

## ETHANOL DRY REFORMING FOR H<sub>2</sub>-RICH SYNGAS PRODUCTION OVER Ce-Ni/Al<sub>2</sub>O<sub>3</sub> CATALYST

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### ABSTRACT

The transformation of greenhouse gas, CO<sub>2</sub> to fuels using heterogeneously catalytic processes has received significant attention due to the depleting petroleum resources, associated environmental problems and stringent environmental regulations. CO<sub>2</sub> reforming of CH<sub>4</sub> is considered as a suitable method for producing syngas to substitute petroleum-based energy. However, CH<sub>4</sub> is an unrenewable resource and will probably be depleted next century. Thus, there is requirement of an alternatively sustainable and green approach for H<sub>2</sub> synthesis. The production of H<sub>2</sub> from ethanol dry reforming seems to be a promising method since it utilizes both bio-derived ethanol regarded as renewable resource and undesirable CO<sub>2</sub> as feedstocks. However, the knowledge about CO<sub>2</sub> reforming of ethanol is still limited. Hence, the aim of this research was to examine the physicochemical properties of 3%Ce-10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and study the influence of both reaction temperature and reactant partial pressure on activity and selectivity of CO<sub>2</sub> reforming of ethanol. Co-impregnation method between Ce(NO<sub>3</sub>)<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> precursor solutions and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support thermally pretreated at 973 K was used for synthesizing 3%Ce-10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Ethanol dry reforming runs were carried out in a quartz fixed-bed reactor placed vertically in a split tubular furnace at reaction temperature range of 873 - 973 K under atmospheric pressure. Approximately 0.1 g<sub>cat</sub> of catalyst was sandwiched by quartz wool in the middle of the reactor. Gas hourly space velocity, GHSV= 42 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and mean particle size of 100-140  $\mu$ m were used for all runs to ensure that the negligible internal and external transport resistances was present. The ratios of CO<sub>2</sub> to C<sub>2</sub>H<sub>5</sub>OH were varied from 1:1 to 2.5:1 and vice versa. CO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH mixture was diluted in N<sub>2</sub> flow acting as a tie component for material balance purposes and ensuring the total flowrate of 70 ml min<sup>-1</sup>. 3%Ce-10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst possesses high surface area of 138.56 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup> with pore volume and pore diameter of 0.23 cm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> and 59 nm, respectively. The BET area of catalyst was close to that of calcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support suggesting the fine metal dispersion on support surface. In fact, the well dispersed metal on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface was also captured by SEM analysis. The derivative weight profiles of temperature-programmed calcination revealed two characteristic peaks indicating the completely thermal decomposition of metal precursors and subsequent oxidation to metal oxides at below 600 K. The X-ray patterns of calcined Al<sub>2</sub>O<sub>3</sub> support and 3%Ce-10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst confirm that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NiO, CeO<sub>2</sub> and NiAl<sub>2</sub>O<sub>4</sub> phases were formed on catalyst surface during calcination. Both CO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH conversions initially decreased with time-on-stream and appeared to be stable at ca. 4-5 h. A reduction in H<sub>2</sub>/CO ratio from 20 to 5 was observed with increasing reaction temperature from 873 K to 973 K probably due to the enhancement of reverse water-gas shift reaction. The consumption rate of C<sub>2</sub>H<sub>5</sub>OH and CO<sub>2</sub> was improved with increasing partial pressure of CO<sub>2</sub>, P<sub>CO2</sub>. Interestingly, C<sub>2</sub>H<sub>5</sub>OH and CO<sub>2</sub> conversions also enhanced with growing P<sub>C2H5OH</sub> and approached the maximum at around 30-35 kPa.

**Keywords:** Ni-based catalyst; Ethanol dry reforming; Hydrogen; Syngas; Ce-Ni catalyst