

# A Comparison of Rh and Base Metal Catalysts for the Conversion of Syngas to Ethanol

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## Introduction

Catalytic synthesis of ethanol from syngas derived from coal or biomass provides an energy-efficient route to relieve the demand for imported crude oil [1, 2]. Rh-based catalysts have been shown to have relatively high activity for the synthesis of C<sub>2</sub>-oxygenates due to the unique carbon monoxide adsorption behavior on Rh [3, 4]. Non-noble metal-based catalysts include modified methanol synthesis catalysts based on Cu-ZnO/Al<sub>2</sub>O<sub>3</sub>, modified Fischer-Tropsch synthesis catalysts based on Co, Fe and Ru, and Mo-based catalysts [1, 2]. The main challenge in the heterogeneous catalytic processes for converting syngas to ethanol is the low yield and poor selectivity using most known catalysts due to the complicated required reaction characteristics.

Although extensive research has been carried out to search for an efficient catalyst and to investigate the effects of supports and promoters for the conversion of syngas to higher oxygenates, few studies have been done with respect to the catalytic nature at the atomic level of different catalysts for the oxygenate synthesis from syngas. The focus of this work was to compare the characteristic of CO hydrogenation on Rh- and Fe-based catalysts using various characterization techniques including *in situ* FTIR spectroscopy and steady-state isotopic transient kinetic analysis (SSITKA).

## Materials and Methods

Catalysts were prepared by sequential or co-impregnation of silica gel with an aqueous solution of Rh(NO<sub>3</sub>)<sub>3</sub> or Fe(NO<sub>3</sub>)<sub>3</sub> hydrate and aqueous solutions of promoter precursors to incipient wetness, followed by drying at 90°C for 4 h and then at 120°C overnight before being calcined in air at 500°C for 4 h. The catalytic activities were tested in a fixed bed reactor at 230°C and 1.8 atm using a H<sub>2</sub>/CO ratio of 2.

A Nicolet 6700 FTIR spectrometer equipped with a Harrick DRIFT (diffuse reflectance infrared Fourier transform) cell was employed for the IR study. The sample was reduced *in situ* at 500°C in a flow of H<sub>2</sub> for 0.5 h, followed by He flushing at 500°C for 0.5 h. After cooling down to the desired temperature in He, a background spectrum was taken, then the reactant gas flow was started to the cell and the infrared spectra were taken. A SSITKA system as described elsewhere [5] was used for isotopic reaction analysis. Isotopic transient measurements were carried out after reactions reached steady state.

## Results and Discussion

As presented in Table 1, non-promoted Rh/SiO<sub>2</sub> showed relatively low activity and low selectivity towards C<sub>2</sub><sup>+</sup> oxygenates. It could also be seen that the addition of different

promoters to Rh/SiO<sub>2</sub> could significantly improve the activity and selectivity of a Rh catalyst for the synthesis of ethanol from CO hydrogenation. The better performance observed for the multiply-promoted Rh/SiO<sub>2</sub> suggested that the addition of a single promoter may not fulfill all the characteristics required for a catalyst to carry out CO hydrogenation to make ethanol.

Fe/SiO<sub>2</sub>, La-promoted Fe/SiO<sub>2</sub> and commercially available Fe-containing spinel-typed catalysts all exhibited poor selectivity towards C<sub>2</sub><sup>+</sup> oxygenates. From the IR study, it was found that the behavior of CO adsorbed on different catalysts was very different. SSITKA also suggested that the surface reaction parameters varied significantly on different catalysts during CO hydrogenation. One possible problem related to Fe-based catalysts for ethanol synthesis may be that Fe has high ability in CO dissociation and chain growth, making CO insertion (an importance step for the formation of oxygenates) less feasible.

**Table 1. Comparison of catalytic activities for CO hydrogenation**

Catalyst	SS Rate (umole/g/ s) <sup>a</sup>	Selectivity (%)					
		CH <sub>4</sub>	C <sub>2</sub> <sup>+</sup> HC	MeOH	Acetalde hyde	EtOH	Other C <sub>2</sub> +oxy
Rh(1.5)/SiO <sub>2</sub>	0.03	48.1	28.7	1.2	6.5	15.6	0
Rh(1.5)-Fe(0.8)/SiO <sub>2</sub>	0.14	47.1	15.8	15	2.5	18.3	1.3
Rh(1.5)- La(2.6)/V(1.5)/SiO <sub>2</sub>	0.28	14.4	51.8	2.9	7.1	21.6	2.2
Rh(1.5)-Fe(0.8)- La(2.6)/V(1.5)/SiO <sub>2</sub>	0.21	17.3	35.4	5.0	6.6	33.2	3.2
Fe(1.6)/SiO <sub>2</sub>	0.11	22.2	67.4	3.8	1	4.9	0.8
Fe(5.0)-La(2)/SiO <sub>2</sub>	0.50	23.0	69.2	3.7	0.4	2.8	1.6
(Fe, Cr)(Fe, Co) <sub>2</sub> O <sub>4</sub>	0.03	31.4	56.0	6.7	0	5.8	0
(Mn, Cu)(Fe, Mn) <sub>2</sub> O <sub>4</sub>	0.05	12.6	80.0	2.1	0	5.3	0

<sup>a</sup> Catalyst: 0.3 g; Inert :  $\alpha$ -alumina 3 g; Pretreatment: 500°C in 30 mL/min H<sub>2</sub>;

Reaction conditions: T = 230°C, P = 1.8 atm, flow rate = 45 mL/min (H<sub>2</sub>/CO = 2), data taken at 15 h after steady state reached; experimental error:  $\pm$ 5%.

## Significance

Unlike costly Rh-based catalysts, non-noble metal-based catalysts could be prepared using inexpensive precursors, which offers possibilities for making ethanol from syngas more economic. By comparing the characteristics of Rh-based and Fe-based catalysts, this study provides insights for the improvement of the catalytic performance of non-noble metal-based catalysts for the ethanol synthesis.

## References

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