

HIGHER ALCOHOL SYNTHESIS OVER A Cs-Cu/ZnO/Cr₂O₃ CATALYST: EFFECT OF THE REACTION TEMPERATURE ON PRODUCT DISTRIBUTION AND CATALYST STABILITY

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ABSTRACT

The influence of reaction temperature on methanol and higher alcohol synthesis has been investigated in the range of 310-340°C. Optimal conditions for selective production of 2-methyl primary alcohols was identified with $T = 340^\circ\text{C}$ and synthesis gas $\text{H}_2/\text{CO} = 0.75$. Deactivation features were observed after 300 hr on stream, but no significant growth of Cu crystals or reduction in surface area was observed for the catalyst after testing.

INTRODUCTION

The Cu/ZnO/M₂O₃ systems (M = trivalent metal) are well-known catalysts for methanol and higher alcohol synthesis (HAS) [1-4]; their performances are reported in the literature with particular attention being paid to the optimization of both the catalyst composition (amount of alkaline dopant, metal ion ratios) and the operating conditions [2-5]. The application of these catalysts is commonly limited to reaction temperatures not exceeding 310-325°C in order to avoid sintering phenomena that are recognized as the major constraint and drawback of all the copper-containing catalysts. At these temperatures, methanol formation is highly favored, and only by carrying out the reaction at low H_2/CO ratios can significant quantities of C₂⁺ oxygenates be obtained. No specific studies have so far addressed the thermal stability of Cu/ZnO-based systems at high temperatures. However, the strong demand for selective production of branched higher oxygenates supports more extensive exploration of the range of allowable reaction temperatures that can be utilized with copper-based catalysts. Indeed, an increment in the temperature is expected to result in the desired promotion of higher alcohol production and a concurrent decrease in methanol formation. In the following, a study of the effect of reaction temperature on HAS over a Cs-doped Cu/ZnO/Cr₂O₃ catalyst is presented, and the principal interests are the changes in the product distribution and the catalyst thermal stability.

EXPERIMENTAL

Catalyst Preparation. The methodology has been described by Nunan et al. [3,6], which consists of the precipitation of a hydrotalcite-like precursor $\text{Cu}_{2.4}\text{Zn}_{3.6}\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ [7], followed by stepwise calcination to 350°C to give the mixture of oxides, CuO/ZnO/Cr₂O₃. Cesium doping was achieved by adding the catalyst to a N₂-purged aqueous solution of CsOOCH, which was then slowly evaporated to dryness under flowing N₂. The amount of dopant (3 mol%) was chosen on the basis of previous studies of the optimal catalyst composition with respect to higher alcohol synthesis [3]. The catalyst was finally reduced with a 2 mol% H₂/N₂ mixture at 250°C.

Activity Tests. The apparatus has been extensively described elsewhere [8]. It is noted that charcoal and molecular sieve traps, an internally copper-lined stainless-steel reactor, as well as a copper thermocouple-well were used during the catalytic testing to prevent the formation and deposition of iron-carbonyls, which are well-known deactivating agents [9,10]. The catalysts were tested under steady state conditions at 7.6 MPa with synthesis gas of various H₂/CO compositions flowing with a gas hourly space velocity of 5300 l/kg cat/hr. The reaction temperature was varied between 310 and 340°C.

The exit product mixture was sampled every 30-60 min using an in-line, automated, heated sampling valve and analyzed in a Hewlett-Packard 5390 gas chromatograph. The products were analyzed via a Poraplot-Q capillary column alternatively connected to a flame

ionization detector and to a thermal-conductivity detector (TCD) and a Molsieve capillary column connected to TCD. The sensitivity factors of the instrument were determined on the basis of calibrated mixtures. The gas-phase on-line analyses were coupled with the analysis of liquid samples collected downstream from the reactor (atmospheric pressure) by liquid nitrogen cooled traps. The identification of the products (more than 50 components) was obtained by comparison of their retention times with those of known standards and from analysis of the liquid samples by a HP GC/MS instrument. All of the experimental data were obtained in a steady-state regime that was reached about 6-8 hr after setting the operating conditions.

Catalyst Characterization. BET measurements and XRD analyses were performed at each stage of the catalyst preparation and after testing to determine the catalyst surface area and crystalline phases, respectively.

RESULTS

Effect of the Reaction Temperature on the Product Distribution. In Fig. 1, the productivities of the most abundant oxygenated products are reported as a function of the reaction temperature, which was increased from 310°C up to 340°C over a period of about 160 hr. As the temperature was increased, a decrease of methanol productivity was observed, in line with the thermodynamic constraints that govern methanol synthesis. As shown in Fig. 1(a), the productivities of all the linear higher alcohols exhibited decreasing trends with increasing reaction temperature. In fact, the product mixture tends to become depleted in intermediate species (ethanol, propanol) and more enriched in the branched oxygenates that play a terminal role in the chain-growth process. At 325°C, a promotion of all the 2-methyl alcohols was observed (Fig. 1-b). It is noted that the molar ratio between methanol and the totality of α -branched alcohols passed from a value of about 16 at 310°C to the value of about 5 at 340°C. In the case of secondary alcohols (whose productivities are summed in Fig. 1-c with those of the corresponding ketones), it is observed that high temperatures favor the formation of high molecular weight species (e.g. 2-methyl-3-pentanol) at the expense of the intermediate species (e.g. 2-butanol).

The formation of methane and C_2^+ hydrocarbons was also observed to increase with increasing reaction temperature (Fig. 2). The overall production of hydrocarbons, equal to 15.7 g/kg cat/hr at 310 °C, grew to the value of 39.4 g/kg cat/hr at 340°C. It is worth noticing that, contrary to the case of oxygenates, hydrocarbons appear to keep an almost constant relative product distribution, which could support the hypothesis of a formation pattern independent from the higher alcohol chain-growth process.

Finally, it is noted that the productivities of all the methyl-esters detected in the product mixture decreased monotonically with increasing reaction temperature. This trend was especially evident in the case of methyl-formate and methyl-acetate, while it was less pronounced for the higher homologs (methyl-propionate, methyl-isobutyrate, methyl-butyrate).

High Reaction Temperature: Effect of H_2/CO Ratio. At the reaction temperature of 340°C, kinetic runs were performed to investigate the combined effects of high temperature and H_2/CO feed ratio on HAS product distribution. The results are reported in Fig. 3, and the data show that an excess of H_2 exclusively promoted methanol formation. The production of higher oxygenates appears to be significantly inhibited at high H_2/CO ratios. Specifically, all of the primary alcohols tended to show a maximum in productivity, with the highest value being associated with the H_2/CO value of 0.75 (Fig. 3 a-b).

With respect to the formation of hydrocarbons, the data reported in Fig. 4 indicate that while the synthesis of C_2^+ hydrocarbons is strongly slowed down by decreasing CO partial pressure, methane productivity was approximately constant as a function of the H_2/CO ratio.

High Reaction Temperature: Catalyst Stability. The operating conditions of $T = 340^\circ\text{C}$, $H_2/CO = 0.45$, 7.6 MPa, and GHSV = 5300 $\ell/\text{kg cat/hr}$ were periodically reproduced in order to check the stability of the catalyst. The results of the experiments are

reported in Fig. 5, where the averaged FID signals, in arbitrary units, for the most abundant products have been plotted vs the time of testing. As previously noted, a period of about 160 hr occurred before reaching the final temperature of 340°C, and at this high temperature a stable catalytic activity was observed during 125 hr. Subsequently, a slow loss of selectivity of the higher oxygenates in favor of an increment in methanol productivity was detected. Similar results were obtained in the past when studying deactivation caused by the deposition of iron-carbonyls onto Cu/ZnO catalysts [9]. Even though the cause of the origin of the behavior shown in Fig. 5 cannot be assessed, Cu sintering can be excluded as playing a major role, where the XRD pattern of the tested catalyst (300 hr on stream at 340°C) revealed the presence of metallic copper with crystallite size in the range of 100Å, which is comparable with the dimension of Cu crystallites observed in the binary Cu/ZnO systems after the reduction stage and before testing [9]. Moreover, BET measures showed that no reduction in the catalyst surface area occurred during the kinetic runs, being 85 m²/g and 89 m²/g the surface area values before and after testing, respectively.

CONCLUSIONS

The presented experimental results suggest that:

- (1) the productivity of α -branched species benefits significantly from an increment of the reaction temperature to 325°C. For further increments of temperature, the productivities of higher alcohols are almost constant but the methanol/higher alcohols molar ratio increases progressively.
- (2) at high temperature, the H₂/CO feed ratio of 0.75 is optimal with respect to higher oxygenate formation. Under such conditions, an equal amount of methanol but *twice* the amount of branched higher alcohols can be obtained, compared to the optimal low temperature conditions (T = 310°C, H₂/CO = 0.45).
- (3) no significant Cu sintering or surface area reduction occurred upon testing at the reaction temperature of 340°C; but iron-carbonyl formation and deactivation of the catalysts under high temperature conditions needs to be studied further.

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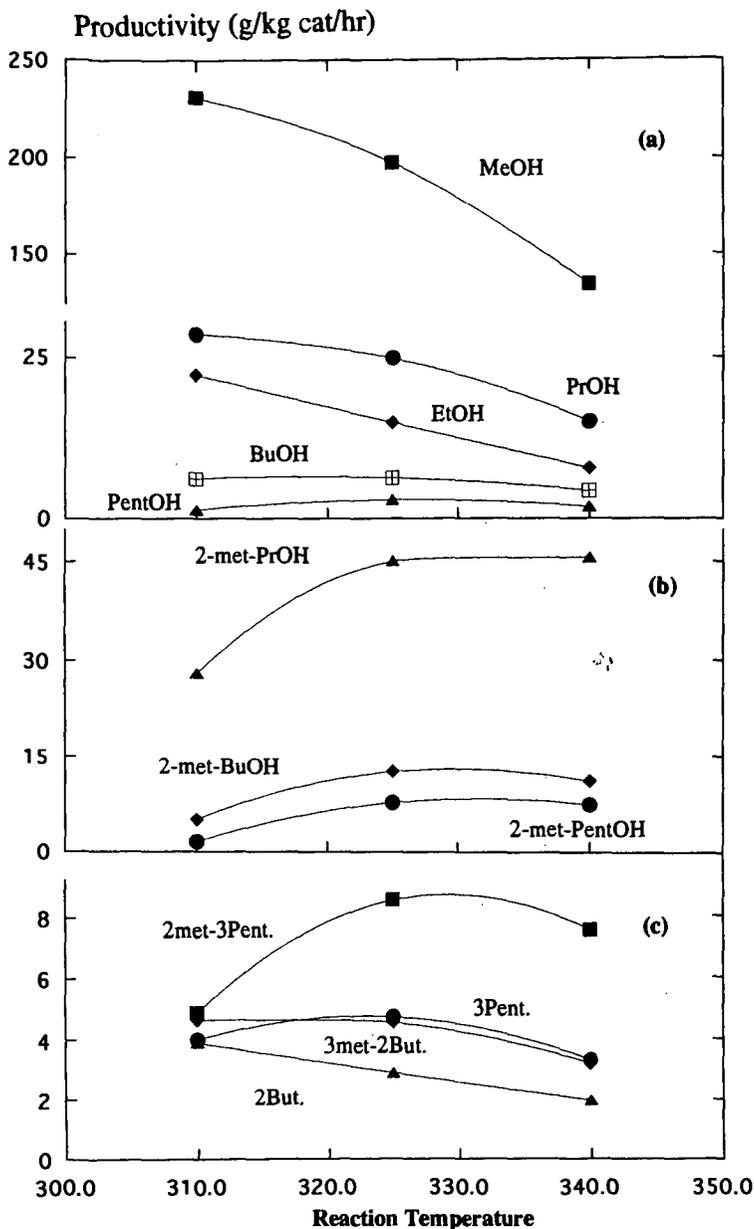


Fig. 1. Experimental effect of reaction temperature on methanol and higher oxygenates productivities. In 1-c: 2met-3Pent = 2methyl-3-pentanol + 2-methyl-3-pentanone, 3-Pent. = 3-pentanol + 3-pentanone, 3met-2But. = 3-methyl-2-butanol + 3-methyl-2-butanone, 2-But. = 2-butanol + 2-butanone. Operating conditions: $H_2/CO=0.45$, $P=7.6$ MPa, $GHSV=5300$ l/kg cat/hr.

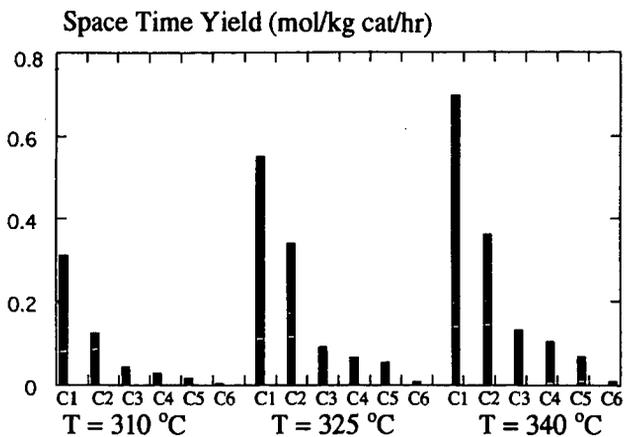


Fig. 2. Effect of temperature on C₁-C₆ hydrocarbon production and distribution.

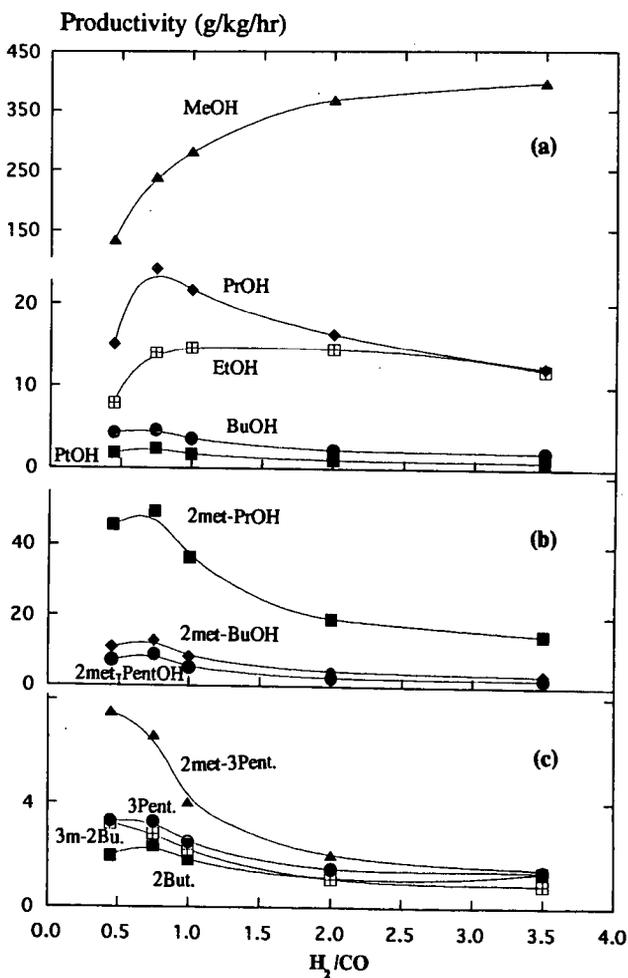


Fig. 3. Effect of H₂/CO ratio; T = 340°C, P = 7.6 MPa, GHSV = 5300 l/kg cat/hr.

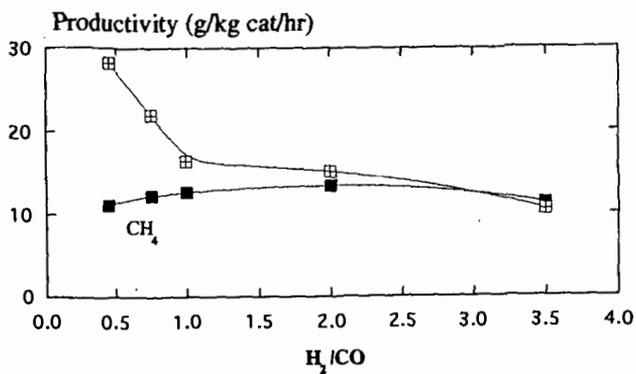


Fig. 4. Effect of H₂/CO ratio hydrocarbon formation. Conditions as in Fig. 3.

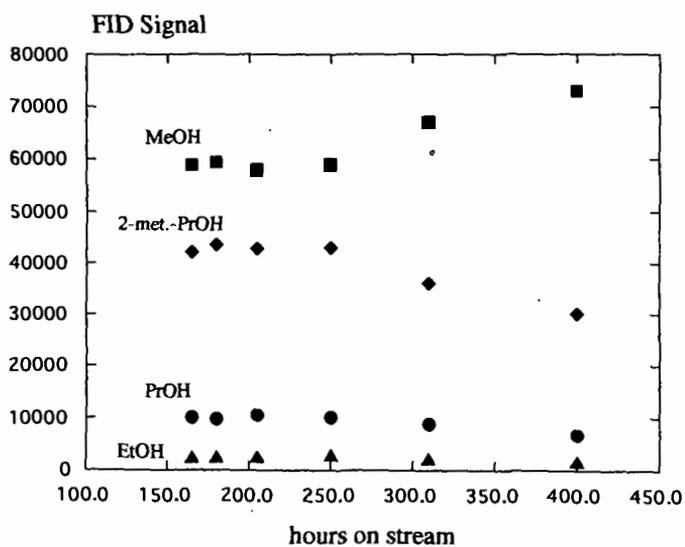


Fig. 5. Change of product distribution with time as detected by FID.