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Integrated bi-modal fluidized bed reactor for butane dehydrogenation to corresponding butylenes

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HIGHLIGHTS

- Integrated production process for butenes via direct dehydrogenation.
- The state-of-the-art reactor design of bi-modal particle gas–solid–solid fluidization (GSS–FBR).
- Promising operational advantages in light alkane dehydrogenation.
- New FBR catalyst for Pt–Sn/Al_2O_3–SAPO-34.

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ABSTRACT

The direct butane dehydrogenation to corresponding butenes (1-butane and/or iso-butene) is the most economical route. The reaction is complex as reaction engineering constraints are very much tide up with engineering constraints due to high endothermic requirements, equilibrium limitations and selectivity control. The state-of-the-art idea of bi-modal particle gas–solid–solid fluidization (GSS–FBR) system was introduced in order to overcome light alkane dehydrogenation reaction barriers (i.e. continuous heat input for endothermic reaction) in a fluidized bed technology. In this study, both n-butane and iso-butane dehydrogenation reactions were studied in an integrated fluidized bed reactor (see Fig. 1), using Pt–Sn/Al_2O_3–SAPO-34 novel catalyst at 590 °C. The results of integrated bi-modal particle fluidized bed reactor were compared with fixed bed micro-reactor, and parametrically characterized. The results showed that above 95% total olefins selectivity with feed conversion between 20 and 40 wt.% from end-of-run (8 h) to the start-of-run (10 min) in GSS–FBR. This significant enhancement is achieved for continuous longer reaction duration by using novel bi-modal particle fluidization system, owing to uniform heat transfer throughout the reactor and transfer of coke from principal catalyst to secondary catalyst, which increases principal catalyst's stability. The secondary catalyst (fine particles), i.e. heat carrier and may serve as a catalyst in secondary reactor for olefin inter-conversion reaction and/or cracking, if integrated setup is designed. Experimental investigation reveals that the novel Pt–Sn/Al_2O_3–SAPO-34 catalyst and proposed intensified design of fluidized bed reactor is a promising commercialization opportunity for light alkane (in particular propane, *n*-butane, and iso-butane, etc.) dehydrogenation to the corresponding olefins, with both economic and operational benefits.

1. Introduction

The light alkane dehydrogenation has been in practice since 1930 as it produces intermediate feed stocks for polypropylene, propylene oxide, MTBE (Methyl Tertiary Butyl Ether), and many other polymers, etc. [1]. Iso-butane (from isomerization) and n-butane are cheap and easily available from crackers, while, iso-butylene and butane-1 market demand is growing 5–7% annually [2–4]. Iso-butene is the feedstock for oxygenates (MTBE, ETBE, etc.) and butane-1 is an important polymer grade intermediate (for butadiene, butyl rubber, polybutene, and isoprene); and is a most profitable part of petrochemical industry. At present both chromium oxide and platinum based catalysts were used for alkane dehydrogenation and hydrogenation with alumina oxide support. Modern catalytic developments shaped advancement in dehydrogenation technology.

The first butane dehydrogenation unit was designed by UOP (Universal Oil Products of USA) and ICI (Imperial Chemical Industries of England) in 1940 [5]. Soon after, other companies, Phillips

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Petroleum, Houdry, Shell, Yarsintez/Snamprogetti and Dow, also built similar dehydrogenation technologies. Phillips Petroleum built a dehydrogenation reactor in 1943 [1]. Houdry designed Catadiene dehydrogenation adiabatic fixed bed process operates below atmospheric pressure, for the production of butenes using chromia–alumina catalyst. Later upgraded same technology renamed to Catofin and licensed by ABB Lummus for propane and isobutene; and above ten units were commercialized [6,7]. In 1970s, most of the light olefins were produced in bulk by thermal and catalytic cracking by-products; threaten on-purpose olefins production. Later in 1990s, due to high gasoline and MTBE demand on-purpose olefins production again comes in picture. After fixed bed technologies various fluidized bed technologies were successfully installed for isobutene and isopentene production in Russia and Saudi Arabia. Fluidized bed iso-butane dehydrogenation unit for about 450,000MTA iso-butylene was commercialized by Snamprogetti (Yarsintez design) to SADAF in Saudi Arabia [8–10]. Uhde also installed one multi-tubular fixed-bed reactor in Egypt for propylene [11]. UOP commercialized slowly moving bed, a typical radial flow adiabatic fixed-bed design using modified Pt-based catalysts [1]. Recently, Mitsubishi Chemical also claimed novel process for oxidative dehydrogenation of alkane by using fixed bed reactor [12].

Recently, Pt-based catalysts supported on amorphous (Al_2O_3, SiO_2, etc.) and zeolites (ZSM-5, SAPO-34, etc.) supports were extensively studied and demonstrated with promising results [13–20]. The dehydrogenation performance of Pt-based catalysts depends largely on the promoter (generally Sn with alkali or alkaline earth metal like Na, Zn, La, Ca, Ce, etc.) and support interaction [21–27]. The development of a highly selective Pt–Sn/SAPO-34–Al_2O_3 catalyst at Tsinghua University (FLOTU) gives a new technological trend in light olefin's production via direct dehydrogenation route [13,14]. The catalyst demonstrates better selectivity control towards light olefins in particular propylene and highly resistant towards regeneration with steam [13,14]. The recent process has been designed by considering the active nature of Pt–Sn/Al_2O_3–SAPO-34 novel catalyst for butane dehydrogenation. The intensified bi-modal fluidized bed reactor system was proposed and is applied first time for butane dehydrogenation to corresponding butylenes. The pilot plant study is conceived to explore reaction engineering pedagogy of butane dehydrogenation using proposed fluidized bed technology.

2. Experimental

2.1. Catalyst preparation

The SAPO-34 and 20% Al_2O_3 support was prepared as per prior art and then calcined, having BET surface area 440 m^2/g [2,4]. The bimetallic Pt-based catalyst was prepared by sequential impregnation method [13,14,28,29]. The mixed support after pelletizing was first impregnated with an aqueous solution of $SnCl_2.2H_2O$ to dope 1 wt.% Sn in the catalyst at 76 °C. After impregnation, the samples were dried at 105 °C for 3 h, and calcined at 525 °C for 4 h. Prepared Sn/Al_2O_3–SAPO-34 was further impregnated with an aqueous solution of H_2PtCl_6 at 70 °C to give a 0.5 wt% Pt in the final catalyst i.e. Pt–Sn/Al_2O_3–SAPO-34 (coarse particles). The metallic content in the prepared sample was confirmed by X-ray fluorescence (XRF) analysis using a Shimadzu XRF 1700 fluorimeter (see Table 1). The catalysts were dechlorinated at 490 °C for 2 h with diluted steam and then reduced under flowing H_2 (8 ml/min) at 500 °C, for 4 h. SAPO-34 without impregnation of metals is used as secondary heat carrier catalyst in the system, as it can be used further in many downstream applications.

Table 1
XRF analysis of Pt–Sn/Al_2O_3–SAPO-34 catalyst.

SAPO-34 supported	Pt content (wt.%)	Sn content (wt.%)	Al content (wt.%)
Pt–Sn/Al_2O_3	0.46	0.87	17.1

2.2. Feed

The 99.6% pure *n*-butane and iso-butane were used in current experimentation. The reaction mixture composed of H_2 and *n*/*i*-C_4H_{10} was charged into the reactor. The mixture was composed of H_2/C_4H_{10} molar ratio of 0.2.

2.3. Experimental setup

The performance of catalyst was first tested at a fixed bed micro reactor for butane dehydrogenation. The measured amounts of prepared catalyst were loaded into the reactor in order to obtain the WHSV 5.6/h and operated at fluidization velocity between 0.1 and 0.2 m/s and 590 °C. The principal dehydrogenation catalyst (large particles) and heat carrier catalyst (small particles) used in this study having spherical shape and size ∼2 mm and 0.1 mm, respectively. The optimum operating parameters and the technology design features of GSS–FBR can be found elsewhere [24,28,30–35]. The butylenes product distribution was analyzed by an online gas chromatography system equipped with a FID and TCD detectors. The values presented here are in weight percentages and using generalized conversion and selectivity relationships [13–17].

The pilot unit of fluidized bed reactor used for butane dehydrogenation was designed and shown in Fig. 1-left. The stainless steel fluidized bed reactor of 180 mm long and ID 20 mm placed coaxially in a furnace coil. The operational specification are: feed rate of gas: 2–10 L/min, catalyst reserve: 10–50 g, temperature: 580–600 °C, H_2/C_4H_{10} molar ratio: 0.1–0.3, WHSV: 3–9/h, regeneration temperature with steam: 550–650 °C. The Pt-based SAPO-34 supported dehydrogenation catalyst remains active for 8–12 h for dehydrogenation, but still we need continuous process to supply heat to the reactor. In laboratory setup for easy control, we run it isothermally for 8 h followed by in situ regeneration. Therefore, there is no solid flow going out of reactor in laboratory setup. In conceptual continuous design for commercial scale-up, the fine (small) particles were circulated between reactor and regenerator in order to carry heat form regenerator to reactor (as shown in Fig. 1-right). The circulation rate will be the controlling parameter for the reactor temperature.

3. Results and discussion

The concept of co-fluidized bed comes due to heat integration and superior fluidization behavior than single particle fluidization [35]. The experimental results of *n*-butane and iso-butane dehydrogenation using novel catalyst Pt–Sn/Al_2O_3–SAPO-34 were compared for fixed bed micro-reactor and pilot bi-modal fluidized bed reactor, in Fig. 2. The influence of fluidization dynamics in an integrated bi-modal particle fluidized system was also investigated for higher olefins productivity. It is observed that the butylenes selectivity in a pilot fluidized bed reactor was improved, when the reactor reached steady state conditions. The steady and uniform trend conversion and yield is also achieved, these results are consistent with previous studies [13,31,32,36]. In fixed bed reactor coke deposition is relatively high as compared to bi-modal fluidized bed reactor as shown in Table 2. In the co-fluidized system it was observed that the coke deposited on SAPO-34 (fine catalyst particles or support) is higher than on the metal incorporated