

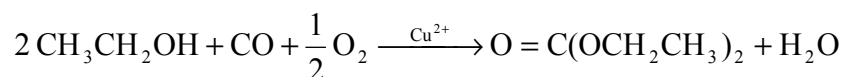
## Synthesis of Organic Carbonates as Possible Transportation Fuel Additives

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### Introduction

Acting on the counsel of the CFFLS Industrial Advisory Board (IAB) (given at a meeting held November 17, 1999), the University of Utah research team terminated a study of the synthesis of dimethyl carbonate (DMC) from methanol and carbon monoxide. The results of the DMC study (covering the period May 1, 1999 to approximately November 30, 1999) were reported at the national American Chemical Society meeting in San Francisco, CA on April 29, 2000. These results are published in a Fuels Division preprint.<sup>1</sup>

Diethyl carbonate (DEC) was judged by the IAB to be a more promising oxygenated diesel fuel additive than DMC because of the lower volatility and lower water solubility of DEC. The initial research question was: Can DEC be prepared from ethanol and carbon monoxide over a supported copper catalyst in a batch reactor in a manner similar to the synthesis of DMC? The balanced chemical equation describing the desired reaction is:



The answer to this initial research question is that the reaction does occur but with some unexpected wrinkles: 1) With a  $\text{CuCl}_2/\text{PdCl}_2$  heterogeneous catalyst (supported on activated carbon) and identical starting experimental conditions (except for using ethanol instead of methanol) one obtains about 20% as much DEC as DMC. 2) The DEC synthesis takes about four times as long to reach completion as the DMC synthesis. 3) There is a greater range of product species in the DEC synthesis than was encountered in the DMC synthesis. Thus mass spectrometry turns out to be a more useful tool for tracking the DEC synthesis than was the case in the DMC synthesis. The dominant byproducts of the DEC synthesis are acetaldehyde and ethyl formate. 4) Pretreatment of the  $\text{Cu}/\text{Pd}$  heterogeneous catalyst with one of several metal hydroxides greatly improves the reaction selectivity for the DEC product over acetaldehyde and ethyl formate.

### Experimental

**Catalyst preparation:** To approximately 10 g DARCO 20-40 mesh activated carbon one adds 100 mL of 3%  $\text{CuCl}_2$ , 0.25%  $\text{PdCl}_2$  methanolic solution. The mixture is refluxed for 4

hours with vigorous stirring. Subsequent drying is accomplished in a vacuum oven operated at 26 inches of mercury vacuum and 100 °C. When the effect of hydroxide on the catalyst selectivity for products is to be tested, a metal hydroxide methanolic solution is added to the above described catalyst and is refluxed for 4 hours before redrying in a vacuum oven.

***Batch reactor sample preparation:*** In a typical experiment 3.2 g ethanol (Absolute grade) are poured over the 0.5 g of heterogeneous catalyst sitting in the glass liner of a 625 mL stainless steel reactor. The lid is tightened with 6 bolts and carbon monoxide is admitted to a pressure of 1.7 atm at 25 °C. 3.4 atm of air also is admitted. The reactor is suspended in a preheated fluidized sandbath and the reaction temperature (typically 170 °C) is attained within 20 minutes.

***Product identification and quantitation:*** The first DEC synthesis experiments (in December, 1999) were greatly facilitated by a portable AVS-GC/MS detection system from the laboratory of Prof. Meuzelaar. [AVS stands for ambient vapor sampling.] A two meter long, 50 mm i.d., deactivated fused silica pressure reduction transfer line between the batch reactor and the GC/MS permits real-time monitoring of the volatile reaction products. Most of the experimental DEC data reported below were gathered by on-line GC monitoring with off-line GC/MS product identification after the portable GC/MS was moved by the Meuzelaar group to another experiment.

## **Results**

Better yields of the target DEC are obtained with the  $\text{CuCl}_2/\text{PdCl}_2$  on activated carbon catalyst than with any other heterogeneous catalyst, which we have tested so far, see Fig. 1. In all eight reactions the reaction begins with 3.6 mL of ethanol, a pressure of 1.7 atm of carbon monoxide, 3.4 atm of air, and 0.5 grams of heterogeneous catalyst.

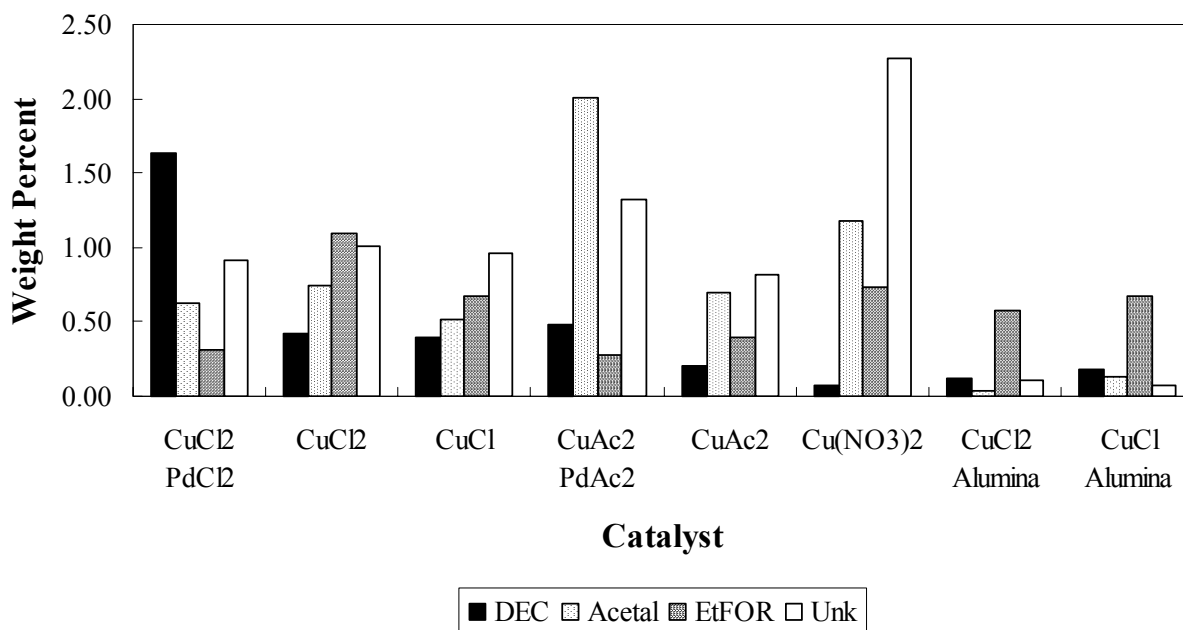
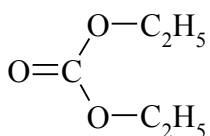
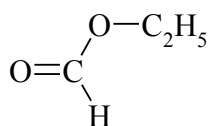


Figure 1. Comparison of product yields after 2 hours at 170 °C for several catalysts. In the first six experiments the support is activated carbon.

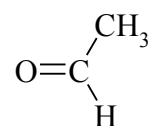
Several reaction products have the formulas shown below:



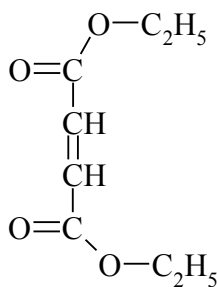
Diethyl Carbonate



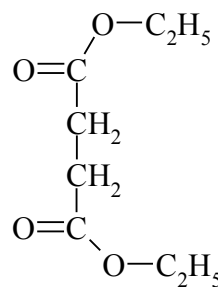
Ethyl Formate



Acetaldehyde



2-Butenedioic acid, diethyl ester



Butanedioic acid, diethyl ester

The influence of hydroxide pretreatment of the heterogeneous catalyst is illustrated in Fig. 2. The yield of the sought after DEC is considerably enhanced by any hydroxide which we have tried with the best results provided by Ba(OH)<sub>2</sub>. It is evident from the results of the last experiment in Fig. 2 that it is possible to have too much of a good thing: Five times as much NaOH largely shuts down the production of DEC.

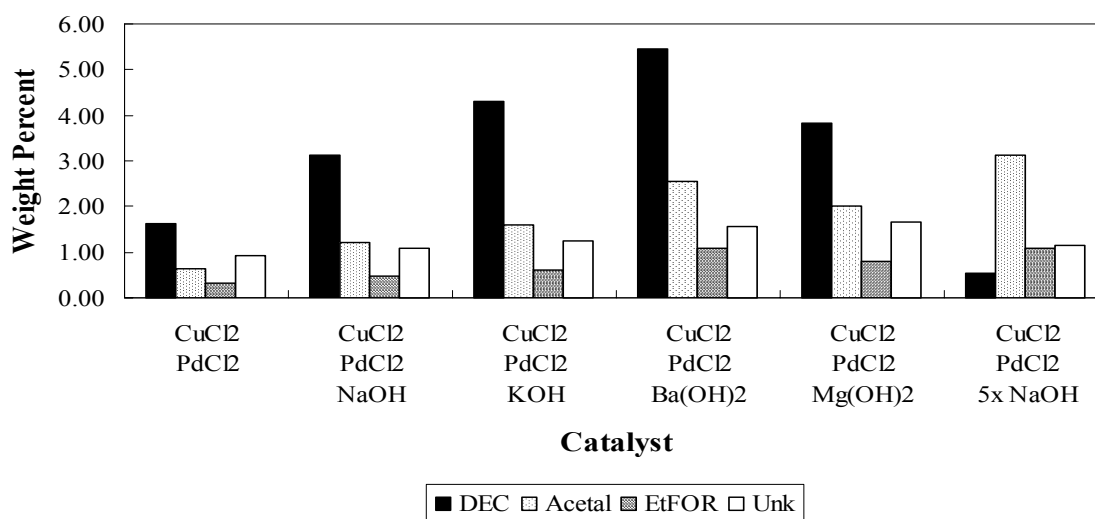


Figure 2. Comparison of product yields at 170 °C and two hours for catalysts pretreated with various metal hydroxides. Note the marked change in the magnitude of the vertical axis from that shown in Fig. 1

In addition to improving product yields the hydroxide pretreatment of the catalyst speeds up the production of DEC. This point is clarified by the time profiles in Fig. 3.

The University of Utah research team has made major strides in two other areas that promise to have a major impact on future research: 1) A flow-through microreactor has been constructed that will address many questions such as the importance of thorough mixing of reactants in the DEC synthesis. It was designed particularly to yield samples of spent heterogeneous catalysts that will be examined by solid state C-13 NMR. 2) A test diesel engine has been acquired and prepared for testing the impact of oxygenated fuel additives on cetane number and composition of engine exhaust.

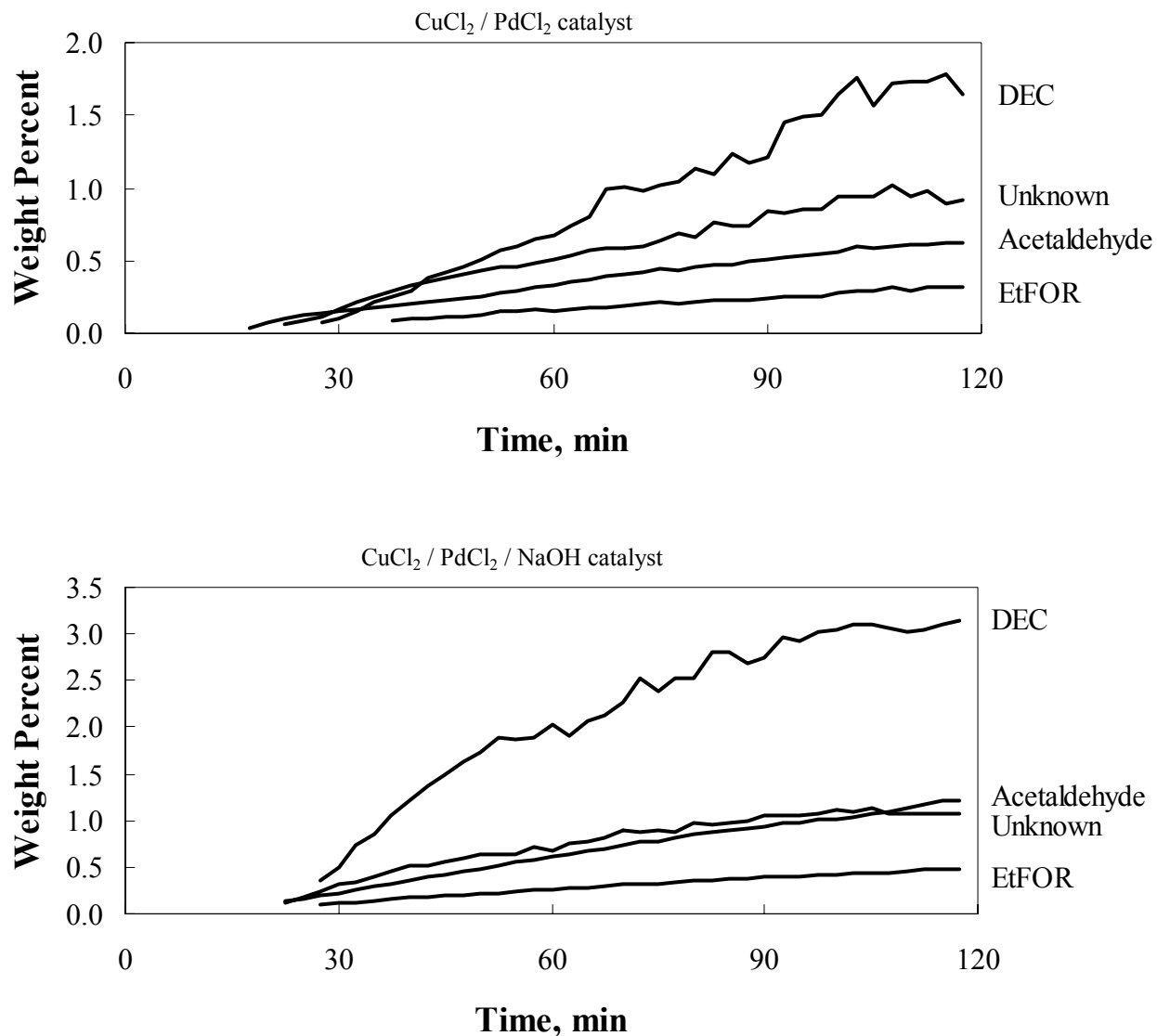


Figure 3. Typical time profiles of heterogeneous reaction showing that hydroxide speeds up the production of DEC.

### **Projections of Further Work**

There are many challenging questions left which merit attention. Some can be resolved more readily than others. Questions are listed below in approximate order of increasing difficulty.

1. What is the oxidation number of the copper species that is catalyzing DEC production?
2. Can better mixing of reactants improve the yield of DEC?
3. Is copper(II) hydroxide the actual catalyst that dramatically enhances selectivity for DEC production?

4. Can an aerogel (a porous glass) provide a better support than activated carbon for the copper clusters that catalyze DEC production?
5. What objective comparisons can be made of cetane number and particulate emissions of oxygenated fuel additives in a diesel engine that will rate DEC against a plethora of other candidate fuel additives?
6. Does the mix of oxygenated products from the copper catalyzed DEC synthesis (from ethanol and CO) work as well in a diesel engine as pure DEC does?
7. Is it true as some have contended that the functional groups in the various potential oxygenated fuel additive molecules are irrelevant to their impact on diesel engine performance and only weight of oxygen in the fuel matters?
8. Over how long a time in a continuous flow reactor will a supported Cu/Pd catalyst continue to put out a reasonable yield of DEC?
9. What are the chemical species left behind on a spent catalyst?

### **Personnel**

People who have participated in this team effort (listed in alphabetical order) are:

Genshan Deng (grad. student), Dr. Brian C. Dunn (post-doc), Dr. Jacek Dworzanski (visiting prof.), Dr. Edward M. Eyring (co-P.I.), Catherine Guenneau (visiting teacher from France), Dan Hopkinson (undergrad.), Dr. Jian Zhi Hu (post-doc), Henk L. C. Meuzelaar (co-P.I.), Jorg Pahnke (visiting grad. student from Germany), Dr. Ronald J. Pugmire (co-P.I.), and Dr. Sidney Thornton (post-doc).

### **References**

1. B.C. Dunn, J. Pahnke, D. Hopkinson, E. M. Eyring, G. Deng, J. Dworzanski, H. L. C. Meuzelaar, R. J. Pugmire, "Direct Observation of the Catalytic Production of Dimethyl Carbonate Using On-Line GC/MS," Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 45 (2), 283-287 (2000).