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PROGRESS REPORT

A NOVEL PROCESS FOR METHANOL SYNTHESIS

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1.0 ABSTRACT

A bench-scale reactor is being used to conduct studies of the conversion of synthesis gas to methanol by a novel process. In previous reports, we provided evidence for a two step reaction in series: the carbonylation of methanol to methyl formate taking place in a non-equilibrium region in the vicinity of the copper chromite surface, and the hydrogenolysis of methyl formate to methanol taking place on the surface of the copper chromite. The synergism between the two catalysts enhances the rate of methanol formation. In this quarter, we tested several copper chromites (with different surface areas and stabilizing agents) on the rate of methanol synthesis. It seems likely that pore diffusion limitations control the hydrogenolysis reaction since the rate of methanol formation is proportional to the square root of the copper chromite surface area. Elemental analyses using Inductively Coupled Plasma analysis and pore size distribution analysis of copper chromite were carried out.

2.0 INTRODUCTION

An experimental investigation of a new process, which we call the concurrent synthesis, for converting synthesis gas to methanol is being carried out in our laboratory. It has advantages over the conventional gas phase synthesis in that the recycle of unreacted material can be virtually eliminated and it operates at lower temperatures. The reaction is not significantly poisoned by low levels of CO_2 or H_2O . It has been demonstrated that the reactions proceed with good rates at 150°C and 6.3 MPa pressure. The overall conversion of synthesis gas to methanol most likely proceeds through methyl formate as an intermediate. However, the nature of the mixed catalyst, comprised of an alkali methoxide (e.g., KOCH_3) and copper chromite, and of the possible intermediates is not understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst(s). This information should help make it possible to scale up the process.

Two papers have been published^{1,2} reporting our studies. One is a study of the individual consecutive reactions: carbonylation of methanol to methyl formate followed by the hydrogenolysis of the methyl formate. The other paper describes the concurrent reaction in which a carbonylation catalyst such as KOCH_3 and a hydrogenolysis catalyst such as copper chromite are used in the same reactor. The current work is part of a three and a half-year project which started in September, 1989.

In this report, a soluble catalyst refers to an alkali salt added as a powder to the reactor (the powder is soluble in methanol); the copper chromite is the heterogeneous catalyst. A homogeneous reaction possibly takes place in the liquid solution, and a heterogeneous reaction takes place on the surface of copper chromite. It is possible that the soluble salt is adsorbed on the copper chromite and the combination then functions as the catalyst or the catalyst precursor.

During this quarter, a paper entitled "The Effect of CO₂ and H₂O and Their Interaction in a Novel Slurry Phase Synthesis of Methanol" was presented at the Eighth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, October 14-18, 1991. A copy is attached.

3.0 RESEARCH OBJECTIVES

Principal research objectives are:

- To find more efficient catalysts for the concurrent synthesis of methanol. We are testing modified copper chromite catalysts and alkali compounds other than methoxides which are soluble in methanol.

- To determine the nature of the active catalyst in the concurrent synthesis and the effect of deactivating agents such as CO_2 and H_2O .

- To determine the rate-limiting step(s) in the concurrent synthesis. The effect of catalyst loading and reactor volume are of special importance.

- To develop mathematical models which can be used to predict the rates of reaction and could be useful in eventual scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, we tested several copper chromites for use in the concurrent synthesis. Results are summarized below.

4.1 Copper Chromites as Hydrogenolysis Catalysts in the Concurrent Reaction

Copper chromite is commonly used as a catalyst for ester hydrogenolysis. It is normally prepared by decomposing a copper ammonium chromate at low temperatures to give a material reported as "copper-chromite"³. Stroupe suggested that the catalyst could be made amorphous or crystalline depending on the decomposition temperature used³. Prior to reduction, copper chromite catalyst consists of an intimate mixture of CuO and CuCr_2O_4 . Stabilizing agents such as BaO or MnO are typically added to prevent complete reduction of the catalyst during use. XRD patterns for barium promoted copper chromite were previously reported⁴. Figure 1 shows XRD traces for two manganese promoted copper chromites before and after reaction. One was obtained from United Catalysts (G-89) and the other from the Calsicat Company. In the unreduced state, G-89 has a more defined crystalline pattern than the other copper chromites which have poorly defined crystalline patterns. After in-situ reduction all copper chromites are essentially amorphous although G-89 retains some crystallinity. Tonner et al. attributed the lack of crystallinity in the barium promoted copper chromite to the decomposition of the BaCrO_4 to BaO and Cr_2O_3 ⁵. Uncertainty exists with regard to the identity of the active species in copper

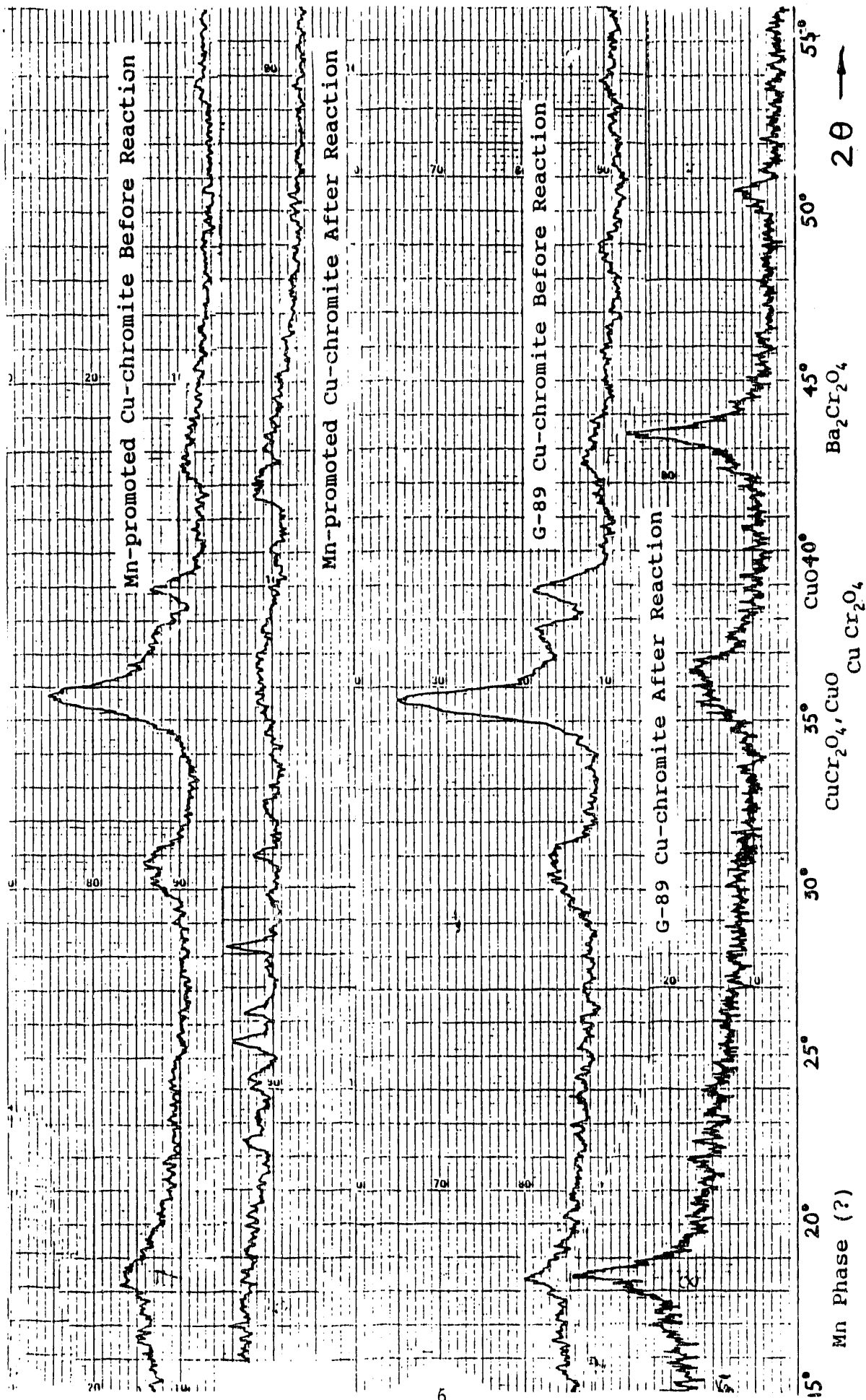


Figure 1: XRD Traces for Mn-promoted Copper Chromite and G-89 Copper Chromite Before and After Reaction.

chromite. Cu^{2+} (Adkins⁶), Cu^0 dispersed on CuCr_2O_4 (Stroupe³), Cu^0 on or mixed with Cr_2O_3 ⁷, Cu_2O or CuO on CuCr_2O_4 or Cu^0 on $\text{Cu}_2\text{Cr}_2\text{O}_4$ have all been proposed⁷. Using XRD and XPS, Monnier et al.⁸ identified Cu^+ in the CuCrO_2 phase formed on reduction of copper chromite as the active site for the direct methanol synthesis at 250°C. It seems likely that Cu^+ is the desired oxidation state in the concurrent synthesis.

The activities of several copper chromites for methanol synthesis are listed in Table 1. The Mn promoted copper chromite has high activity at 40 hrs, but it has a slightly higher rate of deactivation than the high surface area Ba stabilized copper chromite. Three Ba-stabilized copper chromites with different surface areas were examined. The chemical compositions of these catalysts were similar and it is likely that, except for their surface areas, other characteristics are similar. As shown in Figure 2, the rate of methanol synthesis is proportional to the square root of the surface area. This is typical for a pore diffusion limited reaction. Pore diffusion limitations for hydrogenation reactions on copper chromite catalysts have been reported by other investigators⁹.

The pore size distribution of the Ba-stabilized copper chromite catalyst ($S_A = 103 \text{ m}^2/\text{gm}$) is shown in Figure 3. The average pore size is of the order of 40 Å. This size is consistent with pore diffusion limitations particularly since the reactants and products (H_2 , CO , CH_3OH , and KOCH_3) must diffuse into the pores. We have previously reported that cesium methoxide is not as

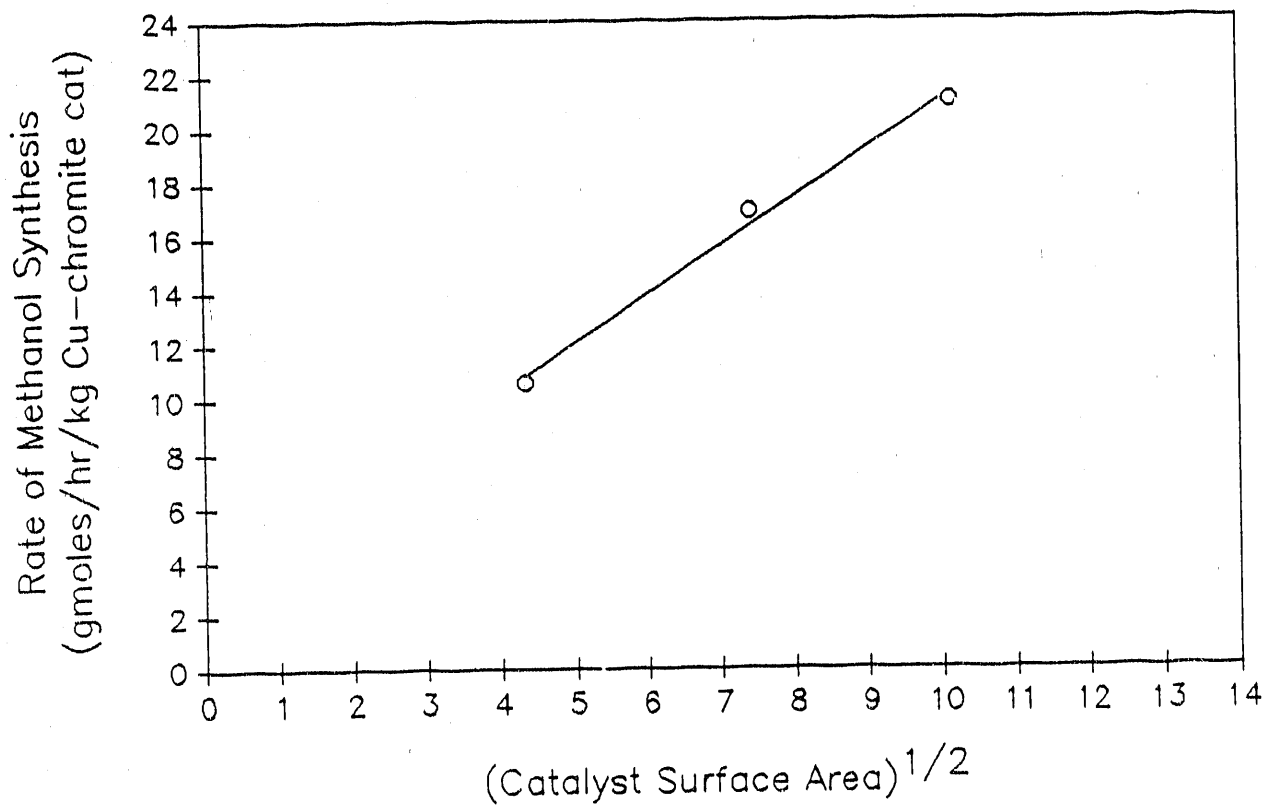


Figure 2: Rate of Methanol Synthesis as a Function of Copper Chromite Surface Area.
 20 gms/lit Cu-chromite, 0.049 gmoles/lit KOMe in 150 cc. MeOH charge, T=150°C, P=63 atm.

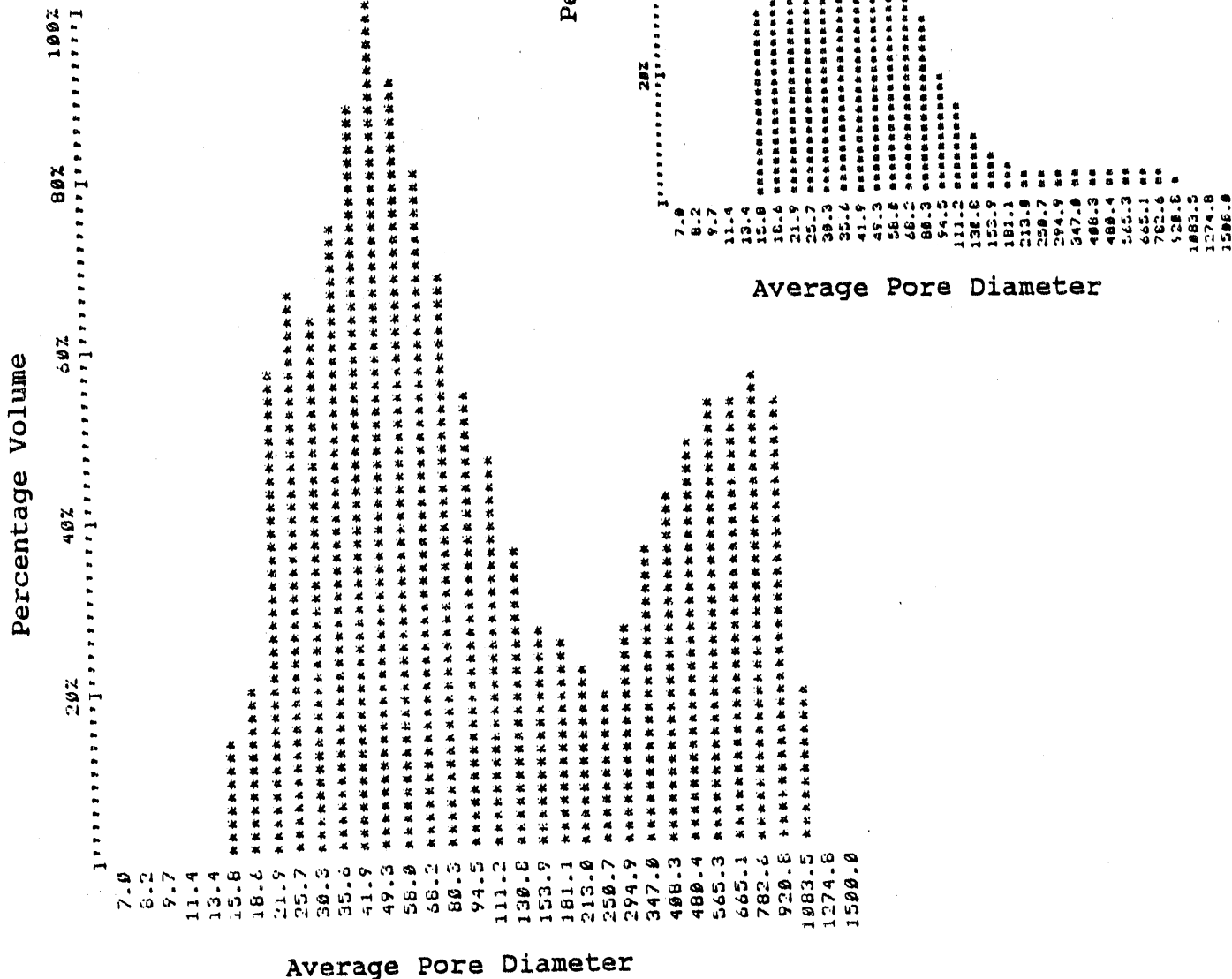


Figure 3: (a) Percentage of Pore Area versus Average Pore Diameter Before Reaction.
 (b) Percentage of Pore Volume versus Average Pore Diameter Before Reaction.

Run No.	Type of Cu-chromite {Composition} (Surface Area)	MeOH Rcn. Rate at 40 hrs. gmoles/hr/kg cat	Average Deactivation Rate %/day
P3	Ba stabilized Cu-chromite - #81C-83B {Cu-32.1(28.33*), Cr-29.0(25.15), Ba-(7.21)} (103 m ² /gm)	21.0	0.37
A36	Ba stabilized Cu-chromite - #42D-04C {Cu-31.7, Cr-28.7} (55 m ² /gm)	16.9	1.04
P13	Ba stabilized Cu-chromite <ppd. by coprecipitation> {Cu/Cr=0.9, Ba/Cu=0.11} (18.785 m ² /gm)	10.6	2.77
A35	Ba stabilized Cu-chromite - #09D-10A {Cu-34.8, Cr-30.4} (area to be determined)	17.0	0.79
A38	G-89 (United Catalysts) {Cu-37.7, Cr-29.1, Ba-0.05, Mn-1.7} (area to be determined)	18.6	1.315
A34	Mn promoted Cu-chromite {Cu-31.1, Cr-32.2} (26 m ² /gm.)	19.0	2.36

Note: All the copper chromites except run A38 (United Catalysts, G-89) and run A13 (prepared by coprecipitation) were supplied by Calscat.

All experiments were carried out with 20 gms/l loading of Cu-chromite and 0.0476 gms potassium methoxide in 150 ml. methanol charge.

* by separate analyses.

Table 1. Properties of copper chromite catalysts used in the concurrent synthesis.

effective a catalyst as potassium methoxide, an unexpected result based on the reduction potentials of cesium and potassium. The explanation may be that this is due to limitations on diffusion of the larger cesium ion.

5.0 FUTURE WORK

We will continue to investigate alternative catalysts for the concurrent methanol synthesis. Emphasis during the next quarter will be to test alternative soluble salts.

The addition of small amounts of methyl formate to the reactor feed will be tried in the hope of decreasing the initial transient period.

Mathematical models for the rate of reaction will be developed and tested.

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6.0 REFERENCES

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