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The Deactivation Modes of $Cu/ZnO/Al_2O_3$ and HZSM-5 Physical Mixture in the One-Step DME Synthesis

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Abstract The CO_2 production by shift reaction and the deactivation process are the drawbacks of the One-Step DME Synthesis. Therefore, this contribution discusses possible deactivation modes taking into account the catalytic performance and the characterization of spent catalysts using XRD, TG and FTIR techniques. For this purpose a physical mixture that contains a commercial methanol catalyst and ZSM-5 was employed. It can be suggested that one of the main modes of catalyst deactivation is the hydrocarbon formation by MTG reactions. Changes in the interaction between Cu^0 and ZnO should also be considered. The results show that both of them are affected by H_2/CO ratio.

Keywords Deactivation · DME · Methanol · ZSM-5 · Copper

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1 Introduction

DME (dimethyl ether) is considered to be the fuel of 21st century. It can be used for power generation, in diesel trucks and fuel cells and it can also replace LPG as cooking gas. This last application is an important alternative for developing countries like China, India and Brazil, which need portable fuel (bottled) for people who live far from the facilities of the big cities. Indeed, many of these populations use wood as fuel for cooking, which implies direct human exposure to particulates air pollution, one of the major causes of health damage [1].

As it is well known, DME is a clean fuel. It is non-toxic and burns without particulate emission. It can make the atmosphere of many dwellings in the countryside of these developing countries much healthier. Moreover, DME can be synthesized from natural gas, coal and also from agriculture residues. The latter is very convenient for the local DME production, also being CO_2 neutral.

Two processes have been claimed so far. The first one uses traditional methanol synthesis followed by a dehydration step. The second generates DME from synthesis gas using a catalyst or a mixture of catalysts which synthesized methanol and ether in the same reactor. The second approach is thermodynamically more favourable, also being an opportunity for the development of a new process. However, two drawbacks of the one-step process should be mentioned: the CO_2 production by shift reaction, which occurs simultaneously with the DME synthesis and the deactivation process. It is worth stressing that there are only few pieces of information available in the literature which focus on the deactivation process of DME One-Step Synthesis.

Peng et al. [2] studied the liquid phase of the One-Step DME Process. They observed a detrimental interaction between the methanol synthesis catalyst and the dehydration catalyst, which was identified as the cause of the rapid, simultaneous deactivation of the catalytic system. The authors suggested this was due to the migration of Zn and Cu species from the methanol catalyst to γ-alumina. Some years later, Ereña et al. [3] observed that the rate of the catalyst deactivation was very low for high concentration of hydrogen in the reaction medium. The same group [4] associated the deactivation process with the presence of coke on the methanol catalyst and also on the acid component. Recently, Luan et al. [5] suggested that this deactivation occurs due to the sintering of Cu particle. They observed that the CO conversion decreases while the turnover frequency (TOF) and DME selectivity were rather stable during 48 h.

As it can be inferred, it is not clear which is the main cause for the decrease of the activity in the DME One-Step Synthesis. Therefore, this contribution aims at further studying this deactivation phenomena focusing on methanol catalyst (Cu/Zn/Al) and ZSM-5 physical mixture. This reaction was analyzed under different conditions and the catalysts were characterized before and after the reaction.

2 Methodology

Physical mixtures of a methanol synthesis catalyst and ZSM-5 were investigated. HZSM-5 sample (SAR = 40) was provided by Petrobras. Only commercially available materials were used.

The DME direct synthesis was carried out using the physical mixtures mentioned above in a continuous unit composed basically of a Berty reactor (Autoclave Engineers, 50 mL of total volume) and a gas chromatograph (Varian CP-3800 equipped with a TCD and a FID) connected in line. The Berty reactor is an internal recycling gradientless reactor, equipped with a fixed basket to hold the catalyst and with a fan over the basket. The reactor was equipped with temperature control and pressure indication. The feed gas flow was controlled by a mass flow meter (Brooks). The output stream and the reactor pressure were controlled by a micrometric valve. The effluent was then analyzed by gas chromatography. In order to prevent methanol and water condensation, the line between the reactor and the chromatograph injection valve, including the micrometric valve, was electrically heated and kept at around 100 °C during the tests. The physical mixture was reduced under H_2/He flow (5% H_2, 30 mL min^{-1}), for 1 h at 250 °C. After reduction, the gas was changed to synthesis gas ($H_2/CO = 1$ or 2) and the reaction conditions (24 mL min^{-1}, 250 °C, 5 MPa) were adjusted. Methanol synthesis catalyst/acid catalyst ratio of one was kept constant in all experiments, except for a few tests in which the ratio 4 was used. After the reaction the catalysts physical mixture was cold down in the reactional atmosphere. The methanol catalyst was kept reduced, due to the CO and CO_2 adsorption (passivation was confirmed heating up the spent catalyst and analyzing the effluent by MS).

The fresh and used catalysts were analyzed using the following techniques.

2.1 Infrared Spectroscopy

Infrared spectra of the catalysts were collected with a Magna 560-Nicolet spectrometer using wafers containing 3 wt.% of the sample in KBr.

2.2 X-Ray Diffraction

X-ray diffraction was performed using a Philips diffractometer, model PW 1410, operating with radiation Cu Kα (40 kV, 30 mA) and a Ni filter. The angular range varied from 20° to 90°, with increments of 0.05° and counting time of 8 s per step. Diffractograms were analyzed by the Rietveld method with fundamental parameters employing the TOPAS program (Bruker AXS, GmbH, version 3.0, Karlsruhe, Germany, 2003). The fit quality was evaluated by the residual (R)-weighted pattern (Rwp) as well as by the goodness of fit (gof). Their maximum values were always smaller than 33.4 and 1.10, respectively.

2.3 Thermal Analysis

Thermal analyses (TG) were performed using a TA Instruments SDT Q 600, flowing N_2 at 40 mL min^{-1} and a heating rate of 20 °C min^{-1}.

3 Results and Discussion

CO consumption rate with time on stream for the DME syntheses, using two different H_2/CO ratios, 1 and 2, are shown in Fig. 1. It can be observed that the H_2/CO ratio play a very important role in the deactivation process, i.e., high H_2 concentration leads to a very low deactivation rate. This result is in line with the observations of Ereña et al. [3].

3.1 The Dehydration Catalyst

Considering the behavior of the catalytic system using $H_2/CO = 1$, the fresh and the used dehydration catalysts were characterized by FTIR. Absorptions bands ranging from 1400 to 850 cm^{-1}, which can be assigned to the structural vibrations of ZSM-5, are displayed in Fig. 2a, b. The spectrum of the aged catalyst also shows low intensity

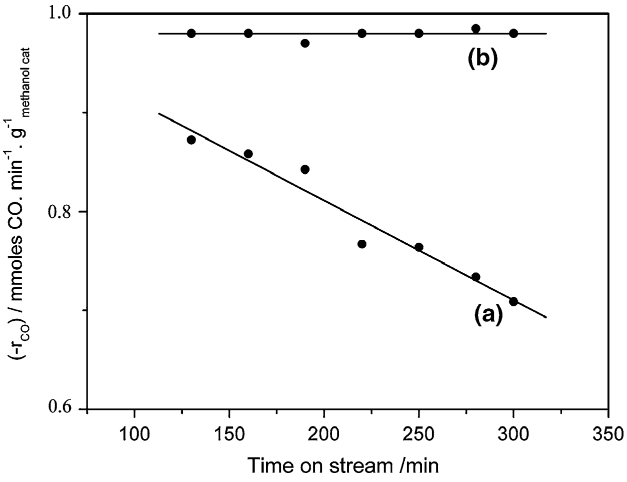

Fig. 1 Effect of the H_2/CO ratio on the CO conversion using methanol catalyst and HZSM-5 physical mixture. The H_2/CO ratio was 1 (**a**) and 2 (**b**)

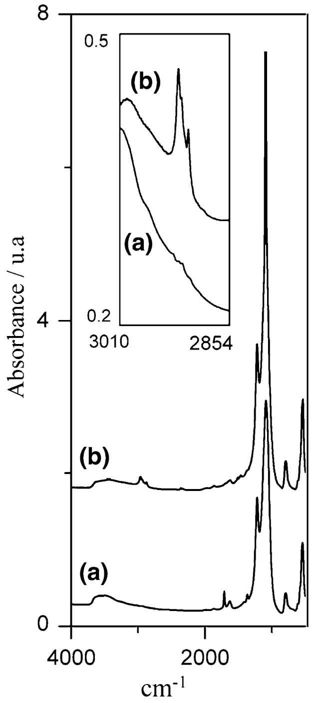

Fig. 2 Infrared spectra of the fresh HZSM-5 catalyst (**a**) and the used one ($H_2/CO = 1$) (**b**)

bands in the range of 3010–2854 cm^{-1}, which can be attributed to the C–H stretching, i.e., to the presence of hydrocarbons on the catalyst surface [6]. However, the spent catalyst that used $H_2/CO = 2$ show also these same bands.

MTG (methanol to gasoline) is a well-known chemical process which produces hydrocarbons from methanol using ZSM-5 as catalyst [7]. DME is one of the intermediate of this process, which is generated by methanol dehydration. It undergoes subsequent reactions via strong Bronsted acid sites to form light olefins over H-ZSM-5. Afterwards, hydrocarbons are produced by these intermediates. It is worth stressing that Ereña et al. [3] observed the formation of light olefins during DME One-Step Synthesis. Therefore, FTIR analyses showed that there are hydrocarbons on the ZSM-5 catalyst, which might be associated to the MTG reactions.

Figure 3 depicts selectivity values towards DME, CO_2 and methanol related to the catalytic test displayed in Fig. 1 for $H_2/CO = 1$. Although a deactivation phenomenon was observed, it can be verified that the selectivity values do not change with time on stream. This result is in good agreement with the data reported by Luan et al. [5]. The same result (Fig. 4) was obtained employing a

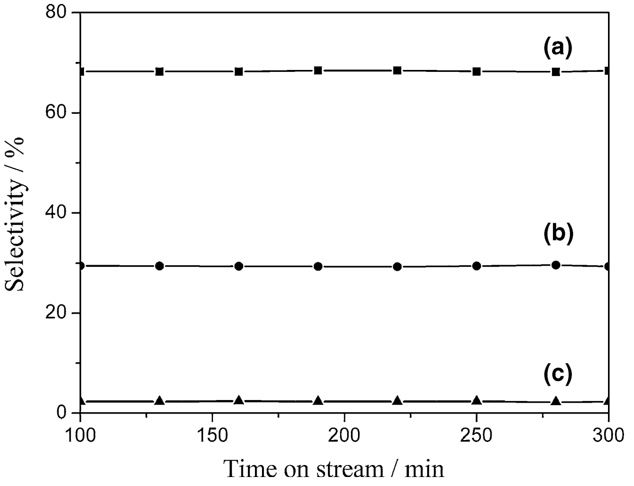

Fig. 3 Selectivity towards DME (■), CO_2 (●) and methanol (▲) for methanol synthesis catalyst and ZSM-5 physical mixture. The methanol catalyst/HZSM-5 and the H_2/CO ratios were 1 and 1, respectively

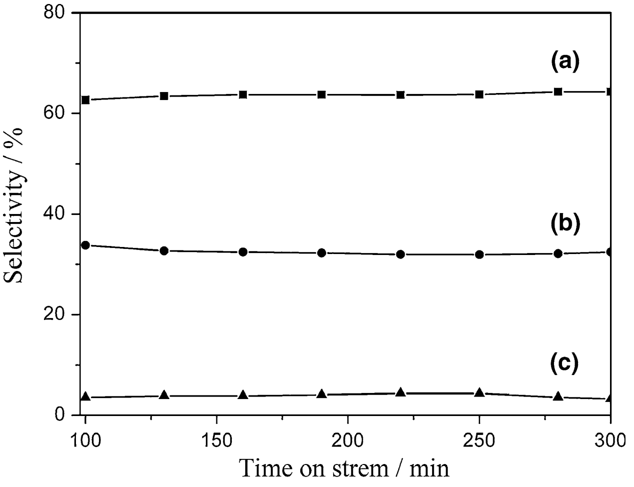

Fig. 4 Selectivity towards DME (■), CO_2 (●) and methanol (▲) for methanol synthesis catalyst and ZSM-5 physical mixture. The methanol catalyst/HZSM-5 and the H_2/CO ratios were 4 and 1, respectively

methanol catalyst/ZSM-5 ratio four times lower than the one used in Figs. 1 and 3. These data show that the dehydration step is not affect by the hydrocarbon formation on ZSM-5 catalyst.

In our previous work [8], it was suggested that the determining step rate of DME direct synthesis is the methanol synthesis in the case of high acidity materials like ZSM-5, sulfated-zirconia, etc. Therefore, it is possible to suggest that the hydrocarbon formation on the dehydration catalyst is not the main deactivation mode in these conditions.

3.2 The Methanol Synthesis Catalyst

According to Twigg and Spencer [9], in normal running conditions of methanol synthesis plants, the most significant mode of deactivation is the sintering of copper crystallites which leads to the loss of copper metal surface area. Indeed, this is due to not only the low Tammann temperature of copper but also the exothermicity of this reaction. Figure 5 shows the rate of CO consumption at two different temperatures: 250 and 260 °C. It can be observed that as the temperature increases, the rate of CO consumption increases as well. At the same time, the deactivation rate decreases (slope), showing that the copper sintering is not a very relevant deactivation mode in these conditions. Indeed, Twigg and Spencer suggested that sinterization is significant for reaction temperatures higher than 300 °C. It is worth stressing that the "Berty" reactor, i.e., the system used in this work provides a very efficient heat transport, avoiding temperature gradients that can promote the sintering process.

Besides sintering, other deactivation modes can also be considered for the methanol synthesis. According to Kung [10], methanol catalyst is very sensitive to sulfur poisoning. Therefore, the sulfur content in the feed stream needs to be reduced to less than 0.5 ppm. This author also reported that Cl facilitates Cu sintering. He also suggested that Fe and Ni carbonyls formation can occur during the reaction. These compounds would be deposited on the catalyst surface and promote the Fischer-Trospch reactions, i.e., hydrocarbon syntheses. Taking into account all these pieces of information, XPS analyses of the spent catalysts were performed. The results showed that none of these elements were identified on the catalysts surface. Therefore, these possibilities can be ruled out.

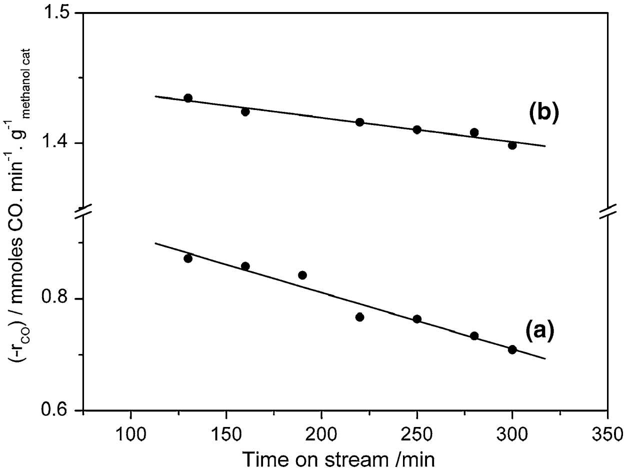

Fig. 5 CO consumption rate of the admixed catalysts of methanol synthesis and HZSM-5 at time on stream at 250 °C (**a**) and 260 °C (**b**), $H_2/CO = 1$

Figures 6 and 7 show the TG and DTG profiles (N_2 flow), respectively, of two methanol catalysts employed in the standard conditions of DME synthesis using $H_2/CO = 1$ and 2. It can be observed that these samples show a loss of mass at temperatures lower then 400 °C, which should be related to the presence of carbonates on the catalyst surface. It is well know that the decomposition of carbonates occurs at low temperatures [11]. Moreover, the low H_2/CO ratio sample also showed a loss of mass at high temperature, which can be attributed to the presence of hydrocarbons on the methanol catalyst surface generated by the acid component. Taking into account that the rate limiting step of the One-Step DME Synthesis is the CO hydrogenation [8] this compound can be associated with the deactivation process (Fig. 1).

Taking into account the FTIR results of the spent ZSM-5 samples, one can suggest that this mode might also occurs

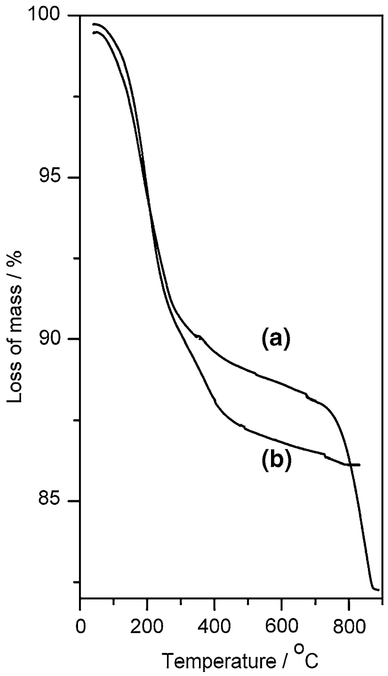

Fig. 6 ATG profile of spent methanol synthesis catalyst used at $H_2/CO = 1$ (**a**) and 2 (**b**)

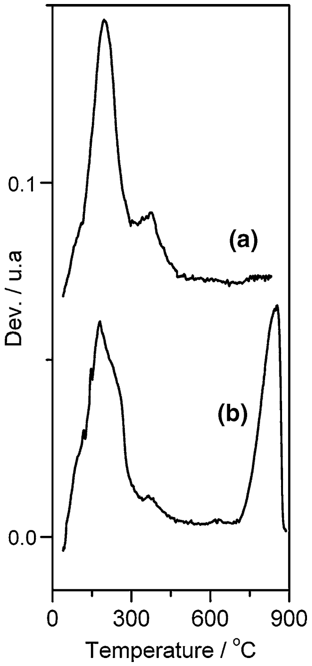

Fig. 7 DTG profile of spent methanol synthesis catalyst used at $H_2/CO = 1$ (**a**) and 2 (**b**)

at $H_2/CO = 2$, although less intense, once it was not possible to observe hydrocarbons on the surface of the methanol catalysts by TG/DTG (Figs. 6 and 7) under these conditions. These results were confirmed by some runs that lasted around 50 h using $H_2/CO = 2$. At the end of these catalytic tests a decrease of activity was observed as well as the presence of hydrocarbons on the methanol catalyst (TG/DTG). Hence, we can infer that the deactivation by MTG reactions occurs during the DME synthesis, being more intense for the $H_2/CO = 1$.

Figure 8a, b show the XRD patterns for the methanol catalysts which were employed in the DME synthesis using two different H_2/CO ratios, 1 and 2, respectively. It can be observed that the intensity of the ZnO diffraction peaks change according to the different H_2/CO ratios. The (101) peak intensity is higher for the $H_2/CO = 2$ ratio. Moreover, asymmetry and shifting of the diffraction peak assigned to the (111) plane of Cu^0 species (small picture) can also be observed. A detailed analysis of the diffractograms by Rietveld method revealed that both samples showed almost the same phases (Table 1), which can be assigned to graphite, ZnO, CuO, $CuAl_2O_4$, Cu_2O, Cu^0.

The graphite phase (type 3R), observed for both H_2/CO ratios, at 26.5° might also be associated with the deactivation process. This result is in line with the data displayed above that show that this phenomenon occurs for both conditions. Some authors also observed the presence of graphite-like compounds on ZSM-5 [12–14]. Indeed, it can be verified that the amount of graphite in both samples (methanol catalysts) is very similar. Therefore, these species might not be very relevant for the deactivation process (see Fig. 1).

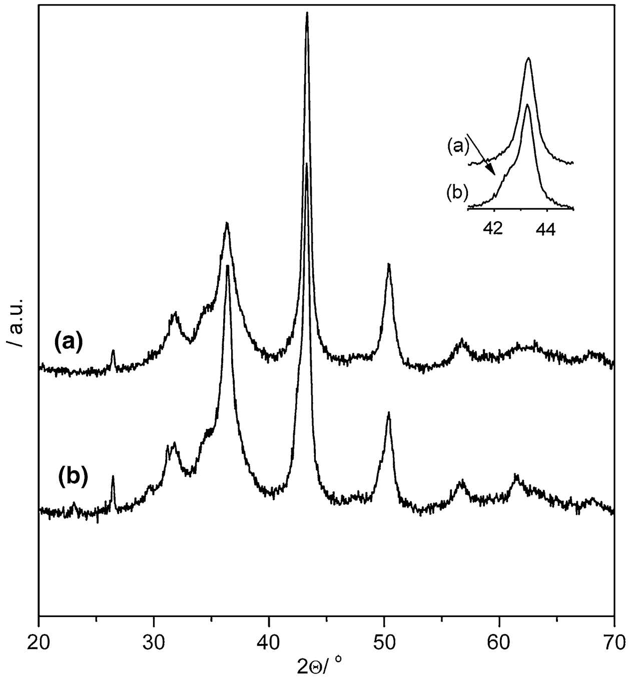

Fig. 8 XRD profiles of spent methanol synthesis catalyst used at $H_2/CO = 1$ (**a**) and 2 (**b**)

Table 1 Crystalline species in spent methanol catalysts (wt.%) and Cu^0 lattice parameter (Å) obtained by Rietveld method

	Sample $H_2/CO = 1$ (%)	Sample $H_2/CO = 2$ (%)
ZnO	33.49	31.76
Graphite 3R	2.46	2.84
$CuAl_2O_4$ (spinel)	17.11	19.97
CuO	5.20	4.96
Cu_2O	7.99	11.2
Cu^0 (a)	33.75	22.80
Lattice parameter	3.619	3.616
Cu^0 (b)	–	6.42
Lattice parameter		3.667

The presence of copper oxides shows that the passivation of the spent methanol catalyst is not perfect since it did not cover all the copper species. The XRD analysis also displayed two kinds of Cu^0 species (a, b) for the sample that used $H_2/CO = 2$. One of then (lattice parameter = 3.616 Å) is consistent with pure copper and can also be observed in the case of the sample that used $H_2/CO = 1$. The other one is related to Cu−0.25Zn alloy, reported by Ng et al. [15]. It is worth stressing that these species were observed for the sample that did not deactivate (Fig. 1b), suggesting that the catalytic activity is related to the alloy presence in the methanol catalyst. Using this analysis it was not observed strain in copper species.

Indeed, Cu/ZnO-based methanol synthesis catalysts have been studied extensively. It is well established that the interaction of the metallic copper particles with the ZnO support is responsible for the catalytic behavior. Some works indicate that the metal-support interaction of Cu/ZnO system depends on the gas environment [16], epitaxial strain [16, 17], shape dynamics [18], and also alloy formation [16, 19] or a combined effect of these phenomena. Although there are many excellent publications concerning this subject, even today it is not clear which one plays the dominating role for the catalyst activity.

Our results clearly show that the atmosphere plays a very important role in the DME synthesis deactivation process. Therefore, it can be suggested that one of the deactivation modes of the catalysts in the One-Step DME Synthesis might be attributed to changes in the metal-support interaction in the Cu/ZnO system promoted by the gas environment.

4 Conclusion

Taking our results into account, it could be suggested that one of the main modes of catalyst deactivation in the One-Step DME Synthesis, is the hydrocarbon formation by MTG reactions. Changes in the interaction between Cu^0 and ZnO should also be considered. It was shown that both deactivation modes are affected by H_2/CO ratio.

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