

# EXAFS and FT-IR characterization of Mn and Li promoted titania-supported Rh Catalysts for CO Hydrogenation

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## Achievement

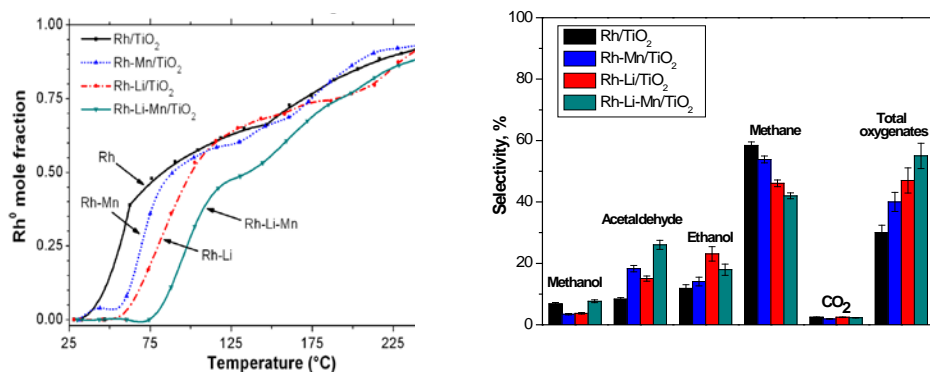
We have investigated the effect of Li and Mn promoters on the structure and selectivity of supported Rh catalysts for CO hydrogenation reaction. The use of alkali promoters has been shown to enhance oxygenate formation by suppressing the hydrogenation activity of Rh, which can lead to the undesired C<sub>1</sub> products (methane and methanol).<sup>1</sup> In our studies, the presence of a promoter slightly decreases the Rh clusters size, however no evidence for an electronic effect induced by the presence of Li and Mn was found. Higher turnover frequencies were found for the single promoted catalysts, which also showed the lower dispersion. The Li promoter introduced a weakened CO adsorption site that appears to enhance the selectivity to C<sub>2</sub>+ oxygenates. The selectivity to C<sub>2</sub>+ oxygenates varies inversely with the reducibility of Rh metal, that is, the lower the Rh reducibility, the higher the selectivity.

## Significance

The catalytic hydrogenation of carbon monoxide into ethanol provides an opportunity to produce a transportable liquid that can be used as a fuel additive, or reformed to produce hydrogen for fuel cells. However, catalytic conversion of syngas to ethanol suffers from yield limitations since methane is the most thermodynamically favorable product. Rh-based catalysts are the most widely studied class of catalyst for hydrogenation of CO to higher oxygenates.<sup>2</sup> This work presents experimental evidence of the effect of promoters on the structure of Rh-based catalyst and how it correlates with their catalytic properties. X-ray absorption near edge spectroscopy coupled with temperature programmed reduction studies show that Li and Mn promoters decrease the reducibility of supported Rh, which correlates strongly with increased selectivity to oxygenates. Fourier Transform Infrared Spectroscopy (FTIR) shows different modes of CO adsorption when Li is added as a promoter. We propose that the observed changes in selectivity are due to interfacial sites between the Rh and the promoter phase. Furthermore, the balance between CO insertion and CO dissociation/hydrogenation (which leads primarily to methane) can be altered depending on the nature of the promoter.

(1) Spivey, J. J.; Egbebi, A. A. *Chemical Society Reviews* 2007, 36, 1514.

(2) Forzatti, P.; Tronconi, E.; Pasquon, I. *Catalysis Reviews-Science and Engineering* 1991, 33, 109.



X-ray absorption results ( left) show that Li and Mn promoters decrease the reducibility of supported Rh, which correlates strongly with increased selectivity to ethanol ( right).

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