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Oxidative dehydrogenation of propane over V_2O_5-MgO/TiO_2 catalyst Effect of reactants contact mode

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Abstract

The performance of the active catalyst 5%V_2O_5-1.9%MgO/TiO_2 in propane oxidative dehydrogenation is investigated under various reactant contact modes: co-feed and redox decoupling using fixed bed and co-feed using fluid bed. Using fixed bed reactor under co-feed conditions, propane is activated easily on the catalyst surface with selectivities ranging from 30 to 75% depending on the degree of conversion. Under varying oxygen partial pressures, especially for higher than the stoichiometric ratio $O_2/C_3H_8 = 1/2$, nor the propane conversion or the selectivities to propene and COx are affected. The performance of the catalyst in the absence of gas phase oxygen was tested at 400 °C. It was confirmed that the catalyst surface oxygen participates to the activation of propane forming propene and oxidation products with similar selectivities as those obtained under co-feed conditions. The ability of the catalyst to fully restore its activity by oxygen treatment was checked in repetitive reduction–oxidation cycles. Fluid bed reactor using premixed propane–oxygen mixtures was also employed in the study. The catalyst was proved to be very active in the temperature range 300–450 °C attaining selectivities comparable to those of fixed bed.

Keywords: Oxidative dehydrogenation; Propane; Vanadia catalyst; Fixed bed reactor; Fluidized bed reactor; Cyclic operation

1. Introduction

The accelerating global demand for propene in the modern petrochemical industry requires the development of on-purpose technologies, which would overcome the disadvantages of the processes used nowadays. Steam cracking and fluid catalytic cracking of heavy petroleum fractions, the two established processes for propene production suffer from low propene selectivity and high separation cost. Propane catalytic dehydrogenation, even though more selective than the established processes, experiences thermodynamic limitations, high-energy consumption, side pyrolysis reactions and coke deposition. Dehydrogenation of propane in the presence of oxygen presents a feasible option. The presence of oxygen raises the thermodynamic restrictions of dehydrogenation and the exothermic character of the reaction renders it an energetically efficient process. The development of efficient heterogeneous catalysts for the gas phase oxidative dehydrogenation of alkanes is of great importance because of the economic benefits of using light paraffins for the production of important base chemicals. However, the yield of alkenes on most of the catalysts used is not satisfactory, due to the side reactions leading to the formation of COx [1].

The development of active and selective catalytic materials for the oxidative dehydrogenation of light alkanes to their corresponding alkenes has been the focus of many academic and industrial research groups [2–11]. Most of the catalysts investigated so far are based on reducible transition metal supported or combined with other oxides. In the presence of transition metal oxides the reaction proceeds through a Mars and van Krevelen mechanism, which involves reduction of the catalyst by the alkane with participation of the lattice oxygen, followed by re-oxidation with oxygen. Vanadia based materials are among the most active and selective catalysts [6–13]. As is well known, the catalyst performance depends on a number of factors, such as the structure of surface species, the chemical nature of the active oxygen species, the redox properties and the acid-base character, which in turn depend on transition metal loading, dispersion and support effects [2–7].

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It is well recognized that increase in selectivity could be achieved not only as intrinsic catalytic function but via engineering route as well, using such reactor designs and operating modes which retard the initial propane and/or sequential propene combustion. A particular way to suppress or limit the total oxidation reactions consists in performing the oxidation in the absence of gas phase oxygen, e.g. decoupling the reduction and reoxidation steps. In this case the catalyst should be exposed to the flow of the hydrocarbon furnishing ‘‘selective oxygen’’ for the formation of products with simultaneous reduction, while in a second step the full oxidation of the catalyst should be accomplished via exposure to oxygen flow. This mode of operation – representing an important breakthrough in the field of selective oxidation – is successfully applied for the production of maleic anhydride via selective oxidation of *n*-butane using recirculating fluid bed reactor system [14]. Advantages of the decoupling process also include the better control of the reaction heat and the avoidance of safety problems. The possibility of implementation of this approach in the oxidative dehydrogenation of lower alkanes has recently attracted the interest of the scientific community. Most of the studies conducted via the decoupling redox mode report an increase in the selectivity to the desired olefin [15–20]. However, this is not the case for all the catalytic materials used. It is reported that the isolation of the active sites, the nature of active species and the degree of conversion are crucial for determining the selectivity to the olefin under anaerobic conditions [19,20].

Apart from high selectivity, factors like the safety of the process – due to the explosivity of the hydrocarbon and oxygen mixtures – and heat management are of paramount importance for the selection of the appropriate reactor system and the reactants contact mode. The use of fluidized bed reactor offers significant advantages to the oxidative dehydrogenation process since it improves the safety of the process, allows very good control of the reaction temperature and thus it is preferred for highly exothermic reactions such as the oxidative dehydrogenation of alkanes [1]. The use of fluid bed where the reduction and reoxidation regimes are separated in situ has been studied in the oxidative dehydrogenation of butane with promising results concerning the selectivity and demonstrating the perspectives of such a reactor concept [21,22]. Other approaches like the use of membrane reactor, with distributed and controlled oxygen feed have also been tested resulting in fairly high selectivity but modest success due to the low productivity and the well known problems related to the inferior stability of the membrane materials [23,24].

Recent studies in our lab showed that a catalyst containing 5%V_2O_5 on TiO_2 promoted with 1.9 wt% MgO, is a very promising one in the oxidative dehydrogenation of propane, achieving very high productivity to propylene (2 kg C_3H_6 per kg catalyst per hour) at relatively low temperature 400 °C [25]. The aim of present study is to improve further the selectivity to propylene not by modification of the catalytic system itself, but by using either different than fixed bed reactor and/or contact mode of the reactants. Here, we present the results obtained applying cyclic operation conditions of the reacting feed by switching the flow between propane and oxygen in the fixed bed reactor and a comparative study of the catalytic performance using fixed and fluidized bed reactors.

2. Experimental

2.1. Catalyst preparation

The support used in the preparation was TiO_2 supplied by Norton with specific surface area 50.8 m^2/g. Prior to impregnation, the support was crushed and sieved to a particle size of 106–180 μm. The catalyst was prepared via sequential wet impregnation of 5%V_2O_5 and 1.9%MgO on TiO_2. The first step was the introduction of MgO using $MgNO_3 \cdot 6H_2O$ (J.T. Baker) as precursor, on TiO_2 followed by intermediate drying at 120 °C and calcination at 600 °C for 3 h in air. In a next step V_2O_5 was deposited, using as precursor NH_4VO_3 (Merck), on MgO-TiO_2 and the sample was dried overnight at 120 °C and finally calcined at 480 °C for 3 h in air. Details on the preparation and the physicochemical properties of the catalyst can be found in a previous publication [25].

2.2. Catalytic experiments

Three different reactor setups were employed for the investigation of the catalytic performance under various operating conditions.

The oxidative dehydrogenation experiments were performed in an experimental unit equipped with quartz tube fixed bed reactor with 9 mm i.d. The temperature monitoring in the catalyst bed was accomplished with a coaxial thermocouple. The catalyst loading (0.1 g) was mixed with equal amount of quartz particles of the same size to avoid hot spots. The catalyst was pretreated in oxygen flow at 500 °C for 0.5 h. The composition of the reacting mixture used was $C_3H_8/O_2/He = 5/5/90$.

Redox decoupling experiments were also conducted in the conventional fixed bed reactor setup with the sampling of the reaction products performed using a Valco 6-positions valve. In addition to this, tests concerning the stability of the catalytic performance under repetitive reduction-reoxidation cycles were performed in a specially designed transients unit with a fast response less than 10 s. The reactor employed was of quartz U type. The composition of the alternate feeds was 5% C_3H_8 and 5% O_2 in He, respectively. The catalyst loading used was 0.1 g.

Experiments under fluid bed conditions were conducted in a 35 mm i.d. and 400 mm long quartz reactor. Inert SiC was added to act as a coadjutant of fluidization, having similar particle size to that of the catalyst used. Approximately 38 g of catalyst and SiC mixture were used (2 g of catalyst and 36 g of SiC). The reactants (propane and oxygen diluted with He) were fed via a quartz distributor at the bottom of the reactor. The gases were passed through a cyclone and a filter to remove solid particles and a liquid receiver (set at 0 °C) to remove the water. Catalyst particles in the range of 106–180 μm showed good fluidization behavior. The minimum fluidization velocity, u_{mf}, as theoretically calculated was 1.75 cm s^{-1}. Tests were