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Selective Cobalt Catalyzed Synthesis of Acetaldehydedimethylacetale (AADMA)

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Abstract

Acetaldehydedimethylacetale (AADMA) is an important material for the synthesis of many kind of pharmaceuticals, fragrances and like the structurally related dimethoxymethane, it can be used as diesel additive to enhance fuels' cetane numbers. Structurally very similar tri-alkoxy alkanes are known to reduce soot emissions during the combustion process of diesel fuels, as known for most oxygenates.[1] The synthesis of AADMA from synthesis gas and methanol has been investigated rather sporadically. Most publications limit themselves to the homogenous route. Walter Reppe, a pioneer in high-pressure chemistry, first patented the direct synthesis of AADMA in 1953 in his publication "oxygen containing organic compounds". Wherein they reported that using Cobalt bromide or Cobalt iodide at elevated pressures led to high methanol conversions and selectivities of up to 77% towards AADMA.[2] Further optimizing this process led to a patent in 1955, where the addition of quartenary alkyl ammonium or phosphonium salts allowed to steer the reaction towards AADMA or other side products like acetic acid, methyl acetate or acetaldehyde by changing the ligand.[3] Long residence times were the major drawback of this reaction. In 1981 Korff et al. further optimized the process by using simple ligands like triphenylphosphine, reducing remarkably the residence times down to 1 h by promoting the catalyst with hydrogen iodide and nickel(II)salts.[4]

We herein present an experimental and theoretical investigation of the above-mentioned reaction using synthesis gas and methanol to generate AADMA. After screening several noble metal-promoted cobalt catalysts, we chose the gold-promoted cobalt catalyst for further investigation of this reaction. It showed enhanced activity (X_{CO} = 42%) at relatively low temperatures (T = 150 °C), pressures and displaying good selectivities towards AADMA (S_{AADMA} = 75%). Variation of reaction control, temperatures, solvents, pressures and CO to H_2 ratios gave interesting insight into the mechanism of the reaction. Furthermore, a broad study on the homogenous route has been conducted as well as a comparison with the results of the heterogeneous catalysts, giving a better understanding of ancillary processes like leaching and partial deactivation of the catalyst.

References:

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