

Homogeneous catalysts stabilized in ionic liquids for conversion of synthesis gas into fuel ethanol via homologation of methanol

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Introduction

Conversion of biomass-derived syngas into fuel ethanol using heterogeneous catalysis has been difficult to commercialize, in part, due to production of side products and especially low-value CH₄ that can consume 10% to over 50% of the CO in the syngas [1]. Homogeneous catalysis offers potential routes to improved selectivity; >99.9% long achieved in the industrial synthesis of acetic acid by the catalytic carbonyl anions, [RhI₂(CO)₂]⁻¹ and [IrI₂(CO)₂]⁻¹, that insert CO into methanol: CH₃OH + CO → CH₃COOH, which is often a critical step in the synthesis of ethanol. A major breakthrough in the field of homogeneous catalysis has been the discovery that a very wide variety of catalytic metals can be stabilized and atomically dispersed in ionic liquids or dispersed as small cluster compounds, maximizing utilization of precious metals. Furthermore, ionic liquids have emerged from laboratory curiosities and solvents for small-scale pharmaceutical synthesis into industrial chemicals, often considered the “green solvents” of the future, minimizing potential air pollution because of their negligible vapor pressure, which also allows distillation of volatile products.

The TDA strategy for ethanol synthesis has been to employ one homogeneous catalyst for rapid conversion of syngas into methanol as an intermediate; a second species for rapid CO-insertion into methanol to form acetic acid, and a species for homogeneous water-gas shift to remove undesired H₂O, while producing H₂ for synthesis [2]. It is preferred not to allow accumulation of acetic acid, in part, due to corrosion issues, and acetic acid is reacted as it forms with excess methanol to produce methylacetate: CH₃COOH + CH₃OH = CH₃COOCH₃ + 2H₂O, which is reduced to form ethanol: CH₃COOCH₃ + 2H₂ → CH₃CH₂OH + CH₃OH; the co-produced methanol being recycled to react with CO and acetic acid. By utilizing both water-gas shift and methanol homologation, less molecular H₂ leading to CH₄ need be added to the system; the overall reaction being: 2CO + H₂ + CH₃OH → CH₃CH₂OH + CO₂.

Many advances in homogeneous catalysis have employed nitrogen-based cations, and especially ammonium, imidazolium and pyridinium salts. Less well appreciated are the advantages of phosphonium ionic liquids that include higher thermal stability, high heat capacity, availability in tonnage quantities at modest cost, and novel catalytic routes involving superacids, superbases and phosphonium ylides and carbanions.

Materials and Methods

Phosphonium ionic liquids (Cytec, Inc., Strem Chemicals, Inc.) and homogeneous catalyst precursors are added to a Pyrex-glass liner of a laboratory-scale, high pressure, continuously stirred, batch reactor (Parr Model 4570) with working volume of 450 cm³, pressurized with pre-mixed syngas (GeneralAir) with varied molecular ratios of H₂/CO of 1/1 or ½ so as to yield pressures of 15-185 bar when heated to a preferred temperature of 220°C [2]. For homologation experiments, methanol is added (SigmaAldrich, reagent grade; ~0.05-

0.25 mol methanol/mol CO), and for homogeneous water-gas shift experiments, H₂ is eliminated and replaced with H₂O. Products are analyzed using three separate, calibrated gas-chromatography instruments (all SRI Models 8610C) with columns and detectors optimized for: 1) Ethanol and other oxygenates extracted into water (Column: Supelco, *Carbowax for Alcoholic Beverage/Fermentation Products in Water*; Detector: SRI Flame Ionization Detector-FID); 2) CH₄ and hydrocarbons (Column: Supelco, *Special Purpose Column for Light Hydrocarbons*, C₁-C₅; Detector: SRI Flame Ionization Detector), and 3) CO and CO₂ (Column: Supelco, *Molecular Sieve 5A/Chromosorb 102*; Detector: SRI Thermoconductivity Detector). Fourier Transform Infrared Spectroscopy (Nicolet Magna-IR Spectrometer 550) is used to examine ionic-liquid solutions, under ambient pressure and temperature, after reaction to identify stable transition-metal carbonyl anions from their characteristic carbonyl stretching frequencies in the range ~2120-1700 cm⁻¹.

Results and Discussion

The highest rate to ethanol achieved directly from syngas (no CH₃OH or H₂O added), while attempting to minimize CH₄ at optimized conditions of 220°C, a 1/1 molar ratio of H₂/CO and initial pressure of 157 bar (dropping to 117 bar after 12 h), was 0.57 mol ethanol/mol catalyst/h, which is comparable on a mass basis, to some of the best sulfided heterogeneous catalysts, but with loss of CO to CH₄ of only 1.8%, with minor 1-propanol as an additional side product. Rate to ethanol was greatly increased by addition of methanol, reaching 5.9 mol ethanol/mol catalyst/h using 0.2 mole methanol added to 0.83 mol CO and 0.83 mol H₂ at 220°C, albeit with losses to CH₄ increasing to 11.8%. Although added or accumulated methanol increases rate to ethanol, it also increases the loss to CH₄. A compromise using 0.05 mol of CH₃OH produced a rate to ethanol of 1.33 mol ethanol/mol catalyst/h, while reducing loss to CH₄ of 2.7%. The rate to ethanol increases linearly with methanol concentration, and the rate increases with syngas pressure. Loss to CH₄ decreases exponentially as pressure is increased. With homogeneous water-gas shift catalysis, ethanol formed without adding any H₂ to the system by the net reaction: H₂O + CO → CH₃CH₂OH + CO₂. Starting with 1.0 mol CO and 0.56 mol H₂O at 120 bar and 220°C, 0.20 mol CH₃OH intermediate formed at a rate of 1.71 mol methanol/mol catalyst/h and 0.00524 mol ethanol formed at a rate of 0.45 mol ethanol/mol catalyst/h, with 0.0019mol of acetic acid intermediate.

Significance

Homogenous catalysis offers potential new routes to production of fuel ethanol from renewable sources of CO + H₂. Selectivity of catalytic metals is enhanced by stabilizing in ionic liquids to form uniform carbonyl anions, and selectivity is further enhanced by operation at lower, uniform temperature in ionic liquids with high heat capacity minimizing thermal excursions.

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References

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