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CO_2 Rich Streams Methanization Intensified by Steam Adsorption with LTA Zeolites in Fluidized Bed Reactor

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Introduction

It is known that CO_2 plays an important role on greenhouse effect, and that up to 412.5 ppm had been measured by 2020 as the highest concentration registered to date. The production of renewable fuels that recycle CO_2 had become relevant. CH_4 is a H_2-rich energy-carrier fuel with a higher energy density compared to H_2 (1).

Surplus renewable energy can be transformed into H_2 by electrolysis. Electrolytic H_2 can react with CO_2 favoring the methanation process through the so-called *Sabatier* reaction, as it is detailed in (r.1) (2). There are also other reactions intervening in the process (r.2, r.3 and r.4):

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H^o_r\text{=-165.1 kJ/mol} \quad \text{(r.1)}$$

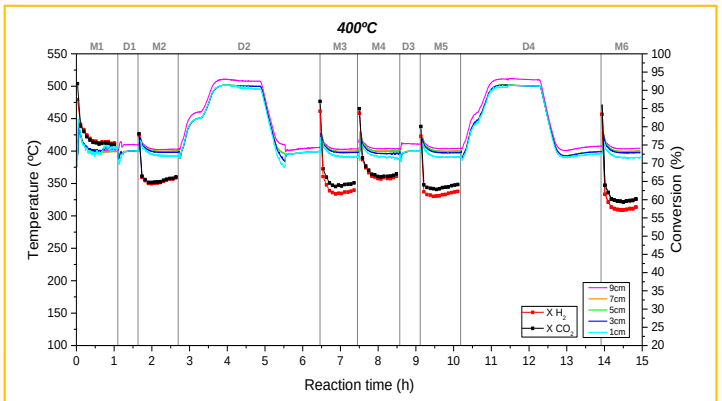
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H^o_r\text{=41.2 kJ/mol} \quad \text{(r.2)}$$

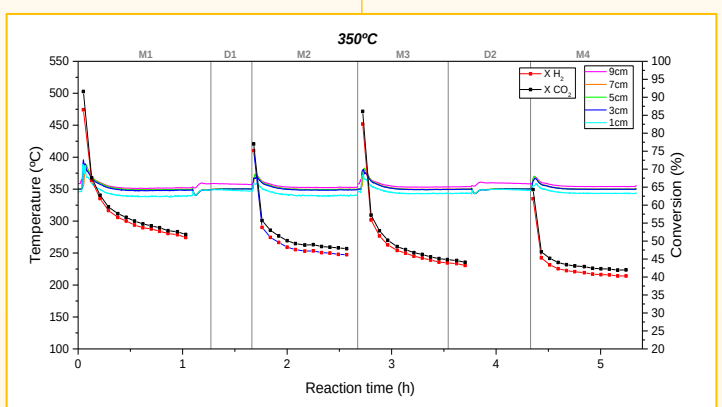
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H^o_r\text{=-206.3 kJ/mol} \quad \text{(r.3)}$$

$$CO_2 \rightleftharpoons C_{(s)} + 2H_2O \quad \Delta H^o_r\text{=-172.5 kJ/mol} \quad \text{(r.4)}$$

Table 1. Reactor characteristics and activation, oxidation, methanation and desorption operating conditions.

Activation		Oxidation	
T (°C)	500	T (°C)	500
P (atm)	1	P (atm)	1
H_2 (^{v}%)	50	O_2 (^{v}%)	2
Ar (^{v}%)	45	Ar (^{v}%)	98
N_2 (^{v}%)	5	N_2 (^{v}%)	0
Flow rate (STPmL/min)	400	Flow rate (STPmL/min)	400
TOS (h)	2	TOS (h)	2
Methanation (M)		**Desortion (D)**	
T (°C)	300/350/400	T (°C)	500
P (atm)	1	P (atm)	1
H_2/CO_2	4	Ar (^{v}%)	93.5
Reactants/inerts	9	N_2 (^{v}%)	6.5
Flow rate (STPmL/min)	570	Flow rate (STPmL/min)	435
TOS (h)	1	TOS (h)	0.5
Reactor characteristics			
Composition		Reactor type	FBR
Zeolite 5A (^{wt}%)	66.67	i.d (mm)	26
Alumina+Ni-Fe (^{wt}%)	33.33	W/q_0 (g_{cat}·min/mL_{STP})	$20 \cdot 10^{-4}$
Catalyst composition (%)	7.5Ni/2.5Fe/Al_2O_3		





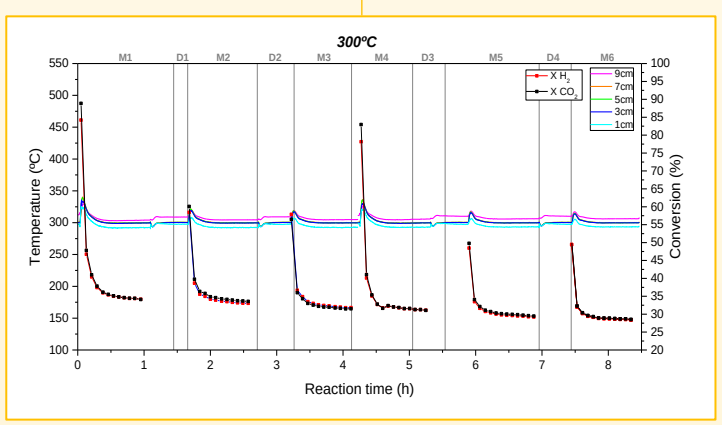
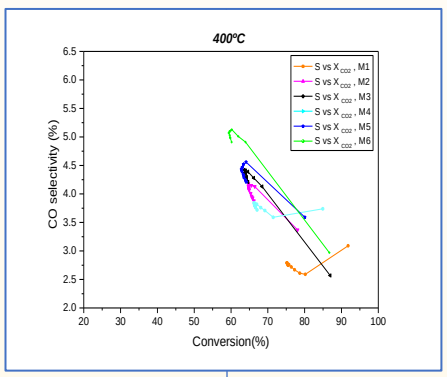
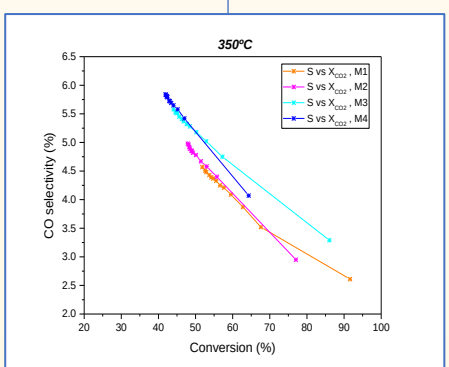


Fig. 1, 2 and 3: H_2 and CO_2 conversions and temperature profiles at different heights for Sorption Enhanced *Sabatier* reaction (SESaR) on a fluidized reactor (M_i: methanation stages, D_i: desorption stages). Methanation conditions: 400ºC, room pressure, H_2:CO_2 = 4:1; reactants:inerts = 9:1. Bed composition: 66.7 ^{wt}% zeolite LTA 5A, 29.5 ^{wt}% alumina, 3.8 ^{wt}% Ni-Fe/Al_2O_3 catalyst.





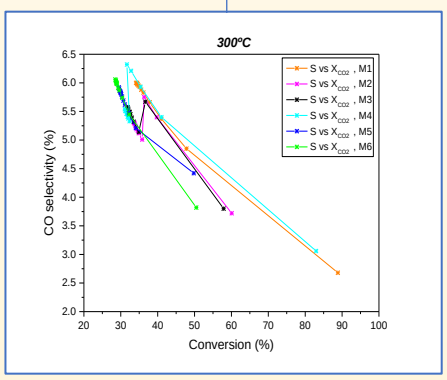


Fig. 4, 5 and 6: CO selectivity versus CO_2 conversion at different methanation operational temperatures for Sorption Enhanced Sabatier reaction (SESaR) on a fluidized reactor (M_i: methanation stages). Other methanation conditions: 400ºC, room pressure, H_2:CO_2 = 4:1, reactants:inerts = 9:1. Bed composition: 66.7 ^{wt}% zeolite LTA 5A, 29.5 ^{wt}% alumina, 3.8 ^{wt}% Ni-Fe/Al_2O_3 catalyst.

Results

Intensification is observed at the beginning of each methanation since H_2O is adsorbed on the zeolite surface (see fig.1, fig. 2 and fig. 3). Later, when the adsorbent gets saturated, conversion stabilizes. It is also noted that as operational temperature decrease from **400ºC**, adsorption capacity and intensification increases, as it takes more time to stabilize the conversions. A drawback is that **lower temperatures entail lower H_2 and CO_2 conversions**.

Fig. 4, fig. 5 and fig. 6 show smooth but **progressive deactivation** and CH_4 selectivity loss is observed along every methanation. Therefore, it **promotes CO forming** by r.2. As a result, **coke is deposited** by r.4, increasing CO generation and CO_2 conversion. To mitigate this effect, an intermediate **oxidation stage** is placed. Catalyst activity is enhanced between M3 and M4 at 400ºC, as **CO selectivity lessens, and conversions rises**. This effect is lower at 350ºC and 300ºC, smoother improvements were identified between M2 and M3 and no CO selectivity reduction was observed. The highest **temperature increments** take place after the oxidation-activation stages.

Conclusions

The sorption enhanced Sabatier process shows its potential, **improving efficiency** and **decreasing the energy requirements** as a benefit of low operating pressure. Moreover, it becomes a sustainable and realistic alternative that could reach the challenging objectives established to **tackle climate change**.

Acknoledgments

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