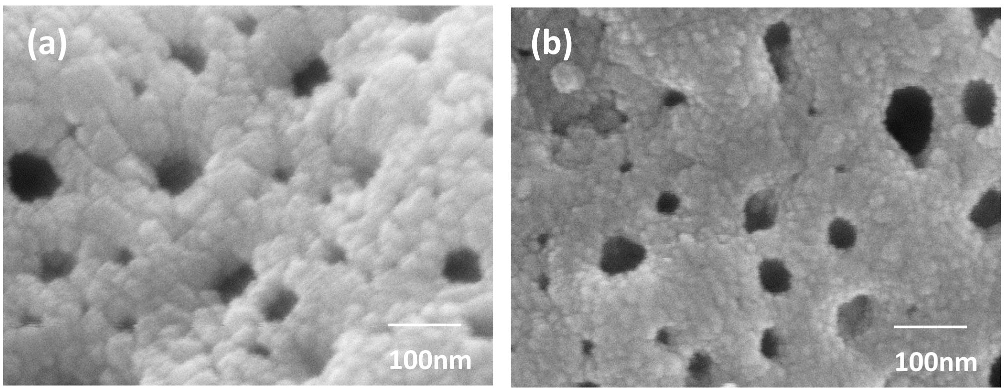



**Figure S1.** Rietveld Refinement of (A) LCRO, (B) MLCRO03, and (C) CLCRO02.




(A)




(B)

**Figure S2.** SEM image of solid solution (A) MLCRO (a) x=0.0, (b) x=0.2, (c) x=0.3 and (B) CLCRO (a) x=0.1 and (b) x=0.2.

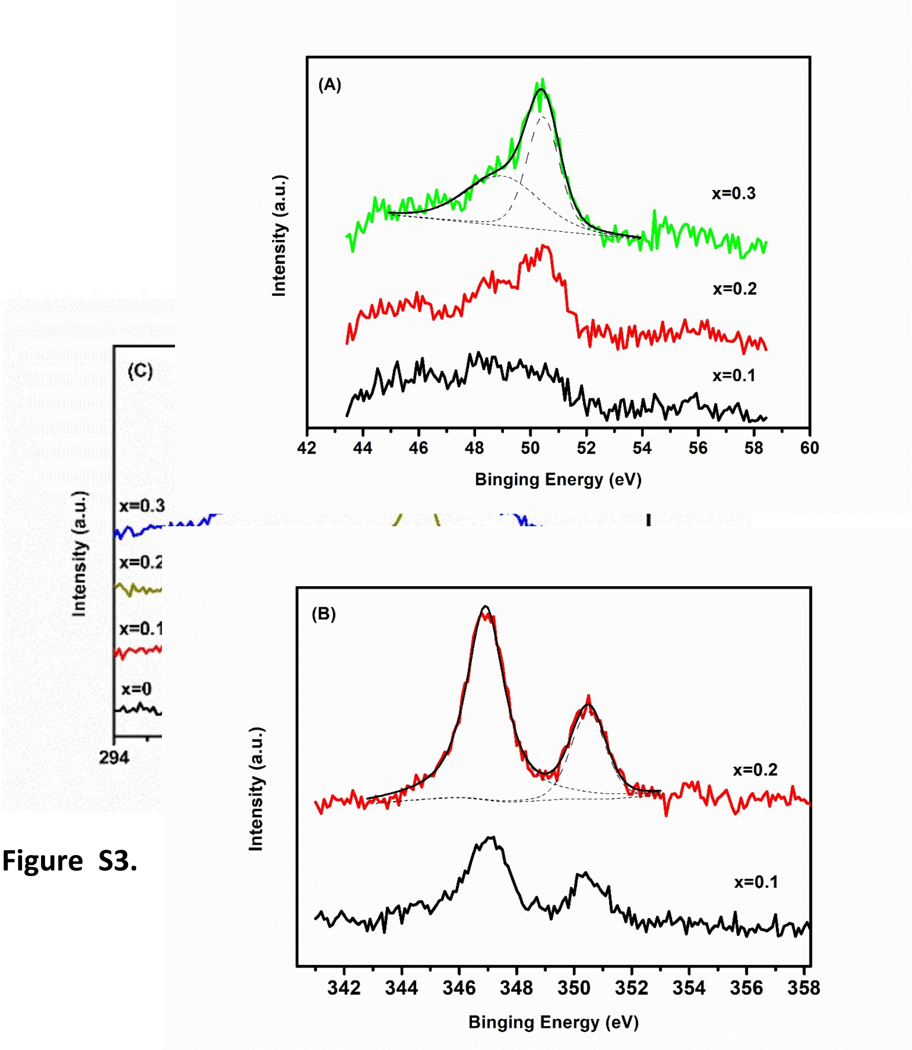



**Figure S3.** X-ray photoelectron spectra of $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca) (A) Mg2p and (B) Ca2p and (C) MLCRO0-03 of Ru3d.

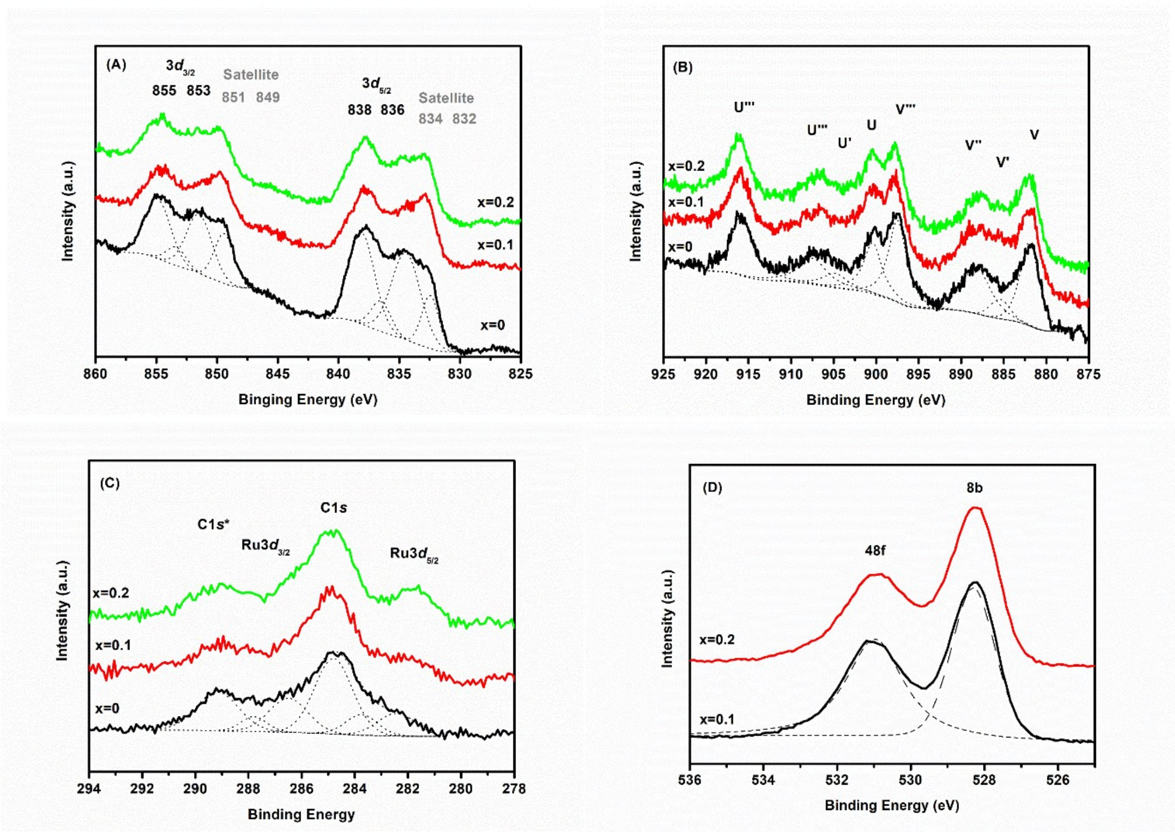



**Figure S4.** X-ray photoelectron spectra of $Ca_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (A) La3*d*; (B) Ce3*d*; (C) Ru3*d*, and (D) O1*s*.

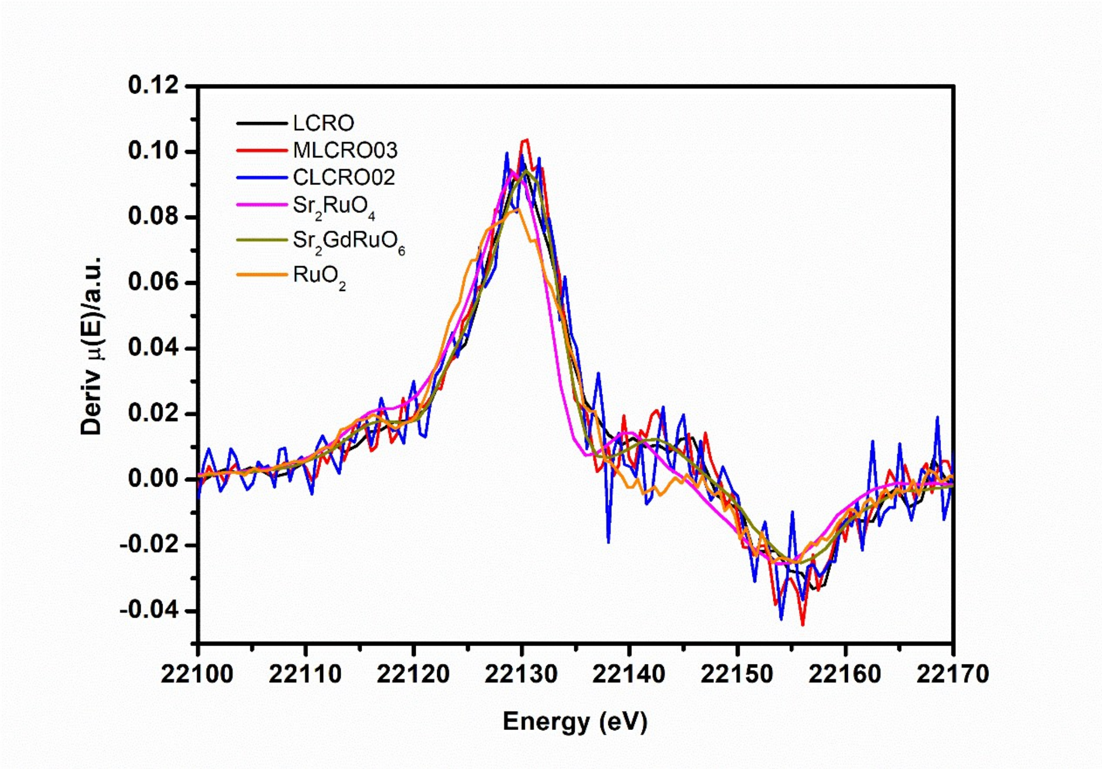



**Figure S5.** The first derivatives of the Ru K-edge XANES spectrum for LCRO, MLCRO03, and CLCRO02 catalysts, and the reference compounds of $Sr_2RuO_4$, $Sr_2GdRuO_6$, and $RuO_2$.

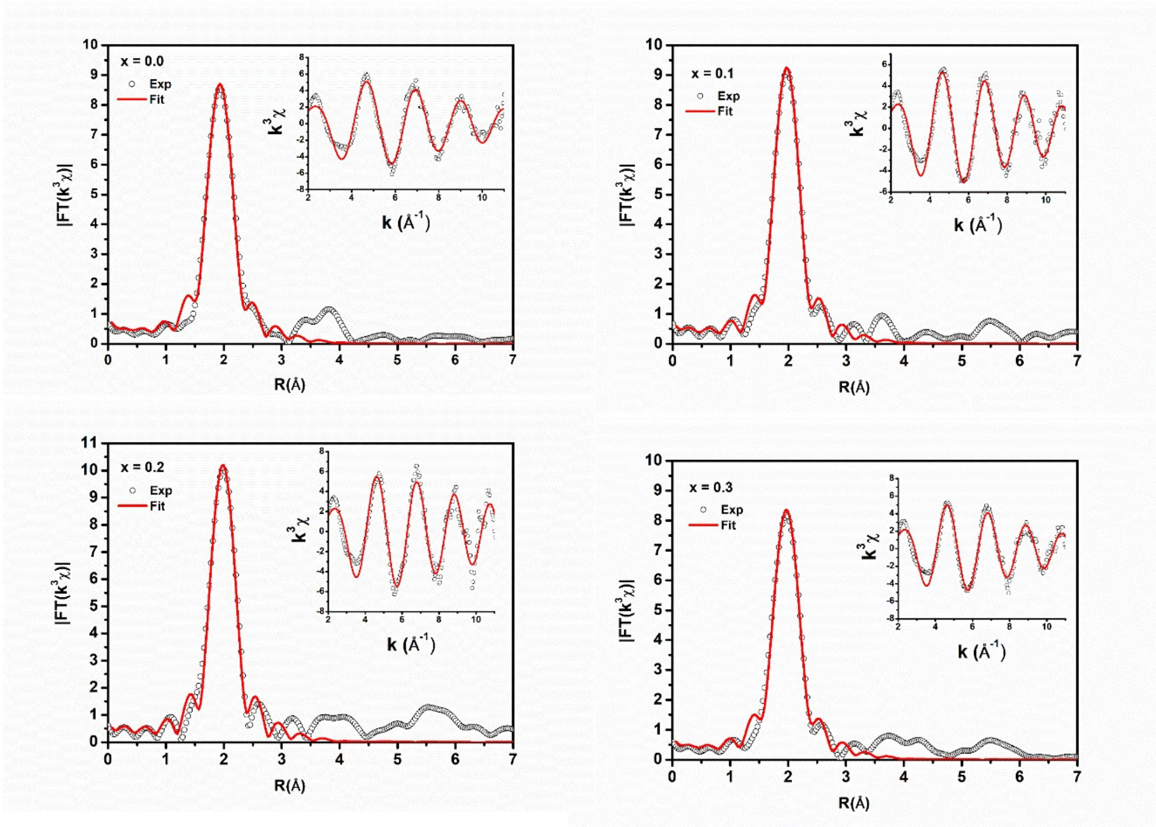


**Figure S6.** The Ru K-edge EXAFS spectra of MLCRO0-03.

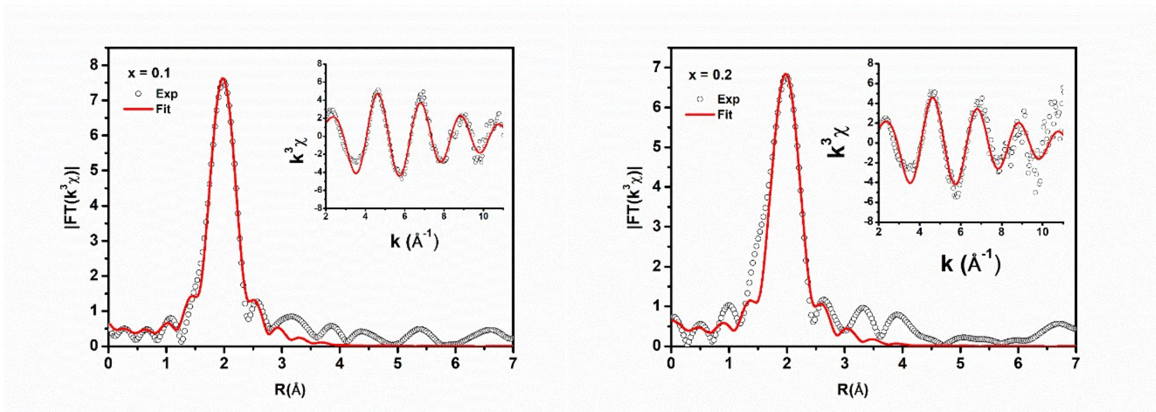
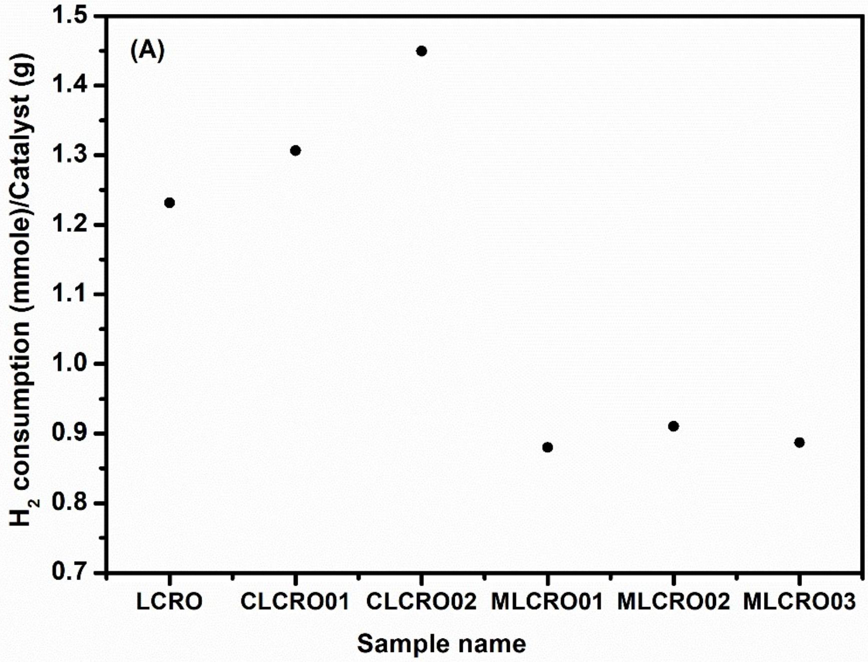


**Figure S7.** The Ru K-edge EXAFS spectra of CLCRO01-02.



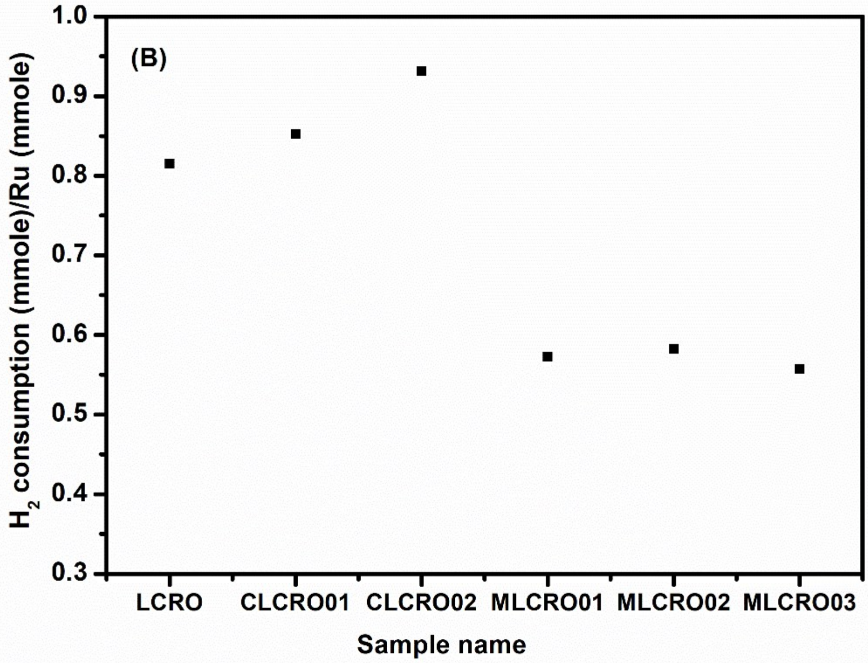




**Figure S8.** Temperature programmed reduction profile of (A) $H_2$ consumption per catalysts of $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca) and (B) $H_2$ consumption per Ru atom of $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca).

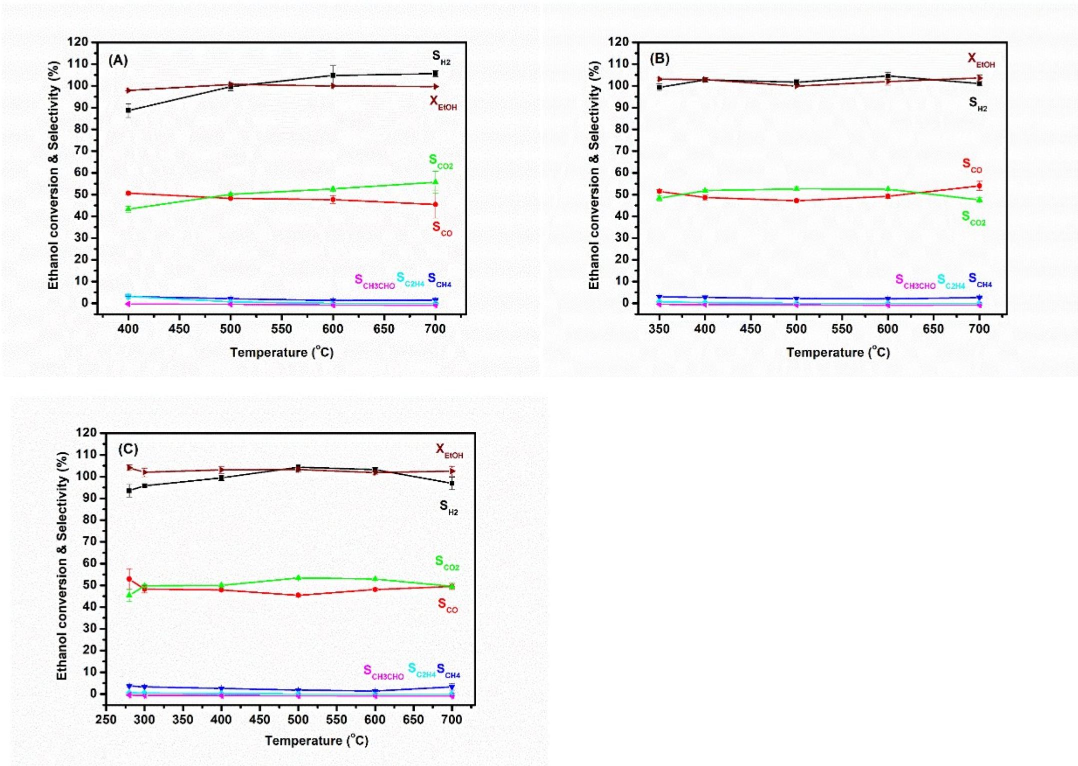



**Figure S9.** The activation temperature of catalysts for (A) LCRO/$Al_2O_3$, (B) MLCRO03/$Al_2O_3$, (C) CLCRO02/$Al_2O_3$ ($H_2O$/ethanol = 3 and GHSV = 1.6 x $10^5$ $h^{-1}$).

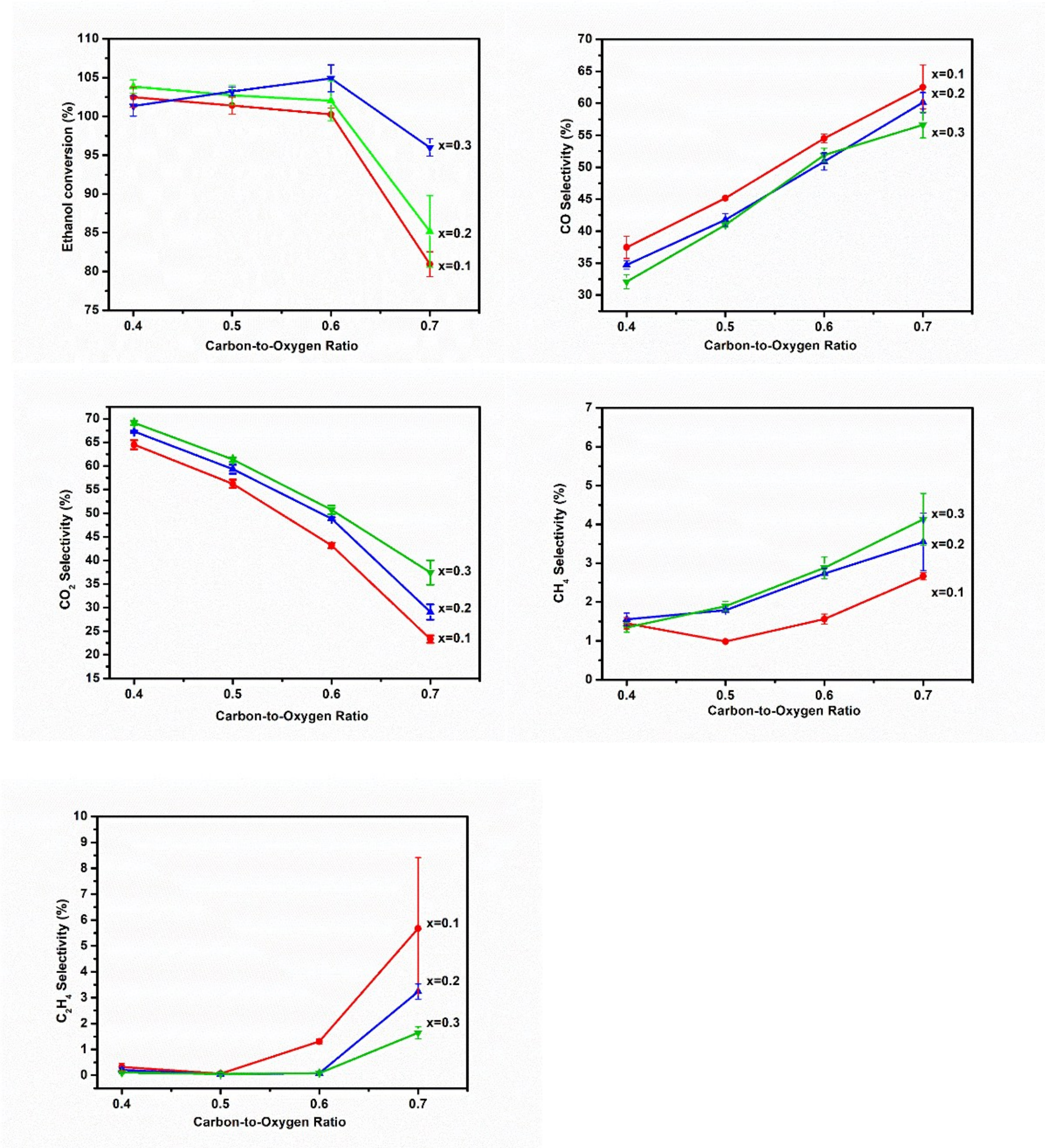



**Figure S10 (A).** Performance in OSRE of $Mg_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}/Al_2O_3$ with Ethanol conversion, CO, $CO_2$, $CH_4$, and $C_2H_4$ selectivity ($H_2O$/ethanol = 3, GHSV = $1.6 \times 10^5$ $h^{-1}$, T = 350$^oC$).

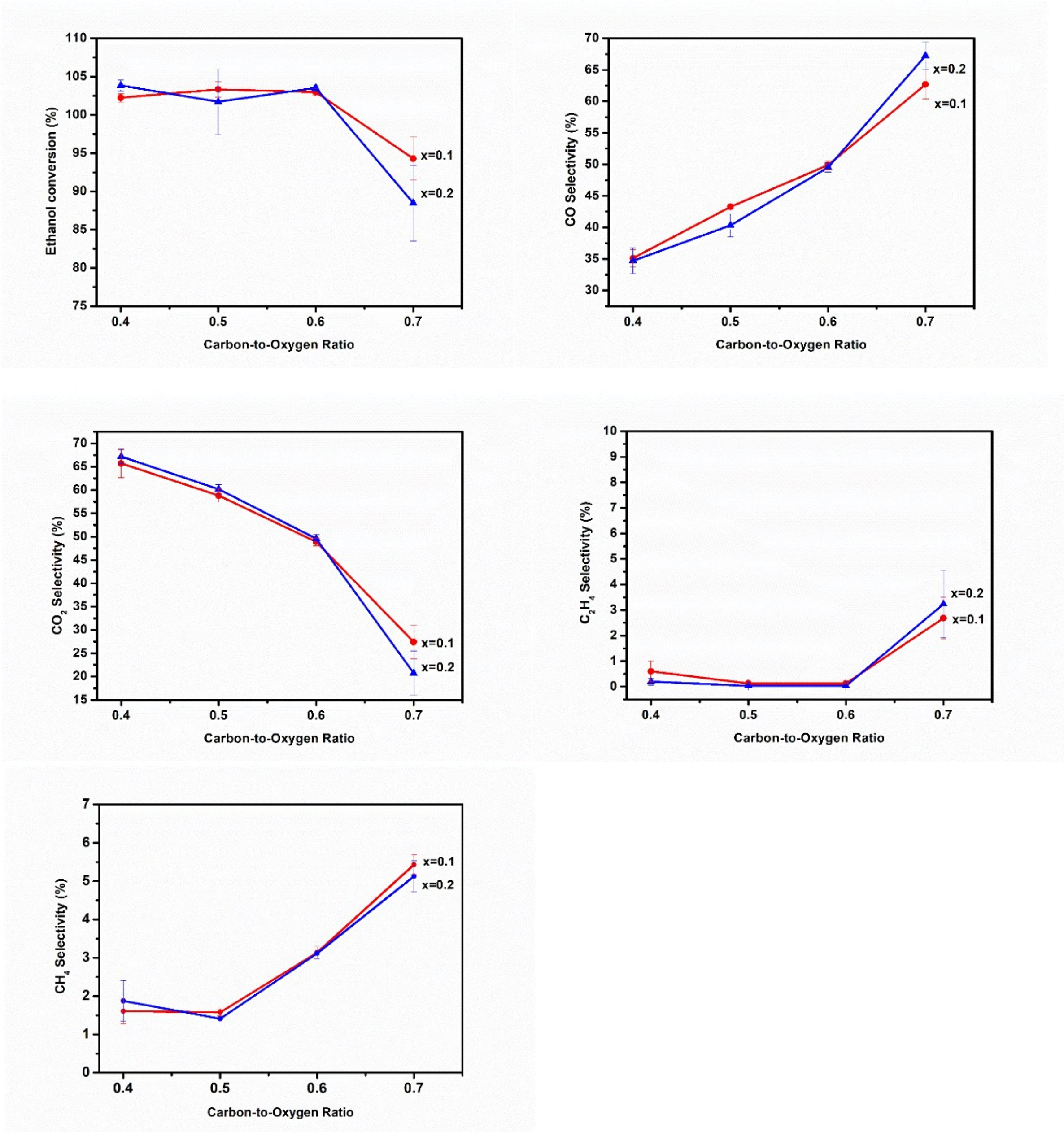



**Figure S10 (B).** Performance in OSRE of $Ca_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}/Al_2O_3$ with Ethanol conversion, CO, $CO_2$, $CH_4$, and $C_2H_4$ selectivity ($H_2O$/ethanol = 3, GHSV = 1.6 x $10^5$ $h^{-1}$, T = 280°C).

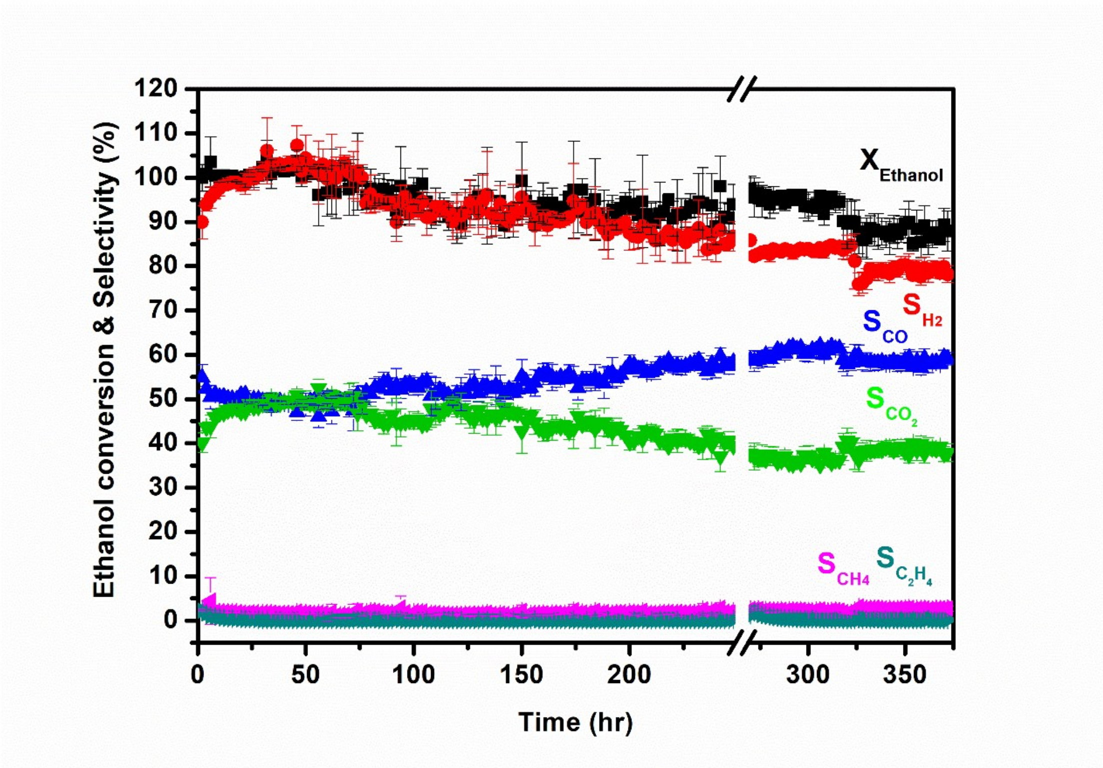



**Figure S11.** Stability test on catalyst MLCRO03/$Al_2O_3$ under T = 350°C, $H_2O$/ethanol = 3, GHSV = 1.6 x $10^5$ $h^{-1}$ condition.

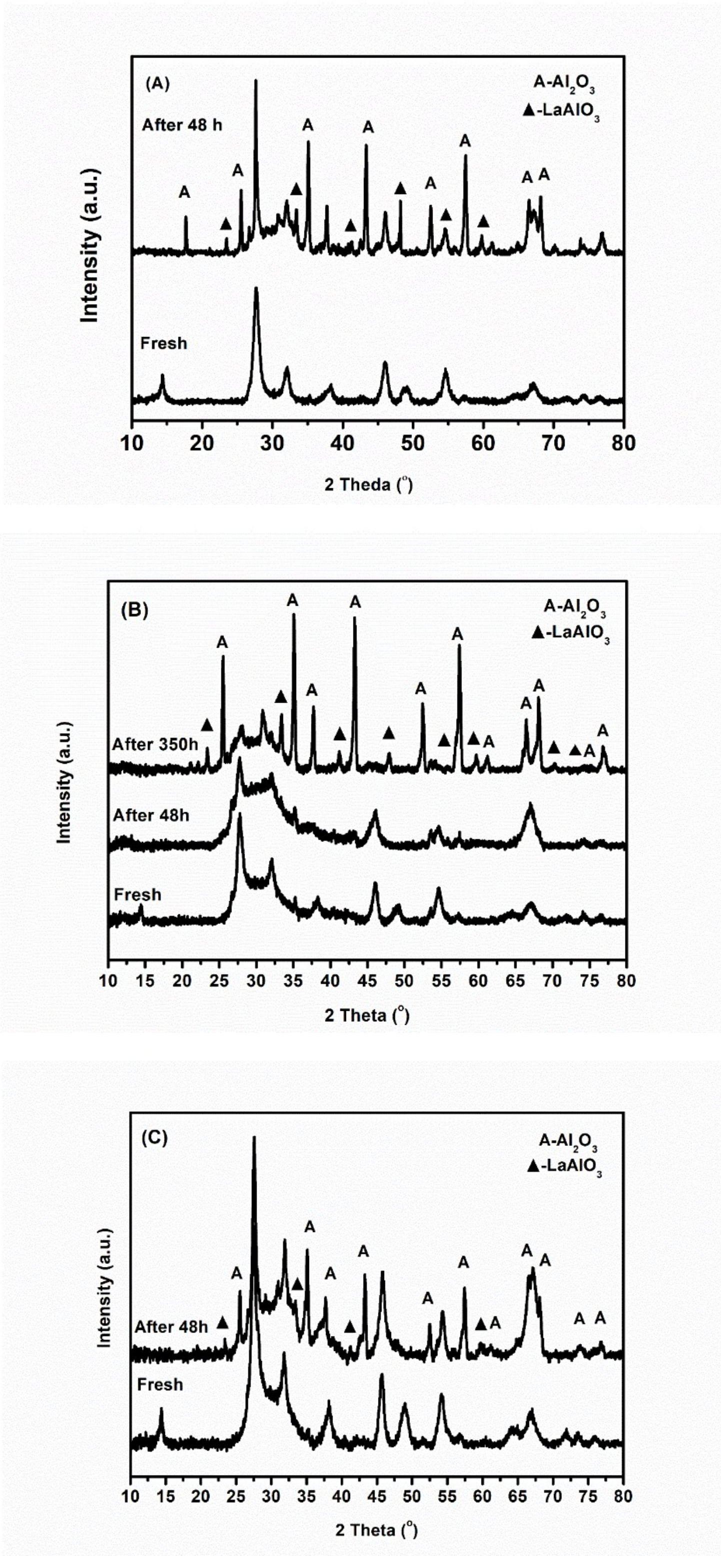



**Figure S12.** Powder X-ray diffraction of (A) LCRO/$Al_2O_3$, (B) MLCRO03/$Al_2O_3$, and (C) CLCRO02/$Al_2O_3$ before and after long-term stability test.

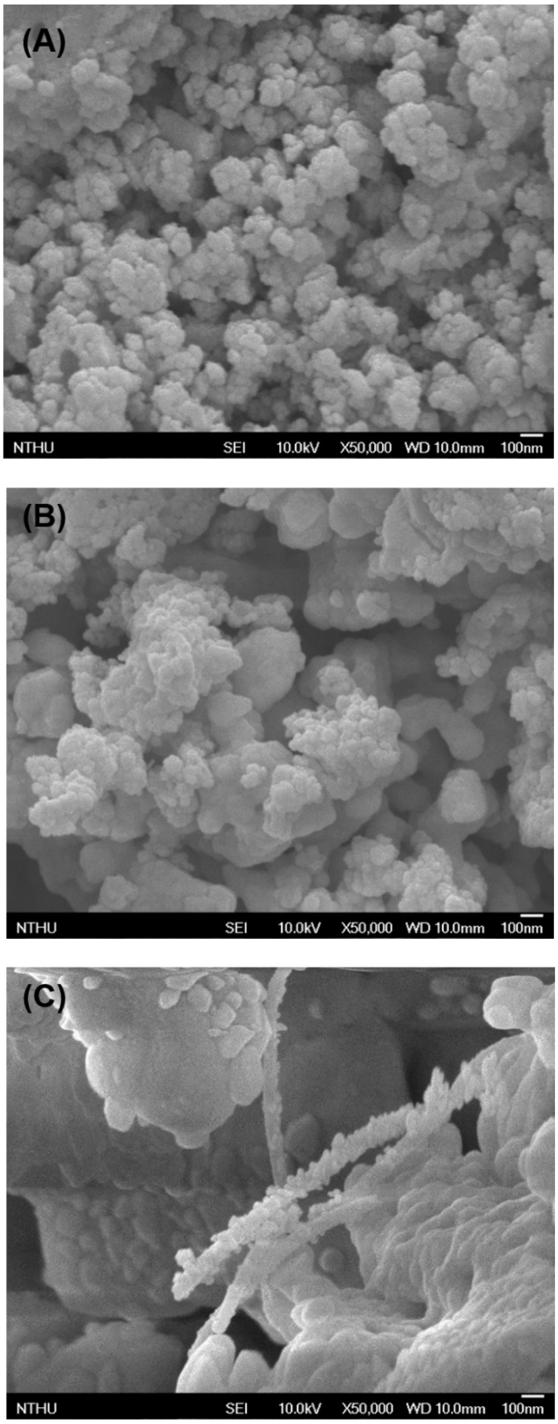



**Figure S13.** SEM for MLCRO03/$Al_2O_3$, T = 350$^{o}$C, $H_2O$/ethanol = 3, GHSV = 1.6 x $10^5$ $h^{-1}$ condition (A) Fresh; (B) after 48 hours; (C) after 350 hours long-term stability test.

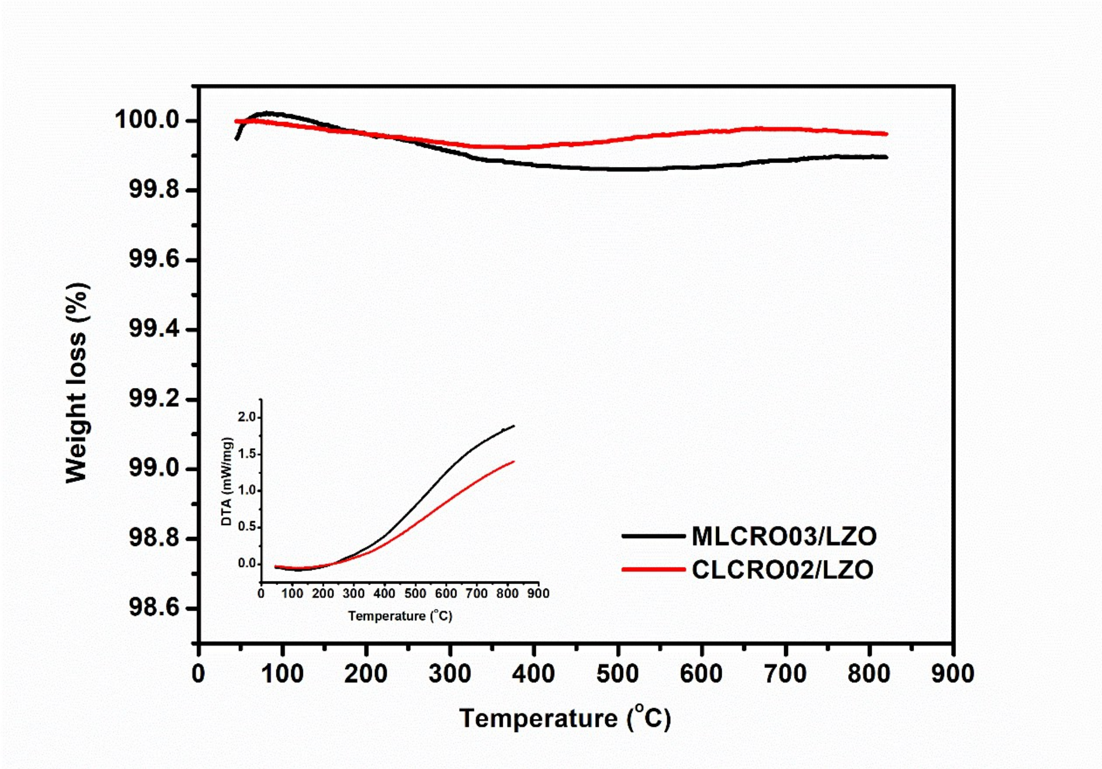



**Figure S14.** TGA and DSC profiles of ATR on LZO catalysts after long-term reaction.

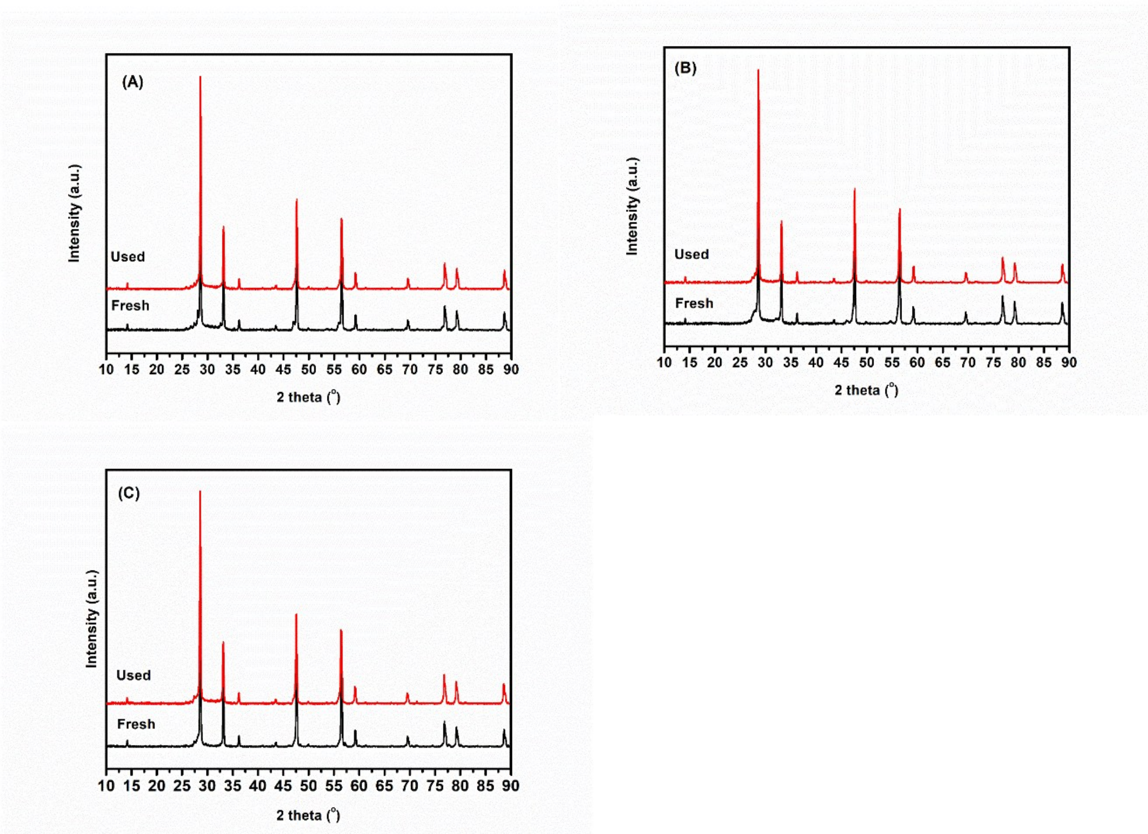



**Figure S15.** Powder X-ray diffraction of (a) LCRO/LZO, (b) MLCRO03/LZO, and (C) CLCRO02/LZO before and after long-term stability test (OSR, $H_2O$/ethanol = 3, GHSV = $1.6 \times 10^5$ $h^{-1}$, T = 400$^oC$).

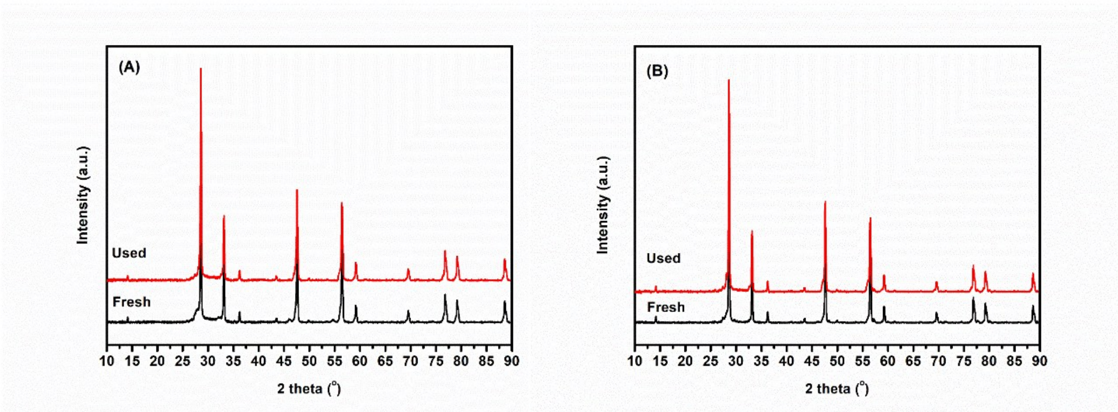



**Figure S16.** Powder X-ray diffraction of (A) MLCRO03/LZO and (B) CLCRO02/LZO before and after long-term stability test (ATR, $H_2O$/ethanol = 3, GHSV = 1.6 x $10^5$ $h^{-1}$).

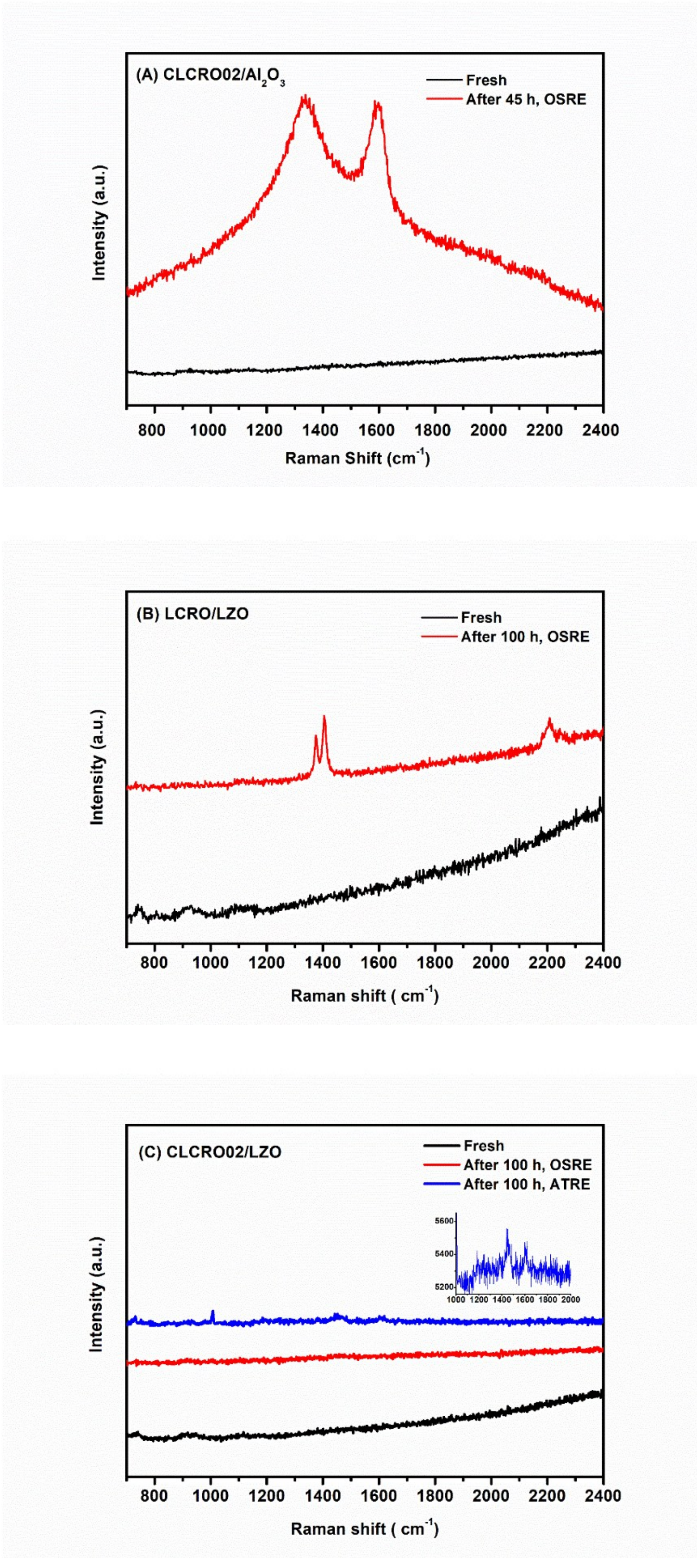
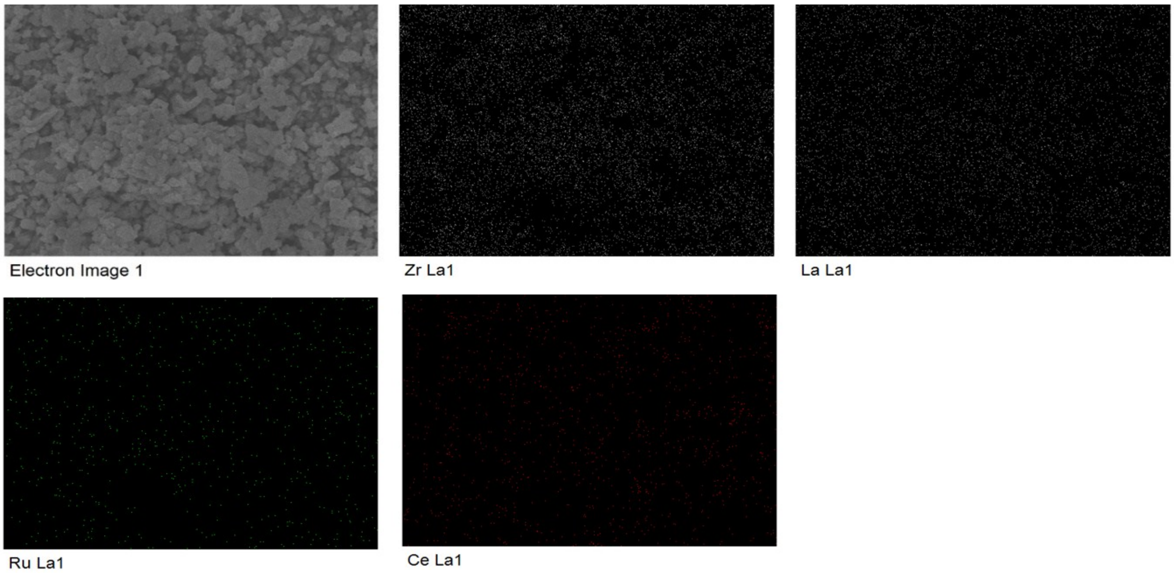



**Figure S17.** The Raman spectrum of fresh and long-termed used catalysts (A) CLCRO02/$Al_2O_3$, (B) LCRO/LZO, (C) CLCRO02/LZO.

(A) LCRO/LZO Fresh




(B) LCRO/LZO Used

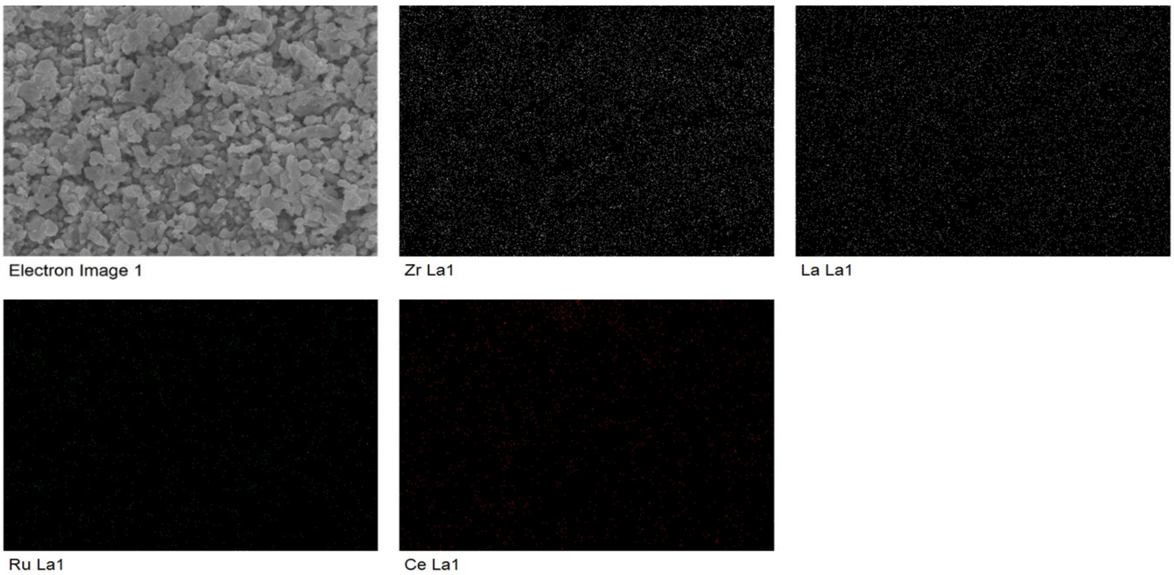
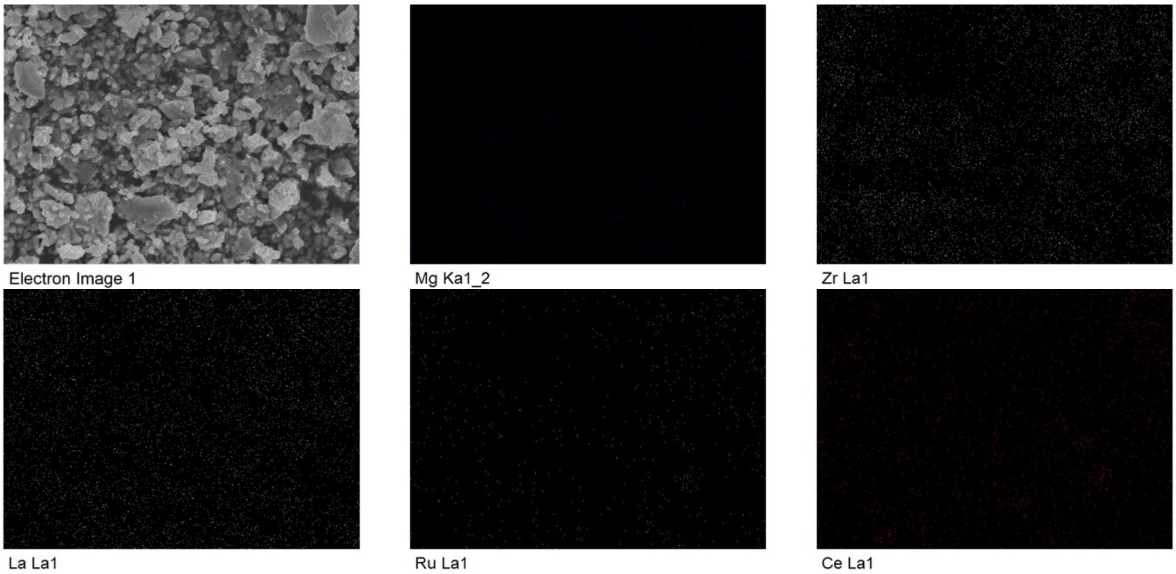



**Figure S18.** SEM and EDX of (A) fresh and (B) used catalyst LCRO/LZO for long-term used in OSRE.

(A) MLCRO03/LZO Fresh




(B) MLCRO03/LZO Used

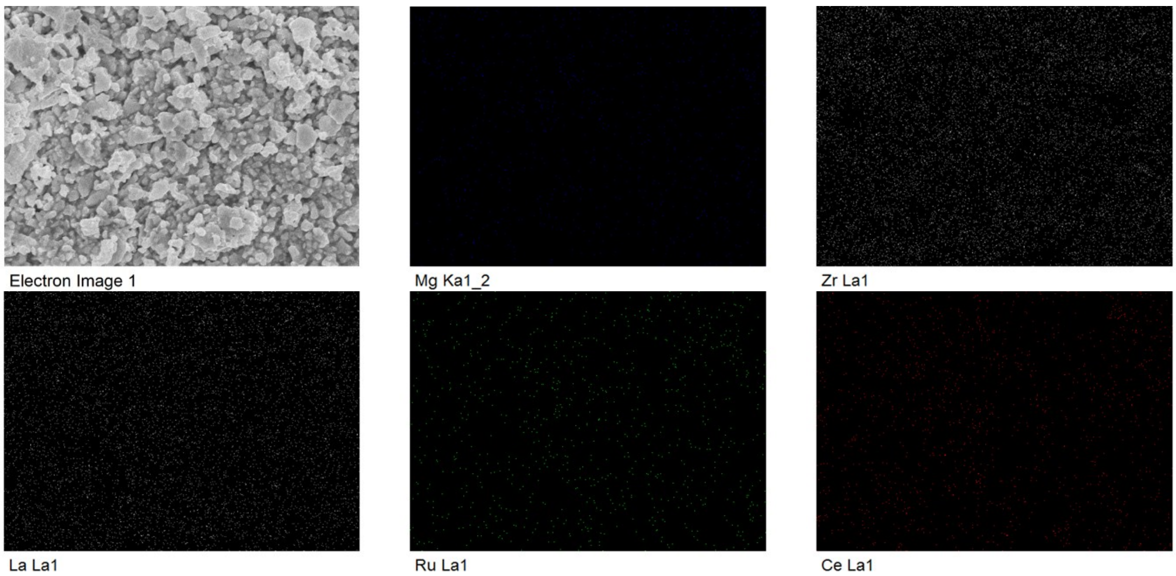
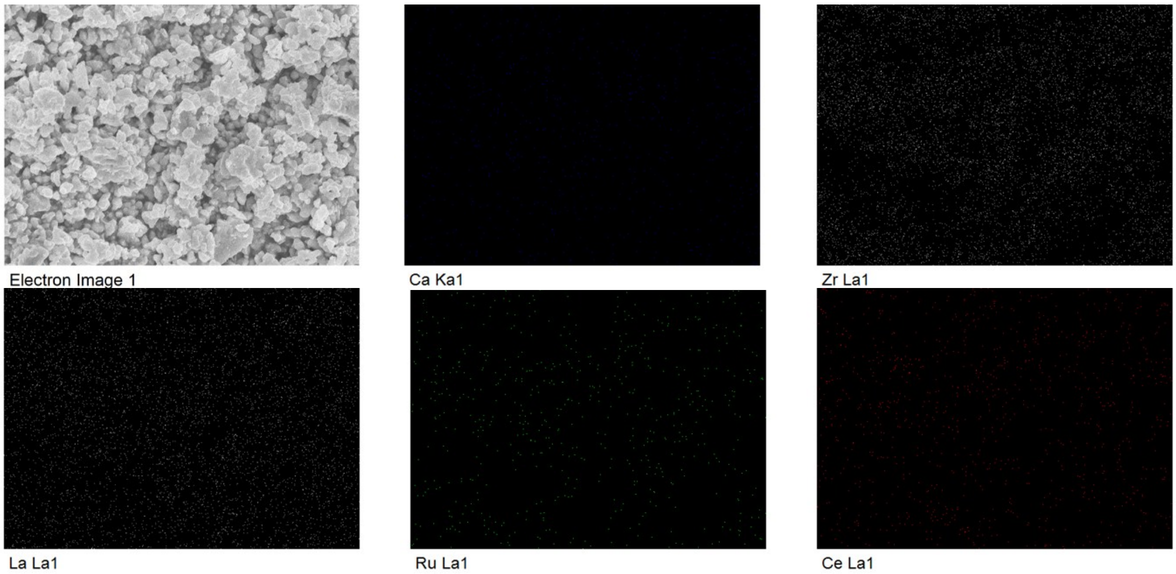



**Figure S19.** SEM and EDX of (A) fresh and (B) used catalyst MLCRO03/LZO for long-term used in OSRE.

(A) CLCRO02/LZO Fresh

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(B) CLCRO02/LZO Used

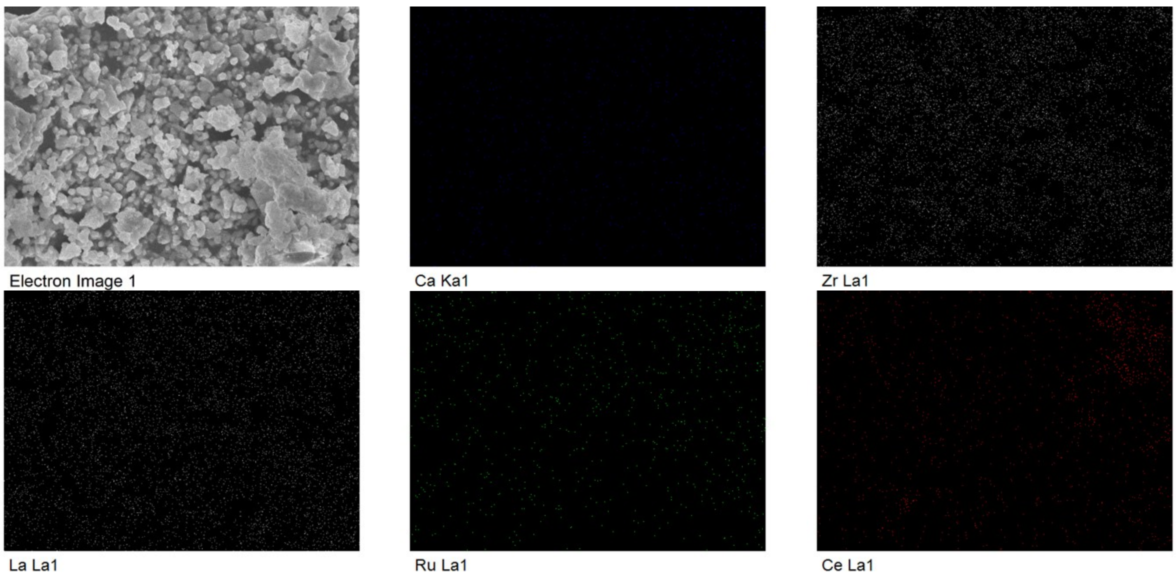
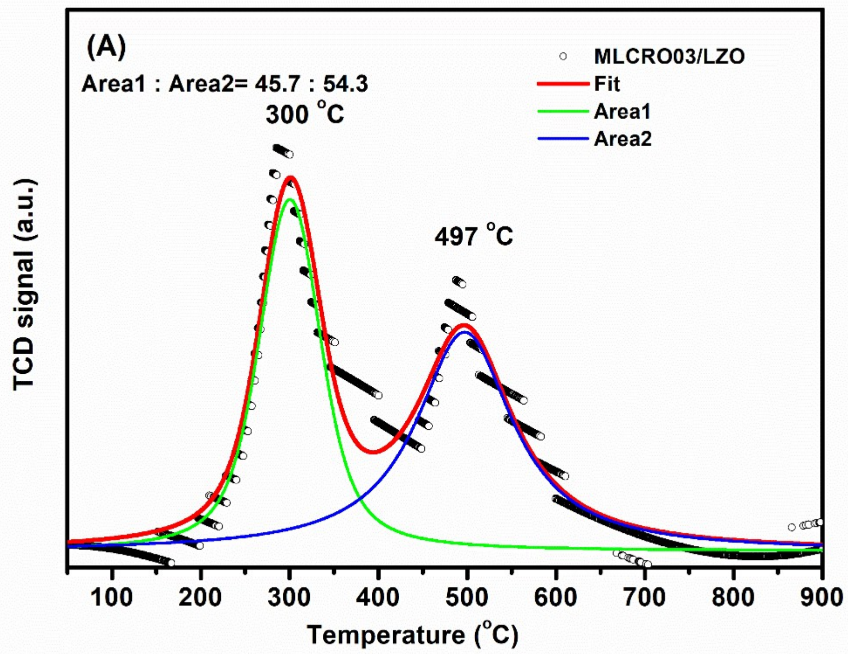



**Figure S20.** SEM and EDX of (A) fresh and (B) used catalyst CLCRO02/LZO for long-term used in OSRE.



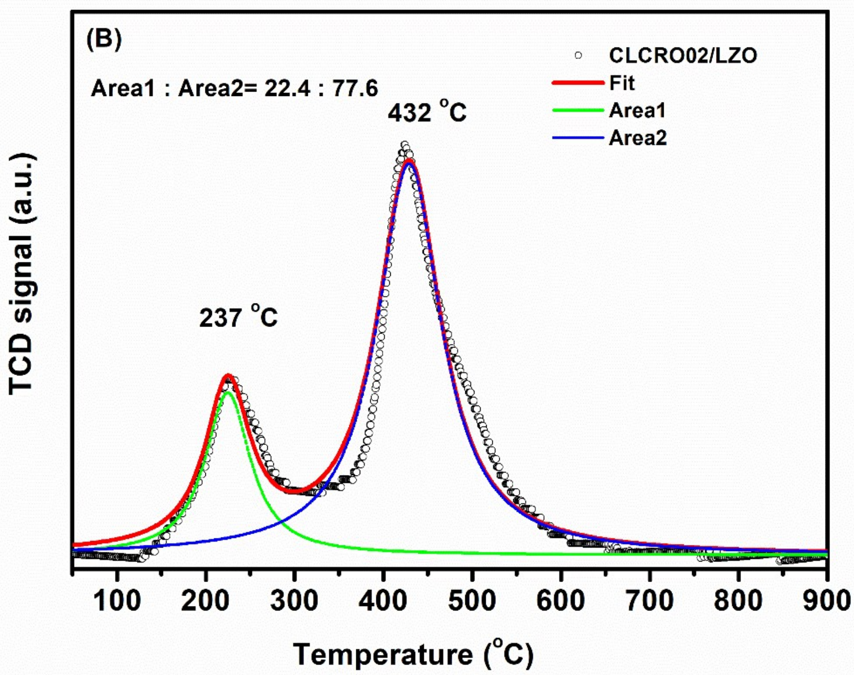
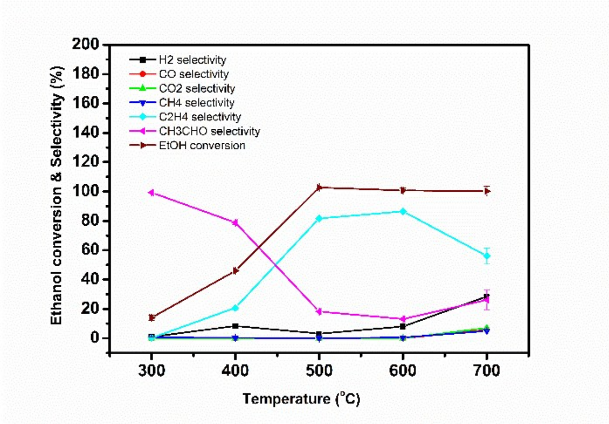
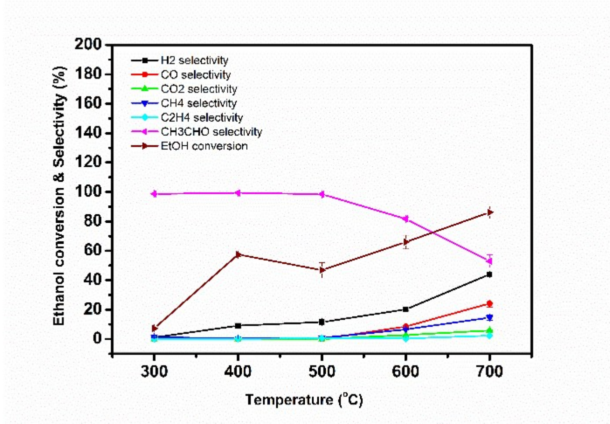



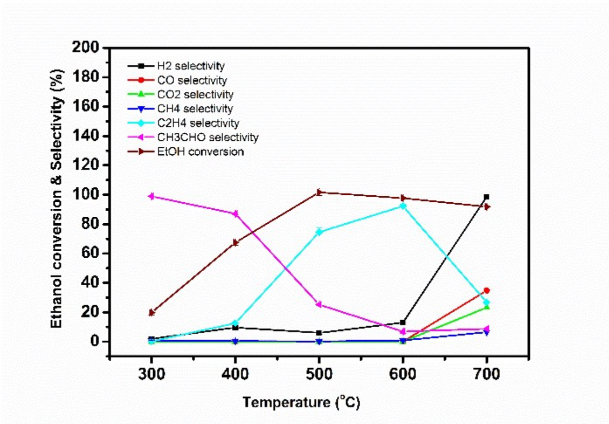

**Figure S21.** Temperature programmed reduction profile of (A) MLCRO03/LZO and (B) CLCRO02/LZO



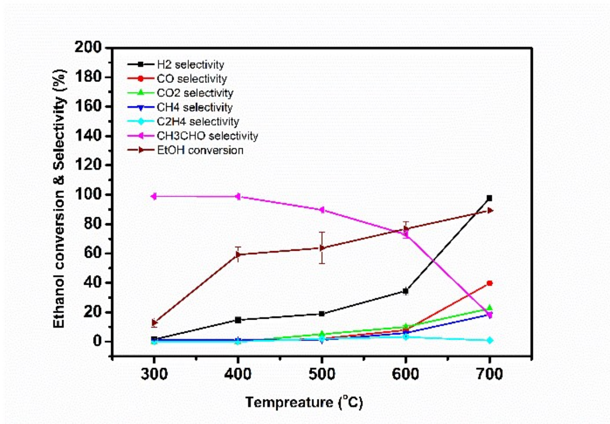

(A)




(B)




(C)




(D)

**Figure S22.** Ethanol conversion on non-oxidative condition ($P(O_2)$ = 0, S/E=3, GHSV=16,000 $h^{-1}$) with catalysts of (A) MLCRO03/$Al_2O_3$, (B) MLCRO03/LZO, (C) CLCRO02/$Al_2O_3$ and (D) CLCRO02/LZO.

**Table S1.** Powder diffraction of $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca) as obtained from Rietveld Refinement of synchrotron diffraction data.

| x | LCRO | MLCRO03 | CLCRO02 |
|---|---|---|---|
| $R_{wp}$ (%) | 5.96 | 6.94 | 9.78 |
| $R_p$ (%) | 4.89 | 5.55 | 8.42 |
| a (Å) | 11.14(1) | 11.11(2) | 11.15(1) |
| *x*(O48f) | 0.367(2) | 0.392(2) | 0.384(3) |
| B-O48f (Å) | 2.36(1) | 2.52(2) | 2.47(2) |
| A-O8b (Å) | 2.412(1) | 2.407(3) | 2.414(2) |
| A-O48f (Å) | 2.46(1) | 2.30(1) | 2.36(2) |
| B-O48f-B (°) | 113.0(12) | 102.3(10) | 105.7(13) |
| A-O48f-A (°) | 111.1(5) | 117.4(12) | 113.4(14) |
| O48f-B-O48f (°) | 107.6(7) | 112.8(4) | 111.3(6) |
| B-48f-A (°) | 109.3(1) | 109.0(1) | 109.3(1) |

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(a) LCRO

| Atom | Site | x | y | z | Occupancy | 100*$U_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|---|
| La | 16*d* | 0.5 | 0.5 | 0.5 | 0.9 | 2.53(2) |
| Ce | 16*c* | 0.0 | 0.0 | 0.0 | 0.9 | 2.53(2) |
| Ru | 16*c* | 0.0 | 0.0 | 0.0 | 0.1 | 2.53(2) |
| O2 | 8*b* | 0.375 | 0.375 | 0.375 | 1.01(2) | 5.3(4) |
| O3 | 48*f* | 0.367(2) | 0.125 | 0.125 | 1.01(2) | 5.3(4) |

(b) MLCRO03

| Atom | Site | x | y | z | Occupancy | 100*$U_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|---|
| La | 16*d* | 0.5 | 0.5 | 0.5 | 0.9 | 2.19(3) |
| Mg | 16*d* | 0.5 | 0.5 | 0.5 | 0.1 | 2.19(3) |
| Ce | 16*c* | 0.0 | 0.0 | 0.0 | 0.9 | 2.19(3) |
| Ru | 16*c* | 0.0 | 0.0 | 0.0 | 0.1 | 2.19(3) |
| O2 | 8*b* | 0.375 | 0.375 | 0.375 | 0.96(2) | 5.5(6) |
| O3 | 48*f* | 0.392(2) | 0.125 | 0.125 | 0.96(2) | 5.5(6) |

(c) CLCRO02

| Atom | Site | x | y | z | Occupancy | 100*$U_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|---|
| La | 16*d* | 0.5 | 0.5 | 0.5 | 0.9 | 2.18(4) |
| Ca | 16*d* | 0.5 | 0.5 | 0.5 | 0.1 | 2.18(4) |
| Ce | 16*c* | 0.0 | 0.0 | 0.0 | 0.9 | 2.18(4) |
| Ru | 16*c* | 0.0 | 0.0 | 0.0 | 0.1 | 2.18(4) |
| O2 | 8*b* | 0.375 | 0.375 | 0.375 | 1.00(2) | 4.6(5) |
| O3 | 48*f* | 0.384(3) | 0.125 | 0.125 | 1.00(2) | 4.6(5) |

**Table S2** Assignments of Ce3*d* XPS lines and calculations of $Ce^{4+}/Ce^{3+}$ of $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca)

$Mg_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$

| $Ce^{4+}/Ce^{3+}$ contribution | Peak | x = 0.0 | | x = 0.1 | | x = 0.2 | | x = 0.3 | |
|---|---|---|---|---|---|---|---|---|---|
| | | Position (eV) | Area | Position (eV) | Area | Position (eV) | Area | Position (eV) | Area |
| IV | V | 882.0 | 8516 | 881.8 | 7822 | 881.9 | 8603 | 881.8 | 8176 |
| III | V' | 885.0 | 2150 | 885.0 | 2139 | 884.9 | 2352 | 885.0 | 2368 |
| IV | V'' | 888.2 | 6826 | 888.0 | 6941 | 888.0 | 6329 | 888.0 | 6149 |
| IV | V''' | 897.5 | 8393 | 897.4 | 7656 | 897.5 | 7241 | 897.5 | 7749 |
| IV | U | 900.5 | 5489 | 900.3 | 5377 | 900.5 | 5173 | 900.4 | 4694 |
| III | U' | 904.8 | 2406 | 904.6 | 1862 | 903.7 | 1845 | 903.9 | 1993 |
| IV | U'' | 907.9 | 3286 | 907.3 | 3441 | 907.4 | 3124 | 907.2 | 3045 |
| IV | U''' | 915.8 | 6539 | 915.9 | 5758 | 915.9 | 5422 | 915.9 | 5785 |
| | $[Ce^{3+}]$ | ***10.45%*** | | ***9.76%*** | | ***10.47%*** | | ***10.91%*** | |
| | $[Ce^{4+}]$ | ***89.55%*** | | ***90.24%*** | | ***89.53%*** | | ***89.09%*** | |

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$Ca_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$

| **Cerium contribution** | **Peak** | **x = 0.1** | | **x = 0.2** | |
|---|---|---|---|---|---|
| | | **Position (eV)** | **Area** | **Position (eV)** | **Area** |
| **IV** | **V** | 881.9 | 8994 | 882.0 | 7898 |
| **III** | **V'** | 885.4 | 4167 | 885.0 | 2785 |
| **IV** | **V''** | 888.5 | 5714 | 888.1 | 5862 |
| **IV** | **V'''** | 897.6 | 7140 | 897.6 | 7128 |
| **IV** | **U** | 900.4 | 5775 | 900.3 | 4862 |
| **III** | **U'** | 903.4 | 2045 | 902.6 | 2162 |
| **IV** | **U''** | 907.0 | 3564 | 906.6 | 4145 |
| **IV** | **U'''** | 916.0 | 5898 | 916.1 | 6078 |
| | **[$Ce^{3+}$]** | ***14.35%*** | | ***12.09%*** | |
| | **[$Ce^{4+}$]** | ***85.65%*** | | ***87.91%*** | |

**Table S3.** Assignments of Ru3*d* XPS lines of $M_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$ (M = Mg, Ca)

$Mg_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$

| | Ru3d3/2 | | C1s | | Ru3d5/2 | |
|---|---|---|---|---|---|---|
| **$Mg^{2+}$ dopant (x)** | **BE (eV)** | **Area (a.u.)** | **BE (eV)** | **Area (a.u.)** | **BE (eV)** | **Area (a.u.)** |
| **0.0** | 286.5<br>287.8 | 1316<br>384 | 284.8 | 2845 | 282.4<br>283.7 | 856<br>656 |
| **0.1** | 286.2<br>287.9 | 967<br>556 | 284.8 | 3139 | 281.9<br>283.3 | 951<br>480 |
| **0.2** | 286.3<br>288.1 | 1066<br>689 | 284.8 | 3243 | 281.7<br>283.4 | 1247<br>663 |
| **0.3** | 286.1<br>287.4 | 1250<br>833 | 284.8 | 2793 | 281.8<br>283.6 | 1052<br>711 |

$Ca_xLa_{2-x}Ce_{1.8}Ru_{0.2}O_{7-\delta}$

| | Ru3d3/2 | | C1s | | Ru3d5/2 | |
|---|---|---|---|---|---|---|
| **$Ca^{2+}$ dopant (x)** | **BE (eV)** | **Area (a.u.)** | **BE (eV)** | **Area (a.u.)** | **BE (eV)** | **Area (a.u.)** |
| **0.1** | 286.2<br>287.9 | 967<br>556 | 284.8 | 3139 | 281.9<br>283.3 | 951<br>480 |
| **0.2** | 286.3<br>288.1 | 1066<br>689 | 284.8 | 3243 | 281.7<br>283.4 | 1247<br>663 |

**Table S4.** The first derivatives of the Ru K-edge XANES spectrum of LCRO, MLCRO03, and CLCRO02 catalysts with reference compounds $RuO_2$.

| Sample | LCRO | MLCRO03 | CLCRO02 | $RuO_2$ |
|---|---|---|---|---|
| Deriv $\mu$(E)/e.V | 22129.73 | 22129.86 | 22129.73 | 22128.57 |

**Table S5.** Review of catalysts tested for hydrogen production from OSRE/SRE.

| Catalyst | T (°C) | $C_2H_5OH/O_2/H_2O$ | $X_{EtOH}$(%) | $H_2$ yield (%) | Ref |
|---|---|---|---|---|---|
| $Ir/CeO_2$ | 550 | 1/0.6/1.8 | 100 | 55[b] | 1 |
| $Ir/CeO_2$ | 650 | 1/0.6/1.8 | 100 | 65[b] | 2 |
| $Rh/CeO_2/Al_2O_3$ | 700[a] (ATR) | 1/1.17/3 | 100 | 68 | 3 |
| $Ru/Ce_{1-x}M_xO_2$ | 700[a] (ATR) | 1/1.17/3 | 100 | 65 | 4 |
| $Rh/CeO_2$ | 800 [a] (ATR) | 1/1.17/3 | 100 | 69 | 5 |
| $Pt/CeZrO_2$ | 500 | 1/0.5/2 | 90 | 55[b] | 6 |
| $CeNiH_zO_y$ | 280 [a] (ATR) | 1/1.6/3 | 100 | 45[b] | 7 |
| $NiAl_2O_4$-$FeAl_2O_4$ | 600 | 1/0.5/3 | 100 | 65 | 8 |
| $LaNiO_3$ | 500 | 1/0.5/3 | 60 | 60[b] | 9 |
| $Ni/La_2O_3$ | 500 | 1/0.5/3 | 100 | 55[b] | 9 |
| $Ni/CeO_2$ | 650 | 1/0.8/8.8 | 75 | 80[c] | 10 |
| Ni/MgO | 650 | 1/0.8/8.8 | 75 | 85[c] | 10 |
| $Co/CeO_2$ | 500 | 1/0.5/3 | 100 | 58[b] | 11 |
| $La_{0.9}Ce_{0.1}NiO_3$ | 500 | 1/0.5/3 | 100 | 50[b] | 12 |
| $La_{1-x}Ca_xFe_{1-x}Co_xO_3$ | 650 | 1/0.5/0.33 | 100 | 68[b] | 13 |
| $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ | 600 | 1/0.5/3 | 100 | 70[b] | 14 |
| $La_2Ce_{1.55}Ni_{0.45}O_7/Al_2O_3$ | 500 | 1/1.17/3 | 100 | 53 | 15 |
| $5\%Ru/CeO_2/Al_2O_3$ | 400 | 1/1.17/3 | 96 | 57 | 16 |
| $5\%Ru/La_2Ce_2O_7/Al_2O_3$ | 400 | 1/1.17/3 | 97 | 56 | 16 |
| $La_2Ce_{1.8}Ru_{0.2}O_7/Al_2O_3$ | 400 | 1/1.17/3 | 100 | 60 | 16 |
| $Li_{0.6}La_{1.4}Ce_{1.8}Ru_{0.2}O_7/Al_2O_3$ | 350 | 1/1.17/3 | 100 | 62 | 17 |
| $Li_{0.6}La_{1.4}Ce_{1.8}Ru_{0.2}O_7$/LZO | 350 | 1/1.17/3 | 100 | 58 | 17 |
| $Li_{0.6}La_{1.4}Ce_{1.8}Ru_{0.2}O_7/ Al_2O_3$ | 372* (ATR) | 1/1.17/3 | 91 | 41 | 17 |
| $Li_{0.6}La_{1.4}Ce_{1.8}Ru_{0.2}O_7$/LZO | 380* (ATR) | 1/1.17/3 | 90 | 43 | 17 |
| $Mg_{0.3}La_{1.7}Ce_{1.8}Ru_{0.2}O_7/Al_2O_3$ | 350 | 1/1.17/3 | 100 | 61 | d |
| $Ca_{0.2}La_{1.8}Ce_{1.8}Ru_{0.2}O_7/Al_2O_3$ | 280 | 1/1.17/3 | 90 | 55 | d |
| $La_2Ce_{1.8}Ru_{0.2}O_7$/LZO | 400 | 1/1.17/3 | 100 | 54 | d |
| $Mg_{0.3}La_{1.7}Ce_{1.8}Ru_{0.2}O_7$/LZO | 400 | 1/1.17/3 | 100 | 54 | d |
| $Ca_{0.2}La_{1.8}Ce_{1.8}Ru_{0.2}O_7$/LZO | 400 | 1/1.17/3 | 100 | 54 | d |
| $Mg_{0.3}La_{1.7}Ce_{1.8}Ru_{0.2}O_7$/LZO | 425* (ATR) | 1/1.17/3 | 94 | 45 | d |
| $Ca_{0.2}La_{1.8}Ce_{1.8}Ru_{0.2}O_7$/LZO | 420* (ATR) | 1/1.17/3 | 100 | 49 | d |

[a] denote ATR experiments were monitored by a K-type thermocouple on the reaction tube;
[b] mole% ; [c] Selectivity(%); [d] this study

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