Supplementary materials: Cu-Mg-Fe-O-(Ce) complex oxides as catalysts of selective catalytic oxidation of ammonia to dinitrogen (NH_3-SCO)

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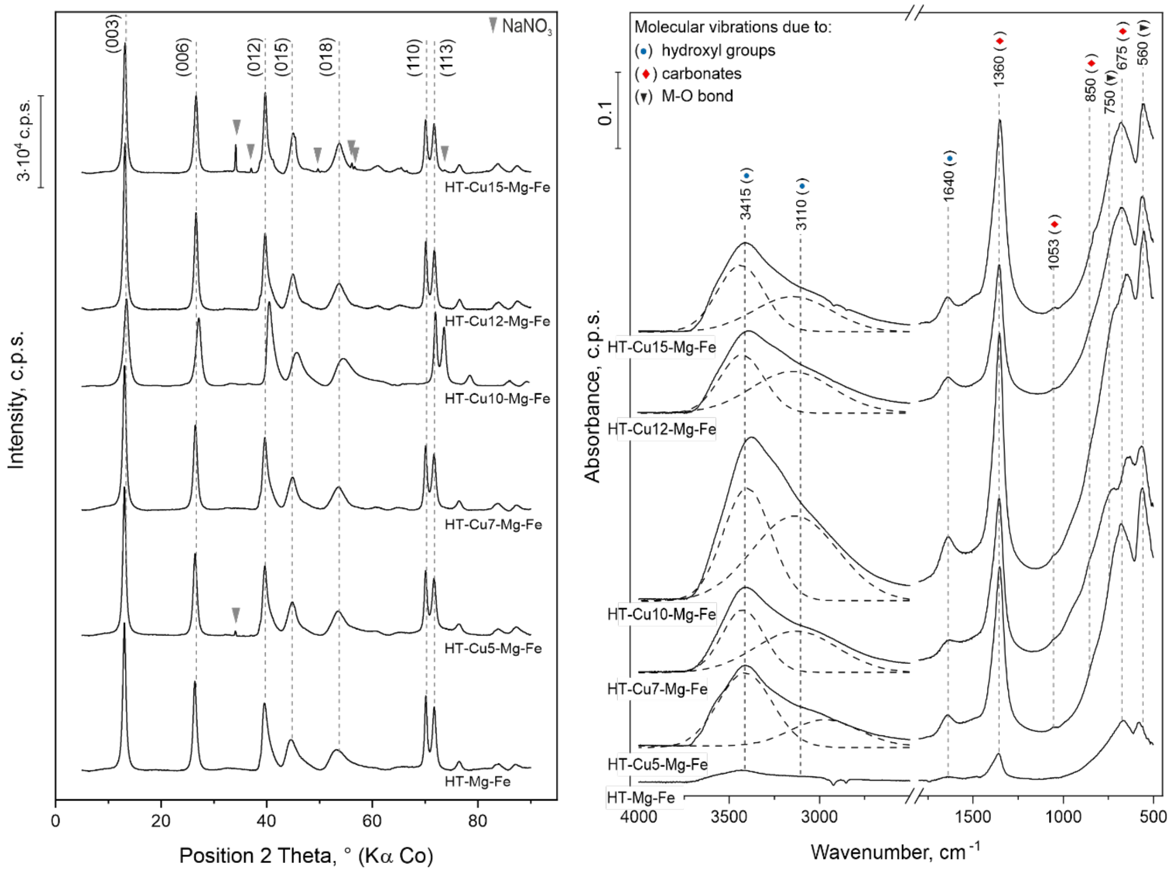
Characterisation of hydrotalcite-like materials

XRD results

Position of XRD patterns corresponds directly to the pyroaurite structure (ICCD pdf card: 01-089-5434). Pyroaurite ($Mg_6Fe_2CO_3(OH)_{16} \cdot 4H_2O$) belongs to the group of hydrotalcite-like materials and is characterized by the cell parameters a = 0.311 nm and c = 2.341 nm [28]. Calculated values of parameters a and c were the same for all synthesized materials (a = 0.311 nm and c = 2.320 nm), with exception of HT-Cu10-Mg-Fe (Table 1), confirming structural similarity of synthesized materials. Parameter a that corresponds to the average cation-cation distance in octahedral network of hydrotalcite, was calculated from the d-spacing of the (110) reflection ($a = 2d_{110}$). Parameter c that is related to thickness of the hydrotalcite layer and the interlayer space, was calculated from the d-spacing of the (003) and (006) reflection ($c = (3d_{(003)}+6d_{(006)})/2$). Shift of (110) and (113) position, noticeable for HT-Cu10-Mg-Fe, could be connected with non-stoichiometric precipitation during synthesis. It could cause not homogenous distribution of cations in hydrotalcite octahedral network and formation of cation aggregates. Parameter a calculated for HT-Cu10-Mg-Fe sample is 0.305 nm, what means that cations in octahedral network are closer packed in comparison to other samples. Analysis of diffractograms of HT-Cu15-Mg-Fe and HT-Cu5-Mg-Fe allow noticing additional patterns ascribed to $NaNO_3$ phase. Occurrence of $NaNO_3$ is related to post-synthesis impurities and do not influence formation of typical hydrotalcite structure.

FT-IR results

Frequency observed at 560 and 750 cm^{-1} could be ascribed to lattice vibrations and is related to transitional motions of the oxygen-metal bond in octahedral-layer network [29]. Other assigned frequencies could be ascribed to molecular vibrations of CO_3^{2-} and OH^-. Maxima at approx. 675 cm^{-1}, 850 cm^{-1}, 1053 cm^{-1} and 1360 cm^{-1} are related to the characteristic vibrations of interlayer carbonates at D_{3h} point group [29–31]. Frequencies represent bending angular (ν_4, E′), torsion mode (ν_2, A2′′), bending non-polar mode (ν_2, A_2''), anti-symmetric stretching C=O bond ($\nu 3$, E′), respectively. The most intensive maximum at approx. 1360 cm^{-1} is related to interaction between CO_3^{2-} and OH^- groups. Frequencies mode of water molecules are represented by maxima at approx. 1640 cm^{-1}, 3100 cm^{-1} and 3415 cm^{-1} that are related to (i) bending mode $\delta(A_1)$, (ii) H_2O-CO_3 bond at interlayer space and (iii) τH_2O stretching mode of metal-OH bond, respectively [29–31].



(**a**) (**b**)

Figure S1. Results of the characterization of HT-Cu-Fe samples (**a**) XRD phase analysis (**b**) infrared spectroscopy measurements.

Properties of the mixed metal oxides

Reducibility and redox properties

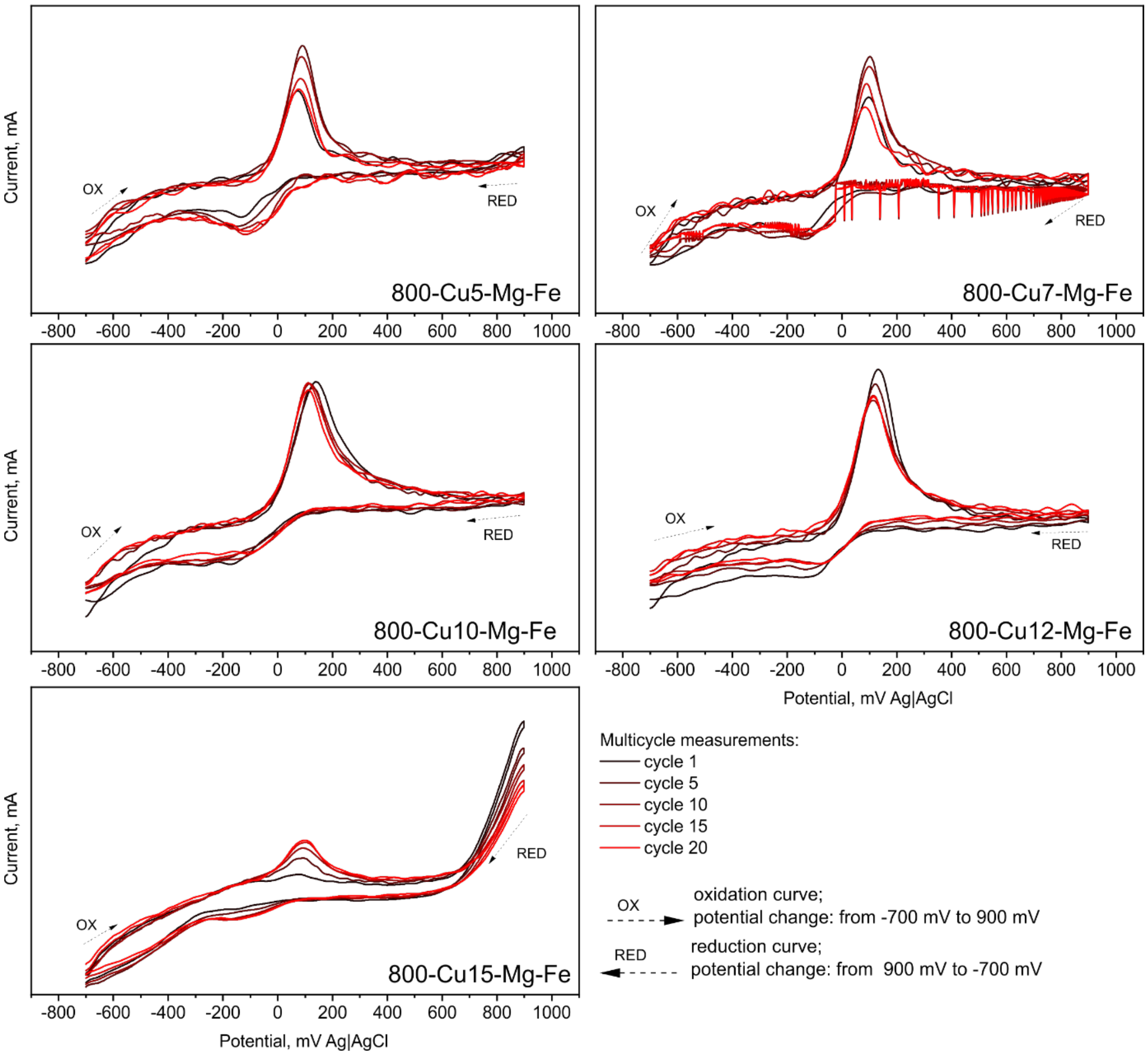


Figure S2. CV multi-cyclic curves registered vs Ag|AgCl electrode at potential window from -700 to 900 mV at acetate buffer (pH=4.6) for 800-Cu-Mg-Fe-O catalysts; OX – oxidation curve, RED – reduction curve; direction of potential change for OX and RED curves is described by arrows.

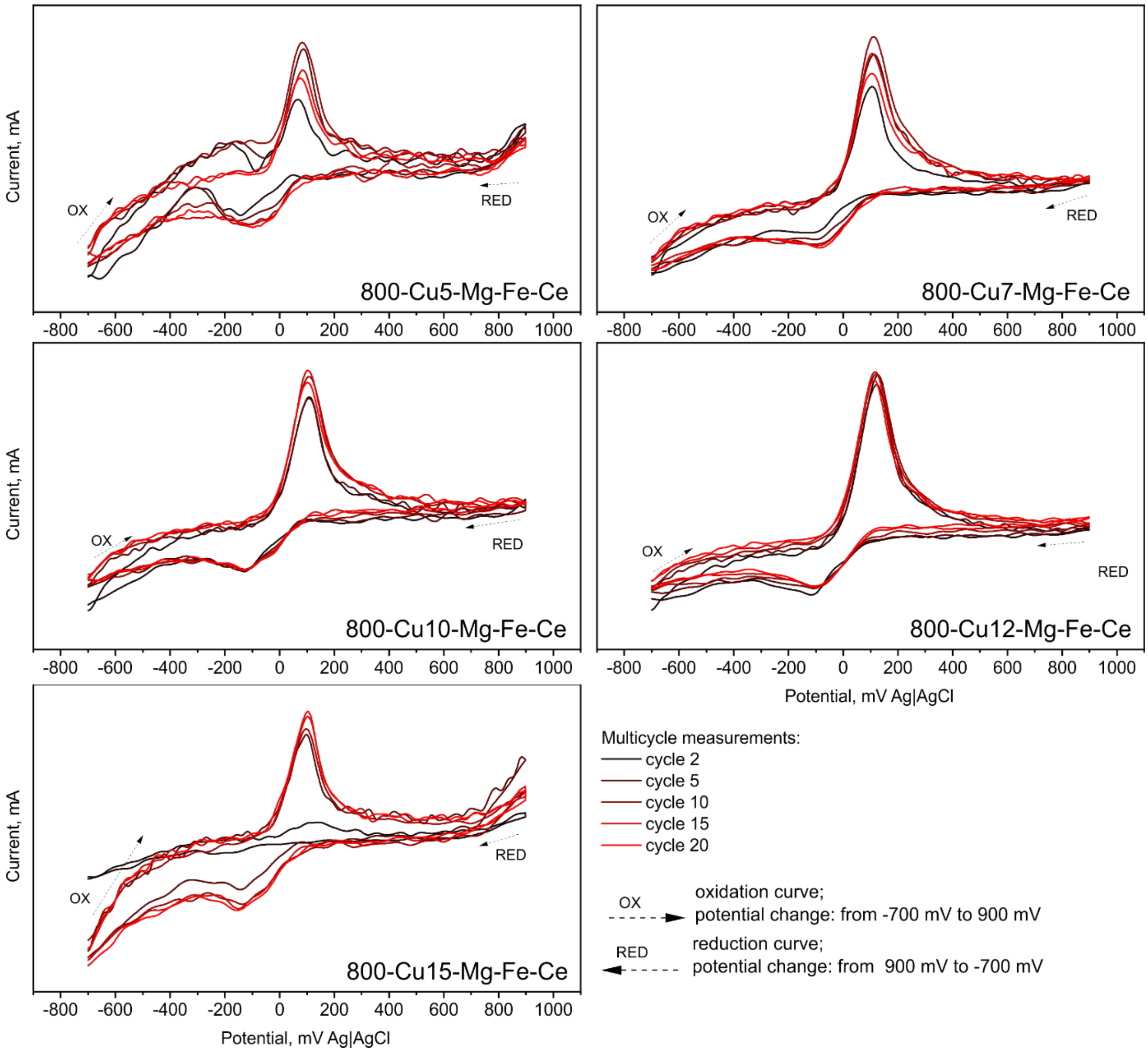


Figure S3. CV multi-cyclic curves registered vs Ag|AgCl electrode at potential window from -700 to 900 mV at acetate buffer (pH=4.6) for 800-Cu-Mg-Fe-O-Ce catalysts; OX – oxidation curve, RED – reduction curve; direction of potential change for OX and RED curves is described by arrows.