In-situ ATR-IR study of Layered Double Hydroxides as potential electrocatalysts for CO_2 reduction reaction

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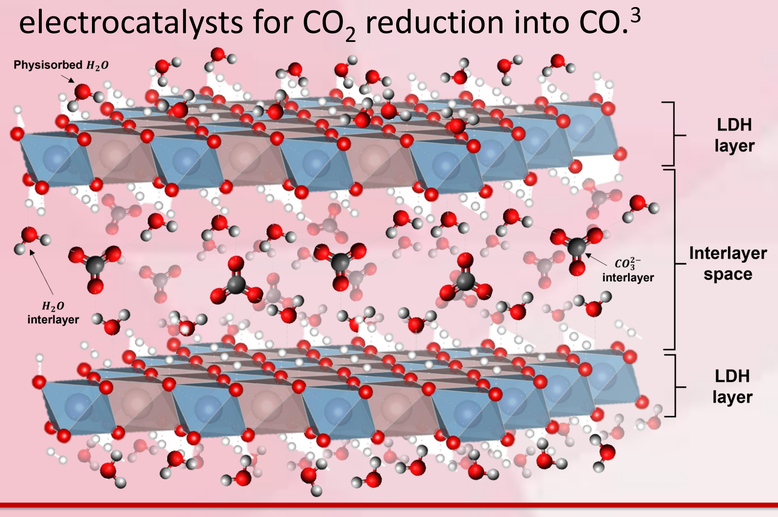
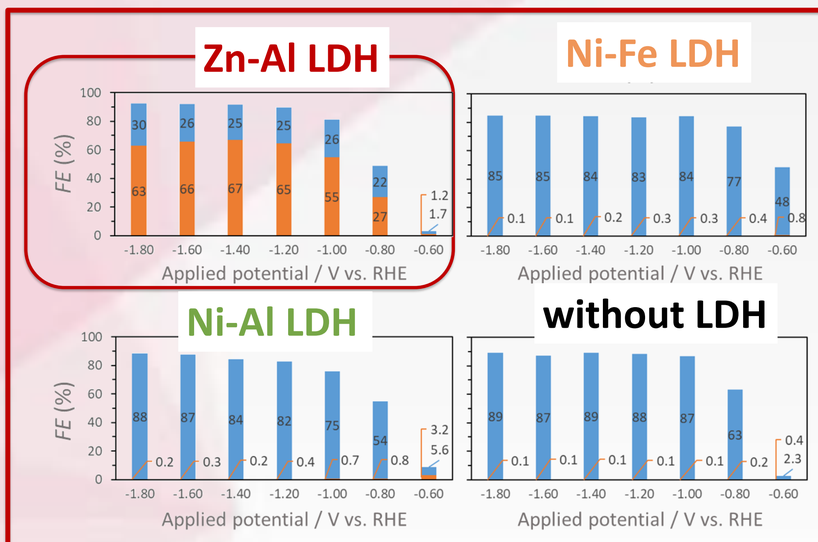
The **electrochemical CO_2 reduction reaction** (CO_2RR) is considered **a promising strategy** for CO_2 conversion and ultimately **for lowering greenhouse gasses emissions**.[1] Recently, **layered double hydroxides (LDHs)** attracted increasing attention as **an alternative to precious metal** catalysts thanks to its strong affinity with CO_2 in water, stability in basic electrolytes, affordability of its components and high ion conductivity.[2]

Materials and methods

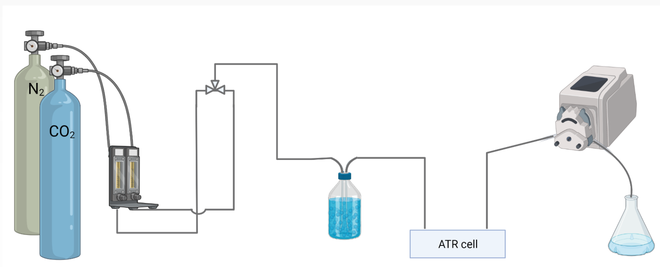
Three LDH with different chemical composition **Ni-Al** and **Ni-Fe** and **Zn-Al LDH** (2:1) were synthesized, characterized (using XRD, TGA, EDX and volumetry) and evaluated as potential electrocatalysts for CO_2 reduction into CO.[3]





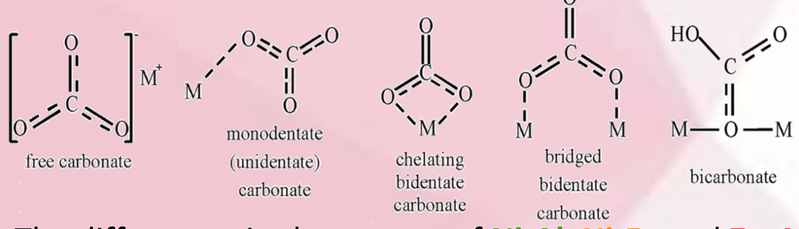
Zn-Al LDH shows a **67%** selectivity for **CO** and 92% selectivity for CO and H_2 at -1.4V vs. RHE with $KHCO_3$ as an electrolyte

A preliminary ***in-situ* ATR-IR** spectroscopical characterization was performed **miming the electrocatalytic conditions** studying the CO_2 **adsorption in absence of potential to explain the different performances into CO evolution reaction.**

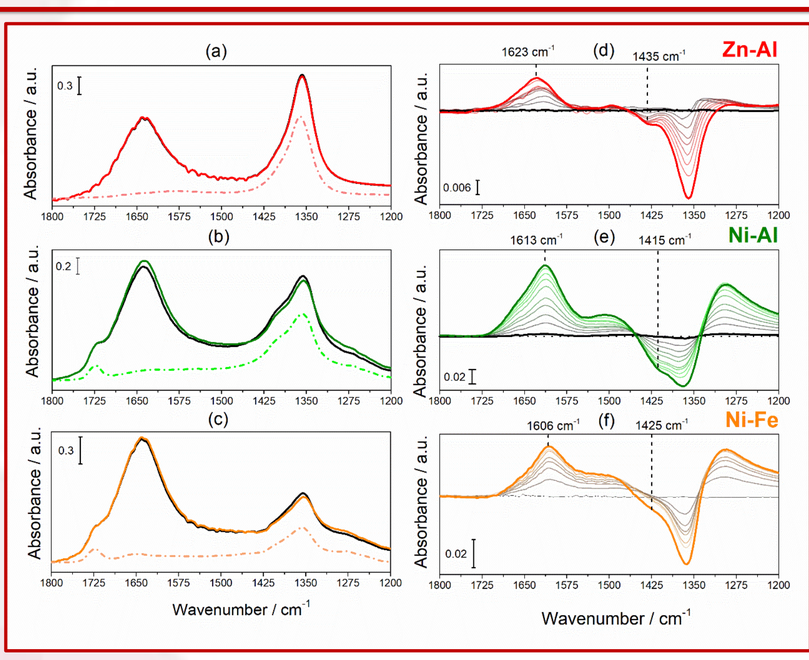


Results and…

The interaction of CO_2 with LDHs show different carbonates evolution.[4]

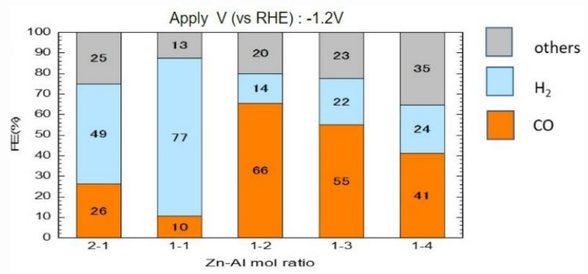


The differences in the spectra of **Ni-Al**, **Ni-Fe** and **Zn-Al** suggest the formation of different families of **bidentate carbonates** with different strength and stability, which might suggest a different catalytic behavior in the tree LDHs.

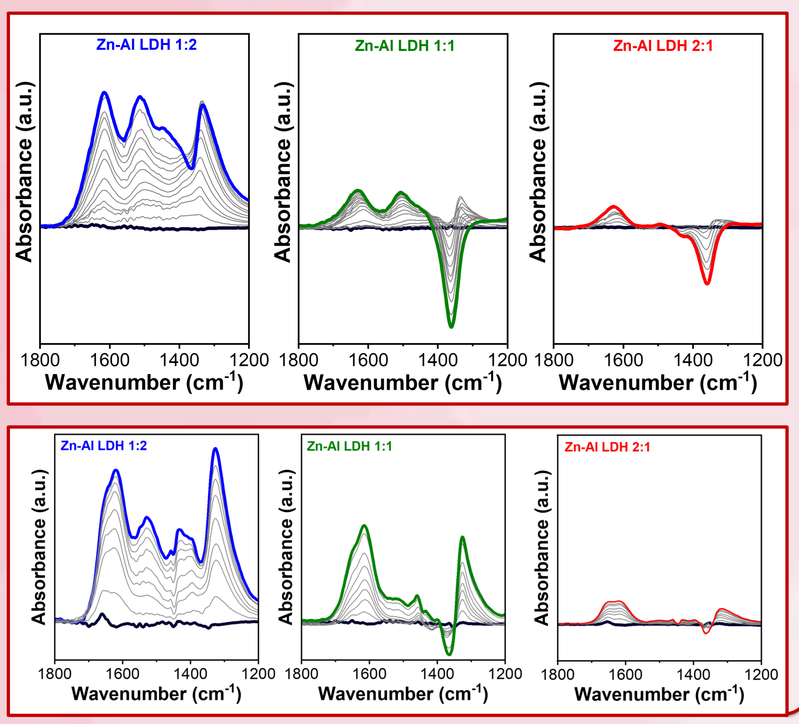


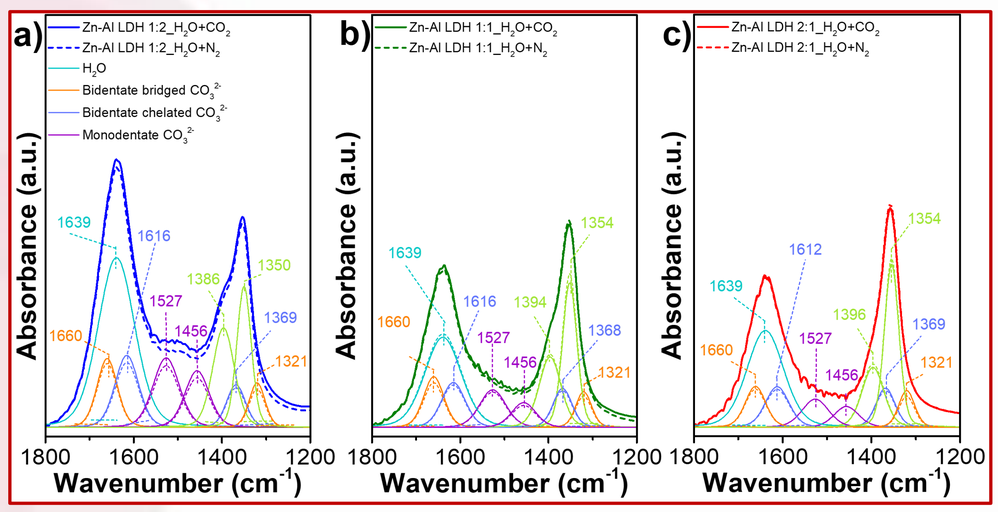
…next steps

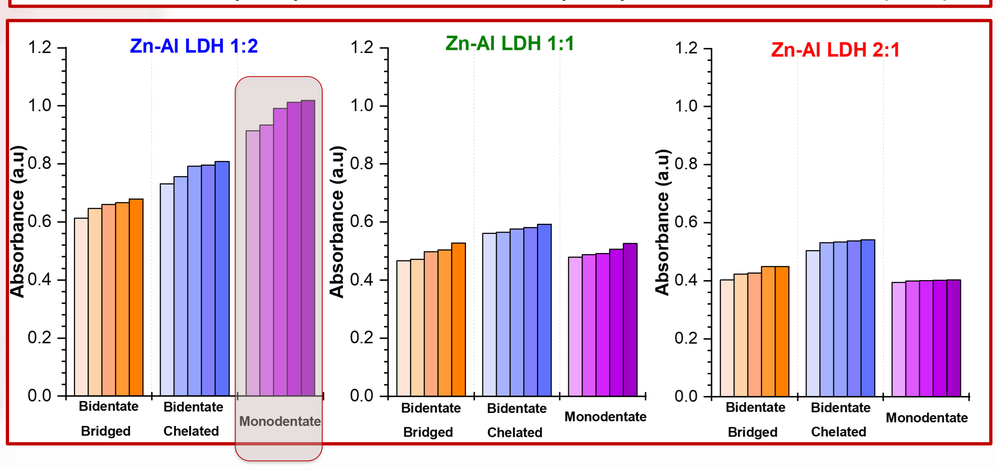
Given the highest CO evolution of **Zn-Al LDH 2:1,** the same sample with other two different stoichiometry were synthetized and tested:
Zn-Al LDH 1:2, Zn-Al LDH 1:1



In-situ ATR-IR spectroscopy







The *in-situ* ATR-IR spectroscopic characterization was performed in both H_2O and C_6H_{12}.
Thanks to this characterization it was possible to perform a deconvolution of the carbonate species

Conclusion

- The **Zn-Al LDH 1:2** which is showing **the best electrocatalytic performances** is characterized by an **higher evolution in monodentate carbonates**.
- **Ni-Al, Ni-Fe** and **Zn-Al** LDH (2:1) show differences only in the evolution of **bidentate carbonates species.**
- The formation of monodentate carbonate is probably associated to an higher electrocatalyst reactivity.

In future a real *operando* spectroscopic characterization will be performed *(*i.e. in presence of potential).

ACKNOWLEDGMENTS & REFERENCES

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101022633. This project is supported by Japan Science and Technology Agency (JST) (Grant Agreement No JPMJSC2102) and São Paulo Research Foundation (FAPESP) (Grant number 2022/04751-0).

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