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Isobutanol-Methanol Mixtures from Synthesis Gas

Quarterly Technical Progress Report

Period Covered: 1 April to 30 June 1995

Contractor

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EXECUTIVE SUMMARY

Three types of catalytic materials for alcohol coupling and isobutanol synthesis reactions have been prepared and characterized by BET surface area and x-ray diffraction methods. The materials consist of (i) modified low-temperature methanol synthesis catalysts and their constitutive components, (ii) high temperature isobutanol synthesis catalysts consisting of Mn-Zn-Zr mixed oxides promoted with Cu, and (iii) high surface area basic oxides prepared from hydrotalcite precursors and active in alcohol coupling reactions.

Mechanistic and kinetic studies of methanol and ethanol coupling reactions using labeled compounds have shown that the reaction proceeds via an intermediate dehydrogenation reaction that form aldehydic intermediates. Ethanol is much more reactive than methanol because it forms a more thermodynamically stable acetaldehyde intermediate with kinetically available aldol condensation pathways for the formation of higher oxygenates. The presence of Cs in this catalysts decreases dehydrogenation rates but prevents the decomposition of methanol and ethanol to CO and H_2.

Construction and start-up of the Catalytic Microreactor Unit (CMRU) for high pressure isobutanol synthesis studies has been completed. A certification run has been performed using a BASF modified methanol synthesis catalysts supplied by Air Products. CO conversion rates are very similar to those obtained in backmixed reactors at Air Products and Chemical but the isobutanol synthesis selectivity is significantly lower. The catalyst behaves as a very active and selective methanol synthesis catalysts in the initial CMRU run. We are presently repeating this run and exploring catalyst or reactor differences between the two tests that may account for these differences.

The design and construction of the Temperature-Programmed Surface Reaction Unit (TPSR) for the study of the adsorption and reaction properties of alcohols and other oxygenates on isobutanol synthesis catalysts and components is about 70% complete. No APCI subcontracting activities were performed during this reporting period.

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1. CONTRACT OBJECTIVES AND TASKS

The contract objectives are:

1. To design a catalytic material for the synthesis of isobutanol with a productivity of 200 g isoalcohols/g-cat-h and a molar isobutanol/methanol ratio near unity

2. To develop structure-function rules for the design of catalysts for the selective conversion of synthesis gas to isoalcohols

The research program has been grouped into four specific tasks and a set of project management and reporting activities. The abbreviated designations for these tasks are:

- Project Work Plan ***(Task 1)***

- Catalyst Synthesis (***Task 2***)

- Catalyst Evaluation in Laboratory Scale Reactors (***Task 3***).

- Identification of Reaction Intermediates (***Task 4***)

- Bench-Scale Catalyst Evaluation at Air Products and Chemicals (***Task 5***).

2. SUMMARY OF ACTIVITIES

Activities during this period have focused on:

- synthesis and characterization of (i) literature modified methanol synthesis catalysts and their individual components, (ii) high surface area alcohol coupling basic catalysts prepared from novel hydrotalcite precursors, and (iii) high temperature isoalcohol catalysts based on Zn-Mn-Zr oxides promoted with Cu

- mechanistic studies of methanol and ethanol coupling reactions on ZnO, Cs-ZnO, Cu-ZnO, and Cs-Cu-ZnO catalysts using labeled alcohol compounds

- start-up of CMRU Unit and initial certification runs of this high pressure microreactor using an APCI-supplied Cu-Cs/ZnO catalyst manufactured by BASF

- continued construction of Temperature-Programmed Surface Reaction Unit for studies of the adsorption and surface reactions of alcohols and other oxygenates on isobutanol synthesis catalysts and components

3. STATUS, ACCOMPLISHMENTS, AND RESULTS

Task 1: Management Plan

No activities were carried out during this reporting period.

Task 2: Catalyst synthesis

Two types of catalytic solids have been prepared using precipitation methods at constant pH. High surface area basic oxides have been prepared from hydrotalcite precursors in order to test their properties as aldol condensation catalysts, the last step in the synthesis of isobutanol from CO and H_2. Also, modified methanol synthesis catalysts reported in the literature to form isobutanol at target conditions (300-350 C, 50 bar) have been prepared in order to test their catalytic performance in CO hydrogenation reactions. Based on their performance, two of these materials will be selected for detailed mechanistic studies using isotopic and kinetic methods. Finally, individual components of these literature catalysts have been prepared as pure compounds in order to test the intimacy requirements among the various required functions in physical mixtures of these individual components.

During this reporting period, surface area and diffraction characterization of materials previously prepared has also been completed.

<u>Aldol coupling catalysts</u>

Coupling reactions of aldehydes and alcohols are important steps in the synthesis of isobutanol from CO and H_2. The coupling between two aldehydes containing β–hydrogens to form a branched aldehyde requires basic catalysts. An alcohol coupling reaction, our reaction of interest would require dehydrogenation of the alcohols before aldol condensation on these basic oxides. It appears that the dehydrogenation step occurs on the Cu metal function also used for methanol synthesis during CO hydrogenation. This behavior is consistent with the widely reported aldehyde hydrogenation properties of Cu-

based catalysts. During this reporting period, we have focused on the synthesis of Mg-Al basic oxides from hydrotalcite precursors.

Hydrotalcites are aluminum-stabilized magnesium hydroxycarbonates that form layered structures and which decompose to high surface basic mixed Mg-Al oxides upon calcination at 773 K. They exhibit a potentially advantageous compositional flexibility. In our work, hydrotalcite materials have been synthesized in two different batches, A and B, using identical procedures while varying the Mg:Al atomic ratio in the synthesis mixture. Samples of batch A with atomic composition 10:1 MgAl-A and 5:1 MgAl-A showed BET surface areas (N_2 physisorption at 77 K) of 130 m^2/g and 230 m^2/g, respectively, after calcination. These samples had been precipitated at a pH of 8.5. The increase in surface area with increasing Al content is consistent with the sintering stability imparted by the Al component to MgO.

Samples in batch-B contained Mg:Al atomic ratios of 10:1, 5:1 and 3:1. X-ray diffraction analysis shows the formation of hydrotalcites, characterized by diffraction lines at low angles caused by the repeating hydrotalcite layered structure (Figures 1 and 2). X-Ray diffraction patterns after calcination are consistent with the formation of mixed Mg-Al oxides. Line breadth analysis shows that the presence of Al decreases the crystallite size of the metal oxides, consistent with the higher surface area obtained when Al oxide is present in MgO samples. Transmission electron microscopy studies of the 10:1 MgAl-B sample after drying shows the characteristic layered structure of the undecomposed hydrotalcite.

Isobutanol Synthesis Catalysts and Components

The synthesis of higher alcohols from methanol and ethanol requires at least two functions (hydrogenation/dehydrogenation and condensation) provided by metal and basic sites. The hydrogenation component is required to hydrogenate CO and to form aldehydic species from alcohols. Basic sites are then used to form higher aldehydes and alcohols via aldol-type condensation reactions of aldehydic intermediates. The required level of intimacy between these functions remains one of the fundamental issues preventing the development of isobutanol synthesis catalysts from physical mixtures of independently optimized functions. The catalysts described in Table 1 have been prepared in order to examine these intimacy requirements. These materials have also been used in alcohol coupling studies (Task 3) in order to examine their properties for the aldol coupling steps involved in the isobutanol reaction sequence.

Table 1. Modified Methanol Synthesis Catalysts and Components

1. Cu/ZnO (30:70 at.; precipitated using K_2CO_3 at a pH of 9.0);Cu-Zn-9-1

2. Cs/Cu/ZnO (0.4:30:70 at.; precipitated with K_2CO_3 at pH 9.0); Cs-Cu-Zn-9-1

3. Cs/ZnO (0.4 at. % Cs; ZnO precipitated using NH_4OH) Cs-Zn-9-1

4. ZnO (precipitated using NH_4OH) Zn-9-1

5. ZnO (precipitated using K_2CO_3 at a pH of 9.0). Zn-K_2CO_3-9-1

Sample 5 was recently prepared in an attempt to improve the surface area of sample 4, which used NH_4OH instead of K_2CO_3 as the precipitant. Precipitation with K_2CO_3 leads to the formation of hydroxycarbonate species that may have been responsible for the higher surface area of the Cu/ZnO samples (Table 2). This procedure, however, did not increase the surface area of pure ZnO and for that reason we have not included this sample in our reactivity studies within Task 3.

These catalysts were subjected to a treatment procedure previously reported by the Klier group (Inorg. Chem. 28 (1989) 3868). The catalysts were first heated to 350 C in air at the rate of 5 C per minute and then maintained at 350 C for 3 h. The samples were then reduced at 350 C in 10% H_2 /He for 1 h before reactivity studies.

Surface Area Characterization

Surface areas of all samples above have been obtained using dinitrogen physisorption at its normal boiling point. A summary of the values obtained is shown in the Table below. These surface area values will ultimately be used to calculate areal rates from catalytic measurements.

Table 2. Surface Area of Modified Methanol Synthesis Catalysts and Components

Catalyst	BET Surface Area (m^2g^{-1})
1. Cu-Zn-9-1	58.0
2. Cs-Cu-Zn-9-1	38.0
3. Cs-Zn-9-1	3.5
4. Zn-9-1	1.8
5. Zn-K_2CO_3-9-1	4.1
6. Cu-Zn-Mn-431-9-1	90.0

We have been unable to prepare ZnO samples with high surface areas using simple precipitation techniques. The presence of Cu appears to be required to stabilize intermediate hydroxycarbonate precursors that cannot form during precipitation of pure Zn hydroxycarbonates.

The synthesis of the Cu-Zn-Mn catalyst was reported in the previous Technical Quarterly Report.

Task 3: Catalyst evaluation in laboratory scale reactors

Activities in this task have focused on:

(i) Isotopic Tracer and Kinetic Studies of Alcohol Coupling Reactions in a Low-Pressure Microreactor

(ii) Start-up of Catalytic Microreactor Unit (CMRU)

(iii) Isobutanol Synthesis Studies on Cs/Cu/ZnO BASF Catalyst in CMRU

Isotopic Tracer and Kinetic Studies of Alcohol Coupling Reactions

We have conducted a preliminary study of alcohol coupling reactions on Cu/ZnO, (0.4% at. Cs) Cs-Cu/ZnO, and Cu:Zn:Mn (4:3:1 at. ratio) oxide catalysts using a gradientless recirculating reactor. We have also examined the chemical and isotopic composition of products of $^{13}CH_3OH/C_2H_5OH$ mixtures and measured the rate and selectivity of the alcohol coupling reactions. We have adapted calculation procedures in order to be able to estimates the content and location of ^{13}C atoms in reaction products. We are currently modifying the codes to include also the presence of about 12 % ^{18}O in the $^{13}CH_3OH$ in the isotopic calculations. This ^{18}O isotopic impurity complicates the calculation of the number of ^{13}C-atoms in reaction products but avoids the extreme expense of ^{18}O-free methanol.

Acetaldehyde appears to be an intermediate in the formation of condensation products from an ethanol-methanol mixture. Reactions of ^{13}C-methanol-ethanol mixtures at 325 C suggest that methanol is converted to formaldehyde and CO/H_2, while ethanol is converted to acetaldehyde and subsequently to isobutyraldehyde, butyraldehyde, methyl ethyl ketone (2-butanone), and higher aldehydes and ketones. C_2+ products contain predominantly ^{12}C from ethanol without significant isotopic enrichment from $^{13}CH_3OH$. Subsequent experiments at 250 C using neon as an internal standard confirmed these findings and allowed quantitative measurements of the rate of CO/H_2 formation. Data analysis is still in progress but some initial results are reported below.

A typical range of products formed from reactions of methanol-ethanol mixtures is shown in Figure 3. Identification was carried by capillary chromatography with mass spectrometric detection: CO and H_2 products of methanol decomposition and aldehydes and ketones, products of the aldol condensation reactions of acetaldehyde, are the predominant reaction products. This product distribution is consistent with that reported

by Elliot and Pennella [J. Catal. 119 (1989) 359]. No esters are found among the reaction products, suggesting that direct condensation and dehydration reactions of alcohols do not occur. The absence of dimethylether from reaction products confirms the absence of residual acid sites on these catalysts.

The conversion-time data obtained on Cu-ZnO in a gradientless recirculating batch microreactor is shown in Figure 4a. Methanol and ethanol conversions, calculated by using Ne as an internal standard, were very similar. Conversion rates, calculated from the slope of the data in Figure 4 and from the initial concentrations of methanol and ethanol in the reactant stream (2:1 mol. methanol:ethanol) were about two-fold higher for methanol. The predominant product formed from methanol was CO (and H_2) possibly through the intermediate formation of formaldehyde, which is thermodynamic unstable and would decompose very rapidly at these reaction conditions. It appears that aldol condensation reactions of formaldehyde with other unsaturates do not occur at these reaction conditions because condensation products contain only trace amounts of carbon-13 when labeled methanol is used as part of the reactant mixture.

The addition of Cs to Cu-ZnO catalysts markedly inhibits the decomposition of methanol to CO/H_2. For example the methanol conversion after 50 min. on Cu-ZnO is 56% (Figure 4a) but less than 1% on Cs/Cu-ZnO (Figure 4b). Ethanol conversion decreases only from 59% to 47% when Cs is added (Figures 4a and 4b). This lower ethanol conversion value is likely the result of the lower surface area of the Cs-promoted sample (38 vs. 58 m^2g^{-1}). Clearly, the deep dehydrogenation activity of the Cu-ZnO sample and its strong tendency to form CO and H_2 from methanol is strongly influenced by the presence of alkali. This inhibition of dehydrogenation reactions prevents the loss of alcohol precursors to CO and H_2 before the aldol condensation reactions of these alcohols occur. The areal rate of ethanol reactions, however, is not influenced strongly by the presence of Cs.

The presence of MnO in Cu-ZnO catalysts also inhibits methanol conversion rates but actually increases the rate of ethanol conversion (Figures 4a and 4c). The underlying mechanism for this behavior is unclear at this time. It may simply reflect the higher surface area of the Mn-promoted sample (90 vs. 58 m^2g^{-1}). Cu dispersion and changes in the interaction strength between Cu crystals and the doped ZnO supports as a function of Mn content may also account for this behavior. We will examine the Cu dispersion and reduction behavior in order to examine these effects during the next two reporting periods.

The selectivity to condensation products is calculated as the fraction of the carbon atoms in the converted alcohol feed that appear as C_3+ products. This selectivity is calculated on a CO-free basis. The data obtained on the three catalysts tested are shown in Figure 5. On all catalysts the condensation selectivity increases with increasing contact time (and conversion). This behavior is consistent with a sequential reaction in which acetaldehyde intermediates are initially formed and then react in condensation steps to give higher molecular weight products. The addition of Cs appears to have a beneficial effect on the condensation selectivity, consistent with an increase in the rate of aldol

condensation reactions with increasing basicity of the ZnO components in these catalysts (Figures 5a and 5b). The presence of Mn in Cu-ZnO catalysts also increases condensation selectivity (Figures 5a and 5c). The basic properties of Mn-Zn mixed oxides have not been reported in the literature but the use of Mn components in high temperature isobutanol synthesis and isosynthesis processes has been reported by the Keim group and by others. The effects of Mn on the density and basicity of surface sites will be examined in detail by TPSR studies during the second year of this research program.

The analysis of isotopic tracer experiments using labeled methanol on Cs-Cu/ZnO shows evidence of incorporation of ^{13}C and ^{18}O form the labeled methanol into reaction products in spite of the inhibited chemical conversion of the methanol reactant on this catalyst. On Cu/ZnO and Cu/Zn/Mn, the isotopic distribution of the acetaldehyde did not significantly differ from the one produced from unlabeled ethanol, showing that acetaldehyde is formed exclusively from the ethanol reactant in methanol-ethanol mixtures. The analysis of the content and location of ^{13}C on other reaction products formed on these catalysts is in progress.

These experiments will be continued during the next two reporting periods. Specifically, the intimacy requirements between the Cu and Cs-ZnO components for the combined alcohol dehydrogenation-aldol condensation steps and the catalytic properties of Mg-Al oxides prepared from hydrotalcite precursors will be examined when the recirculating batch reactor becomes again available.

Start-up of Catalytic Microreactor Unit (CMRU)

CMRU construction was completed by the end of the previous reporting period. Start-up activities during the current period included leak testing, flow meter calibrations, and the measurement of response factors and retention times for oxygenates using a typical APCI La Porte product mixture.

A blank reactor run using acid-washed quartz chips as the reactor charge was carried out at 350 C and 750 psig in order to test for background reactivity and operational reliability of the CMRU high pressure microreactor. The background catalytic activity was very low even at these high temperatures. At gas hourly space velocities of 1000, the CO conversion was less than 2% and the reaction products were exclusively C_1-C_4 paraffins with trace amounts of methanol.

An initial run with the BASF Cs-modified Cu/ZnO catalyst (CMRU-0) was carried out to test reactor isothermality and product analysis. This run served to optimize the chromatographic conditions. The capillary column was able to separate with baseline resolution all major product peaks. The reactor axial temperature profile was constant within +/- 1.5 C throughout the entire range of space velocity. Data acquisition was hampered by a gas chromatograph leak that developed during cryogenic cooling. This prevented calculations of CO conversions and product selectivities for this run.

Isobutanol Synthesis Studies on Cs/Cu/ZnO BASF Catalyst in CMRU

We have carried the planned certification runs of the CMRU unit using the Cs-promoted Cu/ZnO catalysts provided by APCI. Initial experiments (CMRU-1; 0.5 g catalyst, 300 C, 735 psig, $H_2/CO = 0.5$) were carried out without catalyst pre-reduction. Reaction rates were significantly lower than in the LaPorte APCI run and methanol and carbon dioxide accounted for >90% mol. of the products. Differences in pretreatment procedures between the two tests appear to cause this discrepancy in catalyst activity. Pretreatment of this catalyst charge after reaction tests failed to increase the reaction rate, apparently because CO hydrogenation at 350 C during the initial run caused significant deactivation by Cu crystallite growth. These initial experiments were also used to obtain response factors for typical reaction products, to test the liquid introduction system, and to gain operating experience in data acquisition and calculations. The liquid introduction system has not performed to specification; we are presently considering the options of troubleshooting or replacing it.

A new charge of the BASF catalyst was tested after following the APCI recommended pretreatment required to reduce the catalyst before CO hydrogenation reactions (CMRU-2; 0.8 g). This pretreatment consisted of passing a stream of 2% H_2/He (100 psig) over the catalysts while the temperature is increased according to the following program:

(i) Room temperature to 100 C over 1.5 h
(ii) 100 C to 240 C over 14 h
(iii) 240 C to 300 C over 1.5 h followed by introduction of CO and H_2

The reaction conditions and results of this initial run are shown in Table 3. Feed composition and reaction conditions were chosen to duplicate those of the La Porte run. Ar was used as the internal standard to calculate CO conversion while N_2 was used to calculate an absolute value for CO_2 selectivity. CO conversion in the CMRU-2 run was slightly higher than in the LaPorte run. This approximate agreement in catalyst productivity and the lack of severe deactivation during CMRU-2 confirm the integrity of the feed purification and metering trains in CMRU.

CMRU-2 selectivities, however, were significantly different than those obtained in the LaPorte tests of the BASF catalyst. Small differences could be explained by the different levels of backmixing in the two types of reactors. The observed differences, however, suggest differences beyond those attributable to hydrodynamics. The Cs/Cu-ZnO BASF catalysts behaves as a very selective methanol synthesis catalyst in CMRU-2 with very low selectivity to higher alcohols. In addition, CMRU-2 mass balances based on the Ar internal standard were unsatisfactory (60-80%) and showed significant transient behavior over > 8 h. The following possibilities are being explored in order to finalize CMRU certification:

(i) Significant migration of Cs to quartz diluent or reactor walls; CMRU-3 will be carried out with a much larger amount of catalyst (3 g vs. 0.8 g) and without quartz diluent

(ii) Impurities in the quartz diluent

(iii) Condensation of higher alcohols in the transfer lines to gas chromatograph; lines are being retraced and more extensively insulated.

(iv) Mass flow meter transients at low flow rates; CMRU-3 will be run at higher flow rates and a larger catalyst charge while maintaining a GHSV of 5000.

Table 3. Comparison of La Porte Pilot Plant Slurry Run and CMRU Fixed Bed Run

	La Porte	CMRU-2
Feed Composition (% mol)		
Hydrogen	30.32	27.03
Carbon Monoxide	65.62	54.05
Carbon Dioxide	3.03	2.70
Argon	0	13.51
Nitrogen	1.03	2.70
Temperature (C)	300	300
Pressure (psig)	750	735
GHSV (h^{-1})	5000	4995
CO Conversion (%)	13.8	16.4
Carbon Selectivity (%)		
Methanol	30.6	51.2
Isobutanol	1.8	0.1
Methane	1.0	0.07
Carbon Dioxide	28.5	7.3

Task 4: Identification of reaction intermediates

Activities have focused on the construction of the TPSR unit and on the feed metering and purification manifold for both the TPSR and in-situ infrared equipment.

The design of the Temperature Programmed Surface Reaction (TPSR) unit was modified during this reporting period in order to minimize dead volumes that would broaden dosing pulses and desorption peaks. A schematic diagram of the unit design is shown in Figure 6. The Leybold Inficon mass spectrometer and its computer interface have been installed on a cart to allow mobility of the unit between our temperature programmed surface reaction unit and the microreactor unit. The interface between the mass spectrometer and the atmospheric pressure sample stream has also been modified to include a much shorter capillary transfer line in order to minimize sample dispersion and peak broadening.

The construction of Temperature Programmed Surface Reaction (TPSR) Unit is about 70% complete. Start-up activities will begin during October 1995.

Task 5: Bench Scale Testing at Air Products and Chemicals

Subcontract activities were limited to consulting contacts with Dr. Bernard Toseland regarding operational and design details of CMRU. All subcontract documents have been forwarded to Air Products and Chemicals for their approval and signatures.

4. PARTICIPATING PROJECT PERSONNEL

Sara Yu
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Post-doctoral Fellow

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Graduate Student

Sergio Mendez
Undergraduate Researcher

Bernard A. Toseland
Sub-Contractor Manager
Air Products and Chemicals

Enrique Iglesia
Principal Investigator

FIGURES

Figure 1. Powder X-Ray diffraction pattern for 5:1 Mg:Al hydrotalcite precursor

Figure 2. Powder X-Ray diffraction pattern for 10:1 Mg:Al hydrotalcite precursor

Figure 3. Capillary chromatogram of products of methanol-alcohol mixtures on Cu-Cs-ZnO Catalyst; product identification by mass spectrometry

Figure 4. Methanol and ethanol conversion vs. time in batch recirculating reactor (methanol: ethanol 2:1 mol, 250 C, 22 mg catalyst charge)

a) Cu-ZnO (58 m^2 g^{-1})

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b) Cs-Cu-ZnO (38 m^2 g^{-1})

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c) Cu-ZnO-MnO (90 m^2 g^{-1})

Figure 5. Fractional selectivity to condensation products in batch recirculating reactor (methanol: ethanol 2:1 mol, 250 C, 22 mg catalyst charge)

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Figure 6. Schematic diagram of the Temperature-Programmed Surface Reaction/ Infrared Apparatus (TPSR/IR)

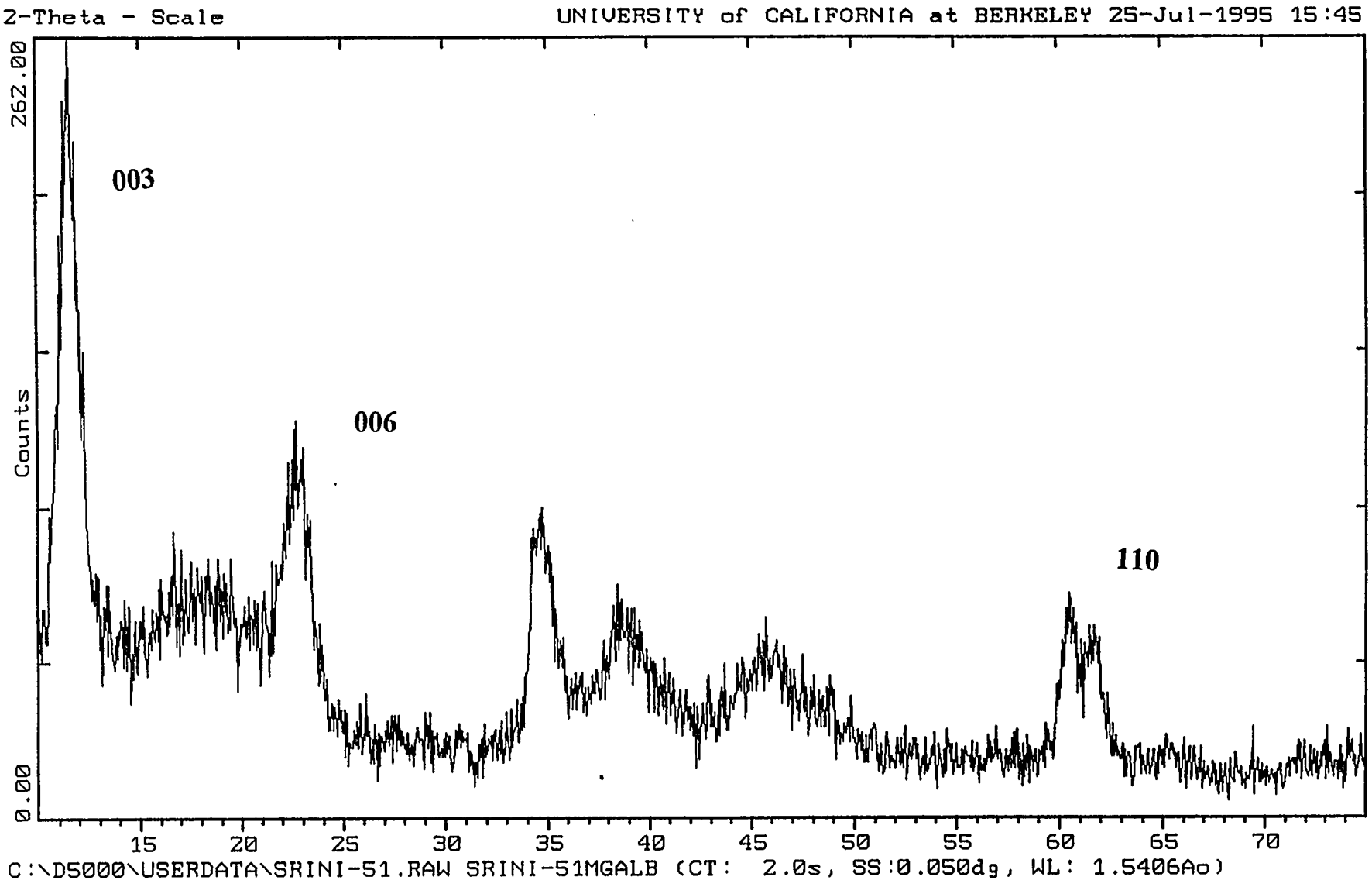


Figure 1. Powder X-Ray diffraction pattern for 5:1 Mg:Al hydrotalcite precursor

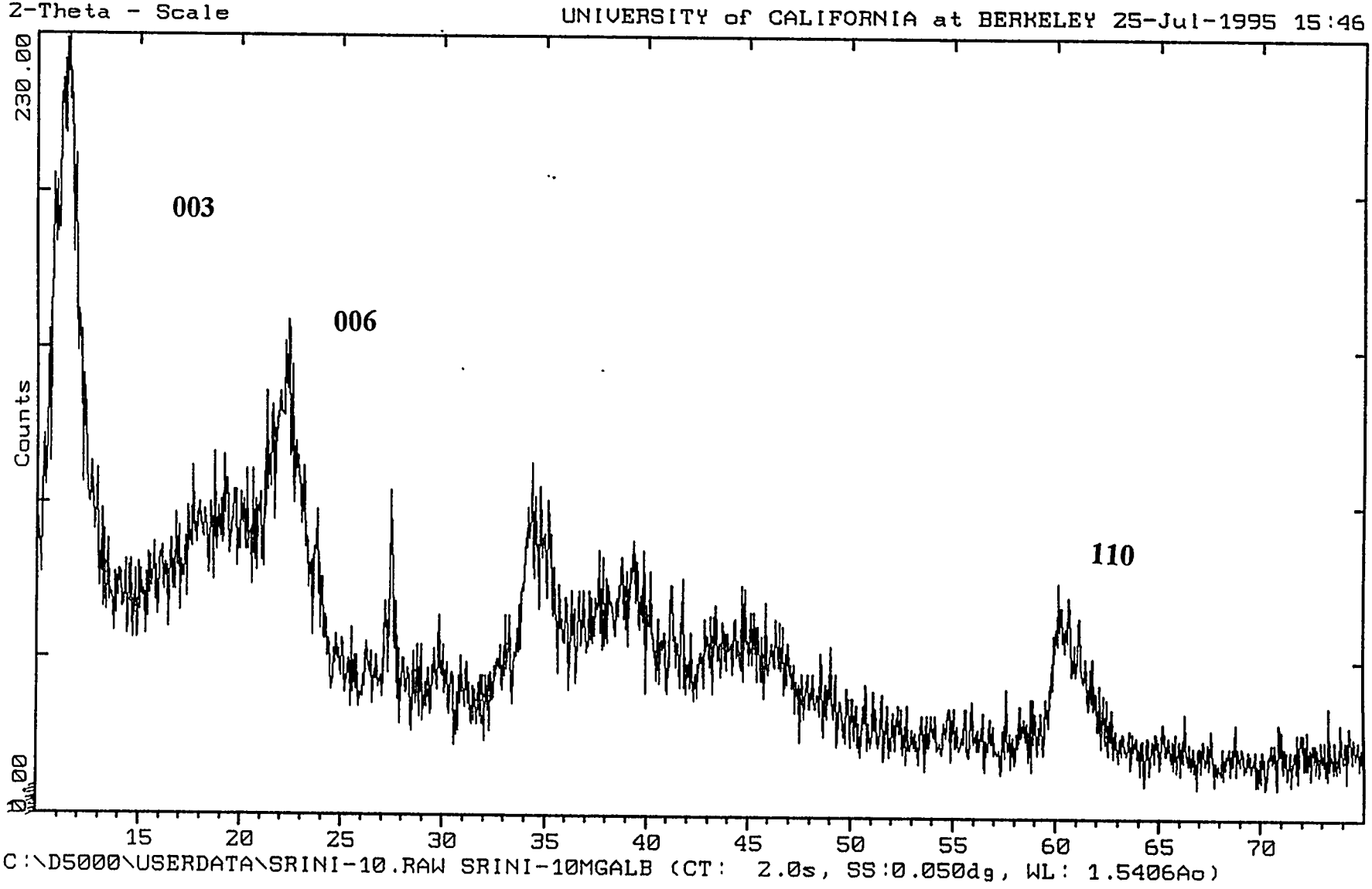
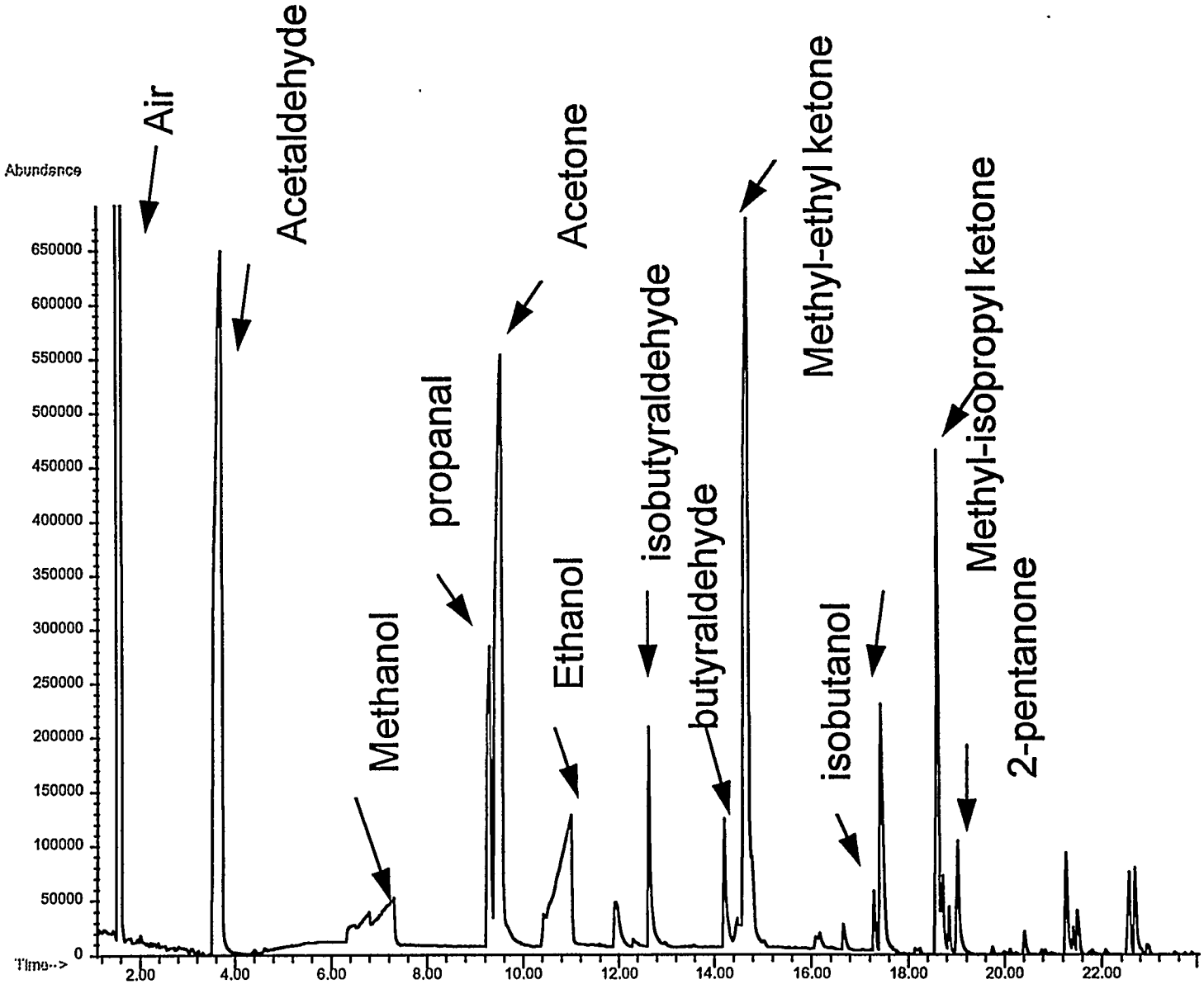


Figure 2. Powder X-Ray diffraction pattern for 10:1 Mg:Al hydrotalcite precursor



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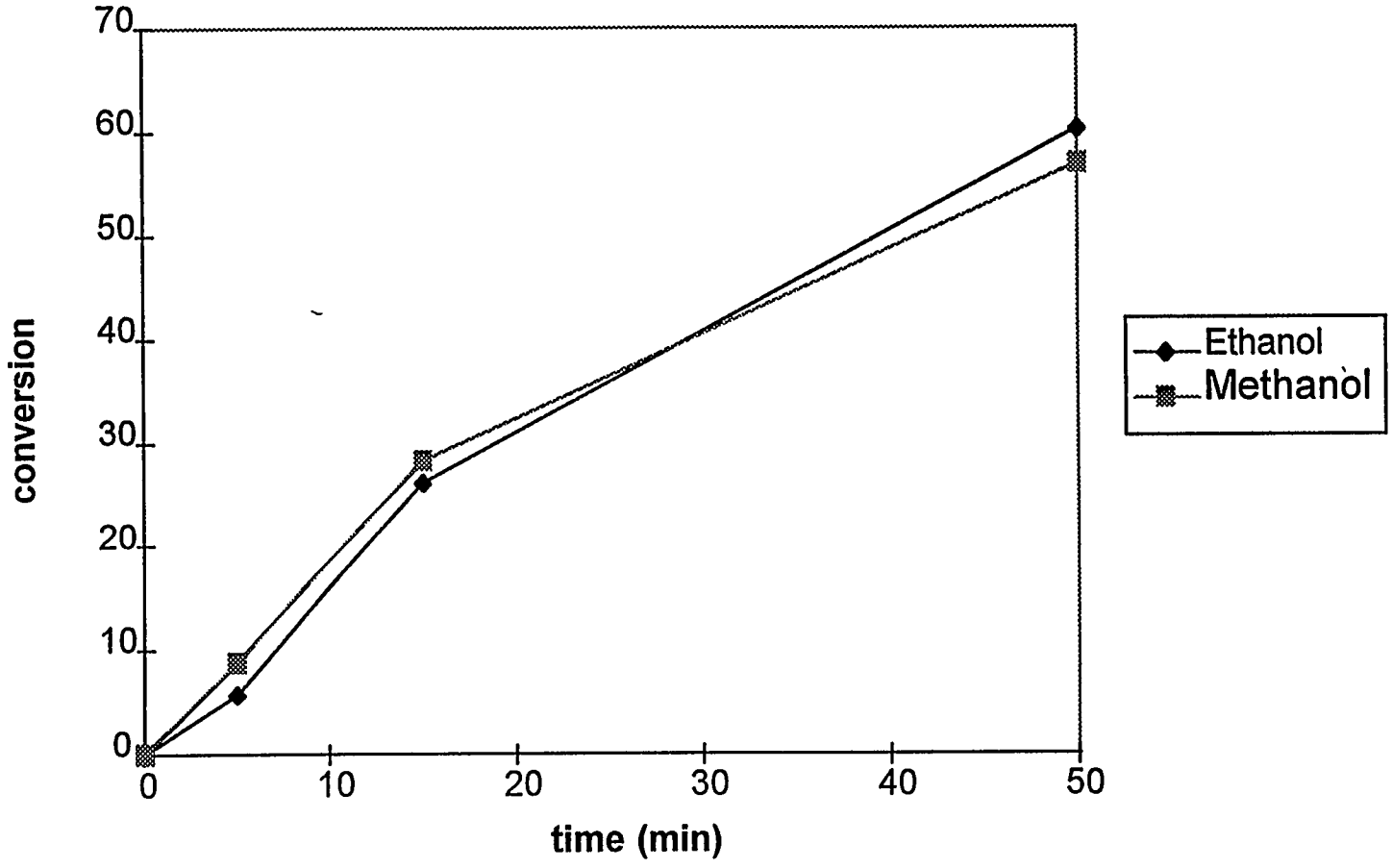

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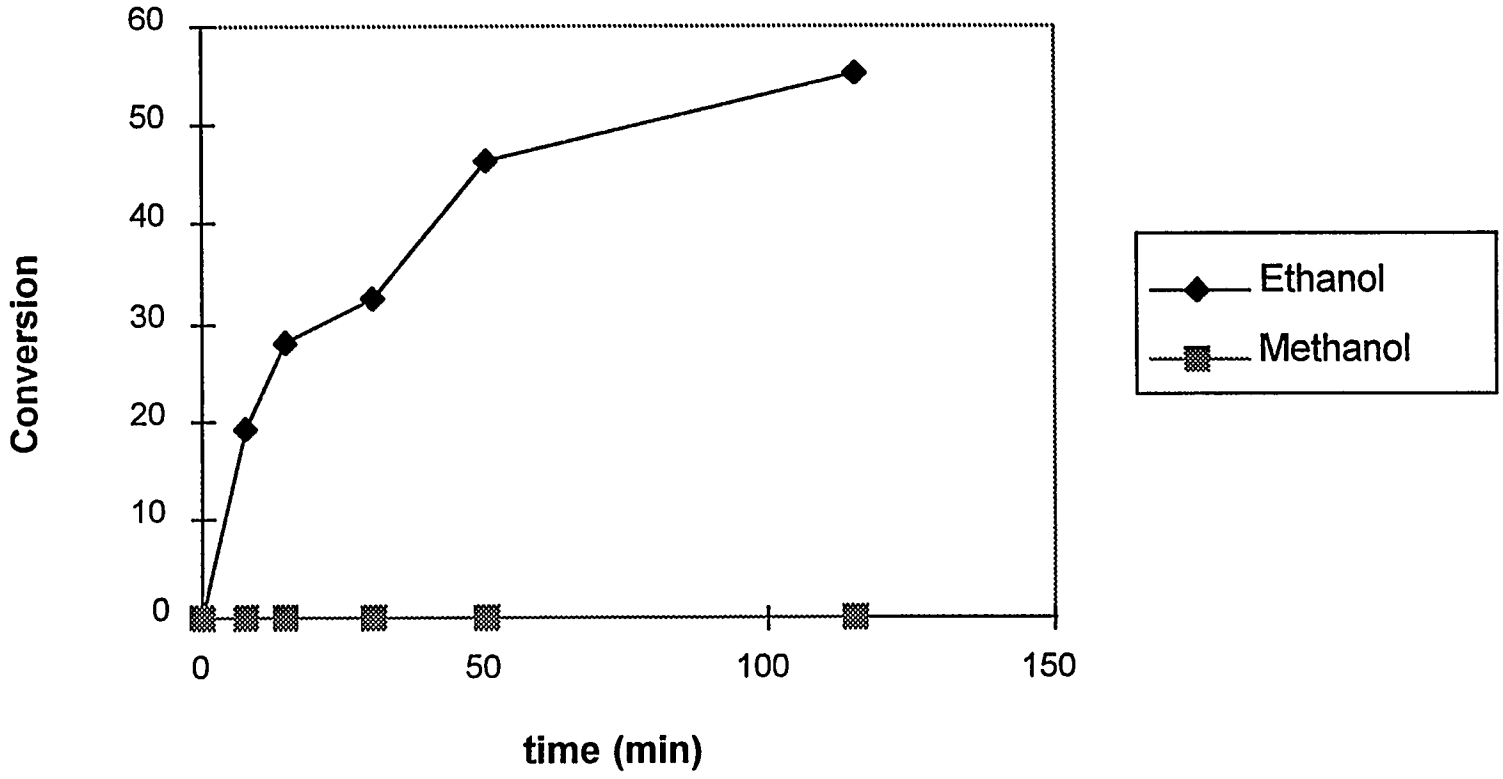
b) Cs-Cu-ZnO (38 m^2 g^{-1})



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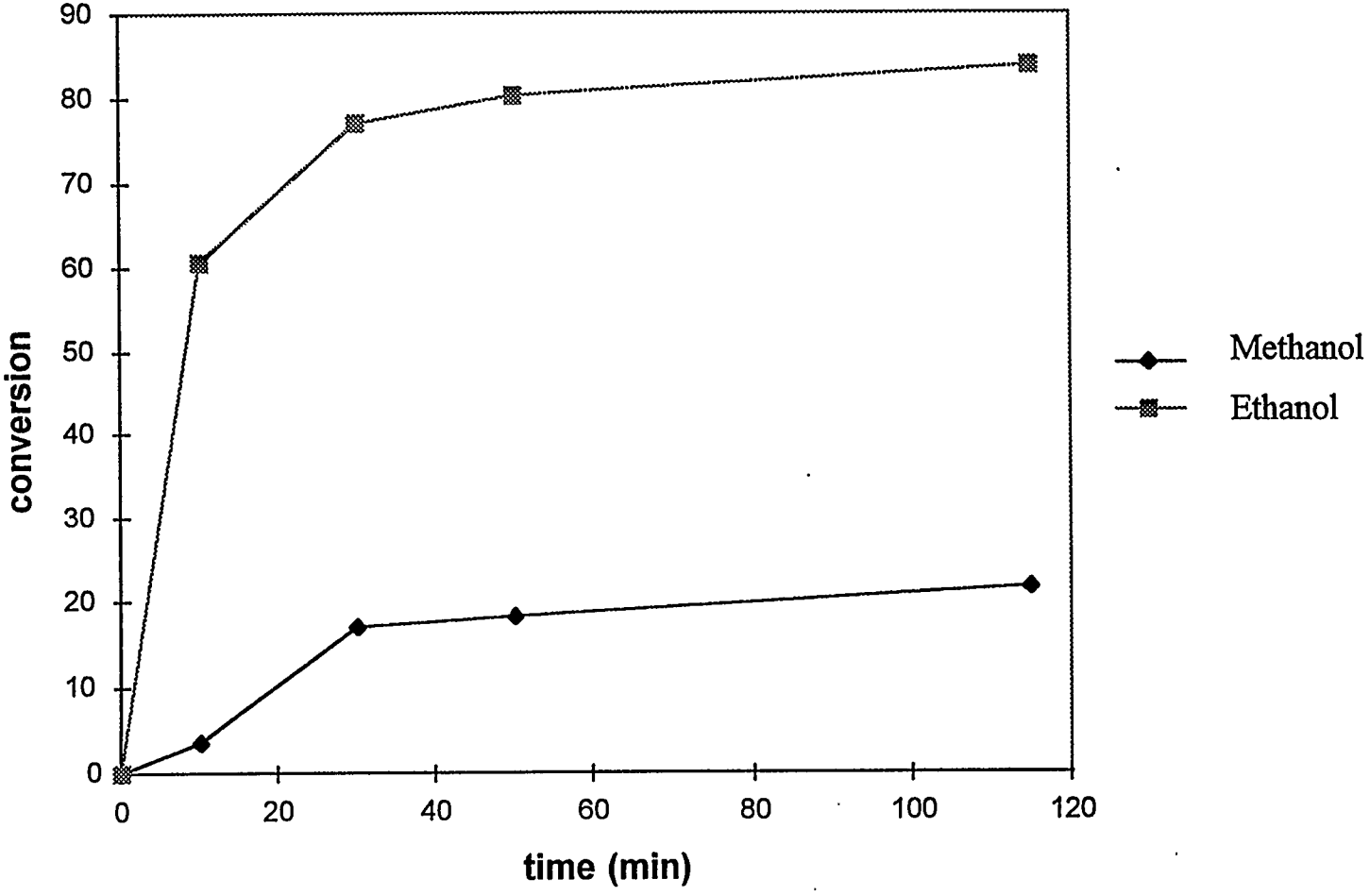

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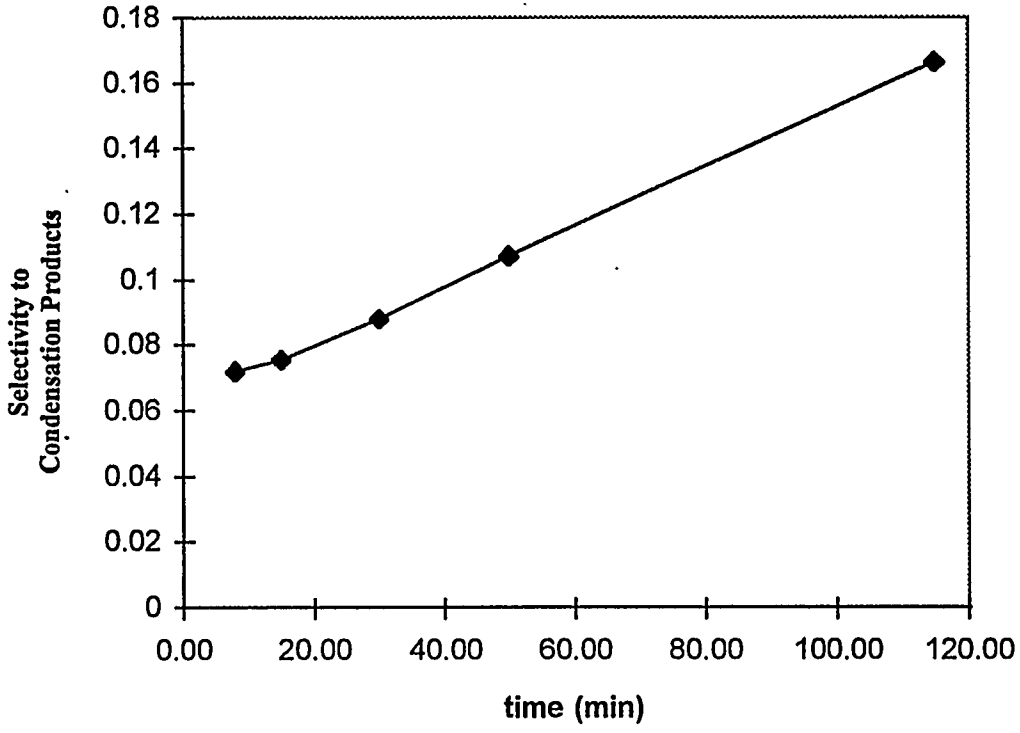

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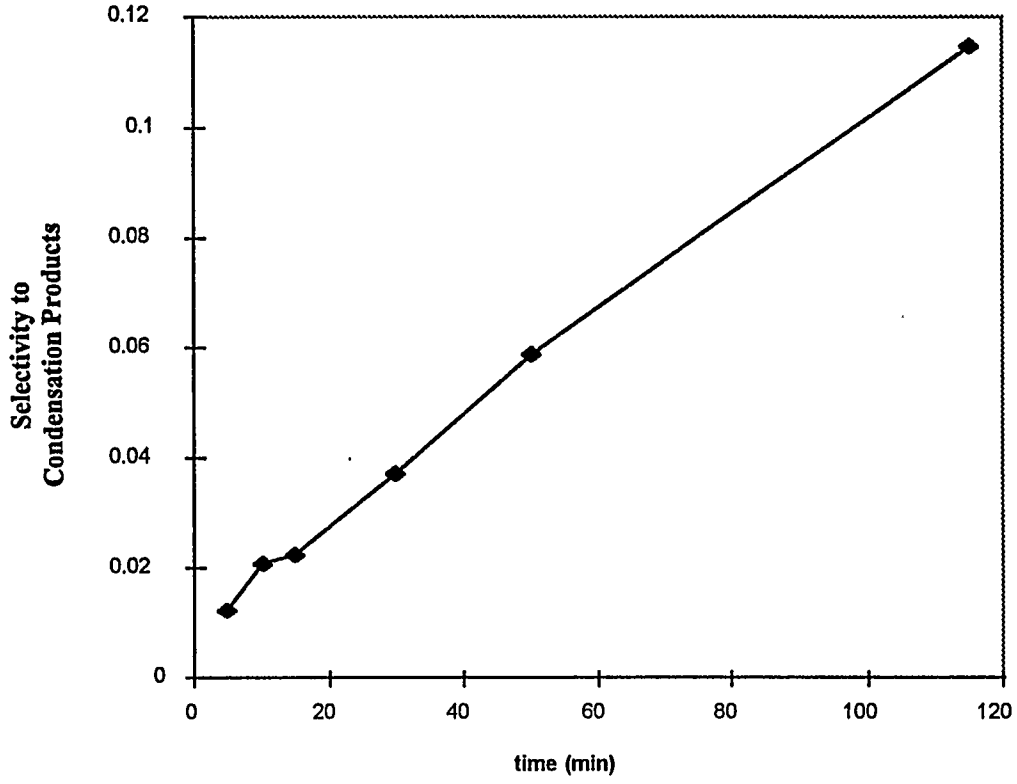

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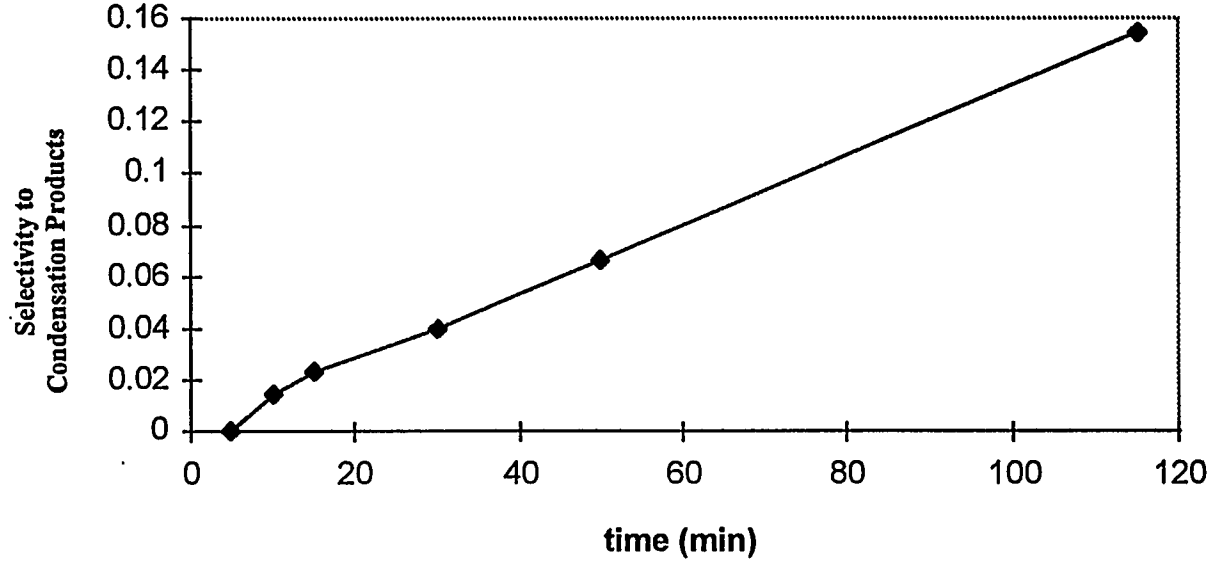

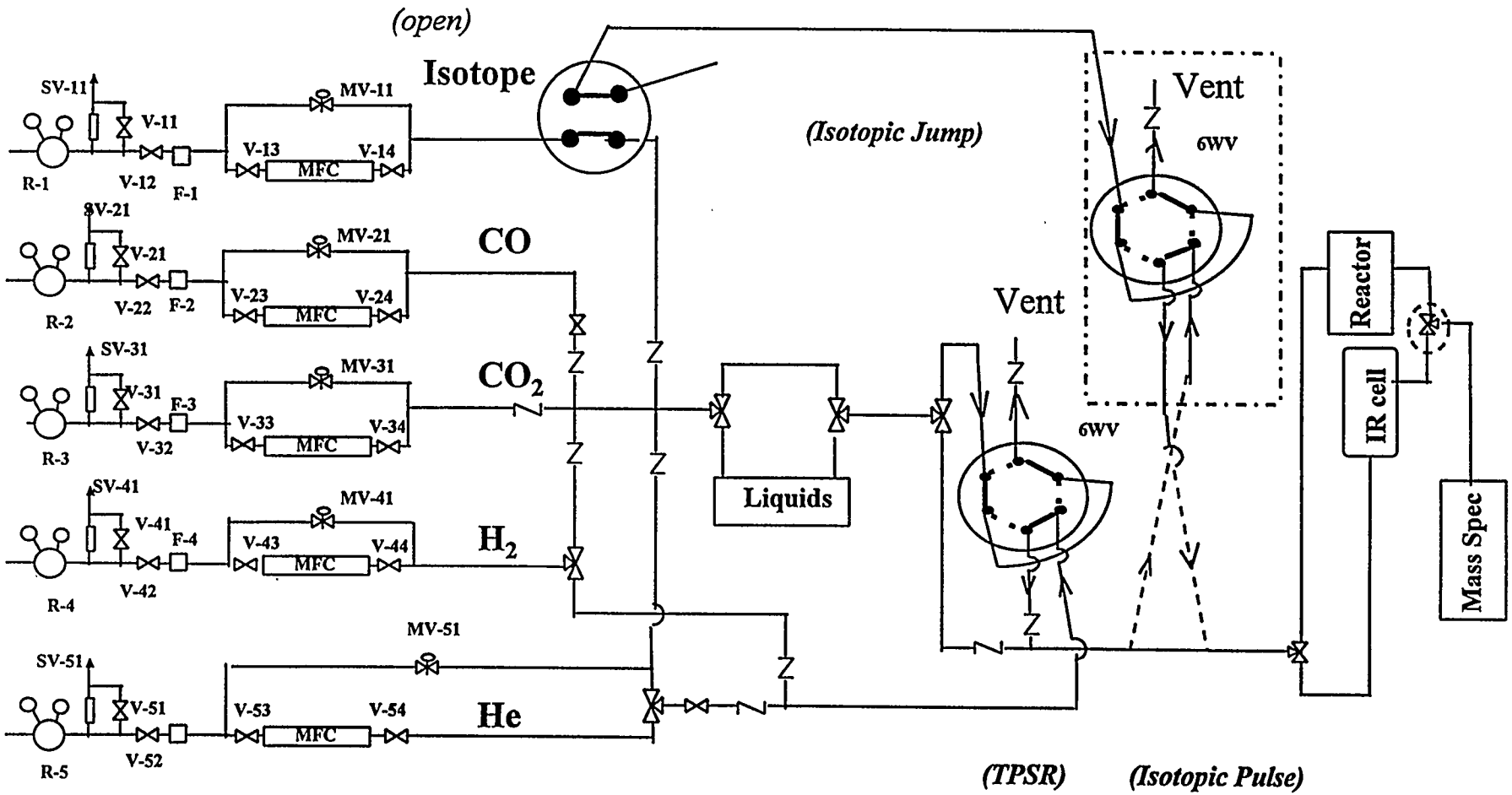

Figure 6. Schematic diagram of the Temperature-Programmed Surface Reaction/ Infrared Apparatus (TPSR/IR)