Highly Stable Catalysts for Ethanol Steam Reforming

Ayman M. Karim, James J. Strohm, Vanessa Lebarbier, Guosheng Li,
David King and Yong Wang
Pacific Northwest National Laboratory, Richland WA 99354

Introduction

In an effort to reduce pollutants and green house gas emissions, hydrogen is seen as a promising energy carrier. Hydrogen use, either in a fuel cell or in an internal combustion engine, produces water as the only product. However, in order to move forward towards a hydrogen economy, hydrogen production from renewable sources is required. Ethanol can be produced by the fermentation of biomass and therefore is a renewable source. Steam reforming of ethanol has gained a lot of interest in the past few years and several catalyst systems have been found promising (e.g. Rh/Ce-Zr and Co/ZnO). Catalyst deactivation, mainly due to active site blockage by carbonaceous deposits [1, 2], is a major obstacle hindering commercial practicability. Catalyst supports with high oxygen storage capacity and oxygen mobility (e.g. CeO_2 and CeO_2-ZrO_2) have been studied in an effort to reduce the rate of coking and catalyst deactivation [1, 2]. For cobalt based catalysts, several groups suggested that Co^{2+} might be playing a role in increasing the catalyst stability and selectivity to CO_2 [3, 4].

In this work, we studied two different catalyst systems for ethanol steam reforming, namely Co-based and Rh-based catalyst systems. The aim of the work is to develop a highly stable catalyst for steam reforming of ethanol by studying the factors leading to catalyst deactivation. We show that catalyst deactivation can be minimized by controlling the properties of the support, mainly oxygen mobility and stability under reducing conditions. We also studied the effect of changing the ratio of Co/Co^{2+} on the Co-based catalyst selectivity and stability.

Materials and Methods

$Rh/Ce_{0.9}Pr_{0.1}0_2$, Rh supported on yttria stabilized ceria, Co/ZnO, Co/ZrO_2 and Co/MgO, were prepared by either impregnation or co-precipitation. The catalysts were characterized by *in situ* Raman spectroscopy, *in situ* XPS, XRD, TEM, temperature programmed reduction, temperature programmed oxidation and H_2 chemisorption. Reactivity measurements for steam reforming of ethanol were performed in a packed-bed reactor. Ethanol partial pressure was varied between 0.056 and 0.13 atm. The reactor effluent was analyzed by an online HP 5890 using an FID detector and an Agilent micro-GC using a TCD detector.

Results and Discussion

Figure 1 shows ethanol conversion with time on stream for three different Rh-based catalysts. The most stable catalyst was the 2% Rh/CePr owing to its high dynamic oxygen storage capacity. The dependence of catalyst deactivation rate on support properties (oxygen mobility and oxygen storage capacity) will be discussed. Co/ZnO catalysts showed higher CO_2 selectivity (and lower CH_4 selectivity) but lower activity than Rh based catalysts, as shown in Figure 2. The catalyst selectivity changed drastically during the first few hours, we attribute the change to reaching an equilibrium Co/Co^{2+} ratio. The effect of Co/Co^{2+} ratio on catalyst activity and selectivity was studied and will be discussed. Finally, we will discuss advantages and disadvantages of both catalyst systems for hydrogen production from ethanol under realistic reaction conditions.

Significance

We show that for the Rh-based catalyst, deactivation can be mitigated by balancing the activity of the support and that of the noble metal. For the Co-based catalyst, control of Co oxidation state distribution is important for maximizing activity and selectivity.
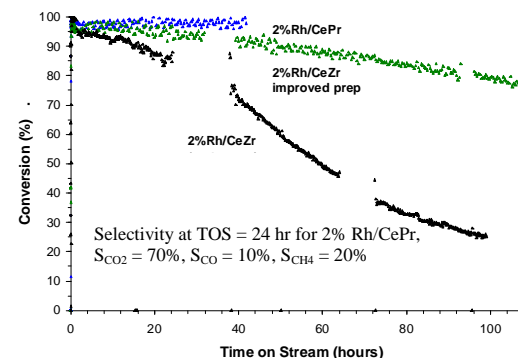

Figure 1. Conversion of ethanol on 2 wt% Rh on different supports. 25 mg catalyst diluted with 125 mg SiC. T= 550 °C, N_2:C_2H_5OH:H_2O = 9:1:8 molar, space velocity = 1.2 $mol_{EtOH}/_{gcat}$/hr, selectivity at time on stream = 24 hr for the 2% Rh/CePr was, S_{CO2} = 70%, S_{CO} = 10%, S_{CH4} = 20%.
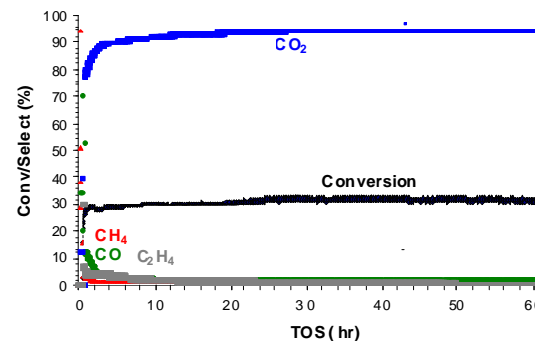

Figure 2. Ethanol conversion and product selectivity on 10% Co/ZnO, 100 mg diluted with 500 mg SiC. T = 450 °C, N_2:C_2H_5OH:H_2O = 0.5:1:8 molar, sv = 0.278 $mol_{EtOH}/_{gcat}$/hr.

References

1. Platon, A., Roh, H.S., King, D.L., and Wang, Y. *Top. in Catal.* 46(3-4), 374 (2007.).
2. Roh, H.S., Platon, A., Wang, Y., and King, D.L. *Catal. Lett.* 110(1-2), 1 (2006.).
3. Tuti, S. and Pepe, F. *Catal. Lett.* 122(1-2), 196 (2008.).
4. Vargas, J.C., Libs, S., Roger, A.C., and Kiennemann, A. *Catal. Today* 107-08, 417 (2005.).