

Cyclic separation of pure hydrogen from synthesis gas via ethanol intermediate

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Introduction

Hydrogen is acclaimed as a promising future fuel alternative to gasoline. However it does not exist in its pure form on Earth and thus has to be produced. Reforming or partial oxidation of carbonaceous feed stocks represents a viable production alternative to energy intensive electrolysis of water. However, the hydrogen stream thus produced contains significant amounts of carbon monoxide which acts as a catalyst poison in low temperature fuel cells and therefore has to be removed. The current separation technologies suffer energy, material and investment cost issues.

This project proposes a novel cyclic separation process which produces high purity and possibly high pressure carbon monoxide and hydrogen streams. In the first step, incoming synthesis gas is used to hydrogenate acetaldehyde to ethanol, which can be easily condensed. A purified CO stream is also produced. In the second step of the cycle, ethanol is dehydrogenated back to acetaldehyde, again condensable specie that can be easily separated from hydrogen. A pure hydrogen stream is then obtained. Eventually, the CO exiting from the first step can be further water-shifted to produce second grade hydrogen.

Materials and Methods

Different supported and unsupported copper-based catalysts were prepared for the hydrogenation and dehydrogenation steps by impregnation and precipitation, respectively. Their activities, selectivities and long-term stabilities were studied in a conventional atmospheric fixed-bed down-flow quartz reactor with an on-line gas chromatograph. The reaction variables included temperature, catalyst loading and feed composition. The catalytic performance was evaluated based on ethanol/acetaldehyde conversion, hydrogen productivity and main/side products selectivities.

Results and Discussion

15% Cu supported on silica was found to yield the highest conversion in ethanol dehydrogenation. The catalyst was stable and conversion increased with increasing temperature up to 300°C. At 350°C, the catalyst was subject to quick deactivation caused by sintering of copper particles. Increase in ethanol conversion had an adverse effect on acetaldehyde selectivity, due to acetaldehyde involvement in subsequent reactions leading to C₄ species, particularly to ethyl acetate. Higher catalyst loading also resulted in higher ethanol conversion, however the reaction is equilibrium limited and therefore the optimum loading exist after which the conversion becomes unaffected by any additional increase. The water content in ethanol feed had no effect on ethanol conversion, but affected acetaldehyde selectivity. With increasing ethanol molar ratio, more acetaldehyde was converted to undesirable ethyl acetate. Hydrogen yield was in all cases unaffected by declining acetaldehyde yield as extra mole of

hydrogen is produced when ethyl acetate is formed. Figure 1 depicts results achieved at optimum reaction conditions for ethanol dehydrogenation.

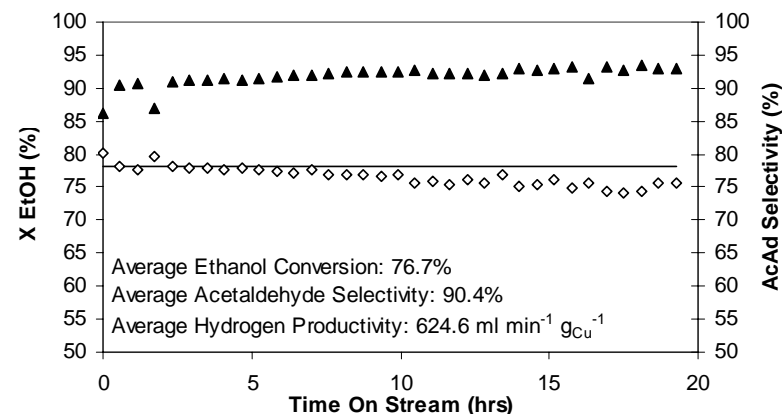


Figure 1. Acetaldehyde Selectivity (▲) and Ethanol Conversion (◇) compared to equilibrium conversion (-). Reaction conditions: 0.5g 15%Cu/SiO₂, 300°C, 0.1 MPa, 0.2 ml min⁻¹ of liquid 1:1 molar EtOH:H₂O feed.

The screening study for acetaldehyde hydrogenation is currently under way. Unsupported copper-zinc and copper-iron precipitated mixed oxides are compared to copper-zinc and copper-iron catalysts supported on high surface silica. The reaction is studied in the temperature range of 150-250°C, with CO:H₂ ratio 1:3 and with varying molar ratios of liquid acetaldehyde: water feed.

Significance

The proposed cycle represents a novel process that combines the advantages of low investment and operating costs, and which is versatile enough to accommodate different scales of operation. Adaptable to different sources of syngas, it can provide high-purity pressurized hydrogen to be used as a fuel for fuel cells, therefore contributing to reducing world's dependency on petroleum.