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Partial oxidation of butane to syngas using nano-structure Ni/zeolite catalysts

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ABSTRACT

In this study, performance of nano-structure Ni over different zeolite supports in partial oxidation of butane was investigated. First, partial oxidation process was performed without catalyst to evaluation of optimal conditions. For in situ reduction of catalysts, H_2 produced from homogenous reaction was used. Catalytic partial oxidation was carried out using nano-structure nickel catalysts supported by ZSM5, mordenite and Y. Each catalyst was synthesized through reverse microemulsion method. The catalysts were characterized by BET surface area, XRD, SEM and TGA. Highest butane conversion (≈89%) observed in the presence of Ni/Y catalyst. Also Ni/Y shows the highest overall selectivity to CO and H_2 as the most desired partial oxidation products. Results from TGA showed that the minimum quantity of formatted coke was related to Ni/Y, which confirmed the stability of butane conversion versus time for this catalyst.

1. Introduction

Syngas can be produced via various methods such as auto thermal reforming (ATR) [1–4], catalytic partial oxidation (CPO) [5–8] and steam methane reforming (SMR). Recently, catalytic partial oxidation has gained an important consign in syngas production. The first mechanism for syngas production from hydrocarbons reaction was proposed by Hickman and Schmidt [9]. This mechanism described base on partial and total oxidation (with steam and dry reforming) of hydrocarbons. Partial and total oxidation of hydrocarbons can be described by the following reactions:

$$C_nH_m + 0.5nO_2 \rightarrow 0.5mH_2 + nCO \quad (\Delta H^{\circ}_{298} < 0) \tag{1}$$

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow 0.5mH_2O + nCO_2 \quad (\Delta H^{\circ}_{298} << 0) \tag{2}$$

Both of these reactions are exothermic, but total oxidation is more exothermic and resulted in no syngas production. Reaction (1) is partial oxidation referred to the direct mechanism and result in H_2 and CO production.

Previous studies indicated that it is more appropriate to describe catalyst partial oxidation (CPO) using an indirect mechanism [10]. In indirect mechanism, first, total oxidation of hydrocarbons proceeds, in which hydrocarbons react with oxygen to form H_2O and CO_2, accompanied by the release of heat. Subsequently, the endothermic steam reforming and CO_2 (dry) reforming occur [10]. Steam and dry reforming of hydrocarbons can be respectively written as the following:

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m}{2} + n\right)H_2 \quad (\Delta H^{\circ}_{298} > 0) \tag{3}$$

$$C_nH_m + nCO_2 \rightarrow 2nCO + \frac{m}{2}H_2 \quad (\Delta H^{\circ}_{298} > 0) \tag{4}$$

Reihani and Jackson [11] showed that views of direct and indirect mechanism of catalytic partial oxidation of hydrocarbons may not be effective performance on selectivities of H_2 and CO. Rather, competition between adsorption and desorption of reactants and products was premier factor.

Catalytic partial oxidation of hydrocarbon fuels (methane, ethane, propane, butane, etc.) has been considered because the rapid kinetics permit volumetrically efficient syngas production without excessive amounts of fuel preheating. Results of previous studies indicated that nickel catalysts were more efficient to reform hydrocarbons. Most of the existing studies have focused on syngas production from methane. Compared to methane, butane has higher energy density, lower storage pressure, and higher H_2 and CO yields [12]. Some studies were performed to investigate the syngas production from butane [13–17]. In these studies, nickel and rhodium used as an active metals for catalyst partial oxidation

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of butane. Hotz et al. investigated the capability of Rh/ceria/zirconia nanoparticles as a catalyst for the production of syngas from butane at 550 °C [18]. They achieved high selectivities toward H_2 and CO up to 92% and 82%, respectively, and complete C_4H_{10} conversion. On the other hand, very high catalytic activity along with long-term stability reveals high performance of catalyst during the operation. Liu et al. studied the effect of Ni/γ-Al_2O_3, Ni/Mgo and Ni/SiO_2 catalysts on catalytic partial oxidation of butane, results showed that the Ni/γ-Al_2O_3 compared to other catalysts is more suitable [16].

Fonesca et al. investigated the performance of Ni/Al_2O_3 catalysts which was prepared through impregnation method in the partial oxidation of methane. The results showed the 70% conversion and also their catalysts had a better syngas selectivity than commercial Rh/Al_2O_3 catalyst. Ni/Al_2O_3 had a favorable stability during the process, although a significant sintering and coke formation were observed [19].

In another work, the performance of Ni/$Ce_{1-x}Zr_xO_2$ in partial oxidation of methane to syngas were examined. With increasing of Zr/Ce ratio in catalyst, activity of catalyst became better along with higher selectivity of syngas. Also by increasing of Zr content, the catalyst surface area and Ni dispersion increase. At Zr/Ce ratio of 3, higher stability and lower coke formation were established [20].

Ruiyan et al. investigated the mesoporous Co/Al_2O_3 catalyst in methane partial oxidation to syngas. The catalyst prepared through one-pot synthesis method. Due to the usage of this mesoporous catalyst, the conversion of CH_4 and selectivity of CO becomes 87% and 32%, respectively. The CH_4 conversion increased as well as higher Co loading in catalysts [21].

Catalytic performance of Ni/SiO_2 promoted with CeO_2 with different content of Ce/Ni ratio investigated in partial oxidation of methane by Li et al. results showed that this promoter caused better catalyst activity and stability compared to other promoter (Pt, Sm and Co). With Ce/Ni ratio increment, from 0.17 up to 0.84, methane conversion increased from 74% to 91%, and also hydrogen selectivity enhanced (38% up to 46%), but higher Ce/Ni ratio had no significant effect on produced hydrogen compared to CO production [22].

The catalystic performance of Ni/SiO_2 depends on particle size and dispersion of Ni in catalyst. Different kinds of preparation of catalyst method effect on size and dispersion significantly. Sol–gel method examined in synthesis of Ni/SiO_2 catalyst by Xia et al. showed that this method resulted in better dispersion and size reduction compared to typical methods such as impregnation. Although favorable dispersion achieved, size reduction of Ni had negative impact of reducibility of catalyst. Conversion of methane, selectivity of syngas increased as well as catalyst became more stable [23].

Li et al. investigated the core–shell structure of Ni/SiO_2 in partial oxidation of methane to syngas. in this structure, the interval of particle size distribution was narrow. Because of this unique structure of core–shell, the conversion of 94% for methane achieved. Selectivity of H_2 leads to 93% and more suitable durability was established [24].

In previous studies, most considered catalyst for partial oxidation were metal oxides. Zeolites are an important category of crystalline alumina silicates, which have been widely used as heterogeneous catalysis because of their well-defined pore structures, having high surface area and surface acidity [25]. In this study, first, non-catalytic partial oxidation of butane performed to find optimum temperature and molar ratio of air/butane in feed. Then different Ni/zeolite catalysts used for catalytic partial oxidation of butane and their performance compared to metal oxide supported catalysts. In addition, method of catalysts reduction was a new route. In this method, produced hydrogen in homogenous section was used for reduction of catalysts.

2. Experimental

2.1. Materials

Microemulsion was prepared from cyclohexane (Cyclohexane ≥99.5%, PRA grade, Sigma–Aldrich), hydrazine hydrate (reagent grade, 98%, Sigma–Aldrich, USA), tetrahydrofuran (THF) (Sigma–Aldrich, USA), poly vinyl pyrolidone (PVP) (Sigma–Aldrich, USA). Aqueous solution of nickel chloride hexahydrate (Sigma–Aldrich, USA) was prepared by using triple distilled water. Three types of different zeolites (Y, mordenite and ZSM5) were provided from the Zeolyst Company (USA). The specification of each used zeolite reported in Table 1.

2.2. Catalyst preparation

Nickel nano particles were synthesized in a reverse microemulsion using PVP and cyclohaxane as stabilizer and oil phase, respectively. The main advantages of microemulsion method, compared to other typical methods are better control on particle size distribution, favorable dispersion, surface area and reducibility. All of these, affect on the performance of catalyst significantly. The concentration of nickel was adjusted using 10 wt.% loading of aqueous $NiCl_2{\cdot}6H_2O$. The average size of nanoparticles was controlled using water/PVP with the ratio of 5. After stirring for 30 min, a microemulsion was obtained. For reduction of nickel oxide and formation of micelles cores, 6 cm^3 solution of hydrazine hydrate (50, v/v% hydrazine hydrate + 50, v/v% water) was added to the microemulsion. Appropriate weight of zeolite added to the emulsion and stirred for 3 h. At the end, the reverse micelles were broken by adding THF. The obtained precipitates were filtered, washed several times with deionized water at 323 K and dried at 365 K for 12 h. After that each catalyst was calcinated under argon in 773 K for 6 h.

2.3. Characterization of the catalysts

The surface area and pore volume of the catalysts were measured by an ASAP-2000 system from Micromeritics. The samples were degassed at 250 8C for 3 h under 70 mTorr vacuum and their BET area and pore volume were determined. For Ni/ZSM5, Ni/Y and Ni/mordenite, X-ray diffraction patterns were obtained with an X-ray diffractometer (D/max-rB 12 kW Rigaku, Japan; 45 kV, 40 mA) operated at 50 mA and 50 kV from 108 to 808. The morphology of catalysts with different zeolite supports were characterized by scanning electron microscopy (SEM) using Cam Scan (MV2300). The amounts of coke deposited on the applied catalysts were measured by thermo-gravimetric analysis (TGA) using a TGA/SDTA851e. Samples (ca. 0.5 g) were pretreated for 1.5 h at 150 °C in N_2 atmosphere to eliminate absorbed water, then heating conducted from room temperature to 800 °C at a rate of 10 °C/min. The exact loading of Ni in the calcinated catalysts measured by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) system after complete dissolution of the catalysts (5 mg) in 5 ml of HNO_3/HCl solution (1/3 volume ratio).

Table 1
SiO_2/Al_2O_3 molar ratio and Na_2O weight percent for each used zeolite support.

Zeolite	SiO_2/Al_2O_3 molar ratio	wt.% Na_2O
ZSM5	50	0.05
Y	80	0.03
Mordenite	90	0.05