



Malic acid oxidative dehydrogenation over iron-cobalt mixed oxides

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INTRODUCTION

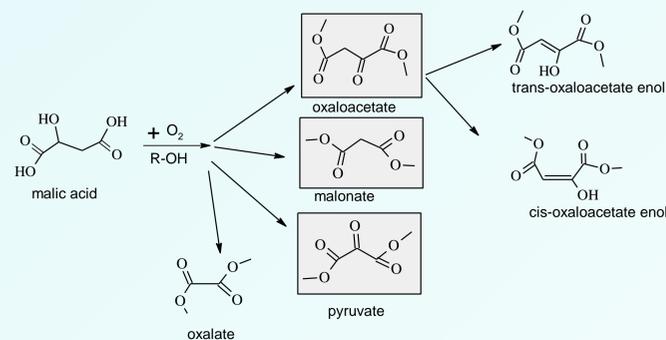
- ❖ Malic acid is a chemical platform for oxaloacetic acid (OAA) and pyruvic acid (PA) synthesis¹.
- ❖ OAA and PA are raw materials for essential aminoacids synthesis.
- ❖ Malic acid is a viable alternative due to its great potential to be produced from biomass.

OBJECTIVES

- ❖ Iron-cobalt oxides $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0; 0.05; 0.1; 0.15$) synthesis by coprecipitation method;
- ❖ Samples characterization by XRD, XPS;
- ❖ Malic acid oxidative dehydrogenation, following the influence of: cobalt content, solvent and malic acid concentration.

RESULTS AND DISCUSSION

- ❖ The presence of $\alpha\text{-Fe}_2\text{O}_3$ rhombohedral hematite phase with Co atoms well incorporated in this structure and the surface elemental composition were determined by XRD and XPS;
- ❖ An increase in the cobalt loading leads to an increase in malic acid conversion and pyruvic acid yield;
- ❖ Oxaloacetic acid yield reaches a maximum on Co_3Fe (10%), while malonic acid is obtained in higher amounts on Co_2Fe ;
- ❖ The increase of malic acid concentration leads to a decrease in its conversion.



Scheme 1. Possible reaction products in the oxidative dehydrogenation of malic acid.

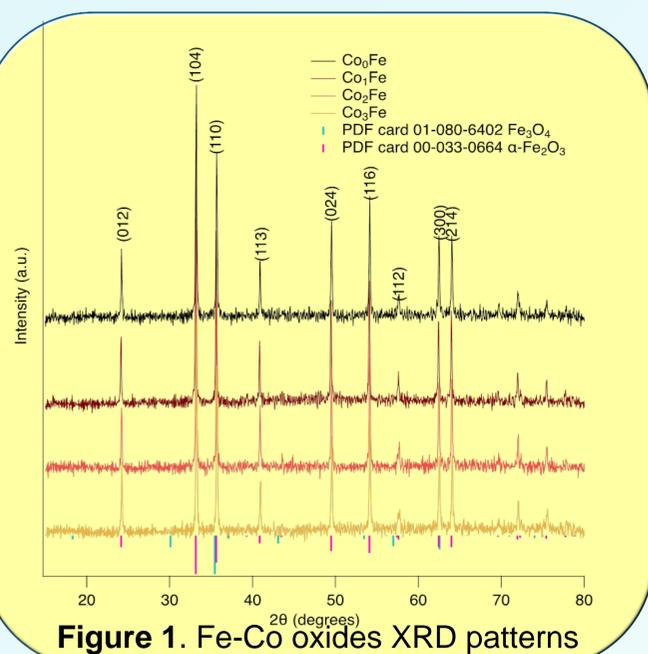


Table 1. The elemental composition of iron-cobalt oxides from XPS

	C	Fe	Co	O	Co/Fe	Fe/O
Co_0Fe	37.5	21.8	0.0	40.7	0	0.54
Co_1Fe	30.1	24.5	0.2	45.2	0.008	0.54
Co_2Fe	29.9	27.6	0.4	42.1	0.014	0.66
Co_3Fe	41.0	17.4	2.2	39.5	0.126	0.44

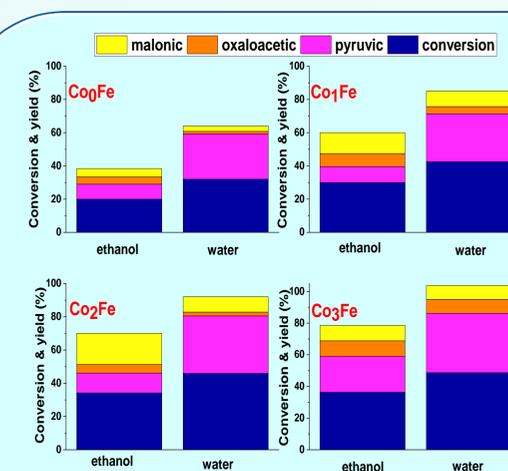


Figure 2. Malic acid conversion and products yield (time 1h, 25°C, 1% catalyst, 2% malic acid)

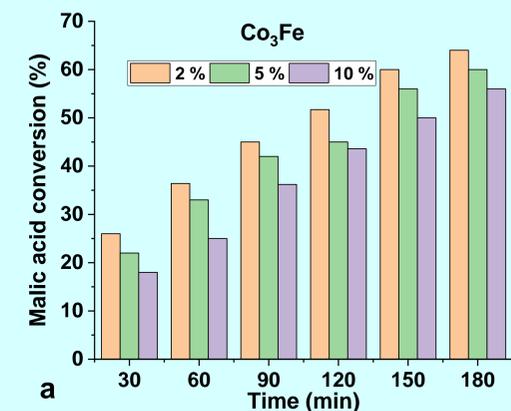


Figure 3. Effect of malic acid concentration on conversion (time 1h, 25°C, 1% catalyst)

CONCLUSIONS

- ❖ The malic acid conversion, in oxidative dehydrogenation reaction, is dependent on the Co/Fe ratio and on the malic acid concentration.
- ❖ The higher Co/Fe ratio, the higher is the yield in pyruvic acid. As solvent, water is preferred to ethanol: higher conversions and yields are obtained in water.

Acknowledgements:

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References: A. Drif, A. Pineda, D. Morvan, V. Belliere-Baca, K. De Oliveira Vigiera, F. Jérôme, *Green Chem.*, 2019,21, 4604-4608;