Optimization of Operating Conditions for Methanol Synthesis via Catalytic CO_2 Hydrogenation in a Fixed-Bed Reactor

D. Flores-Calvo*, R. González-Pizarro, S. Renda, J. Lasobras, J. Soler, M. Menéndez, J. Herguido

Catalysis and Reactor Engieering Group (CREG)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
e-mail: *842620@unizar.es*

Abstract

This work aims to optimize methanol synthesis via catalytic CO_2 hydrogenation by comparing Cu/ZrO_2 and $Pd/In_2O_3/ZrO_2$ systems. A Doehlert experimental design is used to analyze the influence of operating variables and develop a mathematical model to maximize efficiency in Power-to-Liquid processes.

Introduction

Global primary energy demand experienced a 2.3% increase in 2024, which has led to a historical peak of anthropogenic CO_2 emissions into the atmosphere [1]. In response to this environmental crisis, many alternatives to fossil fuels have been developed in recent years. In this context, and with the aim of correcting the dependency of renewable energies on meteorological conditions, Power-to-Liquid (PtL) technology emerges. This alternative enables the transformation of renewable energy surpluses and green hydrogen into renewable liquid fuels. The methanol synthesis process is a complex system where competing reactions coexist, with the reaction under study being the direct hydrogenation of CO_2 (r.1).

$$CO_2 + 3\ H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H^o_R = -49{,}8\ kJ/mol$$

It is an exothermic process that involves a volumetric contraction. This competes directly with the Reverse Water Gas Shift *(RWGS)* reaction (r.2).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^o_R = 41{,}2\ kJ/mol$$

Which is endothermic and favored by an increase in temperature. In this work, the response of a copper catalyst (Cu/ZrO_2) is evaluated against a palladium-indium one ($Pd/In_2O_3/ZrO_2$) using the design of experiments to optimize and model the process, due to the predictive capability it possesses over the reactor responses.

Materials and Methods

A multivariable Doehlert matrix was implemented to model the effect of temperature (240-300 ºC), weight hour space velocity (WHSV), and the H_2:CO_2 ratio. The solids were synthesized by wet impregnation following the procedures detailed in [2-3] and were subjected to physicochemical characterization using TPR, XRD, and BET techniques to correlate their porosity and active sites with the observed activity. The experimental data were processed with AZURAD software, generating second-degree polynomial models based on coded variables that allow quantifying the sensitivity of each operating parameter, as the direct comparison of variables is meaningless when quantifying the effects they have on the system, given the different units and physical magnitudes that define them.

Results and Discussion

Table 1 shows the reaction parameters of the 13 experiments carried out, with their respective coded values.

Table 1. Experimental (values and codification) planification

	Valores Experimentales			*Valores Codificados*		
Nº exp	***H_2:CO_2***	***WHSV ($L_{STP}\,g^{-1}\,h^{-1}$)***	***T (ºC)***	***H_2:CO_2***	***WHSV ($L_{STP}\,g^{-1}\,h^{-1}$)***	***T (ºC)***
1	3	20* / 16**	240	0	0,5	-0,866
2	3	16 */ 12**	240	0	-0,5	-0,866
3	4	18* / 14**	250	0,817	0	-0,577
4	2	20* / 16**	260	-0,817	0,5	-0,289
5	2	16* / 12**	260	-0,817	-0,5	-0,289
6	3	22* / 18**	270	0	1	0
7	3	18* / 14**	270	0	0	0
8	3	14* / 10**	270	0	-1	0
9	4	20* / 16**	280	0,817	0,5	0,289
10	4	16* / 12**	280	0,817	-0,5	0,289
11	2	18* / 14**	290	-0,817	0	0,577
12	3	20* / 16**	300	0	0,5	0,866
13	3	16*/ 12**	300	0	-0,5	0,866

** Catalizador de Cu/ZrO_2*

*** Catalizador de $Pd/In_2O_3/ZrO_2$*

The experimental results are shown below in **Figure 1**, which details the achieved methanol selectivity and CO_2 conversion.

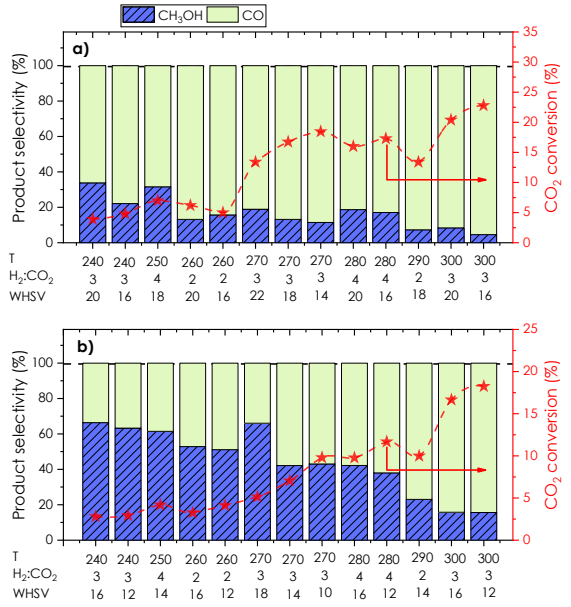

Figure 1. CO_2 conversion and CH_3OH/CO selectivities. (**a**) Cu/ZrO_2; (**b**) $Pd/In_2O_3/ZrO_2$

The increase in temperature raises CO_2 conversion through kinetic enhancement in both catalysts. The copper system is more active than the palladium one due to the low intrinsic activity of indium oxide. However, copper exhibits significantly lower methanol selectivity than palladium. This selectivity decreases with increasing temperature due to the exothermic nature of the reaction and the associated thermodynamic limitations. It is concluded that the Pd system is less active for hydrogenation but much more selective than Cu one. This capability allows the pallsadium system to maintain its specificity, avoiding the limitations that affects copper.

Figure 2 shows the CH_3OH space-time yield (STY_{CH_3OH}) values

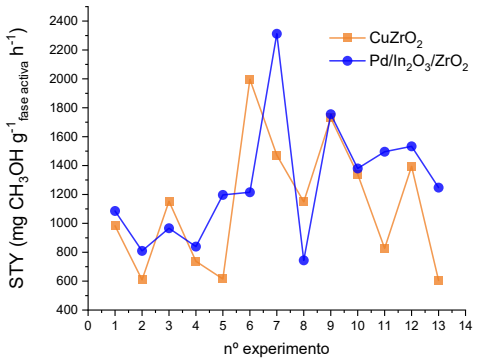

Figure 2. Study of the STY_{CH_3OH} ($mg_{CH_3OH}\ g_{active\ phase}^{-1}\ h^{-1}$)

At low temperatures, kinetics limits production (STY_{CH_3OH}) in both systems, with both reaching their maximum yield at 270 ºC. In the 280 to 300 ºC range, the palladium catalyst is more efficient thanks to its oxygen vacancies, preserving selectivity against heat. Finally, the palladium system manages to overcome the thermodynamic limitations that restrict the copper system.

To transform the results of the 13 experiments into a tool with analysis and prediction capabilities, an empirical mathematical model based on a second-degree polynomial was generated. The polynomial is as follows:

$$Y = b_0 + b_1\,WHSV + b_2\,T + b_3\,H_2{:}CO_2 + b_{22}\,T^2 + b_{33}\,H_2{:}CO_2^2 + b_{12}\,WHSV\,T + b_{13}\,WHSV\,H_2{:}CO_2 + b_{23}\,T\,H_2{:}CO_2$$

Where the b_0 term represents the center point of the experimental domain, the linear coefficients b_1, b_2, and b_3 indicate the direct sensitivity of the response to the variable, the quadratic coefficients b_{22} and b_{33} model the curvature of the response, and finally, the interaction coefficients b_{12}, b_{13}, and b_{23} represent synergistic or antagonistic effects between the variables.

Conclusions

It is concluded that the copper system exhibits higher intrinsic activity, while the palladium-indium system stands out for being significantly more selective toward methanol production. The Doehlert model identifies temperature as the most critical variable and reveals key synergistic relationships, allowing productivity to be optimized by combining high space velocities with a higher H_2:CO_2 ratio.

References

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