Designing reforming catalysts for biomass derived syngas conditioning for fuel synthesis

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Introduction

The efficient thermochemical gasification of biomass to syngas for liquid fuels production requires the use of a catalytic steam reforming process to remove tars. This approach to produce clean syngas additionally maximizes the use of the biomass carbon and hydrogen content. The catalysts used in the steam reforming reactor can comprise a significant portion of the overall process cost to produce biofuels. In order to reduce the catalyst cost and improve the overall fuel synthesis economics, highly active and stable catalysts are required. To achieve this goal, we are using rational catalyst design to understand, design, and synthesize robust, multi-functional catalysts capable of handling biomass-derived impurities such as tars, polyaromatic hydrocarbons (PAHs), and H_2S. Results of catalyst performance are discussed.

Materials and Methods

The catalysts were prepared via incipient wetness impregnation. The support material consisted of a hard, attrition-resistant spray dried alumina designed for operating in a fluidized bed reactor (CoorsTek). The catalyst preparation parameters that were varied included Ni, Mg, and K content and the addition of a 2nd metal. These compositions were based on commercial reforming catalyst compositions that demonstrated good reforming performance but attrited significantly under fluidized bed operations. Five sets of NREL catalysts were created with low, medium, and high levels of magnesium oxide and potassium oxide. Each set had a different nickel loading. A sixth set consisted of four catalysts containing a second metallic species. Precursor materials used in the preparation of these catalysts comprised nitrate salts: Ni $(NO_3)_2\cdot6H_2O$, Mg $(NO_3)_2\cdot6H_2O$, and KNO_3 (Alfa Aesar). One step impregnation of the supports was conducted with addition of an aqueous solution of the salts to incipient wetness followed by calcination in air at 650 °C for two hours to convert the salts to oxides. Prior to use, all catalysts were reduced in flowing hydrogen at reaction temperature (850 °C).

Reaction experiments to assess catalyst steam reforming activity were conducted with 1) ethylene as a surrogate tar, 2) ethylene in model syngas containing hydrogen sulfide, and 3) ethylene after steam regeneration in a microactivity test system (MATS)[1] equipped with a rapid scanning gas chromatograph (Varian Micro) that measured permanent gases, hydrocarbons, and sulfur species contained in the process gas. Steam regeneration and hydrogen reduction were conducted after each reforming reaction to regenerate the sulfided catalyst surface and reduce NiO to Ni, respectively, prior to evaluating further reforming performance. Regeneration was conducted at 850 °C in steam for 1 hour with subsequent reduction occurring at the same temperature in 10% H_2 in He for 1 hour. Initial performance was obtained in pure ethylene and differential performance in model biomass derived syngas containing CO, CO_2, H_2, CH_4, C_2H_4, and C_6H_6.

Results and Discussion

Results from the initial catalyst screening phase are summarized in Table 1. In general, catalysts doped with magnesium oxide performed better than those without magnesium oxide. Those catalysts with a ratio of NiO:MgO of ~2:1 showed higher conversion of ethylene than catalysts with the same NiO content and other MgO loadings. The previously studied NREL Catalyst 32a, which has been used with raw syngas, was used as a benchmark to compare catalyst activity for the initial screening phase. The addition of other metallic species improved catalyst regenerability after reaction in hydrogen sulfide.

Table 1: Ethylene conversion obtained with varied Ni-alumina steam reforming catalysts.

Catalyst	% C_2H_4 Conversion[1]	% C_2H_4 Conversion[2]	% C_2H_4 Conversion[3]	% C_2H_4 Conversion[4-5]	
Cat 34a	30	20	18		
Cat 34b	19	19	48		
Cat 34c	52	70	95		
Cat 34d	37	37	37		
Cat 34e	96	43	100		
Cat 34f	91	37	69	85	78
Cat 34g	80	30	87		
Cat 34h	82	21	82		
Cat 34i	78	16	76		
Cat 34j	94	55	30		
Cat 34k	86	58	95		
Cat 34l	88	38	92		
Cat 34m	98	73	100	87	90
Cat 34n	95	49	NA	88	82
Cat 34o	93	53	100	78	90
Cat 35a	79	12	79		
Cat 35b	68	20	71		
Cat 35c	61	8	60		
Cat 35d	82	16	82		
Cat 32a	97	13	98	83	79

[1] Steady state ethylene steam reforming [2] in 20 ppmv H_2S; [3] after steam regeneration and hydrogen reduction; [4] in model syngas; and [5] in model syngas after regeneration from reforming with 20 ppm H_2S.

Significance

This work demonstrates the optimum composition of a fluidizable Ni-Mg-K-alumina catalyst for reforming tars contained in biomass derived syngas.

References

1. Magrini-Bair, K., Czernik, S., French, R., Parent, Y., Chornet, E., Dayton, D., Feik, C., Bain, R. Applied Catalysis 318, 199-206 (2007).