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Alcohol synthesis in a high-temperature slurry reactor

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Abstract

A family of hydrocarbon liquids has been discovered that is stable at temperatures up to about 400°C in the presence of synthesis gas. The performance of a commercial, 'zinc chromite', 'high pressure' methanol synthesis catalyst was evaluated in a slurry reactor using two of these liquids, decahydronaphthalene and tetrahydronaphthalene, to suspend the catalyst. The evaluation covered a range of temperatures from 275° to 425°C, total pressures from 6.9 to 17.2 MPa, H_2/CO ratios from 0.5 to 2.0 and space velocities from 1500 to 10 000 sl kg(catalyst)$^{-1}$ h^{-1}. Methanol was the only significant product at the lower end of this temperature range. The methanol synthesis reaction was close to equilibrium at the highest temperature, and there were significant quantities of dimethyl ether, olefins, methane and carbon dioxide in the product. Catalyst performance was sensitive to the composition of the slurry liquid, but was relatively stable in decahydronaphthalene over a long period of time.

Keywords: Decahydronaphtalene; Methanol; Slurry reactor; Tetrahydronaphtalene; Zinc chromite

1. Introduction

The production of higher (C_2^+) alcohols from synthesis gas, a mixture of H_2 and CO, has been an active area of research for more than fifty years. A variety of materials can catalyze this reaction, as recently reviewed by Forzatti et al. [1]. Some catalysts produce an Anderson–Schulz–Flory (ASF) product distribution, in which the concentration of each alcohol declines with its carbon number. However, Minahan et al. [2], Heydorn et al. [3], and Minahan and Nagaki [4] have pointed out the potential advantage of an alcohol synthesis process that could produce $\approx$1 mol of methanol plus ethanol and 1 mol of a 2-methyl-1-alcohol, e.g., isobutanol (2-methyl-1-propanol). This kind of product distribution could provide the raw materials that are needed to produce octane enhancers such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME). If a catalyst were sufficiently selective to 2-methyl-1-alcohols, only relatively small amounts of methanol, ethanol, propanol, etc. would have to be sold as by-products. Obviously, catalysts that produce an ASF distribution of alcohols are not appropriate for this objective. However, certain modified methanol synthesis catalysts have yielded product distributions in which methanol and isobutanol are the predominant products [2–12]. These catalysts consist of either of the two commercial methanol synthesis catalysts, the 'low-pressure' Cu/ZnO catalyst or the 'high-pressure', 'zinc chromite' catalyst, promoted with alkali metals such as K, Rb or Cs.

The synthesis of alcohols from CO and H_2 is highly exothermic. In case of methanol synthesis, excellent

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temperature control is essential for high conversions because of the reversibility of the reaction. Moreover, the deactivation rate of the Cu/ZnO methanol synthesis catalyst increases rapidly with temperature [13], adding emphasis to the need for good reactor temperature control. The synthesis of C_2^+ alcohols from H_2/CO mixtures is more exothermic than the synthesis of methanol. Although reversibility is not an issue with the higher alcohols at typical operating conditions [14], good temperature control is important to reaction selectivity and catalyst life. Because of their inherently isothermal nature, slurry reactors have been the subject of considerable research and development for methanol synthesis [13,15,16], for the synthesis of higher alcohols [3,17–19], and for dimethyl ether (DME) synthesis [20]. Table 1 summarizes some of the general advantages of slurry reactors.

Previous research on alcohol synthesis and related reactions in slurry reactors has been carried out at temperatures below approx. 300°C. Much of this work has involved the Cu/ZnO methanol synthesis catalyst, and variations thereof. This catalyst is active at temperatures in the region of 250°C, but it deactivates rapidly above approx. 300°C [5,13]. The 'zinc chromite' methanol synthesis catalyst requires an operating temperature of 350 to 400°C. However, as discussed in more detail below, the liquids that have been used to slurry the Cu/ZnO catalyst are unstable at temperatures significantly in excess of 300°C, in the presence of high partial pressures of H_2.

The objectives of this work were: (1) to extend the operating range of slurry reactors for synthesis gas reactions to a temperature of appprox. 400°C and (2) to characterize the performance of a commercial, 'zinc chromite', 'high-pressure' methanol synthesis catalyst in a slurry reactor in this temperature region. This research was intended to provide a basis for the evaluation of promoted 'zinc chromite' catalysts for the production of higher alcohols in a slurry reactor. It has been established that adding alkali metals such as cesium and potassium to 'zinc chromite' catalysts increases the production of higher alcohols [6–8,11]. The 2-methyl-1-alcohol/methanol molar ratios that have been achieved with promoted 'zinc chromite' catalysts are comparable to those obtained with promoted Cu/ZnO catalysts. For example, the highest reported molar *i*-butanol/methanol ratio for a promoted Cu/ZnO catalyst is approx. 0.65 [12], whereas the highest reported molar ratio for a promoted 'zinc chromite' is in the range of 0.50 to 0.75 [11]. However, neither the promoted nor unpromoted versions of the 'zinc chromite' catalyst have been run previously in a slurry reactor.

Table 1
Advantages of slurry reactors

- Essentially isothermal
- Small catalyst particles minimize mass and heat transfer effects
- Liquid vaporization removes heat
- Greater flexibility in catalyst design:
  - compositions that cannot be pelletized
  - physical mixtures

2. Equipment

The experimental equipment used for this research has been described in some detail in Refs. [18] and [19]. Basically, gases were fed from cylinders through activated carbon traps to remove impurities, including metal carbonyls, and then through mass flow controllers to measure and control the flow rates. The individual gas streams were mixed and compressed to the desired pressure. The compressed gas was passed through another activated carbon trap to remove any iron and/or nickel carbonyls that may have formed during and after compression. The gas was then fed into a 300 cm^3 stirred autoclave reactor. The reactor was initially charged with 20 g of catalyst and 80 g of the slurry liquid. The gas leaving the reactor passed into a gas/liquid separator containing a cooling coil to control the temperature of the separator. The gas then passed through a back pressure regulator, through heated lines to prevent condensation and through a wet test meter to measure the gas flow rate. Samples of the reactor feed and effluent were periodically diverted to a dual-column gas chromatograph containing a Carboxen 1000 column followed by a thermal conductivity detector and a Poroplot Q column followed by a flame ionization detector. The former system was used to measure the fixed gases, H_2, N_2, CO, CO_2 and H_2O. The organic species were measured on the second system.

The autoclave reactor was mechanically agitated to ensure complete backmixing, and to ensure that gas/

liquid mass transfer did not influence the reaction rate. Because the reactor was backmixed, the rates of formation or disappearance for the various species could be calculated directly from the inlet and outlet compositions and flow rates. The system was operated continuously for periods of one to four weeks. All data were taken at steady-state conditions.

3. Results and discussion

3.1. Liquid stability testing

The 'zinc chromite' catalyst is typically run at temperatures of 350° to 410°C in commercial, fixed-bed methanol synthesis reactors [21–23]. Moreover, research on the addition of alkali metals to this catalyst, aimed at shifting the product distribution toward the higher alcohols [6–8,11,24], has involved similar temperatures. Therefore, an initial target temperature of 375°C was set for slurry reactor operation.

A 'thermal' stability test was carried out by charging a measured amount of the liquid to the stirred autoclave reactor, pressurizing to 7.0 MPa with H_2, heating to 375°C, continuously sparging H_2 through the liquid and holding the system at these conditions for about 3 days. The catalyst was not present during this test. The gas leaving the reactor was analyzed periodically by gas chromatography to determine whether any hydrocarbons were present, and, if so, their identities and concentrations. At the end of the test period, a number of analyses were carried out on the liquid remaining in the reactor, including molecular weight, density, refractive index, nuclear magnetic resonance (NMR) spectroscopy, and gas chromatography/mass spectrometry (GC/MS). Table 2 shows data for five different liquids.

Drakeol® 34 is a saturated mineral oil comprised of 68% paraffins and 32% naphthenes. It is typical of the liquids used for methanol synthesis [13], DME synthesis [20], higher alcohol synthesis [3] and isobutanol dehydration [25] in slurry reactors. Durasyn® 180, a mixture of saturated oligimers of 1-decene, is totally paraffinic. Similar liquids have been used for methanol synthesis [15] and higher alcohol synthesis [17] in slurry reactors. All these referenced studies were conducted at temperatures between 200 and 320°C, and all the alcohol synthesis research was conducted with Cu/ZnO catalysts. Decalin® is a trade name for decahydronaphthalene, and Tetralin is tetrahydronaphthalene. Decalin, Tetralin and perhydrofluorene have fused-ring, cyclic structures with no alkyl groups. Decalin and perhydrofluorene are completely saturated; Tetralin is partially saturated. Table 2 shows that all the three fused-ring compounds were much more thermally stable than either Drakeol 34 or Durasyn 180, as indicated by both the gas production/liquid loss rates, as well as by the changes in molecular weight. NMR (^1H and ^{13}C) and GC/MS analyses carried out on samples of Decalin and Tetralin taken from the reactor at the end of the thermal stability test showed no significant evidence of low-molecular-weight, hydrocracked products.

3.2. Catalyst performance

All the research discussed below was carried out with a commercial, 'high-pressure' methanol synth-

Table 2
Thermal stability of various liquids

Liquid	Run duration [a] (h)	Molecular weight reduction [b] (%)	Rate of liquid loss via C_1–C_4 gas production (wt% of initial charge h^{-1})	
			Maximum	Steady-state
Drakeol®34	69	35	1.2	0.10
Durasyn®180	65	86	1.8	0.12
Perhydrofluorene	71	(1)	0.44	0.044
Decalin® [c]	73	3	0.095	0.0040
Tetralin	72	0	0.012	0.0020

[a] At a temperature of 375°C, H_2 pressure of 7.0 MPa and H_2 flow rate of 3.8 sl min^{-1}.
[b] Initial minus End of Run.

esis catalyst (Zn-0312 T1/8) from Engelhard, which was obtained in a reduced and stabilized form. The catalyst contained 60 wt% Zn and 15 wt% Cr, with ZnO and $ZnCr_2O_4$ phases detectable by X-ray diffraction. The as-received BET surface area was 145 $m^2 g^{-1}$. The catalyst was ground and sieved to −120 mesh prior to use. Most runs were made with a 20 wt% slurry of catalyst in Decalin. A limited number of runs were made with the same catalyst concentration in Tetralin, in order to compare the effect of these two liquid compositions on reaction rate and selectivity. The catalyst was activated in situ by: pressurizing the reactor to 7.0 MPa with N_2 and heating it to 130°C while sparging N_2 through the slurry; heating from 130 to 300°C at about 40°C h^{-1} with a sparge gas consisting of 5% H_2 in N_2; heating to 375°C at 25°C h^{-1} while progressively increasing the H_2 mole fraction in the sparge gas from 0.05 to 1, and; holding at 375°C with a pure H_2 sparge until no water was present in the gas leaving the reactor.

Four series of experiments were conducted at total pressures between 6.9 and 17.2 MPa, temperatures in the range of 275 to 425°C and gas hourly space velocities (GHSV) between 1500 and 10 000 sl $kg^{-1} h^{-1}$. The feed was a mixture of H_2 and CO, with H_2/CO ratios between 0.5 and 2. A typical operating pressure for a methanol synthesis process based on the 'zinc chromite' catalyst is about 30 MPa [21–23]. When methanol is the desired product, a high pressure is required in order to overcome equilibrium constraints and achieve practical effluent concentrations of methanol at the operating temperature of the 'zinc chromite' catalyst. However, in a higher-alcohols process, it is desirable to limit the amount of methanol formation. One way to do this is to operate at lower pressures, since the equilibrium concentration of methanol decreases as pressure is decreased. The total pressures used in this research are similar to those used by Tronconi and coworkers [6–8,11] in their studies of higher alcohol synthesis over promoted 'zinc chromite' catalysts.

Fig. 1 shows the product distributions that were obtained in two runs, one at 300°C and the other at 375°C, with otherwise constant conditions: 5000 sl $kg^{-1} h^{-1}$ GHSV, 6.9 MPa total pressure, a H_2/CO ratio of 0.5, and Decalin as the slurry liquid. Carbon selectivity is defined as the percentage of the CO molecules that actually react and are converted to the products indicated. At both temperatures, methanol was the only alcohol in the outlet stream, and DME was the only other oxygenate present in significant quantities. DME probably formed by the condensation of two molecules of methanol, a reaction that is catalyzed by mildly acidic surfaces such as γ-alumina [20,26]. At 375°C, a portion of the product, about 10% of the carbon atoms, was C_2–C_4 olefins. Olefin formation in these quantities has not been reported previously for this type of catalyst in gas-phase fixed-bed reactors. However, the formation of C_2–C_4 alcohols has been reported with an unpromoted 'manganese chromite' catalyst [6]. It is possible that the olefins observed in this study resulted from dehydration of the corresponding alcohol, consistent with the hypothesis advanced by Tronconi and coworkers [8,11]. The dehydration of isobutanol to isobutene is catalyzed by the same kind of acidic surfaces that catalyze the formation of DME from methanol [25]. The paraffins formed at 375°C were predominantly methane with a small amount of ethane. The formation of a large quantity of CO_2 demonstrates that the catalyst has a substantial activity for the water-gas-shift reaction. The water produced by the formation of alkanes, olefins and DME was shifted to CO_2 essentially quantitatively.

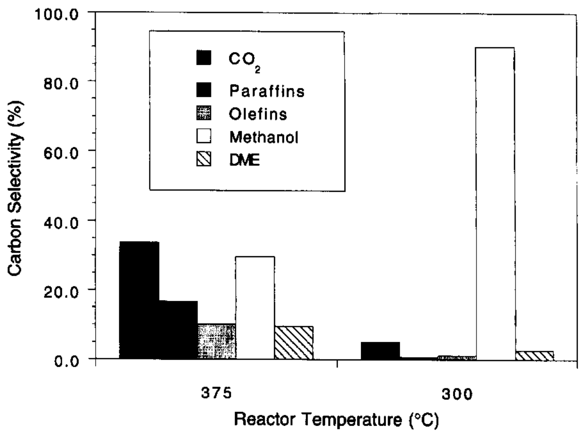

Fig. 1. The effect of reactor temperature on product distribution (GHSV=5000 sl $kg^{-1} h^{-1}$; total pressure=6.9 MPa; H_2/CO feed ratio=0.5; Decalin).

At 300°C, methanol was the only product formed in substantial quantities. The production of hydrocarbons and DME was small, which implies a low rate of water formation. This lack of water formation is

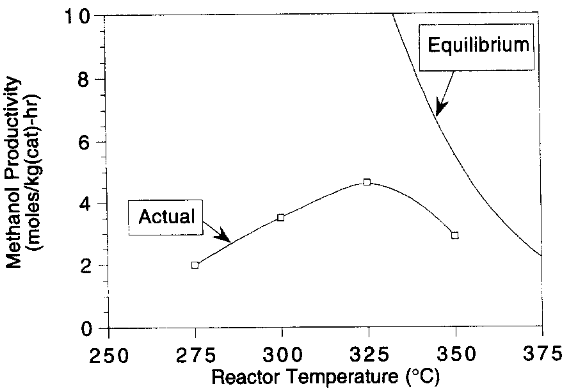

Fig. 2. The effect of reactor temperature on the rate of methanol formation (GHSV=5000 sl kg^{-1} h^{-1}; total pressure=7.0 MPa; H_2/CO feed ratio=2; Decalin).

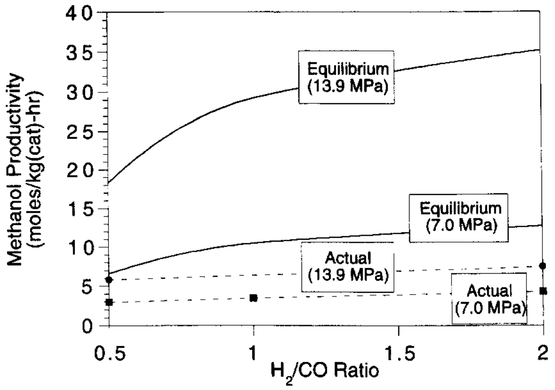

Fig. 3. The effect of H_2/CO ratio on the rate of methanol formation at various total pressures (GHSV=5000 sl kg^{-1} h^{-1}; reactor temperature=325°C; Decalin).

responsible for the low apparent selectivity to CO_2 at 300°C, relative to the selectivity at 375°C.

In Fig. 2, experimentally measured rates of methanol production are compared to the rates that would be observed if chemical equilibrium were achieved, for a pressure of 7.0 MPa, a GHSV of 5000 sl kg^{-1} h^{-1}, a H_2/CO ratio of 2, and with Decalin as the slurry liquid. Catalyst productivity is defined as the rate of methanol formation (mol h^{-1}) divided by the weight of catalyst in the reactor. The 'equilibrium' catalyst productivity was calculated by assuming that the methanol synthesis reaction was at equilibrium in the gas stream leaving the reactor, at the temperature of the reactor. This defined the effluent flow rate of methanol at equilibrium. The 'equilibrium' catalyst productivity was then calculated by dividing this effluent methanol flow rate by the catalyst weight.

The measured and theoretical reaction rates were reasonably close at 350°C, i.e., the effluent methanol concentration was >50% of the equilibrium value. The close approach to equilibrium at temperatures this low is somewhat surprising. The high catalyst activity at low temperature in the slurry reactor may be associated to some extent with a reduction in the resistance to pore diffusion as a result of the much smaller particle size of the slurry catalyst [21]. It also suggests that Decalin did not have a significant inhibiting effect on the catalyst, e.g., by competitive adsorption. The shape of the curve in Fig. 2, i.e., the maximum in the reaction rate at a temperature of approx. 325°C, is traditional for reversible, exothermic reactions. It reflects the fact that the reaction rate constant increases as the temperature increases, while the equilibrium constant decreases.

Fig. 3 shows the methanol catalyst productivity as a function of H_2/CO ratio for two pressures, 7.0 MPa and 13.9 MPa, at a space velocity of 5000 sl kg^{-1} h^{-1} and a reactor temperature of 325°C, with Decalin as the slurry liquid. The actual catalyst productivity increased with total pressure by a factor of ≈ 2 at constant H_2/CO ratio. However, the reaction rate was not very sensitive to the H_2/CO ratio at a fixed pressure. The reaction kinetics are substantially less sensitive to both total pressure and H_2/CO ratio than the reaction equilibrium.

Fig. 4 shows the concentration of hydrocarbons in the product as a function of the carbon number for an experiment at 5400 sl kg^{-1} h^{-1} GHSV, a temperature of 375°C, a pressure of 13.9 MPa and a H_2/CO ratio of 0.5, with Decalin as the slurry liquid. Methanol and DME are not included in the concentrations on this plot. The excellent straight line on semilogarithmic coordinates shows that the C_1–C_6 hydrocarbons follow an ASF distribution. Essentially all the C_2^+ hydrocarbons were olefins. The distribution of hydrocarbons produced by the unpromoted 'zinc chromite' catalyst (α=0.38) is similar to the distribution of alcohols produced by a *K*-promoted 'zinc chromite' catalyst (α=0.35), when this catalyst was operated under conditions where the production of branched higher alcohols was suppressed [8]. This tends to support the hypothesis that olefins are formed by alcohol

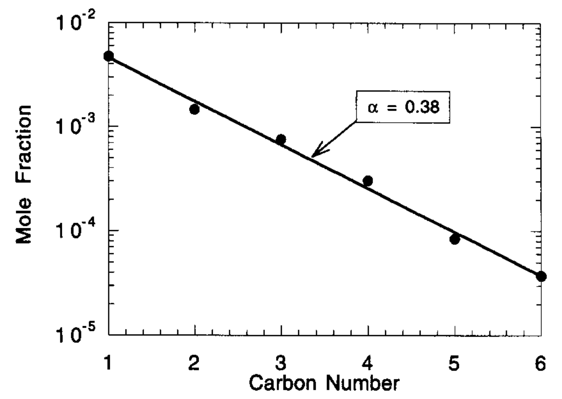

Fig. 4. ASF plot of the hydrocarbon product distribution. Oxygenates are not included. (GHSV =5400 sl kg^{-1} h^{-1}; reactor temperature=375°C; total pressure =13.9 MPa; H_2/CO feed ratio =0.5; Decalin.)

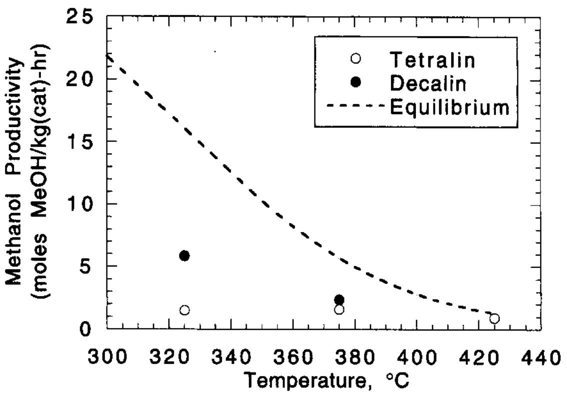

Fig. 5. The effect of reactor temperature on the rate of methanol formation for Decalin and Tetralin (GHSV=4400 sl kg^{-1} h^{-1}; total pressure=13.9 MPa; H_2/CO feed ratio=0.5).

dehydration. On the other hand, the alcohol dehydration hypothesis cannot account for the remarkable fit in case of methane to the line in Fig. 4.

Fig. 5 and Table 3 show comparisons of catalyst performance in Tetralin and Decalin. Firstly, it should be noted from Fig. 5 that Tetralin could be operated at temperatures higher than Decalin, consistent with the higher thermal stability shown in Table 2. At 425°C, a pressure of 13.9 MPa, a H_2/CO ratio of 0.5 and a GHSV of 4400 sl kg^{-1} h^{-1}, the 'zinc chromite' catalyst in Tetralin produced an outlet concentration of methanol that was essentially the same as the equilibrium concentration. At lower temperatures, but otherwise identical operating conditions, the reaction was no longer thermodynamically limited, and the reaction rate was significantly higher in Decalin than in Tetralin. This may result from competitive adsorption of Tetralin onto the catalyst sites that are responsible for the methanol synthesis reaction. Because of its partially-aromatic nature, Tetralin would be expected to adsorb more strongly than Decalin, which is completely saturated. Since the equilibrium constant for adsorption increases with decreasing temperature, the difference between the reaction rates in Decalin and Tetralin also increases with decreasing temperature. Note that the methanol formation rate in Tetralin at 325°C is less than that at 375°C, whereas the rate in Decalin increases as the temperature decreases, for reasons advanced in the discussion on Fig. 2.

Table 3
Effect of liquid composition on dimethyl ether (DME) formation [a]

H_2/CO feed ratio	Rate of DME formation/rate of methanol formation	
	Decalin	Tetralin
0.50	0.20	0.020
2.0	0.045	0.018

[a] Conditions: 375°C; 13.9 MPa; 4 400 sl kg^{-1} h^{-1}.

A similar effect is shown in Table 3, which compares the production of DME in Decalin and Tetralin at 375°C, 13.9 MPa, 4400 sl kg^{-1} h^{-1} GHSV and two different H_2/CO ratios. Both the absolute rate of DME formation and the ratio of the DME formation rate to the methanol formation rate are lower in Tetralin than in Decalin. Since different types of sites are believed to be responsible for methanol synthesis and DME formation, the data in Table 3 suggest that Tetralin also interferes with the reaction that takes place on the methanol dehydration sites.

Since DME is of commercial interest per se, particularly as an additive to or a replacement for diesel fuel, the relationship between the operating conditions and the rate of formation of DME is of some importance. This rate should depend on the concentration of methanol, since DME is formed by condensation of two molecules of methanol. Therefore, the ratio of the rate of DME formation to the total rate of methanol formation, i.e., the rate of methanol formation plus

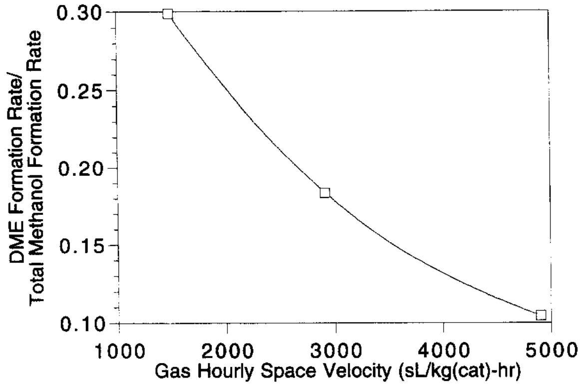

Fig. 6. The effect of GHSV on DME formation (reactor temperature=375°C}}; total pressure=7.0 MPa; H_2/CO feed ratio=1; Decalin).

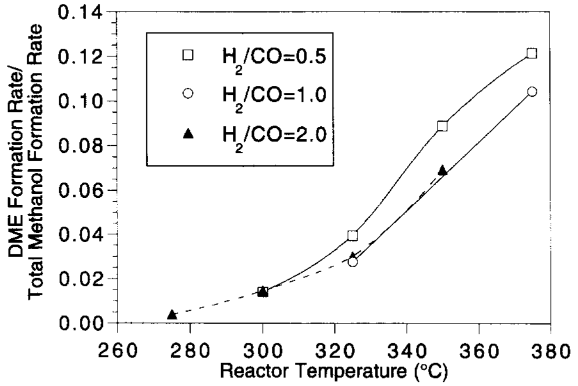

Fig. 7. The effect of reactor temperature and H_2/CO feed ratio on DME formation (GHSV=5000 sl kg^{-1} h^{-1}; total pressure =7.0 MPa; Decalin).

twice the rate of DME formation, has been used to evaluate the effect of operating conditions. This ratio will be abbreviated as DME/TM.

Fig. 6 and 7 show some features of the DME formation rate. The data in both these figures were taken using Decalin as the slurry liquid. Fig. 6 shows that the DME/TM ratio depends significantly on the space velocity, for a total pressure of 7.0 MPa, a H_2/CO ratio of 1, and a temperature of 375°C. Since the space velocity is the inverse of the contact time between the gas feed and the catalyst, i.e., the space time, this plot implies that the kinetics of DME formation are slow relative to the kinetics of methanol formation, even at 375°C.

Fig. 7 shows the effect of temperature and H_2/CO ratio on the DME/TM ratio at a total pressure of 7.0 MPa and a GHSV of 5000 sl kg^{-1} h^{-1}. As noted in connection with Fig. 1, the formation of DME increased significantly as the temperature increased. The effect of H_2/CO ratio was much less pronounced over the range of ratios tested. The DME/TM ratio decreased somewhat as the H_2/CO ratio increased, with most of the decrease taking place at lower H_2/CO ratios.

Since the reactor was operated continuously for periods up to 575 h, it was possible to follow the deactivation of the catalyst by periodically measuring the reaction rate and product distribution at a standard set of conditions: 325°C, 5000 sl kg^{-1} h^{-1} GHSV, 7.0 MPa and a H_2/CO ratio of 2, with Decalin as the slurry liquid. A wide range of operating conditions were tested between these 'standard' runs, so it is not possible to define the effect of individual operating variables, e.g., temperature, on the catalyst deactivation rate. Nevertheless, the results of such tests can indicate whether there is a serious catalyst deactivation issue that must be addressed during subsequent process or catalyst research. The combined data from two separate operating campaigns are shown in Fig. 8. The rate of methanol formation decreased with time on-stream, although the rate of decrease was relatively modest. Of possibly greater concern is the increase in the rate of methane formation with time.

'Post-mortem' analyses were conducted on the catalysts recovered from the reactor at the conclusion

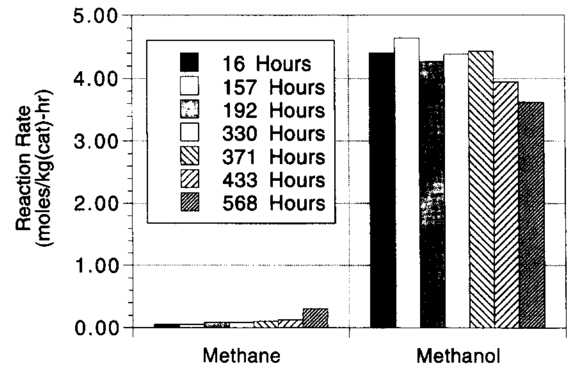

Fig. 8. Change of catalyst activity with time for methanol and methane formation (GHSV=5000 sl kg^{-1} h^{-1}; total pressure =7.0 MPa; reactor temperature=325°C; H_2/CO feed ratio=2; Decalin).

of these tests. The slurry liquid was removed from the used catalysts by heating them in air in an oven at 100°C for ≈12 h. The BET area of the recovered catalysts was about 90 $m^2 g^{-1}$, roughly 40% lower than the 'fresh' value. Interpretation of this result is not straightforward, since some of this loss of surface area may have occurred during the catalyst reduction procedure. Elemental analysis of the used catalyst showed that the concentration of iron increased by several hundred ppm during the run, possibly from the decomposition of iron carbonyl that was formed on the walls of the stirred-autoclave reactor. This iron deposition could have been responsible for both the loss of methanol synthesis activity and the increased methanation activity.

4. Conclusions

Sustained operation of a slurry reactor at temperatures close to 400°C and at high partial pressures of synthesis gas represents a major extension of the operating range for this type of reactor. The fused-ring, cyclic compounds that were used as slurry liquids in this research may find application as a medium for slurry reactors in other areas of syngas chemistry. However, liquid/catalyst interactions can occur that influence both apparent activity and selectivity of the catalyst.

The 'zinc chromite' catalyst appears to be compatible with slurry reactor operation. A high level of activity was observed for methanol formation, relative to the constraints of chemical equilibrium. There was no significant loss of methanol activity over almost 600 h of continuous operation, although the increased rate of methane formation with time on-stream is of concern and warrants further study. The formation of substantial quantities of DME and olefins, and relatively small quantities of paraffins, at 375°C in Decalin are positive features of catalyst performance. Moreover, the high water-gas-shift activity of the catalyst should make it useful with syngas that has a low H_2/CO ratio.

In view of these encouraging results, the next phase of this research will involve the evaluation of alkali-metal-promoted 'zinc chromite' catalysts in a slurry reactor.

Acknowledgements

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