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

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Summary

The **objective** of this study is the **optimization** of the operating conditions for **methanol synthesis** from CO_2 and H_2 in a fixed-bed reactor, employing two distinct catalysts and applying a multivariable experimental design as an optimization tool. The interest of the model lies in analyzing the influence of the operating variables on la X_{CO_2}, S_{CH_3OH}, η_{CH_3OH} and STY_{CH_3OH}. It also constitutes a predictive tool for process optimization.

The reaction of greatest interest in this study is the following:

$$CO_{2(g)} + 3\,H_{2(g)} \rightleftharpoons CH_3OH_{(g)} + H_2O_{(g)} \quad \Delta H^{o}_{R} = -49.8 \text{ kJ/mol}$$

Table 1. Experimental design and values trasnformation.

	Experimental Values			*Encoded Values*		
N° exp	*H_2:CO_2*	*WHSV (L_{STP} g^{-1} h^{-1})*	*T (°C)*	*H_2:CO_2*	*WHSV (L_{STP} g^{-1} h^{-1})*	*T (°C)*
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

** Catalyst Cu/ZrO_2*

*** Catalyst $Pd/In_2O_3/ZrO_2$*

The developed **mathematical model** relates the process variables according to the following **equation** :

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

Table 2. Coeffcient values and p-values of the model:

	X_{CO_2}		*S_{CH_3OH}*		*η_{CH_3OH}*		*STY_{CH_3OH}*	
Coefficient	*Cu*	*Pd*	*Cu*	*Pd*	*Cu*	*Pd*	*Cu*	*Pd*
b_0	0.144	5.74	0.177	42.5	2.44	2.42	1579	1224
b_1	-0.016	-8.82 *	0.043 *	-0.663	0.173	-0.318 *	403**	194 *
b_2	0.100 ***	8.36**	-0.123 **	-27.8 ***	0.244	0.789 *	165	356 *
b_3	0.032 **	2.21 *	0.064 **	5.03 **	1.14 **	1.31 **	417 **	192 *
b_{22}	-0.02 *	5.90**	-0.006	-3.00	-1.46 **	-0.152	-908 ***	-73.8
b_{33}	-0.05 **	0.033	-0.005	1.63	-0.593	0.376	-541 **	183
b_{12}	0.009	-0.851	-0.046	-1.71	0.381	-0.135	240	5.61
b_{13}	0.002	1.24	0.011	8.24 *	-0.135	0.965 *	79.2	468 *
b_{23}	0.006	1.35	-0.049	0.768	-0.091	0.379	-158	105

** 1% < p-value < 5%*

*** 0,1% < p-value < 1%*

**** p-value < 0.1%*

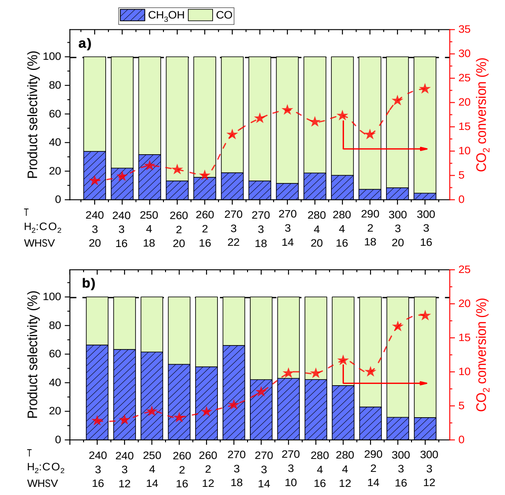

Figure 1. X_{CO_2} and s_{CH_3OH}. Experimental values: Upper graph - Cu/ZrO_2 catalyst, lower graph - $Pd/In_2O_3/ZrO_2$ catalyst.

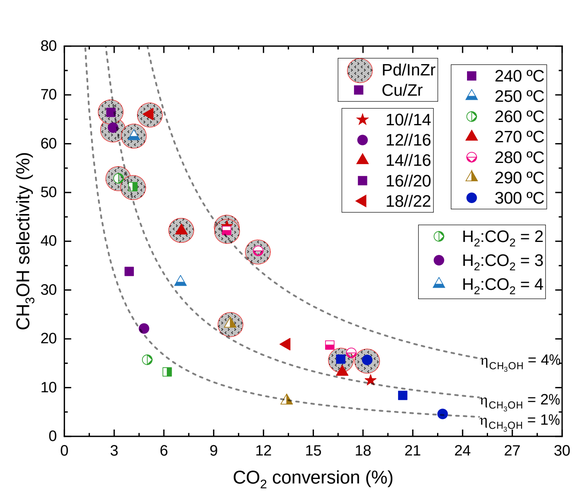

Figure 2. s_{CH_3OH} as a function of X_{CO_2}. Experimental values

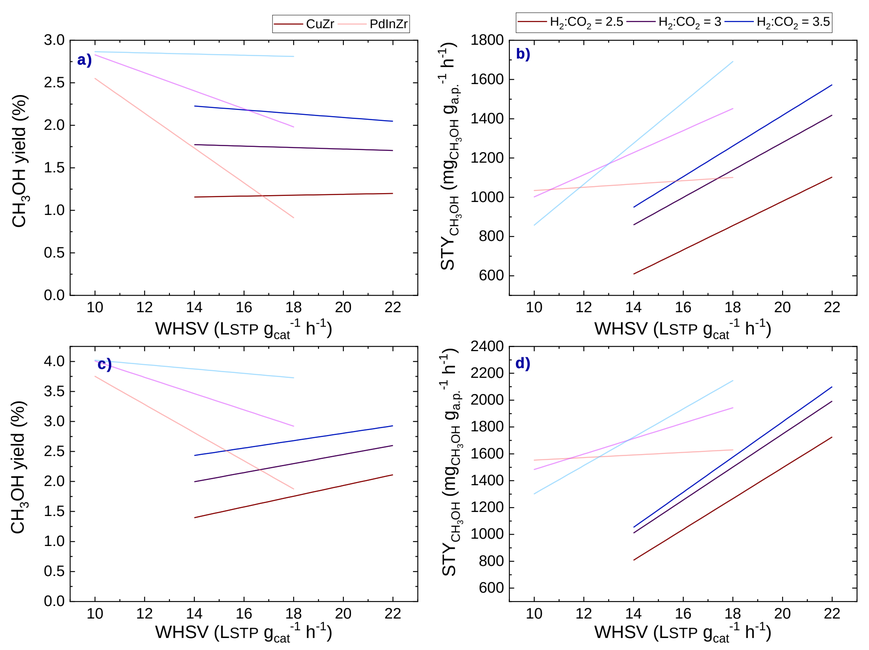

Figure 3. CH_3OH yield (**a**) and (**c**) and CH_3OH space-time yield (**b**) and (**d**) for each different color intensity and ratio represented by different colors; simulated data. (**a** and **c**) 250 ºC; (**b** and **d**) 280 ºC.

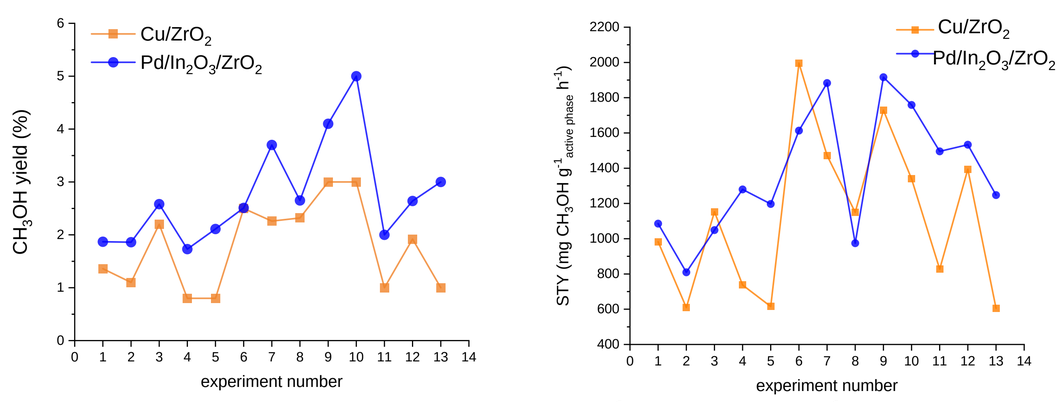

Figure 4. Study of the STY (mg CH_3OH g^{-1} active pase h^{-1}) and CH_3OH yield (%) as a function of the catalytic system used.

Conclusions

- **Design of Experiments (DoE) considerably reduces** the **experimental workload** and is confirmed as a **highly useful tool** in catalysis.
- The **copper** catalyst exhibits a **higher capacity** for **CO_2 conversion**, whereas the **palladium** catalyst proved to be much **more selective** toward the target product
- A significant **synergistic relationship** exists between **T** and **WHSV**, resulting in **high methanol production** at **moderate temperatures and high WHSV**
- The model validates the **thermodynamic limitations** of the process, observing that **T** and the **H_2 / CO_2 feed** present the **most influential coefficients** (*p*-values < 0.05%)

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