Synthesis and Testing of Diethyl Carbonate as a Possible Diesel Fuel Additive

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Typical automotive diesel engine exhaust contains substantial amounts of particulate matter (smoke). Addition of small amounts of oxygenated organic compounds to diesel fuel can diminish the amount of smoke emitted by the engine. A promising oxygenated compound for addition to diesel fuel is diethyl carbonate (DEC), $O=C(OCH_2CH_3)_2$, also called ethyl carbonate, carbonic acid diethyl ester, or Eufin. Its melting point is –43 ^oC, its boiling point is 126 ^oC, and its flash point is 25 ^oC. DEC is readily miscible with diesel fuel and will not phase separate. Its place in a "C-1 chemistry" program is secured by its synthesis from carbon monoxide and ethanol in the gas phase reaction

$$2\,CH_3CH_2OH + CO + \frac{1}{2}O_2 \xrightarrow{cat} O=C(OCH_2CH_3)_2 + H_2O$$

over a heterogeneous catalyst. Carbon monoxide and ethanol are both starting materials for DEC synthesis that can be produced in the huge quantities that would be necessary if DEC became the additive of choice for diesel automotive fuel in the U. S. A further significant advantage of DEC over other oxygenates such as MTBE is that DEC decomposes slowly to CO_2 and ethanol and therefore would not damage an aquifer if DEC accidentally entered the environment.

What we knew on May 1, 2001 was that $CuCl_2$ and $PdCl_2$ supported on activated carbon and subsequently impregnated with a methanolic $Ba(OH)_2$ solution yielded an active catalyst for DEC synthesis. Other reaction products included ethyl formate and acetaldehyde. Hydroxide added to the catalyst significantly improved selectivity for DEC production, but the yield of DEC did not exceed 20 %.

Results

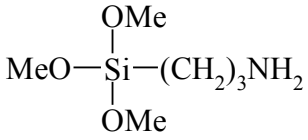
Accumulated since May 1, 2000 include the following:

1) Productive catalysts contain at least two forms of copper. This conclusion is drawn from XRD work done at West Virginia University (Seehra) in which both $CuCl_2$ and $Cu_2(OH)_3Cl$ are detected when the Cu/Pd catalysts are treated with hydroxide during preparation. This is further supported from our observations that kinetic curves, when non-hydroxide treated Cu/Pd catalysts are used, follow an ideal first order process and that when hydroxide treated Cu/Pd catalysts are used, the kinetics are more complex as shown in Figures 1 and 2. As the hydroxide is predicted to have no impact on the activated carbon support, its influence must be localized to the metal salts loaded onto the support prior to its use as a catalyst for the gas-phase oxidative carbonylation of ethanol.

2) Residence times in the flow reactor on the order of ten seconds are optimum for DEC production with longer residence times giving rise to more byproducts such as ethyl formate.

3) When the reaction is carried out at constant reactant composition and 150 ^{o}C, the yield of DEC is greater at higher pressures.

4) With a view to getting copper atoms in the catalyst less agglomerated, sol-gel silica has been used in place of activated carbon as the heterogeneous catalyst support. Starting materials include



the idea being that one amine will complex one copper ion. The sol-gel catalyst has been tried in the batch reactor, and DEC was detected by GC in the reaction products. The effect of changing counter-ions (to enhance DEC yield) and the incorporation of complexed palladium(II) into the sol-gel are both still under investigation.

5) The diesel engine has been moved to a building in downtown Salt Lake City (a little over two miles from the University) where it is being maintained and operated by employees of Prof. Adel Sarofim. Data on particulate matter in the exhaust from this engine operating under idling and load conditions began accumulating after April 30, 2001. Qualitatively, it is clear that DEC has the expected effect of drastically diminishing smoke in the exhaust under all operating conditions of the diesel engine.

Projections of Further Work

Questions that merit answers include the following:

1) Does the mixture of products from the Cu/Pd catalyzed reaction of CO and ethanol perform about as well as DEC when added to diesel fuel?

2) Can unreacted CO and ethanol be recycled efficiently in the DEC synthesis to improve the economics of the DEC synthesis?

3) What is the useful lifetime of the best Cu/Pd supported catalyst?

4) What are the species that remain adsorbed on the spent Cu/Pd supported catalyst?

5) Will a sol-gel supported cobalt catalyst (prepared in a similar manner as the Cu/Pd sol-gel catalyst) work well in a Fischer-Tropsch reaction?

Publications

1. B. C. Dunn, C. Guenneau, S. Hilton, E. M. Eyring, J. Dworzanski, H. L. C. Meuzelaar, J. Z. Hu, and R. J. Pugmire, "Production of Diethyl Carbonate from Ethanol and Carbon

Monoxide over a Heterogeneous Catalyst," Fuel Chemistry Division Preprints **2001**, *46* (1), 236, 237 [San Diego ACS Mtg.].

2. B. C. Dunn, C. Guenneau, S. Hilton, N. S. Rho, E. M. Eyring, J. Dworzanski, H. L. C. Meuzelaar, J. Z. Hu, and R. J. Pugmire, "Diethyl Carbonate Production from Ethanol and Carbon Monoxide," Fuel Chemistry Division Preprints **2001**, in press {Chicago ACS Mtg.].

3. B. C. Dunn, C. Guenneau, S. A. Hilton, J. Pahnke, E. M. Eyring, J. Dworzanski, H. L. C. Meuzelaar, J. Z. Hu, R. J. Pugmire, "Production of Diethyl Carbonate from Ethanol and Carbon Monoxide over a Heterogeneous Catalyst," in preparation.

Personnel

People participating in this team effort (listed in alphabetical order) are: Brian C. Dunn, Jacek Dworzanski, Edward M. Eyring, Catherine Guenneau, Emily Hieder, Steven Hilton, Kerry Kelly, Henk L. C. Meuzelaar, N. S. Rho, Ronald J. Pugmire, Sidney N. Thornton, David Wagner, and Guojin Wang.

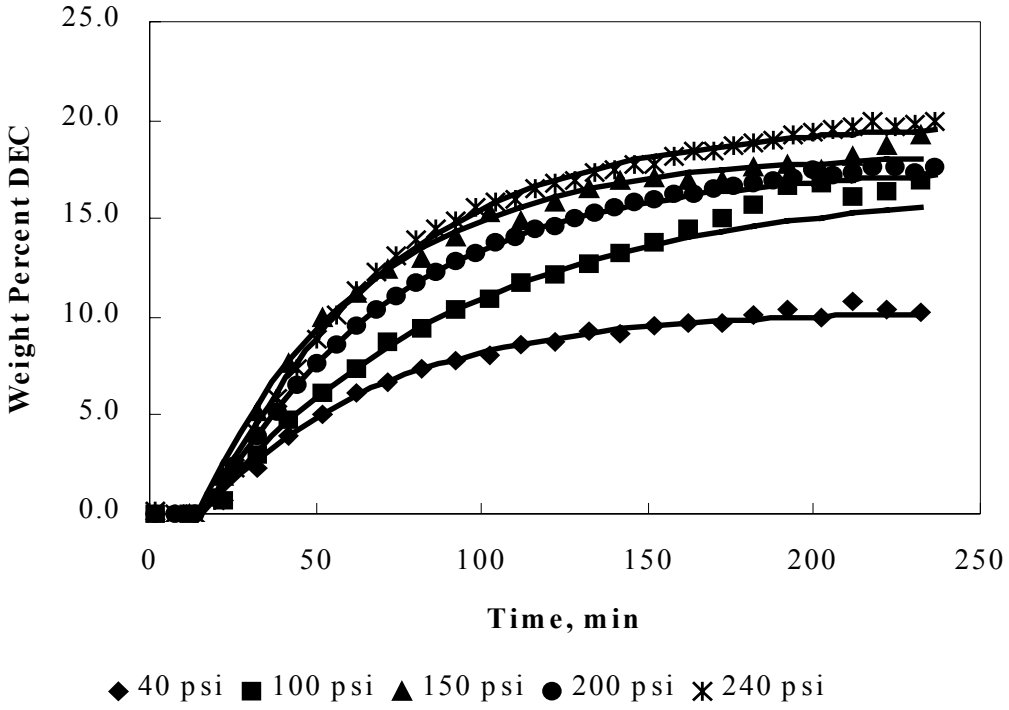


Figure 1. Evolution of DEC with varying amounts of CO. Other conditions: 0.5 g catalyst, 3.6 g EtOH, 60 psi air, 300 psi total pressure, 170 ^{o}C, 4 hrs. Curves are best fit first order kinetic traces.

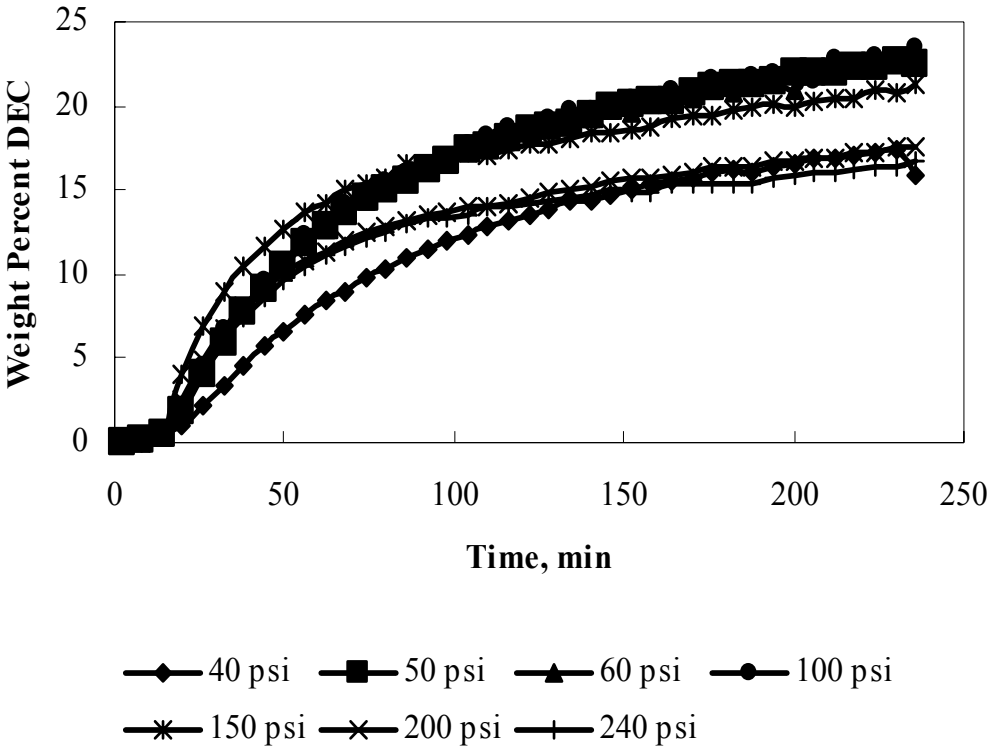


Figure 2. Evolution of DEC with hydroxide treated catalyst with varying amounts of CO. Other conditions: 0.5 g catalyst, 3.6 g EtOH, 60 psi air, 300 psi total pressure, 170 ^{o}C, 4 hrs. Traces do not obey first order kinetics.