

# Effect of Promoters on the Mechanistic Aspects of CO Hydrogenation on Rh/SiO<sub>2</sub>

Jia Gao, Xunhua Mo, and James G. Goodwin, Jr.<sup>1\*</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, SC 29631 (USA)

\*jgoodwi@clemson.edu

## Introduction

The hydrogenation of CO to form hydrocarbon and oxygenated products has been investigated by a lot of research since the 1920s, but it was not until the 1980s that the high ability to selectively produce C<sub>2+</sub> oxygenates of Rh-based catalysts was discovered[1]. Since ethanol is the major fuel additive and a promising fuel alternative, Rh catalyzed CO hydrogenation has been attracting intense attention these years.

The purpose of this study was to probe the mechanism of CO hydrogenation on Rh-based catalysts and the role of different promoters by kinetics analysis. Although there has not been much research concerning the mechanisms of CO hydrogenation on Rh-based catalysts, the thorough studies of Fisher-Tropsch Synthesis on cobalt or nickel may provide a good start for understanding reaction on Rh. Some researchers believe that CO first dissociates to adsorbed carbon and oxygen atoms [2] while others suggest the CO dissociation would be assisted by hydrogen to form the COH or CHOH species on the surface [3-5]. In order to understand the mechanism of CO hydrogenation on Rh-based catalysts at low reaction pressure, a power rate law in the form of  $r = Ae^{-E_a/RT} P_{H_2}^x P_{CO}^y$  can be used. SSITKA was also employed to identify the surface active sites, which leads to a better understanding of the effects of the promoters.

## Materials and Methods

For the catalysts referred to as Rh/M/SiO<sub>2</sub> (M = La or V promoter), silica gel was first impregnated with the aqueous solution containing the precursor of the promoter and then calcined in static air at 500°C for 4 h, followed by impregnation with a Rh(NO<sub>3</sub>)<sub>3</sub> aqueous solution and calcination at 500°C for 4 h. Rh-M/SiO<sub>2</sub> represents a catalyst prepared by co-impregnation. Numbers in parentheses following the symbol for an element indicate the weight percent of that element based on the weight of the silica gel support.

CO hydrogenation was performed in a fixed-bed differential reactor with length ~300 mm and internal diameter ~5 mm. The catalyst (0.3 g) was diluted with inert  $\alpha$ -alumina (3 g) to avoid channeling and hot spots. The catalyst and inert were loaded between quartz wool plugs and placed in the middle of the reactor with a thermocouple close to the catalyst bed. Prior to reaction, the catalyst was heated to 500°C (heating rate ~10°C/min) and reduced with hydrogen (flow rate = 50 mL/min) for 1 h. The catalyst was then cooled down to reaction temperature and the reaction started as gas flow was switched to a H<sub>2</sub>-CO mixture. A schematic diagram and the detailed configuration of a SSITKA reaction system such as used in this study

have been shown elsewhere [6]. The effluent gas was analyzed by an online gas chromatograph and a quadruple mass spectrometer equipped with a high-speed data-acquisition system.

## Results and Discussion

By fitting the results into the power law equation, the apparent orders for the partial pressure of CO and H<sub>2</sub> are shown in Table 1. The orders with respect to CO are negative while H<sub>2</sub> are positive, which may suggest that CO adsorbs preferentially on the Rh and inhibits the adsorption of hydrogen. The SSITKA results indicate that the addition of La may decrease the activity of adsorbed CO, which may explain why the CO orders appear to be more negative in Table 1 for Rh-La/SiO<sub>2</sub>. For Rh/V/SiO<sub>2</sub>, the addition of V decreased CO chemisorption, leading to a decrease in y. The fact that x shows an opposite trend may be because H<sub>2</sub> adsorbed on/near V assists CO dissociation or further chain growth, thus, the reaction rate shows a higher dependency on H<sub>2</sub> partial pressure.

**Table 1. Rate parameters<sup>a</sup> for CO conversion, CH<sub>4</sub> and EtOH formation**

Catalysts	CO Conversion <sup>b, c</sup>		CH <sub>4</sub> Formation <sup>b, c</sup>		C <sub>2</sub> H <sub>4</sub> Formation <sup>b, c</sup>		C <sub>3</sub> H <sub>8</sub> Formation <sup>b, c</sup>		EtOH Formation <sup>b, c</sup>	
	x	y	x	y	x	y	x	y	x	y
Rh(1.5)/SiO <sub>2</sub>	0.55	-0.26	1.03	-0.67	0.61	-0.35	0.07	-0.11	1.02	-0.13
Rh(1.5)-La(2.6)/SiO <sub>2</sub>	0.65	-0.49	0.97	-0.79	0.47	-0.41	0.15	-0.22	0.93	-0.57
Rh(1.5)/V(1.5)/SiO <sub>2</sub>	0.84	-0.31	1.35	-0.71	0.88	-0.41	0.61	-0.26	1.09	-0.22
Rh(1.5)-La(2.6)/V(1.5)/SiO <sub>2</sub>	0.88	-0.37	1.37	-0.74	0.80	-0.40	0.65	-0.32	1.17	-0.45

<sup>a</sup> Error = ±10% of the value measured.

<sup>b</sup> The parameters for each catalyst are determined by fitting a power-law rate expression of the form  $r = Ae^{-E_a/RT} P_{H_2}^x P_{CO}^y$

<sup>c</sup> The parameters are measured at 230°C.

## Significance

By studying the mechanism of the CO hydrogenation, it would shed some light on how the promoters influence the rate and selectivities. Then, a series of Rh-based catalysts can be designed to achieve the aim of this project--improving the ethanol production.

## References

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