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Ethylene glycol dry reforming on Ni/Al₂O₃ catalyst for syngas generation

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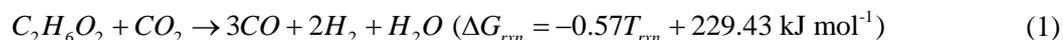
Abstract. It is the first time ethylene glycol dry reforming (EGDR) reaction was carried out for syngas production on 10%Ni/Al₂O₃ catalyst in a tubular fixed-bed reactor at atmospheric condition. Wet-impregnation method was employed for the synthesis of 10%Ni/Al₂O₃ catalyst. The results of X-ray diffraction measurement revealed the presence of γ -Al₂O₃, NiO, NiAl₂O₄, Ni⁰ and graphitic carbon phases on the surface of spent 10%Ni/Al₂O₃ catalyst. H₂ temperature-programmed reduction indicates that NiO and NiAl₂O₄ phases were totally reduced to metallic nickel phase at reduction temperature above 970 K. EGDR activity appeared to be steady with time-on-stream beyond 5-7 h. Catalytic activity was considerably improved with increasing feed ratio of CO₂:C₂H₆O₂ from 1:1 to 2.5:1.

1. Introduction

Syngas referring to the mixture of H₂ and CO has been widely recognized as an economically viable and green energy source to substitute petroleum-based fuels. Typically, this syngas is employed as raw materials in Fischer–Tropsch synthesis (FTS) to produce synthetic liquid fuels and valuable chemicals [1]. Although syngas can be conventionally produced from steam reforming and partial oxidation of methane, high energy consumption due to their endothermic nature and substantial CO₂ greenhouse emission from these industrial processes have induced adversely environmental concerns [2]. Dry reforming of oxygenated hydrocarbons derived from biomass such as ethanol [3] and glycerol [4] has recently gained extensive interests from both academics and industry since this approach not only employs highly available and renewable feedstocks but also mitigates undesirable greenhouse gas discharge by converting it to value-added syngas. However, other types of bio-derived liquids such as ethylene glycol should be also further discovered for syngas generation since it contains the same functional groups present in ethanol and glycerol [5]. In fact, ethylene glycol easily obtained from biomass is also a rich source of hydrogen. Currently, ethylene glycol (EG) aqueous-phase reforming and EG steam reforming have been extensively explored for the production of H₂, but both technologies still contributed to CO₂ emission [6, 7]. Thus, the implementation of dry reforming approach on ethylene glycol could conceivably solve the issue of CO₂ release. Indeed, to the best of our knowledge, research regarding syngas generation from ethylene glycol dry reforming, EGDR (see Eq.(1)) has not been explored before. Based on Gibbs free energy values, it was evident that EGDR



reaction was thermodynamically promising at reaction temperature beyond 406 K which is lower than those of ethanol dry reforming (589 K) and methane dry reforming (906 K) [8-10].



Pt, Pd and Rh based catalysts were reported as outstanding catalysts for syngas production from EG aqueous-phase and steam reforming processes because of their high capacity of C-C bond cleavage, stability and great coking resistance [11-13]. In addition, the employment of those metals during reforming reaction significantly improved the selectivity of H₂. Nevertheless, these noble metals are rarely employed in industrial applications due to limited availability and high cost. Hence, Ni-based catalysts have been considered as favourable catalysts in reforming processes since these non-noble metals are active in cleaving C-C bond and have relatively low cost compared with those precious metals. Thus, the objective of this investigation was to examine the performance of EGDR with time-on-stream (TOS) on 10%Ni/Al₂O₃ catalyst for syngas production.

2. Experimental

2.1. Catalyst synthesis and evaluation

The 10%Ni/Al₂O₃ catalyst was prepared using a conventional impregnation procedure in which Ni(NO₃)₂·6H₂O precursor solution was magnetically mixed with previously pretreated γ-Al₂O₃ support at ambient temperature for 3 h. The resulting solid mixture was subsequently dried for 24 h at 383 K and air-calcined for 5 h at 873 K in flowing air (50 ml min⁻¹). EGDR tests were conducted in a standard stainless steel fixed-bed reactor placed vertically in a divided tubular furnace at temperature range of 873-1023 K and 1 atm. Approximately 0.1 g_{cat} of catalyst sandwiched by quartz wool was initially reduced in situ in 50 ml min⁻¹ of 50%H₂/N₂ reducing mixture at 973 K with a 5 K min⁻¹ heating rate. Sample was kept at that temperature for 2 h before exposing to gaseous reactants for EGDR reaction. Ethylene glycol precisely pumped by a KellyMed KL-602 syringe pump was vaporized in a pre-heater and mixed with CO₂ reactant and N₂ diluent gas regulated by Alicat mass flow controllers.

The catalytic performances of 10%Ni/Al₂O₃ catalyst in EGDR reaction was calculated in terms of C₂H₆O₂ conversion ($X_{C_2H_6O_2}$) and CO₂ conversion (X_{CO_2}) by using Eqs. (2)-(3). Indeed, the conversion of ethylene glycol, $X_{C_2H_6O_2}$ to gaseous products was calculated based on atom-H balance between the inlet and outlet of the reactor.

$$X_{C_2H_6O_2} (\%) = \frac{2F_{H_2,Out} + 4F_{CH_4,Out}}{6F_{C_2H_6O_2,In}} \times 100\% \quad (2)$$

$$X_{CO_2} (\%) = \frac{F_{CO_2,In} - F_{CO_2,Out}}{F_{CO_2,In}} \times 100\% \quad (3)$$

where F_{in} and F_{out} are the inlet and outlet molar flow rates (mol s⁻¹), respectively.

2.2 Catalyst characterization

N₂ physisorption of support and 10%Ni/Al₂O₃ catalyst was performed using Thermo Scientific Surfer unit at temperature of 77 K for investigating Brunauer-Emmett-Teller (BET) surface area, average pore volume and average pore diameter. X-ray diffraction (XRD) measurements of calcined, reduced and spent catalysts were carried out in Rigaku Miniflex II system, in which Cu monochromatic X-ray

radiation (wavelength, $\lambda = 1.5418 \text{ \AA}$) was employed at 30 kV and 15 mA. The AutoChem II-2920 system was used for H_2 temperature-programmed reduction (H_2 -TPR). Sample pre-treated in purging He gas (50 ml min^{-1}) for dehydration at 373 K was exposed to reducing gaseous agent ($10\% \text{H}_2/\text{Ar}$ and 50 ml min^{-1}) from 373 to 1173 K with a ramping rate of 10 K min^{-1} .

3. Results and discussion

3.1. Catalyst characterization

$10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalyst possessed BET surface area of $171.23 \text{ m}^2 \text{ g}^{-1}$, average pore volume of $0.28 \text{ cm}^3 \text{ g}^{-1}$ and average pore diameter of 61.47 \AA . The slightly drop in BET surface compared to $\gamma\text{-Al}_2\text{O}_3$ support ($174.13 \text{ m}^2 \text{ g}^{-1}$) was due to the successful diffusion of NiO nanoparticles into the pore structure of support. XRD measurements of calcined Al_2O_3 support and $10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalyst (including calcined, reduced and spent samples) are displayed in Figure 1. The diffraction peaks belonging to $\gamma\text{-Al}_2\text{O}_3$ phase were detected at $2\theta = 19.45^\circ$, 32.30° , 36.99° , 45.69° and 67.20° for all samples. As seen in Figure 1(b), spinel NiAl_2O_4 phase was observed at $2\theta = 36.99^\circ$ and 49.38° (JCPDS card No. 10-0339) whilst the characteristic peaks for NiO phase were located at 2θ of 36.99° , 43.60° and 63.08° (JCPDS card No. 47-1049) for calcined $10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalyst [14]. However, the NiO phase was not noticed for reduced and spent catalysts (see Figures 1(c) and (d), respectively). In fact, metallic Ni⁰ phase was identified at 2θ angle of 44.56° , 52.04° and 76.26° (JCPDS card No. 04-0850) for these samples [14]. The presence of Ni⁰ phase on catalyst surface was due to the reduction of NiO and NiAl_2O_4 forms during in situ H_2 pretreatment before EGDR reaction in agreement with H_2 -TPR results (see Figure 2). As shown in Figure 1(d), a high intensity peak centred at 2θ of 26.38° for spent $10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalyst belonged to graphitic carbon deposition (JCPDS card No. 75-1621) [15].

Figure 2 shows the H_2 -TPR profile of $10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalyst. The first peak (P1) located at 799 K was due to NiO reduction to metallic Ni⁰ form ($\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O}$) whilst the high temperature peak (P2) detected at 960 K was assigned to the reduction of NiAl_2O_4 phase possessing a strong metal-support interaction ($\text{NiAl}_2\text{O}_4 + \text{H}_2 \rightarrow \text{Ni} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$) [16].

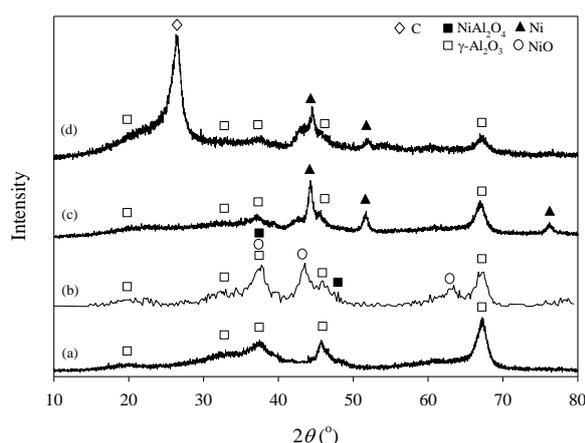


Figure 1. XRD patterns of (a) calcined $\gamma\text{-Al}_2\text{O}_3$ support, (b) calcined $10\% \text{Ni}/\text{Al}_2\text{O}_3$, (c) reduced $10\% \text{Ni}/\text{Al}_2\text{O}_3$ and (d) spent $10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalysts.

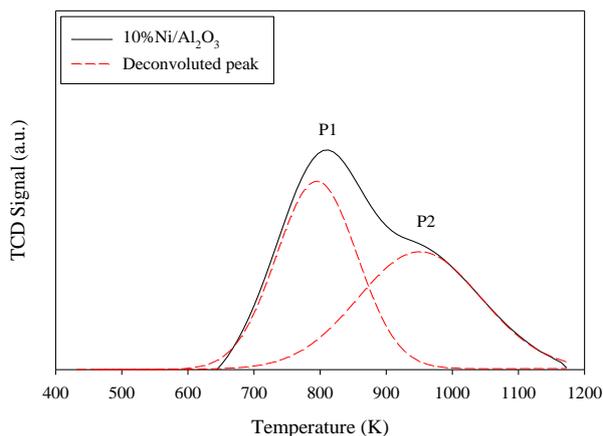


Figure 2. H_2 temperature-programmed reduction profile of $10\% \text{Ni}/\text{Al}_2\text{O}_3$ catalyst.

3.2. EGDR reaction evaluation

The effect of feed ratio on EGDR performance was determined by adjusting the feed ratios of ethylene glycol and CO₂ at about 2.5:1 and 1:2.5. As seen in Figure 3 (a) and (b), the conversions of ethylene glycol and CO₂ for 10%Ni/Al₂O₃ catalyst improved significantly by up to 84.8% and 66.3%, respectively with the rising of CO₂ feed composition. In the CO₂-rich environment, CH₄ intermediate product generated from ethylene glycol hydrogenation (cf. Eq. (4)) could be further consumed in methane dry reforming reaction (cf. Eq. (5)), in turn enhanced the consumption of both reactants [17, 18]. However, it was evident that only conversion of ethylene glycol was slightly improved with the increment of ethylene glycol whilst a decline in CO₂ conversion. This behaviour could suggest that the adsorption of CO₂ on catalyst surface was suppressed by the existence of ethylene glycol-excess environment. In addition, irrespective of feed ratios, the conversion of ethylene glycol was superior to that of CO₂ conversion. This trend could further verify the presence of parallel side reactions during dry reforming of ethylene glycol, i.e., decomposition, dehydrogenation and steam reforming of EG.

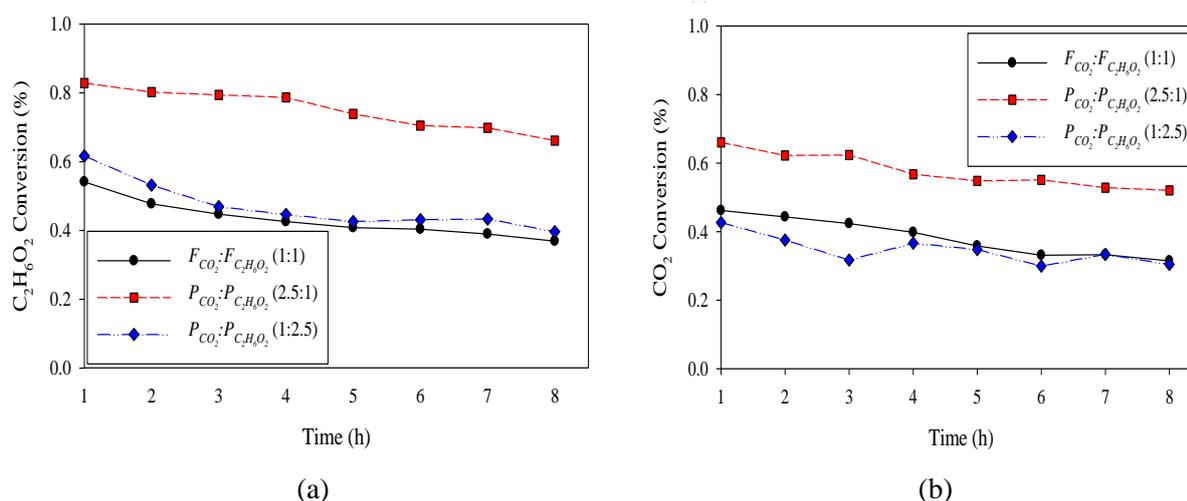
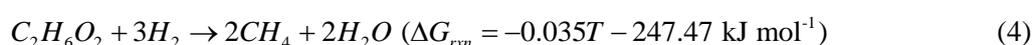


Figure 3. Reactant conversions versus time-on-stream (TOS) during EGDR reaction on 10%Ni/Al₂O₃ catalyst at feed composition of 1:1, 2.5:1 and 1:2.5.

4. Conclusion

The catalytic performance of Ni/Al₂O₃ catalyst prepared by impregnation procedure was successfully investigated in dry reforming of ethylene glycol at different CO₂:C₂H₆O₂ ratios of 2.5:1 to 1:2.5 and temperature of 1023 K. XRD measurement revealed the appearance of γ -Al₂O₃, NiO, NiAl₂O₄, Ni⁰ and carbon phases on the catalyst surface. H₂-TPR revealed that NiO and NiAl₂O₄ phases were reduced to metallic Ni⁰ phase with in the reduction temperature of 799 and 970 K, respectively. At the stoichiometric condition of EGDR reaction, catalytic activity for 10%Ni/Al₂O₃ catalyst achieved stable condition beyond 5 h on stream. Increasing CO₂ feed ratio enhanced CO₂ and C₂H₆O₂ conversions up to 84.8% and 66.3%, respectively owing to the enhancement of methane dry reforming reaction. The decline in CO₂ conversion was experienced with growing ethylene glycol feed composition due to the competing reactant adsorption on catalyst surface in the ethylene glycol-rich environment.

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