Chemical Engineering & Processing: Process Intensification 129 (2018) 103–108

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

The oxidative dehydrogenation of ethane: Convectional vs microwave heating of Ba - containing catalysts

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ARTICLE INFO

Keywords:
Oxidative dehydrogenation
Ethane
Microwave heating
Catalyst

ABSTRACT

The influence of heating method on oxidative dehydrogenation of ethane (ODE) over $BaO–CeO_2–ZrO_2$ and $BaCl_2–TiO_2–SnO_2$ catalysts was studied. Noticeable differences were observed at the ODE under conventional heating and microwave (MW) heating when only the granules of catalyst but not the surrounding gas mixture are heated. The MW heating of the $BaO–CeO_2–ZrO_2$ catalyst resulted in a decrease in selectivity to carbon dioxide and in an increase in selectivity to carbon monoxide. Supposedly, the conventional heating led to gas-phase complete oxidation of carbon monoxide to carbon dioxide. The MW heating of the $BaCl_2–TiO_2–SnO_2$ catalyst suppressed almost completely parallel and consecutive deep oxidation of ethylene but selectivity to ethylene increased remarkably. The study demonstrates potentialities of the MW heating in enhancing the efficiency of ODE. The observed phenomena can be accounted for the effective "quenching" of the target ODE product via inhibiting undesirable homogeneous reactions in the gas phase.

1. Introduction

Ethylene is one of the most important compounds of high demand in chemical industry, being a precursor for production of a wide range of polymers (polyethylene, fibers and plastics). Ethylene also is widely used for synthesis of ethylene oxide, dichloroethane, and ethylbenzene. In industry, ethylene is produced mainly by pyrolysis of hydrocarbons (light $C_2–C_4$ alkanes, gasoline) in the presence of overheated water vapor (the steam cracking or dehydrogenation). Despite the success in the field, there are remarkable disadvantages of these approaches. The principal disadvantage is the high energy consumption for reaching the process temperature above 800 °C and the use of huge amounts of superheated water vapor. Again, hydrocarbon pyrolysis and dehydrogenation are endothermic processes due to necessity to break strong C—C and C—H bonds. The high temperature of pyrolysis leads to a loss of selectivity and favors the occurrence side reactions such as coke formation, etc.; as a result, the yield of the target product ethylene decreases (ca. 50% in the pyrolysis of $C_2–C_4$ alkanes) while numerous pyrolysis by products are formed.

An attractive alternative for petrochemical industry is production of ethylene via the catalytic oxidative dehydrogenation of ethane (ODE). Compared to the steam cracking, and dehydrogenation, ODE is thermodynamically favored and can be performed at lower reaction temperature to prevent the coke formation [1]. A number of heterogeneous catalysts for the oxidative dehydrogenation of ethane to produce ethylene are described (see, e.g. [2]). Among these catalysts, MoVTeNb mixed oxides and Ni-based mixed oxides are shown to operate at moderate temperature (< 500 °C) but the yield of ethylene over these catalysts (typically less than 50%) is still not high enough for commercial applications. However, some catalysts based on oxides promoted by alkaline or alkaline earth metals with a chloride modification provided more than 70% yield of ethylene at temperatures higher than 600 °C [3].

The main problem of ODE is the moderate selectivity of respective catalysts due to high reactivity of ethylene formed at high reaction temperatures (> 600 °C). To increase the ODE selectivity, the consecutive deep oxidation of ethylene via the homogeneous mechanism should be inhibited (quenched) [4].

Microwave (MW) energy becomes more and more attractive for different applications in chemistry and processing of materials. Among the considerable successes are: analytic chemistry, microwave organic synthesis and sintering of ceramics. The developed and produced commercial laboratory MW set up allowed researchers to discover the so called microwave effect that may result in a considerable increase in the rate or reduction of temperature of chemical reactions under microwave power. Furthermore, perspectives of application of MW heating for the process intensification were demonstrated in various catalyzed reactions [5]. That is accounted for by specific features of

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https://doi.org/10.1016/j.cep.2018.05.006
Received 30 December 2017; Received in revised form 28 April 2018; Accepted 11 May 2018

heat transfer at microwave processes: i) rapid heating; ii) selective heating; iii) high efficiency volumetric heating. The most obvious advantage that microwave radiation affords in driving a heterogeneously catalyzed reaction is the ability to selective heating of the catalyst without touching the surrounding gas or liquid phase. The selective microwave heating of the catalyst as compared with the conventional heating allows the creation of conditions where the temperature gradient between the "hot" catalyst and "cold" reaction mixture appears to be considerable [5,6], which favours the quenching of non-desirable transformations of target products evolved into the catalyst surrounding. While quenching of the gas-phase reactions are important to the high temperature ODE mechanism, it is reasonable to admit that occurrence of the process under microwave heating of catalysts should differs from that under conventional heating.

Oxides of alkaline earth metals are known to be quite active catalysts for partial oxidation of alkanes [2]. The reported studies were focused on high temperature ODE under conventional and MW heating of Ba-containing ($BaO–CeO_2–ZrO_2$ and $BaCl_2–TiO_2–SnO_2$) catalysts. Mixed $BaCl_2–TiO_2–SnO_2$ multi-component catalysts demonstrated a good performance for the oxidative dehydrogenation of ethane to produce ethylene under conventional heating [7]. The ZrO_2-CeO_2 system is a highly thermostable system capable of storing oxygen and thus often used in modern three way catalysts for neutralization of motor vehicle emissions [8]. The cerium-zirconium systems were supposed to allow hydrogen evolved during dehydrogenation to be oxidized following the stage mechanism.

2. Materials and methods

2.1. Catalyst preparation

$BaO–CeO_2–ZrO_2$ catalysts were prepared by precipitation. A typical procedure for preparation of $BaO–CeO_2–ZrO_2$ catalyst was as follows: the mixture of 11 g $ZrOCl_2$, 4 g $Ce(C_2H_3O_2)_3$ and 8 g $BaCl_2$ was dissolved in distilled water under vigorous stirring. The obtained aqueous solution was precipitated by ammonia (NH_4OH) until pH = 10.6 and then washed with distilled water until neutral pH. The residue was semidried after the evaporation of this solution at 100 °C, then granulated and calcined in air at 500 °C for 20 min and crushed and sieved to 0.5–1.0 mm before testing. The final composition of the catalyst was 14 wt. % CeO_2, 48 wt. % ZrO_2 and 38 wt. % BaO.

The $BaCl_2–TiO_2–SnO_2$ catalyst with the atomic ratio Ba:Ti:Sn = 1:1:1 was prepared according to the method described elsewhere [7]. All chemicals were purchased from Aldrich (purity > 99%), and used without further purification. A typical procedure for preparation of the $BaCl_2–TiO_2–SnO_2$ catalyst was as follows: the mixture of 1.50 g $BaCl_2{\cdot}2H_2O$, 0.49 g TiO_2 and 0.92 g SnO_2 was moistened with a little amount of deionized water and put in a mortar until it became a hard paste. The sample was dried at 120 °C for 1 h and calcined in air at 800 °C for 3 h, crushed and sieved to 0.5–1.0 mm before testing.

2.2. Dielectric properties measurements

Dielectric constant ε' and loss tangent tanδ of the samples were measured ex situ at room temperature in air using the cavity perturbation technique [9]. A sample loaded in a quartz test tube was positioned along the central axis of the cylindrical cavity and excited by oscillation mode TM_{010}. The following relationships were used to determine ε' and tanδ [9]:

$$\varepsilon' = 1 + 0,54\left(\frac{D}{d}\right)^2\frac{\Delta f}{f_{res}}$$

$$tg\delta_d = \left(\frac{0,27}{\varepsilon'}\right)\left(\frac{D}{d}\right)^2\left(\frac{1}{Q_L} - \frac{1}{Q_{LS}}\right)$$

where D is a diameter of the cylindrical cavity, d is an inner diameter of the quartz test tube, Δf is a shift of the resonance frequency f_{res}, and Q_{LS} and Q_L are quality factors of the cavity with and without the sample inside. To exclude the effect of quartz on the parameters to be measured, the quality factor and frequency for the cavity with the empty quartz tube inside were taken as the initial parameters. Parameters f_{res} and Q were measured using an Agilent PNA -L network analyzer (N5230 A series). The relative errors in ε' and tanδ measurements were 5 and 10%, respectively.

Effective microwave heating of samples was achieved in reactors that were cavities with a high or low mode number. An important characteristic of these devices is the efficiency of MW conversion to sample heat. Generally, MW heating is a complex problem as efficiency of heating depends strongly on dielectric properties, as well as on the sample volume. An original technique was used to identify the optimal conditions for effective heating according to the properties of the sample [10]. This simple technique was based on measuring electrodynamic characteristics of the "cavity + sample" system at a low MW power without heating the sample and made it possible to calculate efficiency of MW conversion to the sample heat in the lab scale set up.

The following relationship was used [10]:

$$\eta = \{1 - (1 + \beta)\frac{Q_{LS}}{Q_0}\}\frac{4\beta}{(1 + \beta)^2}$$

where β is coupling coefficient of the sample-loaded cavity and the feed line, Q_{LS} is quality factor of the sample-loaded microwave cavity and Q_0 is the quality of the empty cavity. The relative error of measurements was 5%.

2.3. Catalytic testing

Catalytic tests were performed at atmospheric pressure in a continuous gas flow system. A flow tubular quartz reactor (internal diameter 16 mm) with the fixed catalyst bed was used. The reactor with the catalyst (total mass m = 2–4 g, particles of 0.5–1.0 mm in size) was heated either by an electric resistance furnace, or by the MW irradiation.

The MW heating was carried out using a lab scale set up (power up to 1 kW) based on a rectangular single-mode cavity with high Q-factor (~6000), which is excited by oscillation mode TE_{102} (Fig. 1).

The reactor with the catalyst was inserted into the cavity so that the catalyst bed was positioned in the E-field node (Fig.2). This is a complex problem to determine temperature during MW heating. The main problems in temperature measurements are described elsewhere [11]; the suggested rather complex approach to solving the problems includes the procedure of successive recalibration. In the present work, the

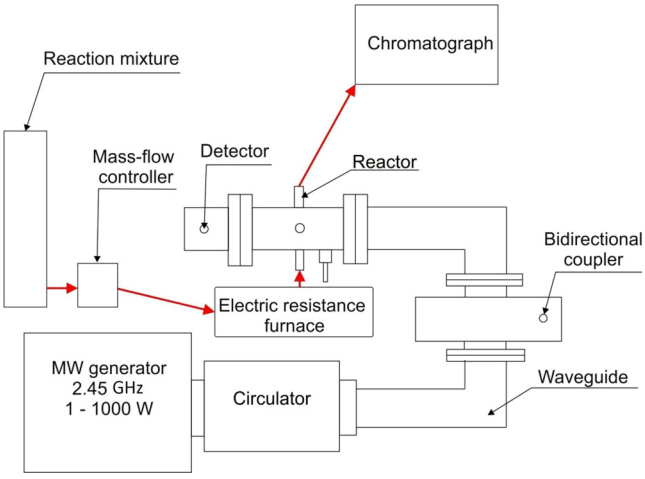

Fig. 1. Block diagram of the MW catalytic testing set up.