# Behavior of CZZr/S Catalysts on the Direct Synthesis of DME from $CO_2$ Containing Feeds
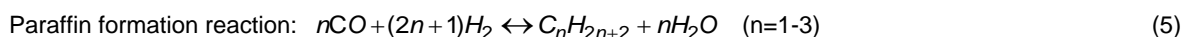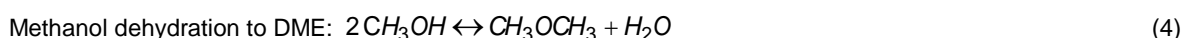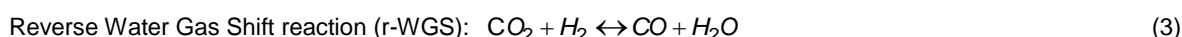
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The catalytic behavior of a $CuO$-$ZnO$-$ZrO_2$/SAPO-18 (CZZr/S) catalyst on the direct synthesis of DME for different feeds of $H_2$+$CO$+$CO_2$ has been studied in runs carried out in a fixed bed isothermal reactor. The effect of the operating conditions (temperature, pressure, $H_2/CO_x$ ratio and time on stream), and especially of $CO_2$ concentration in the feed on the conversion of $CO_X$ ($CO_2$+$CO$), product yield and selectivity, as well as on the coke content, responsible for deactivation, have been quantified. With this catalyst, at 275 ºC, moderate pressure of 30 bar and space time of 10.18 $g_{cat}h(mol_C)^{-1}$, $CO_X$ conversion of 0.28 and oxygenates selectivity (DME + MeOH) over 99 % can be obtained from feeds with a $CO_2/CO_X$ ratio of 0.25. The presence of $CO_2$ in the feed limits coke formation, and therefore, attenuates the deactivation of the catalyst.

## 1. Introduction

DME is receiving great interest in the last decades, not only as an environmentally friendly fuel and key intermediate for olefin or $H_2$ production, but also because its production is an alternative route for the large-scale valorization of $CO_2$ when it is fed together with syngas (Olah et al., 2009). Nowadays the direct synthesis of DME using bifunctional catalysts (STD process) is preferred over the conventional two-step process, due to the lower thermodynamic limitations and economical features (Ateka et al., 2016a), the process involves the reactions described in Eqs. (1) - (5).

CO hydrogenation: $CO + 2H_2 \leftrightarrow CH_3OH$ (1)

$CO_2$ hydrogenation: $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ (2)

Reverse Water Gas Shift reaction (r-WGS): $CO_2 + H_2 \leftrightarrow CO + H_2O$ (3)

Methanol dehydration to DME: $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ (4)

Paraffin formation reaction: $nCO + (2n+1)H_2 \leftrightarrow C_nH_{2n+2} + nH_2O$ (n=1-3) (5)

Seeking for active and stable catalysts for this purpose, the addition of $ZrO_2$ to the conventional $CuO$-$ZnO$ metallic function improves the dispersion of Cu and stability due to its good water tolerance (Bonura et al., 2014, 2013). On the other hand, SAPO-18 acid function has shown a good dehydration capacity, due to its homogeneous and moderate acidity, which is suitable for minimizing the formation of paraffins in this process (Ateka et al., 2016b, 2016c).
Bearing in mind the need of efficient catalysts for $CO_2$ valorization in the STD process, the aim of this work is to study the effect of the operating conditions, and especially of $CO_2$ concentration in the feed on the conversion of $CO_X$, product yield and selectivity over a $CuO$-$ZnO$-$ZrO_2$/SAPO-18 (CZZr/S) catalyst, as well as on the coke formation, responsible for deactivation.

## 2. Experimental

The CZZr/S bifunctional catalyst in prepared by physical mixing of the $CuO$-$ZnO$-$ZrO_2$ metallic function (for the synthesis of methanol from $CO_2$+$CO$ hydrogenation) and the SAPO-18 acid function (for the selective

dehydration of the formed methanol to DME) described in detail elsewhere (Ateka et al., 2016b). The metallic function has been synthesized following a conventional co-precipitation method from the corresponding Cu, Zn and Zr nitrates and $Na_2CO_3$ aqueous solution, dried (at room temperature for 12 h and at 110 ºC for 12 h) and calcined at 300 ºC for 3h. The acid function has been prepared by crystallization using $Al(OH)_3$, $H_3PO_4$ and $SiO_2$ as Al, P and Si sources respectively, using $C_8H_{19}N$ as organic template, dried (following the same two stage drying procedure) and calcined at 550 ºC for 5 h. The final catalyst has been prepared by mixture of both individual functions using a metallic/acid mass ratio of 2/1, finely grinded, pelletized and sieved to a particle size of 125-500 µm. This catalyst requires a treatment *in situ* in the reactor prior to reaction, which consists of a reduction in $H_2$ atmosphere in order to reduce CuO to the active species in this process, that is, $Cu^0$. The individual functions and the final bifunctional catalyst have been characterized using the following techniques: i) $N_2$ adsorption-desorption analyses to determine the physical properties; ii) X-Ray fluorescence and Inductive Coupling Plasma-Masss Espectrometry to determine the Cu:Zn:Zr ratio (2:0.75:1.5); iii) Selective chemisroption of $N_2O$ to quantify the metallic surface and Cu dispersion; and iv) Thermogravimetric/calorimetric analyses of $NH_3$ adsorption to determine the acid properties. The results of the characterization have been summarized in Table 1. The total coke content has been determined by means of TPO analyses recording the $CO_2$ signal in a mass spectrometer (Gayubo et al., 2014).

The runs have been carried out in a high pressure automated isothermal reaction equipment (PID Eng. & Tech. Microactivity) provided with a fixed bed reactor, connected online to a Varian CP4900 gas-chromatograph for the analysis of the reaction products (Ateka et al., 2016b), under the following operating condition ranges: $CO_2/CO_X$ molar ratio in the feed, 0-0.5; $H_2/CO_X$ molar ratio in the feed, 3-4; 250-300 ºC; 20-30 bar; space time, 10.18 $g_{cat}$ h $(mol_C)^{-1}$; time on stream, up to 30 h.

The studied reaction indexes have been defined as follows:

Conversion of $CO_X$ ($CO_2+CO$):
$$X_{COx} = \frac{F^0_{CO_x} - F_{CO_x}}{F^0_{CO_x}}$$
(6)

Product yield (DME, MeOH, $C_1$-$C_3$ paraffins):
$$Y_i = \frac{n_i - F_i}{F^0_{CO_x}} \cdot 100$$
(7)

Product selectivity (DME, MeOH, $C_1$-$C_3$ paraffins):
$$S_i = \frac{n_i \cdot F_i}{\sum_i n_i \cdot F_i} \cdot 100$$
(8)

*Table 1: Physical, metallic and acid properties of the fresh individual functions and bifunctional catalyst*

| | Physical properties | | | Metallic surface | | | Acid properties | |
|---|---|---|---|---|---|---|---|---|
| | $S_{BET}$ $(m^2g^{-1})$ | $V_{micropore}$ $(cm^3g^{-1})$ | $V_p$ $(cm^3g^{-1})$ | $S_{Cu}$ $(m^2g_{Cu}^{-1})$ | $S'_{Cu}$ $(m^2g_{cat}^{-1})$ | $Cu_{disp.}$ (%) | Average acid strength $(kJ\ mol_{NH3}^{-1})$ | Total acidity $(mmol_{NH3}\ g^{-1})$ |
| CZZr | 123 | - | 0.301 | 78.1 | 22.4 | 12.0 | - | - |
| S | 480 | 0.160 | 0.390 | - | - | - | 130 | 0.42 |
| CZZr/S | 223 | 0.051 | 0.248 | 72.3 | 13.8 | 11.1 | 110 | 0.16 |

## 3. Results and discussion

### 3.1 Feeds composed of $H_2+CO$

The effect of reaction temperature on the reaction indexes at zero time on stream has been studied within the 200-300 ºC range under fixed operating conditions: feed, syngas ($H_2+CO$); $H_2/CO$ ratio, 3; pressure, 30 bar; space time, 10.18 $g_{cat}h(mol_C)^{-1}$; time on stream, 5 h.

In Figure 1 the results of CO conversion and product yield and selectivity are depicted. These results point out that the maximum DME yield and selectivity (36.3 % and 95.8 %, respectively) are obtained at 275 ºC.

Moreover, it is noteworthy that for higher temperatures, paraffin formation starts being significant, which is indicative of the incipient activation of the hydrocarbon pool mechanism. This is to be avoided in this process, since it will give way to the formation of coke species. This effect is more evident in Figure 1c and also when analyzing the evolution of product yield with time on stream (results not shown), where the effect of catalyst deactivation is noteworthy at 300 ºC, as a consequence of coke deposition blocking the active sites of the metallic function, thus, limiting the first step of methanol formation. These results evidence the good kinetic behavior of the CZZr/S catalyst at 275 ºC, with a good compromise between high selectivity to DME, negligible paraffin formation ($C_1$-$C_3$ paraffins) and stability. These results are better than those obtained with the conventional $CuO-ZnO-Al_2O_3/\gamma-Al_2O_3$ (CZA/A) catalyst (Sierra et al., 2010).
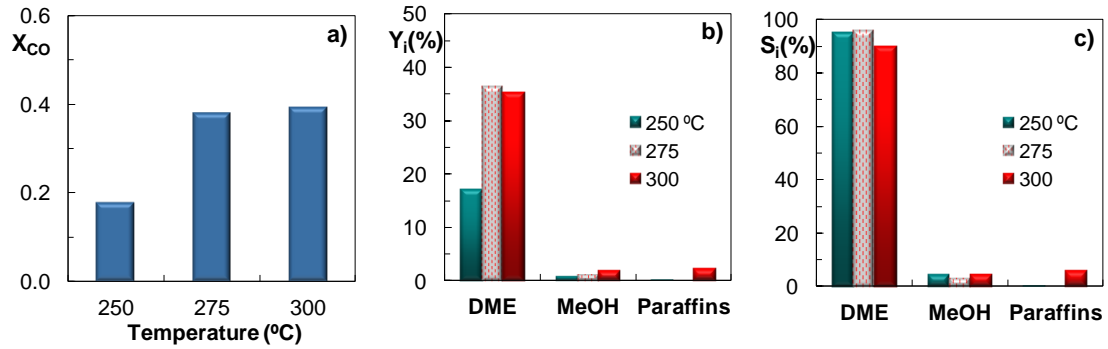
*Figure 1: Effect of reaction temperature on the conversion of CO (a), product yield (b) and selectivity (c). Reaction conditions: 30 bar; 10.18 $g_{cat}$ h $(mol_C)^{-1}$; feed, $H_2+CO$ with a $H_2/CO$ molar ratio of 3.*

The effect of reaction pressure has been studied between 20-40 bar, at 275 ºC and the same operating conditions previously used.

The results of CO conversion and product yield and selectivity are shown in Figure 2. The overall reaction of the process goes through mole number reduction, and consequently, higher pressure enhances the conversion of CO. However, it can be observed in Figure 2 that the effect of this operating condition goes gradually fading, that is, it follows an asymptotic trend and pressure higher than 30 bar does not lead to significant improvement of the reaction indexes to compensate the operating costs.
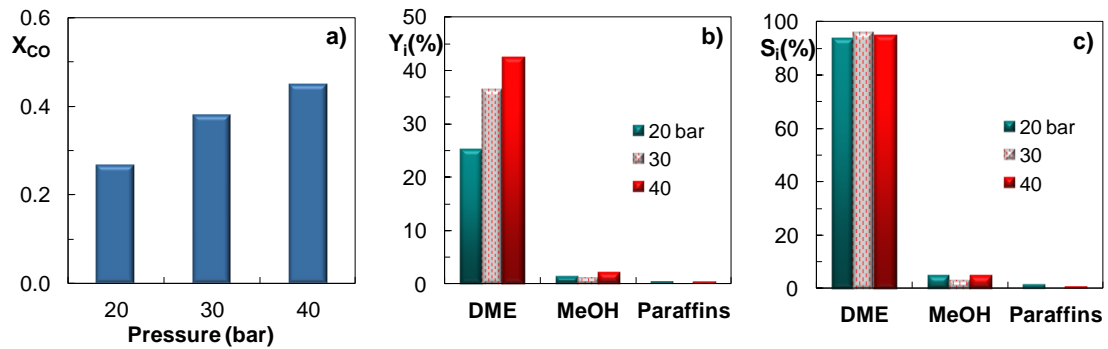


*Figure 2: Effect of reaction pressure on the conversion of CO (a), product yield (b) and selectivity (c). Reaction conditions: 275 ºC; 10.18 $g_{cat}$ h $(mol_C)^{-1}$; feed, $H_2+CO$ with a $H_2/CO$ molar ratio of 3.*

Based on the results and the works in literature where the reaction indexes hardly change above the highest pressure value studied here, a moderate pressure of 30 bar has been selected as suitable, since DME selectivity over 95 % is obtained with negligible paraffin formation.

### 3.2 Feeds composed of $H_2+CO+CO_2$

In the current scenario in which the utilization of $CO_2$ in chemical processes in order to obtain added value products is the pursued goal, the study of the $CO_2$ concentration in the feed is one of the key points for the viability of this process. Consequently, especial attention has been paid to the effect of the $CO_2/CO_X$ ratio in the feed not only over the reaction indexes, but also on the coke content (in the succeeding Section 3.4), responsible for catalyst deactivation. In this section, $CO_X$ conversion and product distribution have been studied for different contents of $CO_2$ in the $H_2+CO+CO_2$ feed, from 0 (syngas, $H_2+CO$) to 0.5 (50 % $CO_2$ + 50 % CO).

The results in Figure 3 evidence that the increase of the $CO_2/CO_X$ ratio in the feed leads to a decrease in the conversion of $CO_X$. Besides, it does not significantly affect product distribution, since the selectivity of DME is over 88 % in all cases, and moreover, the selectivity of oxygenates (DME + MeOH) is almost constant in all cases (above 99 %), indicating the $CO_2$ content in the feed has no effect on the selectivity.

Moreover, it should be noted that all the DME yields obtained with the CZZr/S catalyst, also that obtained using the feed with the highest content of $CO_2$, are higher than those reported in literature for conventional (CZA/A) bifunctional catalysts (Sierra et al., 2010).
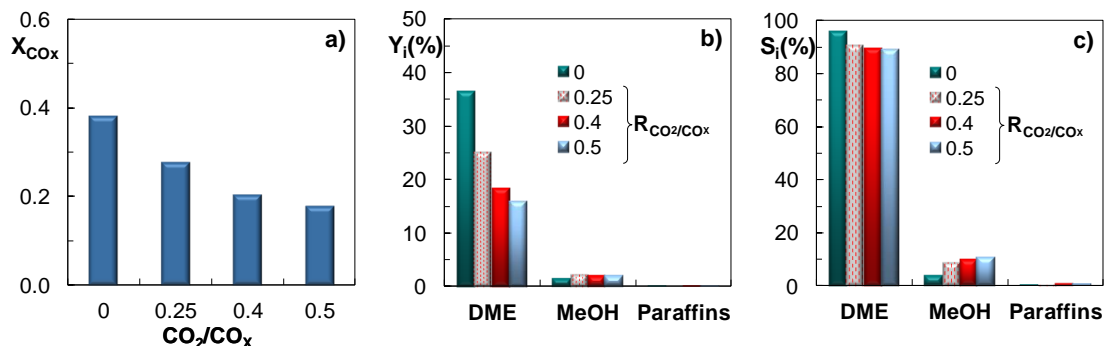
*Figure 3: Effect of $CO_2/CO_X$ molar ratio in the feed on the conversion of $CO_X$ (a), product yield (b) and selectivity (c). Reaction conditions: 275 ºC; 30 bar; 10.18 $g_{cat}$ h $(mol_C)^{-1}$; feed, $H_2+CO+CO_2$ with a $H_2/CO_X$ molar ratio of 3.*

### 3.3 Role of $H_2/CO_X$ molar ratio in the feed

This Section pretends to assess the possible upgrading in the reaction indexes with a higher $H_2/CO_X$ molar ratio than that used in the preceding sections. However, the results in Figure 4 suggest that $H_2$ rich feeds do not lead to any improvement in the kinetic performance of this catalyst, regardless the $CO_2/CO_X$ ratio in the feed. What is more, lower $CO_X$ conversion and DME yield values have been registered for the runs carried out with $H_2/CO_X= 4$ and $CO_2/CO_X$ ratio below 0.4.
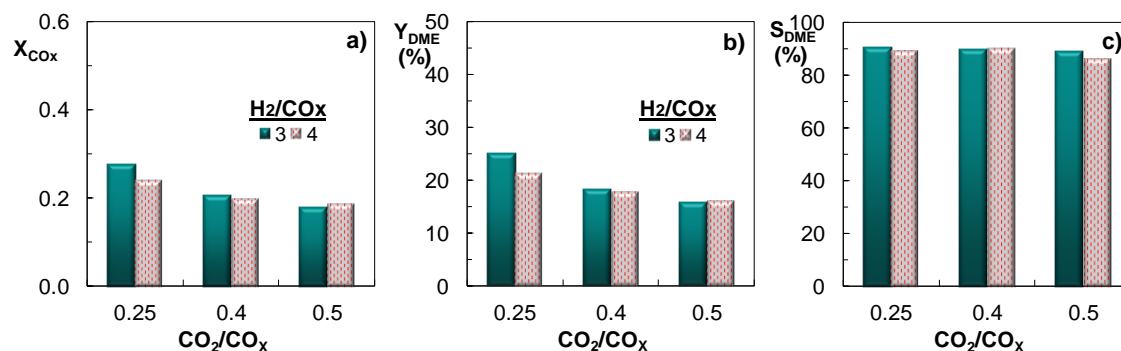


*Figure 4: Effect of the $H_2/CO_X$ ratio on the conversion of $CO_X$ (a), product yield (b) and selectivity (c) for different $CO_2/CO_X$ molar ratios in the feed. Reaction conditions: 275 ºC; 30 bar; 10.18 $g_{cat}$ h $(mol_C)^{-1}$; feed, $H_2+CO+CO_2$.*

### 3.4 Coke deposition

Aiming at the progress in the knowledge of the behavior of the CZZr/S catalyst, the effect of the $CO_2$ content on the feed on the deposited coke content and location has been studied. The content and location of coke conditions the deactivation of the catalyst. Ereña et al. (2008) identify by deconvolution of the TPO profiles three fractions in the coke deposited in a CZA/A catalyst. These authors attribute deactivation to the coke fraction deposited on the metallic function since the catalyst has been prepared with excess of acid function, as in this case, in order to ensure the displacement of the dehydration of methanol to DME. Figure 5a shows as an example the TPO profile and curve deconvolution for a catalyst used in a reaction under the following conditions: 275 ºC, 30 bar, 10.18 $g_{cat}$ h $(mol_C)^{-1}$; $H_2/CO_X$, 3, $CO_2/CO_X$, 0.4. The first type of coke, with a peak maximum at 160 ºC (lowest temperature) is presumably located on the metallic function, which catalyzes the combustion of coke. The second type, has a peak maximum at 200 ºC, and is located on the interface between both individual functions; and type 3, is located in a longer distance to the metallic function, thus, in the acid function, with the combustion peak maximum at 325 ºC. The coke fraction corresponding to this third peak is the most condensed (lowest H/C ratio), due to the capability of the acid sites to catalyze the reactions of hydrocarbon condensation (olefins and aromatics), which are the coke precursors.

Figure 5b shows the effect of the $CO_2/CO_X$ molar ration in the feed on the total coke content deposited on the catalysts after 5 h of reaction, and the distribution of the three different types of coke determined from the

deconvolution of the corresponding TPO curves. From these results, it is evident that increasing $CO_2$ concentration in the reaction medium limits noteworthy the formation of coke, thus, attenuates deactivation, which is consistent with the paraffin formation previously mentioned. This fact is a direct consequence of the higher water content in the reaction medium, resulting from the WGS reaction (Sierra et al., 2011). Among the differences in the coke type distribution regarding the $CO_2/CO_X$ ratio fed, it can be observed that the higher $CO_2$ content in the feed, the higher is the fraction of coke type 2 and coke type 3, what means, that besides the total coke amount is way lower than for syngas feeds, its nature is more evolved. Sierra et al. (2011) have studied the role of water in the reaction medium to attenuate coke formation. This attenuation results from the control of the formation of methoxy ions by the adsorption of methanol and DME on the active sites (both on metallic and acid sites) of the catalyst. Methoxy ions are considered to be the active intermediates in the hydrocarbon pool mechanism for the formation of the coke precursors. It can be observed in Figure 5b that the increase of the $CO_2$ content in the feed, results in a sharp decrease of the total content and of each of the fractions of the deposited coke, indicating that the coke formation steps both in the metallic and acid sites are inhibited.
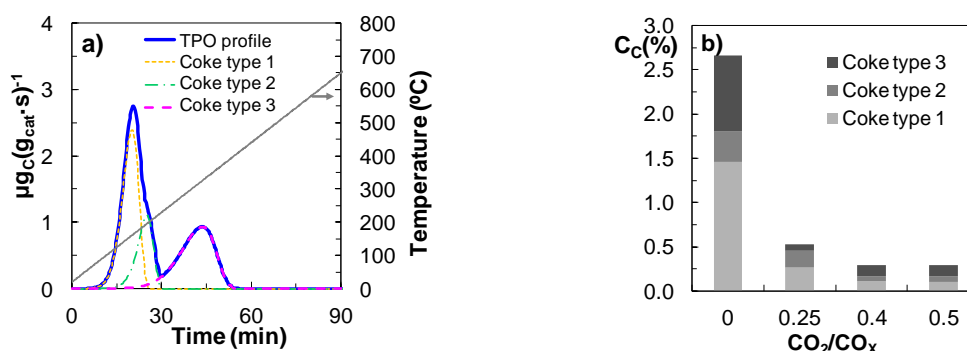


*Figure 5: Identification of the three types of coke by TPO curve deconvolution of a catalyst used in a reaction with the following operating conditions: 275 ºC; 30 bar; 10.18 $g_{cat}$ h $(mol_C)^{-1}$; $H_2/CO_X$, 3; $CO_2/CO_X$, 0.4 (a) and effect of $CO_2/CO_X$ molar ratio in the feed on the coke content (b).*

## 4. Conclusions

CZZr/S catalyst shows a good kinetic performance in the selective hydrogenation of $CO_2+CO$ to DME at 275 ºC and moderate pressure of 30 bar, attaining $CO_X$ conversion values of 0.28 and DME yield and selectivity values of 25 % and 90.3 % respectively, for $H_2+CO_2+CO$ feeds with a $CO_2/CO_X$ ratio of 0.25. The increase of the $H_2/CO_X$ molar ratio in the feed above 3 does not boost the kinetic behavior of the catalyst, therefore, using hydrogen rich feeds is not economically worth it.

However, it should be noted that the DME yields obtained with the CZZr/S catalyst co-feeding $CO_2$ are higher than the yields obtained with a conventional catalyst (CZA/A) feeding $H_2+CO$. On the other hand, although co-feeding $CO_2$ decreases $CO+CO_2$ conversion, and consequently also DME yield, it does not affect the selectivity of oxygenates (DME + MeOH). In addition, co-feeding $CO_2$ diminishes coke deposition on the catalyst, which is interesting for the viability of the process, since it is conditioned by the deactivation of the catalyst.

### Acknowledgments

### Abbreviations

| | |
|---|---|
| $C_1$-$C_3$ | Paraffins with 1 to 3 carbon atoms. |
| $C_C$ | Coke content, wt %. |
| DME, MeOH | Dimethyl ether and methanol, respectively. |
| $F^0_{CO_X}$, $F_i$ | Molar flow rate of $CO_X$ in the feed and of i component in the reactor outlet stream, respectively, $mol_C$ $h^{-1}$. |

| | |
|---|---|
| $n_i$ | Number of carbon atoms in the i product. |
| P | Pressure, bar. |
| $S_{BET}$ | BET specific surface area, $m^2 g^{-1}$. |
| $S_{Cu}$, $S'_{Cu}$ | Cu specific surface area, $m^2 g_{Cu}^{-1}$ and $m^2 g_{cat}^{-1}$, respectively. |
| T | Temperature, ºC. |
| $V_{micropore}$, $V_p$ | Micropore volume and total pore volume, respectively, $cm^3 g^{-1}$. |
| $X_{COx}$ | Conversion of $CO_X$, in C units. |
| $Y_i$, $S_i$ | Yield and selectivity of i component, respectively, %. |

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