Evaluation of the Cu/Zn/Al catalyst deactivation and the effect of γ-Al_2O_3 on the CO_2 hydrogenation to methanol

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Abstract. *With the current scenario of decreasing fossil fuel reserves, the CO_2 hydrogenation to methanol is a promising procedure for the development of alternative energy sources. In this work, the deactivation of the commercial Cu/Zn/Al catalyst and the effect of γ-Al_2O_3 on its performance was investigated by catalytic tests and XRD analysis. The experiments were conducted using temperature, molar ratio and GHSV of 250 ºC, 3:1 (H_2/CO_2) and 3000 h^{-1}, respectively, the studied pressures were 1, 10, 20 and 30 bar. The crystallite size was determined by the Scherrer equation before and after the tests. The reaction at 30 bar presented the highest performance: 4,7% CO_2 conversion and 242,14 methanol STY. The XRD analysis indicated increase in copper crystallite size, most likely due to sintering. The addition of γ-Al_2O_3 had a positive effect on CO_2 conversion and catalyst stability. The results are relevant to improve the industrial methanol synthesis process.*

Keywords: Heterogeneous catalysis; CO_2 conversion; XRD.

1. Introduction

The decreasing fossil fuel reserves along with the climate change effects due to rapidly growing emission levels of greenhouse gases such as CO_2, have caused major worldwide concerns over the past decades. Therefore, the development of novel green alternative energy sources from non-fossil fuels is of utmost importance. In this regard, the CO_2 conversion into fuels and chemicals, including methanol, is emerging as a promising alternative, as it attenuates global climate change effects and may also be economically attractive. In addition to its application as a fuel, methanol is also an intermediate in the production of other fuels and chemicals, such as dimethyl ether (DME), a potential ultra clean fuel and green propellant for jet engines, therefore being a substance of great interest in the aerospace field (OLAH, 2005; ALVAREZ et al., 2017). However, one of the biggest challenges in transforming carbon dioxide into products is the elevated thermodynamic stability of the molecule, requiring high energy input to activate the compound. Thus, the catalytic hydrogenation of CO_2 is a promising procedure (YE et al., 2019). Catalysts for methanol synthesis are mainly composed of a metal and an oxygen-deficient material, such as the Cu/Zn/Al catalysts, which have been widely studied and employed industrially (YANG et al., 2017). As indicated by several authors, γ-Al_2O_3 has a positive effect on the CO_2 conversion, most likely due to its acidity, rendering the substance an important component for the CO_2 hydrogenation catalysts (WANG; ZENG, 2005) (WANG; LEE; HUANG, 2002) (WITOON et al., 2015). Apart from catalyst composition and promoters, the operating conditions such as the reaction temperature, pressure, space velocity and the reactants molar ratio also play a crucial role on the conversion and selectivity. The methanol synthesis (Equation 1) is an exothermic reaction, however, at low temperatures ($< 250°C$) the CO_2 molecule activation is limited due to its thermodynamic restrictions. Also, at high temperature conditions the reverse water gas shift (RWGS) reaction (Equation 2) is favored, leading to the formation of CO and H_2O, thus impacting negatively the methanol and DME selectivity. It is also relevant to highlight that the high amount of H_2O generated during the CO_2 hydrogenation to methanol and DME is a potential cause of catalyst deactivation (TWIGG; SPENCER, 2001). Furthermore, as shown in thermodynamic simulations as well as in experimental results, both the CO_2 conversion and methanol selectivity are favored in high pressure conditions (ALVAREZ et al., 2017).

$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta_{H_{298}} = -49,51\,\text{kJ/mol} \tag{1}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta_{H_{298}} = +41,19\,\text{kJ/mol} \tag{2}$$

In light of the above, the present work had the objective of investigating the deactivation of copper catalysts in the methanol synthesis reaction at different pressure conditions through XRD analysis. The study also focuses on evaluating the effect of physically mixed γ-Al_2O_3 in the stability and performance of the materials.

2. Methodology

The catalytic performance was evaluated in a fixed bed stainless steel tubular reactor (i.d. = 1,2 cm). For each test, the commercial Cu/Zn/Al catalyst was diluted in Silicon Carbide (Sigma-Aldrich) to avoid hot spots in the catalytic bed. Prior to the experiments, the catalysts were reduced under H_2 flow at 300 ºC for 1 hour. After the reduction time, the flow was changed to He and kept at this temperature for 30 min. Then, the reaction temperature was decreased to 250 ºC. All the catalytic experiments were performed using a gas hourly space velocity (GHSV) of 3000 h^{-1}, 3 hours reaction time and the molar ratio of H_2 to CO_2 was 3.0, using a commercial gas mixture. The reactions were carried out at different pressures, 1, 10, 20 and 30 bar.

For the analysis with alumina, the Cu/Zn/Al catalyst was physically mixed with calcined γ-Al_2O_3 in a 1:1 mass proportion. The reaction was performed at the same conditions specified previously, in order to evaluate the effect of the addition of alumina on the catalyst performance.

In all tests, the gas products were analyzed by an online Gas Chromatograph (GC) Clarus 500, equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). The liquid products were collected after the tests and analyzed on a Clarus 580 GC equipped with FID.

To evaluate the modifications on the Cu crystallite size in the structure of the catalytic materials during the tests, X-Ray Diffraction (XRD) analysis were performed before and after the reaction using Cuα radiation source, with 2θ in the range 8 - 90° and 0,02 step. The equipment utilized was a Panalytical Empyrean. The crystallite size was determined by the Scherrer equation (3), where d_p is the average crystallite diameter, $k \sim 1$ is a dimensionless shape factor, λ the X-Ray wavelength, b is the peak full width at half maximum (FWHM) and υ the Bragg angle.

$$d_p = \frac{k\lambda}{b\cos(\upsilon)} \tag{3}$$

3. Results and Discussion

The results for the catalytic tests are presented in terms of CO_2 conversion, methanol Space-Time Yield and CO yield. Carbon monoxide is a product of the reverse water gas shift side reaction. Figure 1 shows the results obtained for the reactions using the Cu/Zn/Al catalyst in each condition. It is observed that performing the hydrogenation reaction at higher pressures result in higher methanol yield, which can be explained by the equilibrium shift towards methanol formation that occurs when the reaction pressure is increased. The result is in accordance with several authors (ALVAREZ et al., 2017; SAEIDI; AMIN; RAHIMPOUR, 2014; YANG et al., 2017; YE et al., 2019). CO Yield increased with pressures up to 20 bar, and then decreased for higher pressures. Industrially, the reactions is carried out at more drastic conditions ($\sim$ 50 - 100 bar) in order to inhibit RWGS, favoring methanol formation and enhancing the selectivity to the desired product. CO_2 conversion showed a similar behavior to methanol STY, with the exception of the reaction performed at 10 bar, which had lower conversion than the experiment at 1 bar. All these factors may explain the lower conversion obtained in the experiment, and were possibly caused by incomplete reduction in the pre-analysis step, even though all reaction followed the same procedure. A possible solution would be increasing the reduction step time, to ensure complete reduction to the active phases. It is important to highlight that the CO_2 conversion was not stable during all experiments, so that by the end of the tests, it had decreased significantly.

One of the crucial aspects of copper catalysts performance is the crystallite size, which was investigated by the XRD analysis using the most intense diffraction lines that were not overlapped. The results obtained by Equation 3 are presented in Table 1. All post reaction samples presented similar crystallite diameter, and so only the result for the experiment performed at 30 bar is shown. It can be observed that the samples used in the catalytic tests presents sharper and more intense peaks, resulting in larger crystallite size. This highly undesirable effect is likely caused by sintering (agglomeration of particles) of the catalyst structure, which is the main cause for deactivation in copper catalysts employed in the methanol synthesis reaction. Other common forms of deactivation are coke deposition, catalyst poisoning by sulfur or chloride species and formation of non active phases such as copper aluminates, however, further investigation is required to analyse and minimize these effects (TWIGG; SPENCER, 2001).

Table 1: Copper crystallite diameter before and after the tests. [Source: Results]

Catalyst	Reaction	2θ(°)	dp (nm)
Cu/Zn/Al	Fresh	58,39	7,6
	P = 30 bar	43,21	13,9

In order to evaluate the effect of the addition of alumina, the experiment with Cu/Zn/Al phys-

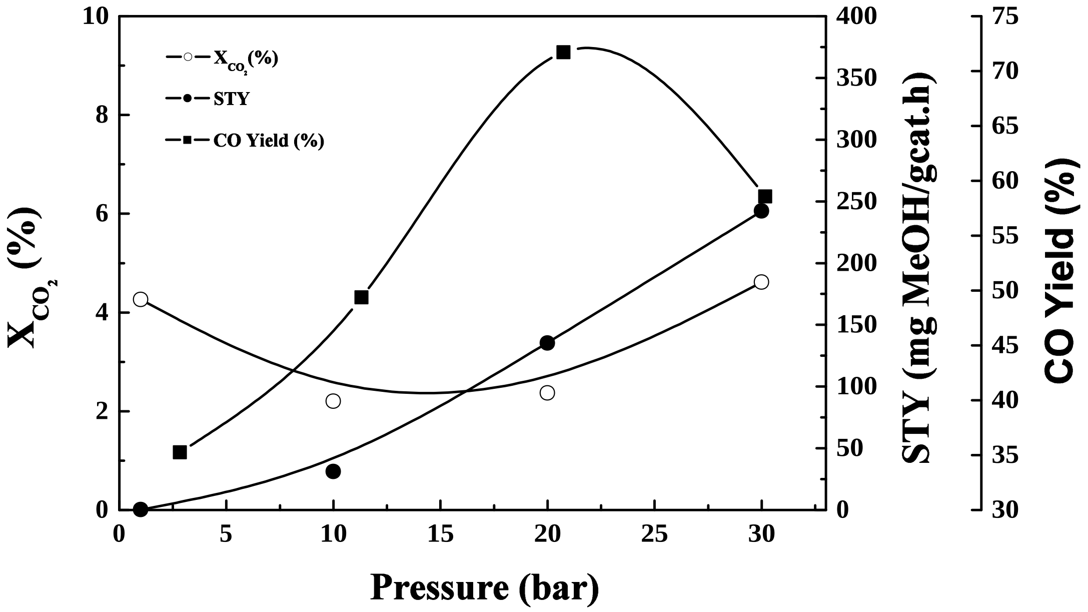

Figure 1. CO_2 conversion, Methanol STY and CO yield obtained in each pressure. [Source: Results]

ically mixed with γ-Al_2O_3 was carried out at P = 30 bar, other parameters such as reduction time, reaction temperature, GHSV and reactant molar ratio were maintained from the previous experiments. The results are presented in Table 2. The experiment resulted in higher CO_2 conversion and lower methanol STY and CO yield in comparison with the reaction performed at 30 bar without γ-Al_2O_3. The CO_2 conversion was also more stable with this catalyst, whereas in the previous experiments, the deactivation occurred more rapidly. Regarding the methanol formation, Spencer, M.S (1999) states that the alkaline property of ZnO removes acidic sites of alumina present in the fresh catalyst, preventing methanol to be further hydrogenated to other products (SPENCER, 1999). Even so, most likely due to the addition of γ-Al_2O_3 causing excess of acidity, other products besides methanol were detected by the Flame Ionization Detector (FID), even though these remain unknowns as the authors did not have the chromatography standards for the substance. This explains why the methanol STY obtained was lower, although CO_2 conversion was higher. Furthermore, it can be noted that the CO yield was significantly lower for the sample with γ-Al_2O_3, indicating that alumina may also have an inhibitory effect on the RWGS reaction.

Table 2: Results obtained with the Cu/Zn/Al + γ-Al_2O_3 physical mixture [Source: Results]

	Result
CO_2 conversion (%)	5,73
STY (mg MeOH/g cat. h)	138,44
CO yield (%)	32,26

4. Conclusion

The deactivation of the commercial Cu/Zn/Al catalyst and the effect of the addition of γ-Al_2O_3 on its performance in the methanol synthesis reaction was investigated. It was observed that alumina has a positive effect on the CO_2 conversion and CO yield, even though it generates other products besides methanol. The XRD analysis indicate that all samples undergone sintering, a common cause for copper catalysts deactivation both on research and industry contexts. In this sense, γ-Al_2O_3 may be an alternative to mitigate the deactivation effect thus improving the catalyst performance, and may also inhibit the RWGS side reaction. The results of the present work are relevant for optimizing the industrial methanol synthesis process, a highly relevant product for this century.

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References

ALVAREZ, A. et al. Challenges in the greener production of formates/formic acid, methanol, and dme by heterogeneously catalyzed co2 hydrogenation processes. *Chemical reviews*, ACS Publications, v. 117, n. 14, p. 9804–9838, 2017.

OLAH, G. A. Beyond oil and gas: the methanol economy. *Angewandte Chemie International Edition*, Wiley Online Library, v. 44, n. 18, p. 2636–2639, 2005.

SAEIDI, S.; AMIN, N. A. S.; RAHIMPOUR, M. R. Hydrogenation of co2 to value-added products—a review and potential future developments. *Journal of CO2 utilization*, Elsevier, v. 5, p. 66–81, 2014.

SPENCER, M. The role of zinc oxide in cu/zno catalysts for methanol synthesis and the water–gas shift reaction. *Topics in Catalysis*, Springer, v. 8, n. 3, p. 259–266, 1999.

TWIGG, M. V.; SPENCER, M. S. Deactivation of supported copper metal catalysts for hydrogenation reactions. *Applied Catalysis A: General*, Elsevier, v. 212, n. 1-2, p. 161–174, 2001.

WANG, J.; ZENG, C. Al2o3 effect on the catalytic activity of cu-zno-al2o3-sio2 catalysts for dimethyl ether synthesis from co2 hydrogenation. *Journal of natural gas Chemistry*, Science China Press, v. 14, n. 3, p. 156–162, 2005.

WANG, J. B.; LEE, H.-K.; HUANG, T.-J. Synergistic catalysis of carbon dioxide hydrogenation into methanol by yttria-doped ceria/γ-alumina-supported copper oxide catalysts: effect of support and dopant. *Catalysis Letters*, Springer, v. 83, n. 1, p. 79–86, 2002.

WITOON, T. et al. Effect of hierarchical meso–macroporous alumina-supported copper catalyst for methanol synthesis from co2 hydrogenation. *Energy Conversion and Management*, Elsevier, v. 103, p. 886–894, 2015.

YANG, H. et al. A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. *Catalysis science & technology*, Royal Society of Chemistry, v. 7, n. 20, p. 4580–4598, 2017.

YE, R.-P. et al. Co 2 hydrogenation to high-value products via heterogeneous catalysis. *Nature communications*, Nature Publishing Group, v. 10, n. 1, p. 1 – 15, 2019.