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Isobutanol-Methanol Mixtures from Synthesis Gas

Quarterly Technical Progress Report

Period Covered: 1 July to 30 September 1995

Contractor

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EXECUTIVE SUMMARY

Mechanistic and kinetic studies of methanol and ethanol coupling reactions on Cs/Cu/ZnO and Cu/ZnO/MnO catalysts using isotopically-labeled compounds have confirmed that coupling reactions proceed via intermediate dehydrogenation of alcohols to aldehydes. Ethanol coupling reactions are much faster than those of methanol because ethanol forms a more thermodynamically favored intermediate (acetaldehyde), with aldol condensation pathways kinetically available for chain growth. Cs decreases the rate of formation of aldehydes in alcohol dehydrogenation reaction and inhibits the undesired conversion of methanol and ethanol to synthesis gas (CO/H_2).

Construction and start-up of the Catalytic Microreactor Unit (CMRU) for high pressure isobutanol synthesis studies have been completed. Initial certification runs have reproduced catalytic CO conversion rates on a standard APCI material ($Cs/Cu/ZnO/Al_2O_3$). Condensation of higher alcohols in the transfer lines appears to be responsible for the observed low apparent selectivity to higher alcohols.

The design and construction of the Temperature-Programmed Surface Reaction (TPSR) Unit for the study of the adsorption and reaction properties of alcohols and other oxygenates on isobutanol synthesis catalysts and components is complete. The reduction of CuO powder and of a Cs/Cu/ZnO catalyst were used to certify the apparatus before proceeding with alcohol adsorption and reaction studies. Several meetings between APCI and UC-Berkeley personnel were held during this reporting period.

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 five 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:

- Documentation of details of synthesis and characterization procedures and results
- Analysis of the mechanistic data related to methanol and ethanol coupling reactions on Cu/ZnO, Cs/Cu/ZnO, Cu/ZnO/MnO (CuZnMn) catalysts
- Initial certification runs on the high pressure microreactor using a standard APCI-supplied Cs/Cu/ZnO catalyst manufactured by BASF and supplied by Air Products and Chemicals Inc.
- Start-up and initial certification runs of the temperature-programmed surface reaction unit for the studies of the adsorption and surface reactions of alcohols and other oxygenates on isobutanol synthesis catalysts and on individual components of such catalysts.

3. STATUS, ACCOMPLISHMENTS, AND RESULTS

Task 1: Management Plan

No activities were carried out during this reporting period.

Task 2: Catalyst synthesis

Synthesis and characterization details for all materials prepared during this project were entered into a data logging system to ensure rapid and accurate data retrieval of all procedures and characterization data. This system is being used to ensure efficient transfer of details among members of the isobutanol team. It includes details on reagent identity and composition, synthesis procedures, pretreatment methods, and surface area and crystallographic data.

Powder X-ray diffraction analyses have been performed for the 10:1 MgAl and 5:1 MgAl hydrotalcite samples. Line breadth analysis of diffraction peaks shows that hydrotalcite crystals are 6-9 nm in diameter. Thus, even if non-porous, such small particles are expected to give very high surface areas.

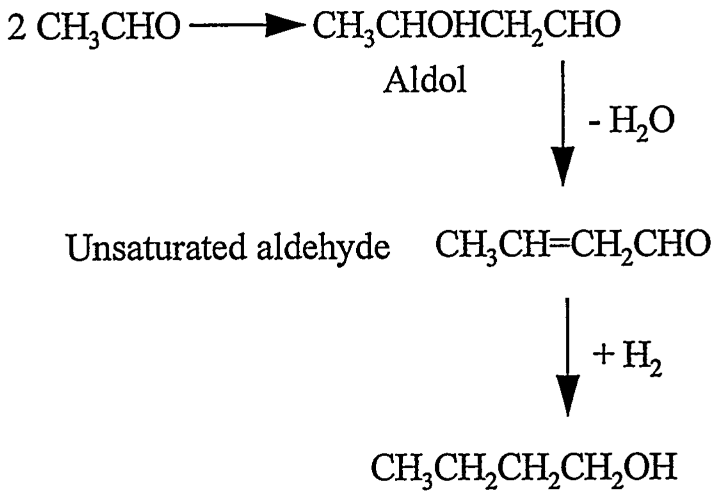
Surface areas obtained by BET methods using dinitrogen physisorption were 140 m^2/g for the 10:1 sample and 238 m^2/g for the 5:1 sample. Thus, hydrotalcite surface area increased with increasing alumina content. Transmission electron microscopy analysis of the 10:1 sample revealed pure MgO particles in regions devoid of Al ions, suggesting that the Mg:Al limiting ratio was met locally during precipitation and that the excess Mg ions precipitated as a segregated MgO phase.

Task 3: Catalyst Evaluation in Laboratory Scale Reactors

3.1 Isotopic Tracer and Kinetic Studies of Alcohol Coupling Reactions

3.1.1 Introduction

A preliminary study of alcohol coupling reactions was carried out using a gradientless recirculating batch reactor. Alcohol coupling reactions consist of a sequence of steps leading to the formation of higher alcohols from C_1 and C_2 alcohols. This sequence includes dehydrogenation steps to form aldehydes, aldol condensation of these aldehydes to an aldol that dehydrates to an α, β unsaturated aldehyde, and finally, the hydrogenation of the α, β unsaturated aldehyde to form an alcohol. Aldol condensation can occur between aldehydes or ketones containing an α–hydrogen in the presence of acidic or basic catalysts. An aldol is a hydroxyaldehyde that is formed when the α–carbon of a molecule attaches to a carbonyl carbon in another; aldols tend to be very easily dehydrated to unsaturated aldehydes or ketones. Ketones are formed as final products if a ketone is a reactant; otherwise, an aldehyde is formed. An example of the aldol condensation scheme for acetaldehyde is illustrated below.



In isobutanol synthesis from synthesis gas, methanol is likely to be the initial alcohol from which higher alcohols and aldehydes are formed [Smith, K.J., Himmelfarb, P.B., Simmons, G.W., and Klier, K., Ind. Eng., Chem. Res., **30**, 61 (1991)]. Therefore, we have chosen to study the coupling reaction between ^{13}C-methanol and unlabeled ethanol. Measurements of reaction rates and selectivity and of the rate of appearance and the location of ^{13}C can reveal the details about the mechanism of alcohol coupling and provide a direct measure of the relative reactivities of methanol and ethanol in coupling reactions. These types of experiments are complicated by the presence of ^{18}O impurity (12% ^{18}O) in ^{13}C-methanol. Therefore, analysis methods are being developed to estimate the content and the location of ^{13}C in reaction products from mass spectral data corrupted by the ^{18}O impurity.

3.1.2 Background

The literature on alcohol coupling reaction suggests that aldehydes formed by dehydrogenation steps are reactive intermediates in chain growth. [Vedage, G.A., Himelfarb, P.B., Simmons, G.W., and Klier, K., ACS Symposium Series, **279**, 295 (1985)]. Studies on Cu/ZnO catalysts by Elliott et al. [Elliott, D.J., and Penella, F., J. Catal, **119**, 359 (1989)] have shown that primary alcohols containing n-carbon atoms condense at atmospheric pressure to form predominantly C_{2n} esters and C_{2n} and C_{2n-1} ketones. These authors report that the presence of CO influences product distributions; esters were formed preferentially in N_2 atmospheres but ketones were favored when CO was present. They have suggested a role for surface oxygen vacancies in the formation of ketones on the basis of the enhanced selectivity to ketones at high CO pressures (~ 65 bar). The role of CO (and H_2) in the formation of surface vacancies was confirmed by the appearance of CO_2 when Cu/ZnO catalysts were exposed to CO and then heated from 25 to 250 ^{0}C. These surface reduction steps are likely to occur during isobutanol synthesis from CO/ H_2 mixtures, where they can also lead to the formation of CO_2.

Elliott and Penella's [Elliott, D.J., and Penella, F., J. Catal, **<u>119</u>**, 359 (1989)] mechanistic proposal can be summarized by the sequence of steps as illustrated below:

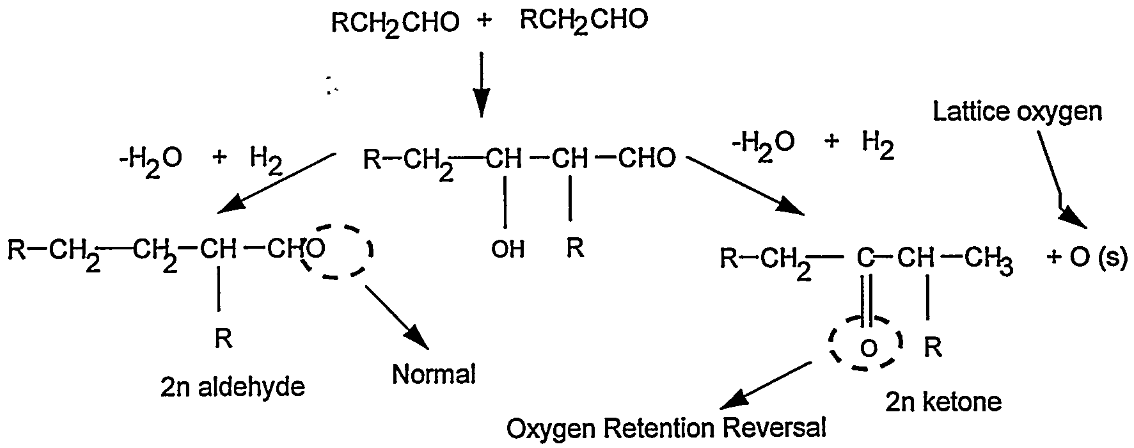
1) The initial formation of a C_n-aldehyde from a C_n-alcohol by dehydrogenation

$$RCH_2CH_2OH \rightleftharpoons RCH_2CHO + H_2$$

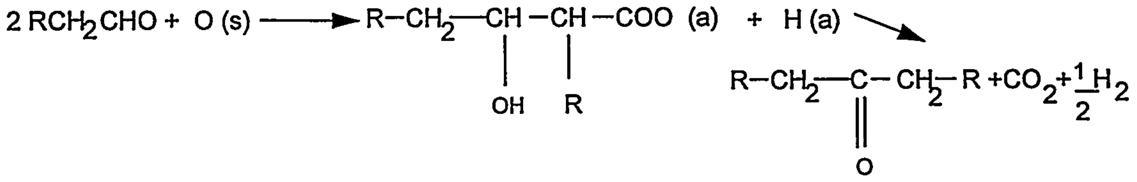
2) The reaction of the C_n-aldehyde with the C_n-alcohol to form the C_{2n}-ester

$$RCH_2CH_2OH + RCH_2CHO \longrightarrow R-CH_2-CO-O-CH_2-CH_2-R$$

3) The self addition of the C_n-aldehyde by aldol-type condensation to yield C_{2n}-aldehydes or ketones



4) The condensation of the C_n-aldehyde to give C_{2n-1}-ketones using up a surface oxygen vacancy



$$2\,RCH_2CHO + O(s) \longrightarrow R-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{R}{\underset{|}{CH}}-COO\,(a) + H\,(a) \longrightarrow R-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-R + CO_2 + \frac{1}{2}H_2$$

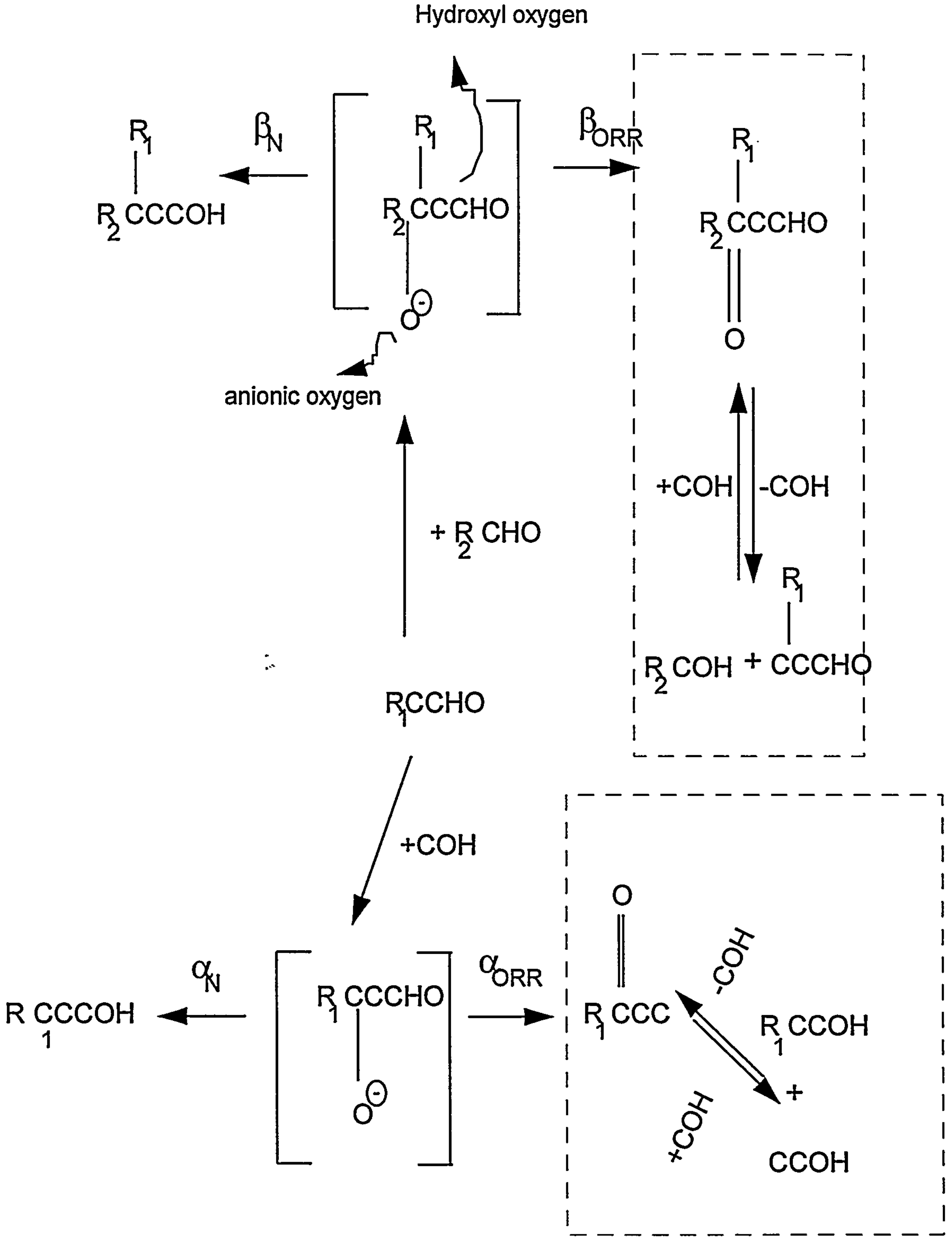
(s enclosed by parenthesis refers to surface species and a enclosed by parenthesis refers to adsorbed species)

This mechanism accounts for the formation of C_{2n}-aldehydes and ketones. Reactions between the C_n-alcohols and aldehydes account for C_{2n}-esters and the self-condensation reaction for C_{2n} aldehydes and ketones. This explanation is identical to the normal and oxygen retention reversal modes of the mechanism proposed by others. [Klier, K., Herman, R.G., Himelfarb, P.B., Young, C.W., Hou, S., and Marcos, J.A., Proc. 10th Intern. Catal. Congr. Congress, Budapest (1992) and Forzatti, P., Tronconi, E., and Pasquon, I., Catal. Rev. Sci. and Eng., **33**, 109 (1992)]. The mechanism proposed by Klier et al. for higher pressure isobutanol synthesis conditions from synthesis gas is shown in the following page.

Tronconi et al. [Tronconi, E., Forzatti, P., and Pasquon, I., J. Catal., **124**, 376 (1990)] have suggested that under high pressure conditions ketones are thermodynamically less favorable (< 2% equilibrium yield at 7.6 MPa) because of an inverse cubic dependence of their equilibrium concentration on reaction pressure. These authors show that primary alcohols and ketones equilibriate rapidly; at high temperatures and contact time this equilibrium tends to favor alcohols over ketones.

The mechanism for the formation of C_{2n-1}-ketones is less apparent. Some authors [Kagan, M.J., Sobolew, I.A., and Lubarsky, G.D., Chem. Ber., **68**, 1140 (1935)] suggest that acetone forms from ethanol via ethyl acetate intermediates. Acetone is not formed on basic MgO catalysts, suggesting that vacancies (not favored in MgO) may be required for ketone formation [Ueda, W., Ohshida, T., Kuwabara, T., and Morikawa, Y., Catalysis Letters, **12**, 97 (1992)]. This redox mechanism for the formation of ketone intermediates may also account for the role of Mn in high performance isobutanol synthesis catalysts, as found in the work of Keim et al.{Keim, W., and Falter, W., Catalysis Letters, **3(1)**, 59-63 (1989)] and Kotowski et al. [Kotowski, W., Kliemiec, J., Lach, J., Gorski, R., Adamus, W., Groschwski, B., and Zalewski, I., Polish Patent PL 130325 (1986) as referred to in the article by Sofianos [Sofianos, A., Catalysis Today, **15**, 149 (1992)]}. MnO is a well known oxidation catalyst and it is expected to contain a high density of oxygen vacancies at reaction conditions. If a molecularly adsorbed acetone was formed as a surface species during synthesis gas conversion at high pressures, it would hydrogenate rapidly to 2-propanol, which can react with formaldehyde on basic sites to form isobutanol. This unexplored pathway can be studied by the addition of ^{13}C-labeled acetone to CO/H_2 feeds and the measurement of isotopic contents in products.

The addition of unlabeled 2-propanol or acetone to CO/H_2 mixtures under higher alcohol synthesis conditions, not surprisingly, gave identical results on a Cs/Cu/ZnO type catalyst. [Vedage, G.A., Himelfarb, P.B., Simmons, G.W., and Klier, K., ACS Symposium Series, **279**, 295 (1985)]. In both cases a significant increase in the yield of ethanol and acetaldehyde was observed under higher alcohol synthesis (HAS) conditions. These studies show that under higher alcohol synthesis conditions two reactions dealing with acetone attain thermodynamic equilibria: between ethanol and acetone and between 2-propanol and acetone.


Hydroxyl oxygen
R1
R2CCCOH
βN
R1
R2CCCHO
O⊖
anionic oxygen
βORR
R1
R2CCCHO
O
+COH
-COH
R1
R2COH + CCCHO
+ R2CHO
R1CCHO
+COH
R1CCCOH
αN
R1CCCHO
O⊖
αORR
O
R1CCC
-COH
+COH
R1CCOH
+
CCOH

$$2CH_3CH_2OH \longrightarrow CH_3COCH_3 + 3H_2 + CO$$

$$CH_3CHOHCH_3 \longrightarrow CH_3COCH_3 + H_2$$

In our initial study of alcohol reactions, we have addressed the mechanism of the formation of aldehyde and ketone synthesis formed from ethanol-methanol mixtures and its relationship to higher pressure alcohol synthesis reactions. We have also explored the potential roles of Mn and Cs components, which are usually present as promoters in isobutanol synthesis catalysts. Specific questions that we continue to explore are:

1. How are ketones and aldehydes formed? Are esters intermediates in the formation of ketones? Is acetone one of the intermediates in isobutyraldehyde formation from syngas via the formation of 2-propanol?

2. How can mechanistic studies of alcohol coupling reactions at low pressures be used to infer mechanisms and performance at high pressures?

3. What are effects of Cs and Mn on the methanol synthesis reaction, on the C_1 to C_2 alcohol conversion, on aldol condensation of C_{2+} aldehydes, on the dehydrogenation of alcohols to aldehydes, and on ketone formation using surface oxygen vacancies?

3.1.3 Experimental Procedures

Alcohol coupling reactions were conducted at 250 ^{0}C in a gradientless recirculating batch reactor at a total pressure of 0.1 MPa. The make-up of the feed was: 30 torr ethanol, 60 torr methanol, 15 torr neon and the balance helium. Cu/ZnO [Cu:Zn at. 30:70], Cs/Cu/ZnO [Cs:Cu:Zn at. 0.4:30:70] and Cu/ZnO/MnO [Cu:Zn:Mn at. 4:3:1] catalysts were evaluated using 22 mg catalyst charges. Products were sampled by syringe extractions from the recirculating stream at approximate intervals of 5, 10, 15, 30, 50 and 115 min. and injected into a gas chromatograph equipped with flame ionization and thermal conductivity detectors.

Methanol and ethanol conversions were calculated from thermal conductivity data using Ne as an internal standard. Ne was used because it was readily separated from CO and CO_2 using our chromatographic set-up (6ft, 1/8″ Porapak Q column; temperature program: 45 ^{0}C for 4 min, heating to 200 ^{0}C at 10 ^{0}C/min). The remaining products were separated using a 5% phenyl-methyl silicone 60 m capillary column (HP-5) and analyzed by flame ionization (temperature program: 50 ^{0}C for 2 min, heating to 210 ^{0}C at 20 ^{0}C/min). CO formation rates were calculated by difference because extensive overlap between CO and the N_2/O_2 peaks (from air leak into the syringe) precluded direct chromatographic measurements of CO concentrations.

The catalysts were prepared by controlled precipitation from an aqueous mixture of the respective metal nitrates. The precipitate was then treated in air to a temperature of 350 ^{0}C using a program consisting of rapid heating to 150 ^{0}C at 5 ^{0}C/min followed by slow heating to 350 ^{0}C at about 1 ^{0}C/ min. The Cs was added as Cs-formate to a Cu/ZnO sample prepared by the above procedure. The sample was then heated to 100 ^{0}C in a nitrogen atmosphere and then calcined as described above. The samples were reduced at 350 ^{0}C in 10% H_2/He before alcohol coupling reaction studies at 250 ^{0}C, as reported elsewhere [Nunan, J.G, Himelfarb, P.B., Herman, R.G., and Klier, K., Inorg. Chem., **28**, 3868 (1989)].

The surface areas of the samples were measured using dinitrogen physisorption and the BET isotherm in a Quantasorb flow adsorption apparatus. A surface area of 90 m^2/g was obtained for Cu/ZnO/ MnO, 58 m^2/g for Cu/ZnO, and 38 m^2/g for the Cs-doped Cu/ZnO catalyst.

3.1.4 Results

Our product formation rates are reported as site (copper)-time yields, based on the total number of copper atoms. This is a convenient choice, as it can be easily converted to the correct site-time yields from independent copper dispersion measurements. Selectivities are reported on a carbon basis, as a fraction, in terms of the moles of carbon appearing within each product formed per mole of carbon in the ethanol and methanol converted.

Reactivity data for the Cs-doped Cu/ZnO methanol synthesis catalyst

The Cs/Cu/ZnO catalyst is a Cs-modified methanol synthesis catalyst and chosen in order to examine the effect of Cs. The conversion of methanol on this sample under our reaction conditions (250 ^{0}C, ~ 0.1 MPa total pressure) was very low (< 1%), while the ethanol conversion was higher and reached an asymptotic value about 60% (Fig. 1(a)). The same behavior is observed when the methanol and ethanol turnovers are plotted as a function of time (Fig 1(b)).

On this sample, the acetaldehyde site-time yield increases initially, reaches a maximum and then decreases (Fig. 2). When the selectivity for acetaldehyde formation is plotted as a function of ethanol conversion, there is also an initial increase in the selectivity, attainment of a maximum and a decrease (Fig. 3). This behavior is expected of a reactive intermediate in a classical series reaction. Therefore, acetaldehyde appears to be a reactive intermediate product in methanol-ethanol coupling reactions. Acetone site-time yields reach a maximum rapidly and then decline to a constant value (Fig. 4). Isobutyraldehyde site-time yields obtained on this catalyst are lower than for acetone but its behavior with increasing contact time is similar. The acetone and isobutyraldehyde selectivities increase monotonically with ethanol conversion (Fig. 5). This behavior suggests they are unreactive products under these conditions on Cs/Cu/ZnO.

The site-time yields of ethylacetate and n-butyraldehyde decline after an initial increase, while the site-time yields of methylethyl ketone and 2-pentanone continue to increase with contact time (Fig. 6), suggesting that both ethylacetate and n-butyraldehyde are reactive. When the ethyl acetate and butyraldehyde selectivities are plotted as a function of conversion, they initially increase, attain maxima at intermediate conversion and decrease (Fig. 7). This confirms that ethylacetate and n-butyraldehyde are intermediates. The selectivities towards methylethyl ketone and 2-pentanone (Fig. 7) increase monotonically as conversion increases, suggesting that are unreacting products.

Reactivity Data for the Mn Containing Cu/ZnO/MnO catalyst

In contrast with Cs/Cu/ZnO, the Cu/ZnO/MnO leads to significant methanol conversion levels (Fig. 8). Methanol conversion turnovers are lower than ethanol turnovers even though the feed contains 30 Torr of ethanol to the 60 Torr of methanol (Fig. 9). Ethanol dehydrogenation is significantly more rapid than methanol dehydrogenation on this catalyst. Acetaldehyde site-time yields show an initial increase with increasing contact time, then a maximum value and ultimately, a decrease (Fig. 10). The intermediate nature of acetaldehyde is consistent with changes in acetaldehyde selectivity with ethanol conversion (Fig. 11).

Acetone shows similar behavior on Cu/ZnO/MnO. It behaves as an intermediate on the Cu/ZnO/MnO with a maximum in acetone site-time yield at intermediate times (Fig. 12). Among the condensation products, butyraldehyde and ethyl acetate appear to be reactive intermediates whereas isobutyraldehyde, methylethyl ketone, and 2-pentanone appear to be unreacting species (Figs. 12 and 13).

Reactivity data on Cu/ZnO methanol synthesis catalysts

It is interesting to compare the activity of Cu/ZnO with the Cs-promoted Cu/ZnO methanol synthesis catalyst. Methanol shows a non-zero conversion on Cu/ZnO (Fig. 14), methanol turnover-time curves lie above the ethanol turnover-time curves (Fig. 15). As on Cs/Cu/ZnO and Cu/ZnO/MnO systems, it is found that acetaldehyde is an intermediate in methanol-ethanol coupling reactions (Fig. 16, 17). Acetaldehyde site-time yields are similar in magnitude to those on the other two catalyst systems.

Among the condensation products, acetone and n-butyraldehyde are intermediates whereas isobutyraldehyde, methylethyl ketone, and 2-pentanone are unreactive products. The magnitudes of the site-time yields (Fig. 18) of these condensation products are much greater on the Cs/Cu/ZnO and Cu/ZnO/MnO catalysts.

3.1.5 Discussion

Ethanol and methanol reactivities

It appears that on the modified and unmodified methanol synthesis catalyst surfaces, the ethanol dehydrogenation rates were higher than those of methanol reactions. On the Cs-modified Cu/ZnO, the methanol was not converted. On Cu/ZnO/MnO catalysts, the ethanol turnovers were higher than methanol turnovers at all times during the run. Only for the unmodified Cu/ZnO, ethanol turnovers were lower than those of methanol.

On each catalyst, ethanol conversions reach a constant value (~ 60%) with increasing contact time. We conclude that ethanol conversion reaches the equilibrium for the predominant reaction of ethanol dehydrogenation to acetaldehyde.

The role of the alkali might be two-fold: 1.) modification of methanol formation and decomposition sites and 2.) stabilization of the intermediate necessary for the formation and decomposition of ethanol. Our experimental evidence suggests that Cs inhibits methanol decomposition to CO and H_2 because undoped Cu/ZnO is very active for methanol conversion to CO and H_2. It is possible that alkali decreases the size of Cu ensembles available for dehydrogenation..

Reactive Intermediates and Unreactive Product Species

On all three catalyst formulations, acetaldehyde, the most abundant product, seems to be a reactive product that undergoes significant secondary reactions. The formation of all the other species depends on the condensation of acetaldehyde either with itself (self-condensation) or with formaldehyde. The condensation steps are slower than the ethanol dehydrogenation step to form acetaldehyde or methanol dehydrogenation to form formaldehyde. The major secondary products that are formed on all of the catalyst formulations are: acetone, isobutyraldehyde, and methylethyl ketone. All aldehydes except isobutyraldehyde are intermediates and all ketones, except acetone are unreactive products.

Acetone seems to be an intermediate species as well. The presence of acetone (the (2n-1) ketone) among reaction products is due to the presence of the CO product of methanol decomposition [Elliott, D. J., and Penella, F., J. Catal, **119**, 359, (1989)]. These authors have suggested that CO was necessary for the formation of oxygen vacancies.

The condensation products of the reaction can be grouped into two categories, those that can form directly from ethanol and those that require methanol-ethanol reactions. Acetone, ethyl acetate, methyl-ethyl ketone, n-butyraldehyde and 2-pentanone can form from ethanol, while propionaldehyde and isobutyraldehyde require formaldehyde reactants for their synthesis. The presence of the isobutyraldehyde and propanal as reaction products suggests that low concentration of reactive formaldehyde species are available from methanol dehydrogenation.

As expected, the methanol synthesis component (Cu/ZnO) of the higher alcohol synthesis catalyst also acts as a dehydrogenation function. On Cu/ZnO, the condensation site-time yields are much lower than on the Cs/Cu/ZnO and Cu/ZnO/MnO catalysts. Therefore, Cs and Mn appear to be important functions for the condensation steps. The effect of Cs seems to better defined as the precursor of the Cs-modified catalyst was none other than the unmodified Cu/ZnO sample.

Conclusions

Thus, in summary, the analysis of the recirculating batch reactor data leads to the following conclusions:

1. The presence of Cs inhibits the methanol decomposition to synthesis gas. On all catalysts, the ethanol conversion reaches a maximum asymptotic value of about 60% as contact time increases in the recirculating batch reactor. This suggests that the predominant reaction, ethanol dehydrogenation to acetaldehyde, reaches thermodynamic equilibrium. Thus, conversion of acetaldehyde to higher molecular weight condensates is slow and rate-limiting at these reaction conditions.

2. Acetaldehyde is the most abundant product. The selectivity to acetaldehyde reaches a maximum at intermediate conversions, suggesting that acetaldehyde is the predominant reactive intermediate in the conversion of ethanol to higher oxygenates. Formaldehyde, though not observed by us experimentally because of its low equilibrium concentrationat these reaction conditions appears to be formed and involved in the synthesis of propionaldehyde and isobutyraldehyde.

3. The main products of the reaction are acetaldehyde and acetone (by acetaldehyde self-condensation), ethyl acetate (by acetaldehyde-ethanol condensation), methyl-ethyl ketone and 2-pentanone (from acetaldehyde condensation), propionaldehyde (from aldol-type condensation of acetaldehyde with formaldehyde), butyraldehyde (from condensation of acetaldehyde), and isobutyraldehyde (from condensation of formaldehyde and propionaldehyde).

4. Formaldehyde species formed by methanol dehydrogenation decompose rapidly to CO and H_2 , which are the predominant products of methanol reactions in $^{13}CH_3OH/C_2H_5OH$ mixtures. High CO selectivities are consistent with previous studies. In addition, the work of Elliott and Penella [Elliott, D.J., and Penella, F., J. Catal, **<u>119</u>**, 359, (1989)) shows that inert atmospheres favor the formation of ethyl acetate from ethanol. The presence of CO favors condensation reactions leading to acetone. Our observation of high selectivity to condensation products is consistent with the presence of significant CO partial pressures during reactions of $^{13}CH_3OH/C_2H_5OH$ mixtures.

5. Significant ^{13}C contents within reaction products were only observed on Cs/Cu/ZnO catalysts. Smaller amounts of ^{13}C were also found in all the higher carbon number

condensation products formed in the reactions of $^{13}CH_3OH/C_2H_5OH$ mixtures on the other two catalysts (Cu/ZnO/MnO, Cu/ZnO).

6. Acetaldehyde and acetone site-time yields are significantly higher on the Cs/Cu/ZnO catalyst than on the other two catalysts. Site-time yields increase in the order of Cs/Cu/ZnO >CuZnMn>>Cu/ZnO for these products.

7. All aldehydes, except isobutyraldehyde, appear to be reactive intermediates at these reaction conditions. Their site-time yield-time curves show maxima at intermediate contact time. All ketones, except acetone, all ketones appear to be unreactive products and their site-time yields increase monotonically with contact time.

These findings have suggested several additional experiments. First, the use of unlabeled and singly-labeled ethanol (with the ^{13}C in the α-carbon) can be used to determine whether ethanol is the only required reactant in the condensation reactions or whether methanol (through formaldehyde intermediate) also participates. Labeled ethanol also contains much lower levels of ^{18}O than ^{13}C labeled methanol (4%). A comparison of the catalytic behavior of these materials with that reported on other basic oxides such as MgO shows that MgO catalyzes isobutanol synthesis selectively from methanol-ethanol reactions via hydrogen transfer from methanol to isobutyraldehyde to form isobutanol. This provides the required thermodynamic and kinetic driving force for the formation of formaldehyde, a reactant required for the formation of isobutyraldehyde on Cu-based isobutanol synthesis catalysts. On our Cu-based catalysts, this hydrogen transfer mechanism does not occur. The predominant reaction is aldol condensation of two acetaldehyde molecules to give n-butyraldehyde. On these catalysts, surface hydrogen atoms formed in the dehydrogenation steps appear to recombine to form dihydrogen molecules, whereas on MgO they remain on the surface and are used in the hydrogenation of aldehydic products of the aldol condensation step. These catalytic differences are poorly understood and deserve further attention by using deuterated methanol as a probe of hydrogen transfer pathways. These studies will be continued following the completion of the RRU equipment described below.

3.2 Design of Recirculation Reactor Module

Design and specifications for a recirculating reactor module (RRU) dedicated to this project have been completed and most parts have been ordered during this reporting period. The feed introduction, metering and purification systems will be independent of that of the CMRU in order to allow independent use of the CMRU and the RRU equipment. The additional expenses associated with this redesign are being covered by cost savings in the APCI subcontract. (Task 5).

3.3 Isobutanol Synthesis at High Pressure in the CMRU

We have continued the CMRU (Catalytic Microreactor Unit) certification runs using the Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst provided by APCI. A charge of 0.8 g catalyst with 0.8 g quartz diluent (CMRU-2) resulted in selectivities significantly different from those obtained in CSTR tests of this catalyst at APCI. Additionally, CMRU-2 mass balances based on the argon internal standard were unsatisfactory (60-80% of the converted CO appearing in the products). The latter was attributed to poor resolution of the argon and carbon monoxide peaks in the thermal conductivity analysis. The chromatography temperature program was modified to provide complete resolution of these peaks.

In CMRU-3, the BASF catalyst (2.4 g) was charged to the reactor. The higher catalyst loading was chosen in order to run at higher flow rates while maintaining the CMRU-2 gas hourly space velocity of 5000 cm^3/g-cat.-h. Because Cs promotion increases selectivities to higher alcohol products, CMRU-3 was carried out without quartz diluent in order to eliminate the potential for Cs migration to quartz diluent, a process which may have led to the low selectivity toward higher alcohols obtained in CMRU-2.

Initial CMRU-3 results gave very high methanol selectivities. However, analysis of the data highlighted the gas chromatograph response factors as a possible source of error. Using known mass flow rates, the inlet gas composition as determined by thermal conductivity analysis was used to verify current response factors. Calculations yielded response factors varying as much as 35% from those reported by Dietz [Dietz, W. A., *Journal of Gas Chromatography*, 5, 68 (1967)]. We have since obtained and incorporated response factors from APCI, values measured specifically for alcohols at low concentrations. These response factors resulted in more reasonable methanol selectivities of 25-55%. A new 50 m HP-5 column with a thicker film was purchased and installed to provide for better chromatographic separation of alcohols. The new column has resulted in complete resolution of all components and significantly decreased tailing of the alcohols.

Certification of the CMRU using the Cs-promoted $Cu/ZnO/Al_2O_3$ catalyst provided by APCI was continued in order to study the effects of varying gas hourly space velocity (GHSV) and temperature. CMRU-3 was conducted with a 2.4 g catalyst charge over a GHSV range of 625-2500 scm^3/g-cat.-h and temperatures 300-360 °C. Decreasing the GHSV resulted in the expected increase of CO conversion from 10% at 2500 scm^3/g-cat.-h to 22% at 1250 scm^3/g-cat.-h, at 300 °C. Additionally, lower space velocities gave higher isobutanol selectivities. As temperature increased, CO conversion to methanol became thermodynamically unfavorable and the isobutanol selectivity increased. At 625 scm^3/g-cat.-h and 354 °C, conversion was low (5.2%) but the highest isobutanol-to-methanol ratio (0.062) was achieved.

One of the primary goals of CMRU-3 was to determine whether inability to attain a selectivities sum of unity was the consequence of alcohols condensation in the lines or erroneous calculation methods. Data from three different days (Table 1) of CMRU-3 are given below:

Table 1: CMRU-3 - Summary

Time on stream (h)	4	144	168
GHSV (scm^3/g-cat.-h)	2500	625	2500
Temperature (°C)	300	354	360
CO Conversion	**19.8%**	**5.2%**	**8.2%**
Selectivities (fractional)			
CO_2	0.08	0.31	0.24
methanol	0.54	0.18	0.29
isobutanol	0.0023	0.0091	0.0054
Selectivity sum	**0.65**	**0.58**	**0.61**

As conversion decreased, the sum of all selectivities decreased to the lowest sum of 0.44 at a conversion of 4.2%. This trend is partly explained by the selectivity calculation which requires dividing by the conversion, a very small number as shown at 144 h and 168 h. Failure to attain a sum of selectivities near unity must be attributed to alcohols condensation in the lines.

In an attempt to detect any condensation during the experiments, the lines downstream from the reactor were heated to 230 °C, 30 °C higher than the usual value. Unfortunately, this led to the destruction of the Teflon seal and diaphragm of the back pressure regulator before the question of alcohols condensation was resolved. Additionally, two valves had to be replaced as a consequence of operating near their maximum temperature specification. The regulator has been repaired and the unit reconstructed using valves rated to higher temperatures. We are currently leak testing the unit and re-installing the heat tracing to provide better thermocouple placement and insulation of the heated lines.

The high pressure syringe pump has been calibrated and installed. Upon completion of leak testing, we plan to introduce liquid n-butanol in helium in order to obtain an independent measure of the n-butanol response factor required for more accurate selectivity calculations. Also, we will increase the n-butanol introduction rate until the area of the n-butanol peaks no longer increases. This experiment should provide the minimum line temperature at which n-butanol begins to condense.

A sample septum and a liquid collection system were installed downstream from the gas chromatograph in order to allow for off-line GC-MS analysis of the reactor effluent. Mass spectrometric measurements will become essential as we need to identify the composition of complex higher mixtures formed and as we introduce ^{13}C or D labeled reactants and products into the feed mixtures. A smaller volume sample loop for the GC 10-port valve was purchased in order to allow the use of the high sensitivity setting in the thermal conductivity detector. At low thermal conductivity detector sensitivity, the only peak detected by both the thermal conductivity and the flame ionization detectors is that of methanol. Additional cross-correlation peaks between the two columns/detectors should provide a more accurate selectivity calculation and identify any potential mass discrimination artifacts in the capillary column inlet.

We have received a new batch of the BASF Cs-promoted Cu/ZnO/Al_2O_3 catalyst from APCI. CMRU-4 will be conducted with this catalyst. APCI will also test this catalyst in a fixed-bed reactor to complement their current data, which were previously obtained using a backmixed reactor.

Task 4: Identification of Reaction Intermediates

Activities have focused on the final stages of the construction of the TPSR unit and on the design and construction of the feed metering and purification systems shared between the TPSR unit and the in-situ infrared spectrometer.

The design of the Temperature Programmed Surface Reaction (TPSR) unit was modified during this reporting period in order to minimize dead volumes, which could broaden dosing pulses and desorption peaks. 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 and microreactor units. 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.

Using CuO and Cs/Cu/ZnO samples, we have conducted certification and comparison tests of the TPSR system. The plots show the results of the temperature-programmed reduction (TPR) conducted on CuO powder and on Cs/Cu/ZnO catalysts. The standard experimental procedure consisted of heating a known weight of the sample in flowing hydrogen [4.6% H_2 in He] at the rate of 10 ^{0}C/min and measuring the hydrogen consumption rates. The hydrogen consumption rate obtained from the mass spectrometer signal is plotted against temperature in Figures 19 and 20.

As part of the certification procedure, these TPR data from the TPSR system were compared with a similar run that was carried out in a different apparatus. We used a modified Quantasorb surface area measurement unit with a thermal conductivity detector for the comparison. The material chosen for comparison was CuO and the results obtained on the Quantasorb are shown in Fig. 21.

On CuO, the onset of reduction occurs at around 230 ^{0}C for the CuO sample, with a well defined peak maximum at around 305 ^{o}C (Fig. 19). The completion of the bulk reduction of the sample occurs around 340 ^{0}C. The behavior of the Cs/Cu/ZnO is slightly different. The results of the temperature programmed reduction on this sample suggest that there are actually three peaks which have some overlapping regions. The onset of reduction on this sample occurs at 200 ^{0}C (Fig. 20), corresponding to the first of the three deconvoluted peaks. The reduction regime corresponding to this peak is completed at

310 ^{0}C. The peak with the largest area in the Cs/Cu/ZnO TPR spectrum is similar in shape to the reduction peak seen on the TPR of the CuO powder and has a reduction onset at 240 ^{0}C. The reduction regime corresponding to that peak is completed around 340 ^{0}C. The third peak has a reduction onset around 270 ^{0}C and this reduction is completed around 340 ^{0}C.

The hydrogen consumption as calculated from the total integrated area in the case of the unsupported CuO (Fig 19) is within 2% of the amount based on the catalyst stoichiometry and loading. In the case of the Cs/Cu/ZnO (Fig. 20), the hydrogen consumed is in excess of that required for the reduction of only the copper present on the sample. The appearance of three overlapping peaks also suggests that the supported Cu oxide perhaps shows a different reduction behavior from that of the unsupported CuO.

Figure 21 shows the results of a temperature programmed reduction of CuO conducted using the Quantasorb apparatus. The gas mixture used was 20% hydrogen in helium, as compared to the 4.6% hydrogen in helium used in the TPR experiment conducted on the TPSR apparatus. The onset of the reduction occurs around 180 ^{0}C, the peak maximum around 230 ^{0}C, and, the completion of the reduction around 300 ^{0}C. The comparison of the two sets of results seem to be consistent with the analysis of Monti and Baiker [Monti, D.A.M., and Baiker, A., J. Catal., <u>83</u>, 323 (1983)] who showed that reduction temperatures decrease with increasing hydrogen concentration.

After these certification runs, all transfer lines in the TPSR unit have been heated to ~ 100 ^{0}C in order to minimize of adsorbing and eluting products on walls. A thermostated saturator has also been introduced in order to allow controlled dosing of alcohols and other oxygenates. Measurement of flow rates have shown that the differentially pumped sampling system is extracting too large a fraction of the flowing stream from the analysis stream that enters the mass spectrometer. We have ordered a fine metering valve to reduce the pumping speed and thus eliminate this problem.

The construction of Temperature Programmed Surface Reaction (TPSR) Unit is thus 100% complete. Initial activities will focus on the study of surface species formed by interaction of alcohols and other oxygenates with catalytic surfaces and on the detection of their decomposition products upon heating.

Task 5: Bench Scale Testing at Air Products and Chemicals

Activities during this reporting period have included meetings between the UCB program manager and Drs. Richard Underwood and Bernard Toseland at Berkeley, at the DOE Contractor's Meeting in Pittsburgh, and during the Fall Meeting of the American Chemical Society in Chicago.

Extensive interactions between APCI and UCB have addressed the initial difficulties in obtaining > 97% total carbon mass balances and in reproducing the APCI backmixed reactor data on the standard BASF catalyst. APCI will be testing the standard BASF catalyst in their fixed-bed reactor during the next reporting period. In addition, initial discussions on the use of APCI's extensive data set for the purposes of kinetic modeling at UC-Berkeley have taken place. APCI will be providing the details of such data within the next reporting period.

The principal investigator attended the DOE Contractor's Meeting in Pittsburgh. As a part of this meeting, all DOE-funded investigators in the area of isobutanol synthesis met separately from the meeting and agreed to a standard set of conditions for the testing of catalytic materials and to the sharing and cross-testing of individual catalytic solids.

4. PARTICIPATING PROJECT PERSONNEL

Srinivasan Sundararajan
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Brandy. L. Stephens
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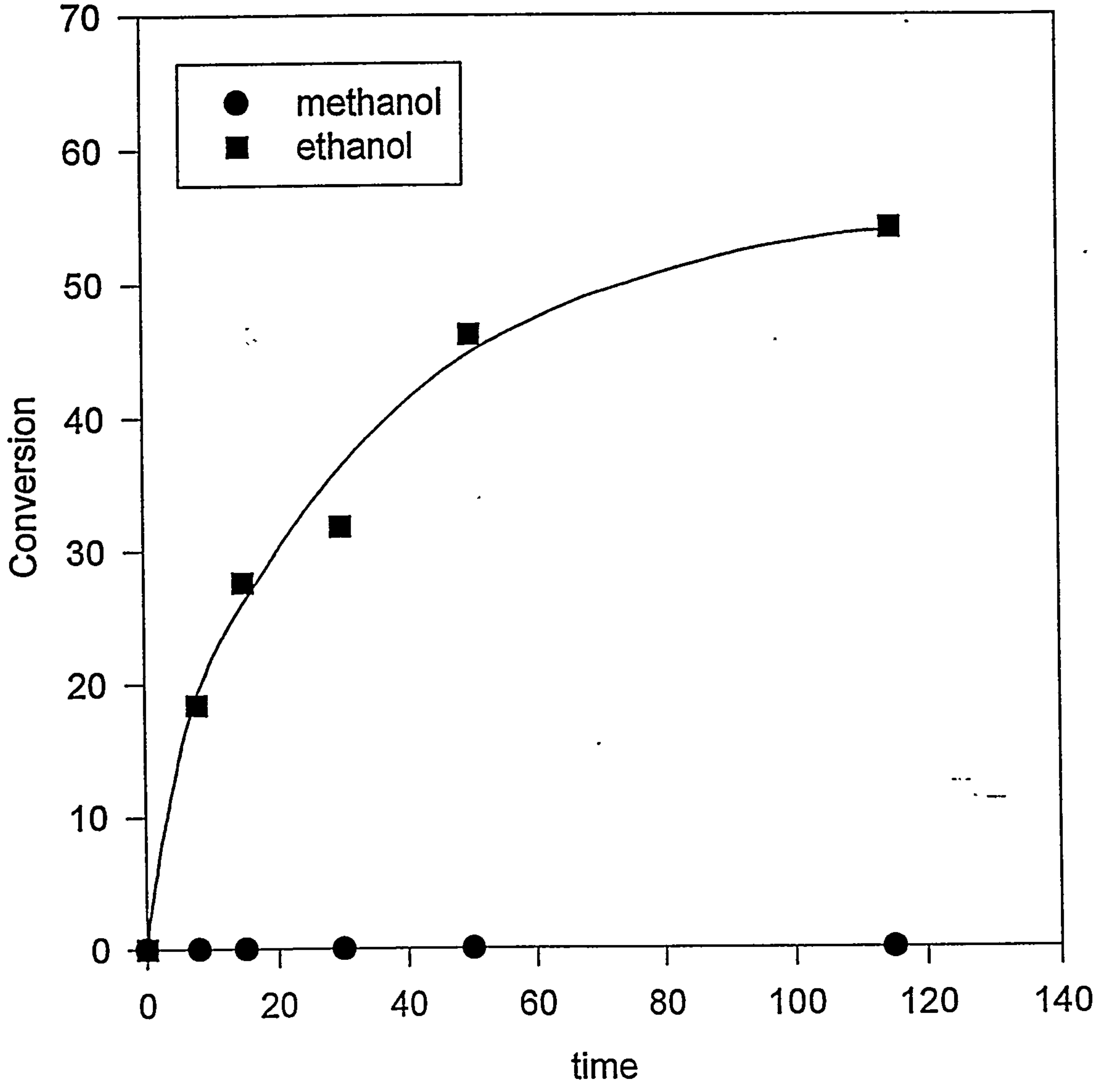
Sergio Mendez
Undergraduate Researcher

Tom Wang
Undergraduate Researcher

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

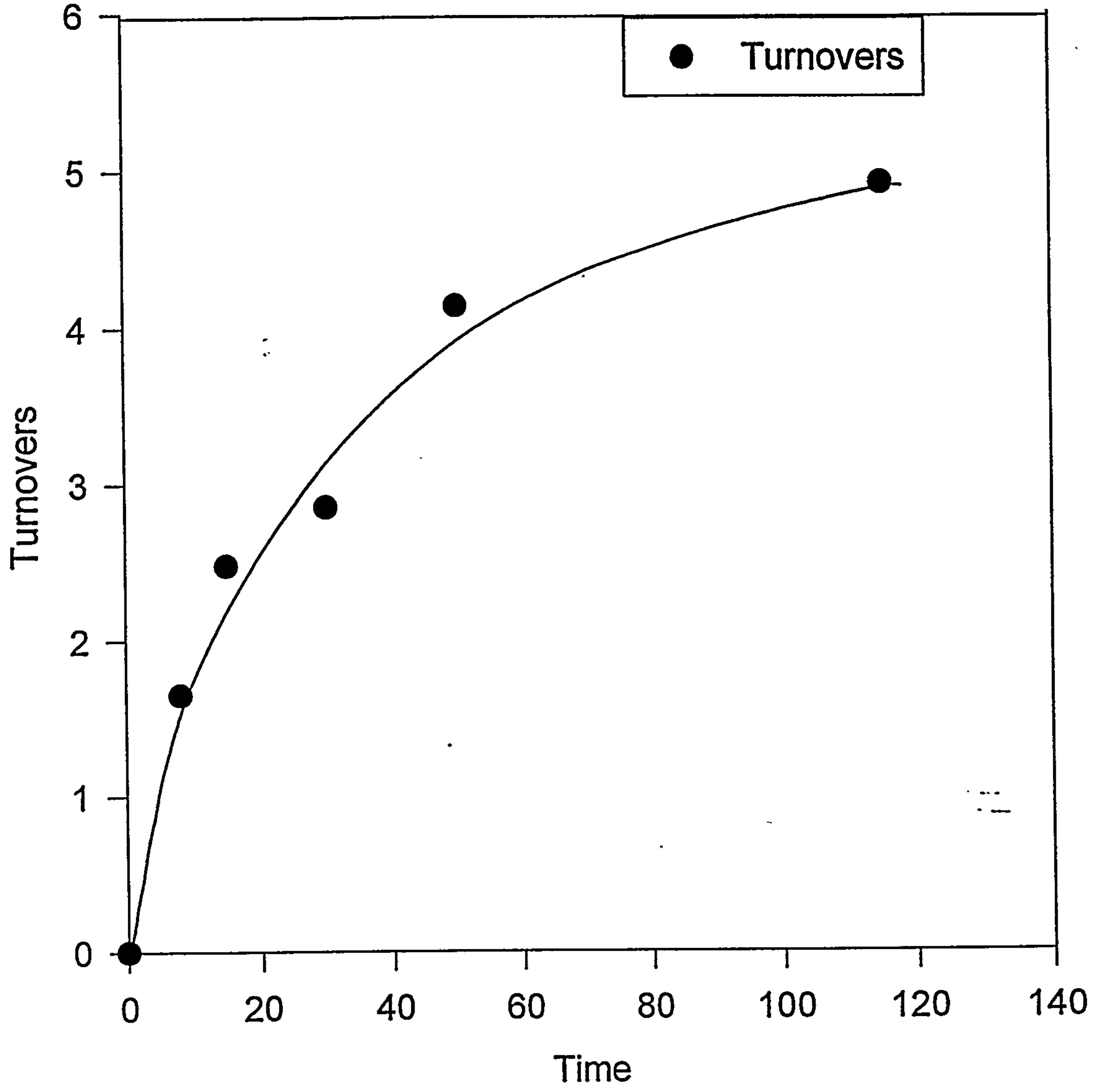
Enrique Iglesia
Principal Investigator

Fig. 1(a) Conversion vs time on Cs/Cu/ZnO catalyst for the alcohol coupling reaction.



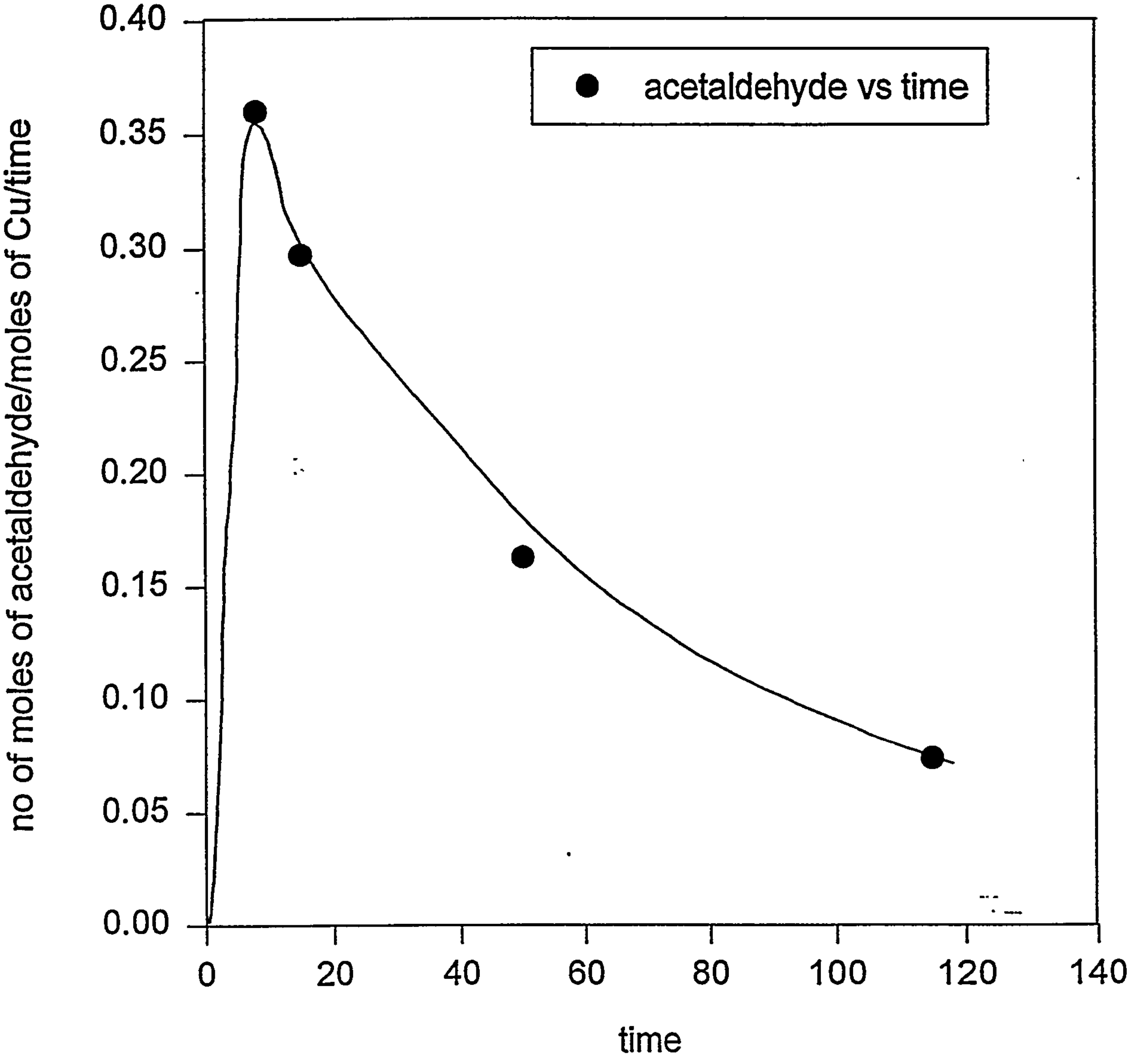
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst

Fig. 1(b) Turnovers vs time on Cs/Cu/ZnO catalyst for the alcohol coupling reaction.



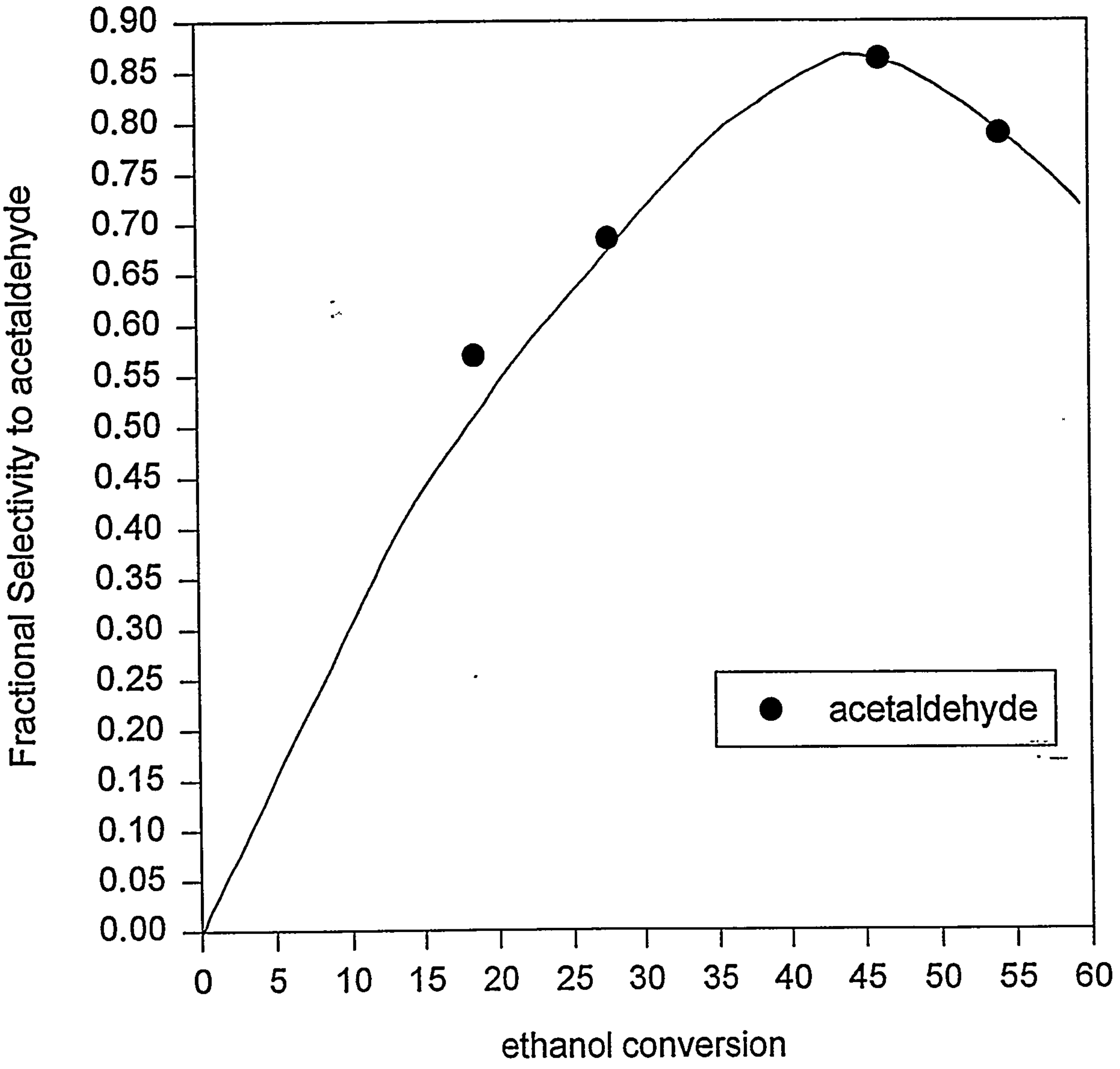
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Turnovers based on Cu atoms in sample

Fig. 2 Site-time yields vs time on Cs/Cu/ZnO catalyst for the alcohol coupling reaction.



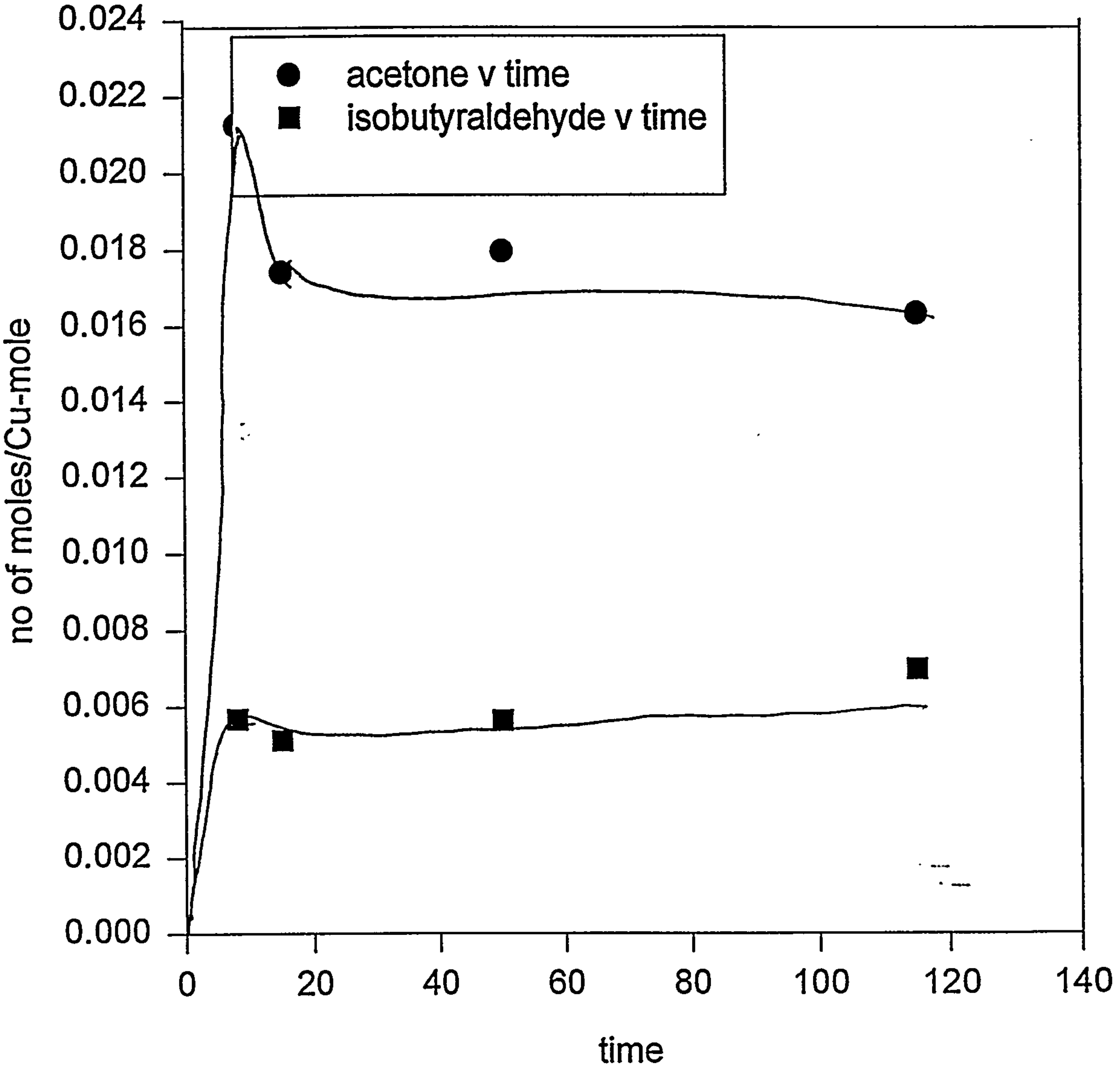
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Based on the number of Cu atoms in sample

Fig. 3 Selectivity conversion plot for products for alcohol coupling reaction



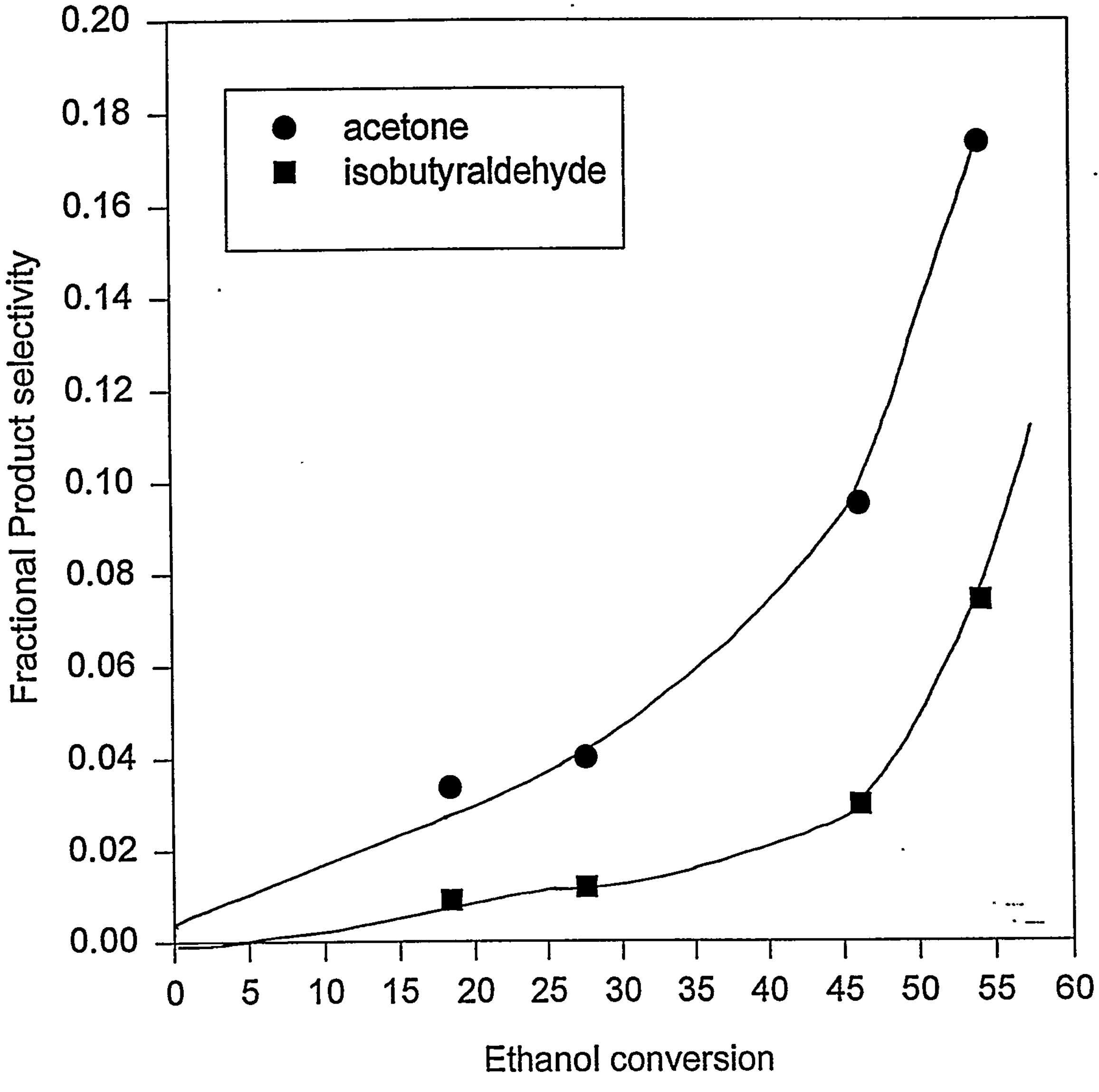
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Selectivity based on moles of ethanol converted

Fig. 4 Site-time yields vs time on Cs/Cu/ZnO catalyst for the alcohol coupling reaction.



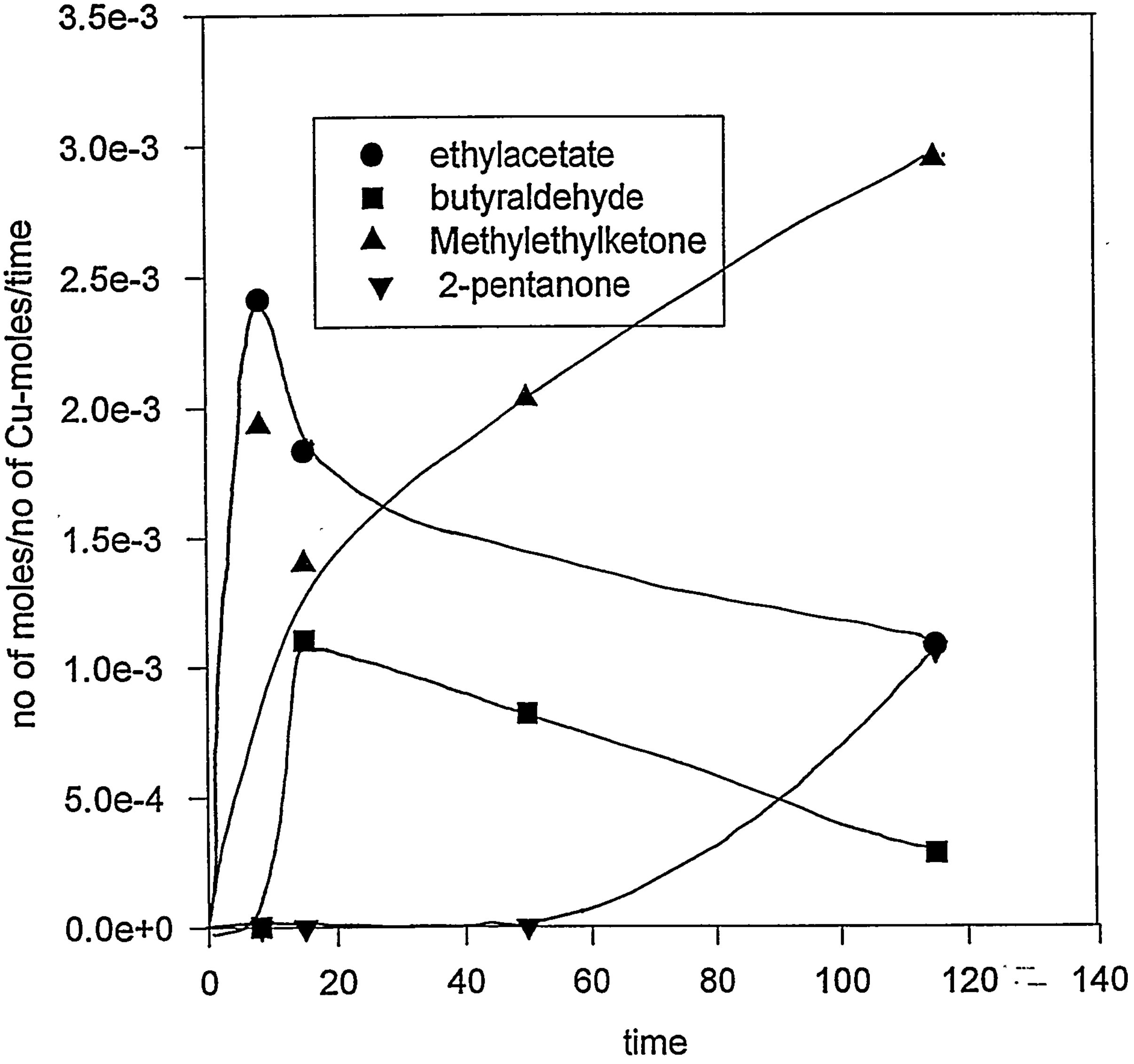
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Based on the number of Cu atoms in sample

Fig. 5 Selectivity conversion plot for products for alcohol coupling reaction



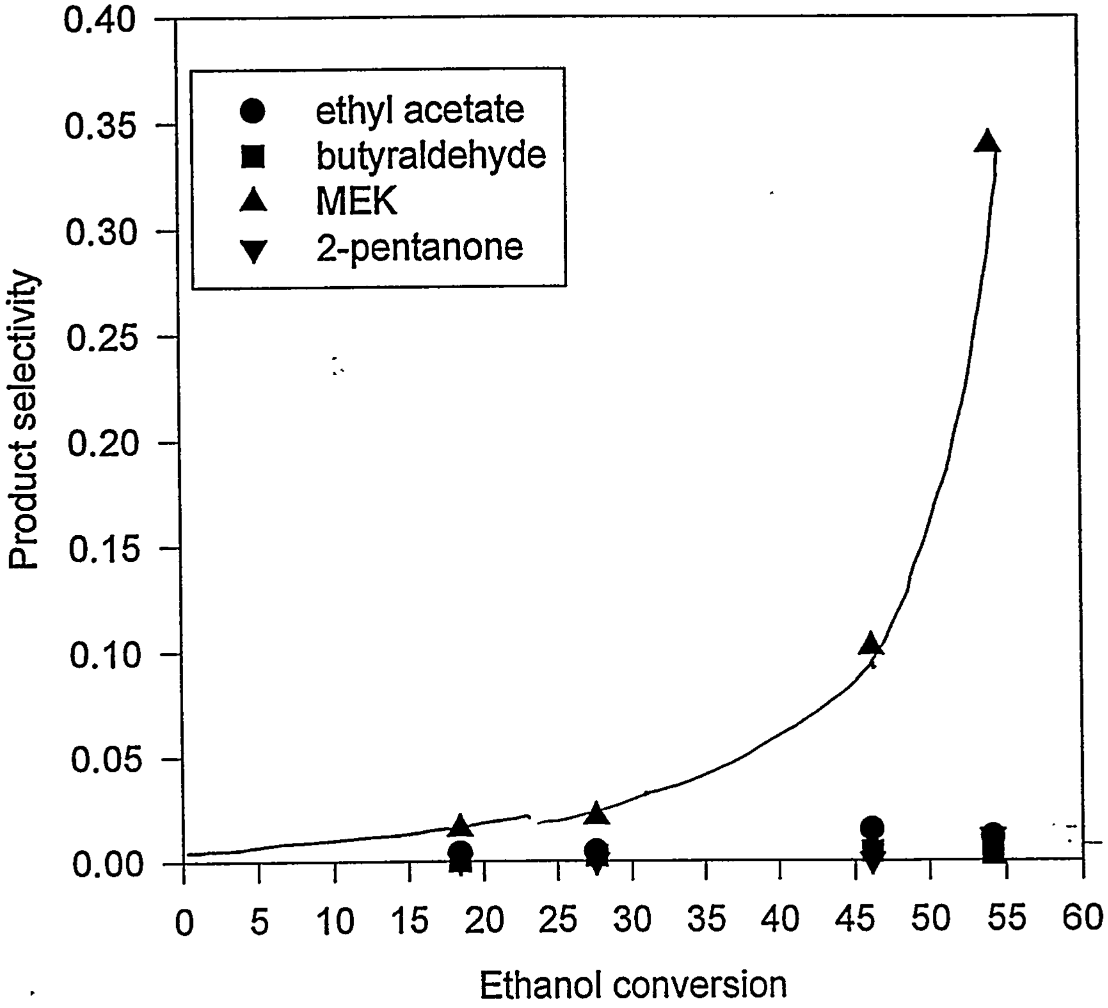
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Selectivity based on moles of ethanol converted

Fig. 6 Site-time yields vs time on Cs/Cu/ZnO catalyst for the alcohol coupling reaction.



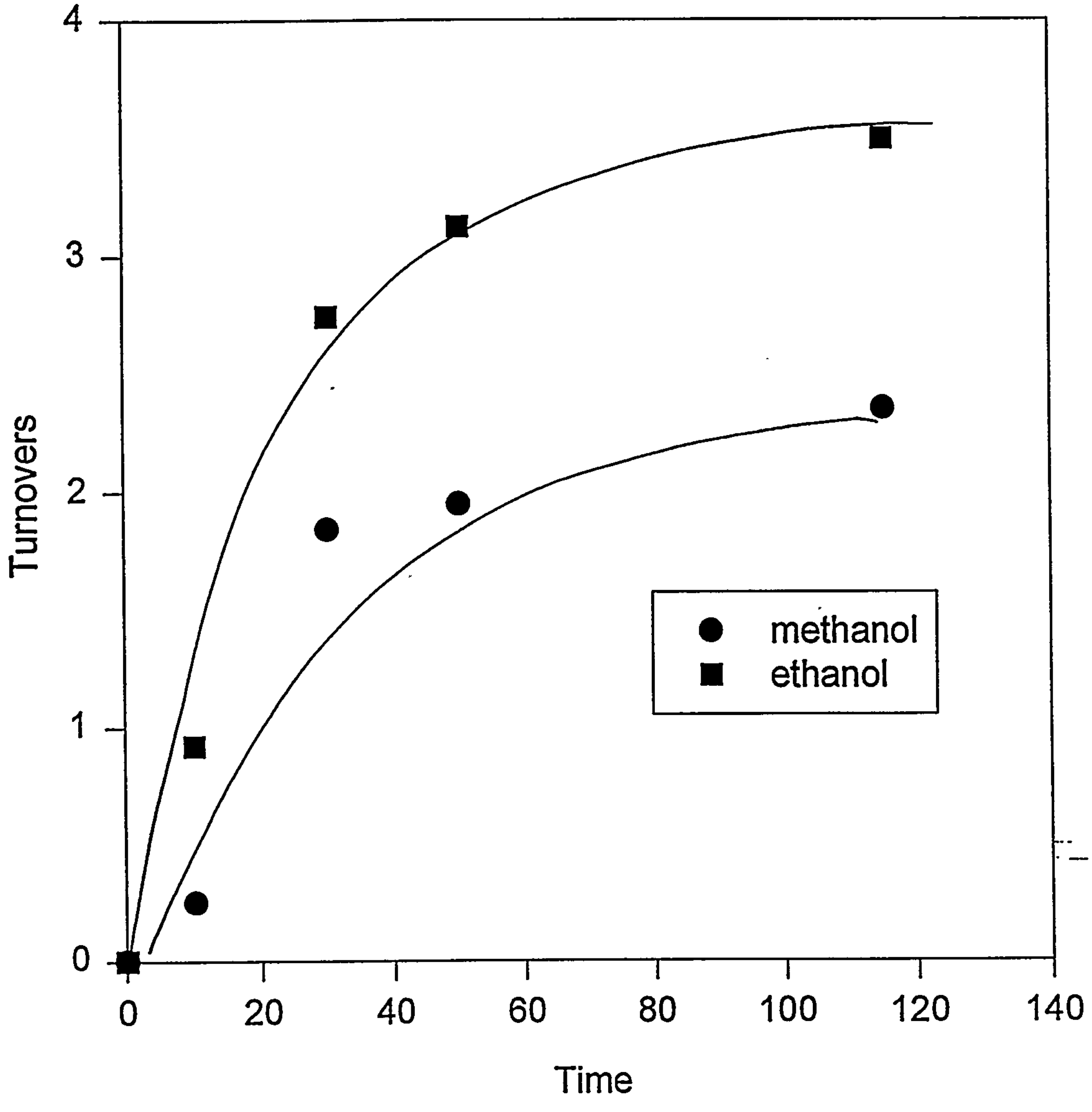
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Based on the number of Cu atoms in sample

Fig. 7 Selectivity conversion plot for products for alcohol coupling reaction



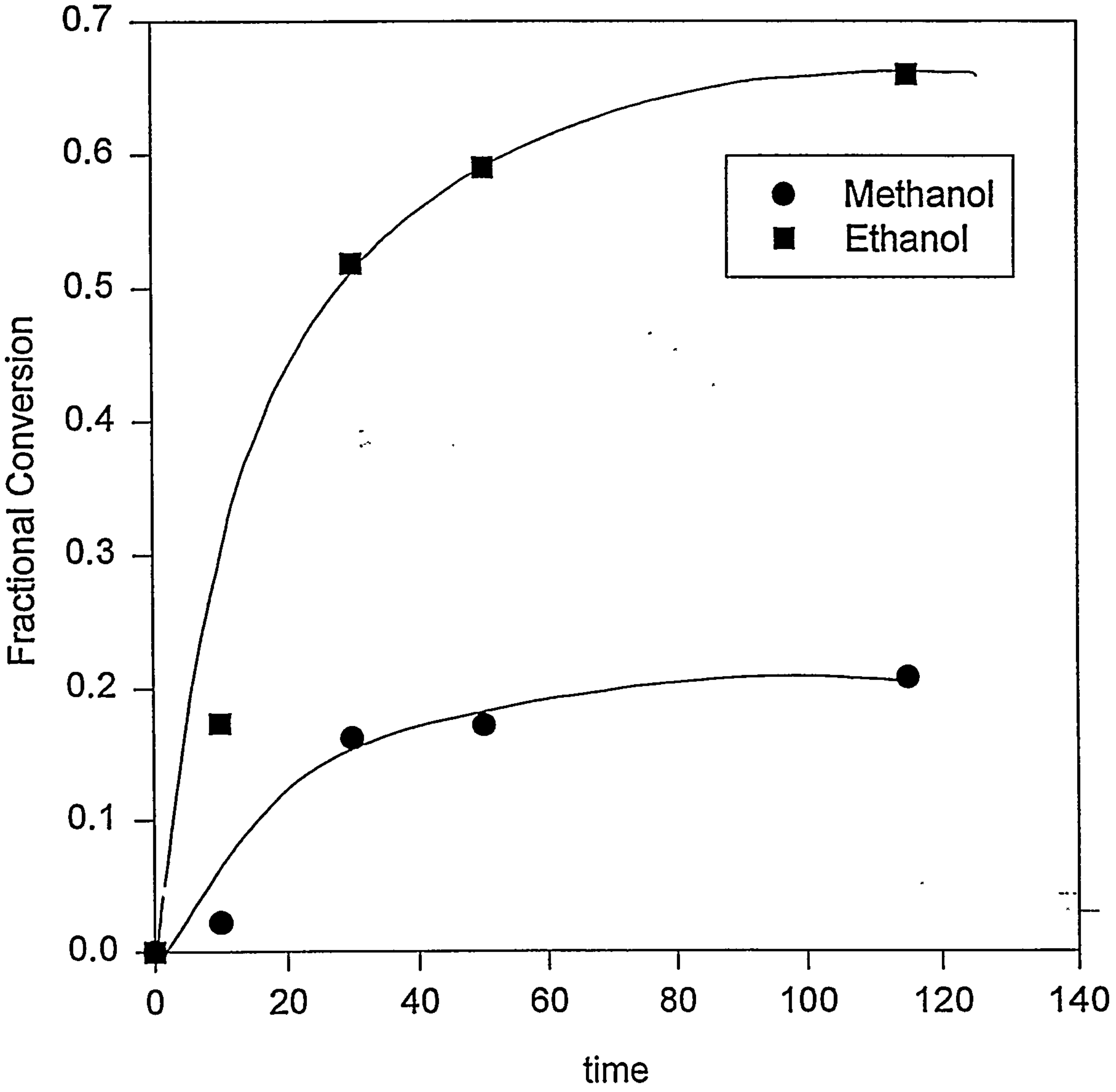
Reaction conditions: 250 C, 1 atm, 22 mg Cs/Cu/ZnO catalyst
Selectivity based on moles ethanol converted

Fig. 8 Turnoovers vs time plot for CuZnMn catalyst for the alcohol coupling reaction.



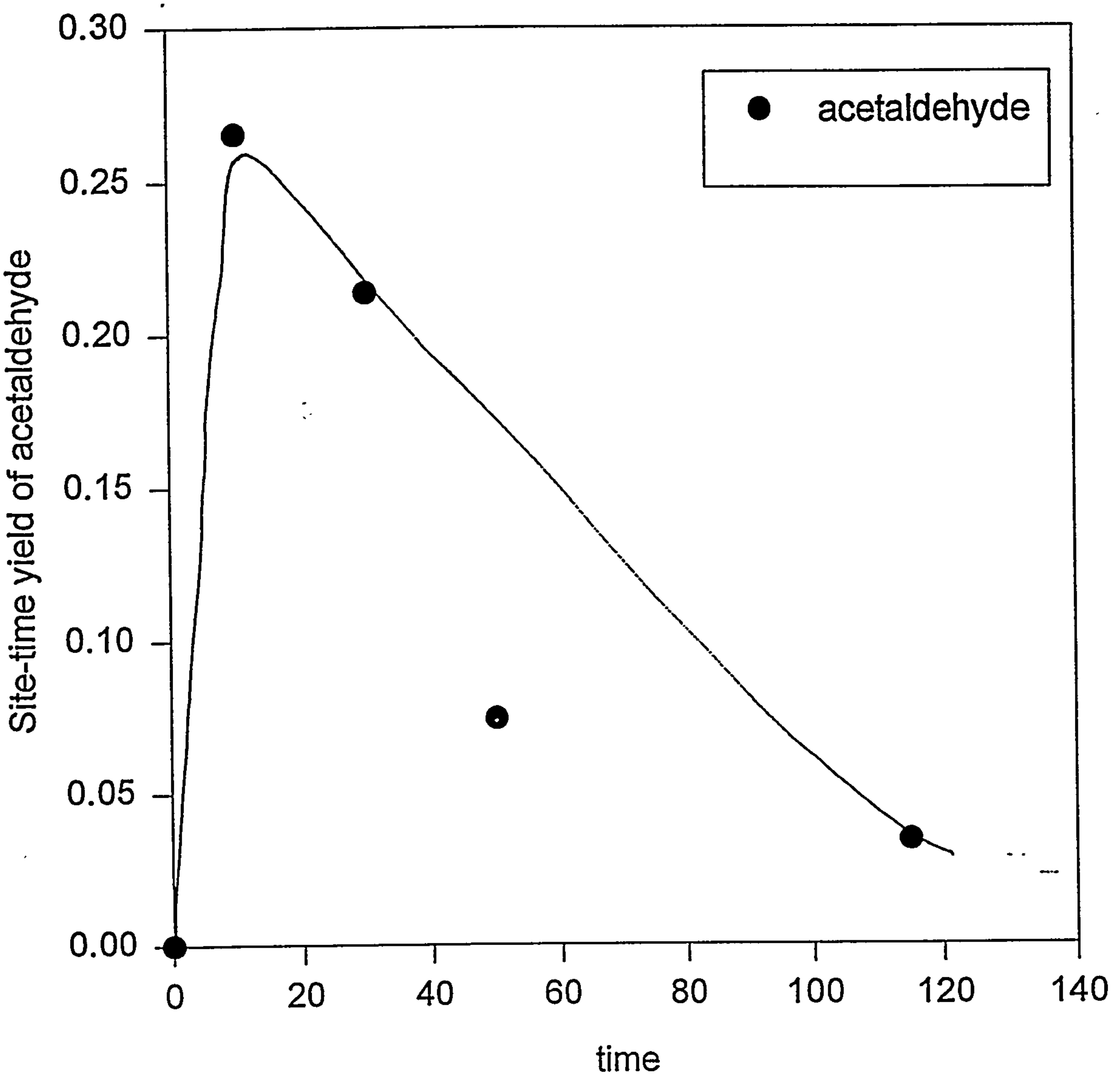
Reaction conditions: 250 C, 1 atm, 22 mg CuZnMn catalyst
Turnovers based on # of Cu atoms in sample

Fig. 9 Conversion vs time plot for CuZnMn catalyst for the alcohol coupling reaction.



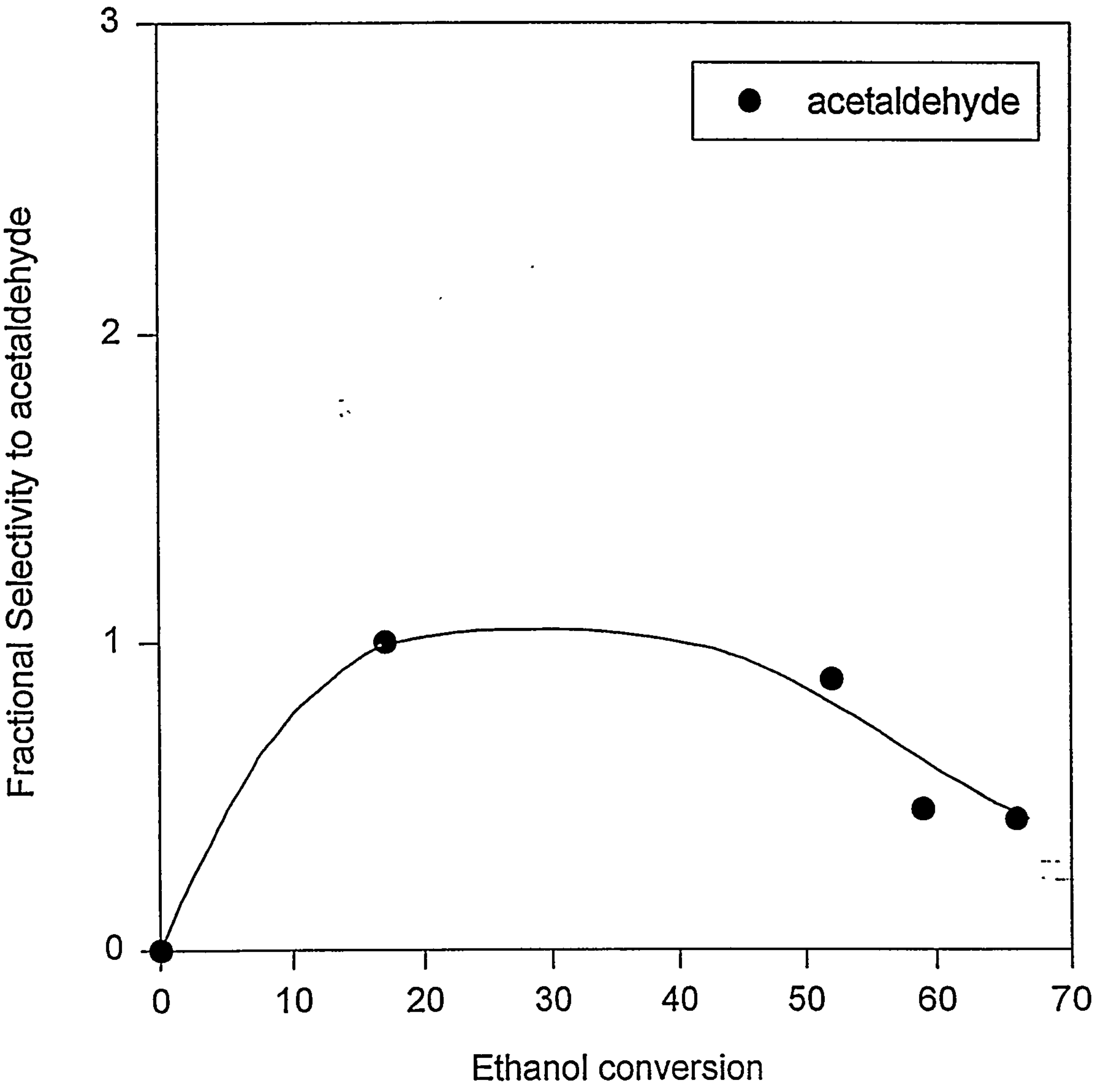
Reaction conditions: 250 C, 1 atm, 22 mg CuZnMn catalyst
Turnovers based on # of Cu atoms in sample

Fig. 10 Site-time yields vs time on CuZnMn catalyst for the alcohol coupling reaction.



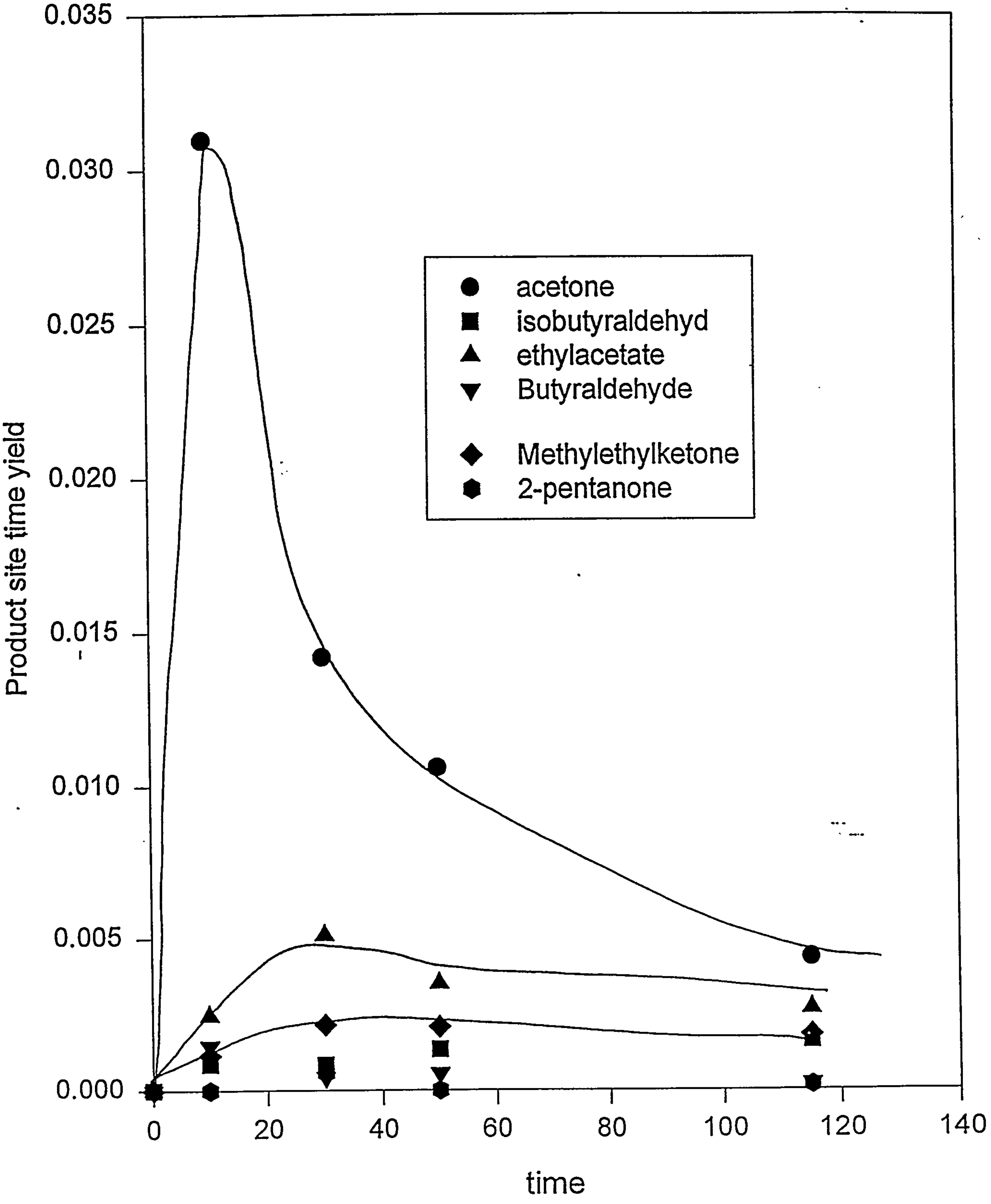
Reaction conditions: 250 C, 1 atm, 22 mg CuZnMn catalyst
Based on the number of Cu atoms in sample

Fig. 11 Selectivity-conversion plots for CuZnMn catalyst for the alcohol coupling reaction.



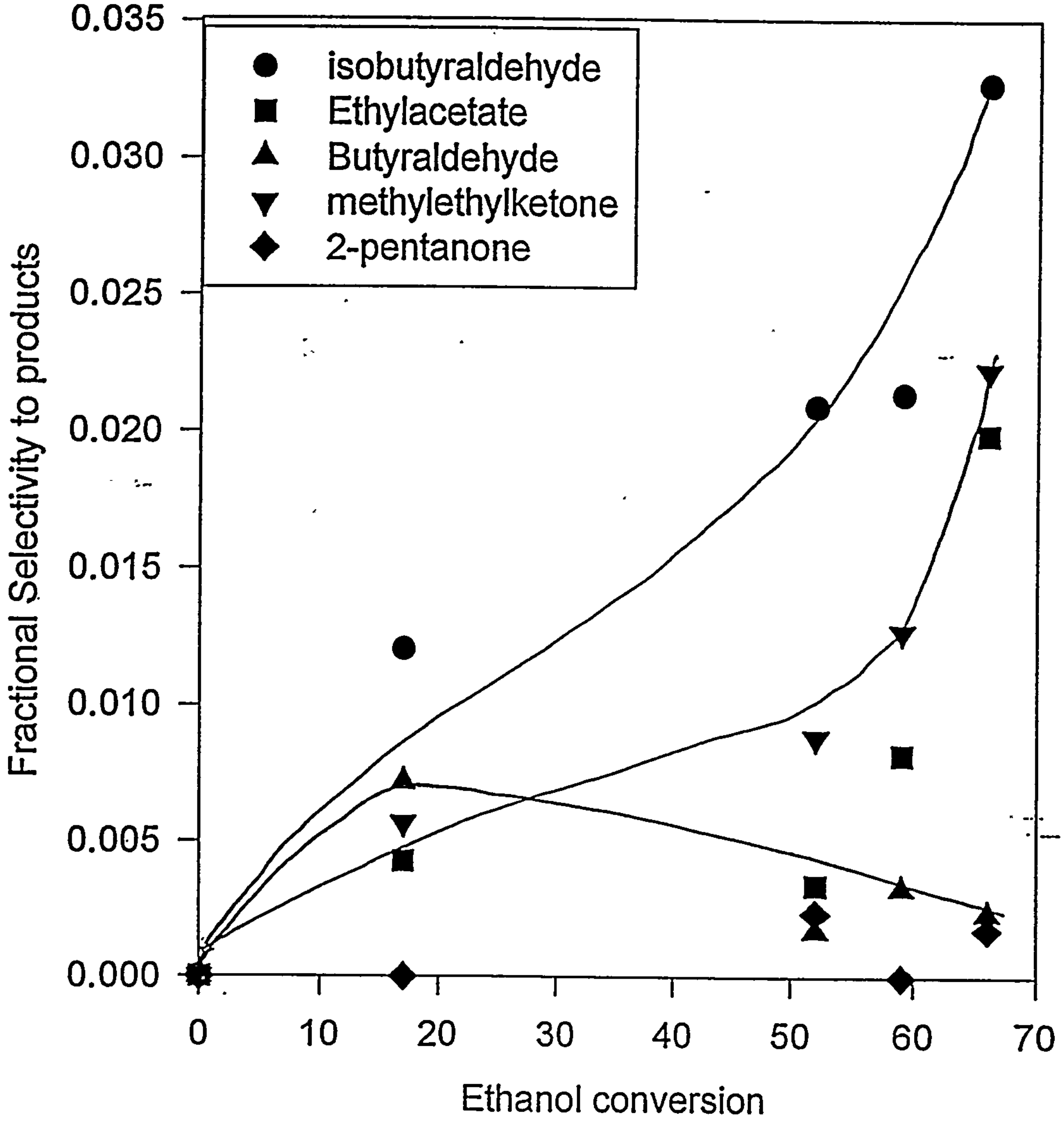
Reaction conditions: 250 C, 1 atm, 22 mg CuZnMn catalyst
Selectivity based on moles of methanol and ethanol converted

Fig. 12 Site-time yields vs time on CuZnMn catalyst for the alcohol coupling reaction.



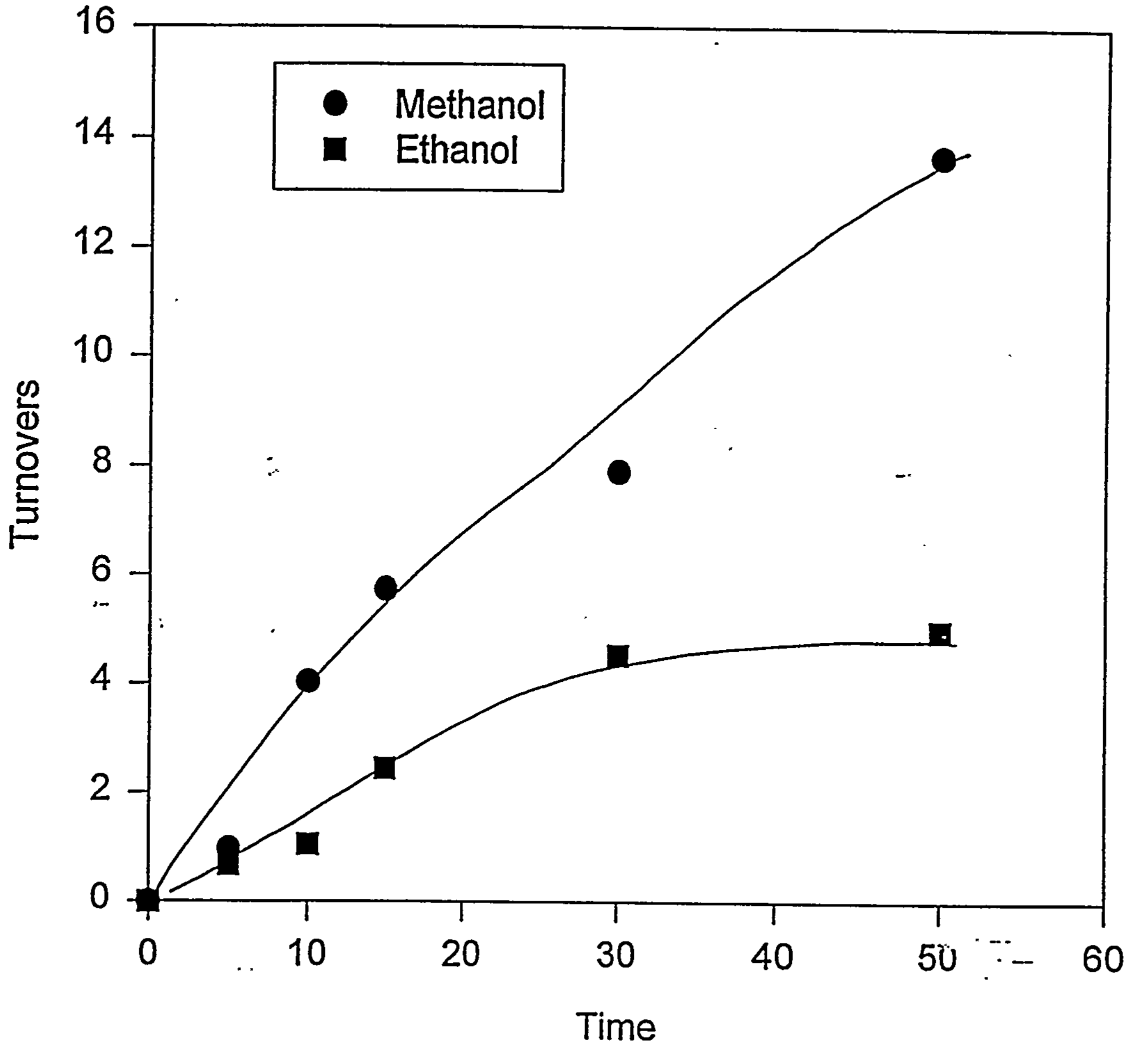
Reaction conditions: 250 C, 1 atm, 22 mg CuZnMn catalyst
Based on the number of Cu atoms in sample

Fig. 13 Selectivity-conversion plots for CuZnMn catalyst for the alcohol coupling reaction.



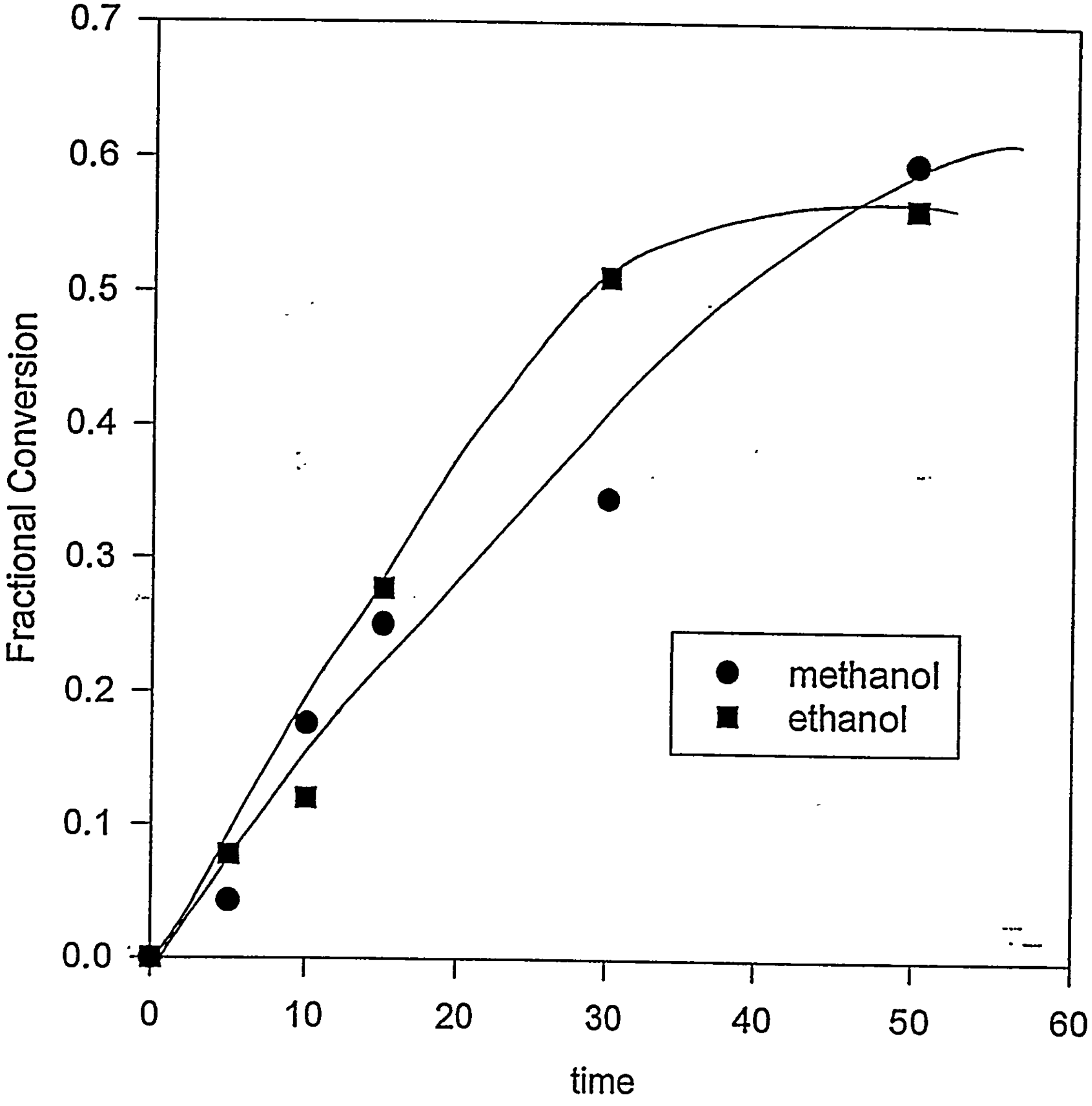
Reaction conditions: 250 C, 1 atm, 22 mg CuZnMn catalyst
Selectivity based on moles of methanol and ethanol converted

Fig. 14 Turnovers vs time on Cu/ZnO catalyst for the alcohol coupling reaction.



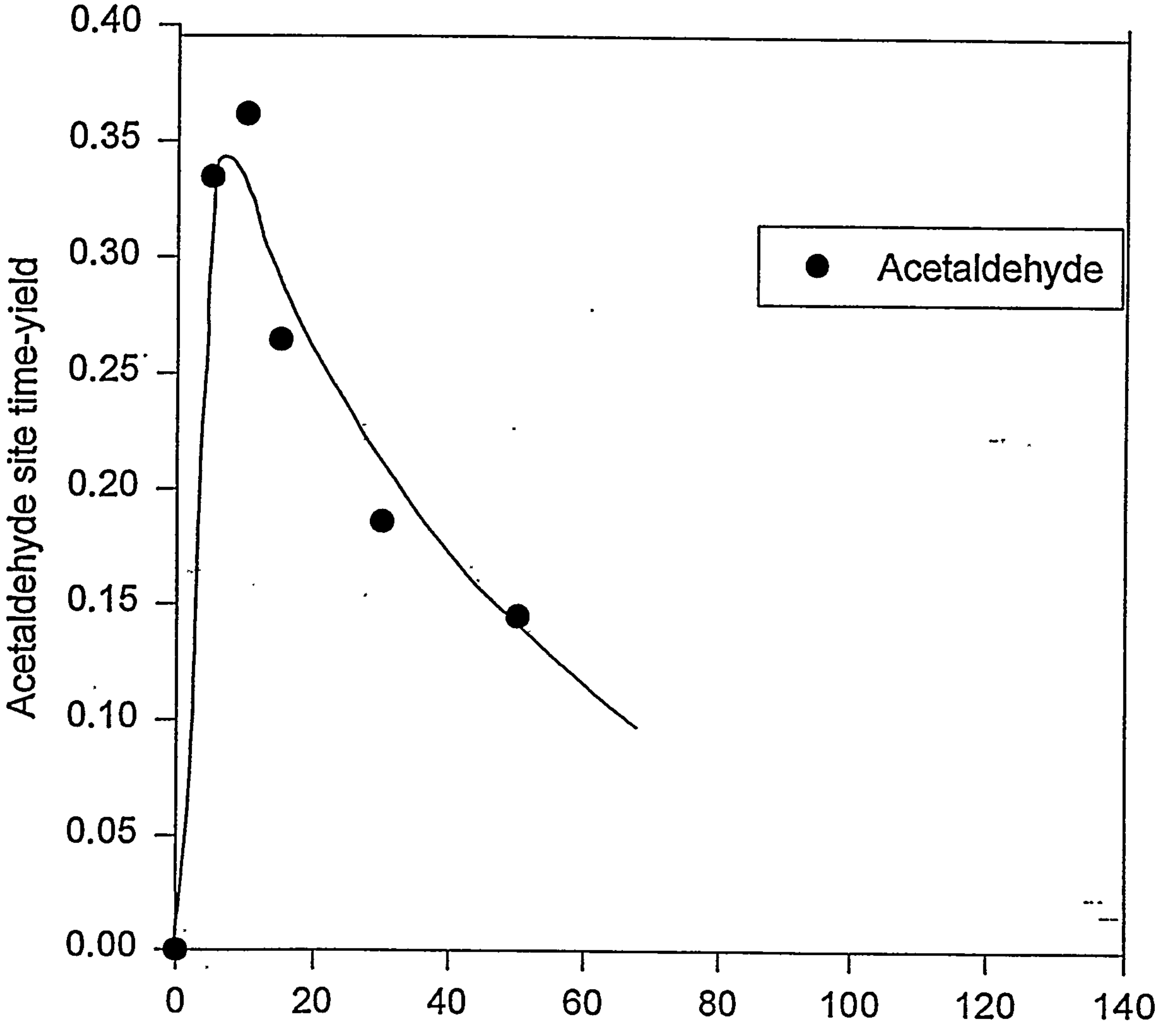
Reaction conditions: 250 C, 1 atm, 22 mg Cu/ZnO catalyst
Sites based on the number of Cu atoms.

Fig. 15 Conversion vs time on Cu/ZnO catalyst for the alcohol coupling reaction.



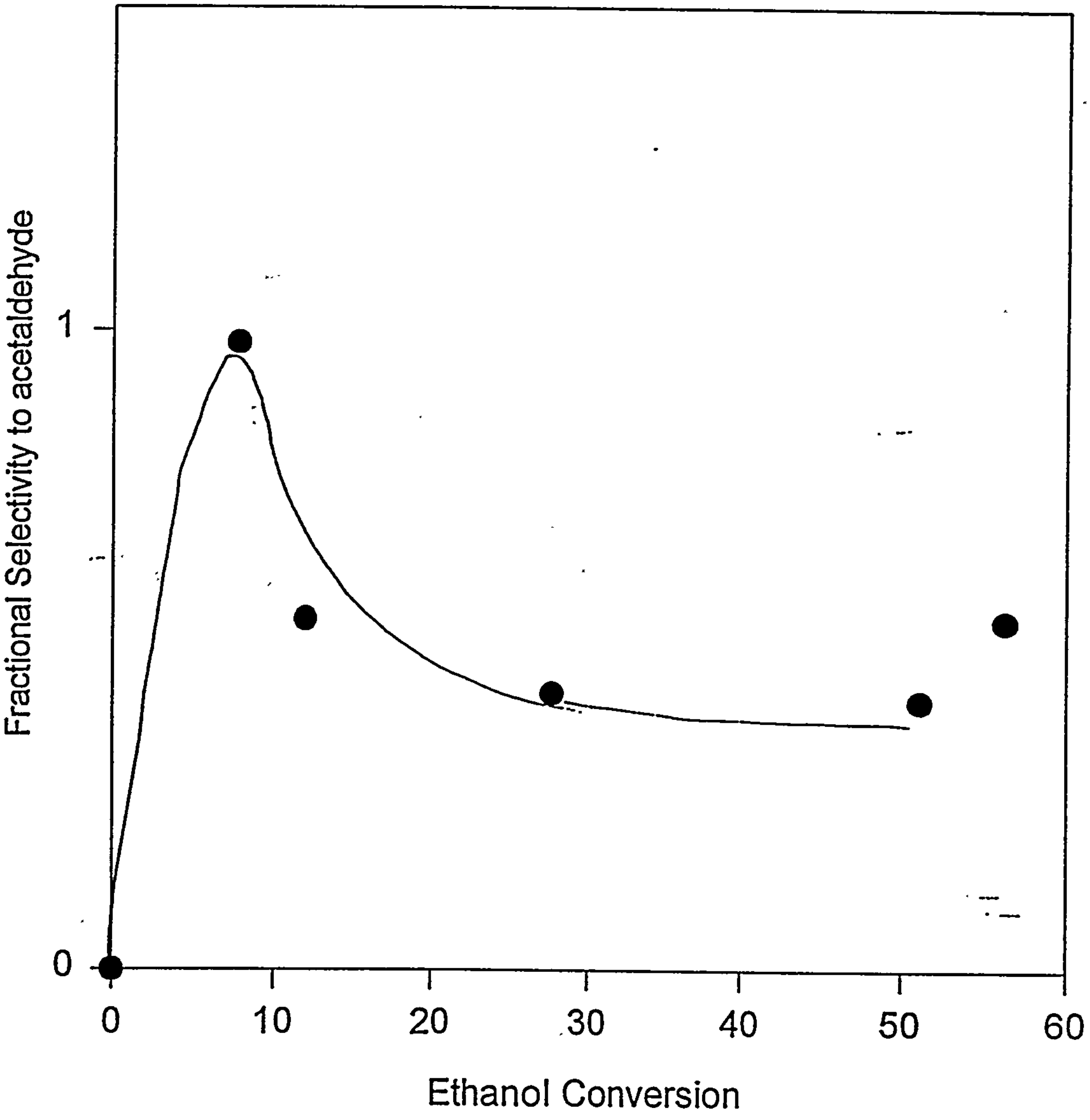
Reaction conditions: 250 C, 1 atm, 22 mg Cu/ZnO catalyst
Sites based on the number of Cu atoms in sample

Fig. 16 Site time yield vs time on Cu/ZnO catalyst for the alcohol coupling reaction.



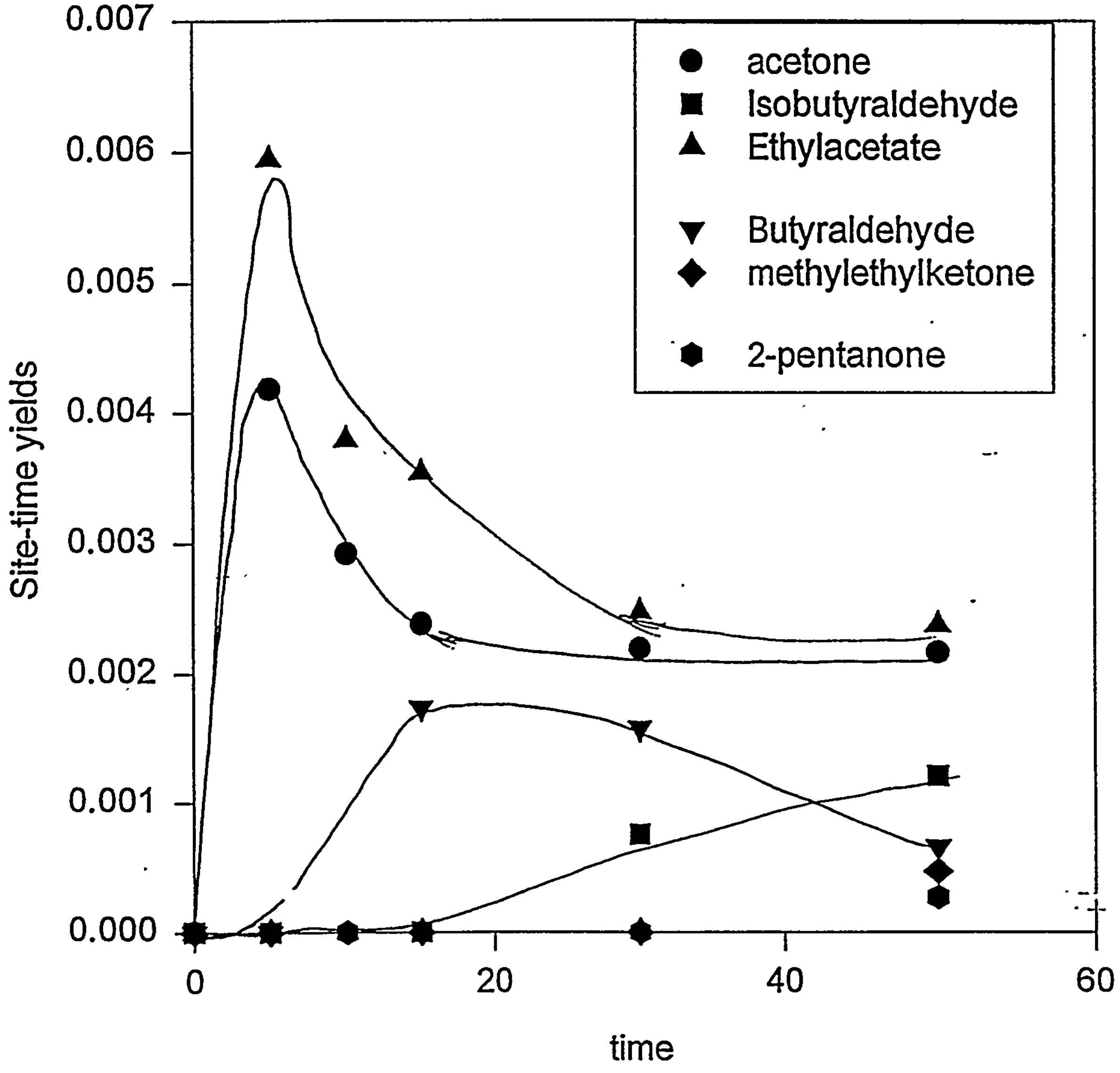
Reaction conditions: 250 C, 1 atm, 22 mg Cu/ZnO catalyst
Sites based on the number of Cu atoms in the sample

Fig. 17 Selectivity -conversion plots on Cu/ZnO catalyst for the alcohol coupling reaction.



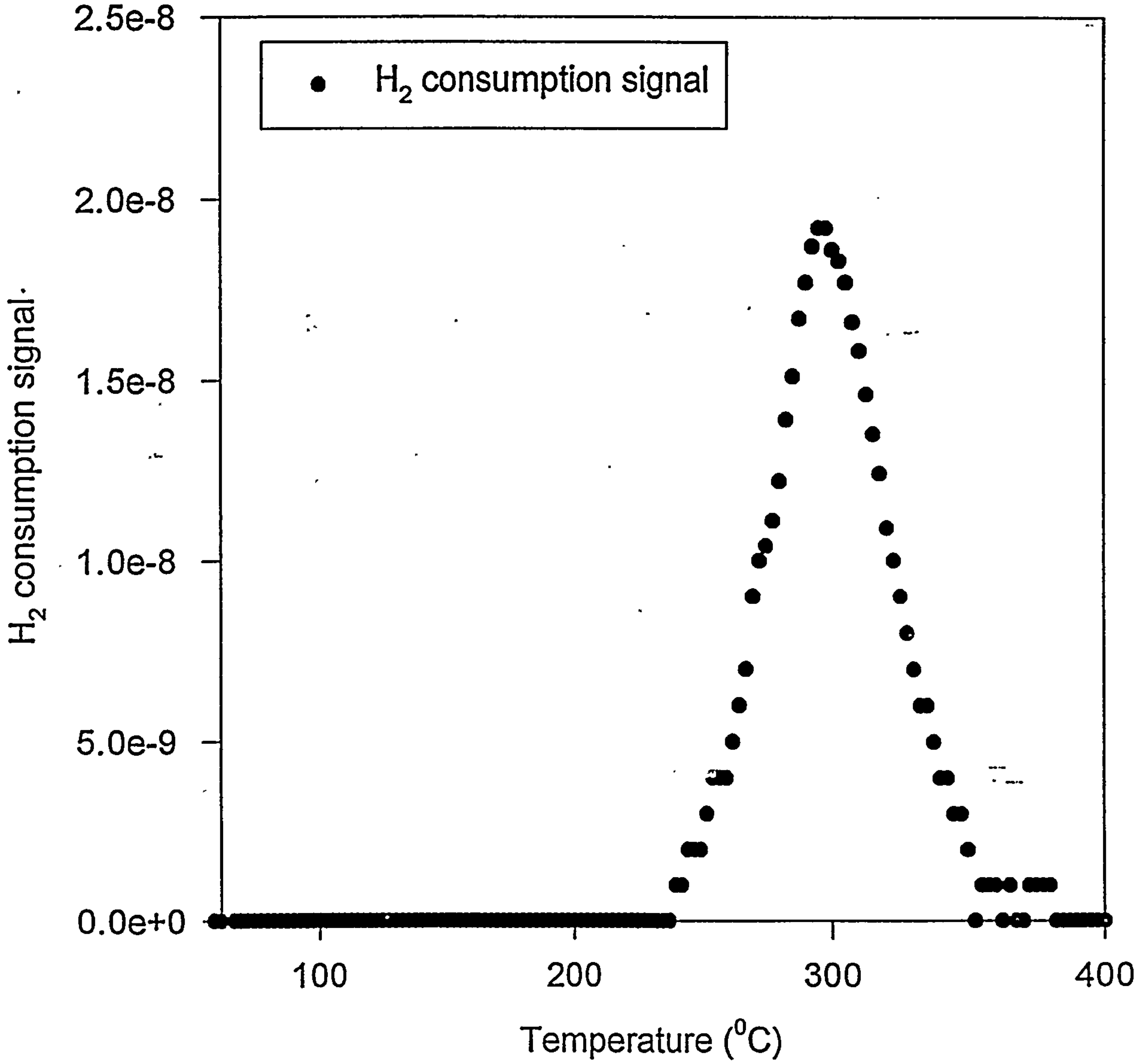
Reaction conditions: 250 C, 1 atm, 22 mg Cu/ZnO catalyst
Selectivity based on moles of ethanol+methanol converted.

Fig. 18 Site time yield vs time on Cu/ZnO catalyst for the alcohol coupling reaction.



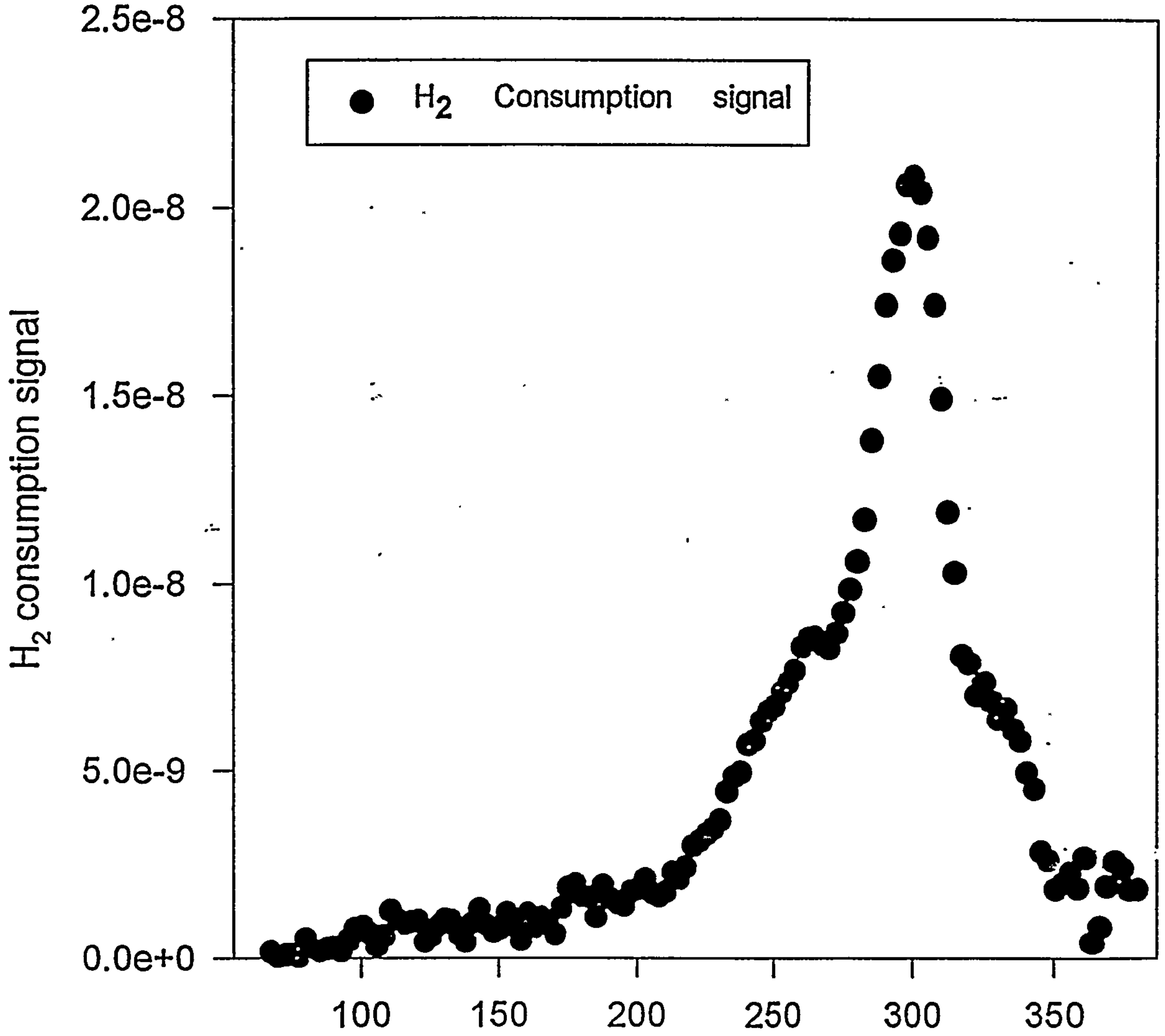
Reaction conditions: 250 C, 1 atm, 22 mg Cu/ZnO catalyst
Sites based on the number of Cu atoms in sample

Fig. 19 Temperature programmed reduction of CuO



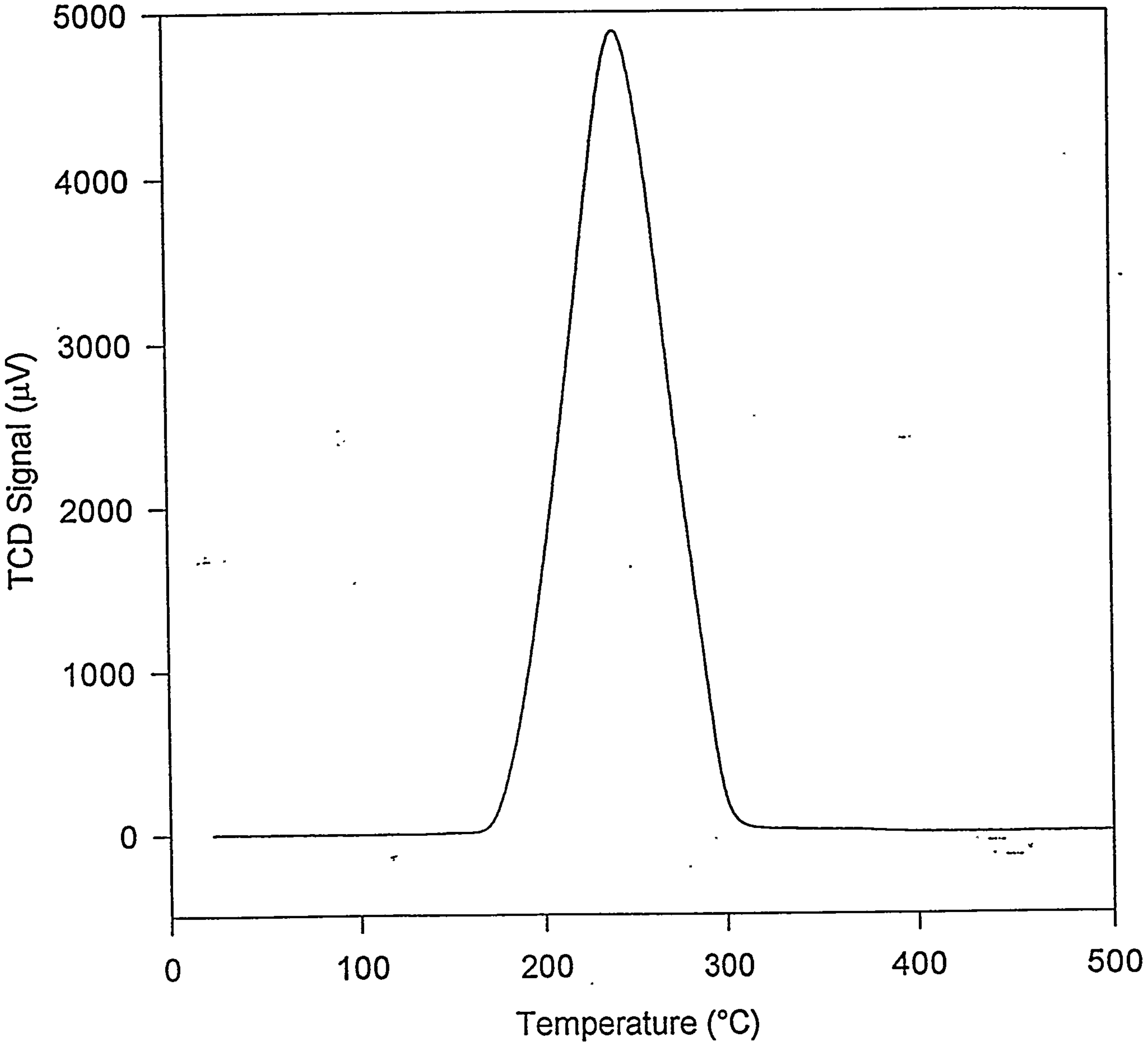
Temperature programmed reduction of CuO carried out in 4.6 mol% H_2 / He

Fig. 20 Temperature programmed reduction of Cs/Cu/ ZnO



Temperature programmed reduction of Cs/Cu/ ZnO carried out in 4.6 mol% H_2 / He

Fig. 21 Temperature programmed reduction of CuO in the Quantasorb apparatus.



The temperature programmed reduction was carried in 20% H_2/ He