

# Kinetic and mechanistic implications of CO<sub>2</sub>-assisted ethane dehydrogenation over Fe-based catalysts

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## Highlights

- Iron oxide-based catalysts were found to be selective towards the C-H bond cleavage, with the best candidate, labelled as Fe-700(5h), attaining ethylene selectivity ~90% at conversion >20%.
- The enhanced performance of Fe-700(5h) catalyst was attributed to a structural modification of Mg and Fe atoms, as it was proven by XRS data at Mg L<sub>2,3</sub> edge.
- Mechanistic studies performed using C<sup>18</sup>O<sub>2</sub> isotope in the feed suggested towards an indirect reaction mechanism for CO<sub>2</sub>-EDH.

## 1. Introduction

Ethylene is one of the most valuable commodities in the petrochemical industry. The global demand of ethylene production is constantly increasing, while its annual growth rate is expected to be equal to 5.5% by 2029[1]. Currently, ethylene is mainly produced from thermal steam cracking of hydrocarbons, such as naphtha and ethane, a process that takes place in high temperatures (>800°C) and thus, is very energy demanding. The abundance of the stranded gas reserves in combination with the so-called “shale gas revolution” have revitalized the research interest for on-purpose ethylene production, through ethane utilization. CO<sub>2</sub> can act as a mild oxidant for ethane dehydrogenation, shifting the reaction equilibrium, via H<sub>2</sub> consumption through the Reverse Water-Gas Shift reaction. The research challenge during CO<sub>2</sub>-EDH is the selective C-H bond scission and consequently, ethylene production. Iron oxide-based catalysts have been found to be selective towards the C-H bond cleavage, attaining a single-pass ethylene yield of ~14 %, at 600°C [2]. In the present work, the nature of active sites of iron oxide-based catalysts is investigated, along with the kinetic and mechanistic implications on the best Fe-based candidate.

## 2. Methods

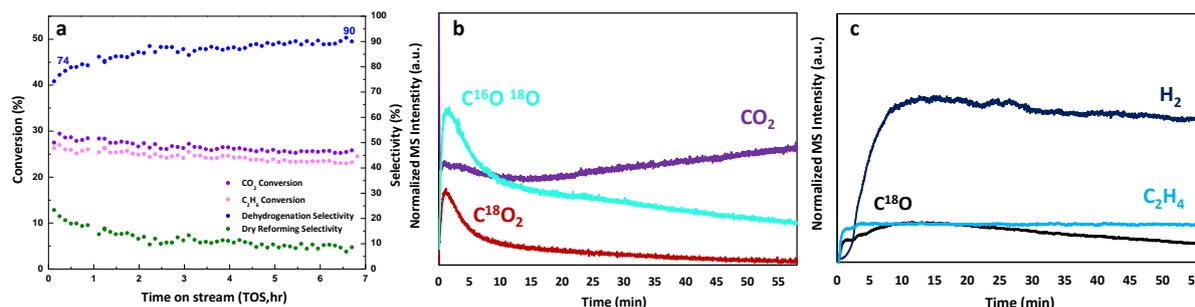
**Support and catalyst preparation:** The synthesis procedure took place in two consecutive steps: a) the support synthesis followed by b) the catalyst synthesis. The 10wt%-NiO-MgO-ZrO<sub>2</sub> support material was prepared using a sol-gel auto-combustion method [3]. 5wt% Fe catalyst was prepared by wetness impregnation of the Fe precursor on the mixed oxide support. The catalyst was calcined at 700°C for 5 hours, under continuous air flow and then labeled as Fe-700(5h). **Catalyst Characterization:** Advanced characterizations techniques were performed at BM23 and ID20 beamlines of European Synchrotron Radiation Facility (ESRF). Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) were performed at Fe and Ni K edges, while X-ray Raman Scattering spectroscopy (XRS) at O K and Mg L<sub>2,3</sub> edges. **Experimental:** a) Mechanistic insights: The mechanism of CO<sub>2</sub>-EDH reaction was examined via a series of isotopic experiments, using <sup>18</sup>O<sub>2</sub> for exchange of the catalyst oxygen and C<sub>2</sub>H<sub>6</sub> and the isotope C<sup>18</sup>O<sub>2</sub> as feedstock, at 101.3kPa. Typically, 400mg of catalyst were placed in a U – shape quartz reactor. The products as well as the unconverted amount of the reactants were detected at the outlet of the reactor, using a Quadrupole Mass Spectrometer (MS). b) Kinetic experiments: All the experiments at varying temperature, W/F and reactants’ partial pressures were conducted at the same fixed bed reactor unit under conditions ensuring that the resistances of external and internal mass transfer limitations were negligible. The products and the unconverted C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> were detected at the outlet using an Agilent® 7890A GC system for online analysis.

### 3. Results and discussion

Activity tests were performed for the Fe-based catalysts during CO<sub>2</sub>-EDH, using an equimolar feed ratio of 1 and temperature of 650°C. Fe-700(5h) achieved the best performance, reaching 90% selectivity towards ethylene production, at 23.3% conversion (Fig.1a). The enhanced performance of Fe-700(5h) catalyst was attributed to a structural modification of Mg atoms geometry and the formation of a spinel like arrangement between Mg and Fe atoms, as it was revealed by XRS data at Mg L<sub>2,3</sub> edge.

A series of isotopic labelling experiments were conducted in order to get insights into the dominant reaction mechanism for CO<sub>2</sub>-EDH on the best candidate, Fe-700(5h) catalyst. There are two main proposed reaction mechanisms for CO<sub>2</sub>-EDH: 1) a direct redox mechanism that occurs in-situ under reaction conditions. During the direct mechanism, oxygen from the catalyst lattice participates in order to produce C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>O. The consumed catalyst lattice oxygen is replenished by CO<sub>2</sub>, which is reduced to CO. 2) an indirect mechanism in which the catalyst acts as a dehydrogenation catalyst, producing C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>. H<sub>2</sub> is consumed by CO<sub>2</sub> in a next step via the RWGS reaction. The formation of H<sup>18</sup>O<sub>2</sub> was not observed during any of the experiments performed, while the main observed products being C<sub>2</sub>H<sub>4</sub>, C<sup>18</sup>O, and H<sub>2</sub> (Fig.1b,c). The latter suggests that the indirect mechanism is more possible to occur during CO<sub>2</sub>-EDH using iron oxide-based materials at temperature range of 600-650°C.

A preliminary kinetic model was developed using the power-law model for the competitive reactions of CO<sub>2</sub>-EDH and ethane dry reforming. Similar reaction orders, ~1, were calculated for the ethane consumption in both ethane dehydrogenation and dry reforming reaction. On the other hand, the model revealed that CO<sub>2</sub> partial pressure does not play a crucial role for ethylene production, during CO<sub>2</sub>-EDH. A more advanced kinetic model, that takes into consideration other possible reaction mechanisms, such as Langmuir-Hinshelwood, Eley Rideal and Mars-van Krevelen, is under development.



**Figure 1:** a) Activity test of Fe-700 (5h). Conversion (%) of C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub> and selectivity (%) towards dehydrogenation (C<sub>2</sub>H<sub>4</sub>) and dry reforming reaction (syngas), as a function of time on stream (TOS). Conditions: 650°C, CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> =1, W<sub>cat</sub>/F<sup>0</sup> =10.8 kg<sub>cat</sub>·s·mol<sup>-1</sup>, P = 101.3 kPa. (b,c) Temperature programmed <sup>18</sup>O<sub>2</sub> isotope exchange experiment took place on Fe-700(5h), from 400°C up to 600°C, until full exchange between lattice and inlet flow oxygen, followed by isothermal experiment, using 1% CO<sub>2</sub> + 1% C<sub>2</sub>H<sub>6</sub>, in Ar. Conditions: 600°C, 101.3 kPa, W<sub>cat</sub>/F<sup>0</sup> =19.5 kg<sub>cat</sub>·s·mol<sup>-1</sup>. (b) CO<sub>2</sub>, C<sup>18</sup>O<sub>2</sub> and C<sup>16</sup>O<sup>18</sup>O and (c) C<sup>18</sup>O and H<sub>2</sub> normalized signals.

### 4. Conclusions

Iron oxide-based Fe-700(5h) was the most selective towards C<sub>2</sub>H<sub>4</sub> production, achieving ~21% ethylene yield at 650°C. The structural modelling of XRS data, revealed a spinel like arrangement between Mg and Fe atoms for Fe-700(5h), which led to an enhanced catalytic performance during CO<sub>2</sub>-EDH, with the latter exceeding by far the performance of previously reported Fe- and Ga-based catalysts. The mechanistic studies that were performed for the same catalyst indicated towards an indirect reaction (CO<sub>2</sub>-EDH) mechanism and thus, a dehydrogenation ability of the studied Fe-based catalyst.

### References

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### Keywords

CO<sub>2</sub> valorization; ethylene; reaction mechanism; oxidative dehydrogenation.