



Short Communication

Creation of a continuous process for bio-ethanol to butadiene conversion via the use of a process initiator

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ABSTRACT

One of the major constraints to the efficiency of Lebedev's process for butadiene production is the deposition of soot on the active sites of the catalyst which results to the reduction of catalyst activity and the periodic regeneration of catalyst thereby increasing time and energy spent on the process and subsequently, cost. The use of a process initiator has been found to be a possible solution to the above mentioned challenges. A synergetic effect was observed during the initiation of the catalytic process. Furthermore, the interdependence between the efficiency of the process initiator and the morphology of Al_2O_3 , linear velocity of the feed stream and other process parameters was observed.

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1. Introduction

Butadiene, which is an important building block for the chemical industry is produced by (1) pyrolysis of butane–butylene fraction of petroleum [1], (2) as a byproduct of ethylene production from steam crackers [2] and (3) combined process of ethanol dehydrogenation and dehydration (Fig. 1) [1].

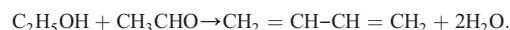
Butadiene in the 1930s was produced by a one-step catalytic process of both dehydrogenation and dehydration in the Soviet Union [3–14]. During the Second World War, about 60% of butadiene produced in the United States was via a two-step process commonly known as Ostromislensky process [15], in which ethanol is oxidized to acetaldehyde which then reacts with additional ethanol over a tantalum-promoted silica catalyst to yield butadiene [16]

One-step process:

$$T = 430\text{--}450^\circ\text{C}, \text{ZnO}/\text{Al}_2\text{O}_3$$



Two-step process:

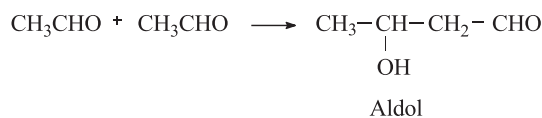


The mechanism of the ethanol to BD transformation is extremely complicated and is still a subject of debate. However, one generally accepts the involvement of the following principal steps [17–30]:

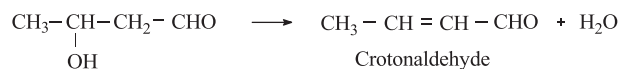
Step 1 Production of acetaldehyde from ethanol under the influence of the dehydrogenating centers of the catalyst.



Step 2 Condensation of acetaldehyde to form aldol under the influence of the dehydrating sites of the catalyst.



Step 3 Dehydration of aldol to form crotonaldehyde



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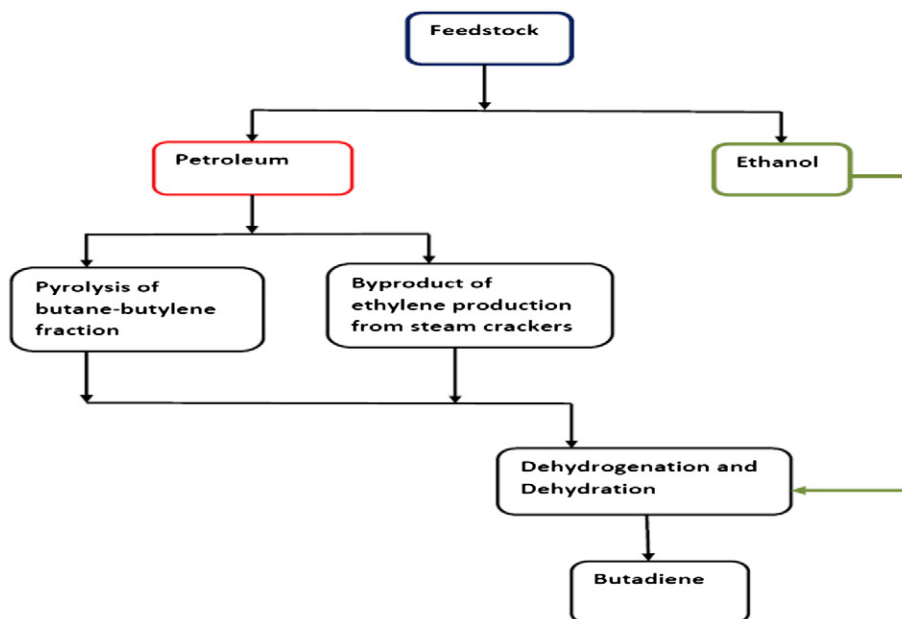
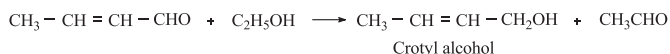
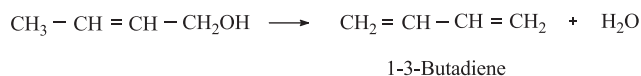


Fig. 1. A brief overview of butadiene production.

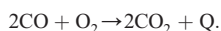
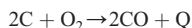
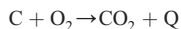
Step 4 Meerwein–Ponndorf–Verley reaction between crotonaldehyde and ethanol to obtain Crotyl alcohol and acetaldehyde.



Step 5 Formation of butadiene from Crotyl alcohol on the dehydrating sites of the catalyst.



Soot formation is one of the numerous side reactions that take place in the process of butadiene formation. It forms on the surface of the catalyst there by blocking the access to active sites. This process of soot formation results to the periodic regeneration of the catalyst in a stream of hot air as shown below:



The aim of this study was to achieve a continuous process void of catalyst regeneration and to show the correlation between the efficiency of the process initiator and the morphology of Al_2O_3 , linear velocity of the feed stream, temperature and selectivity of the process.

2. Experimental section

2.1. Catalyst preparation

Catalysts were prepared mainly by mechanical mixing and impregnation based on the different morphologies of aluminium oxide

i.e. gamma and alpha. Sample **A** was prepared by mechanical mixing of zinc oxide with $\gamma\text{-Al}_2\text{O}_3$, **B** by impregnation of $\gamma\text{-Al}_2\text{O}_3$ with mixed aqueous solution of aluminium and zinc nitrate and **C** by mechanical mixing zinc oxide with $\alpha\text{-Al}_2\text{O}_3$.

Impregnation of $\gamma\text{-Al}_2\text{O}_3$ was carried out using mixed aqueous solution of aluminium and zinc nitrates at 80°C for 2 h. The precursor samples were later dried for 6 h. Further thermal treatment was carried out in a muffle furnace for 3 h at 300°C with subsequent expulsion of nitrogen oxides for an additional 3 h.

The precursor samples were loaded into a glass reactor and calcined at 450°C for 3 h. At this same temperature, activation of catalyst samples was done in a stream of hydrogen. Further activation was done at 400°C using bio-ethanol for 6 h at a flow rate of 1 h^{-1} . The drying, calcination and activation process for all samples A, B and C were the same [31,32].

2.2. Catalyst testing and initiator introduction

The catalytic conversion of bio-ethanol to BD was carried out in an integral quartz reactor with a catalyst loading of 10 cm^3 , in the presence and absence of the initiator (hydrogen per oxide) with a flow rate of $1.2\text{--}4.4\text{ h}^{-1}$ at $390\text{--}420^\circ\text{C}$. Kinetic studies were also carried out using a micro reactor with a catalyst loading of 1 cm^3 . Products were analyzed by gas chromatograph (GC, Crystal-2000M made in Russia by Chromatec). The experiments were tested for reproducibility several times and the data was averaged and results were verified with independent gas-mass spectrometry equipment, model – Finnigan MAT 95 XL. Besides butadiene some amounts of methane, propylene, butylenes, butane, acetaldehyde, diethyl ether and other oxygenated compounds were found as by-products. The conversion of ethanol and the theoretical yield of butadiene were found to be 42% and 88% respectively with the use of the initiator. Samples prepared using $\gamma\text{-Al}_2\text{O}_3$ were found to be more active (concentration of BD in the gaseous phase was between 65 and 70%), and stable; not losing activity for over 120 h of testing in a glass reactor. The duration of work on this sample without the use of an initiator (hydrogen per oxide) was 48 h with subsequent decrease in activity. However, testing in the presence of the initiator resulted to unabated activity of catalyst sample for 120 h which gives the basis to believe the possibility of creating a continuous process needless of

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