

SYNTHESIS OF OXYGENATE PRODUCTS FOR HIGH-VOLUME FUELS APPLICATIONS

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BACKGROUND AND OBJECTIVES

Task 2.1 Investigate improved syntheses of dimethyl carbonate via oxidative carbonylation of methanol and/or dimethyl ether.

Liquid and gas-phase processes for synthesis of dimethyl carbonate (DMC) via Cu(II)-catalyzed oxidative carbonylation of methanol (MeOH) offer limited reactor performance as the result of the effects of water formed as a coproduct. Reactor water inhibits the catalytic reaction and limits reactant conversion to 30-40%⁽¹⁾. In halide-containing fixed bed catalyst systems water leaches halide away from the catalyst resulting in long-term deactivation and excessive corrosion of metallic reactor and downstream hardware components⁽²⁾. A major goal of this subproject is to limit water formation and improve reactor performance by incorporation of DME as a dehydrated methanol equivalent into the reactor feedstream. DME is less expensive to produce than MeOH on a methanol equivalent basis and its oxidative carbonylation to DMC would not produce water as a coproduct.

Task 2.2 Investigate upgrading of dilute acetylene-containing feedstreams via reactive extraction of acetylene with MeOH and/or DME to produce 1,1-dimethoxyethane, a useful liquid oxygenate fuel.

The liquid-phase reaction of acetylene with MeOH to yield 1,1-dimethoxyethane (DMOE) has long been known to occur in high yield via the action of strongly acidic catalysts in the presence of Hg(II) cocatalysts⁽³⁾. Conditions are necessarily mild in order to inhibit violent polymerization of acetylene. Little is known regarding the efficiency of this reaction carried out with feedstreams of dilute acetylene in nitrogen, hydrogen (from rapid coal or HC pyrolysis), or synthesis gas (from oxidative pyrolysis of methane or HC). An efficient reactive extraction of acetylene to DMOE would afford a value-added conversion of acetylene to a useful oxygenate fuel/chemical as well as an alternative to solvent extraction of the acetylene with a polar aprotic compound such as NMP. A goal of this subproject is to test this concept with methanol reactant and with DME/water as a low-cost methanol equivalent.

Task 2.3 Investigate upgrading of dilute acetylene-containing feedstreams via gas-phase conversion of acetylene with MeOH and/or DME to light alcohols.

A variety of methods have been reported regarding the conversion of acetylene in dilute feedstreams to useful oxygenate fuels/chemicals using conventional synthetic reactions and typically incorporating multistep pathways⁽⁴⁾. As a result of the complexity of these overall syntheses, they have not represented low-cost methods for utilization of dilute acetylene.

The patented gas-phase synthesis of light alcohols (propanol, i-butanol) via the saturated alcohol condensation of MeOH and EtOH with modified MgO catalysts was pioneered in our Amoco laboratories in the mid-80s⁽⁵⁾. Later this technology was extended to include the synthesis of light alcohols (including EtOH) from the condensation of MeOH and ethylene⁽⁶⁾. A goal of this subproject is to successfully achieve the condensation of MeOH and/or DME with dilute acetylene feedstreams to yield similar useful light alcohols products.

Task 2.4 Investigate new methods for direct conversion of dilute acetylene feedstreams to useful liquid oxygenate products.

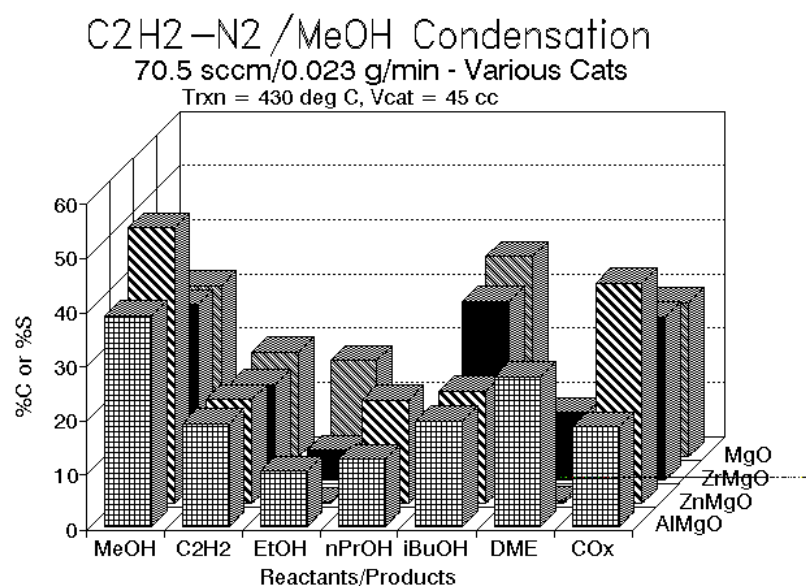
Direct conversions of acetylene in diluted process streams to useful products are little known in the literature and are limited mostly to conversion of acetylene to complex mixtures of aliphatic and/or aromatic hydrocarbons over solid acid catalysts. The direct conversion of dilute acetylene in synthesis gas to liquid oxygenates, especially with co-conversion of the synthesis gas, would represent a potentially valuable method for synthesis of high-value fuels/chemicals from a relatively inexpensive feedstream. A goal of this subproject is to test various acetylene-containing streams for conversion (in the presence of water as a co-reactant) to oxygenates with MgO-based condensation catalysts.

RESULTS AND DISCUSSION

Light Alcohols

Previous research at Amoco has uncovered novel and moderately high-yield gas-phase syntheses of n-propanol/i-butanol mixtures via gas-phase condensation of methanol with ethanol or ethylene over specially prepared MgO catalysts⁽⁵⁾. The most effective catalysts for these reactions were MgO materials prepared by low-temperature calcination (e.g., 450°C) of Mg(OH)₂. Catalysts prepared by other methods and/or those calcined at high temperatures (e.g., 538°C) exhibited lower activity. We now report an efficient and novel synthesis of mixtures of ethanol, n-propanol, and i-butanol from the condensation of methanol with acetylene utilizing similar catalysts. A key to this synthesis is a new catalytic reaction, reductive hydration of acetylene with methanol/water to yield ethanol, CO, and H₂. Reasonably high activity is obtained with dilute acetylene streams (e.g. 10 v/v% in N₂ or CO/H₂), and product formation is observed throughout a reaction temperature range of 370-450°C. In a typical example, a 2:1 mole ratio of methanol:acetylene is passed over a catalyst bed of MgO heated to 430°C at a GHSV of 100 hr⁻¹. Reactant conversion of methanol and acetylene was 57% and 32%, respectively; and carbon selectivity to ethanol, n-propanol, and i-butanol was 9%, 16%, and 34%, respectively. Carbon selectivity to CO was 23%. Reactant conversion is somewhat lower at lower reaction temperatures and significantly more ethanol is formed. Results at 430°C obtained with a variety of catalysts are shown in the graph.

Incorporation of low levels of aluminum into the catalyst composition does not significantly diminish its basic condensation activity, and yet imparts mild catalyst acidity and activity for alcohol-ether interconversion. Thus, with methanol/acetylene feed and a catalyst consisting of 1% Al₂O₃/MgO, similar reactant conversions were obtained (56% and 30%, respectively, under similar reaction conditions) and formation of methyl ether products was observed in addition to alcohols. In this example, selectivities to EtOH, nPrOH, and



iBuOH were 2%, 19%, and 20%, respectively. Selectivity to DME was 16% and selectivities to the methyl ethers of the C₂+ product alcohols were several percent each.

With the low-Al catalyst it is also possible to utilize DME in the feed and realize a net conversion of DME to higher products. With a feed consisting of DME:MeOH:H₂O reactant conversions were 11%, 24%, and 15%, respectively with 5%, 26%, and 27% selectivity to the three product alcohols, respectively.

Several modifications of the MgO catalyst were prepared and tested including Zn- and Zr-containing materials with metal loadings equivalent to the Al in the 1%_{Al}/MgO catalyst described above. For the condensation of MeOH with CH₂ the following general results are summarized for each catalyst: MgO provided a balanced distribution of alcohol products and exhibited higher selectivity to EtOH than the other catalysts. AlMgO provided a balanced distribution of alcohol products as well as low levels of their methyl ethers and moderate levels of DME formed via dehydration of MeOH. ZnMgO exhibited the highest reactant conversions (up to 67% MeOH conversion) and the highest activity for CO_x formation (up to 48%), probably via direct decomposition of methanol to CO_x. This catalyst exhibited higher selectivity to nPrOH than the other catalysts. ZrMgO yielded primarily iBuOH as the alcohol product with very low formation of the lower alcohols and some formation of DME, suggesting mild catalyst acidity in this material.

Dimethyl Carbonate Synthesis

A catalyst consisting of Cu/C (Darco active carbon), known to be active for the oxidative carbonylation of methanol/CO to DMC was found to be inactive for oxidative carbonylation of DME. At all conditions tested low levels of CO₂ was the only product detected. A catalyst consisting of Cu/AMSAC (an acidic molecular sieve) was also inactive and produced significantly more CO₂, suggesting that the sieve-supported Cu(II) species was more of a deep oxidation catalyst than the C-supported material. In the presence of a small amount of water added to promote initial hydrolysis of DME to methanol, the sieve-based catalyst generated a significant amount of MeOH in addition to the CO₂ but no DMC product. A third catalyst, consisting of an admixture of Cu/C and AMSAC was tested with DME/water feed. In this case methanol was formed but with no DMC production. Very little CO₂ was formed with this catalyst so returning the Cu(II) to the C support eliminated the deep oxidation activity.

Productive results were obtained with the admixture catalyst and with a DME/MeOH cofeed consisting of DME/MeOH/CO₂/O₂ (1/1.1/7.2/1.2 mole ratio). Throughout a 1100 minute test, carried out at 125 °C, conversion of DME was steady at 30-33%. Methanol conversion was **negative** at -20% to -30%, thus indicating net production of methanol via hydrolysis of DME. Two principle products, DMC and dimethoxymethane (DMM), were formed, each in about 50% selectivity, and methyl formate and methyl chloride were observed in trace quantities. We have calculated the net conversion of the total methoxy functionality in the feed to take into account the negative conversion (or production) of methanol. This value ranged from 10-16% over the course of the study. To our knowledge this finding represents the first known net conversion of DME to DMC in an oxidative carbonylation reaction.

The high production of DMM in this study was not anticipated. The formation of this compound, the dimethyl acetal of formaldehyde, suggests that some of the methanol has undergone conversion to formaldehyde and subsequently reacted with methanol to form the acetal. Acidic molecular sieves are well known catalysts for acetal formation, and this reaction would be heavily favored in a low-water reaction environment.

DMOE Synthesis

A variety of experiments were carried out in an attempt to determine the reactivity of DME/water for the synthesis of DME with superacid catalysts and Hg(II) cocatalysts. With a variety of BF₃-based catalysts and at conditions ranging from 20°C and ambient pressure to 40°C and 30 psig, no DMOE formation was observed and a significant amount of the acetylene was merely hydrated to acetaldehyde. In a separate experiment acetaldehyde and DME were tested as potential reactants for the DMOE synthesis, but no reaction was observed.

In contrast, methanol/acetylene was found to yield DMOE at high conversions of acetylene even when the acetylene was diluted down to 10% (v/v) in N₂ synthesis gas. In a typical experiment 10% acetylene in N₂ was sparged at ambient temperature and pressure into a methanolic solution containing BF₃ dimethyletherate and mercuric acetate over a period of 1100 minutes. Overall conversion of H₂C was 74% with >95% selectivity to DMOE. Conversion of methanol was 23%. Very similar results were obtained at the same conditions with a feedstream consisting of 10% acetylene diluted in synthesis gas (2:1 volume ratio of H₂:CO).

Conversion of Dilute Acetylene Streams

Dilute acetylene (10% v/v) in either N₂ or synthesis gas was found to undergo an interesting conversion to mixtures of acetaldehyde and ethanol with either a pure MgO catalyst or the AlMgO catalyst. Conversion of acetylene ranges from 5% at a reaction temperature of 375°C to 45% at 456°C. At the lowest reaction temperatures acetaldehyde is strongly favored with the MgO catalyst although the aldehyde/alcohol ratio diminishes as temperature is increased, suggesting an acetaldehyde reduction to ethanol that is more favorable with increasing temperature. In a typical experiment with the H₂/N₂ feed a 15% conversion of acetylene was obtained at a reaction temperature of 433°C with 55% selectivity to acetaldehyde and 33% selectivity to ethanol. The mechanism of acetaldehyde reduction to ethanol is not understood although it is suspected that hydride transfer from an adsorbed acetaldehyde species with resultant formation of a more highly oxidized C species (e.g., acetic acid) may be an important process. Formation of significant levels of CH₄, CO and CO₂ (3%, 6%, and 10% selectivity, respectively, at 456°C) suggest decomposition of the oxidized C species via decarboxylation or decarbonylation. Low levels of hydrocarbons up to 6% were observed in the product mixtures, especially at higher reaction temperatures.

Slightly different results were observed with acetylene feed diluted with synthesis gas. In this case low net conversions of CO (up to 5%) were obtained, and low levels of methyl ether products were observed, in addition to higher levels of CO than observed with the CH₂/N₂ feed. Thus, there is a slight indication that CO/H₂ might be involved in a reduction to methanol which, in turn, undergoes condensation and etherification to these products.

CONCLUSIONS AND RECOMMENDATIONS

Acetylene and methanol undergo a facile conversion to C₄ alcohols via the catalytic action of pure MgO (obtained by low-temperature calcination of Mg(OH)₂) or modified MgO-based catalysts containing other metallic oxides. Incorporation of Al into the MgO results in a catalytically active material that produces some etheric products, mostly DME. The AlMgO also catalyzes the conversion of DME in DME/methanol mixtures to similar products. Formation of CO as a coproduct suggests some of the methanol is consumed as a reducing agent in the overall conversion of acetylene to saturated alcohol products. In future research it would be desirable to utilize a feed consisting of acetylene diluted in synthesis gas and incorporate the synthesis gas as the reducing agent for this process. This would require additional catalyst development to

define a component that would catalyze reduction of acetaldehyde to ethanol with and/or CO under similar reaction conditions.

A traditional catalyst for the oxidative carbonylation of methanol and CO to DMC admixed with a mildly acidic molecular sieve catalyst allows for the oxidative carbonylation of DME/methanol mixtures to DMC. In these initial studies DMM is formed as a coproduct. Future research should focus on methods for controlling the DMC/DMM ratio and on methods to increase reactant conversion.

Attempts to utilize DME/H₂O as a reactant in an acid-catalyzed liquid-phase condensation reaction with acetylene did not produce DMOE as a product. However, it was found that methanol reacts readily with dilute acetylene streams to yield DMOE in high yield. Either synthesis gas or nitrogen is a useful inert diluent. A process variables study will be required to determine optimum reaction conditions for this synthesis.

Dilute acetylene in the presence of water undergoes a reductive hydration to ethanol via the catalytic action of an MgO catalyst. In nitrogen diluent acetaldehyde, formed as a coproduct, apparently acts a self-reducing agent for its conversion to ethanol and the observed CO_x products. It would be desirable to incorporate synthesis gas for this reduction and the reduction of CO to methanol under appropriate reaction conditions. This would allow for the direct conversion of acetylene-containing synthesis gas to C₂-C₄ alcohols.

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