

## EXECUTIVE SUMMARY

A series of  $\text{CuMgCeO}_x$  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  $\text{N}_2\text{O}$  titration at 90 °C.  $\text{CeO}_x$  does not contribute to the measured copper dispersion in  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  samples and the high dispersion value indeed reflects the presence of Cu metal small crystallites.

Kinetic studies of methanol and propionaldehyde coupling reactions on  $\text{K-Cu/MgO/CeO}_2$  and  $\text{MgO/CeO}_2$  catalysts indicate that Cu enhances the rates of alcohol dehydrogenation. The cross-coupling reactions of propionaldehyde and  $^{13}\text{C}$ -labeled methanol produce singly-labeled isobutyraldehyde, a precursor to isobutanol, suggesting that it forms by the condensation of propionaldehyde and a reactive intermediate derived from methanol. Singly-labeled propionaldehyde formed by the reverse aldol condensation of 2-methyl-3-hydroxy-propionaldehyde. The latter formed by the cross coupling between propionaldehyde and  $^{13}\text{C}$ -labeled methanol followed by hydrogen transfer from  $\gamma$ -carbon atom and hydroxyl group to the carbonyl group. Methanol reactions on MgO form only CO and  $\text{CO}_2$  with trace amounts of methyl formate. The addition of  $\text{AlO}_x$  to MgO leads to the formation of dimethylether (DME), suggesting the presence of acid sites resulting from the separate phases of  $\text{AlO}_x$ . DME-to- $\text{CO}_x$  ratio increases with increasing Al content.

High-pressure isobutanol synthesis from  $\text{CO}/\text{H}_2$  has been studied on  $\text{Cu}_{0.5}\text{Mg}_5\text{O}_x$  catalysts at 593 K and 4.5 MPa.  $\text{Cu}_{0.5}\text{Mg}_5\text{O}_x$  catalysts show high hydrocarbon and low isobutanol selectivities compared to  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ , suggesting the presence of residual acidity in  $\text{Cu}_{0.5}\text{Mg}_5\text{O}_x$ . Methanol turnover rates on  $\text{Cu}_{0.5}\text{Mg}_5\text{O}_x$  are higher than on  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ , suggesting that the active site (Cu) for methanol synthesis is inhibited by reaction products such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The small Cu crystallites resulting from the interaction between copper and cerium oxides are more likely to be oxidized by  $\text{CO}_2$  and/or  $\text{H}_2\text{O}$ .

The density and strength of available basic sites are determined using a  $^{13}\text{CO}_2/^{12}\text{CO}_2$  isotopic exchange method. Addition of  $\text{CeO}_x$  to MgO increases not only MgO surface area but also the density and strength of available basic sites at 573 K. The presence of Cu has little effect on basic site density and strength in  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$ . Yet, K increases both the density and strength of basic sites.  $\text{Mg}_5\text{AlO}_x$  mixed-oxides exhibit lower basic site density and strength compared to MgO.

Two manuscripts "*Isobutanol and Methanol Synthesis on Copper Catalysts Supported on Modified Magnesium Oxide*" and "*Isotopic Switch Methods for the Characterization of Basic Sites in Modified MgO Catalysts*" are 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>, and MgAlO<sub>x</sub> catalysts
- Measurements of Copper Surface Area
- 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
- Isotopic tracer studies of alcohol coupling reactions on MgO/CeO<sub>2</sub> and MgO/Al<sub>2</sub>O<sub>3</sub>-based catalysts
- Evaluation of high-pressure isobutanol synthesis reactions on Cu<sub>0.5</sub>Mg<sub>5</sub>O<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*

CuCeMgO<sub>x</sub> and its individual components were prepared by coprecipitation of 1 M mixed metal nitrate solutions with a mixed solution of potassium hydroxide (2 M) and potassium carbonate (1 M) at 338 K and a constant pH of 9 in a computer-controlled well-stirred batch reactor. The precipitates were filtered, washed with de-ionized water at 338 K, and then dried at 353-363 K overnight. The resulting materials were calcined at 723 K for 4 h to obtain the mixed oxides. The detailed procedures have been described by Apesteguia et al. [1]. K-containing samples were prepared by incipient wetness impregnation using K<sub>2</sub>CO<sub>3</sub> (0.25 M) solutions. The nominal potassium concentration was 1.0 wt.%. Catalyst properties are summarized in Table 1.

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

Sample	Nominal composition	Mg/Cu	Mg/Ce	K (wt.%) AAS	S.A. (m <sup>2</sup> /g)
MG 3 - 5 O/K	Cu <sub>0.1</sub> MgO <sub>x</sub>	8	---	1.1	112
MG 3 - 7 O/K	Mg <sub>5</sub> CeO <sub>x</sub>	---	5.2	0.7	155
MG 3 - 8 O/K	MgO	---	---	---	129
MG 3 - 9 O	CeO <sub>2</sub>	---	---	< 0.01	80
MG 3 - 12 O	Mg <sub>5</sub> CeO <sub>x</sub>	---	4.8	0.01	183
MG 3 - 13 O	Cu <sub>0.5</sub> Mg <sub>5</sub> CeO <sub>x</sub>	8.3	4.3	< 0.01	160

As mentioned in the previous report (3Q, FY'96), the amount of residual potassium on MG3-3 O (CeO<sub>2</sub>), left behind during co-precipitation, was very high, resulting in a material with low surface area (S.A.=0.2 m<sup>2</sup>/g). Another CeO<sub>2</sub> sample (MG3-9 O) was prepared by co-precipitation methods. The precipitates were filtered and *thoroughly washed* with distilled water at 338 K, resulting in a cerium oxide with low potassium content and high surface area (Table 1). New batches of Mg<sub>5</sub>CeO<sub>x</sub> (MG3-12 O) and Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> (MG3-13 O) were synthesized in order to verify the reproducibility in catalyst preparation and to provide large amounts of sample for testing in CMRU.

At this point, we decided to prepare several new catalytic materials in order to 1) avoid CO<sub>2</sub> inhibition on Cu (by removing CeO<sub>x</sub> to avoid Cu-Ce interaction) and on basic sites (by varying basic strength), 2) increase surface area (by Zr, Zn, and Mn addition) and basic site density and strength (by Li addition) of basic oxides, and 3) improve the chain growth by incorporating a chain growth component (Co) into the best CuMgMeO<sub>x</sub> material (Me=Ce, Al). Some of these materials have been prepared in collaboration with Professor Carlos Apesteguia's research group in the Department of Chemical Engineering

at Universidad Nacional del Litoral in Santa Fe (Argentina). A list of the materials being synthesized is given in Table 2.

**Table 2.** Catalysts being synthesized.

<b>Catalyst</b>	<b>Synthesis Method</b>
CuZnAlO <sub>x</sub>	Coprecipitation
CuZnAlO <sub>x</sub> /(K)MgCeO <sub>x</sub>	Coprecipitation and Physical Mixtures
CuZnAlO <sub>x</sub> /(K)MgAlO <sub>x</sub>	Coprecipitation and Physical Mixtures
CuZnAlO <sub>x</sub> /(K)MgOx	Coprecipitation and Physical Mixtures
CuCoMgCeO <sub>x</sub>	Coprecipitation
CuMgAlO <sub>x</sub>	Coprecipitation
CuCoMgAlO <sub>x</sub>	Coprecipitation
MgAlO <sub>x</sub>	Coprecipitation

Cu<sub>0.5</sub>Mg<sub>5</sub>Al<sub>10</sub>O<sub>x</sub> (MG3-15 P), Cu<sub>0.5</sub>Co<sub>0.1</sub>Mg<sub>5</sub>Al<sub>10</sub>O<sub>x</sub> (MG3-16 P), and MgAlO<sub>x</sub> samples were provided by Apesteguiá's research group. These samples were prepared by co-precipitation of 1.5 M mixed metal nitrate solutions with a mixture of KOH (2M) and K<sub>2</sub>CO<sub>3</sub> (1M) at 333 K and a constant pH of 10 in a stirred-batch reactor following the procedures described by Apesteguiá et al. [1]. The precipitates were filtered, washed with 600 ml of distilled water at 333 K and dried at 348 K overnight. Then, the precursors were crushed and suspended in 300 cm<sup>3</sup> of hot water, washed again with 600 cm<sup>3</sup> of hot water, filtered and dried at 348 K. The resulting precursors will be calcined at 723 K for 4 h to obtain the mixed oxides. The amount of residual potassium, determined by atomic analysis, was less than 0.05 wt.%.

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

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

Alcohol coupling reactions require a sequence of steps leading to the formation of higher alcohols from C<sub>1</sub> and C<sub>2</sub> alcohols [2,3]. These steps include alcohol dehydrogenation to aldehydes, aldol condensation of aldehydes to higher aldehydes and ketones, and the subsequent hydrogenation to higher alcohols. It is believed that aldehydes are the reactive intermediates in chain-growth reactions that occur on basic sites [4,5].

Ethanol dehydrogenation-coupling reactions were reported for K-Cu-Ce-Mg catalysts in the previous report (3Q, FY'96). Ethanol is a useful and simple probe molecule to test the metal and basic functions of isobutanol synthesis catalysts. Ethanol reactions, however, lead only to acetone and n-butyraldehyde (precursors to 2-propanol and 1-butanol, respectively), neither of which can form isobutanol precursors (e.g. isobutyraldehyde and propionaldehyde) during CO hydrogenation.

<sup>13</sup>C-tracer studies of methanol/propionaldehyde cross-coupling reactions were carried out in order to examine chain-growth reaction pathways leading to C<sub>4</sub> oxygenates.

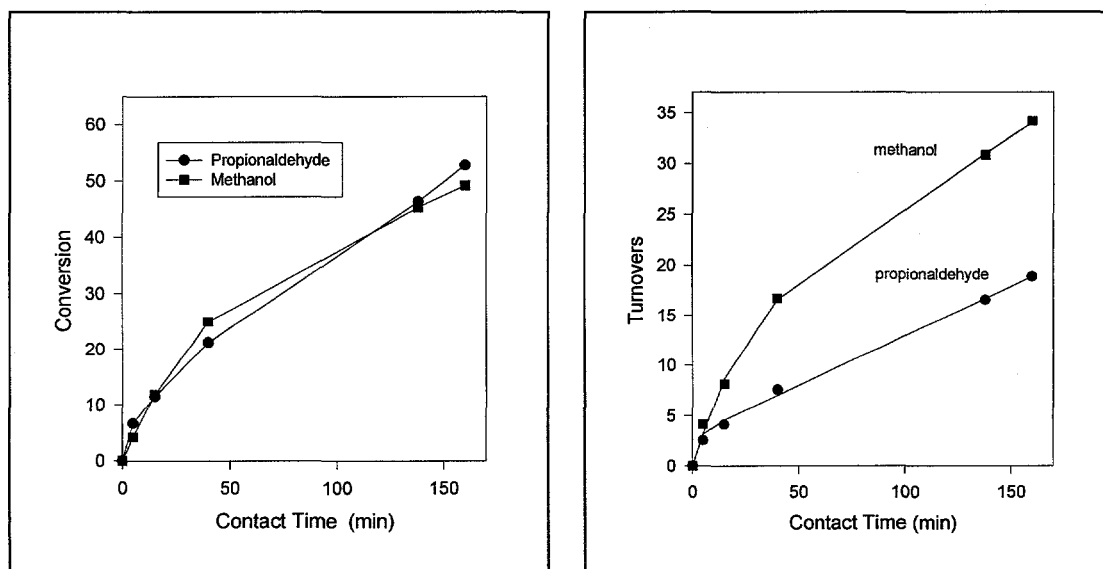
Catalysts (22 mg) were charged into a gradientless batch reactor. The samples were reduced in 10 % H<sub>2</sub> (balance He) at 623 K for 30 min. After the desired reaction temperature was reached, reactants were fed to the reactor. For the cross-coupling reactions of methanol and propionaldehyde on K-CuMgCeO<sub>x</sub> catalysts, the feed gas composition was <sup>12</sup>C<sub>3</sub>H<sub>6</sub>O/<sup>13</sup>CH<sub>3</sub>OH/CH<sub>4</sub>/He = 4/8/2.7/86.6 kPa (methane was used as an internal standard). The reaction was carried out at 573 K and 101.3 kPa in the recirculating reactor unit (RRU). 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.

Results of methanol and propionaldehyde cross-coupling reactions on low-Cu catalysts (Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>) are summarized as follows:

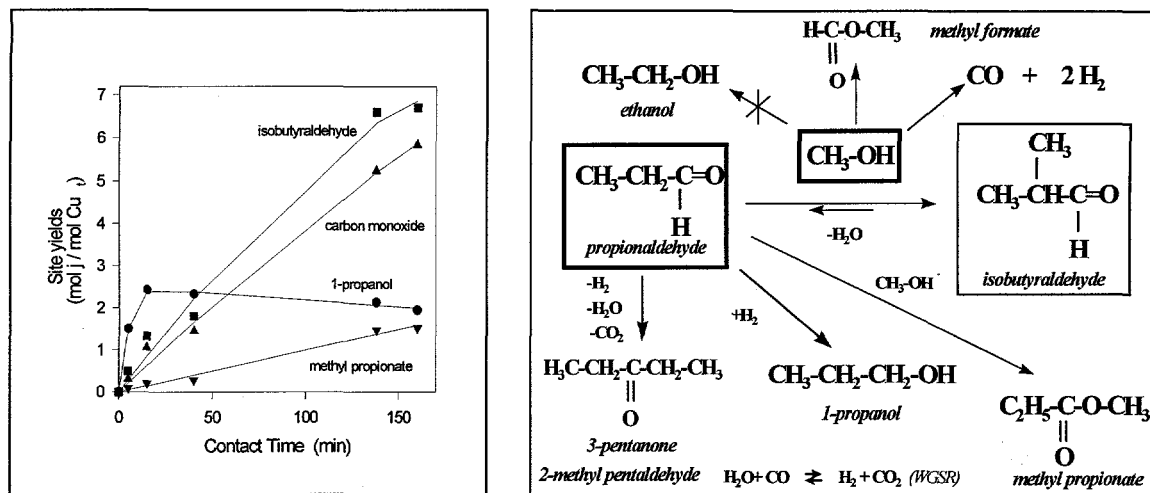
a) The conversion of methanol was comparable to that of propionaldehyde (Figure 1a). The turnovers of both methanol and propionaldehyde (moles converted per total number of Cu atoms) as a function of contact time are shown in Figure 1b.

b) Isobutyraldehyde, 1-propanol, and methyl propionate were the main reaction products (Figure 2).

c) Other products included CO (from methanol decomposition), CO<sub>2</sub> (from CO via water-gas shift reaction), methyl formate, 3-pentanone (propionaldehyde self-coupling followed by decarboxylation), 2-methyl-pentaldehyde (from propionaldehyde self-condensation) and 2-hydroxy-2-methyl-pentaldehyde. 2,2-Dimethyl butyraldehyde (from cross coupling of isobutyraldehyde and C<sub>1</sub> species) was not observed. Neither ethanol nor acetaldehyde formed during the cross-coupling reactions.



**Figure 1.** Methanol-propionaldehyde reactions on Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>/K catalysts. (a) Methanol and propionaldehyde conversion as a function of contact time. (b) Methanol and propionaldehyde turnovers as a function of contact time.

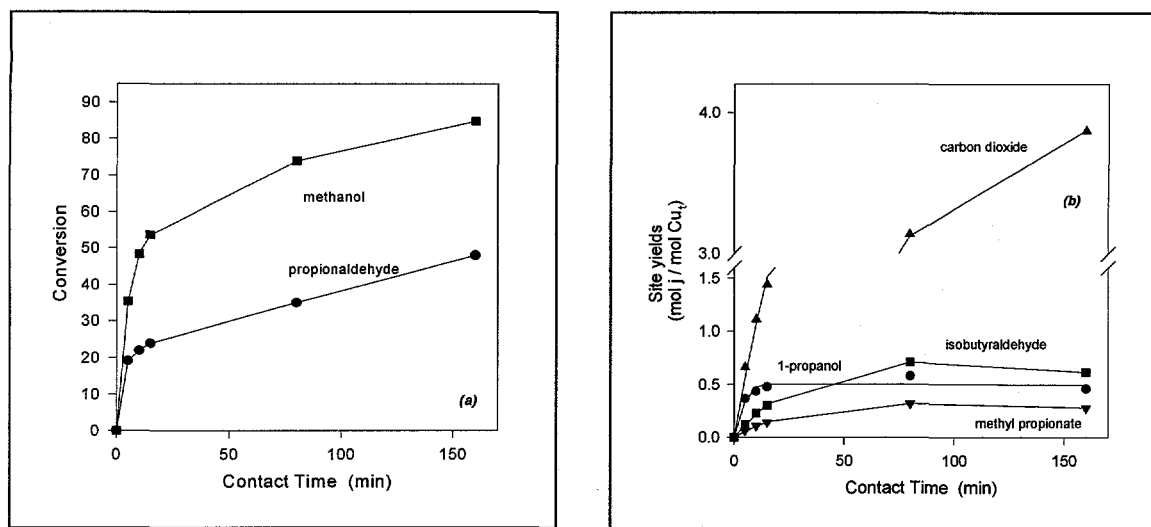


**Figure 2.** Methanol-propionaldehyde reactions. (a) Site yields as a function of contact time on  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x/\text{K}$ ; (b) Simplified reaction scheme for methanol-propionaldehyde reactions.

Catalytic activity and product distributions obtained in methanol/propionaldehyde coupling reactions on high-Cu loading catalysts ( $\text{Cu}_{7.5}\text{Mg}_5\text{CeO}_x/\text{K}$ ) are summarized as follows:

a) Methanol conversion was higher than that of propionaldehyde at all contact times (Figure 3a). The initial methanol turnover rate, calculated from the slope at zero contact time, was higher than that of propionaldehyde by a factor of two.

b) The reaction products are similar to those obtained on low-Cu catalyst with isobutyraldehyde, 1-propanol, methyl propionate, and  $\text{CO}_2$  as the main products. The site-yields of these main products are shown in Figure 3b.



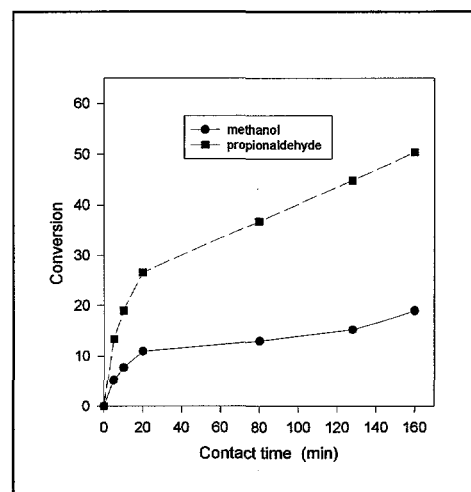
**Figure 3.** Methanol-propionaldehyde reactions on  $\text{Cu}_{7.5}\text{Mg}_5\text{CeO}_x/\text{K}$  catalysts. (a) Methanol and propionaldehyde conversions as a function of contact time. (b) Site-yields as a function of contact time on  $\text{Cu}_{7.5}\text{Mg}_5\text{CeO}_x/\text{K}$ .

The methanol conversions obtained on  $\text{MgO}$  and  $\text{Mg}_5\text{CeO}_x$  were lower compared to that obtained on Cu-containing catalysts (Table 3 and Figure 4), but the propionaldehyde conversion was similar. The main reaction products were 1-propanol, 2-methyl-3-butenal, and isobutyraldehyde. The minor products included CO (from methanol decomposition), methyl propionate, and 3-pentanone.

**Table 3.** Effect of each catalyst component on the rates of methanol/propionaldehyde reactions.

Catalyst	$r_0^{\text{methanol}}$	$r_0^{\text{propanal}}$
$\text{MgO}$	$1.1 \times 10^{-5}$	$1.4 \times 10^{-5}$
$\text{Mg}_5\text{CeO}_x$	$4.7 \times 10^{-6}$	$9.1 \times 10^{-6}$
$\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x/\text{K}$	$1.5 \times 10^{-5}$	$1.1 \times 10^{-5}$
$\text{Cu}_{7.5}\text{Mg}_5\text{CeO}_x/\text{K}$	$1.1 \times 10^{-4}$	$5.5 \times 10^{-5}$

$r_0$  are expressed as  $\text{mol} / \text{s} \cdot \text{g}_{\text{cat}}$



**Figure 4.** Methanol and Propionaldehyde conversions as a function of contact time on  $\text{MgO}$ .

Quantitative analysis of isotopic contents in products of  $^{13}\text{C}$ -labeled methanol/propionaldehyde reactions was performed using a spreadsheet, which computes the  $^{13}\text{C}$  contents in different molecules using a matrix deconvolution method [6]. The results obtained for  $^{13}\text{C}$ -methanol/propionaldehyde reactions on  $\text{K-Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  are shown in Table 4.  $\text{CO}_2$  molecules were predominantly labeled (87%  $^{13}\text{C}$ ) and formed from  $^{13}\text{CO}$  via water-gas shift reactions. Unlabeled  $\text{CO}_2$  was formed via the decarboxylation reactions leading to 3-pentanone (Figure 3b). Propionaldehyde acquired some  $^{13}\text{C}$  during reaction. The increment in the  $^{13}\text{C}$  content of propionaldehyde molecules as a function of contact time can be explained by the scheme showed in Figure 5. The apparent presence of propionaldehyde with two  $^{13}\text{C}$  atoms is an artifact caused by  $^{18}\text{O}$ , which is present as an impurity in  $^{13}\text{CH}_3\text{OH}$ .

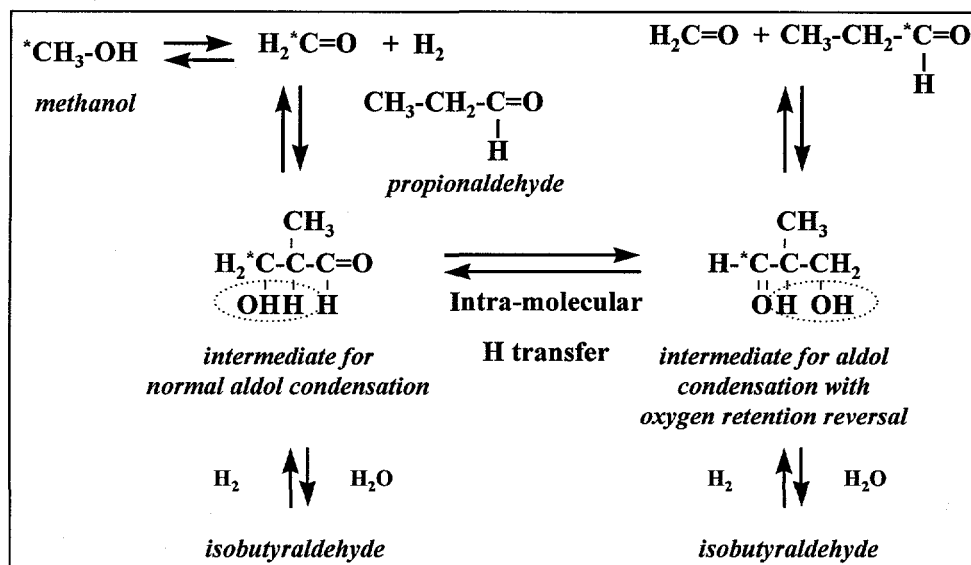
**Table 4.** Quantitative analysis of  $^{13}\text{C}$  contents on reactant and products of  $^{13}\text{CH}_3\text{OH}/^{12}\text{C}_3\text{H}_6\text{O}$  cross-coupling reactions.

Time (min)	0	5	10	20	40	80
<b><math>\text{CO}_2</math></b>						
0		0.181	0.197	0.153	0.146	0.131
1		0.819	0.803	0.847	0.854	0.869
% $^{13}\text{C}$		0.819	0.803	0.847	0.854	0.869
<b>Propionaldehyde</b>						
0	0.997	0.973	0.960	0.942	0.912	0.889
1	-0.001	0.008	0.013	0.022	0.032	0.047
2	0.004	0.018	0.025	0.034	0.051	0.059
3	0.000	0.001	0.002	0.003	0.004	0.005
% $^{13}\text{C}$	0.002	0.016	0.023	0.033	0.049	0.060
<b>Isobutyraldehyde</b>						
0		0.064	0	0	0.039	0.039
1		0.849	0.927	0.874	0.810	0.800
2		0.064	0.052	0.087	0.099	0.101
3		0.024	0.021	0.034	0.044	0.050
4		0	0	0.005	0.008	0.009
% $^{13}\text{C}$		0.261	0.273	0.293	0.293	0.298
<b>Methyl propionate</b>						
0			0	0	0.091	0.075
1			1.059	84.8	0.738	0.793
2			-0.061	0.057	0.057	0.041
3			0.002	0.096	0.116	0.093
4			0	-0.002	-0.002	-0.002
% $^{13}\text{C}$			0.236	0.311	0.298	0.286

Isobutyraldehyde is predominantly labeled with one  $^{13}\text{C}$  (Table 4), suggesting that it formed by cross-coupling reactions between  $^{13}\text{C}$ -labeled methanol and propionaldehyde. Isobutyraldehyde with two  $^{13}\text{C}$  atoms formed in the aldol condensation reaction of methanol ( $^{13}\text{C}_1$  aldehyde-type intermediate) and propionaldehyde (with one



<sup>13</sup>C). Methyl propionate contained mainly one <sup>13</sup>C atom. Both carbon atoms of methyl formate were labeled, indicating that it formed from two molecules of methanol.



**Figure 5.** Reaction pathways leading to labeled propionaldehyde.

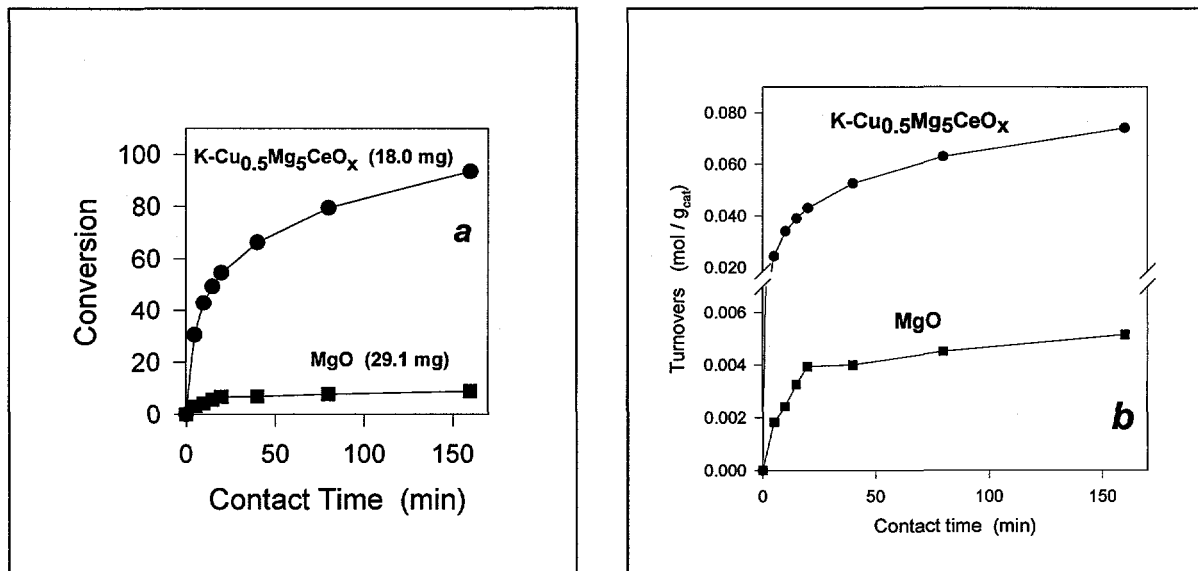
CH<sub>3</sub>OH reactions were carried out in order to explore chain growth pathways leading to higher alcohols on base catalysts. In a typical experiment, the catalyst (18 mg) was charged into a gradientless batch reactor and reduced in 10 % H<sub>2</sub> (balance He) at 623 K for 30 min. After the desired reaction temperature was reached, reactants were fed to the reactor. For the methanol decomposition reaction on K-CuMgCeO<sub>x</sub> and MgO catalysts, the feed gas composition was CH<sub>3</sub>OH/CH<sub>4</sub>/He = 4.0/2.7/94.6 (methane was used as an internal standard). The reaction was carried out at 573 K and 101.3 kPa in the recirculating reactor unit (RRU).

Results of methanol decomposition reactions on K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> and MgO can be summarized as follows:

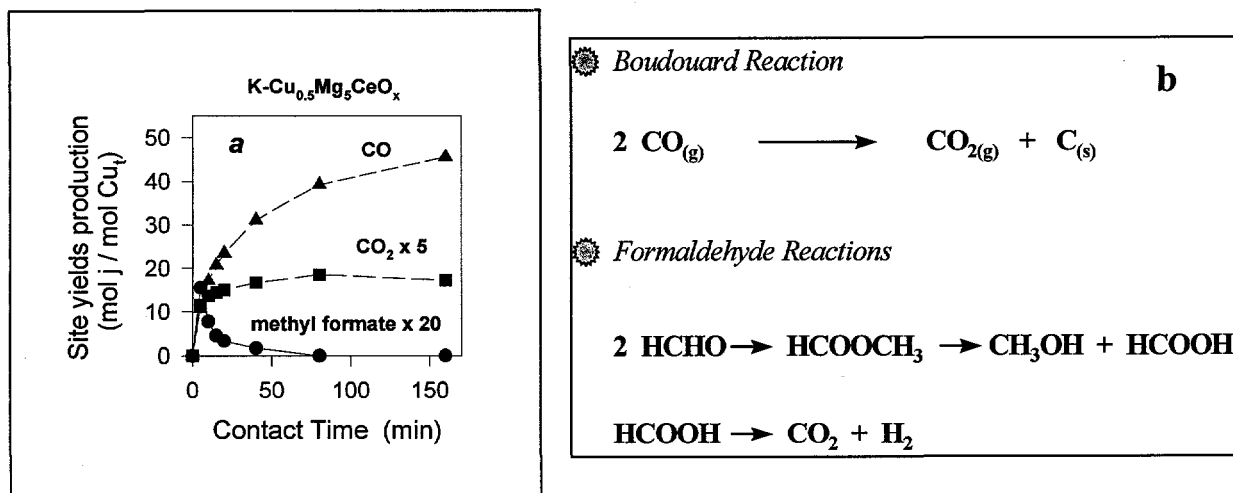
a) CO and H<sub>2</sub> were the most abundant products on both catalysts. The methanol conversions as a function of contact time are shown in Figure 6a. The methanol turnovers (moles converted per gram of catalyst) as a function of contact time on both K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> and MgO are shown in Figure 6b. The initial rate is higher for copper-containing catalysts ( $r_0 = 7.6 \times 10^{-5}$  mol / g<sub>cat</sub> s) than for pure MgO ( $r_0 = 4.0 \times 10^{-6}$  mol / g<sub>cat</sub> s).

(b) In addition to CO and H<sub>2</sub>, small amounts of methyl formate (from methanol condensation) and CO<sub>2</sub> (Figure 7a) were produced. CO<sub>2</sub> is formed from Boudouard reaction and/or methyl formate decomposition (Figure 7b). Ai and co-workers [6] studied the vapor-phase aldol condensation of formaldehyde with acetaldehyde over various metal oxides supported on silica gel. They found that the incorporation of an oxide of

transition metal, like CuO, promoted the formation of CH<sub>3</sub>OH and formic acid. These two products are believed to form from HCHO via the process showed in Figure 7b. Basic sites favor the decomposition of formic acid to CO<sub>2</sub> and H<sub>2</sub> [7].



**Figure 6.** Methanol decomposition reaction on K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub> and MgO catalysts. (a) Methanol conversion. (b) Methanol turnovers.



**Figure 7.** Methanol decomposition reaction on K-Cu<sub>0.5</sub>Mg<sub>5</sub>CeO<sub>x</sub>. (a) Site-yields as a function of contact time; (b) Pathways of carbon dioxide production.

Methanol decomposition on Cu-based catalysts without using methane as internal standard was carried out in order to determine whether methane is produced from methanol under these conditions. The amount of methane produced was low (< 0.5%

selectivity). Alcohol decomposition occurs primarily through its dehydration or dehydrogenation on acidic or basic sites, respectively. In order to establish a correlation between the catalytic activity for methanol consumption and surface acid-base properties in MgO, Mg<sub>5</sub>AlO<sub>x</sub> and MgAlO<sub>x</sub>, methanol dehydrogenation and dehydration reactions were investigated on these samples.

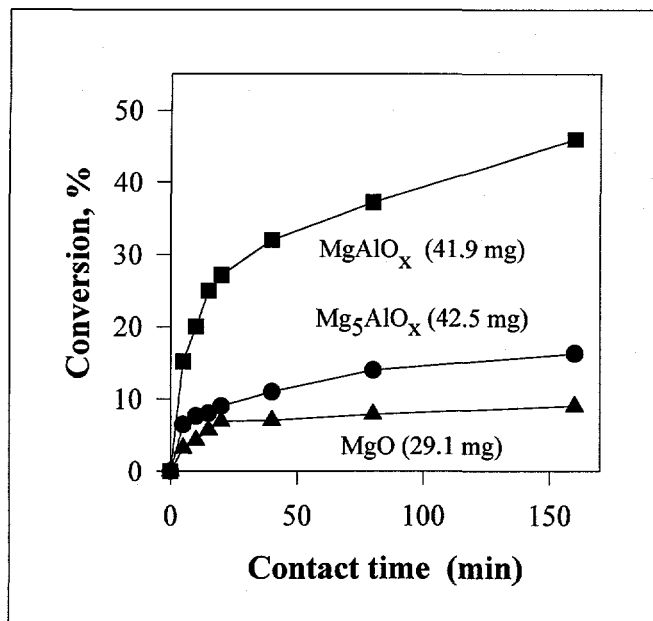
In a typical experiment, catalysts (30-40 mg) were charged into a gradientless batch reactor and pretreated in 10 % H<sub>2</sub> (balance He) at 623 K for 30 min. After the desired reaction temperature was reached, reactants were fed to the reactor. For the methanol decomposition reaction on MgAlO<sub>x</sub> and MgO catalysts, the feed gas composition was CH<sub>3</sub>OH/CH<sub>4</sub>/He = 2.6/2.4/89.5 (methane was used as an internal standard). The reaction was carried out at 573 K and 101.3 kPa in the recirculating reactor unit (RRU).

Reaction rates, expressed as mol/g<sub>cat</sub>-s, for each sample are shown in Figure 8. The initial rates of methanol consumption along with the catalyst properties are summarized in Table 5. CO<sub>2</sub>, CO and H<sub>2</sub> were the only products, and DME and hydrocarbons were not formed on pure MgO. CO<sub>2</sub> formed via methyl formate decomposition [8,9] or from carbonaceous deposits (C<sub>n</sub>H<sub>x</sub> oxygen deficient compounds) that remained on the surface. On Mg<sub>5</sub>AlO<sub>x</sub> and MgAlO<sub>x</sub> samples, DME, CO<sub>2</sub>, and CO were detected. DME was formed via dehydration of methanol on acid sites [8,9].

**Table 5.** Properties and rates of methanol conversion.

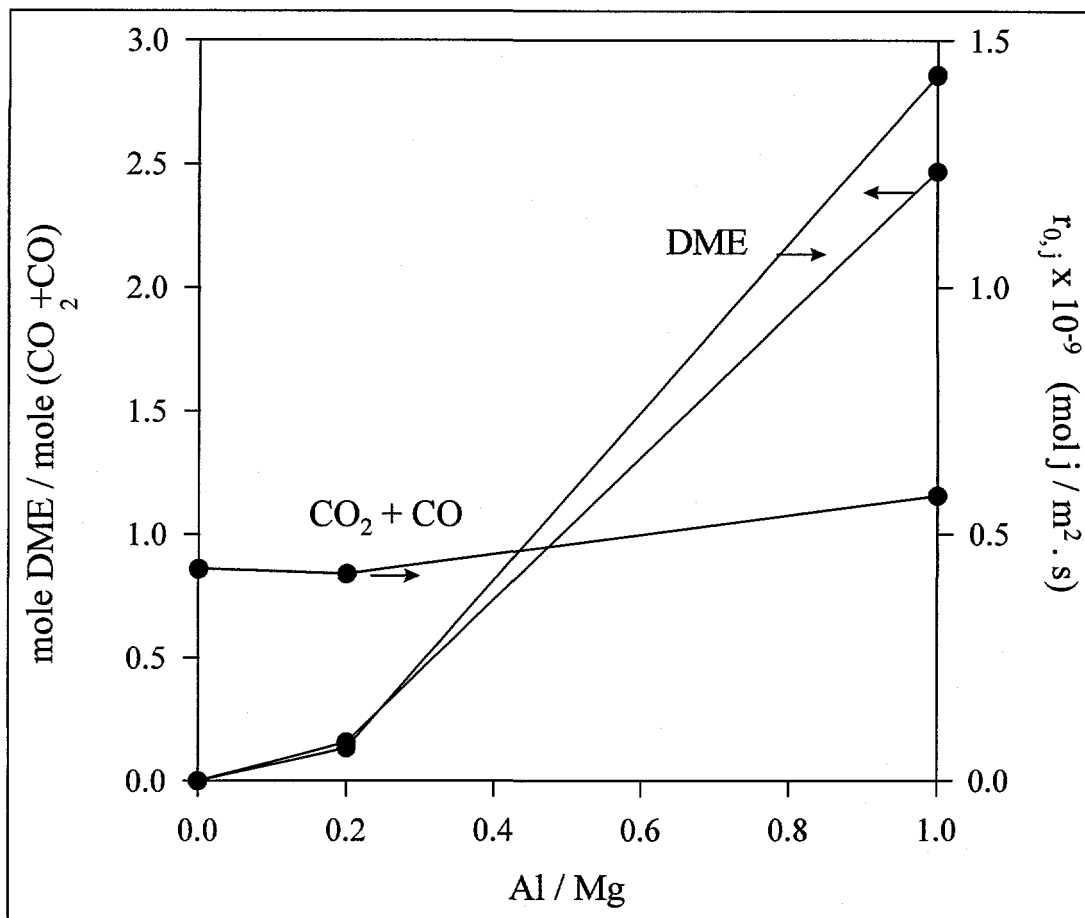
Catalyst	Al/Mg	K	S.A.	<sup>13</sup> CO <sub>2</sub> / <sup>12</sup> CO <sub>2</sub>	r <sub>0</sub>	r <sub>0</sub>
		wt. %	m <sup>2</sup> / g	exchange at 573 K	mol / g <sub>cat</sub> -s	mol / m <sup>2</sup> -s
				x 10 <sup>-6</sup> μmol / m <sup>2</sup>		
MgO	0	0.2	194	0.38	4.0 x 10 <sup>-6</sup>	2.1 x 10 <sup>-8</sup>
Mg <sub>5</sub> AlO <sub>x</sub>	0.2	0.02	184	0.10	2.7 x 10 <sup>-6</sup>	1.5 x 10 <sup>-8</sup>
MgAlO <sub>x</sub>	1	0.08	230	0.21	4.7 x 10 <sup>-6</sup>	2.0 x 10 <sup>-8</sup>

r<sub>0</sub> is the rate of methanol consumption, and is expressed in mol/g<sub>cat</sub>-s or mol/m<sup>2</sup> total.s.



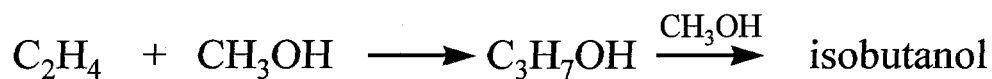
**Figure 8.** Methanol conversion as a function of contact time on different  $\text{MgAlO}_x$  catalysts. [ $T_r=573$  K,  $P_{\text{methanol}}=2.6$  kPa,  $P_T=101.3$  kPa].

The ratio of the initial rates of DME and  $\text{CO}_x$  formation as a function of Mg/Al ratio on different Mg-Al samples is shown in Figure 9. The DME/ $\text{CO}_x$  ratio increases monotonically with increasing Al content. This ratio reflects the relative number of acid and basic sites in the catalyst. Acid sites lead to DME and basic sites are responsible for  $\text{CO}_x$  formation. For  $\text{MgAlO}_x$ , the amount of DME produced is higher than  $\text{CO}_2$  and CO; whereas less DME and more  $\text{CO}_x$  formed on  $\text{Mg}_5\text{AlO}_x$  than on  $\text{MgAlO}_x$ , suggesting  $\text{MgAlO}_x$  is less basic and more acidic than  $\text{Mg}_5\text{AlO}_x$ . DME was only observed on Al-containing MgO samples, suggesting that Al cations increase the acidity of MgO.



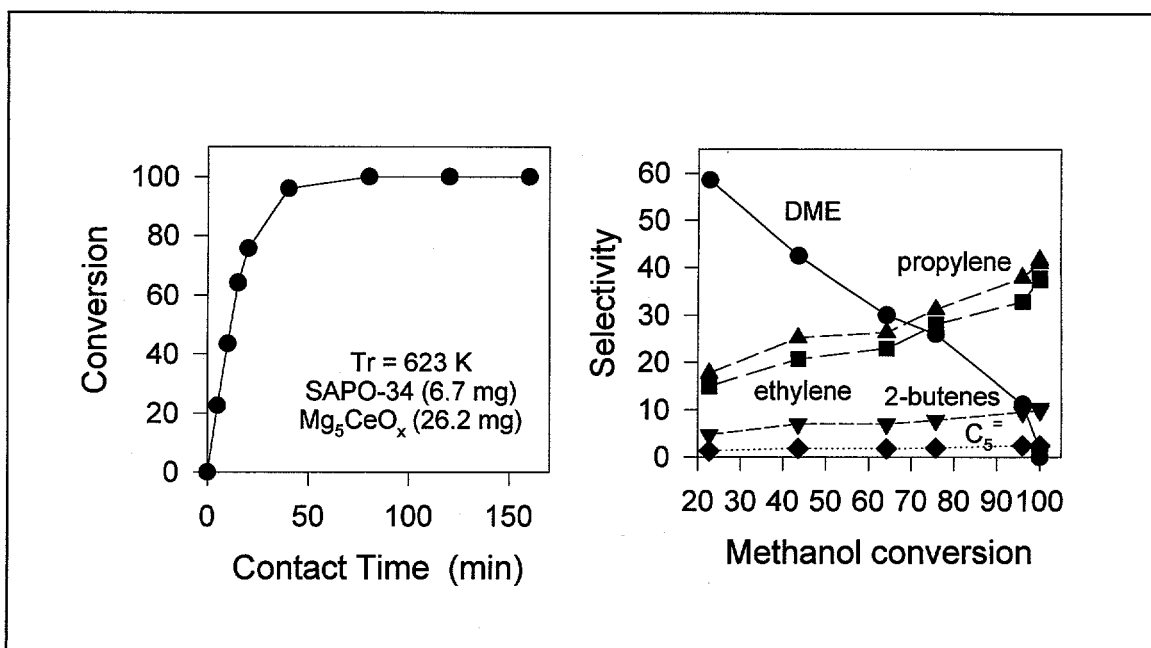
**Figure 9.** Methanol reaction on  $\text{MgAlO}_x$  catalysts: Effect of Mg/Al ratio on product distribution. [ $T_r=573$  K,  $P_{\text{methanol}}=2.6$  kPa,  $P_t=101.3$  kPa].

In recent Amoco patents [10,11], the following reaction was carried out on modified MgO catalysts for the synthesis of higher alcohols from methanol in the presence of ethylene:



It is known that SAPO-34 (acid catalyst) converts methanol to olefins (selectivity higher than 80% to  $\text{C}_2^-$  and  $\text{C}_3^-$ ) and MgO (base catalyst) catalyzes the condensation reactions between olefins and methanol to produce isobutanol [10,11]. It is possible to produce 1-propanol and isobutanol from methanol in one step by using a physical mixture of SAPO-34 and  $\text{Mg}_5\text{CeO}_x$ . To verify this, a physical mixture of SAPO-34 (6.7 mg) and  $\text{Mg}_5\text{CeO}_x$  (26.2 mg) was charged into a gradientless batch reactor and pretreated in 10 %  $\text{H}_2$

(balance He) at 623 K for 30 min. The feed gas composition was  $\text{CH}_3\text{OH}/\text{He} = 5.8/90.0$  kPa. The reaction was carried out at 623 K and 101.3 kPa in the recirculating reactor unit (RRU). The results are summarized in Figure 10.



**Figure 10.** Methanol reactions on a physical mixture of SAPO-34/ $\text{Mg}_5\text{CeO}_x$  (6.7/26.2 mg). a) Methanol conversion vs. contact time, b) product selectivity vs. methanol conversion [ $T_r=623$  K,  $P_{\text{methanol}}=5.8$  kPa,  $P_t=101.3$  kPa].

Methanol was predominantly converted to propylene and ethylene. Other products included DME, CO,  $\text{CO}_2$ , methane, ethane, propane, butane, pentane, 1-butene, 2-butene, and 1-pentene. The product distribution was similar to that obtained on pure SAPO-34 catalyst charge and no alcohols were detected. Neither isobutanol nor its precursor was observed. Methanol conversion to olefins was much faster than condensation reactions between olefins and  $\text{C}_1$  intermediate species.

Future work in the alcohol coupling reactions includes:

1. Competitive reactions between  $^{13}\text{CH}_3$ - $^{13}\text{CHO}$  and  $\text{CH}_3\text{CH}_2\text{OH}$ , to explain the rate of acetone in ethanol dehydrogenation and coupling reactions on  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  catalyst.
2. Reactions of  $^{13}\text{CH}_2\text{O}$  with acetaldehydes on different catalysts to explore the chain-growth ability of different materials.
3. Reactions between  $^{13}\text{CH}_2\text{O}$  and  $\text{CH}_3\text{CH}_2\text{CHO}$  on  $\text{Cu}_{0.5}\text{Mg}_5\text{CeO}_x$  catalysts.
4.  $^{13}\text{C}$ -tracer studies of methanol-acetaldehyde (or methanol-propionaldehyde) cross-coupling reactions in order to examine reaction pathways leading to chain growth and  $\text{C}_3$  oxygenates on catalytic materials described in the synthesis section.