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ROLE OF NANOPARTICLE SIZE ON PERFORMANCE OF PARTIAL OXIDATION OF BUTANE PROCESS TO SYNGAS

MAHDI.FAKOORI[1], BIZHAN.HONARVAR[2]*

[1]*Department of Process, South Pars Gas Complex, Assalouyeh, Iran*
[2]*Department of Chemical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran*

ABSTRACT

In this study, performance of nano structure Co/γ-Al_2O_3 catalysts in partial oxidation of butane was investigated. The catalysts were produced through chemical reduction and incipient wetness impregnation methods. Prepared catalysts were characterized with X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM),N_2 adsorption/desorption (BET), temperature programmed reduction (TPR) and thermal gravity analysis (TGA).The characterization results confirmed the uniform dispersion of Co nanoparticles over γ-Al_2O_3 by using chemical reduction. Butane conversion, H_2 and CO selectivities increased by decreasing of Co particle size due to higher dispersion and reducibility. The optimum value of H_2/CO ratio of 2 obtained from chemical reduction technique. The results showed that the stability of catalyst produced by chemical reduction method was higher than incipient wetness impregnation ones.

Keywords: Partial oxidation, butane, Co/γ-Al_2O_3, particle size, selectivity.

INTRODUCTION

In recent years, a catalytic partial oxidation of butane has attracted much attention because the reaction can produce H_2/CO ratio of 2 which is suitable for feed of Fischer–Tropsch reaction [1]. It is well known that high butane conversion, H_2 and CO selectivities can be obtained over catalysts containing transition metals (Ni, Co, Cu and Fe), noble metals (Pt, Pd, Rh, Ru and Ir) and metal oxides [2].Among those, the catalysts based on noble metals are more active than Co-based catalysts. However, because of the very high cost of noble metals, Co-based catalysts are usually used for butane reforming reactions especially due to their low cost [2]. One of the important parameters in catalytic reactions is particle size of active species. Iglesia [3] reported a significant increase in the activity of Fischer-Tropsch synthesis reaction when the cobalt particle size was decreased from 50 to 9 nm. The particle size has a important role on the interaction between cobalt species and support, Therefore it can influences on the reducibility of cobalt species [4]. Hence the methods of catalyst synthesis result in the uniform size, homogeneous distribution and higher reducibility of metal species are important factors for the higher activity in partial oxidation of butane [4].

Sun et al. [5] reported the preparation of Co/SiO_2 catalyst with high cobalt dispersion through the mixture cobalt acetate and cobalt nitrate precursors and reached to higher number of active sites. Bezemer et al. [6] investigated the effect of particles size of Co/CNT catalyst on the performance of FTS reaction and founded that optimum conditions obtained by particles larger than 5-6 nm. Mosayebi and abedini. [1] reportd the synthesize of Ni/Zeolite catalyst with size-controlled Ni nanoparticles by using microemulsion method and reached to high degree of reducibility.

In recent years, the chemical reduction method for catalyst synthesis used in different catalytic process by scholar [7]. This technique led to uniform distribution and higher dispersion (smaller particle size) of metal species and finally increase in reactants conversion and selectivity of desired products.

In this study, the Co/γ-Al_2O_3 catalysts prepared by using chemical reduction method and its structural properties, performance in partial oxidation of butane was compared with catalyst produced through incipient wetness impregnation technique, which was no reported in the literature since now.

EXPERIMENTAL

Catalyst preparation

In first method, the Co/γ-Al_2O_3nano-structure catalysts were synthesized using a chemical reduction. In detail, 0.5 g of γ-Al_2O_3 (Merck) was dispersed in 60 ml ethanol–water (Volume ratio = 1:1) solution by ultrasonic at 323 K for 30 min. Then, 0.025 g of $CoCl_2.6H_2O$ (Sigma Aldrich) aqueous solution was added into the suspension, stirred and purged by N_2 for 90 min. Suspension was saturated of N_2, $NaBH_4$ prepared solution as reducing, is added dropwise into the solution under stirring at room temperature. After the suspension stirred for 12 h. The solid sample is filtrated using circle filtration paper and washes several times with ethanol and deionized water. The catalysts are dried in vacuum condition at 373 k for 12 h. In order to remove impurities and residuals, the catalysts are calcined at 773 k for 6 h.

In second method, Nano-structure Co/γ-Al_2O_3 catalyst were synthesized using an incipient wetness impregnation.$Co(NO_3)_2.6H_2O$. At first, Co/γ-Al_2O_3 was prepare using the dispersion of γ-Al_2O_3 powder (Merck) in an aqueous solution (30 mL) of $Co(NO_3)_2.6H_2O$ (Merck) as a Co precursor. Then, solution stirred for 2 h followed by drying at 100 °C in vacuum condition for 12 h.In order to remove the impurities, the catalysts were calcined at 500 °C for 4 h. In each two synthesize technique, Co loading was 20 wt.%, which verified by an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) system.The Co/γ-Al_2O_3 catalysts prepared through chemical reduction and incipient wetness impregnation were noted as CR and IW, respectively.

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 °C for 3 h under 70 mTorr vacuum and their BET area and pore volume were determined. For Ni/ZSM5, Ni/Y and Ni/Mordenit, 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 TPR experiment is carried out using Quantachrome chemBET-3000 so that the 0.05 g of catalyst is placed in a quartz tubular reactor. Prior to the temperature-programmed reduction measurement, the calcined catalysts are heated to 150 °C in a pure N_2 steam and held at this temperature for 30 min in order to remove water or impurities. The sample is then cooled down to the room temperature in N_2 and the gas is switched to 5% H_2/Ar, then catalyst temperature increases to 1073 k at 10 k. min^{-1}. The morphology of catalyst is specified using Philips CM30 high resolution transmission electron microscopy (HRTEM).Thermo gravimetric analyses (TGA) of prepared catalysts after FTS reaction were conducted by using TGA/SDTA851e apparatus to investigate the carbon deposition on the catalysts. The test was carried out in an air flow of 50 ml/min in the range of 300 K to 1000 K at a rate of 30 K/min.

reactions testing

The partial oxidation of n-C_4H_{10} was performed in a fixed-bed reactor. The schematic representation of the set up used is shown in Fig. 1. The reactor (ID = 30 mm, OD = 35 mm and L= 70 cm) was made of 316 stainless steel and located in a furnace. Air and fuel were fed to the reactor via thermal mass flow controllers (Brooks 5850). Product stream was analyzed by online TCD-gas chromatography with a column consisting of molecular sieve 5A and 13x and helium as carrier gas at 353 K. Before being tested, the catalysts are reduced at 600°C in atmospheric pressure for 3 h by a flow of pure hydrogen (50 mL/min). The reactant feed composed of butane and air with ratio of 2 to 1 (V/V) was introduced into the reactor at operation conditions of 700-800 °C, space velocity of 1300 1/h (30 mL/min) and atmospheric pressure.Conversion of butane and selectivity of products were calculated as follow:

$$\text{Conversion}=\frac{\text{amount of butane in inlet-amount of butane in outlet}}{\text{amount of butane in inlet}} \qquad (1)$$

$$\text{Selectivity}=\frac{\text{amount of desired product}}{\text{sum of products in outlet}} \qquad (2)$$

e-mail: Mahdi.Fakoori@gmail.com

$$\text{Yield of } H_2 = \frac{\text{mole of } H_2 \text{ produced}}{\text{total mole of } C_4H_{10} \text{ fed}} \qquad (3)$$

RESULTS AND DISCUSSION

Characterization of catalysts

The BET surface areas of the catalysts are presented in Table 1. The BET surface area and porosity amount of the loaded catalysts are clearly lower than γ-Al_2O_3. The dilution effect of the support and partial blockage of its pores by active components (Co) during the catalysts preparation are responsible for reducing in the surface area and porosity amounts [8]. Of course, it be should noted that decrease in surface area and porosity of prepared catalyst by IW was more than CR.

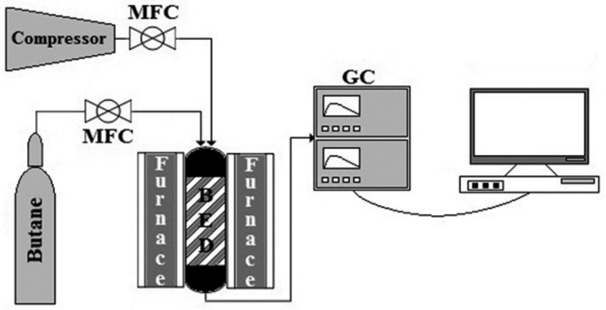

Fig. 1: A schematic of the experimental set-up which used.

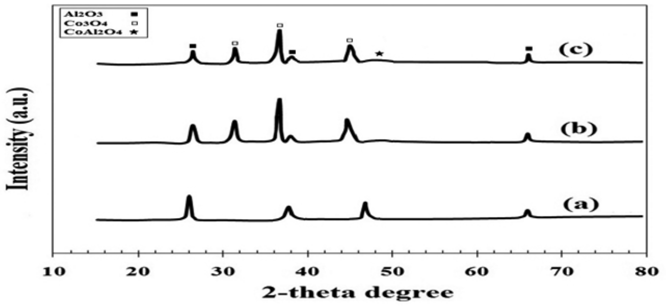

Fig. 2: XRD patterns of the catalysts (a) Alumina support; (b) IW catalyst; (c) CR catalyst.

XRD patterns of the three prepared samples are shown in Fig. 2.The diffraction patterns (Fig.2a) show the broad peaks at 2θ= 25.58°, 37.74° and 66.2° corresponding to γ-Al_2O_3 [9]. After the introduction of Co to support in two synthesize method, the intensity of γ-Al_2O_3 peaks decreased. In Fig. 2 (b and c), the intense peaks at 2θ= 31.46°, 36.9°, 44.8° are observed that is attributed to Co_3O_4 with cubic structure [10]. The 48.4° peak in the spectrum of IW and CR catalysts were ascribed to formation the cobalt aluminate due to a strong interaction between cobalt and the alumina support [10]. However, the intensity of this peak in two catalysts were low. The average Co_3O_4 particle size of the catalysts is measured by the XRD pattern using scherrer equation at 36.9°, as shown in Table 1. This peak for CR catalyst was broader and smaller than IW, indicated the cobalt oxide nanoparticle size of IW (9.12 nm) was higher than CR (7.32 nm). The enhacement in nanoparticle size lead to lower number of cobalt oxide crystallization sites, thus the dispersion of cobalt oxide was decreased [7]. As was shown in Table 1, the dispersion of CR catalyst (13.11%) was more than IW catalyst (10.52%).Park et al. [4] observed that the Co_3O_4 particle diameter enhanced through increasing of catalyst synthesis temperature.

The HRTEM images describe the crystallite structure of prepared catalysts as shown in Fig. 3. As it can be seen in Fig. 3(a, b), in CR catalyst, the spherical shape of cobalt oxide nanocrystals uniformly dispersed on the support external surface that it indicates the advantage of this synthesis method compared to incipient wetness impregnation technique. The CoO average particle size for CR and IW catalysts were 8.92 nm and 11.26 nm, respectively, which these values were almost coincided with the values measured by XRD as given in Table 1. Fig. 4 shows the reduction behavior of the catalysts that are shown through the TPR experiments.In this work, two typical steps during the reduction in the flow of H_2, i.e. Co_3O_4 to CoO and then CoO to Co, which was in agreement with literature [7].we observed two main peaks in prepared catalysts, could be attributed to reduction of Co_3O_4 to CoO and CoO to metallic cobalt, which is in accordance to the results of XRD test.

For each two catalyst, the low temperature peak (300–400 °C) was assigned to reduction of Co_3O_4 to CoO [11].The second broad peak (400–500 °C) was related to reduction of small CoO to Co0 species [11].The high temperature reduction peaks a (545°C for CR catalyst and 560°C for IW catalyst) would be assigned to reduction of cobalt aluminate formation due to a strong interaction between cobalt and the alumina support, which is in agreement with results of XRD analysis [7]. According to Fig. 4, the deposition of cobalt nanoparticles synthesized by chemical reduction on the alumina support shift the reduction temperature of the Co_3O_4 to CoO species (first peak in 358°C) to a lower temperature compared to the catalyst prepared by the incipient wetness impregnation method (380°C), which indicated higher reducibility for uniform particles of CR catalyst [11]. Interestingly, the temperature of the first reduction peak decreased with decreasing cobalt oxide nanoparticle size from 9.12 to 7.32 nm.

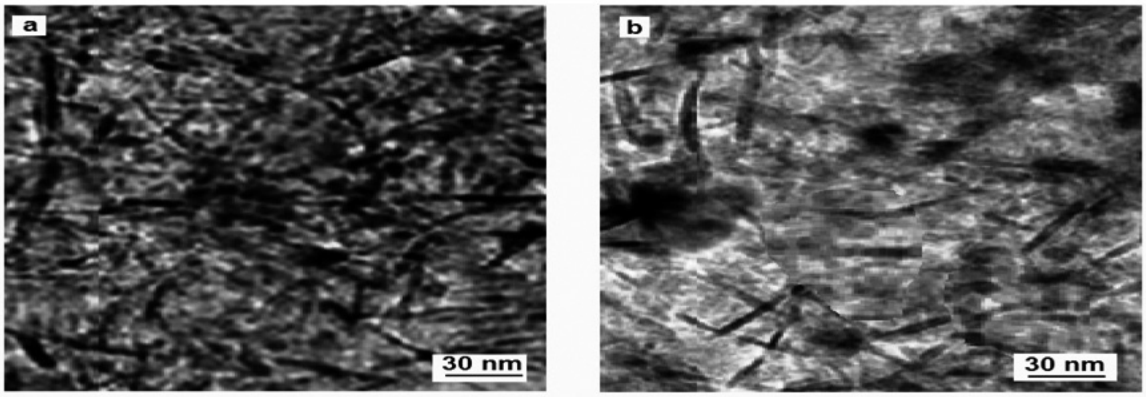

Fig. 3: HR-TEM images of (a) CR and (b) IW catalysts.

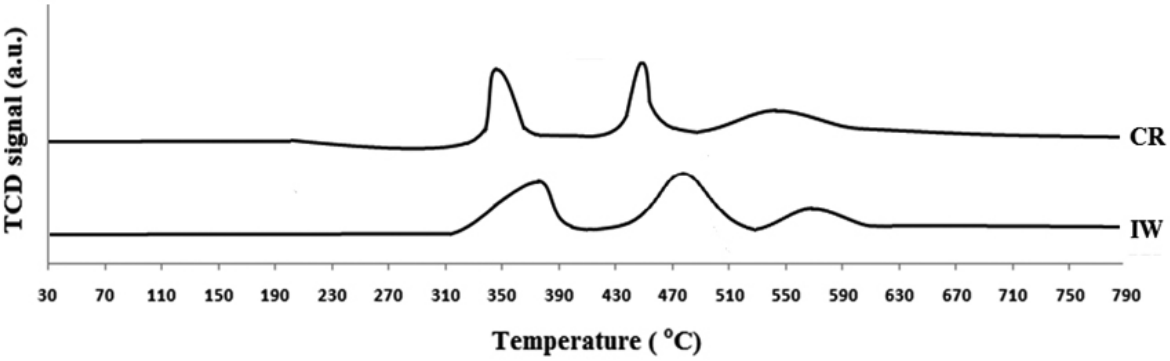

Fig. 4: TPR curves of CR and IW catalysts.

Table 1 . The textural parameters of used catalysts in this study.

Sample	Surface area (m^2/g)	Pore radius (nm)	Pore volume (cm^3/g)	XRD d(Co_3O_4) (nm)	Dispersion (%)	HRTEMd(Co_3O_4) (nm)	Reduction degree (%)
γ-Al_2O_3	720	8.6	0.36	---	---	---	---
CR	524	7.8	0.31	7.32	13.11	8.92	86.39
IW	458	7.2	0.29	9.12	10.52	11.26	67.13

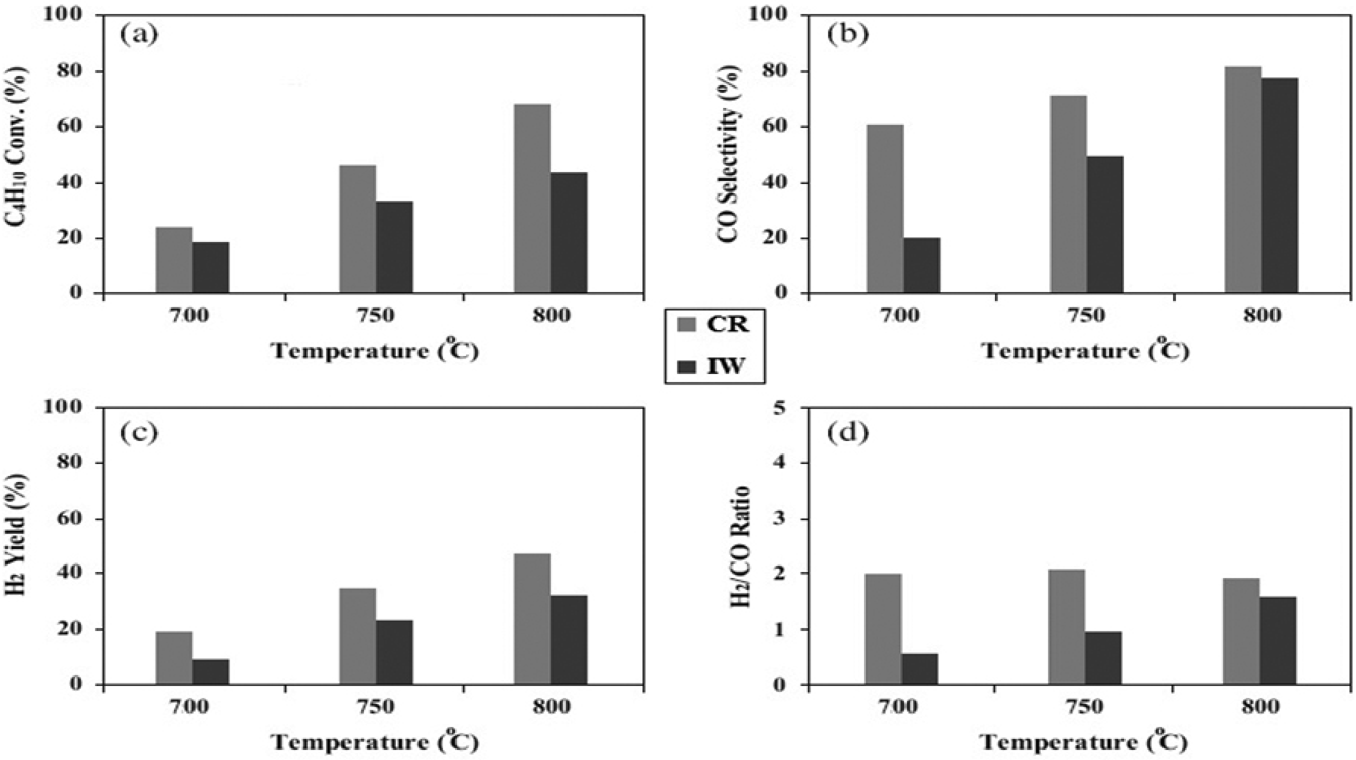

Fig. 5: (a) The butane conversion; (b) CO selectivity; (c) H2 Yield; (d) H2/CO ratio over catalysts.

Terapnier et al [11]. Observed that the reduction temperature of the first peak decreases with decreasing cobalt particle size from 10 to 3 nm.The second reduction peak for IW catalyst shifts to higher temperatures (473 °C) compared to CR catalyst (455 °C). In the literature [11], It is observed that second reduction peak shifted to lower temperature by increasing in nanoparticle size (> 10 nm). Therefore, the catalyst prepared by chemical reduction displayed displays better reducibility than incipient wetness impregnation method.

Fig. 4 indicated that by increasing the cobalt nanoparticle size, the broad shoulder of the TPR peak becomes larger, suggesting more difficult reduction process for cobalt oxide species.

The reduction degree at 150–500 °C are calculated by the TPR test, as depicted in Table 1. The using of chemical reduction method leads to considerable growth in the reduction degree from 67.13% to 86.39%.The growth in reduction degree leads to an increase of cobalt oxide nanoparticle size. However, Haghtalab et al. [7] reported that the reduction degree increased with increasing of cobalt oxide nanoparticle.

Table 2. The comparison between this work and other studies.

Catalyst	Conversion of butane (%)	CO selectivity (%)	H2 Yield (%)	Ref.
Ni/MgO	10.0	64.7	---	[16]
Ni/SiO_2	11.0	39.6	---	[16]
$Rh/Ce_{0.5}Zr_{0.5}O_2$	90.2	10.4	---	[17,18]
$Co/\gamma\text{-}Al_2O_3$	76.4	87.5	51.2	This study

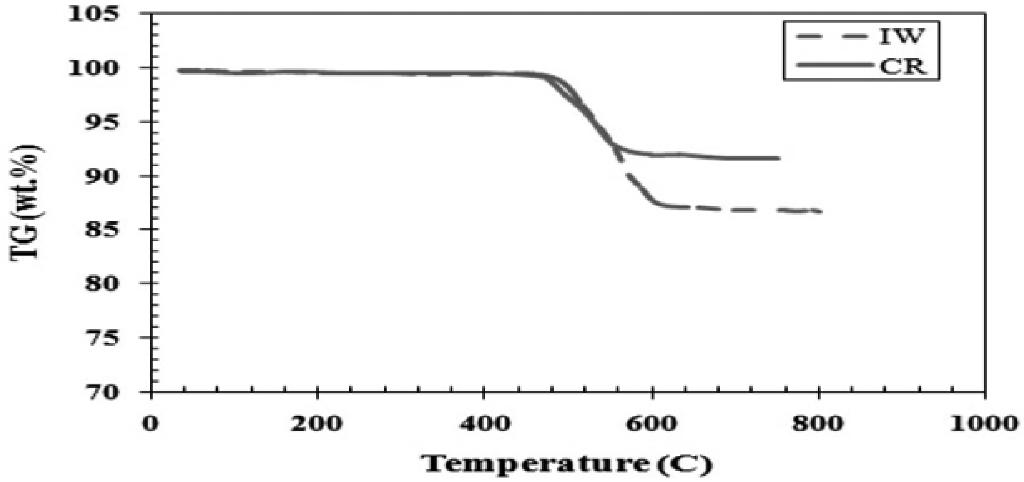

Fig. 6: TGA curves of each catalyst

Performance of catalysts in Partial Oxidations

Partial oxidation of butane was studied over CR and IW catalyst at the temperature range of 700–800°C. The catalytic performance of the samples is influenced by operating conditions (Fig. 5). The butane conversion increased with temperature for catalysts which are prepared (Fig.5 (a)). These results are in agreement with previously reported studies indicating that a higher operating temperature results in a shift in catalyst activity towards higher CH_4 conversion [12]. Because of higher reduction degree and dispersion, values of butane conversion for CR catalyst was more than IW catalyst in any values of temperature range of 700-800°C. The maximum and minimum of butane conversion observed at 800°C for CR (68.1%) and 700 °C for IW (44.2%), respectively. The CO and H_2 selectivities were found to increase with temperature for two catalysts which are studied (Fig. 5(b and c)). As can be observed the IW catalyst sample requires temperature above 700 °C, to start and to show high level of catalytic activity (in production of CO and H_2). The maximum CO and H_2 production are observed at 800 °C. For CR sample, the lowest butane conversion is observed at 700 °C. In this condition,the least amount of carbon monoxide product and the major product is carbon dioxide. In contrast, at 850 °C, represents the maximum amount of butane consumption, formation of carbon monoxide and efficiency of hydrogen. This trend is consistent with published results by other scholars [12]. Among the catalysts, the CR catalyst showed the most effective performance, and the H_2/CO ratio of about 2 was obtained for this catalyst at 700–800°C(Fig. 5(d)). This ratio is suitable for feed of FTS process.

In recent literature [13,14], the partial oxidation of butane was studied over bimetallic oxides such as nickel–lanthanide, Ce–Fe and Ni-Mg by investigators. The selectivity of the bimetallic oxides is clearly different from that of single metal oxides.The existence of an synergism effect between the two metal oxide phases that lead to higher conversions of butane and higher selectivities for H_2 and CO [15].

To investigate the stability of the catalysts, the amount of deposited coke on the catalyst was measured by TGA method. The results of this analysis are shown in Fig. 6. Formation of coke on the catalyst surface leads to less number of active sites may be exposed to the reactants over time, which consequently caused the rate of butane conversionis reduced [1]. At temperature of 500 °C for all two catalysts, there is a dramatic drop. IW Catalyst has the highest drop. This indicates that the amount of coke produced for this catalyst is more compared to CR. TGA results for CR catalyst showed that this catalyst has less drop, resulting information of lower amount of coke on the catalyst during the process. So changing of butane conversion of CR catalyst with time was less than IW catalyst.

Table 2, shows the comparison between this work and other research where used metal oxide as a support. Table 2 reveals that $Co/\gamma\text{-}Al_2O_3$ catalyst, which was examined in this study has higher syngas compared to author catalysts. This favor-able performance of $Co/\gamma\text{-}Al_2O_3$ can be related to its high surface area, suitable dispersion of Co in zeolite based catalyst and more pore volume where caused better accessible of butane to Co clusters.

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CONCLUSIONS

In this study, the performance of IW and CR catalysts in partial oxidation of butane reaction were investigated. The results of characterization tests showed that oxide cobalt nanoparticles well dispersed on the support by using the chemical reduction method compared to the convential ones. CR catalyst had a higher activity in partial oxidation of butane than IW catalyst because of higher dispersion and reduction degree. The maximum value of selectivities of H_2 and CO obtained in temperature of 800 °C. Due to lower formatted coke over active sites, CR catalyst had the higher stability along the partial oxidation of butane process, which resulted in lower changes of butane conversion in reaction time.

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