

LIQUID/CATALYST INTERACTIONS IN A SLURRY REACTOR FOR METHANOL SYNTHESIS USING "ZINC CHROMITE" CATALYST

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INTRODUCTION

The synthesis of methanol and higher alcohols from mixtures of H₂ and CO (synthesis gas) is a promising approach to producing high-value fuels and chemicals from feedstocks such as natural gas, coal, coke and waste biomass. Slurry bubble column (SBC) reactors have been the focus of considerable attention for alcohol synthesis because the reactions are highly exothermic. Close temperature control is necessary to prevent excessive catalyst deactivation and to achieve high selectivity to oxygenates. The technology for producing methanol in a SBC reactor has been developed on a pilot scale, and is currently being commercialized [1,2,3]. This work has been based on Cu/ZnO, the conventional, low-pressure methanol synthesis catalyst. In addition, laboratory and pilot-plant studies have been conducted using cesium-promoted Cu/ZnO catalyst in a slurry reactor for the synthesis of higher alcohols [4,5]. Alkali-metal-promoted catalysts for higher-alcohol synthesis have evolved from the early work of Anderson and co-workers and Klier and co-workers [e.g., 6-9]. Unpromoted Cu/ZnO catalysts for methanol synthesis typically are operated at about 250°C, and the promoted Cu/ZnO catalysts for higher-alcohol synthesis have been evaluated over a temperature range of roughly 250 to 325°C.

"Zinc chromite", the high-pressure methanol synthesis catalyst, also is a promising starting point for the synthesis of higher (C₂⁺) alcohols. However, this catalyst requires a much higher operating temperature, about 400°C, than Cu/ZnO. The liquids that traditionally have been used to slurry the Cu/ZnO catalyst are not thermally stable at this temperature [10-12]. In previous research, a family of liquids was identified that are sufficiently stable, thermally and chemically, to be used in a slurry reactor with the "zinc chromite" catalyst [10-13]. The objective of the present investigation was to explore the performance of an unpromoted "zinc chromite" catalyst in three of the most stable liquids, decahydronaphthalene (DHN or Decalin[®], C₁₀H₁₈), tetrahydronaphthalene (THN or tetralin, C₁₀H₁₂) and tetrahydroquinoline (THQ, C₉H₁₁N). Unpromoted "zinc chromite" is essentially a methanol-synthesis catalyst. It is no longer competitive for methanol synthesis with the Cu/ZnO catalyst, which is more active and therefore can operate at lower pressures and temperatures. However, when promoted with alkali metals, "zinc chromite" can produce substantial yields of higher alcohols, particularly 2-methyl-1-alcohols such as isobutanol [14-17]. These alcohols might serve as alternative raw materials for the synthesis of established octane enhancers such as methyl tertiary butyl ether (MTBE). Thus, the present study of interactions between the unpromoted "zinc chromite" catalyst and the three slurry liquids was intended to provide a basis for using of one or more of these liquids as a slurry medium for an alkali-metal-promoted "zinc chromite" catalyst.

EXPERIMENTAL

The equipment used for this research has been described previously in some detail [10-13]. 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 cm³ stirred autoclave reactor. The reactor was charged with 20 grams of catalyst and 80 grams of the slurry liquid. The catalyst was a commercial, high-pressure methanol synthesis catalyst (Zn-0312 T1/8) from Engelhard Corporation, which was obtained in a reduced and stabilized form. The catalyst contained 60 wt% Zn and 15

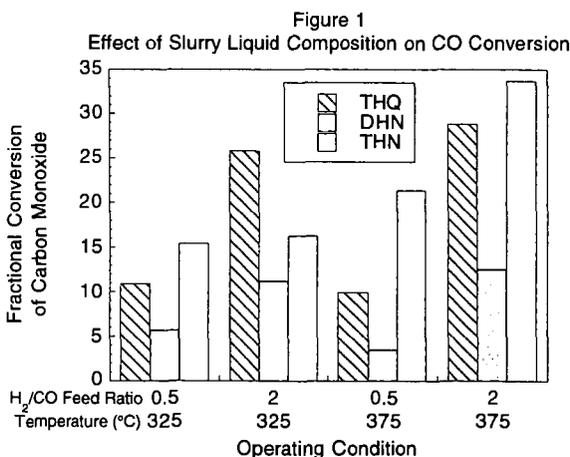
wt% Cr, with the ZnO and ZnCr₂O₄ phases detectable by x-ray diffraction. The as-received BET surface area was 145 m²/g. The gas leaving the reactor passed into a gas/liquid separator containing a cooling coil to control the temperature of the separator. The gas then passed through a back pressure regulator, 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, H₂, N₂, CO, CO₂ and H₂O. 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 of 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 was taken at steady state conditions.

A matrix of four experiments was run in each liquid. Two experiments were at a temperature of 375°C, one with a H₂/CO ratio of 0.5 in the feed gas and the other with a feed ratio of 2. The remaining two experiments were at 325°C, at the same two H₂/CO feed ratios. For all experiments, the total pressure was 13.8 MPa and the space velocity was about 5000 sL/kg(cat)-hr.

RESULTS

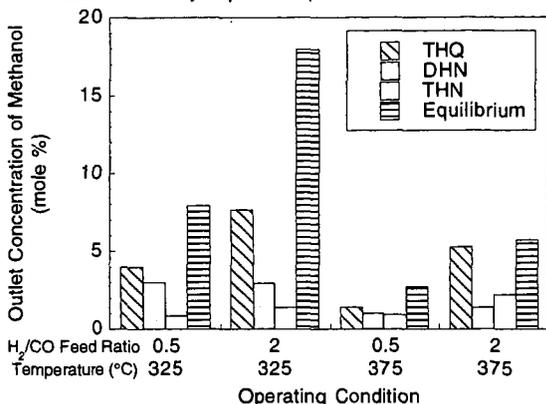
Figure 1 shows the fractional conversion of carbon monoxide at each of the four operating conditions, in each of the three slurry liquids. The difference in conversion between slurry liquids was substantial. At all four operating conditions, the ratio of the highest conversion to the lowest was between about 2 and 6. The difference in apparent catalyst activity from liquid to liquid was even greater, since the actual partial pressures of CO and H₂ in the reactor were lower in the high-conversion experiments than they were in the low-conversion experiments. The CO conversion was lowest in DHN at all four conditions. At three of the four conditions, the CO conversion was highest in THN. The exception was at 325°C and a H₂/CO ratio of 0.5, where the conversion was higher in THQ than THN.



The CO conversion generally increased as the H₂/CO ratio increased from 0.5 to 2. The influence of temperature on conversion depended on the liquid employed. With THN, "normal" behavior was observed, i.e., conversion increased substantially with temperature. However, with DHN and THQ, the effect of temperature on conversion was small. The reason for this difference in behavior is discussed below, in connection with Figure 3.

Figure 2 shows the concentration of methanol in the outlet gas from the reactor at each of the four operating conditions, in each of the three slurry liquids. For comparison, the equilibrium methanol concentration at the specified reactor temperature, with the specified feed gas, also is shown.

Figure 2
Effect of Slurry Liquid Composition on Methanol Production



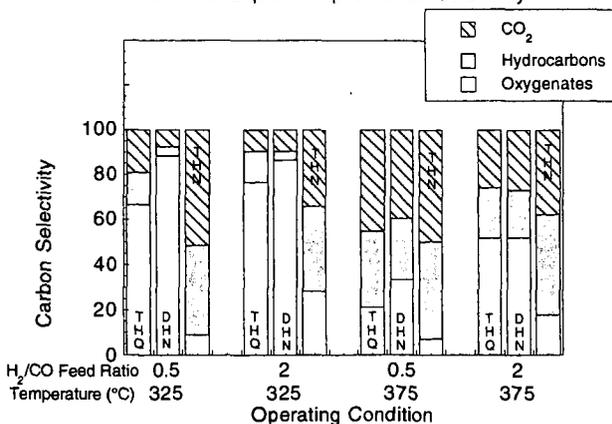
Once again, there was a substantial difference in catalyst performance from liquid to liquid. At all four conditions, the rate of methanol production was higher when THQ was used as the slurry liquid than with either THN or DHN. With the exception of the condition at 375°C and H₂/CO = 2, the rate of methanol synthesis was lowest in THN. At the lower temperature, where the reaction is not as close to equilibrium, the effect of liquid composition on the methanol production rate was substantial. For example, at H₂/CO = 2 and 325°C, this rate was about a factor of 6 higher in THQ than in THN and about a factor of 2.5 higher in THQ than in DHN.

At both temperatures, the methanol concentration generally increased as the H₂/CO ratio increased, with a given liquid. However, the effect was not as significant with DHN as with the other liquids. In fact, at 325°C with DHN, there was a slight decrease in methanol concentration as H₂/CO increased from 0.5 to 2.

The methanol production rate decreased with temperature at both H₂/CO ratios in THQ and DHN, reflecting the lower equilibrium concentration at the higher temperature. The methanol concentration increased as the temperature increased with THN, probably because the reaction was far from equilibrium in this liquid, at both temperatures.

Figure 3 shows that liquid composition also had a pronounced effect on reaction selectivity. The oxygenates were mostly methanol, plus some dimethyl ether and minor amounts of higher alcohols, primarily ethanol and isobutanol. The hydrocarbons were mostly methane, ethane and ethylene, plus lesser amounts of higher olefins.

Figure 3
Effect of Liquid Composition on Selectivity



The most significant difference between liquids was the low oxygenate selectivity and high hydrocarbon selectivity in THN, relative to the other two liquids. These effects were especially pronounced at 325°C. The oxygenate selectivity, which never exceeded 30% in THN, was always a factor of about 3 to 10 higher in the other two liquids. Moreover, the high CO₂ selectivity with THN is a direct consequence of the high hydrocarbon selectivity, since "zinc chromite" is an excellent catalyst for the water-gas-shift reaction.

The selectivity to both hydrocarbons and CO₂ increased as the temperature was raised from 325 to 375°C, for all three liquids. The increase was especially pronounced for THQ and DHN since the oxygenate selectivity at 325°C was quite high for both of these liquids. In part, this reflects the fact that the methanol synthesis reaction is close to equilibrium in THQ and THN at 375°C, as shown in Figure 2. This close approach to equilibrium limited the quantity of methanol, the major component of the oxygenates, that could be produced. The oxygenate selectivity generally increased as the H₂/CO ratio was raised from 0.5 to 2 at constant temperature, for all three liquids.

The different product distributions that occur with the three liquids are consistent with the effect of temperature on CO conversion, as noted in connection with Figure 1. The primary products with THN are hydrocarbons and CO₂, and there are no significant equilibrium limitations to the formation of these products at the conditions of these experiments. Therefore, the CO conversion increases with temperature, reflecting the "normal" influence of temperature on reaction kinetics. With THQ and DHN, methanol is the primary product at 325°C. The equilibrium concentration of methanol decreases with temperature, partially offsetting the effect of temperature on reaction kinetics. As a result, the effect of temperature on CO conversion with THQ and DHN is relatively weak.

DISCUSSION

The chemical mechanism(s) that are responsible for the large differences in apparent catalyst activity and selectivity from liquid to liquid are not clear at this time. There has been very little detailed information published on the behavior of the unpromoted "zinc chromite" catalyst in the absence of a liquid, e.g., in a fixed- or fluidized-bed reactor. The problem of comparison is compounded by the fact that the present studies were carried out at a much lower total pressure than typically is used in a methanol synthesis plant employing the "zinc chromite" catalyst. This low pressure probably is characteristic of those that would be used with the promoted "zinc chromite" catalyst for higher-alcohol synthesis. However, the pressure difference makes it difficult to determine which of the liquids most closely approximates "normal" behavior. It is clear that the very low oxygenate selectivity that was observed with THN cannot be typical of conventional, vapor phase operation. The high hydrocarbon and CO₂ selectivities of this liquid, coupled with the high CO conversions, suggest some sort of liquid/catalyst interaction that inhibits methanol synthesis and dramatically increases the rate of hydrocarbon formation.

The methanol-synthesis activity of the "zinc chromite" catalyst in THQ is probably greater than the vapor-phase activity, based on the fact that the methanol synthesis reaction essentially came to equilibrium at 375°C and a H₂/CO ratio of 2 with THQ as the slurry medium. This enhanced rate of reaction may be related to the ability of secondary amines such as THQ to react with oxygenate and/or hydrocarbon fragments on the surface of the catalyst. Analyses of samples of THQ taken during and after reactor operation showed that some alkylation of THQ took place. Moreover, the alkylation of other amines has been reported to occur over various Fischer-Tropsch catalysts during vapor-phase operation, at substantially lower temperatures than those used in this research [18-22]. A mechanistic understanding of the chemistry of the interactions between THQ and the catalyst surface may lead to further improvements in rate and selectivity that can be applied to the synthesis of higher alcohols.

CONCLUSIONS

The composition of the slurry liquid had a major effect on both the apparent activity and selectivity of "zinc chromite" catalyst for the synthesis of methanol in a slurry reactor. Tetrahydronaphthalene (THN) does not appear to be a promising liquid because it causes low rates of oxygenate formation and low oxygenate

selectivities. In contrast, the rate of methanol synthesis was very high in tetrahydroquinoline (THQ), and the oxygenate selectivity was good, especially considering that the rate of the methanol synthesis reaction was retarded by a close approach to equilibrium.

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