

## EXECUTIVE SUMMARY

A series of MgO-based Cu catalysts have been prepared by coprecipitating the corresponding metal nitrates with a mixed solution of potassium carbonate and potassium hydroxide. The bulk composition of the catalyst has been measured by atomic absorption (AA) analysis and the Cu dispersion has been determined by  $N_2O$  titration at 363 K.

Kinetic studies of ethanol coupling reactions on  $Cu_{0.5}Mg_5CeO_x$  and 1.0 wt % K- $Cu_{0.5}Mg_5CeO_x$  catalyst indicates that at similar steady-state acetaldehyde concentrations, the presence of K increases the rates of base-catalyzed aldol coupling reactions to acetone and butyraldehyde. Aldol coupling chain growth reaction rates on 1.2 wt % K- $Cu_{7.5}Mg_5CeO_x$  are higher than on 1.0 wt % K- $Cu_{0.5}Mg_5CeO_x$  even though basic site densities are similar on both samples, suggesting that Cu metal sites are also involved in rate-determining steps required for condensation reactions. Cu appears to enhance the desorption of  $H_2$  via the migration of H species from basic to Cu sites and makes the basic sites available for subsequent C-H bond activation steps. Addition of  $CO_2$  decreases the rate of base-catalyzed chain growth reaction to acetone, but does not affect the rate of ethanol dehydrogenation reaction on Cu metal sites

High-pressure isobutanol synthesis from  $CO/H_2$  has been studied on 1 wt % K- $Cu_{0.5}Mg_5CeO_x$  catalysts at 593 K and 4.5 MPa. The catalyst deactivates continuously during the run, and CO conversion decreases from 12.5 % to 7.5 % after 140 h on stream. Methanol and isobutanol productivities decrease with the addition of 0.047 MPa of  $CO_2$  into  $CO/H_2$  feed. Methanol productivity recovers upon the removal of  $CO_2$  from the feed.  $CO_2$ , however, irreversibly inhibits isobutanol production. Addition of 1-propanol to  $CO/H_2$  feed increases isobutanol productivity on 1 wt % K- $Cu_{0.5}Mg_5CeO_x$  catalysts by an order of magnitude, suggesting that 1-propanol is the precursor to isobutanol.

The reduction behavior of a series of MgO-based Cu catalysts was investigated using temperature-programmed reduction. The presence of  $CeO_x$  decreases CuO reduction temperature, and the promoting effect of  $CeO_x$  on CuO reduction increases with increasing Ce/Mg ratio. In contrast to  $CeO_x$ , K addition to Cu-containing samples inhibits CuO reduction. The presence of  $K_2O$  in CuO may inhibit to some extent  $H_2$  activation and increase the bond strength of CuO and therefore retard CuO reduction.

The density and strength of available basic sites have been determined using a  $^{13}CO_2/^{12}CO_2$  isotopic exchange method. The number of available basic sites measured at different flow rate is similar; the slope of the transient curve, however, changes with flow rates due to the readsorption of  $^{13}CO_2$ . Mathematical treatment reveals that the curve slope is a function of both exchange rate constant and gas residence time.

The manuscript "*Isobutanol and Methanol Synthesis on Copper Catalysts Supported on Modified Magnesium Oxide*" has been submitted to the Journal of Catalysis for publication. A manuscript titled "*Isotopic Switch Methods for the Characterization of Basic Sites in Modified MgO Catalysts*" is in the final draft and will be submitted for publication during the next 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-to-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:

- Preparation of a series of K-Cu/MgO/CeO<sub>2</sub>, CuCoMgCeO<sub>x</sub>, CuZnAlO<sub>x</sub>, and CuMgAlO<sub>x</sub> catalysts
- Kinetic studies of ethanol and acetaldehyde coupling reactions on K-Cu/MgO/CeO<sub>2</sub>
- Investigation of the reduction behavior of MgO-based Cu catalysts
- Studies of the effect of total flow rate on the determination of basic site density and strength at reaction temperatures using <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> switch methods
- Evaluation of high-pressure isobutanol synthesis reactions on K-CuMg<sub>5</sub>CeO<sub>x</sub> catalysts

### 3. STATUS, ACCOMPLISHMENTS, AND RESULTS

#### *Task 1: Management Plan*

No activities were carried out during this reporting period.

#### *Task 2: Catalyst Synthesis*

CuZnAlO<sub>x</sub> (MG4-2 O) and Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-13 O) prepared in previous reporting periods were impregnated with Cs and K, respectively. These materials were prepared to verify the reproducibility in catalyst preparation and to provide large amounts of samples for CO<sub>2</sub> and alcohol addition and isotopic tracer studies in CMRU. The precursor (MG3-15 P) of Cu/Mg/Al samples provided by Dr. Carlos Apesteguia (UNL, Argentina) was calcined at 723 K for 4 h to obtain the mixed oxide (MG3-15 O). K- and Cs-promoted CuMgAlO<sub>x</sub> catalysts were prepared by incipient wetness of the oxidized samples using K<sub>2</sub>CO<sub>3</sub> (0.25 M) and CH<sub>3</sub>COOCs (0.25 M) aqueous solutions (K<sub>2</sub>CO<sub>3</sub>: Fisher Scientific, A.C.S. certified; CH<sub>3</sub>COOCs: Stream Chemicals, 99.9%). Catalyst properties are summarized in *Table 1*.

**Table 1.** Composition and surface areas of metal oxides.

Sample	Nominal composition	Alkali (wt.%)	
		AAS	S.A. (m <sup>2</sup> /g)
MG 4 - 2 O/Cs	1.2 wt % Cs-CuZnAlO <sub>x</sub>	1.25	74
MG 3 - 13 O/K	1.0 wt % K-Cu <sub>0.5</sub> Mg <sub>5</sub> CeO <sub>x</sub>	1.03	150
MG 3 - 15 O	Cu <sub>0.5</sub> Mg <sub>5</sub> Al <sub>10</sub> O <sub>x</sub>	0.05	327
MG 3 - 15 O/K	1.0 wt % K-Cu <sub>0.5</sub> Mg <sub>5</sub> Al <sub>10</sub> O <sub>x</sub>	1.15	264
MG 3 - 15 O/Cs	3.4 wt % K-Cu <sub>0.5</sub> Mg <sub>5</sub> Al <sub>10</sub> O <sub>x</sub>	2.88	258

Based on the catalyst composition reported by Keim [1] and more recently by Dombeck [2] for higher alcohol synthesis from CO and H<sub>2</sub>, new catalytic materials containing Pd were prepared by incorporating Pd into the modified MgO catalysts (K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> and K(Cs)-Mg<sub>5</sub>CeO<sub>x</sub>) in order to increase total alcohols and isobutanol productivities and isobutanol/methanol ratio. These samples will be tested in CMRU in the next reporting period.

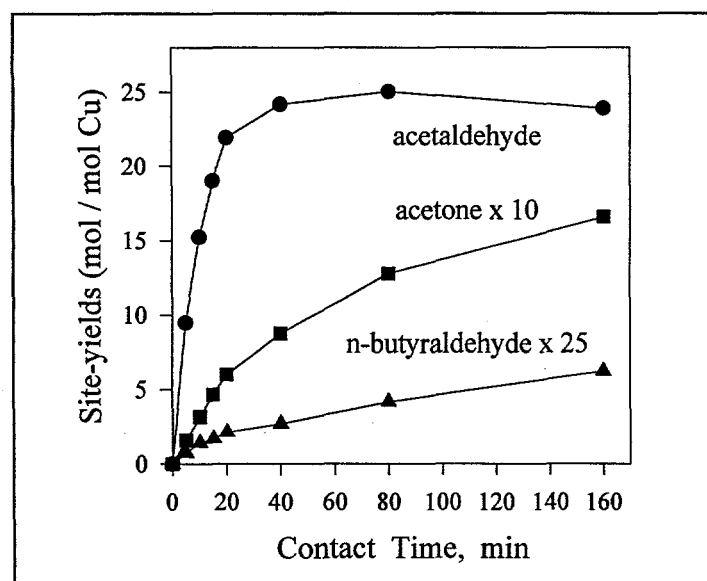
#### *Task 3: Catalyst Evaluation in Laboratory Scale Reactors*

##### *3.1. Kinetic Studies of Alcohol Coupling Reactions*

Dehydrogenation and condensation reactions of ethanol were investigated on Mg<sub>5</sub>CeO<sub>x</sub> (MG3-7 O), Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-11 Ow), 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-11 Ow/K), and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-6 Ow/K) in order to address the role of each individual catalyst component in chain growth reactions. The experiment was carried out in a gradientless

recirculating reactor unit (RRU). The catalyst (19.0 mg) was first reduced in H<sub>2</sub> (10 % H<sub>2</sub>/He) at 623 K for 0.5 h. The temperature was lowered to 573 K and ethanol was introduced along with a small amount of methane, used as an unreactive internal standard (reaction mixture: C<sub>2</sub>H<sub>5</sub>OH/CH<sub>4</sub>/He = 4.0/2.7/94.6 kPa; C<sub>2</sub>H<sub>5</sub>OH: Fisher Scientific, A.C.S. certified; CH<sub>4</sub>: Matheson, ultra high purity). Products were sampled by syringe extraction from the recirculating stream at different contact times, and injected into a gas chromatograph equipped with flame ionization and thermal conductivity detectors. Mass spectrometry after chromatographic separation was used to confirm the identity of each reaction product.

Acetaldehyde was the initial product of reactions of pure ethanol on 1 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (Figure 1). Dehydrogenation reactions occur much faster than the chain growth reactions to acetone, n-butyraldehyde, and other oxygenates. Acetaldehyde reaches a maximum concentration at intermediate contact times during ethanol reactions and then decreases gradually, suggesting that acetaldehyde is involved in subsequent chain growth reactions or reaches the equilibrium and is converted back to ethanol. Acetone and n-butyraldehyde were the predominant condensation products. The non-zero initial slopes of acetone and n-butyraldehyde curves are not expected for products formed through consecutive reactions. Therefore, acetone and n-butyraldehyde are formed either by ethanol condensation or by acetaldehyde condensation with zero-order kinetics. Methyl-ethyl ketone (by acetaldehyde condensation with oxygen retention reversal [3, 4], 2-pentanone (by acetaldehyde-acetone condensation), and ethyl acetate (by ethanol-acetaldehyde) were detected among reaction products in much smaller concentrations.



**Figure 1.** Site yields as a function of contact time on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> in ethanol reactions. [ 573 K, 101.3 kPa total pressure, 4.0 kPa ethanol, balance He].

Reaction pathways involved in the formation of all detected products are shown in Figure 2. Acetaldehyde is formed via ethanol dehydrogenation (step I) and undergoes subsequent condensation reactions (steps II-XII). The self-condensation of acetaldehyde by an aldol-type condensation produces n-butyraldehyde (steps II-IV) and methyl-ethyl ketone (steps

II-V) [3]. The aldol species is converted to the keto form via H transfer (step VI). The dehydration-dehydrogenation reactions of the keto form (step VII) lead to methyl-ethyl ketone. Acetone is formed via two pathways: by reaction of aldol intermediates with surface oxygen followed by decarboxylation (steps VIII-IX) and by reverse aldol condensation of the keto form (step X). Formaldehyde formed in the latter reaction decomposes rapidly to CO and H<sub>2</sub>. 2-Pentanone is formed by condensation of aldol-type intermediates formed in acetone-acetaldehyde self condensation reactions (steps XI-XII). Ethylacetate forms via the reaction of ethanol and acetaldehyde (step XIII) [3].

The rates of ethanol conversion and acetaldehyde, n-butyraldehyde, and acetone formation were measured and the results are summarized in *Table 2*. Initial reaction rates were obtained from the slopes of site-yield plots at short contact times using total surface area, MgCeO<sub>x</sub> surface area (estimated from the difference between the total and the copper surface area), and Cu metal surface area of each sample.

**Table 2.** Effects of Cu- and K-loading on Ethanol Consumption and Product formation on Mg<sub>5</sub>CeO<sub>x</sub>.

wt. % Cu	wt. % K	Ethanol dehydrogenation		Formation rates of			
		areal rate ( <sup>1</sup> )r <sub>1</sub>	Turnover rate ( <sup>2</sup> )r <sub>1</sub>	Acetone ( <sup>3</sup> )r <sub>2</sub>	( <sup>4</sup> )r <sub>2</sub>	Butyraldehyde ( <sup>3</sup> )r <sub>3</sub>	( <sup>4</sup> )r <sub>3</sub>
0	0	1.3 x 10 <sup>-8</sup>	/	6.2 x 10 <sup>-11</sup>	6.5 x 10 <sup>-5</sup>	( <sup>5</sup> )	( <sup>5</sup> )
7	0.1	3.6 x 10 <sup>-7</sup>	0.24	3.0 x 10 <sup>-9</sup>	2.2 x 10 <sup>-3</sup>	4.5 x 10 <sup>-10</sup>	3.4 x 10 <sup>-4</sup>
7	1.0	2.4 x 10 <sup>-7</sup>	0.23	4.3 x 10 <sup>-9</sup>	1.8 x 10 <sup>-3</sup>	7.6 x 10 <sup>-10</sup>	3.2 x 10 <sup>-4</sup>
49	1.2	9.4 x 10 <sup>-7</sup>	0.24	4.4 x 10 <sup>-8</sup>	1.0 x 10 <sup>-2</sup>	1.2 x 10 <sup>-9</sup>	2.8 x 10 <sup>-4</sup>

(<sup>1</sup>) r<sub>1</sub> is the rate of ethanol consumption, and is expressed in mol/m<sup>2</sup> total · s.

(<sup>2</sup>) Turnover rates per Cu surface atom, and is expressed in s<sup>-1</sup>.

(<sup>3</sup>) r<sub>2</sub> and r<sub>3</sub> are the rates of product formation, and are expressed in mol/m<sup>2</sup> MgCeO<sub>x</sub> · s.

(<sup>4</sup>) Turnover rates per accessible basic site from <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> measurements and is expressed in mol/mol CO<sub>2</sub> exchange·s.

(<sup>5</sup>) Not detected.

Ethanol dehydrogenation rates were much higher on Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> catalysts than on Mg<sub>5</sub>CeO<sub>x</sub>, suggesting the involvement of Cu metal sites in the dehydrogenation of ethanol to acetaldehyde. The presence of K decreased areal ethanol dehydrogenation rates because of a concomitant decrease in Cu dispersion (4Q, FY1996). Ethanol dehydrogenation turnover rates (normalized by exposed Cu atoms) on Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> catalysts were 0.24, 0.23, and 0.24 s<sup>-1</sup>, respectively. Thus, ethanol dehydrogenation occurs predominantly on exposed Cu atoms, which become inaccessible for both N<sub>2</sub>O decomposition and alcohol dehydrogenation by blocking with K species. Dehydrogenation turnover rates were not affected by Cu crystallite size or by the titration of Cu surface atoms with K.

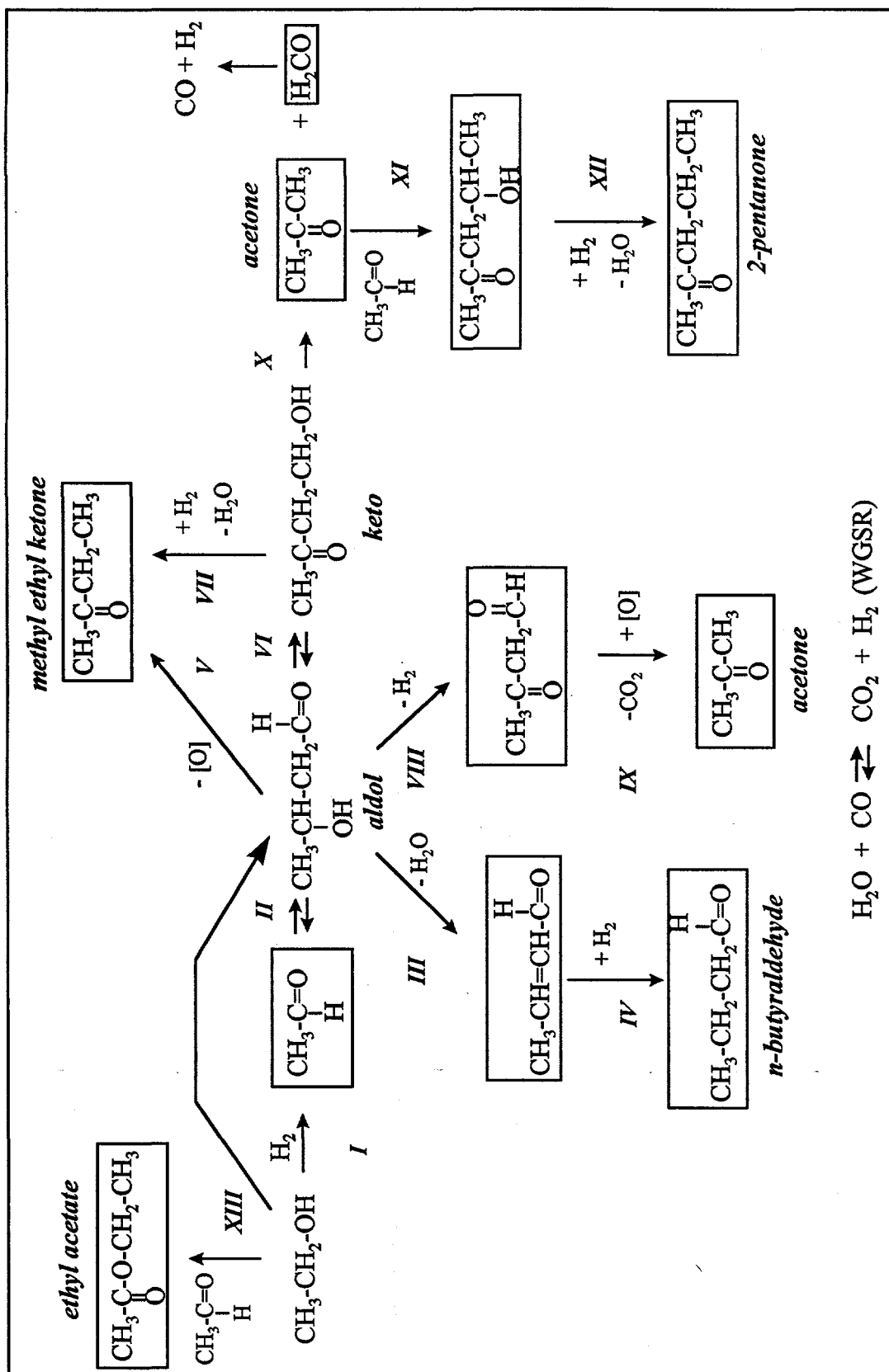
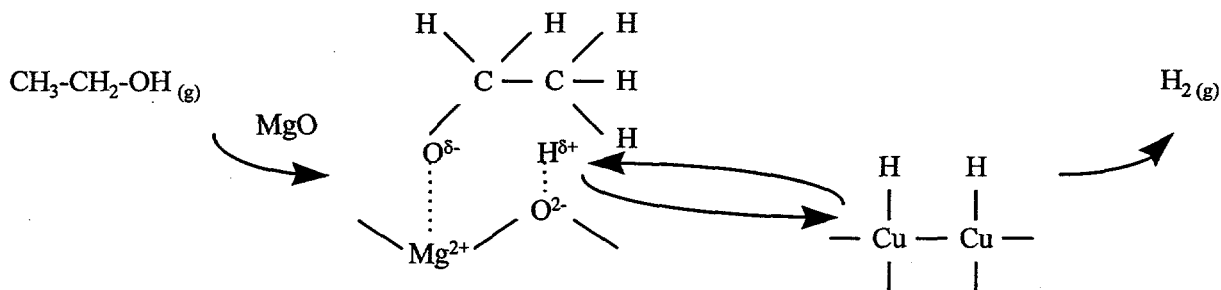


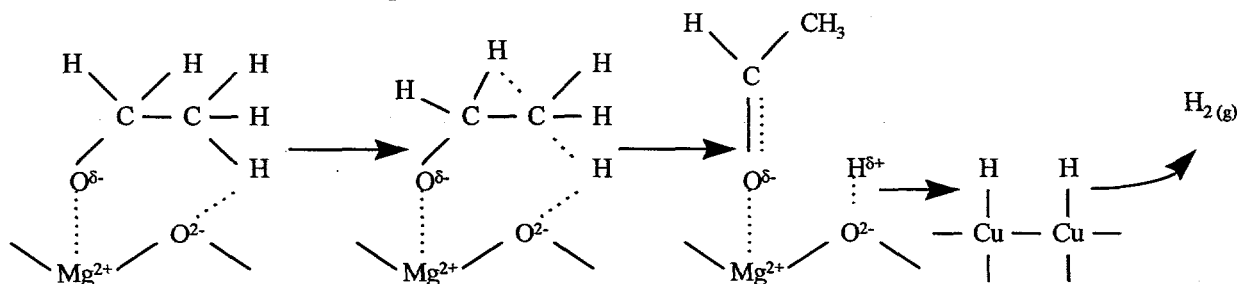
Figure 2. Reaction scheme for ethanol reactions.

Aldol coupling chain growth rates are lower on  $\text{Mg}_5\text{CeO}_x$  than on  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  because of the lower acetaldehyde in the former. At similar steady-state acetaldehyde concentrations on  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  and 1.0 wt %  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  catalysts, the presence of K increases the rates of base-catalyzed aldol coupling reactions to acetone and butyraldehyde (Table 2). Thus, it appears that the higher basic site density and strength measured by  $^{13}\text{CO}_2/^{12}\text{CO}_2$  isotopic switch measurements lead to higher rates of aldol condensation reactions. The rates of base-catalyzed aldol coupling reactions, when normalized by the number of accessible basic sites, are similar on  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  ( $2.2 \times 10^{-3} \text{ s}^{-1}$ ) and  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  ( $1.8 \times 10^{-3} \text{ s}^{-1}$ ). Aldol coupling chain growth reaction rates on 1.2 wt %  $\text{K-Cu}_{7.5}\text{Mg}_5\text{CeO}_x$  (49 wt % Cu, 0.047 Cu dispersion) are, however, much higher than on  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ , even though basic site densities are similar on both samples. The difference in chain growth rates indicates that Cu metal sites are involved in rate-determining steps required for condensation reactions. This is confirmed by the lower aldol coupling reaction rates observed on Cu-free catalysts, which are caused not only by the lower concentrations of required acetaldehyde intermediates but also by the absence of Cu sites required in condensation steps.

The role of copper suggests a bifunctional mechanism for aldol condensation. Ethanol adsorbs dissociatively on MgO surface to form ethoxide and hydrogen species. Hydrogen species are removed by migration to Cu sites, reaction with another H species, and desorption as  $\text{H}_2$ :

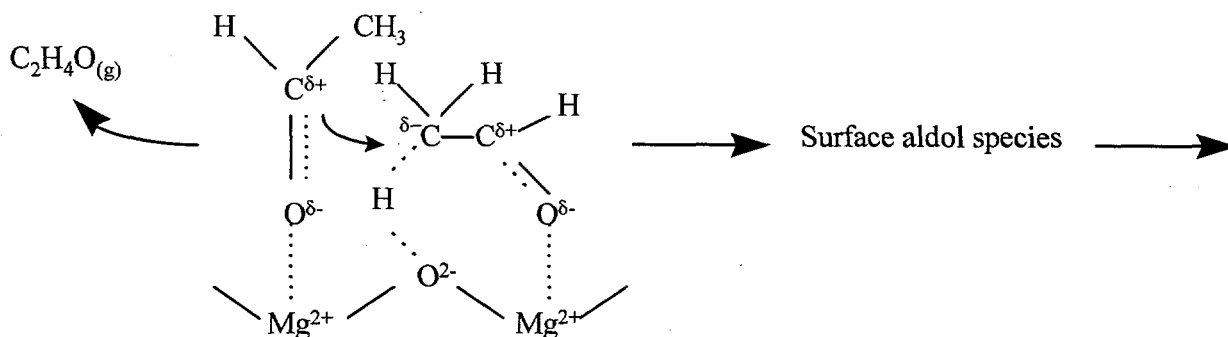


The ethoxide species then loses a  $\beta$ -H via intermolecular hydrogen transfer to oxygen ions and forms surface acetaldehydic species:



H species migrate from basic to Cu sites and recombine on Cu sites to form  $\text{H}_2$ ; as a result, basic sites become available for another turnover. H-H recombination rates increase with increasing ratio of surface Cu atoms to basic sites, which is reflected in the ratio of Cu surface area to oxide surface area on  $\text{K-Cu}_{7.5}\text{Mg}_5\text{CeO}_x$  (0.31) and  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  (0.07) at similar basic site density. The high Cu-to-oxide surface area ratio on  $\text{K-Cu}_{7.5}\text{Mg}_5\text{CeO}_x$  (0.31) leads to higher

aldol-condensation rates. Adsorbed acetaldehyde species can either desorb as acetaldehyde or react with other surface species to form aldol condensation products:

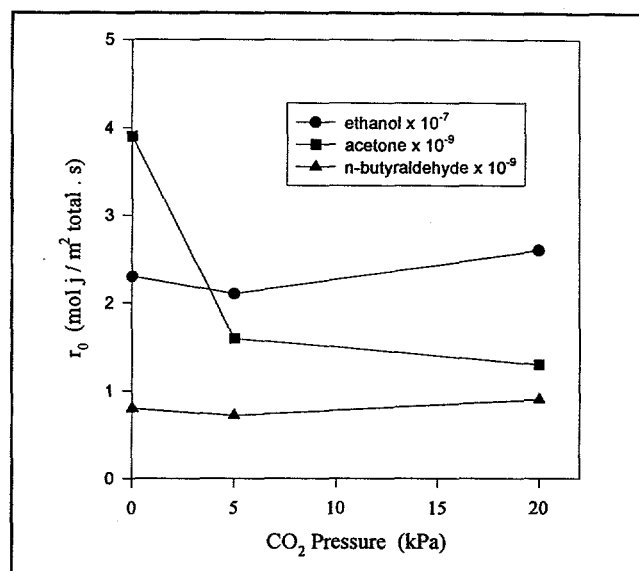


Surface aldol species can undergo further reactions via the pathways shown in *Figure 2*. In these reactions, the presence of copper sites enhances H mobility and provides H species for the hydrogenation of unsaturated species (steps IV, VII, and XII, *Figure 2*). It should be pointed out that the rates of the final products formed through consecutive reactions should have zero initial slopes, unless the formation of the product has a zero-order kinetics. The non-zero initial slopes of acetone and n-butyraldehyde curves (*Figure 1*) would be explained by the mechanism proposed above because it provides a pathway for direct conversion of ethanol to condensation products without the requirement for gas phase acetaldehyde.

The effect of  $\text{CO}_2$  on ethanol dehydrogenation and coupling reactions was examined on a 1.0 wt %  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  catalyst (19 mg) by adding  $\text{CO}_2$  (3.5 kPa and 20.0 kPa) to ethanol/ $\text{H}_2$  (4.0/29.3 kPa) reactant mixtures in a gradientless batch reactor. The results are shown in *Figure 3*. Ethanol dehydrogenation reaction rates do not change with increasing  $\text{CO}_2$  pressure, suggesting that Cu sites were not inhibited by  $\text{CO}_2$ . Also,  $\text{CO}_2$  does not affect the rate of n-butyraldehyde formation. These data are not consistent with the observed decrease in methanol and isobutanol synthesis rates as  $\text{CO}_2$  is added to  $\text{CO}/\text{H}_2$  feeds in CMRU. It appears that the higher  $\text{CO}_2$  pressures under typical isobutanol synthesis conditions reduces the number of Cu sites required for alcohol synthesis. On catalyst compositions leading to selective methanol synthesis i.e.,  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ , the presence of  $\text{CO}_2$  in modest concentrations (1-2 % mol) actually increases methanol synthesis rates [3]; higher  $\text{CO}_2$  concentrations (>10% mol), however, lead to the oxidation of surface Cu atoms and consequently to the inhibition of methanol synthesis [3]. The strong inhibition effect of  $\text{CO}_2$  on methanol synthesis rates has been reported for catalysts containing Cu and Ce [6]. Competitive adsorption between  $\text{CO}_2$  and aldehyde on basic sites may account for the observed inhibition of condensation reactions on 1.0 wt %  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  catalysts under high pressure isobutanol synthesis conditions. The ratio of  $\text{CO}_2$  and aldehydic intermediates is much higher under the high-pressure isobutanol synthesis conditions than in low-pressure ethanol reaction experiments, because of the lower aldehyde/alcohol ratio at higher  $\text{H}_2$  pressure in the former.  $\text{CO}_2$  competition for basic sites, therefore, is not favorable and aldol coupling reactions are not influenced strongly by  $\text{CO}_2$  in the former. The rate of acetone formation, however, decreased when  $\text{CO}_2$  was present during ethanol reactions.  $\text{CO}_2$  inhibition effect on acetone production could be a result of several factors: 1) the presence of  $\text{CO}_2$  reverses the reaction step that forms acetone and  $\text{CO}_2$  (steps IX



and X, Fig. 9), or 2) acetone is produced following a different parallel reaction path using stronger basic sites which are inhibited by CO<sub>2</sub>.



**Figure 3.** Rates of ethanol consumption and product formation as a function of CO<sub>2</sub> initial pressure on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>. [573 K, 101.3 kPa total pressure, 4.0 kPa ethanol, 26.7 kPa dihydrogen, balance He].

Condensation and hydrogenation reactions of acetaldehyde were investigated on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-11 Ow/K) and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-6 Ow/K) in a gradientless recirculating reactor unit (RRU). These experiments were performed in order to determine whether Cu sites are required for acetaldehyde reactions, as proposed previously for ethanol reactions.

Catalytic activity and product yields for acetaldehyde reactions on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> are shown in *Figure 4*. Acetone and crotonaldehyde are the predominant condensation products. Carbon dioxide, n-butyraldehyde, methyl propenyl ketone, and 2-pentanone were also detected in small concentrations among reaction products. Ethanol was the product of acetaldehyde hydrogenation. An aldol-type self-condensation of acetaldehyde produced crotonaldehyde, some of which is hydrogenated to n-butyraldehyde. Acetaldehyde may also polymerize to yield dimer and trimer compounds, which remained on the catalyst surface and led to poor mass balances (<50 %). Reaction pathways involved in the formation of the all observed products are shown in *Figure 5*.

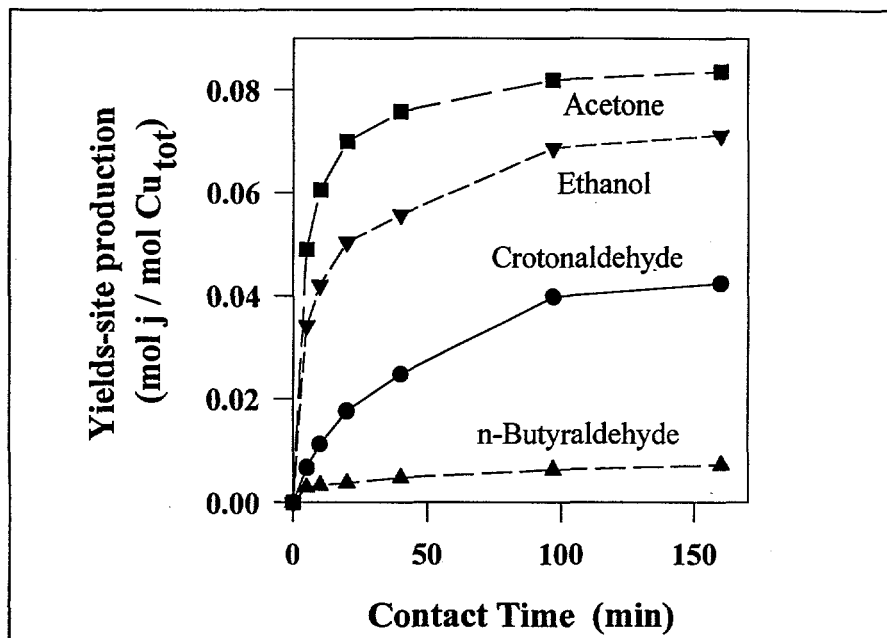


Figure 4. Acetaldehyde reactions. Site yields as a function of contact time on 1.2 wt. % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>. [573 K, 101.3 kPa total pressure, 7.0 kPa acetaldehyde, balance He].

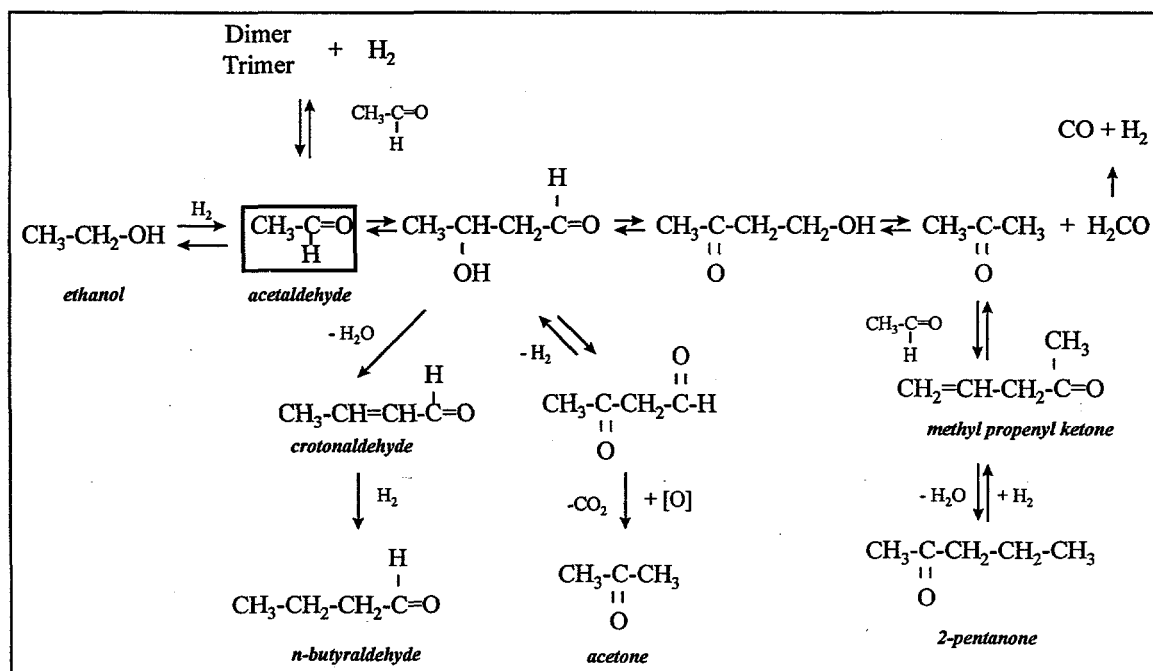
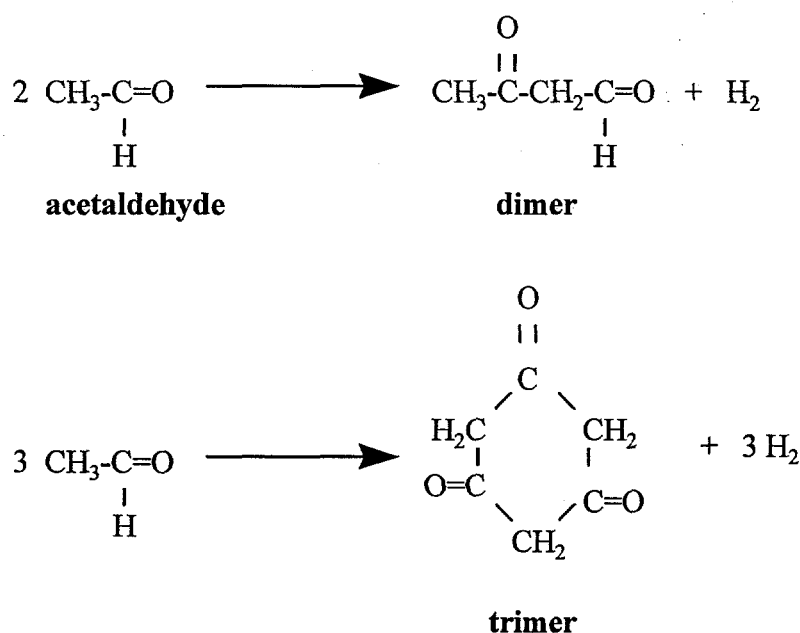


Figure 5. Reaction scheme for acetaldehyde reactions.

Hydrogenation products such as ethanol and n-butyraldehyde were formed by using H<sub>2</sub> generated in acetaldehyde polymerization reactions:



The initial reaction rates for acetaldehyde consumption and product formation on the low- and high-Cu catalysts are listed in *Table 3*. The rates of acetaldehyde consumption and acetone formation are higher on high Cu catalysts than on low Cu catalysts. Since the basicity of these two samples is comparable acetaldehyde reaction rate increases with increasing Cu loading possibly due to the enhancement of H mobility by Cu sites. The lower turnover rates of ethanol formation on high Cu catalysts may be caused by the limited supply of H atoms from acetaldehyde polymerization reactions.

**Table 3.** Effects of Cu on the rates of acetaldehyde consumption and product formation on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>.

wt % Cu	wt % K	Formation rates of			
		<sup>(1)</sup> Acetaldehyde	<sup>(2)</sup> Ethanol	<sup>(3)</sup> Crotonaldehyde	<sup>(3)</sup> Acetone
7	1.0	8.2 x 10 <sup>-8</sup>	4.8 x 10 <sup>-3</sup>	2.3 x 10 <sup>-9</sup>	4.0 x 10 <sup>-9</sup>
49	1.2	1.3 x 10 <sup>-7</sup>	2.4 x 10 <sup>-3</sup>	2.5 x 10 <sup>-9</sup>	1.8 x 10 <sup>-8</sup>

<sup>(1)</sup> Rate of acetaldehyde consumption, in mol/m<sup>2</sup> total · s.

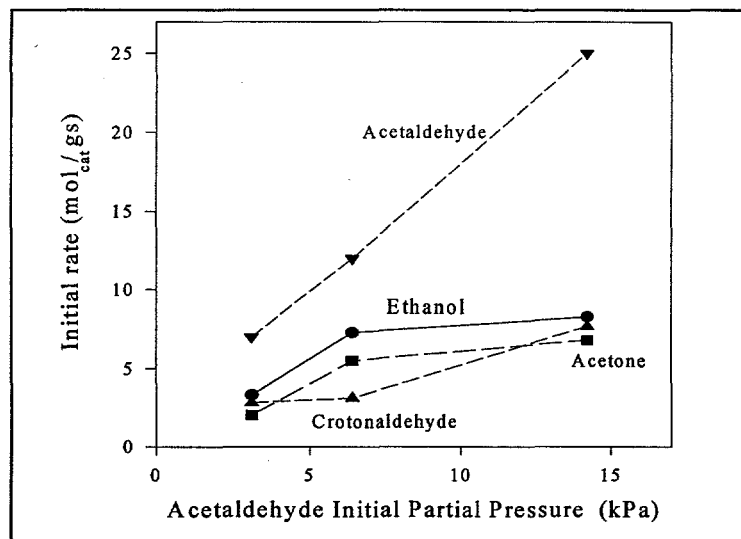
<sup>(2)</sup> Turnover rates per Cu surface atom, in s<sup>-1</sup>.

<sup>(3)</sup> Rates of product formation, in mol/m<sup>2</sup> base · s.

The effect of acetaldehyde partial pressure (3.1-14.6 kPa) on acetaldehyde reaction rates and product selectivity has been investigated on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-11 Ow/K) in order to determine the reaction order with respect to acetaldehyde partial pressure. The reaction was carried out at 573 K with a reaction mixture of C<sub>2</sub>H<sub>4</sub>O/CH<sub>4</sub>/He = 7.0/2.7/90.6 kPa (C<sub>2</sub>H<sub>4</sub>O:

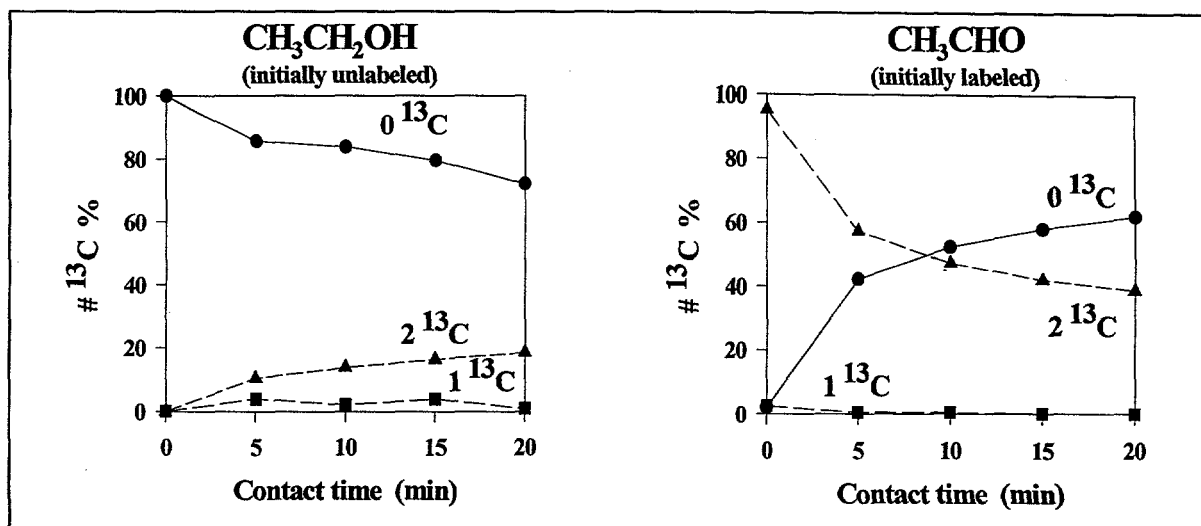
Fisher Scientific, Reagent Grade; CH<sub>4</sub>: Matheson, ultra high purity). Methane was used as an unreactive internal standard.

The initial reaction rates at different initial partial pressures of acetaldehyde are shown in *Figure 6*. The reaction rates of condensation products (acetone and crotonaldehyde) depend on the initial partial pressure of acetaldehyde. Kinetic reaction orders of 0.7 for crotonaldehyde and 0.8 for acetone were obtained by employing a like power law kinetic expression ( $r_j = k_j \cdot P_{\text{acetal}}^n$ ). These results indicate that the reaction kinetics is not zero-order with respect to acetaldehyde, as suggested previously for ethanol reactions on a similar catalyst.

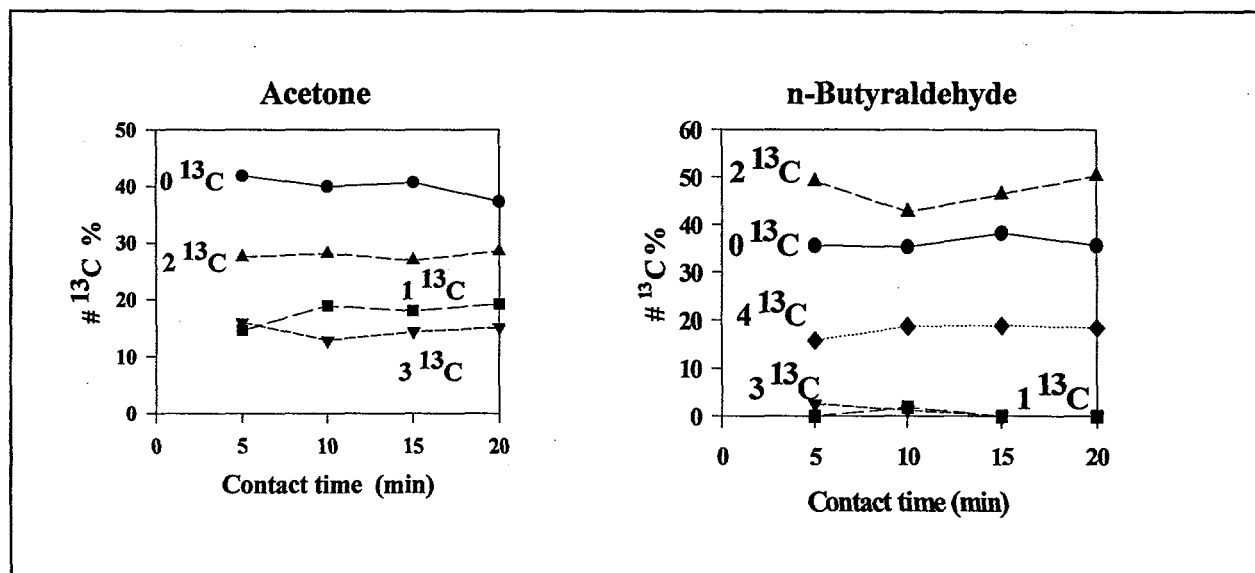


**Figure 6.** Effect of acetaldehyde partial pressure on the initial rates of acetaldehyde reaction and product formation 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>. [573 K, 101.3 kPa total pressure, 3-15 kPa acetaldehyde, balance He].

Competitive reactions between <sup>12</sup>C<sub>2</sub>H<sub>5</sub>OH and <sup>13</sup>C<sub>2</sub>H<sub>4</sub>O were examined on a 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-11 Ow/K) in order to probe the mechanistic significance of the non-zero initial rate of acetone formation in ethanol dehydrogenation and coupling reactions. The catalyst (20 mg) was charged into a gradientless batch reactor. The sample was reduced in 10 % H<sub>2</sub> (balance He) at 623 K for 0.5 h. Reactions were conducted at 523 K and 101.3 kPa in a recirculating reactor unit (RRU) with a reaction mixture of <sup>13</sup>C<sub>2</sub>H<sub>4</sub>O/<sup>12</sup>C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>/CH<sub>4</sub>/He = 1.3/3.7/21.2/2.4/72.7 kPa. (<sup>13</sup>C<sub>2</sub>H<sub>4</sub>O: Isotec Inc., 2 <sup>13</sup>C: 99 %; C<sub>2</sub>H<sub>5</sub>OH: Fisher Scientific, A.C.S. certified; CH<sub>4</sub>: Matheson, ultra high purity). The results are shown in *Figures 7 and 8*.



**Figure 7.** Carbon-13 distribution of reactants in  $^{13}\text{C}_2\text{H}_4\text{O}-\text{C}_2\text{H}_5\text{OH}-\text{H}_2$  reactions on 1.0 wt %  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  as a function of contact time. [523 K, 101.3 kPa total pressure, 1.3 kPa acetaldehyde, 3.7 kPa ethanol, balance He].

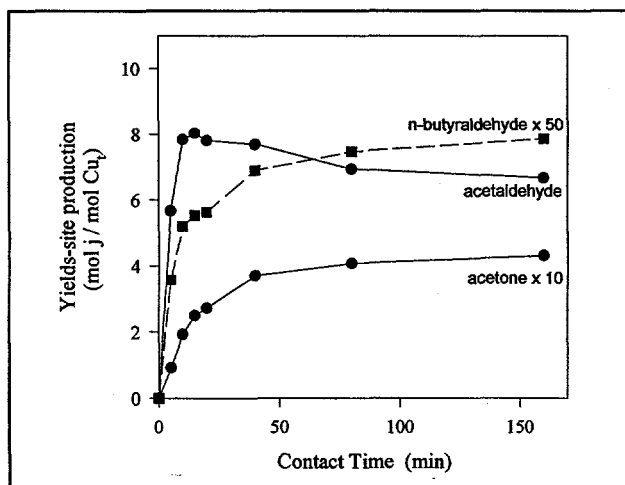


**Figure 8.** Carbon-13 distribution of products as a function of contact time in  $^{13}\text{C}_2\text{H}_4\text{O}-\text{C}_2\text{H}_5\text{OH}-\text{H}_2$  reactions on 1.0 wt %  $\text{K}-\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ . [523 K, 101.3 kPa total pressure, 1.3 kPa acetaldehyde, 3.7 kPa ethanol, balance He].

The carbon-13 distributions of products showed in *Figure 8* do not change with contact time, but the carbon-13 distributions in reactants change significantly (*Figure 7*), suggesting that the reactants may form polymer species on the surface, which decompose to give the observed products. From the total carbon-13 content we are not able to determine if acetone (40% of  $^{13}\text{C}$ , 1.2  $^{13}\text{C}$ ) or n-butyraldehyde (40% of  $^{13}\text{C}$ , 1.7  $^{13}\text{C}$ ) comes from ethanol or acetaldehyde (reaction mixture contents 26.5% of  $^{13}\text{C}$ ) because both lose their isotopic identities.

Dehydrogenation and condensation reactions of ethanol were investigated on a physical mixture of K-Mg<sub>5</sub>CeO<sub>x</sub> (MG3-7 O/K) and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> in order to address whether the proximity between Cu and basic sites are required for the base-catalyzed condensation reactions. This physical mixture was prepared in order to simulate the low-Cu catalyst (same number of Cu sites and the same number of basic sites as it had in 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> sample). The catalyst (22.8 mg) was first reduced in H<sub>2</sub> (10% H<sub>2</sub>/He) at 623 K for 0.5 h. The temperature was lowered to 573 K and ethanol was introduced along with a small amount of methane, used as an unreactive internal standard (reaction mixture: C<sub>2</sub>H<sub>5</sub>OH/CH<sub>4</sub>/He = 4.0/2.7/94.6 kPa; Fisher Scientific: C<sub>2</sub>H<sub>5</sub>OH A.C.S. certified; Matheson: CH<sub>4</sub> ultra high purity).

Acetaldehyde was the initial reaction product of pure ethanol feeds on Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (Figure 9). Dehydrogenation reactions occur much faster than the chain growth reactions to acetone, n-butyraldehyde, and other oxygenates on all the catalysts tested. The initial reaction rates for acetaldehyde reaction and product formation are shown in Table 4. The turnover rate of ethanol dehydrogenation on the physical mixtures was surprisingly twice as much as that observed on low and high-Cu catalysts. No explanation was found for this result. The rate of acetone formation on high-Cu catalysts was higher than that on low-Cu catalyst and the physical mixture, suggesting that the proximity between Cu and basic sites favors the production of acetone, but not n-butyraldehyde. On the other hand, n-butyraldehyde formation rate is an order of magnitude higher for the physical mixture than for the low or high Cu catalysts.



**Figure 9.** Ethanol reactions. Site yields as a function of contact time on a physical mixture of K-Mg<sub>5</sub>CeO<sub>x</sub> (MG3-7 O/K) and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>. [573 K, 101.3 kPa total pressure, 3.5 kPa ethanol, balance He].

**Table 4.** Effect of the proximity between Cu and basic sites on ethanol consumption and product formation on 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, and a physical mixture of K-Mg<sub>5</sub>CeO<sub>x</sub> and 1.2 wt % K-Cu<sub>7.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>.

Catalyst	Ethanol dehydrogenation		Formation rates of			
	areal rate ( <sup>1</sup> )r <sub>1</sub>	Turnover rate ( <sup>2</sup> )r <sub>1</sub>	Acetone ( <sup>3</sup> )r <sub>2</sub>	Butyraldehyde ( <sup>4</sup> )r <sub>2</sub>	( <sup>3</sup> )r <sub>3</sub>	( <sup>4</sup> )r <sub>3</sub>
low-Cu	2.4 x 10 <sup>-7</sup>	0.23	4.3 x 10 <sup>-9</sup>	1.8 x 10 <sup>-3</sup>	7.6 x 10 <sup>-10</sup>	3.2 x 10 <sup>-4</sup>
high-Cu	9.4 x 10 <sup>-7</sup>	0.24	4.4 x 10 <sup>-8</sup>	1.0 x 10 <sup>-2</sup>	1.2 x 10 <sup>-9</sup>	2.8 x 10 <sup>-4</sup>
mixture	4.6 x 10 <sup>-7</sup>	0.46	6.9 x 10 <sup>-9</sup>	3.1 x 10 <sup>-3</sup>	5.2 x 10 <sup>-9</sup>	2.4 x 10 <sup>-3</sup>

(<sup>1</sup>) r<sub>1</sub> is the rate of ethanol consumption, and is expressed in mol/m<sup>2</sup> total · s.

(<sup>2</sup>) Turnover rates per Cu surface atom, and is expressed in s<sup>-1</sup>.

(<sup>3</sup>) r<sub>2</sub> and r<sub>3</sub> are the rates of product formation, and are expressed in mol/m<sup>2</sup> MgCeO<sub>x</sub> · s.

(<sup>4</sup>) Turnover rates per accessible site from <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> and is expressed in mol/mol CO<sub>2</sub> exchangeable·s.

### 3.2. Isobutanol Synthesis at High Pressure in CMRU

#### 3.2.1. Methanol turnover rates

Table 5 shows methanol turnover rates found for some methanol synthesis catalysts in the literature [7-10] and for the most recent CMRU runs. The methanol turnover rates for the CMRU runs are calculated at a gas hourly space velocity of 6000 cm<sup>3</sup>/g/h. All literature values are measured at lower temperature (493-523 K) and at different feed gas compositions compared to our catalysts. Both the low- and high-Cu K-CuMgCeO<sub>x</sub> catalysts, and the catalyst without Ce give similar methanol turnover rates. This is consistent with the fact that methanol productivity is proportional to Cu surface sites.

**Table 5.** Methanol synthesis turnover rates .

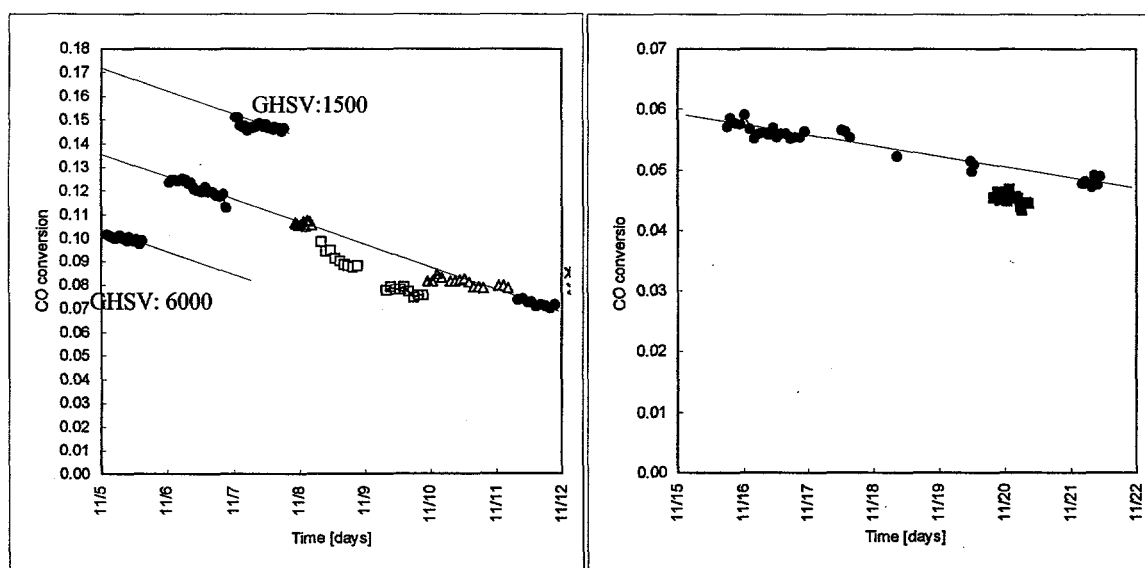
	Catalyst	Methanol turnover rate [mmol MeOH/mol Cu s]	Ref.
Literature <sup>1</sup>	Cu/ZnO	15.7	[7]
	Cu/Zn/Al	15.7	[8]
	Cu/SiO <sub>2</sub>	4.2	[9]
This study <sup>2</sup>	Cu <sub>0.5</sub> Mg <sub>5</sub> O <sub>x</sub> <sup>#</sup>	9.0	run 22
	K-Cu <sub>0.5</sub> Mg <sub>5</sub> CeO <sub>x</sub> <sup>*</sup>	7.9	run 19
	K-Cu <sub>0.5</sub> Mg <sub>5</sub> CeO <sub>x</sub> <sup>*</sup>	8.2	run 20
	K-Cu <sub>0.5</sub> Mg <sub>5</sub> CeO <sub>x</sub> <sup>**</sup>	9.1	run 23
	K-Cu <sub>0.5</sub> Mg <sub>5</sub> CeO <sub>x</sub> <sup>**</sup>	8.9	run 24
	K-Cu <sub>7.5</sub> Mg <sub>5</sub> CeO <sub>x</sub>	8.7	run 21

<sup>1</sup> 493-523 K, 5-7 MPa, CO<sub>2</sub>/CO/H<sub>2</sub> feeds. <sup>2</sup> 593 K, 4.5 MPa, 6000 cm<sup>3</sup>/g<sub>cat</sub> h. \* MG3-11 Ow/K

\*\* MG3-13 O/K. # Incorrect value and catalyst identity reported in the November monthly report

### 3.2.2. Deactivation during CMRU-23

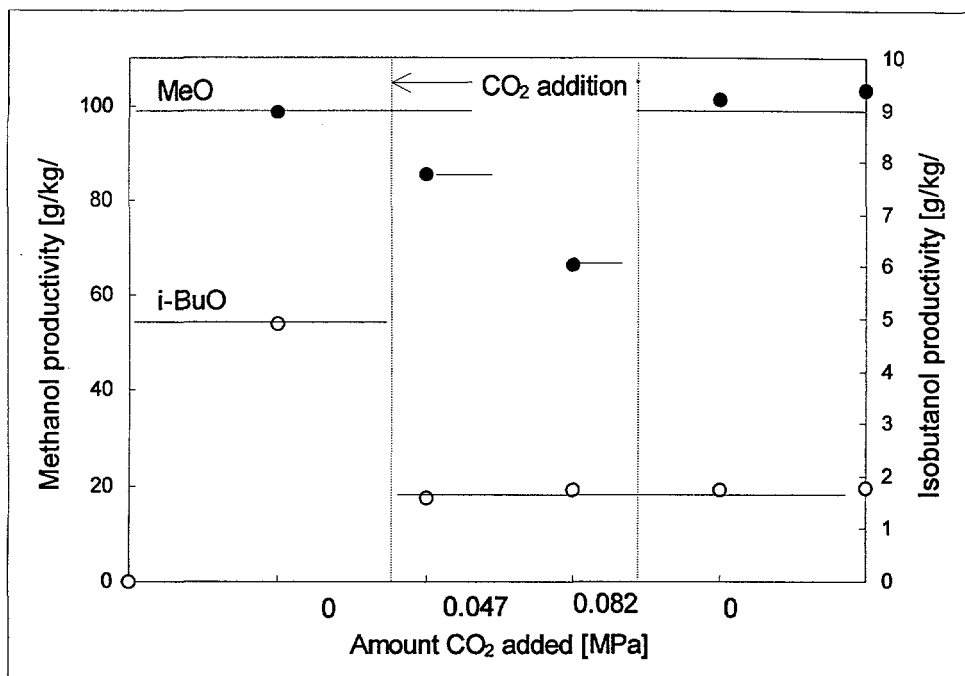
The plot of CO conversion versus time on stream (*Figure 10*) reveals that the catalyst deactivates continuously during the run. The deactivation rate decreases with time but the catalyst is still losing activity after 14 days on-stream. The solid symbols represent the data obtained at 593 K and the open symbols at 603 K. It can be seen that an increase in the temperature by 10 K has essentially no effect on CO conversion when the deactivation is taken into account. Methanol selectivity, however, decreases with increasing temperature, resulting in a decrease in methanol yield. This is similar to what was found by Apesteguia et. al. [11]. They found essentially no change in CO conversion but a decrease in methanol selectivity with increasing temperature. The decrease in methanol yield is probably caused by lower equilibrium conversion levels for methanol synthesis at higher temperature.



Open symbols: 603 K  
Filled symbols: 593 K  
Squares: CO<sub>2</sub>-addition

**Figure 10.** CO conversion vs. time-on-stream on 1 wt% K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> catalysts (MG3-13 O/K). (593-603 K, 4.5 MPa, H<sub>2</sub>/CO = 1, GHSV = 1500-6000 cm<sup>3</sup>/g/h).





**Figure 11.** Effect of CO<sub>2</sub> addition on methanol and isobutanol productivities (after corrected for deactivation). ( $H_2/CO = 1$ ,  $T = 603$  K,  $P = 4.5$  MPa,  $GHSV = 3000$  cm<sup>3</sup>/g cat/h).

Figure 11 shows the changes in methanol and isobutanol productivities when CO<sub>2</sub> is added to the feed gas. The CO conversion used for calculating the productivities has been corrected for the observed deactivation with time. When 0.047 MPa of CO<sub>2</sub> is added to the feed, isobutanol productivity is reduced to about 1/3 of the value before CO<sub>2</sub> addition. No further decrease was observed when the amount of CO<sub>2</sub> added was increased to 0.082 MPa, and the productivity was not recovered when the CO<sub>2</sub> addition was stopped. This suggests that the basic sites are irreversibly poisoned. The procedures for CO<sub>2</sub> addition were different for this run compared to earlier CO<sub>2</sub> addition runs for which no irreversible poisoning was detected. In this case the CO<sub>2</sub> was added directly during synthesis (without flushing the catalyst with H<sub>2</sub> before and after the CO<sub>2</sub> addition). The space velocity was kept constant and CO<sub>2</sub> added at two different levels in contrast to earlier runs where CO<sub>2</sub> was added in a certain amount and the space velocity was varied during the CO<sub>2</sub> addition.

The methanol productivity also decreased when CO<sub>2</sub> was added, but the productivity was recovered when the CO<sub>2</sub> addition was stopped. CO<sub>2</sub> seems to reversibly inhibit the methanol productivity. It is possible that the added CO<sub>2</sub> results in the oxidation of Cu (either directly or via H<sub>2</sub>O). When the CO<sub>2</sub> is removed, the same CO/H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O ratio as before is recovered, the Cu is reduced back again. It is also possible that the water-gas-shift reaction could influence on the measured CO conversion by converting some of the added CO<sub>2</sub> to CO. A decreased CO<sub>2</sub> selectivity would then be expected. Instead, an increased CO<sub>2</sub> selectivity was observed in the current run (possibly due to the uncertainty in correcting the measured CO<sub>2</sub> for the CO<sub>2</sub> added).

After the CO<sub>2</sub>-addition studies, the catalyst had lost over 50% of its original activity and the CO conversion was so low that accurate measurements were difficult. It was therefore

decided to end the experiment at this point. After the experiment was ended the catalyst was removed from the reactor in four sections from the inlet of the reactor to the outlet. This was done in order to detect whether the extent of catalyst deactivation depends on its position in the reactor.

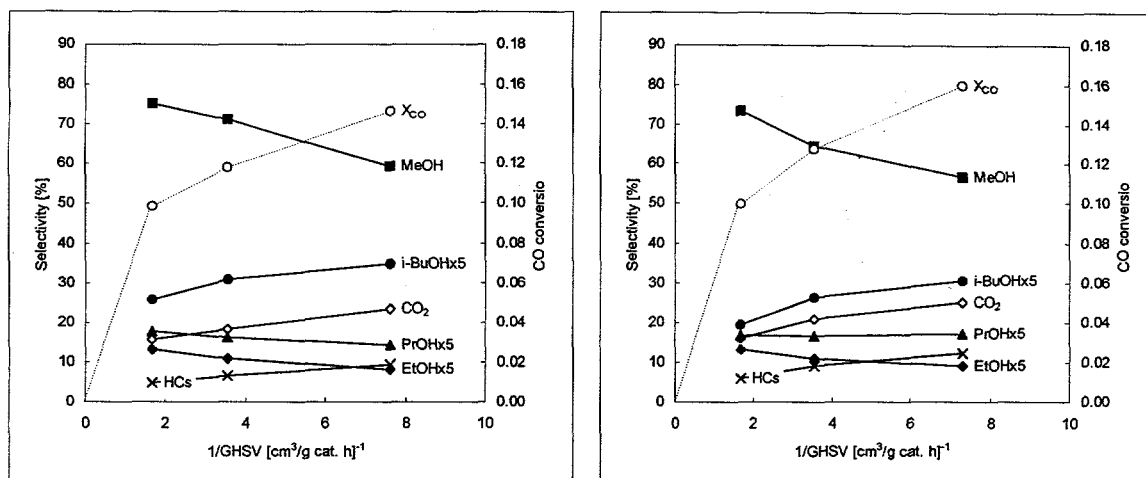
The total BET surface areas of the various portions of the used catalyst were measured. The results are presented in Table 6. The total surface area decreased to almost the half of the surface area of the fresh catalyst. If the catalyst deactivated only due to oxidation of Cu during reaction, a large decrease in total surface area is unlikely and sintering of the support seems therefore to be a more likely explanation. The reduction in total surface area could, however, be caused both by pore blocking by coke and by sintering of the catalyst, and it is not possible to discriminate between these two causes by the BET measurements. No difference could be detected between the inlet and outlet section of the catalyst bed by the BET measurements.

**Table 6.** BET surface area measured before and after methanol-isobutanol synthesis (CMRU 23).

MG3-13 O/K	BET surface area [m <sup>2</sup> /g cat.]	Cu dispersion (%)
Fresh catalyst	150	15.8
Used catalyst - Inlet	84	3.6
Used catalyst - Outlet	85	1.2
<sup>a</sup> Used catalyst - Inlet	84	20.6

<sup>a</sup> After O<sub>2</sub> treatment at 723 K

A new sample of catalyst MG3-13 O/K was charged to the CMRU in order to carry out ethanol and propanol addition studies. This also provides an additional test of the reproducibility of the CMRU unit since a sample of the same batch of 1.0 wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> catalyst was charged. The same amount of catalyst as in CMRU-23 was charged and initially the same space velocity study was performed. *Figure 12* shows the conversion and selectivities for the two comparable runs (CMRU-23 and -24) and *Table 7* shows comparison of the two runs at 6000 cm<sup>3</sup>/g-cat.h. The reproducibility is excellent, but a somewhat lower isobutanol (3.2 % vs. 4.3 % at 10 % conversion) and higher hydrocarbon selectivity (5.9 vs. 4.7 %) were observed in CMRU-24.

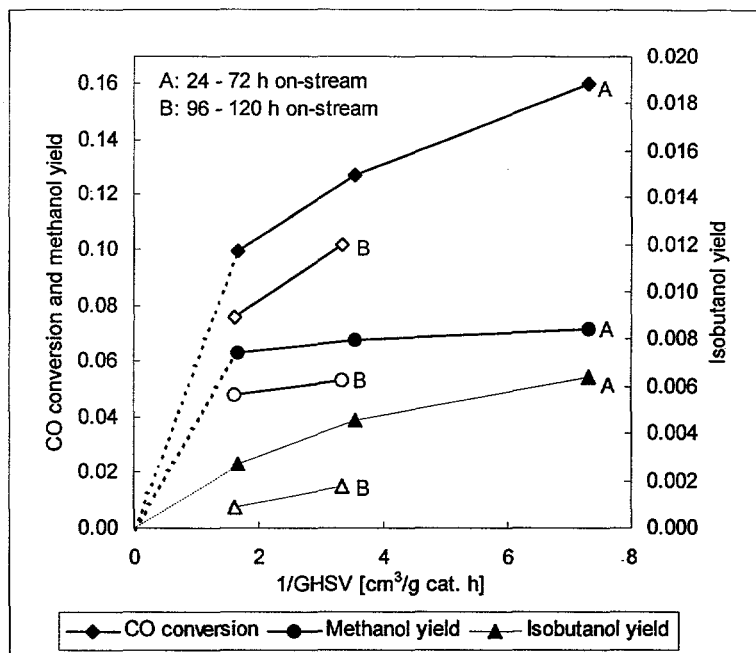


**Figure 12.** CO conversion and product selectivities for CMRU-23 and -24. [Catalyst: 1%K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, 2.06 g, 4.5 MPa, 593 K, H<sub>2</sub>/CO=1, 1500-6000 cm<sup>3</sup>/g-cat.h.]

**Table 7.** Comparison of CMRU-23 and -24. [Catalyst: 1wt % K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>, 2.06 g, 4.5 MPa, 593 K, H<sub>2</sub>/CO=1, 6000 cm<sup>3</sup>/g-cat.h.]

RUN	CMRU-23	CMRU-24
Catalyst	MG3-130/K	MG3-130/K
amount [g]	2.06	2.06
GHSV [cm <sup>3</sup> /g cat. h] <sup>-1</sup>	6000	6000
CO conversion [%]	9.9	10.0
Rate of Reaction (mmol CO converted/g. cat.*hr.)	10.9	11.1
Methanol Productivity (g/kg*hr)	227.8	224.2
Isobutanol Productivity (g/kg*hr)	7.5	5.6
Selectivities (CO <sub>2</sub> -free)		
CO <sub>2</sub> (%C)	15.6	16.1
Methanol	75.2	73.5
Ethanol	2.6	2.6
1-Propanol	3.6	3.4
Isopropanol	1.0	1.3
2-butanol	0.07	0.15
Isobutanol	4.3	3.2
1-butanol	0.00	0.27
1-pentanol	0.18	0.11
2-methyl-1-butanol	0.49	0.48
2-methyl-2-butanol	0.12	0.18
2-methyl-1-pentanol	0.14	0.14
1-hexanol	0.00	0.00
2-methyl-1-hexanol	0.02	0.00
Methane	3.6	4.4
C <sub>2+</sub> Paraffins	1.1	1.5
Alcohols Selectivity	88.9	86.6
Paraffins Selectivity	4.7	5.9

After decreasing the space velocity from 6000 to 1500  $\text{cm}^3/\text{g-cat h}$ , the space velocity was increased again to 6000  $\text{cm}^3/\text{g-cat h}$  and then decreased to 3000  $\text{cm}^3/\text{g-cat h}$ . The results showed that the catalyst had deactivated. The CO conversion decreased from 10% to 7.5% at 6000  $\text{cm}^3/\text{g-cat h}$  (Figure 13). Both the methanol and isobutanol yield decreased.



**Figure 13.** CO conversion, methanol and isobutanol yields as a function of space velocity and time. [CMRU-24, 593 K, 45 MPa,  $\text{H}_2/\text{CO}=1$ , 1500-6000  $\text{cm}^3/\text{g-cat h}$ .]

### 3.3.3. 1-Propanol addition

1-Propanol addition were studied earlier on high Cu catalysts. In this case, 1-propanol was added to the syngas feed for the low Cu-containing catalyst (1 wt %  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ ) after initial space velocity studies. The amount of 1-propanol added was much higher than the amount of methanol produced due to experimental problems. It was originally intended to add about 20% of the methanol produced. The large amounts of alcohol added possibly result in a more pronounced competition with CO for active sites, resulting in a decrease in CO conversion. Only a slight decrease was observed previously when less propanol was added for the high Cu-containing catalyst.

The propanol was degassed with inert gas before it was charged to the pump and the alcohol was added to the feed after first measuring catalyst activity without propanol addition. Catalyst activity was also measured after propanol addition. The results are shown in Table 8. Isobutanol selectivity increased by an order of magnitude when propanol was added to the feed. The significant increase in isobutanol selectivity upon propanol addition is consistent with earlier results from this group and also with results reported for other higher alcohol catalysts ( $\text{Cs-Cu/ZnO/Cr}_2\text{O}_3$ ) by Campos-Martin et al. [12]. Isobutanol is formed by condensation of  $\text{C}_1$  intermediate derived from methanol or CO and 1-propanol or propionaldehyde. A large