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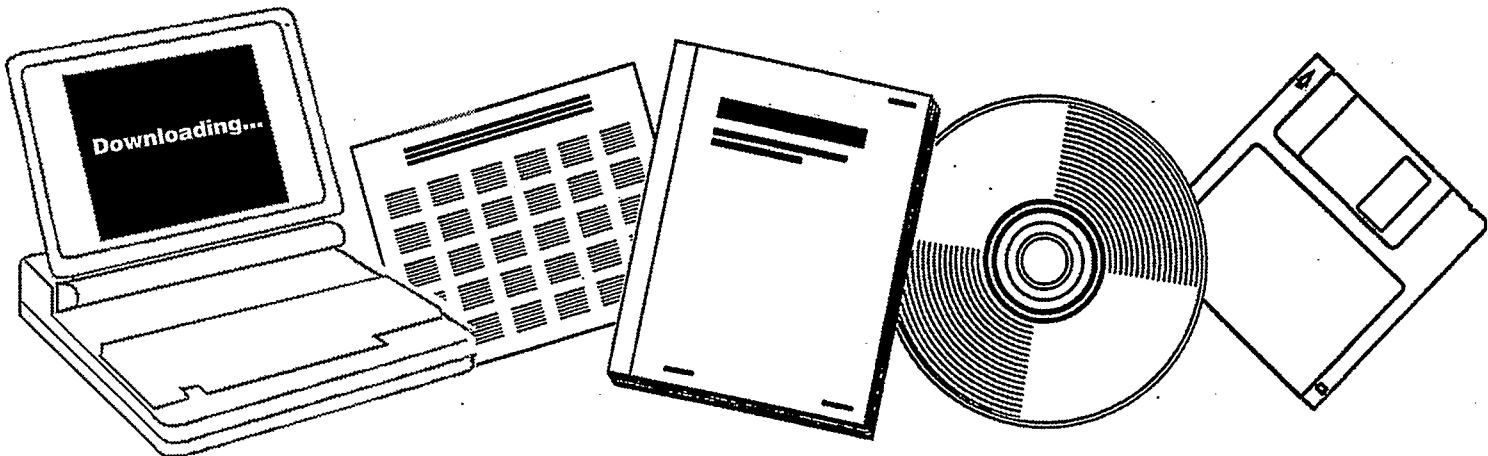
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**NOVEL PROCESS FOR METHANOL SYNTHESIS.
PROGRESS REPORT, SEPTEMBER 1,
1990--NOVEMBER 30, 1990**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

1990



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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. During the last quarter, we investigated the nature of the reactions involved and the nature of the Cu-chromite catalyst being used. There is evidence that methanol is formed via a two step reaction with a methyl formate intermediate rather than by the direct hydrogenation of CO. The carbonylation reaction predominantly takes place in the liquid phase while the hydrogenolysis reaction is restricted to the surface of Cu-chromite. At steady state, the carbonylation reaction taking place in the region close to the Cu-chromite surface is probably the main source of MeF. This model also explains the increased tolerance of the process to CO. A mechanistic model is proposed to explain the interaction of different species in the reaction mixture. The topography of the Cu-chromite surface is also investigated by X-ray diffraction and scanning electron microscopy.

2.0 INTRODUCTION

An experimental investigation of a new process, developed in our laboratory, for converting synthesis gas to methanol is being carried out. It has significant 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 CO_2 or H_2O . It has been demonstrated that the reaction proceeds with good rates at 150°C and 6.3 MPa pressure. It is likely that the overall reaction proceeds through methyl formate as an intermediate. However, the nature of the mixed catalyst comprised of an alkali methoxide (e.g. KOMe) and Cu-chromite and of the possible intermediates is not well understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst. This information should make it possible to scale up the process.

Two papers have been published^(1,2) reporting our studies. One is on the individual reactions: (a) carbonylation of methanol and (b) hydrogenolysis of methyl formate. The other paper is on the concurrent reaction in which a carbonylation catalyst (e.g. potassium methoxide) and a hydrogenolysis catalyst (e.g. Cu-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.

Two papers were presented during the last quarter, one at the AIChE Annual Meeting, Chicago, November 11-16, entitled The Synthesis of Methanol by a Novel Method⁽³⁾ and the other at the Seventh Annual International Pittsburgh Coal Conference, Pittsburgh, September 10-14, entitled A Novel Synthesis of Methanol⁽⁴⁾. Copies of the two papers are attached as Appendix I. Mr. Vishwesh Palekar prepared a proposal for his PhD. dissertation entitled "A Novel Synthesis of Methyl Alcohol". It was approved by his doctoral committee.

In this report, a soluble catalyst refers to an alkali salt (e.g. potassium methoxide)

added as a powder to the reactor (the powder is soluble in the solution). The Cu-chromite powder is referred to as a heterogeneous catalyst. A homogeneous reaction is thus one which takes place in the liquid solution (not on the surface of Cu-chromite) and a heterogeneous reaction is one which takes place on the surface of Cu-chromite.

3.0 RESEARCH OBJECTIVES

Principal research objectives are,

1) To determine the effect of alternate catalysts on the synthesis. This will include modified copper chromite catalysts in addition to soluble catalysts in the form of methoxides or similar salts.

2) To determine the nature of the active catalyst in this reaction and the effect of deactivating agents such as CO_2 , H_2O and CO .

3) To determine the rate limiting steps in this reaction so that proper scale-up is possible. The effect of catalyst loading and reactor volume are of special importance.

4) To develop mathematical models which can be used to predict the rates of reaction and are suitable for scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, we studied the nature of the reactions (whether homogeneous/heterogeneous or just heterogeneous) involved and also looked at the surface of Cu-chromite by XRD and SEM.

4.1 Sequence of reactions

From our previous studies^(1,2) it seems likely that the formation of MeOH in the concurrent synthesis proceeds through two steps: the carbonylation of MeOH to MeF and the successive hydrogenolysis of the MeF to two moles of MeOH. The net result is the reaction of CO with H₂ to give MeOH. This is supported by the high MeOH formation rates obtained at 150°C for a KOME/Cu-chromite combination in comparison to a KOME/Cu-ZnO mixed catalyst, as shown in our previous report⁽⁵⁾. The depletion of CO leading to the formation of MeF was rapid followed by a slow rise in the H₂ conversion as shown in Figure 1. This shows that a certain amount of MeF needs to be formed before the H₂ can be consumed, supporting the two step scheme rather than the direct hydrogenation of CO on the Cu-chromite surface as reported by Onsager et al.⁽⁶⁾. The carbonylation reaction is in equilibrium (about 4% MeF is present in the liquid at steady state) and the hydrogenolysis reaction is the rate determining step (refer to Table 1). It is proposed that although the carbonylation reaction is in equilibrium in the bulk liquid, it may not be in equilibrium in the film close to the heterogeneous surface.

Table 1 : Comparison of Calculated and Experimental Equilibrium Ratios for Carbonylation of MeOH and Hydrogenolysis of MeF

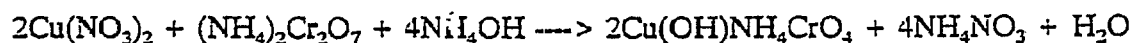
Reaction (Ratio)	Equilibrium	
	Calculated	Experimental
Carbonylation ($C_{MeF}/C_{MeOH}P_{CO}$)	0.00285*	0.00253
"	0.00263**	
Hydrogenolysis ($P_{MeOH}^2/P_{MeF}P_{H_2}^2$)	80.19*	3.0E-4

* Data from Liu⁽⁷⁾

** Data obtained from Onsager et al.⁽⁸⁾

4.2 Nature of the Concurrent Reaction

To study the location of the reaction active sites, a Ba-stabilized Cu-chromite catalyst containing potassium in the bulk was prepared by coprecipitation. This method suggested by Adkins et al.⁽⁹⁾ involves precipitating an ammonium salt according to the reaction,



The basic ammonium salt is then decomposed according to the reaction,



Use of $K_2Cr_2O_7$ instead of $(NH_4)_2Cr_2O_7$ results in Cu-chromite containing potassium in the bulk. If MeF is predominantly formed in the liquid phase, potassium is likely to diffuse out of the bulk matrix into solution. This should result in a delayed induction period for the formation of MeF. As seen in Figure 2, in comparison to a run for KOMe/Cu-chromite, a much longer induction time was observed for MeF generation corresponding to the time required for diffusion to the surface. This is in agreement with the assumption that MeF is formed predominantly in the liquid phase.

4.3 Nature of the Cu-chromite Catalyst

The Cu-chromite catalysts (commercial as well as prepared by coprecipitation) were examined under X-ray diffraction (XRD). The commercial Cu-chromite showed very poor crystallinity; mainly $BaCrO_4$ crystalline peaks were identified. However, both catalysts after reaction seemed to lose their crystallinity (the catalyst after reaction was amorphous). The XRD peaks are compared in Figure 3. For the Ba-stabilized Cu-chromite prepared by coprecipitation with and without K, crystalline phases of CuO and $CuCr_2O_4$ were identified on the surface of the catalyst. This observation is supported by Trimm et al.⁽¹⁰⁾ who identified CuO and $CuCr_2O_4$ in Cu-chromite which were used as catalysts for the hydrogenolysis of MeF.

Cu-chromite as well as K promoted Cu-chromite were characterized by SEM. At a magnification of 20,000, the Cu-chromite seemed to contain discrete flat particles. The

surface also showed a number of small patches of elongated particles. These would be expected to have higher surface areas. SEM pictures for Cu-chromite is shown in Figure 4.

Size analysis of the Cu-chromite particles before reaction obtained in a Microtrac Size Analyzer, showed a size distribution in the range 2 to 88 microns, mainly concentrated in the range 5.5 to 62 microns.

4.4 Proposed Model for the Concurrent Synthesis

Studies of the concurrent synthesis show that there are considerable differences between the predicted performance based on studies of the individual reactions and the actual performance. At least two explanations are possible. One is that the reaction pathway in the concurrent synthesis involves adsorption of an alkali metal on the surface of Cu-chromite, the reaction(s) being heterogeneous in nature. Another is that the reactions are essentially unchanged, but the environment in which they take place is changed. Based on studies done earlier a mechanistic model is proposed for the nature of the concurrent reaction.

A Model for the Concurrent Synthesis

The basic assumption is that the reaction proceeds by the carbonylation of methanol to MeF with the subsequent hydrogenolysis of the MeF to MeOH. This assumption is

justified in light of the fact that MeOH production rate picks up only after considerable MeF is formed (Figure 1). Also, high rates are obtained at 150°C in contrast to Monnier at al.'s claim that Cu-chromite is active only at temperatures around 250°C⁽¹¹⁾. Thus, it is proposed that the carbonylation reaction takes place homogeneously in the liquid phase while the hydrogenolysis reaction takes place on the surface of alkali promoted Cu-chromite (heterogeneous reaction). We know that if no heterogeneous catalyst is present, the only reaction which takes place is carbonylation and if no alkali or suitable alkali compound is present as catalyst, MeOH is formed at a greatly reduced rate.

The volume of liquid is large compared to the catalyst volume, so it is expected that the bulk mixture would contain an equilibrium amount of MeF and MeOH and this has been verified experimentally. However, for the hydrogenation reaction to take place on the Cu-chromite surface, the MeF must diffuse onto the surface. It is the region adjacent to the Cu-chromite surface which is of prime importance in influencing the environment under which the reaction takes place. As MeF is disappearing on the surface, there exists a concentration gradient from the bulk liquid concentration to the surface concentration. Since the MeF concentration in this region will be less than the equilibrium value, reaction with CO will occur. It seems quite possible that all or most of the homogeneous reaction is taking place in this layer. The net effect is that a CO gradient exists between the bulk and the surface concentration. This model helps explain some of the effects noted in the concurrent reaction.

- The rate limiting step is the hydrogenolysis of MeF. If the carbonylation reaction is not taking place in the surface layer, the concentration of MeF will drop (probably linearly) from the bulk concentration to the surface concentration. If the carbonylation reaction does take place in the film, it will yield a higher value for the surface concentration of MeF. This is shown in Figure 5. The higher surface concentration would be expected to produce a higher reaction rate. This could explain the higher rate of MeOH formation obtained in comparison to the summation of the individual reactions.

- If no homogeneous catalyst is present but CO is present, it has been observed that the hydrogenolysis reaction is inhibited⁽⁷⁾. However, if the homogeneous catalyst is present, the reaction seems to be tolerant to CO^(3,4). With no homogeneous catalyst, the CO on the surface is essentially that in the bulk. The net effect of the homogeneous reaction is that of reducing the surface concentration of CO and thus its effect in inhibiting the reaction.

- If no Cu-chromite is present, the presence of H₂O in the reaction mixture is a poison for the carbonylation reaction. A white precipitate of sodium formate is observed when NaOMe is used as the catalyst. Other alkali methoxides are removed by conversion to the corresponding formates⁽¹²⁾. In the presence of Cu-chromite, the reaction proceeds without a poisoning effect on the homogeneous catalyst. This is explained by considering a Cu-chromite

regeneration cycle as shown in Figure 6. The methoxide ion is regenerated from the formate in the presence of a good ester hydrogenolysis catalyst such as Cu-chromite. Thus, it is proposed that the methoxide ion is the carbonylation catalyst. This is substantiated by the fact that KOMe gave the highest rates. H_2O has a greater tendency to interact with alkali than with Cu-chromite. This interplay can explain the tolerance of the reaction to the presence of H_2O .

- As the CO is introduced into the reaction mixture containing MeOH, the catalyst which is reduced at $170^\circ C$ in situ and about 1.5-2% H_2O (which is formed as a result of catalyst reduction), it is possible that the CO takes up the labile oxygen from the Cu-chromite catalyst, and forms CO_2 , which keeps increasing in concentration. The labile oxygen in the catalyst is the only source of free oxygen available in the reaction mixture. This is supported by the observation that the maximum amount of CO_2 reached is a function of the reduction temperature or the temperature at which the Cu-chromite is activated prior to the reaction. In situ reduction in the liquid phase has been known to result in incomplete reduction of the Cu-chromite catalyst⁽¹³⁾.

- The presence of CO_2 is detrimental to both the reactions⁽¹⁾. However, its effect on the Cu-chromite catalyst for MeF hydrogenolysis is known to be reversible⁽¹⁾. The maximum always occurs at around 4 hrs into the reaction.

The CO_2 concentration rapidly reaches equilibrium at about 8 hrs into the reaction supposedly by the water-gas shift reaction since it is observed that the H_2O concentration in the liquid phase decreases. Until then the MeF builds up slowly due to the regeneration of the CH_3O^- group. However, only when the CO_2 reaches a mole fraction of 0.4-0.8% in the gas phase (steady state level), does the MeOH production rate really pick up. This shows that CO_2 reversibly deactivates the Cu-chromite. The reason for the tolerance of the process to this level of CO_2 in comparison to higher amounts of CO_2 which are detrimental is not yet clear. It may be that this is connected with the maintenance of Cu in the Cu^+ state for its activity.

• The MeOH formation rate follows the MeF rate with a small time lag. However, it soon catches up and then the two rates go hand in hand. This implies that the reason for the MeOH induction time is the formation of MeF and CO_2 , while that for MeF is the formation of CO_2 (since the buildup of CO in the reaction medium is rapid). It is likely that the carbonylation reaction is catalyzed by the CH_3O^- group in a reaction sequence proposed by Christiansen⁽¹⁴⁾ while the hydrogenolysis reaction proceeds through the decomposition of a hemiacetal intermediate⁽¹⁵⁾ resulting in the formation of a surface formyl species which is rapidly hydrogenated to MeOH. It is likely that the presence of CO is detrimental to the hydrogenation of the formyl species as proposed by Monti et al.⁽¹³⁾ especially since trace amounts of

formaldehyde were noted in the gas phase analysis (< 0.05%).

5.0 FUTURE WORK

Studies will be carried out to investigate the activity and nature of the reactions with other catalysts for MeOH synthesis. Different salts will be investigated for their catalytic activity and to test the Cu-chromite regeneration hypothesis. The effect of addition of small amounts of MeF to the reaction feed would be tested in the hope to decrease the initial transient period. Cu-chromites with different surface areas would be tested to investigate any effect on the rate of MeOH synthesis. The effect of different amounts of CO₂ and H₂O in the reaction mixture will be investigated.

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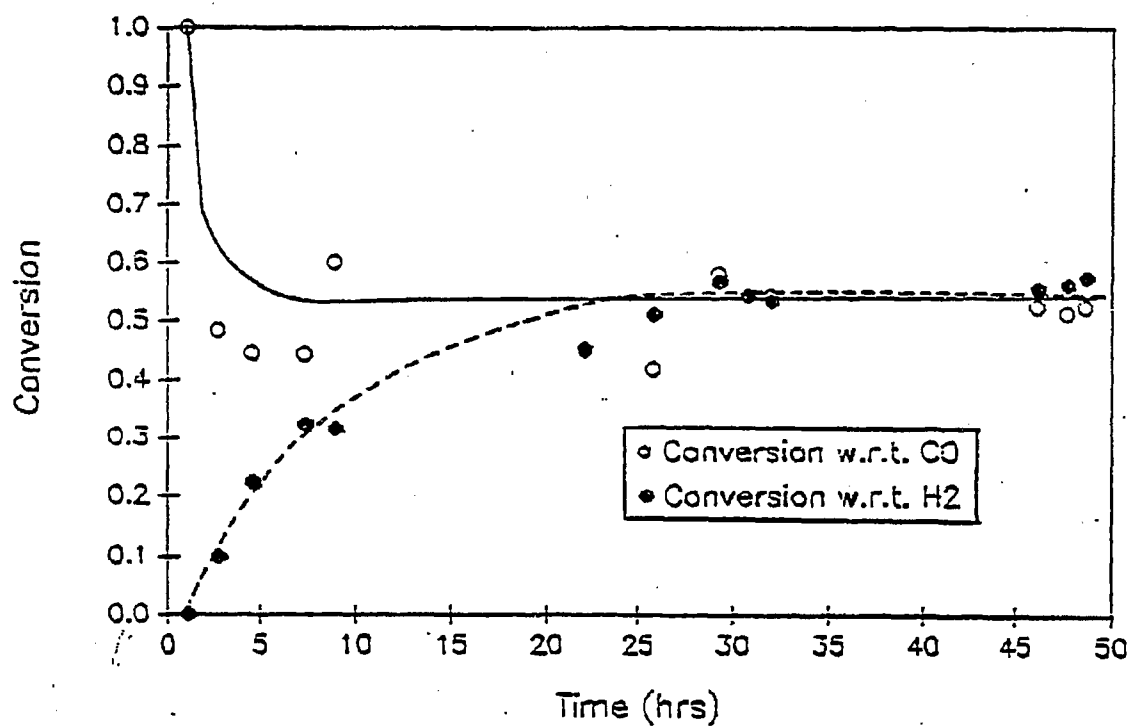


Figure 1: Typical Conversion of CO and H₂ with Time

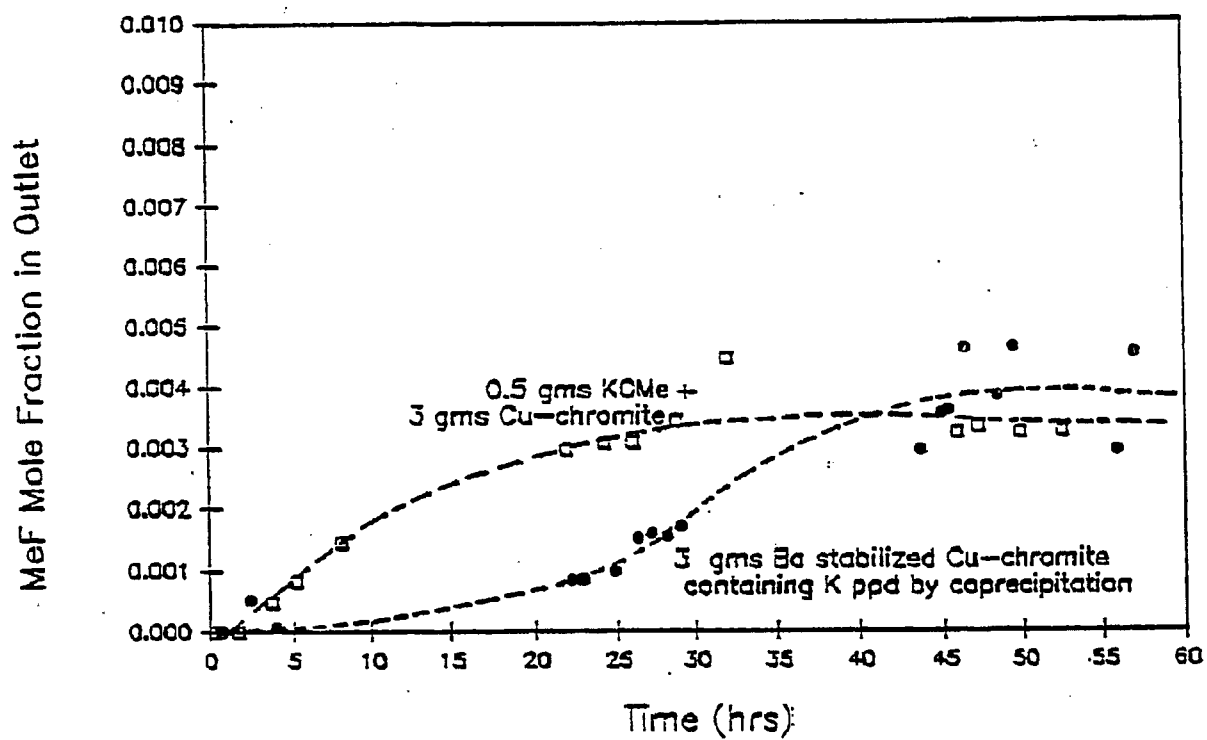


Figure 2: Mole Fraction MeF using Various Catalyst Systems

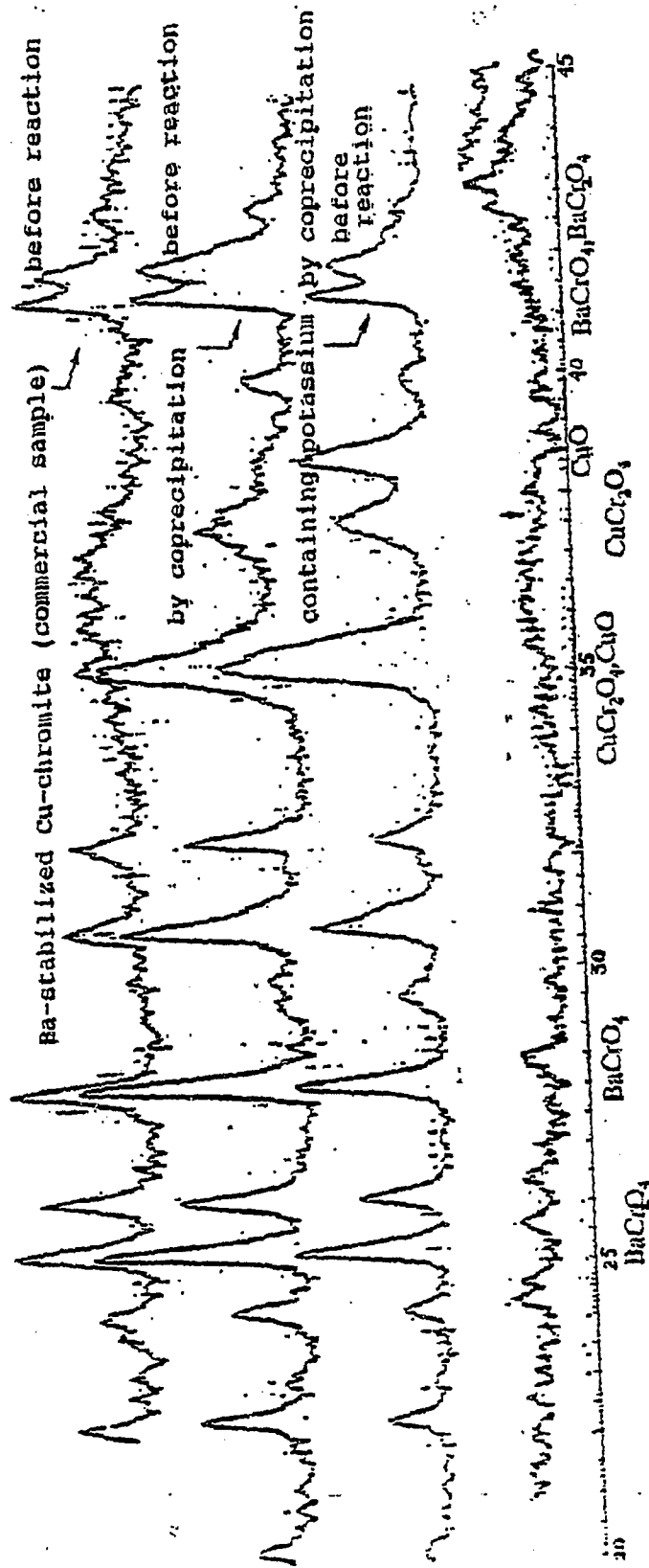


Figure 3: XRD Spectra for the Various Cu-chromite Catalysts

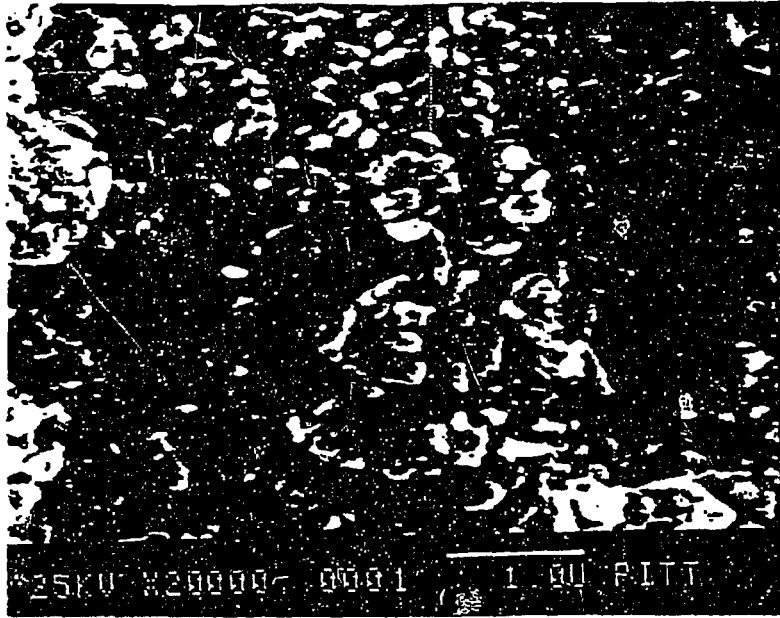
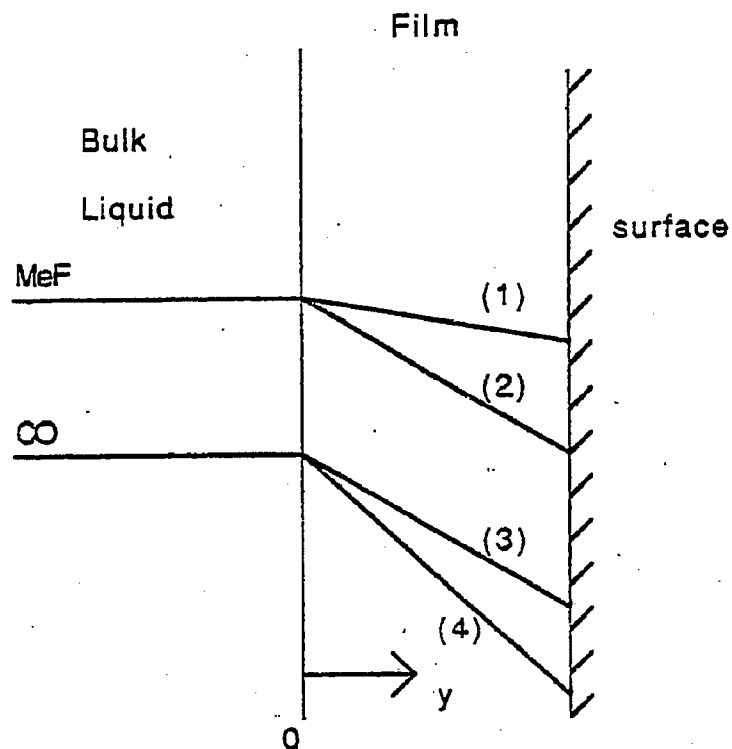


Figure 4: Surface Morphology by SEM of Cu-chromite Catalysts



- (1) Actual MeF gradient in the reaction mixture
- (2) MeF gradient in the absence of the carbonylation reaction.
- (3) CO gradient in the absence of the carbonylation reaction
- (4) CO gradient in the reaction mixture.

Figure 5: MeF and CO Concentration in the Region Close to the Cu-chromite Surface

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