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ALCOHOL SYNTHESIS FROM CO OR CO₂

RELATED APPLICATIONS

In accordance with 35 U.S.C. sect. 119(e), this application claims priority to U.S. Provisional Application Nos. 60/751,144 filed 16 Dec. 2005 and 60/823,093 filed 21 Aug. 2006.

GOVERNMENT RIGHTS

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FIELD OF THE INVENTION

The invention relates to methods of alcohol synthesis, catalysts for alcohol synthesis, and systems for synthesizing alcohols. Methods of reacting alcohols are also included in some aspects of the invention.

INTRODUCTION

The Pd/Zn on alumina catalyst is known as a catalyst for the alcohol steam reforming reaction. See, for example, U.S. Published Patent Application 20040223908 and Iwasa et al., "Steam Reforming of Methanol over Pd/ZnO: Effect of the formation of Pd/Zn alloys upon the reaction," Appl. Catal. A: General 125 (1995) 145-147. The mechanism for steam reforming and dehydrogenation of methanol are discussed in Takezawa et al., "Steam Reforming and dehydrogenation of methanol: Difference in the catalytic functions of copper and Group VIII metals," Cat. Today, 36 (1997) 45-56. Although the mechanism for the synthesis of alcohols from CO₂ over Pd/Zn is not known, the mechanism over Cu/ZnO is discussed by Fujita et al. in "Mechanisms of Methanol Synthesis from Carbon Dioxide and from Carbon Monoxide at Atmospheric Pressure over Cu/ZnO," J. Catal. 157, 403-413 (1995).

The synthesis of ethanol and higher alcohols from CO₂ is possible via the use of composite catalysts that include a Fisher-Tropsch catalyst. Inui and Yamamoto, in "Effective synthesis of ethanol from CO₂ on polyfunctional composite catalysts," Catalysis Today vol. 45, pp. 209-214 (1998), reporting using a combination of catalysts, either mixed or in series, to synthesize ethanol and higher alcohols.

SUMMARY OF THE INVENTION

In one aspect, the invention comprises the staged reaction of hydrogen with C₁⁺ oxygenates to form C₂⁺ oxygenates. The staging can either be conducted along the length of a microchannel; and/or by reacting C₁⁺ oxygenates with hydrogen in a first microchannel or first section of microchannel, followed by providing additional hydrogen and again exposing the reaction mixture to reaction conditions in a microchannel. "Reaction conditions" include the presence of a catalyst at a suitable temperature. In some preferred embodiments, the reaction involves the staged addition of hydrogen to a feed stream comprising CO. As alternatives to staging hydrogen, CO and/or CO₂ can be added in a stagewise fashion; likewise C₁⁺ oxygenates can be added in a staged fashion; furthermore, mixtures of these, such as a mixture of H₂ and CO₂ can be added in a stagewise fashion to a microchannel reaction channel (also called microchannel reaction chamber). In preferred embodiments, the microchannel reaction chamber comprises an alcohol synthesis catalyst as described herein. Microchannel apparatus for staging other

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reactions is known and such apparatus can be adapted for the inventive processes. For example see, U.S. Published Patent Application 2006/0129015 by Tonkovich et al. (synthesis of hydrogen peroxide) and U.S. Pat. No. 7,442,360 also by Tonkovich et al; which are both incorporated herein.

In another aspect, the invention provides a method of synthesizing alcohols comprising: contacting hydrogen and CO over an alcohol catalyst in a microchannel. This method is further characterized by any of the results described herein. For example, at CO conversions of at least 20%, the method surprisingly results in a selectivity to C₂⁺ oxygenates (preferably selectivity to ethanol) of at least 30%, more preferably at least 40%, and still more preferably at least 50%, and in some embodiments a selectivity of 40 to about 60%, in some embodiments up to about 56%. This can be compared with a selectivity reported in the literature of only 20%. Preferably, the process is conducted at a relatively high throughput, such as a GHSV of at least 1000 h⁻¹, more preferably at least 3000 h⁻¹, in some embodiments 2000 to 100,000 h⁻¹, in some embodiments 2000 to about 4000 h⁻¹. The use of a microchannel reactor enables highly exothermic CO hydrogenation reaction to be operated in an isothermal mode to achieve high productivity. Integration of a catalyst in a microchannel reactor allows hydrogenation to alcohols at high throughput and high space time product yield and surprisingly increased product selectivity. Heat flux from the reaction microchannel is preferably at least 5 W/cc, and in some embodiments is in the range of 5 to 8 W/cc, where the "cc" volume is the volume of the reaction chamber (i.e., the portion of the microchannel where catalyst is present in either a flow-by or flow through configuration. The catalyst may further include a Fisher-Tropsch catalyst to increase production of ethanol and higher alcohols.

In another aspect, the invention provides a method of synthesizing alcohols from CO comprising: flowing a reactant gas mixture comprising CO and H₂ into contact with a catalyst; wherein the catalyst comprises Pd and Zn dispersed on alumina; and forming an alcohol or alcohols. In some embodiments, the alcohol or alcohols formed in the step of forming an alcohol or alcohols consists essentially of methanol. The catalyst may further include a Fisher-Tropsch catalyst making it possible for the alcohol or alcohols to contain substantial amounts of ethanol and higher alcohols.

In a further aspect, the invention provides a new method of synthesizing alcohols from CO₂ comprising: flowing a reactant gas mixture comprising CO₂ and H₂ into contact with a catalyst; wherein the catalyst comprises Pd and Zn dispersed on alumina; and forming an alcohol or alcohols.

In a related aspect, the invention provides a method of synthesizing ethanol and higher alcohols from CO₂ comprising: flowing a reactant gas mixture comprising CO₂ and H₂ into contact with a catalyst; wherein the catalyst comprises: (a) Pd—Zn alloy dispersed on alumina and (b) a Fisher-Tropsch catalyst; and forming ethanol and higher alcohols.

In another aspect, the invention provides a method of synthesizing C₂⁺ oxygenates comprising: a first step of subjecting a Rh- or Pd-containing composition to a RedOx treatment to form a catalyst; then, in a subsequent step, contacting a C₁⁺ oxygenate with hydrogen in the presence of the catalyst to form a C₂⁺ oxygenate. The step of contacting a CO₁⁺ oxygenate with hydrogen in the presence of the catalyst is preferably conducted in a microchannel. Rh catalysts are preferred because of their greater selectivity. Rh on silica is particularly preferred. A RedOx treatment comprises a first step of reducing the Rh-containing (or, less preferably, the Pd-containing) composition at elevated temperature. Reduction is preferably carried out in the presence of hydrogen. A