Electronic Supplementary Material (ESI) for Green Chemistry.


**SUPPORTING MATERIAL**

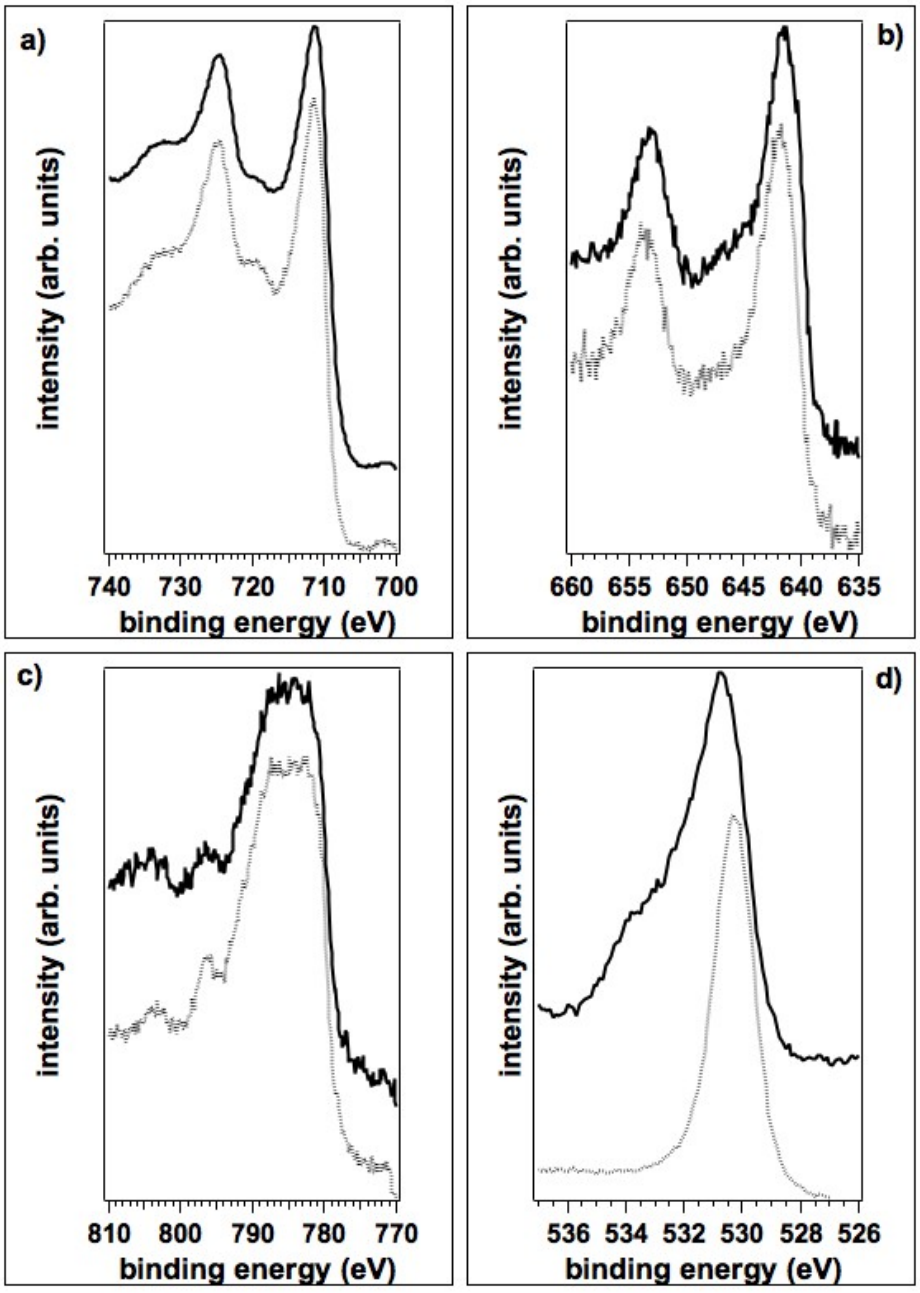


**Figure S1**: (a) Fe 2p,(b)Mn 2p,(c) Co 2p,(d) O1s photoemission spectra of $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ before (solid line) and after (dot line) annealing at 450°C for 30 minutes.

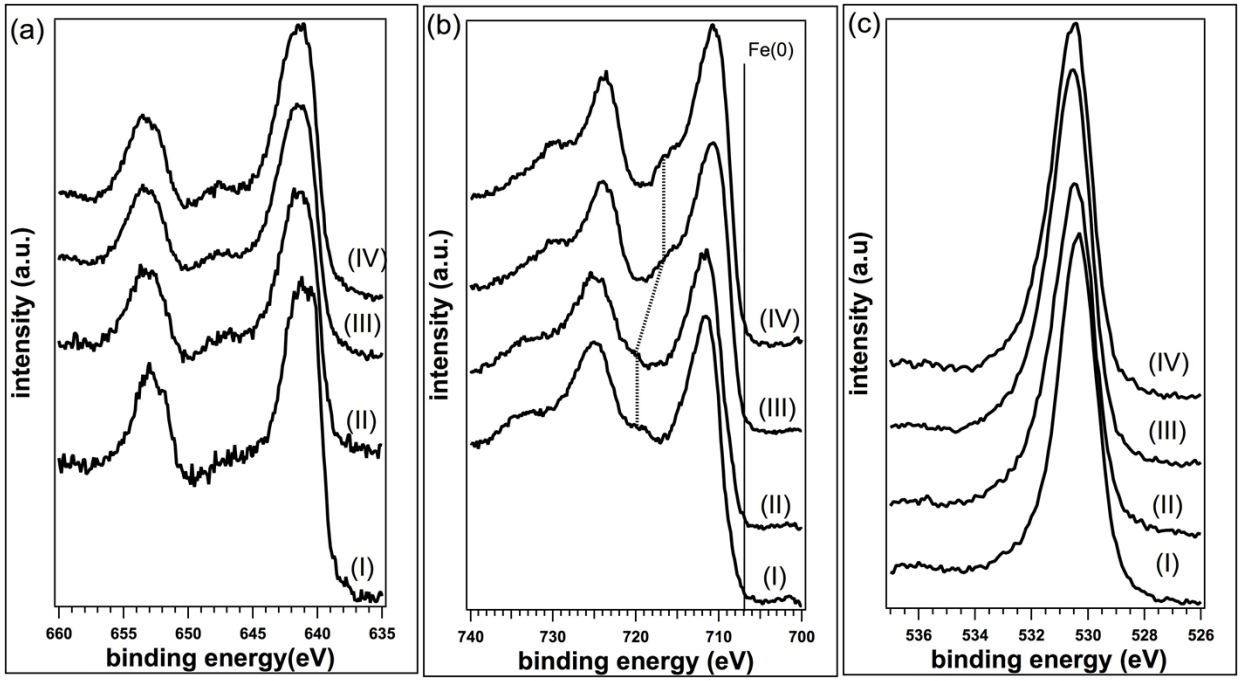


**Figure S2**: (a) Mn 2*p* (b) Fe 2*p* (c) O 1*s* photoemission peak of $Mn_{0.6}Fe_{2.4}O_y$ (i) after annealing at 450°C in UHV for 20 min, and after (II) 20 min, (III) 50, min (IV), 80 min ethanol exposure at 450°C. ($P_{Ethanol}$: $5x10^{-6}$ mbar). In (b) the dotted line shows the change in the position of the satellite of the Fe $2p_{3/2}$ line whereas the solid vertical line indicates the BE position of iron metal.

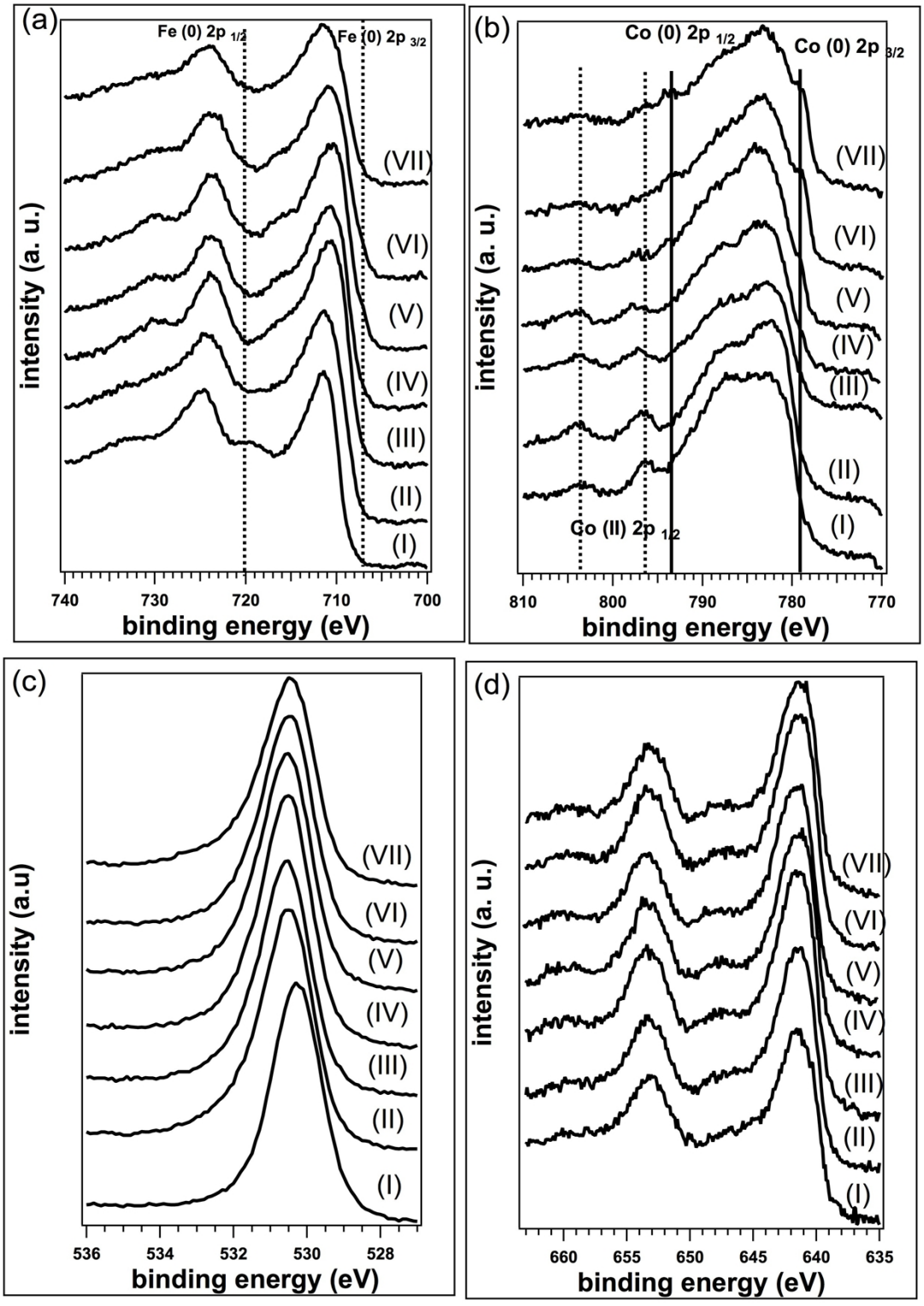


**Figure S3:**(a) Fe 2*p* (b) Co 2*p* (c) O 1*s*(d) Mn 2*p* photoemission peaks of $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (i) after annealing at 450°C in UHV for 20 min, and after (II) 20 min, (III) 50 min, (IV) 80 min,(V) 120 min ethanol exposure at 450°C ($P_{Ethanol}$: $5x10^{-6}$ mbar), and after (VI) 30 min and (VII) 60 min water exposure at 450°C ($P_{water}$: $2x10^{-4}$ mbar). In (a) the dotted vertical line indicates the BE position of iron metal, in (b) the BE position of metal component is shown by solid vertical lines, whereas the position of the Co(II) $2p_{1/2}$peak maximum position and its satellite are indicated by dotted lines.

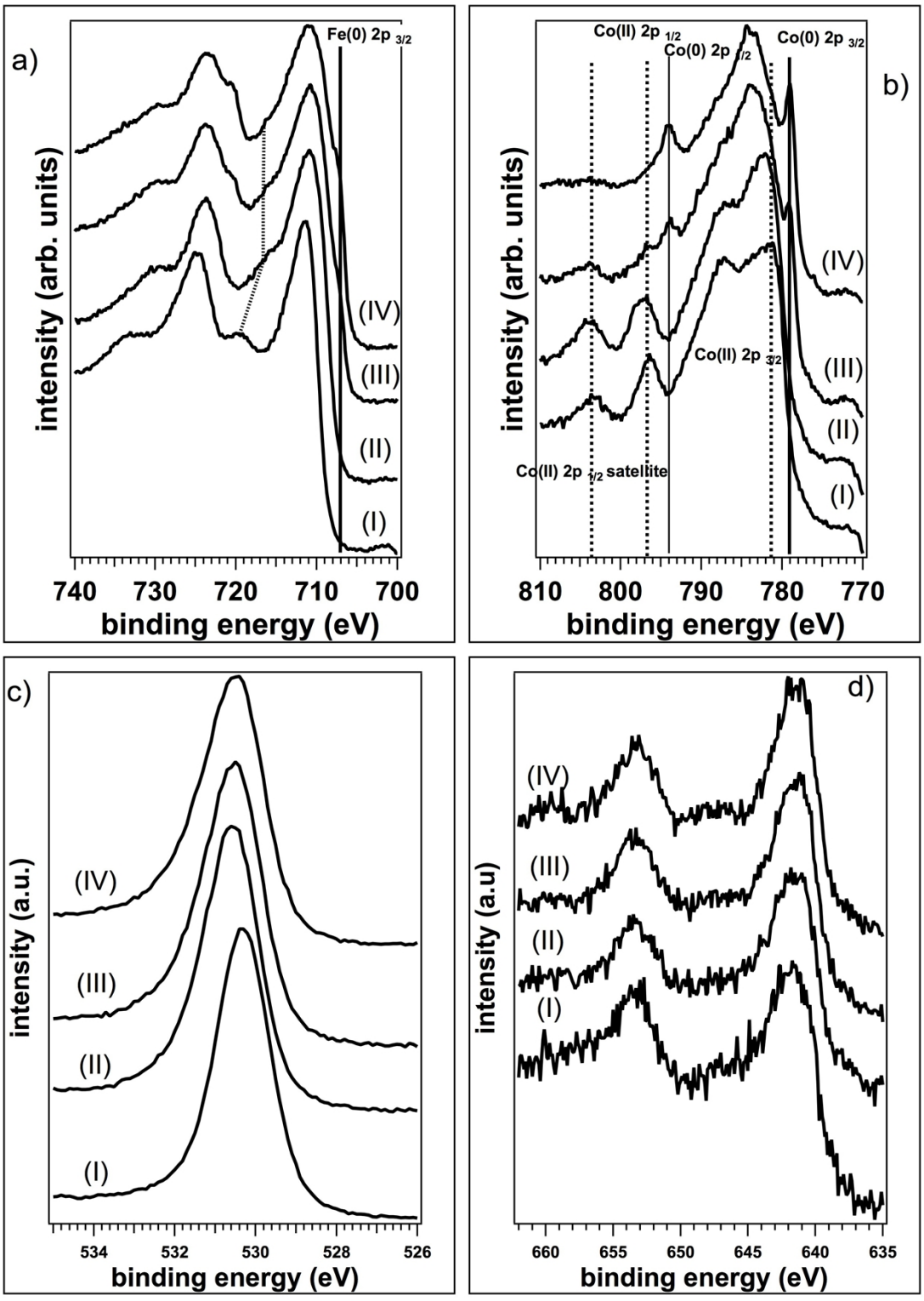


**Figure S4:**(a) Fe 2*p* (b) Co 2*p* (c) O 1*s*(d) Mn 2*p* photoemission peaks of $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (i) after annealing at 450°C in UHV for 20min, and after (II) 20 min, (III) 50 min (IV), 80 min ethanol exposure at 450°C ($P_{Ethanol}$: $5x10^{-6}$ mbar). In (a) the dotted vertical line indicates the BE position of iron metal and whereas the dotted line the shift of Fe $2p_{3/2}$ satellite peak, in (b) the BE position of metal component is shown by solid vertical lines, whereas the position of the Co(II) $2p_{1/2}$peak maximum position and its satellite are indicated by dotted lines.

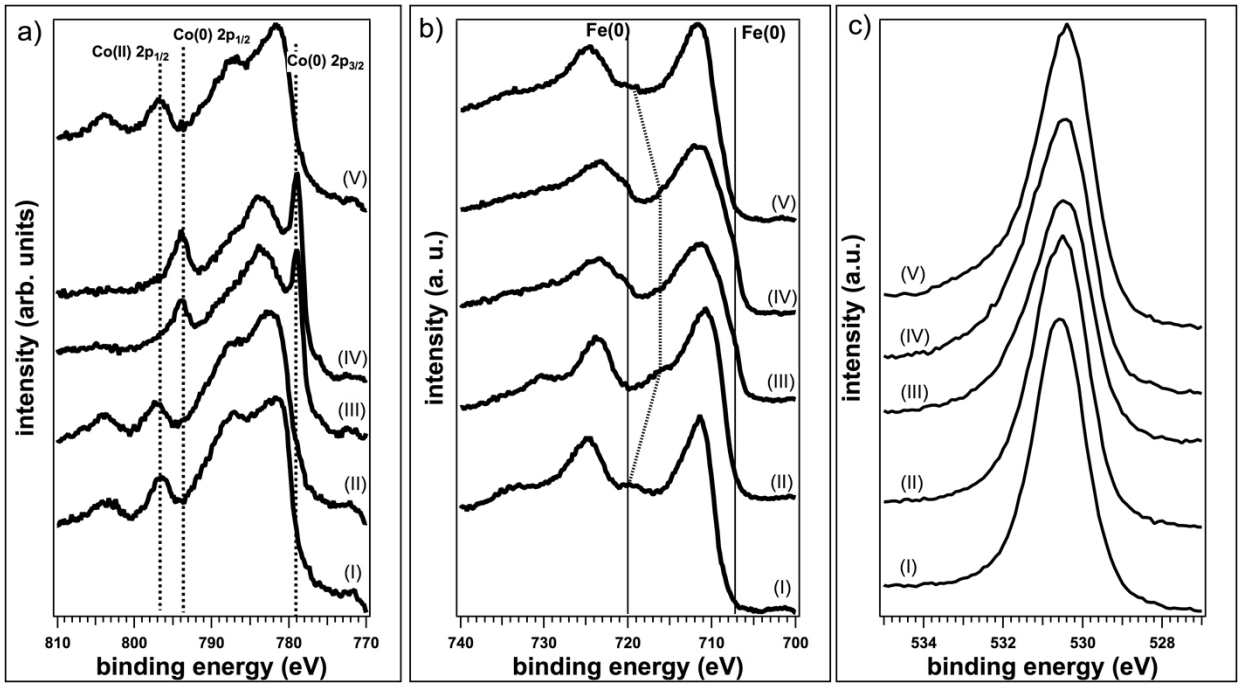


**Figure S5:**(a) Co 2*p* (b) Fe 2*p* (c) O 1*s* photoemission peaks of $Co_{0.6}Fe_{2.4}O_y$ (i) after annealing at 450°C in UHV for 20 min, and after (II) 20 min, (III) 50, min (IV), 80 min ethanol exposure at 450°C($P_{Ethanol}$: $5x10^{-6}$ mbar) and after (VI) 30 min water exposure at 450°C ($P_{water}$: $2x10^{-4}$ mbar).In (b) the dotted vertical line indicates the BE position of iron metal and whereas the dotted line the shift of Fe $2p_{3/2}$ satellite peak.

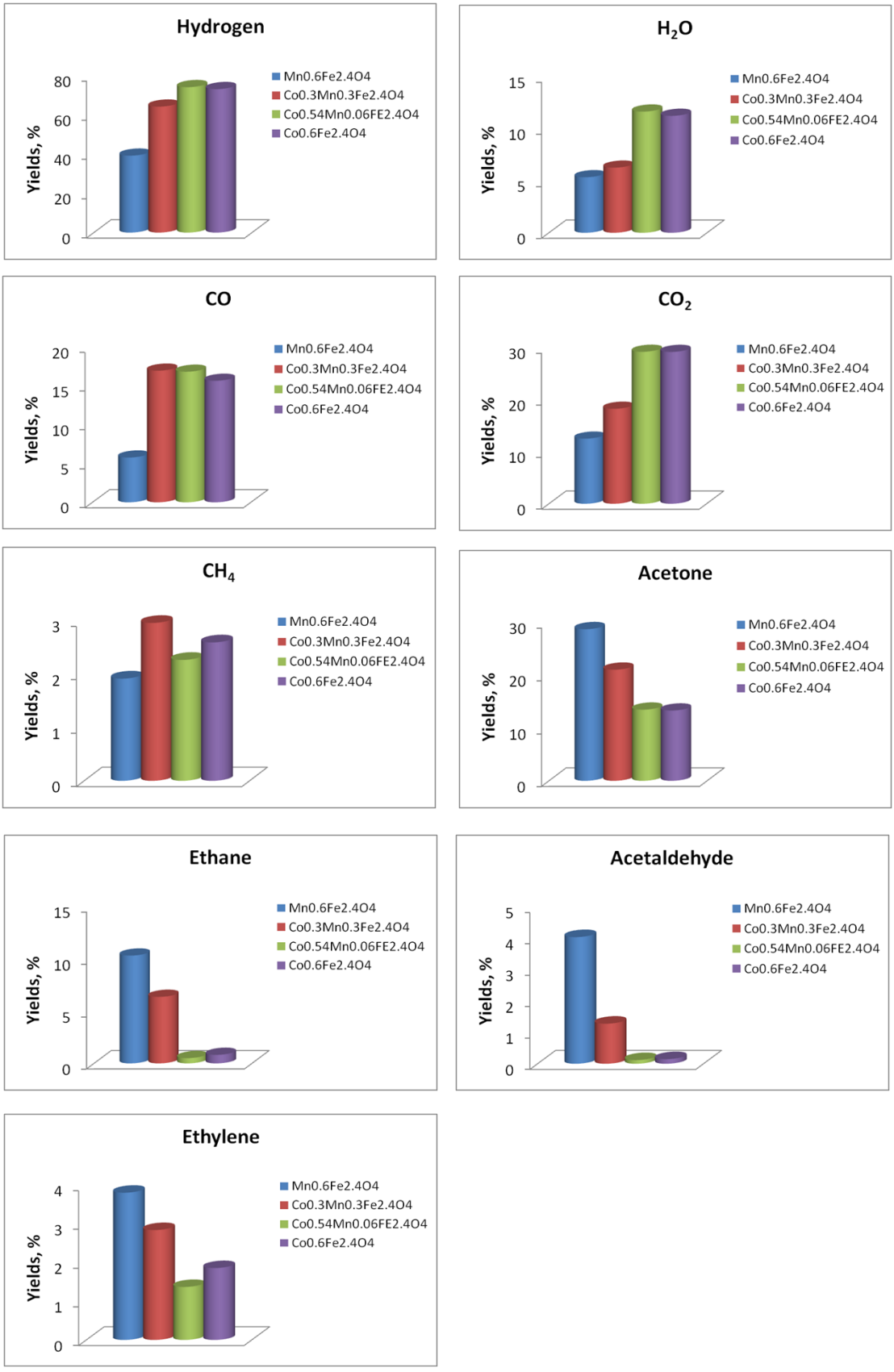


Figure S6. Integrated yields for some products obtained during 20 min reduction with ethanol.

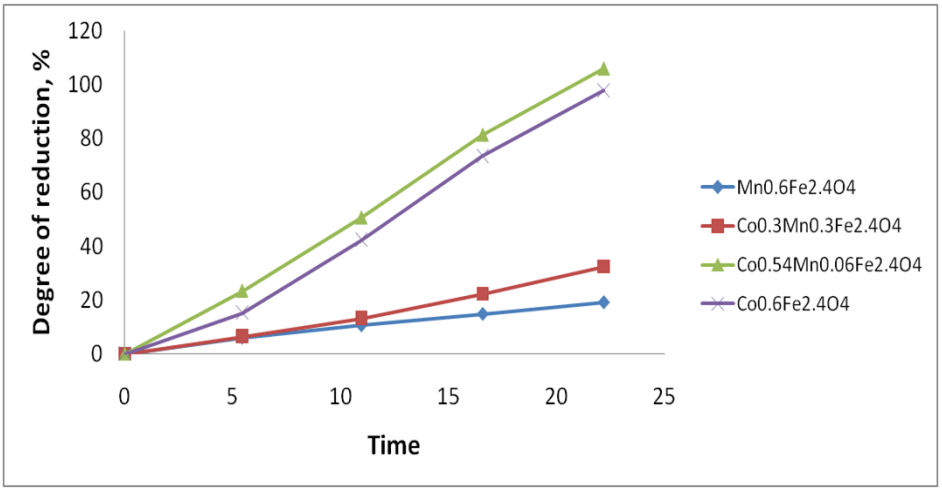


Figure S7. Degree of reduction of M-modified ferrospinels.

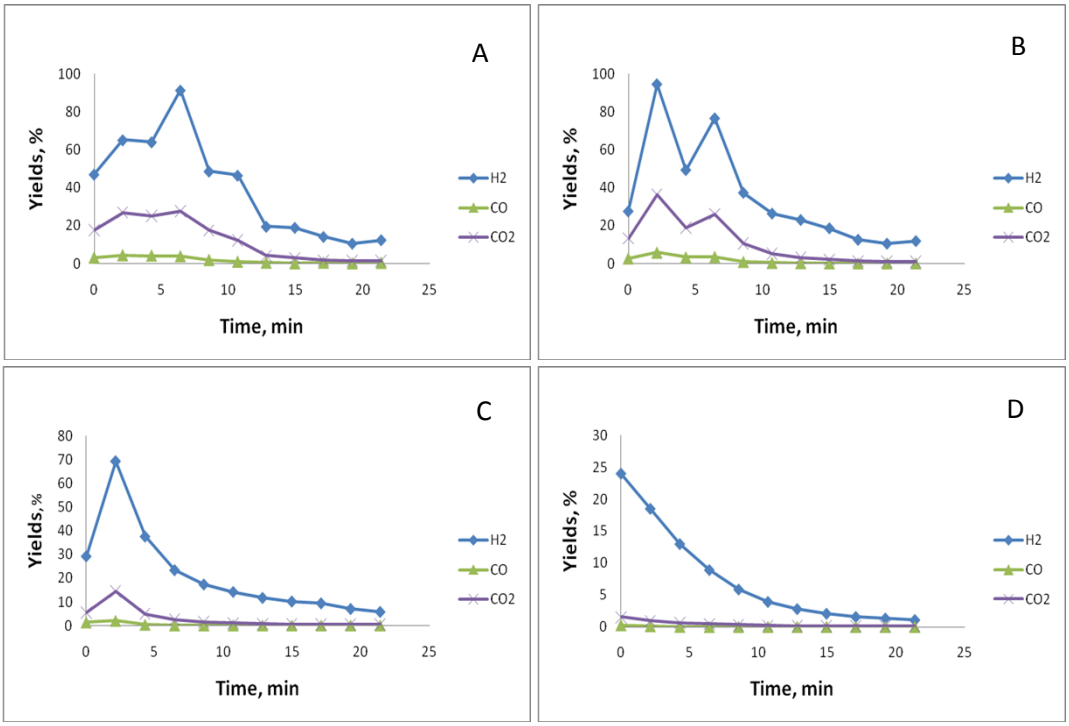


Figure S8. Yields obtained during 20 min of the re-oxidation with water at 450°C over: (A) $Co_{0.6}Fe_{2.4}O_y$; (B) $Co_{0.54}Mn_{0.06}Fe_{2.4}O_y$; (C) $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$; (D) $Mn_{0.6}Fe_{2.4}O_y$.

Table S1. $T_{max}$(°C) values pertaining to each reduction step of M-modified non-stoichiometric ferrospinels.[44–47]

| Sample name | $Fe_2O_3 \rightarrow Fe_3O_4$ | $Fe_3O_4 \rightarrow FeO$ | $FeO \rightarrow Fe$ | Other $M^{n+}$ |
|---|---|---|---|---|
| $CoFe_2O_4$ | 427 | 683 | 795 | $Co_3O_4 \rightarrow CoO \rightarrow 507$<br>$CoO \rightarrow Co \rightarrow 574$ |
| $Co_{0.6}Fe_{2.4}O_y$ | 400 | 690 | 780 | $Co_3O_4 \rightarrow CoO \rightarrow 502$<br>$CoO \rightarrow Co \rightarrow 576$ |
| $Co_{0.54}Mn_{0.06}Fe_{2.4}O_y$ | 412 | 703 | 797 | $Mn^{4+} \rightarrow Mn^{3+} \rightarrow 200$<br>$Mn3+ \rightarrow Mn^{2+} \rightarrow 559$<br>$Co_3O4 \rightarrow CoO \rightarrow 507$<br>$CoO \rightarrow Co \rightarrow 574$ |
| $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ | 402 | 704 | 800 | $Mn^{4+} \rightarrow Mn^{3+} \rightarrow 200$<br>$Mn^{3+} \rightarrow Mn^{2+} \rightarrow 560$<br>$Co_3O_4 \rightarrow CoO \rightarrow 518$<br>$CoO \rightarrow Co \rightarrow 613$ |
| $Mn_{0.6}Fe_{2.4}O_y$ | 380 | 616 | 845 | $Mn^{4+} \rightarrow Mn^{3+} \rightarrow 199$<br>$Mn^{3+} \rightarrow Mn^{2+} \rightarrow 525$ |