TPSR studies of Rh-based catalysts designed for ethanol synthesis from biomass-derived syngas

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Introduction

Ethanol derived from biomass is a renewable source of energy. Ethanol can be used either as an energy carrier or a fuel additive. Virtually all ethanol in the US is produced biochemically, primarily by the fermentation of corn. An alternative route is the thermo-chemical conversion of biomass to syngas, then conversion of the syngas to ethanol. This route might be more desirable because it allows the use of a wider range of biomass feedstocks, such as corn stalks, forest residues and animal wastes.

Rhodium-based catalysts have been found to be most selective for the formation of C_2 oxygenates from the hydrogenation of CO [1]. CO_2 hydrogenation to ethanol, another possible reaction from syngas, is thought to go through a CO intermediate[2] so the conversion of a biomass derived syngas to ethanol involves CO hydrogenation. Thermodynamics have shown that ethanol selectivity is very low unless the formation of methane can be eliminated. To this end, we have studied the effects of Fe, Mn, and Li promoters on alumina and titania supports to examine their effects on the hydrogenation of CO to ethanol on Rh-based catalysts.

Materials and Methods

Rh-Mn-Li-TiO_2 and Rh-Fe-Al_2O_3 catalyst was prepared using conventional impregnation method while a Rh-Al_2O_3 (Alfa Aesar) was used for comparison. Temperature programmed surface reaction (TPSR) of CO-H_2 was conducted at 20 bar by adsorbing CO on the catalyst at room temperature (RT) and ramping the temperature under H_2 flow using a fixed bed micro reactor system equipped with a residual gas analyzer for product analysis. The m/z = 31 signal was used to follow ethanol in the product gas. In all runs, the relative intensities of m/z = 31, 45 and 46 followed those for ethanol [3]

Results and Discussion

Figure 1 shows the profiles of CO-H_2 TPSR carried out at 20 bar on Rh-Mn-Li-TiO_2, Rh-Fe-Al_2O_3 and Rh-Al_2O_3. While atmospheric TPSR shows no sign of alcohol formation on all the catalysts, the TPSR at 20 bar showed ethanol peaks at different temperatures: 255°C, 278°C and 300°C for Rh-Mn-Li-TiO_2, Rh-Fe-Al_2O_3 and Rh-Al_2O_3 respectively. Rh-Mn-Li-TiO_2 gives the highest intensity suggesting it has the highest alcohol activity among the three catalysts. The methane (mass 16) peaks (not shown) appeared at temperatures just higher than those for ethanol, on each catalyst, suggesting that ethanol was formed prior to methane, possibly due to increased CO dissociation activity compared to CO insertion at the higher temperatures. This suggests that a mix of dissociated and non-dissociated CO is necessary for CO-insertion and hence ethanol formation. The CH_4 peak temperatures indicate the highest CO dissociation activity because CO dissociation is very rapidly followed by hydrogenation of carbon to CH_4 on Rh-based catalysts [4]

Significance

Suitably promoted Rh-based catalysts improve ethanol formation from syngas.

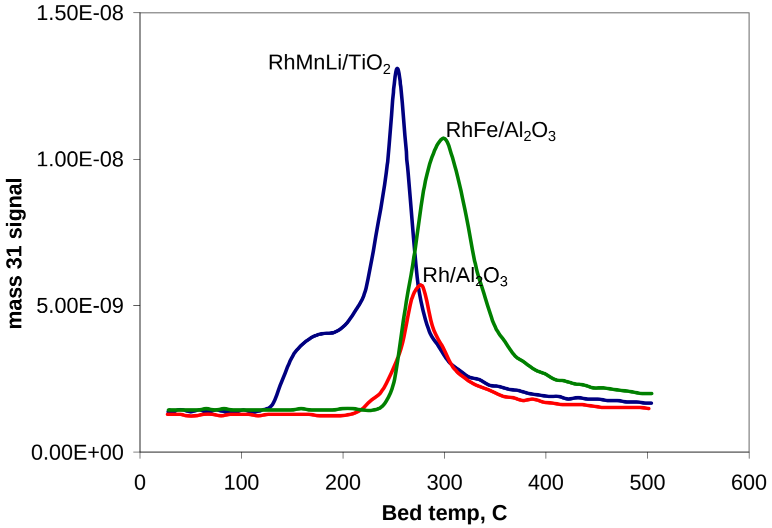

Figure 1. CO-H_2 TPSR profiles of Rh-Mn-Li-TiO_2, Rh-Fe-Al_2O_3 and Rh-Al_2O_3 at 20bar

References

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