

## Ethanol Steam Reforming over a Ni/Mg-Al Mixed Oxide Catalyst

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### Introduction

The production of hydrogen or syngas from renewable, biologically derived feedstocks, such as ethanol, can lessen the demand for, and reliance upon non-renewable fuels. Biologically derived ethanol is a prime candidate since it is produced by the fermentation of a wide variety of carbohydrate sources, which can be obtained from dedicated agricultural products or agricultural and forestry byproducts. Steam reforming of ethanol has been investigated over a wide variety of supported metal catalysts. Supported nickel catalysts have shown good activity, H<sub>2</sub> and CO<sub>2</sub> selectivities however exhibit deactivation typically through coking mechanisms. Our group has found that Mg-Al mixed oxide supported nickel catalysts give improved steam reforming product selectivity and catalyst stability (reduced deactivation) compared to the pure oxide supported catalysts.

This study reports on the effect of temperature, residence time, and feed composition on ethanol conversion, selectivity, catalyst stability, and provides insight into the probable reaction mechanisms.

### Materials and Methods

Performance experiments were carried out in a quartz tube fixed bed reactor over an in-house prepared 10 wt% Ni/Mg-Al mixed oxide catalyst at reaction temperatures ranging 375-650°C, H<sub>2</sub>O:EtOH feed ratios of 1:1 to 8.4:1, and GHSV of 66,000 to 2,500,000 mL<sub>Feed</sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> at atmospheric pressure. The product gas composition was determined by an on-line GC. Catalysts were reduced in situ at 750°C in 200 mL min<sup>-1</sup> with 10% H<sub>2</sub>/N<sub>2</sub>. The prepared catalyst has been characterized prior to and after reaction by several techniques including BET, XRD, TPR, TPD-CO<sub>2</sub>, TPD-NH<sub>3</sub>, and TPO/TGA.

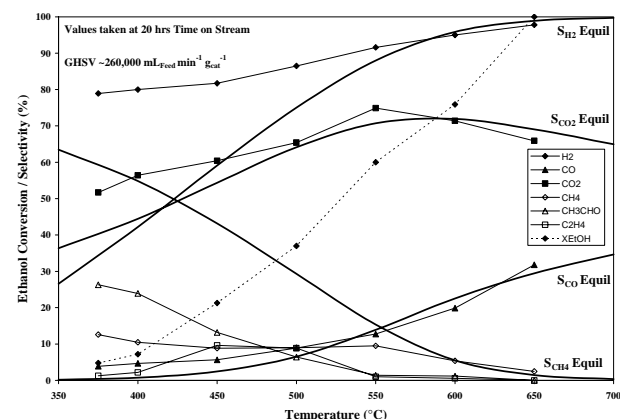
### Results and Discussion

Loss in catalytic activity was observed at all reaction conditions. Deactivation had only a minor effect on product selectivity; most significantly affected was C<sub>2</sub>H<sub>4</sub>. C<sub>2</sub>H<sub>4</sub> selectivity exhibited a nonlinear relationship with time on stream and ethanol conversion suggesting that it was associated with catalyst deactivation.

Figure 1 shows the effect of reaction temperature on product selectivity and ethanol conversion. Ethanol conversion increased monotonically with increasing temperature and attained 100% at 650°C. For temperatures up to 500°C, H<sub>2</sub>, CO, and CO<sub>2</sub> selectivities exceeded equilibrium expectations while CH<sub>4</sub> selectivity was significantly below its equilibrium expected values. It should be noted that C<sub>2</sub>-species, C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>CHO, present in the product stream below 600°C are not thermodynamically favorable at these conditions for temperatures above 200°C. For temperatures above 550°C, product selectivity closely followed equilibrium expectations even with incomplete ethanol conversion. Residence time experiments at 550°C

revealed that steam-reforming products (H<sub>2</sub>, CO, CO<sub>2</sub>) dominated the product gas even at low residence times and ethanol conversions of approximately 10%.

These observations suggest a complex, competitive surface mechanism in which the rate-limiting step occurs early in the mechanism. This is consistent with the findings of ethanol adsorption and decomposition on Ni single crystals. Ethanol decomposition on Ni (111)<sup>1</sup> and (100)<sup>2</sup> proceeded through an ethoxy intermediate and the rate limiting step was found to be the C-H bond scission of the  $\alpha$ -carbon resulting in the formation of surface CH<sub>3</sub> and CO species. At low temperatures, the methyl group would be expected to recombine with surface H and desorb as methane since it is thermodynamically favorable. However, as shown in Figure 1, significant deviation from equilibrium at low temperatures suggests a different mechanism. The authors propose that the most probable route is the rapid dehydrogenation of the methyl group to adsorbed carbon followed by steam gasification forming CO<sub>2</sub> and H<sub>2</sub>.



**Figure 1.** Effect of reaction temperature on ethanol conversion and product selectivity. H<sub>2</sub>O:EtOH = 8.4:1, GHSV = ~260,000 mL<sub>Feed</sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, P = 1 atm, Time on stream = 20 hours. Equilibrium data was obtained by Gibbs' free energy minimization ignoring elemental carbon using AspenPlus 12.1.

### Significance

This work provides insight into the reaction mechanism governing the steam reforming of ethanol over supported nickel catalysts. Of specific relevance is the deviation of H<sub>2</sub> and CO<sub>2</sub> selectivity from equilibrium at low reaction temperatures.

### References

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2. Johnson, S.W., and Madix, R.J. *Surf. Sci.* 115, 61-78 (1982).