

Process intensification of the Sabatier reaction for CO₂ methanation with 13X zeolite

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Summary

Power-to-Gas technologies allow the storage of renewable surpluses through the *Sabatier* reaction. This research evaluates the intensification of the process using 13X zeolite as H₂O adsorbent. The effect of temperature and H₂:CO₂ feed ratio are analyzed comparing their performance with other adsorbent materials.

Introduction

The *Sabatier* reaction is a key catalytic process for CO₂ valorization. This reaction is highly exothermic and is limited by thermodynamic equilibrium.

CO ₂ + 4H ₂ ⇌ CH ₄ + 2H ₂ O	ΔH° _r = -165.1 kJ/mol	(r1)
CO ₂ + H ₂ ⇌ CO + H ₂ O	ΔH° _r = +41.2 kJ/mol	(r2)
CO + 3H ₂ ⇌ CH ₄ + H ₂ O	ΔH° _r = -206.3 kJ/mol	(r3)
2CO ⇌ C + CO ₂	ΔH° _r = -172.5 kJ/mol	(r4)

This work investigates process intensification through the use of 13X zeolite. Its utilization allows the selective removal of water from the reaction medium, shifting the equilibrium toward the products by *Le Châtelier's* principle. Another advantage consists in preventing the deactivation of the Ni (7.5 wt%) - Fe (2.5 wt%) catalyst supported on γ-Al₂O₃ (90 wt%) due to sintering or reoxidation in the presence of high partial pressures of steam. This implies an improvement in CH₄ selectivity and reduces the need for subsequent separation stages [1-3].

Experimental

The experimental procedure consists of two stages. First one is activation, which purpose is to reduce the Ni-Fe/γ-Al₂O₃ catalyst, increasing the temperature up to 400 °C for 3 hours, using H₂ as reducing agent. In the second stage, cycles of reaction (r1-r4), and desorption of the water adsorbed on the zeolite are carried out in order to analyze the achieved intensification. Each experiment consists of three reaction stages (90 min each) interspersed with two desorption stages (30 min each). The experimental conditions are listed in Table 1. The different

experiments performed are detailed in Table 2 and Table 3, where 'O' indicates that the experiment is in progress and '✓' that it has been completed.

Table 1. Experimental process conditions.

Catalyst weight (g)	0.25
Adsorbent material weight (g)	10.25
Particle size (μm)	100 - 200
Total flow rate (mLSTP/min)	250
H ₂ /Ar/N ₂ ratio during activation (vol%)	50 / 45 / 5
Activation time (hours)	3
Ar/N ₂ /reactants ratio during reaction (vol%)	5 / 5 / 90
Reaction time (minutes)	90
Ar/N ₂ ratio during desorption (vol%)	95 / 5
Desorption time (minutes)	30
Pressure (atm)	1
Synthetic biogas ratio CH ₄ : CO ₂	7:3

Table 2. Experiments performed at different temperatures.

CO ₂ experiments	Temperatures (°C)					
	400	375	350	325	300	275
Zeolite 13X	✓	✓	✓	✓	✓	✓
Zeolite 5A			✓	O		
Zeolite 4A				✓		
Blank (Al ₂ O ₃)			✓	✓		
Biogas experiments	Temperatures (°C)					
	400	375	350	325	300	275
Zeolite 13X		✓	✓	✓	✓	
Zeolite 5A				O		
Zeolite 4A				✓		
Blank (Al ₂ O ₃)				✓		

Table 3. Experiments at different H₂: CO₂ feed ratios.

CO ₂ experiments	Ratio (H ₂ : CO ₂)				
	2:1	3:1	4:1	5:1	6:1
Zeolite 13X	✓	✓	✓	✓	✓
Biogas experiments	Ratio (H ₂ : CO ₂)				
	2:1	3:1	4:1	5:1	6:1
Zeolite 13X	O	O	✓	O	O

Process intensification is quantified by integrating the CO₂ conversion versus time curves from the initial transient maximum to convergence at steady state. This “extra” performance (see Figure 1-3) is attributable to the selective adsorption of H₂O by the zeolite following the *Le Châtelier's* principle.

The reference temperature selected to perform the experiments with different $H_2:CO_2$ ratios and adsorbent materials was 325 °C. This value was chosen because it maximizes the net amount of intensified reactant while keeping a relatively high stationary conversion (see Table 4 and Figure 1).

Table 4. Intensified areas for the different temperatures.

Temperatures °C	Intensified area	
	Average absolute area (min^{-1})	Average relative area with respect to the non-intensified area (%)
400	0.10	0.25
375	0.50	1.38
350	1.77	5.60
325	2.49	13.24
300	1.81	14.54
275	0.89	12.77

Results

As observed in Figures 1 and 2, along the first reaction stage CO_2 conversion exhibits an initial maximum and drops exponentially until reaching steady state. At the following desorption stage, the initial conversion is slightly lower than that achieved in the first cycle. Moreover, the steady state achieved along this second cycle is practically identical to that of the first one as is also along the third. This demonstrates that the catalyst does not deactivate in the periods tested. The decrease in intensification may be due to the zeolite not recovering its full adsorption capacity because it does not completely desorb the water. Third reaction stage, following 2nd desorption achieves equivalent values to those obtained in the second. This finding is consistent with incomplete water desorption in the preceding stage. On the other hand, adding methane to the feed used to test the behaviour of a sweetened biogas reduces the conversion compared to CO_2 -only methanation by an amount that corresponds to methane acting as

an inert component. This fact has been checked at different temperatures (Figure 3).

Conclusions

From the experiments performed, it can be concluded that using H_2 and CO_2 as reactants at 325 °C with a 6:1 molar ratio ($H_2:CO_2$) yields the highest intensification when employing 13X zeolite in the fixed-bed reactor under the studied operating conditions, and that desorption periods at the same temperature than reaction ones are not enough to recover the initial water adsorption capacity of the 13X zeolite.

Acknowledgments

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REFERENCES

- [1]. MERCADER, Víctor Daniel, et al. Biogas upgrading by intensified methanation (SESaR): Reaction plus water adsorption - desorption cycles with Ni-Fe/ Al_2O_3 catalyst and LTA 5A zeolite. *Catalysis Today*. 2024. vol. 442. 114919. ISSN 0920-5861.
- [2]. OLUSHOLA, Samuel Babatunde, et al. Durable, hydrophobic and porous zeolite 13X coatings for resisting liquid water during CO_2 desorption. *Materials Today Communications*. 2026. vol. 42. ISSN 2468-0230. Al_2O_3
- [3]. CHEN, Chao y AHN, Wha-Seung. CO_2 capture using mesoporous alumina prepared by a sol-gel process. *Chemical Engineering Journal*. 2011. vol. 166. no. 3. pp. 1151-1155. ISSN 1385-8947.

Figures

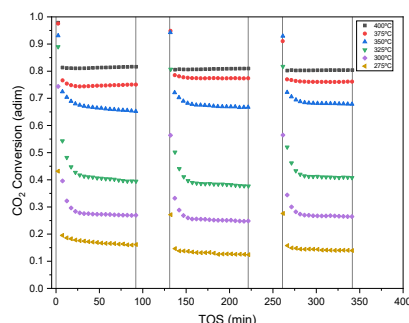


Figure 1. Evolution of CO_2 conversion versus time with 13X zeolite at stoichiometric $H_2:CO_2$ ratio.

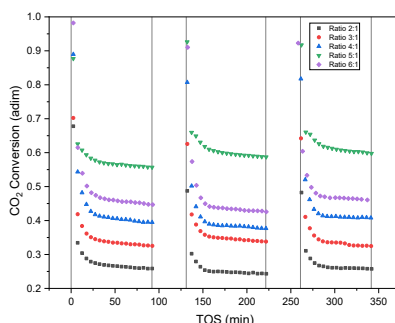


Figure 2. Evolution of CO_2 conversion versus time at 325 °C with 13X zeolite at different $H_2:CO_2$ ratios.

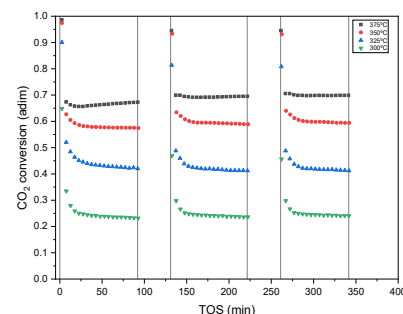


Figure 3. Evolution of CO_2 conversion versus time at different temperatures with stoichiometric $H_2:CO_2$ ratio and 13X zeolite for synthetic biogas.