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Effect of operating conditions on the synthesis of dimethyl ether over a CuO-ZnO-Al_2O_3/NaHZSM-5 bifunctional catalyst

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Abstract

The effect of operating conditions (time on stream, temperature, pressure and space time) on the conversion of CO and CO_2, selectivity to dimethyl ether (DME), yield of DME and product distribution is studied in the DME synthesis from H_2, CO and CO_2 in a single reaction step on a CuO-ZnO-Al_2O_3/NaHZSM-5 bifunctional catalyst. CO conversion is total at 275 °C and 40 bar, with a selectivity to DME of 80% and a yield of DME of 78%, for a space time of 67 (g of catalyst) h/mol of (H_2 + CO) and for a feed made up of H_2/CO = 2/1. Catalyst deactivation under these conditions is insignificant, even when CO_2 is fed and there is a high water concentration in the medium.

Keywords: Dimethyl ether; Syngas; CO_2; Bifunctional catalyst

1. Introduction

DME has certain advantages over methanol as an intermediate product for the valorization of alternative resources to oil via syngas and fewer geographic limitations (coal, natural gas, biomass). Shikada et al. [1] estimated that the production cost of DME from natural gas is 20% lower than the cost corresponding to the production of methanol. DME is a relatively inert compound, non-corrosive for metals (although it attacks rubber and its by-products) and it is not carcinogenic. Its toxicity is much lower than that of methanol [2]. Its physical properties are similar to those of LPG and, consequently, it may be stored and handled under the same conditions as those of easily transported domestic gases [3]. Consequently, it is a raw material that has been successfully used as a substitute for methanol in the production of light olefins [4].

DME is a well-known propellant and coolant and an alternative fuel for diesel engines due to its good properties, such as its high cetane index (>55) and the low emission of CO, NO_x and particulates in its combustion [5,6]. Moreover, as a substitute for LPG, it has the same possibilities for distribution and use in rural areas [7]. In addition to its easy storage for transportation, its volatile nature facilitates its use as a hydrogen source for fuel cells by means of catalytic reforming [8].

Three reactions take place in the syngas-to-DME process:

Methanol synthesis reaction: $CO + 2H_2 \Leftrightarrow CH_3OH$;
Methanol dehydration reaction: $2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$;
Water shift reaction: $CO + H_2O \Leftrightarrow CO_2 + H_2$.

The obtaining of dimethyl ether (DME) in one reaction step using a bifunctional catalyst consisting of a metallic function (composed of oxides such as CuO, ZnO, Al_2O_3 and Cr_2O_3) for the synthesis of methanol and of an acid function (such as γ-Al_2O_3, HZSM-5 or HY zeolites, SAPOs) for the transformation of methanol into DME improves the yield of DME over the two-step process, due to the fact that the dehydration of methanol in the same reactor displaces the equilibrium of the synthesis reaction [9,10]. Consequently, the new process may be carried out at a higher temperature and lower pressure than the synthesis of methanol. Furthermore, the incorporation of CO_2 together with syngas

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DME	dimethyl ether
n_{Ci}	number of carbon atoms for each *i* hydrocarbon in the reactor outlet stream
n_{DME}, n_M	flowrate of DME and methanol in the reactor outlet stream (mol/s)
n_i	flowrate of each *i* hydrocarbon in the reactor outlet stream (mol/s)
$(n_{CO})_0$, n_{CO}	flowrates of CO in the feed and in the reactor outlet stream (mol/s)
$(n_{CO_2})_0$, n_{CO_2}	flowrates of CO_2 in the feed and in the reactor outlet stream (mol/s)
$(n_{CO})_F$, $(n_{CO_2})_F$	flowrates of CO and CO_2 formed in the reaction (mol/s)
S_{DME}	selectivity to DME (Eq. (3))
X_{CO}, X_{CO_2}	conversion of CO (Eq. (1)) and of CO_2 (Eq. (2))
Y_{DME}	yield of DME (Eq. (6))

is thermodynamically more favourable than in the synthesis of methanol [11,12], which is positive for the large-scale sequestration of CO_2. The CO_2 fed intervenes in the previous water shift reaction and also in a methanol synthesis reaction:

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$$

The single step DME synthesis process has been studied in a three-phase slurry reactor and in a gas–solid contactor. In the former case, a paraffin is used to suspend the catalyst, which causes severe limitations on the mass transfer between phases and, consequently, the apparent activation energy is very low [13,14]. Furthermore, as in the synthesis of methanol [15], the equipment required in the former case is more sophisticated because, in addition to the three-phase slurry reactor, a recycling system and a gas–liquid separator are required.

Gas–solid contact allows for eliminating the diffusional restrictions between phases. The more commonly used reactor, either at laboratory or pilot scale, is that of fixed bed [9,10,16–19]. Nevertheless, given the high exothermallity of the two steps carried out simultaneously, the fluidized bed is more suitable for scaling up [20]. The main objective is the attainment of high conversion without the need for recirculation and under moderate pressure. Given that it is a reversible reaction, operation in a fixed bed reactor is an interesting alternative that allows for using an optimum longitudinal profile of temperature, which will be decreased from the inlet to the outlet of the reactor [21]. Thus, the reaction rate is high near the inlet (conversion is far from that limited by thermodynamics) and, by decreasing temperature along the reactor, high conversion is attained at the inlet. Nevertheless, this strategy requires a detailed knowledge of kinetic modelling.

In this paper, the effect of the operating conditions (time on stream, temperature, pressure and space time) on the yields of products and selectivity to DME has been studied in the transformation of H_2, CO and CO_2 on a hybrid catalyst made up of CuO-ZnO-Al_2O_3 and NaHZSM-5 zeolite. The selection of this acid function is especially noteworthy, given that it has been chosen because the HZSM-5 zeolite has no activity limitations due to water adsorption, as in the case of γ-Al_2O_3 [22]. This feature is important when CO_2 is fed in a significant amount, given that water is formed by the water shift reaction and in the synthesis of methanol. Nevertheless, the HZSM-5 zeolite is active, even with a high Si/Al ratio, for the transformation of DME into hydrocarbon by-products (with ethene and propene as primary products), following the well-known mechanism of the methanol to gasoline (MTG) process [23,24]. These hydrocarbons partially evolve into heavy structures (coke) and block the zeolite pores and cause its deactivation. This deactivation is slow due to the high partial pressure of hydrogen that attenuates the mechanisms of coke formation. It has been proven [25] that a suitable concentration of Na in the zeolite moderates the number and acid strength of Brönsted sites in the HZSM-5 zeolite and stops the formation of hydrocarbons from DME. Besides, the optimum acidity required in the single step synthesis of DME is lower than that required for maximizing the yield of DME in the dehydration of methanol [26].

2. Experimental

The active function for the synthesis of methanol is a catalyst made up of CuO-ZnO-Al_2O_3, which has been prepared by coprecipitation at pH 7.0 of the corresponding metallic nitrates with Na_2CO_3 [27]. NaHZSM-5 zeolite has been tried as acid function for methanol dehydration. This zeolite has a low acid strength, which minimizes the proportion of light olefins. The elimination of Na^+ cation in the NaZSM-5 zeolite is only partial and is carried out by ion interchange with 1 M solution of NH_4Cl [28]. In Table 1, the physical properties of the metallic function and of the acidic function of the catalyst determined by nitrogen adsorption–desorption (Micromeritics ASAP 2000) are set out.

Table 1
Properties of the individual functions of the catalyst

Catalyst	BET surface ($m^2\ g^{-1}$)	Micropore surface ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)	Average pore diameter (Å)
CuO-ZnO-Al_2O_3	54	5.9	0.21	0.0026	158.0
NaHZSM-5	474	456.0	0.63	0.23	5.6

The final CuO-ZnO-Al_2O_3/NaHZSM-5 bifunctional catalysts have been prepared by mixing the two functions in aqueous solution (Fig. 1). Subsequently, the suspension is filtered and the solid is washed, dried (in two steps, at 20 and 120 °C for 12 h each step) and calcined (350 °C, 6 h). A mass ratio between the metallic function and the acid one of 4/1 has been chosen, which is the ratio that provides the higher values of conversion and selectivity to DME [28]. The catalyst has an acidity of 0.1 (mmol of NH_3) g^{-1}.

Prior to use, the bifunctional catalysts have been subjected to an equilibration treatment by oxidation–reduction in the reactor itself, which consists of successively exposing them to different streams: (a) a H_2 stream diluted in He (at 10%) at 200 °C for 14 h and (b) a H_2 stream diluted in He (at 20%) at 300 °C for 1 h. The runs have been repeated three times. In the figures corresponding to the experimental results, the values plotted are the average ones, and error bars corresponding to 95% confidence interval have been drawn.

The reaction equipment used, Autoclave Engineers BTRS Jr., allows for working up to 100 bar and up to 650 °C. The reactants are introduced into the reaction oven through a mixer that preheats to 280 °C. The reactor is an isothermal fixed-bed of 6.4 mm internal diameter, 152.4 mm length and with a volume for the catalyst of up to 5 cm^3. The temperatures in the bed and on the internal wall of the reactor are controlled by means of a Eurotherm 847 temperature controller. The flowrates of H_2, CO and CO_2 are controlled by Brooks 5850 mass flow-meters. The reaction mixture is passed through several purifiers to eliminate possible traces of oxygen, water and iron carbonyl that may deactivate the catalyst.

The on-line analysis of reaction products has been carried with an Agilent 6890 gas chromatograph, provided with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The chromatograph is also provided with three columns for the separation of the products into different fractions: a semicapillary column (HP-1 Cross-linked Methyl Silicone, 15 m × 0.530 mm ×1.50 μm) in which the products are separated into the fractions that will be characterized in the TCD and in the FID; a packed column (HP-PLOT/Molsieves15A 30 m × 0.53 mm × 25.0 μm) for the separation of the oxygenate products (methanol and DME) and gases (H_2, CO, CO_2 and methane); a capillary column (PONA Methyl Siloxane, 50 m × 0.20 mm × 0.50 μm) for the separation of hydrocarbons analyzed in the FID (mainly C_2–C_4 paraffins). The collection and the subsequent analysis of the data is carried out by means of Hewlett-Packard software. The transformation of the values of chromatographic peak areas into values of mass is carried out with specific factors.

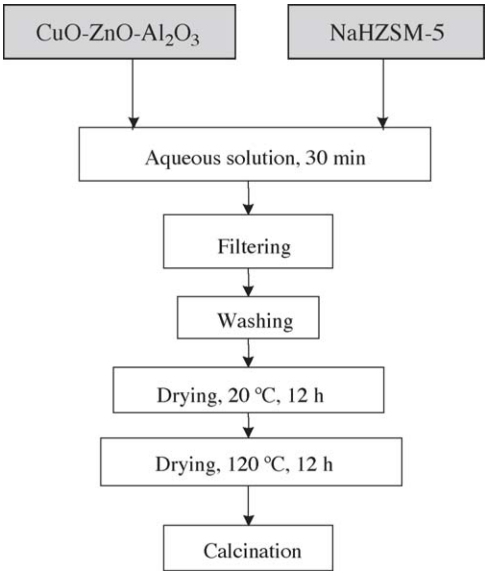

Fig. 1. Preparation of the CuO-ZnO-Al_2O_3/NaHZSM-5 bifunctional catalyst.

The components in the product stream have been identified by coupling an Agilent 6890 gas chromatograph on-line to a Hewlett-Packard 5890 mass spectrometer.

3. Results and discussion

The conversion of CO (X_{CO}) has been calculated by using the flowrates of CO in the feed, $(n_{CO})_0$ and in the reactor outlet stream, n_{CO}:

$$X_{CO} = \frac{(n_{CO})_0 - n_{CO}}{(n_{CO})_0} \times 100 \tag{1}$$

Similarly, the conversion of CO_2 is calculated as follows:

$$X_{CO_2} = \frac{(n_{CO_2})_0 - n_{CO_2}}{(n_{CO_2})_0} \times 100 \tag{2}$$

The selectivity to DME (S_{DME}) is determined as the ratio (expressed in wt%) between the content of carbon in the product DME and the sum of carbon contents corresponding to all the products formed that are present in the reactor outlet stream:

$$S_{DME} = \frac{2n_{DME}}{\sum_i n_{Ci}n_i + 2n_{DME} + n_M + (n_{CO})_F + (n_{CO_2})_F} \times 100 \tag{3}$$

where n_{DME} and n_M are the molar flowrates of DME and methanol in the outlet stream, n_{Ci} the number of carbon atoms for each of the hydrocarbons and n_i is the molar flowrate of these hydrocarbons. The terms $(n_{CO})_F$ and $(n_{CO_2})_F$ correspond to the molar flowrates of CO and CO_2, respectively, formed in the reaction and they are calculated by the difference between the flowrates measured at the reactor outlet, n_{CO} and n_{CO_2}, and the values corresponding to the feed, $(n_{CO})_0$ and $(n_{CO_2})_0$:

$$(n_{CO})_F = n_{CO} - (n_{CO})_0 \tag{4}$$

$$(n_{CO_2})_F = n_{CO_2} - (n_{CO_2})_0 \tag{5}$$

The terms $(n_{CO})_F$ and $(n_{CO_2})_F$ are only considered in Eq. (3) when they have positive values.

The yield of DME (Y_{DME}) is measured as the percentage of carbon atoms fed in CO and CO_2 that converts to DME:

$$Y_{DME} = \frac{2n_{DME}}{(n_{CO} + n_{CO_2})_0} \times 100 \qquad (6)$$

where $(n_{CO} + n_{CO_2})_0$ is the sum of molar flowrates of CO and CO_2 in the feed.

Prior to studying the effect of operating conditions, an analysis has been made of the restrictions of internal diffusion, through the catalyst pores, and external diffusion, through the stationary outside particle layer. From a kinetic point of view, the reaction of transformation of syngas and CO_2 into DME is relatively slow and, consequently, there should be no internal or external diffusion restrictions and the gaseous mixture should reach the whole volume of the catalyst without concentration gradients. In order to confirm this aspect, runs have been carried out varying the particle size (0.2, 0.45 and 0.9 mm) and the molar flowrate of the reactants (0.5, 1.0 and 2.0 mmol of $(H_2 + CO + CO_2)$/min) and maintaining the remaining operating conditions constant at the following values: time on stream, 6 h; temperature, 275 °C; pressure, 40 bar; molar flowrate of reactants, 1 mmol of $(H_2 + CO + CO_2)$/min; $H_2/CO/CO_2$ molar ratio in the feed, 3/1.5/1; space time, 33.33 (g of catalyst) h/mol of $(H_2 + CO + CO_2)$. It is observed that under these operating conditions the reaction is not affected by diffusional restrictions.

3.1. *Effect of time on stream: equilibration period*

A characteristic of the metallic functions used for syngas and CO_2 transformation is the existence of an initial period for which catalyst equilibration occurs as a consequence of the oxidation–reduction of metallic active sites [27]. In this period, catalyst activity increases until a stable condition is reached and, subsequently, the behaviour of the catalyst is only altered by slow deactivation. The duration of this period of catalyst activation depends on operating conditions and especially on specific variables, such as the composition of the catalyst and of the feed and the pretreatment of the catalyst. In order to illustrate the existence of this period, the evolution of CO_2 conversion with time on stream is shown in Fig. 2a for different H_2/CO_2 molar ratios in the feed. Fig. 2b shows the results corresponding to the evolution of DME yield with time on stream for the ratio of $H_2/CO_2 = 3/1$. The results correspond to the following reaction conditions: temperature, 275 °C; pressure, 40 bar; molar flowrate of reactants, 1 mmol of $(H_2 + CO_2)$/min; space time, 33.33 (g of catalyst) h/mol of $(H_2 + CO_2)$.

All the results shown afterwards correspond to the pseudosteady state in which the reactant conversion reaches a maximum. This state is reached after a period of approximately 2 h (as is shown in Fig. 2). Deactivation is insignificant in the 6 h experimentation shown in Fig. 2. In the 12 h experimentation, the coke content deposited on the porous structure of the catalyst is significant only for the ratio of $H_2/CO_2 = 1/1$. This low coke deactivation is explained by the hydrocracking of coke precursors under the reaction conditions. Moreover, taking into account that deactivation is a factor that conditions the use of acid functions in oxygenate transformation reaction (as the secondary reactions of this process), from the point of view of industrial operation, catalyst use time may be increased by raising the content of NaHZSM-5 zeolite.

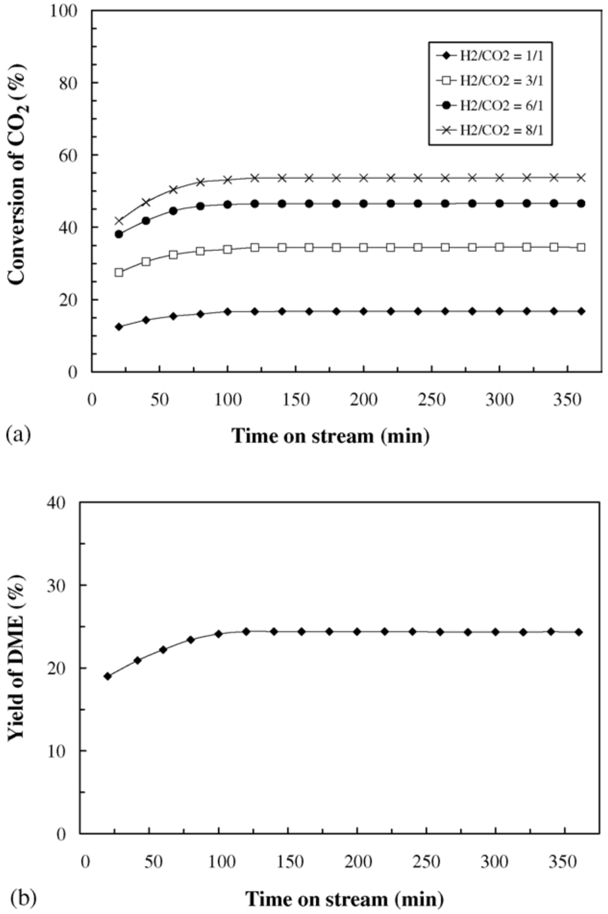

Fig. 2. Initial evolution with time on stream of CO_2 conversion for different H_2/CO_2 molar ratios in the feed (graph a) and of DME yield (graph b) on $CuO-ZnO-Al_2O_3$/NaHZSM-5 bifunctional catalysts.

3.2. *Effect of temperature*

Runs have been carried out by varying the temperature in the 175–350 °C range and maintaining the remaining operating variables constant at the following values: time on stream, 6 h; pressure, 40 bar; molar flowrate of reactants, 1 mmol of $(H_2 + CO + CO_2)$/min; $H_2/CO/CO_2$ molar ratio in the feed, 3/1.5/1; space time, 33.33 (g of catalyst) h/mol of $(H_2 + CO + CO_2)$. In each one of the dynamic runs, temperature has been varied throughout the reaction.

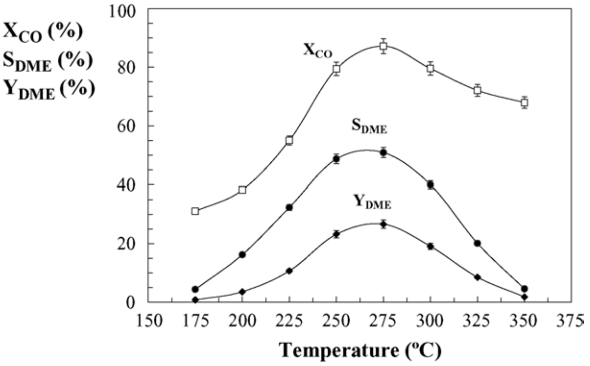

Fig. 3. Effect of temperature on CO conversion (X_{CO}), selectivity to DME (S_{DME}) and yield of DME (Y_{DME}).

Furthermore, two runs have been carried out at constant temperature (275 and 300 °C) and it has been observed that the results are similar to those corresponding to the dynamic runs.

The effect of temperature on CO conversion and on the selectivity to DME and yield of DME is very important (Fig. 3). The low conversion of CO at low temperatures is due to the competitive adsorption between CO and CO_2 on the metallic function of the catalyst. The decrease in conversion as temperature is increased above 275 °C is due, firstly, to the thermodynamic restrictions of the exothermal reaction and secondly, to Cu sintering, which provokes partial loss of catalyst activity [29–31].

Fig. 4 shows the effect of temperature on product distribution (CO_2, DME, methanol and hydrocarbons, which are, according to concentration order and at 275 °C, butane $>$ methane $\gg$ propane $>$ ethane $>$ pentane $>$ hexane). The highest concentration of oxygenates (methanol and DME) is obtained in the 250–300 °C range. Above 300 °C, hydrocracking reactions are favoured, which means that the production of light paraffins (especially methane) becomes important, which leads to a sharp decrease in the selectivity to DME. The cracking of DME produces water, which reacts with CO and gives way to an increase in the yield of CO_2 observed above 275 °C. In view of these results, the temperature of 275 °C has been taken as optimum.

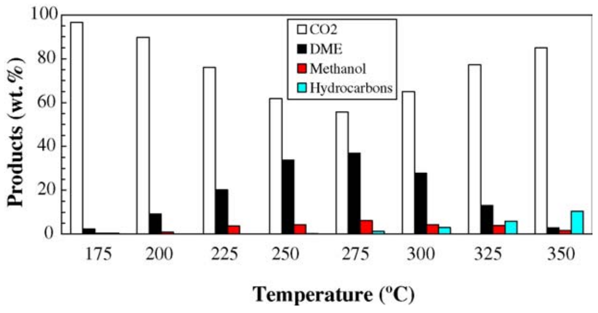

Fig. 4. Effect of temperature on product distribution.

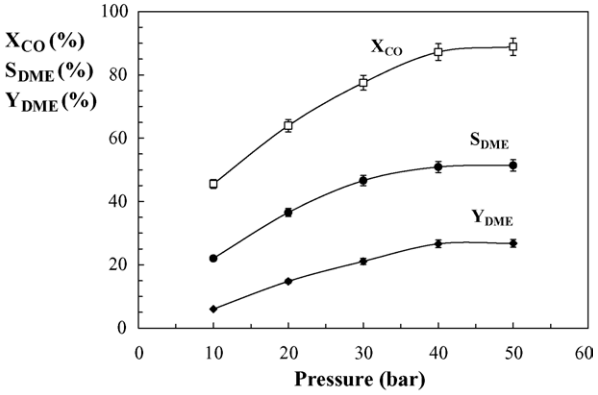

Fig. 5. Effect of pressure on CO conversion (X_{CO}), selectivity to DME (S_{DME}) and yield of DME (Y_{DME}).

3.3. Effect of pressure

Fig. 5 shows the influence of pressure on the conversion of CO and on the selectivity to DME and yield of DME. The results correspond to 275 °C and the remaining operating conditions have been maintained constant at the values used in the experiments described in Section 3.2. As is observed, when pressure is increased in the range from 10 to 50 bar the conversion of CO increases, which is the logical consequence whereby methanol synthesis is the limiting step of the overall reaction. This implies that the reaction of DME production may be carried out under a similar pressure as in the conventional synthesis of methanol.

Jia et al. [32] carried out the direct synthesis of DME under pressures of up to 100 bar and they observed that reaction parameters hardly change above 50 bar. They obtained similar results as those obtained in this paper.

As pressure is increased, the content of CO_2 in the product stream decreases and that of oxygenates increases (Fig. 6), due to the fact that the hydrogenation of CO and CO_2 to methanol gives way to a decrease in the number of moles and, consequently, as pressure is increased, these reactions are favoured over water shift reaction.

Besides, regarding the composition of hydrocarbons in the product stream, as pressure is increased the content of C_1–C_4 paraffins increases and that of C_5^+ paraffins decreases. This result is explained by the fact that pressure

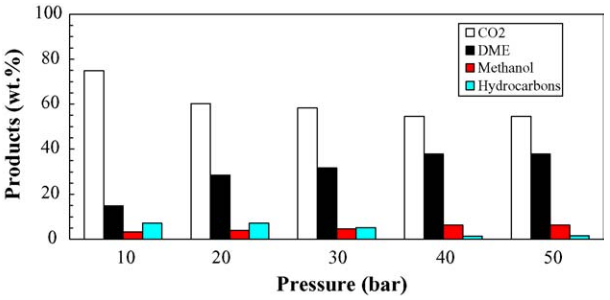

Fig. 6. Effect of pressure on product distribution.

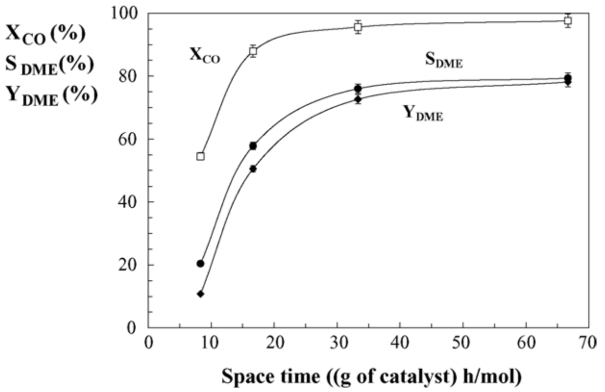

Fig. 7. Effect of space time on CO conversion (X_{CO}), selectivity to DME (S_{DME}) and yield of DME (Y_{DME}) for the feed made up of $H_2 + CO$.

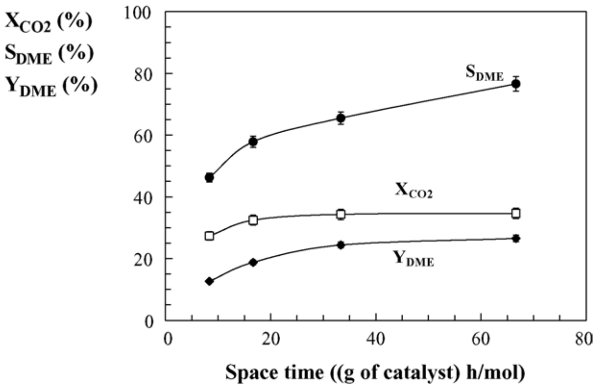

Fig. 9. Effect of space time on CO_2 conversion (X_{CO_2}), selectivity to DME (S_{DME}) and yield of DME (Y_{DME}) for the feed made up of $H_2 + CO_2$.

favours the hydrogenation of light olefins (intermediate products obtained from methanol and DME) and minimizes the single reactions of condensation (oligomerization, alkylation, aromatization).

3.4. Effect of space time

The effect of space time has been studied for the feeds made up of $H_2 + CO$ (with a molar ratio of 2/1) and of $H_2 + CO_2$ (with a molar ratio of 3/1). Runs have been carried out with four values of space time, 8.33, 16.66, 33.33 and 66.66 (g of catalyst) h/mol of reactants, which have been obtained by changing the mass of catalyst (0.5, 1, 2 and 4 g, respectively) and maintaining the molar flowrate of the reactants constant in the feed (1 mmol/min). The maximum value of space time (66.66 (g of catalyst) h/mol of reactants) corresponds to the maximum amount of catalyst that may be introduced into the reactor. The remaining operating conditions are: time on stream, 6 h; temperature, 275 °C; pressure, 40 bar.

Space time considerably affects the results for the feed of $H_2 + CO$ (Fig. 7). It is observed that both the conversion of CO and the selectivity to DME and yield of DME increase sharply for low values of space time and then they increase monotonically to constant values (≈99, 80 and 78%, respectively). From these results it is concluded that the conversion of CO increases rapidly at the beginning of the reactor and is almost complete for a space time of 67 (g of catalyst) h/mol of ($H_2 + CO$), whereas selectivity to DME and yield of DME have equilibrium values close to 80%.

Fig. 8 shows the distribution of products obtained in the range of space time considered. The decrease in the yield of CO_2 is clearly appreciated as space time is increased and an opposite trend in the content of DME is observed. These results are a consequence of the fact that low space time values favour the water shift reaction and high values of space time (above 33 (g of catalyst) h/mol) favour the reaction of dehydration of methanol to DME, as has been observed in the literature [33].

Conversion is partial for a feed made up of $H_2 + CO_2$, CO_2 (Fig. 9) and increases slightly as space time is increased. The high selectivity to DME is noteworthy, increasing linearly with space time. When these results are compared with those corresponding to $H_2 + CO$ (Fig. 7), it is evident that the transformation of $H_2 + CO_2$ is significantly slower.

Regarding the distribution of products (Fig. 10), as space time is increased the content of CO decreases, whereas there is an increase in oxygenates (methanol and DME). It is noteworthy that the content of hydrocarbons is insignificant.

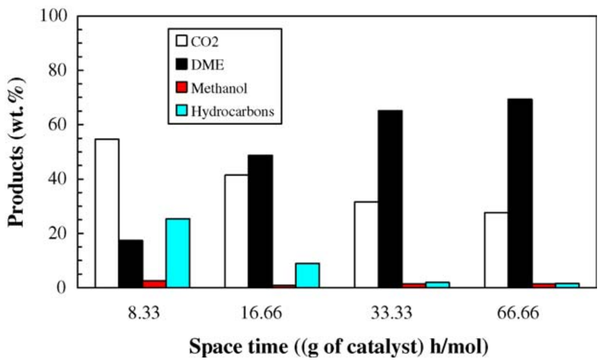

Fig. 8. Effect of space time on product distribution for the feed made up of $H_2 + CO$.

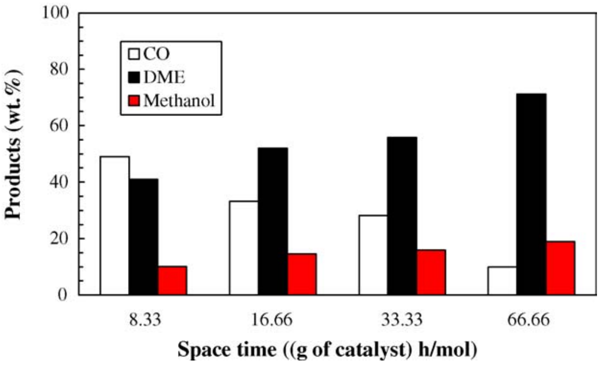

Fig. 10. Effect of space time on product distribution for the feed made up of $H_2 + CO_2$.

4. Conclusions

It has been proven that the bifunctional catalyst made up of CuO-ZnO-Al_2O_3/NaHZSM-5 performs well for obtaining DME directly from H_2, CO and CO_2 in a single reaction step. Consequently, an encouraging avenue is opened for the study of this process, where in addition to obtaining DME, the interest lies in the contribution to CO_2 sequestration. The moderate acid strength of the partially sodic zeolite is a key factor for minimizing secondary reactions of transformation of methanol and DME into hydrocarbons. Furthermore, its activity is not limited by water adsorption under conditions in which CO_2 is fed in a significant amount. Due to the low activity for light olefin formation and to the high concentration of hydrogen in the reaction medium, catalyst deactivation is insignificant.

In order to obtain an almost total conversion of CO from a feed made up of $H_2 + CO$, with 80% DME yield and selectivity, a temperature of 275 °C is suitable, with a space time of 67 (g of catalyst) h/mol of ($H_2 + CO$) and a H_2/CO molar ratio in the feed of 2/1. The transformation of the feed made up of $H_2 + CO_2$ is slower, although for the same space time indicated above and for a H_2/CO_2 ratio of 3/1, a CO_2 conversion of 35% is obtained, with a selectivity to DME of 75% and without hydrocarbon formation.

Acknowledgements

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