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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 conducted at relative velocities varying between 1.1 u_{mf} and 1.4 u_{mf}. The reacting mixture composition and the catalyst pretreatment conditions were the same as in the fixed bed.

The analysis of the reaction products exiting fixed and fluid bed reactor was accomplished via on line connection using a GC equipped with a TC Detector. Two columns in series-bypass configuration were used for the analysis: a Porapak Q and an MS 5A. The reaction products were mainly C_3H_6, CO_2, CO and H_2O. The amount of oxygenates other than COx was negligible at the reactor exit.

The composition of the exit stream in the transients unit was followed by mass spectrometry: An online MS analyzer (Balzers, Omnistar) was used to monitor the evolution of the signals corresponding to various fragments. The main fragments (m/e) recorded were 2, 4, 12, 17, 18, 28, 29, 32, 41, 43 and 44. The intensity of the signal for each reactant/product was normalized, based on the relative sensitivity factor of each species with respect to helium and corrected for contributions from other components, based on the cracking patterns of each molecule.

3. Results and discussion

The catalytic formulation 5 wt% V_2O_5-1.9 wt% MgO on TiO_2 (denoted VMgTi) proved as the optimum one in terms of activity among the various V-Mg on TiO_2 catalysts, studied in propane oxidative dehydrogenation [25]. The main physicochemical properties of the sample are summarized in Table 1. The catalyst has a surface area of 41.3 m^2/g and the only crystalline phase identified is that of titania anatase. Vanadia is highly dispersed on the surface forming a monolayer of VOx species (density 7.7 VOx/nm^2) which are reducible under H_2 flow with T_{max} at 580 °C. The acidity of the catalyst as measured by NH_3-TPD, amounts to 0.63 mmol NH_3/g distributed in sites of weak and medium strength.

The catalytic performance in propane ODH at three reaction temperatures (350–400–450 °C) is presented in Table 2. The catalyst is highly active attaining 30% propane conversion at 450 °C under low W/F (0.06 g s cm^{-3}), which corresponds to a nominal residence time of 50 ms. The products formed are C_3H_6, CO and CO_2 with selectivities depending mainly on the propane conversion and to a lesser extent on the reaction temperature. The selectivity versus conversion relation, obtained from experiments performed at constant temperature (450 °C) and various W/F ratios is rather typical of the parallel/consecutive reaction networks with the selectivity of the desired product decreasing as a function of conversion (Fig. 1). It is clear that the presence of basic MgO improves the dehydrogenation over the whole range of the conversions studied (0–25%) compared to the non-promoted vanadia on titania catalyst. Propene selectivity boosting is almost equally distributed, indicating that the increase of basicity induced by MgO drastically inhibits the initial rates of propane direct combustion to COx.

Table 1
Physicochemical characteristics of the 5 wt% V_2O_5/TiO_2 catalyst promoted with 1.9 wt% MgO [25]

Atomic ratio (V/Mg)	1.16
Surface area BET (m^2/g)	41.3
Crystalline phases	TiO_2 (anatase)
TiO_2 crystal size (nm)	30.6
VOx surface density (nm^2)	7.7
TPR H_2, T_{max} (°C)	580
TPD NH_3 (mmol NH_3/g cat.)	0.63
Weak/medium acid sites	1.74

Table 2
Reactivity of 5 wt%V_2O_5-1.9 wt%MgO/TiO_2 catalyst in propane ODH (W/F = 0.06g s/cm^3, C_3H_8/O_2/He = 5/5/90)

Temperature (°C)	350	400	450
Conversion (%)			
C_3H_8	6.30	15.01	30.15
O_2	10.75	34.20	84.47
Selectivity (%)			
C_3H_6	65.71	46.55	30.35
CO	22.23	35.37	45.37
CO_2	12.06	18.08	24.27

To further investigate and evaluate the performance of the VMgTi catalyst under variable oxygen pressures a series of experiments was performed at temperature 400 °C, maintaining the partial pressure of the propane constant (50 mbar). The oxygen partial pressure varied from 10 to 100 mbar, while the total inlet flow was kept constant by balancing with He. The effect of oxygen partial pressure on the conversion/selectivity patterns is depicted in Fig. 2(a and b). Increase of the oxygen concentration in the feed stream up to the stoichiometric ratio for ODH reactions ($O_2/C_3H_8 = 1/2$) affects positively the conversion of the alkane. Further increase of the O_2 pressure does not have any effect to the propane conversion. Concerning the selectivities to the products (Fig. 2b) the differences observed in the range up to 25 mbar oxygen pressure are not significant, well explained by the change in propane conversion. For higher than stoichiometric ratio, propene, CO and CO_2 with selectivities 65, 21 and 13%, respectively, retain their

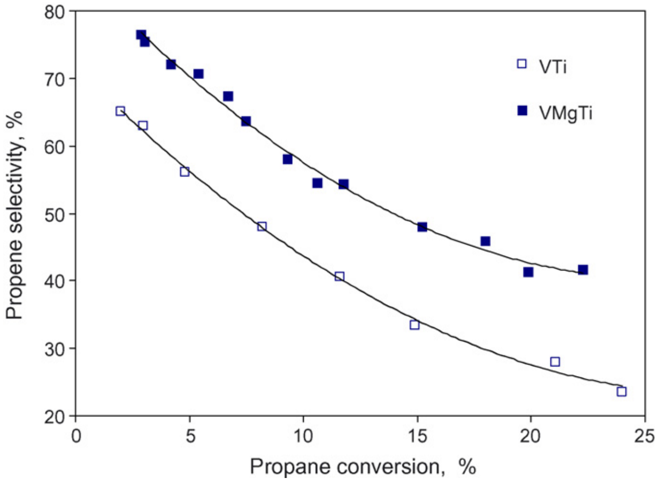

Fig. 1. Propene selectivity vs. conversion obtained at variable W/F ratios over 1.9 wt% MgO promoted and non-promoted 5 wt% V_2O_5 on TiO_2 catalysts (T = 450 °C, C_3H_8/O_2/He = 5/5/90).

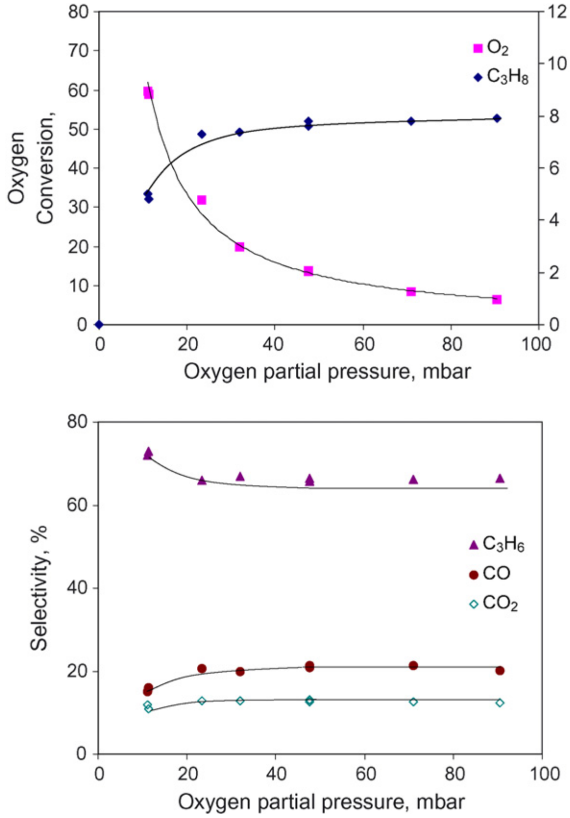

Fig. 2. Effect of oxygen partial pressure to (a) conversion of propane and (b) product selectivities obtained over VMgTi catalyst at constant propane pressure = 50 mbar and temperature 400 °C.

proportions even in the presence of large excess of oxygen. These results imply that the extent of consecutive reactions with the participation of gas phase oxygen is rather limited under the conditions studied (relatively low conversion) and that the catalyst oxygen drives both the selective and the unselective paths in product formation. The zero order dependence on oxygen partial pressure especially when oxygen in the feed exceeds the stoichiometric ratio for oxidative dehydrogenation has been also pointed in the literature [2,26]. However, according to a recent review on kinetics of oxidative dehydrogenation of lower alkanes, the participation or not of gas phase oxygen to primary and consecutive pathways largely depends on the catalytic system used and the feed concentrations [27].

To clarify the role of the catalyst oxygen and its contribution to the selective formation of propene, reactivity tests were carried out in the flowing fixed bed reactor system at 400 °C under redox decoupling conditions using in the feed only propane in dilution with He. Before the entrance of the alkane, the catalyst was treated at 500 °C in flowing oxygen. The profiles of the conversion and selectivities attained in the absence of the gaseous oxidant are compiled in Fig. 3 for the duration of 40 s. Indeed, the catalyst oxygen is very active. It activates propane achieving an instant conversion around 10% after 10 s of propane flow. The decrease of propane conversion obtained, is due to the progressive reduction of the catalyst and loss of active oxygen [18]. One might expect that lattice oxygen is more selective favoring the propene formation route. However, this is not the case with the catalyst VMgTi. Lattice oxygen promotes not only the selective routes of the reaction but the unselective as well. The direct formation of appreciable amounts of CO and CO_2 from propane accompanies the formation of propene. Cyclic experiments carried out in a TAP reactor over the VMgTi catalyst led to the same conclusions [28]. The increase in propene selectivity from 60 to 70% observed in the course of time, cannot be ascribed to the existence or participation of more selective oxygen species, but to the lower activity of the catalyst which decreases to 2.5% after 40 s exposure to the reducing stream.

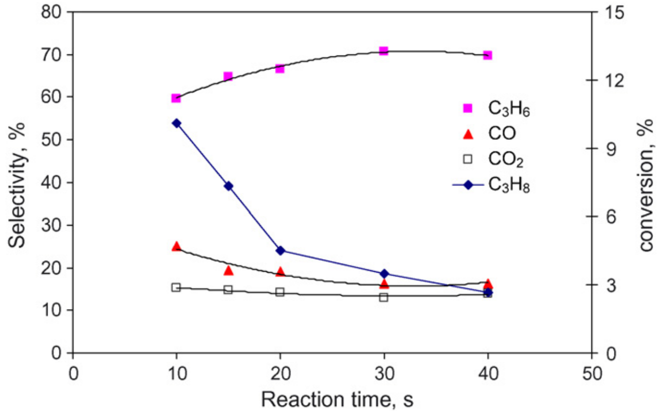

Fig. 3. Catalytic performance of VMgTi sample in the absence of gas phase oxygen ($T = 400$ °C).

Data in the literature concerning the nature of lattice oxygen and its selective participation to the reaction are not scarce. In most of the cases, operation under redox decoupling conditions leads to significantly higher alkene selectivities (15–20) offering thus a strong incentive and advantage of using such a mode of operation under industrial conditions. However, the absence of gas phase oxygen does not necessarily favor the alkene selectivity. Systematic work conducted by Cavani group showed that the active participation of the lattice oxygen to the unselective routes depends on the type of transition metal used and even on the density of the MOx moieties on the support surface. It was nicely demonstrated that high densities of active species, which implies that the isolation of the active sites is not possible, do not favor the selective activation of the alkane, resulting to similar selectivity patterns under both anaerobic and aerobic conditions [20].

The catalyst used in the present study contains 5 wt% V_2O_5 dispersed on the TiO_2 surface in the form of oligomers as demonstrated by in situ Raman measurements [29]. The VOx surface coverage is considered to be close to monolayer since the density is around 7.7 VOx/nm^2. Site isolation, which according to [20], favors high selectivities under redox decoupling conditions, cannot be claimed for the catalyst under study. Of interest to point that the selectivity pattern obtained at 400 °C under co-feed conditions using propane/oxygen ratio 1/1 is exactly the same with that observed under alternate feed mode in the absence of oxygen as clearly shown in Fig. 4. The results confirm the crucial role of the catalyst oxygen to the distribution of the products.

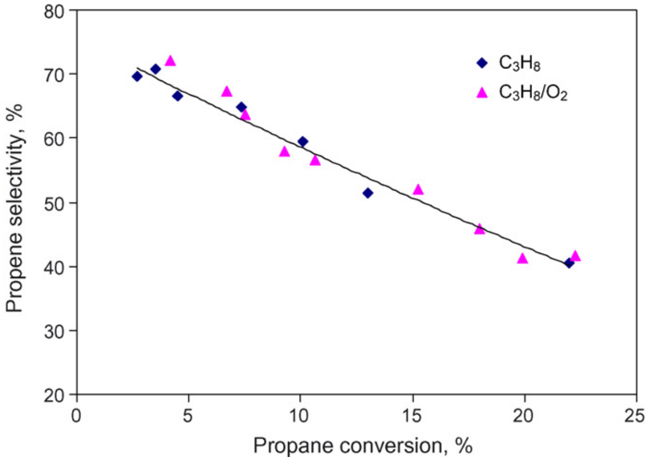

Fig. 4. Propene selectivity as a function of conversion under co-feed and redox decoupling conditions at constant reaction temperature 400 °C.

Exposure of the catalyst to the reducing agent (propane) results in a drastic decrease of the conversion due to the progressive reduction of V^{5+} to V^{4+}. In order to investigate the capability to maintain its activity after repeated cycles and the rate of reoxidation of the catalyst we performed a series of experiments in a fast responding transient reactor system with online continuous monitoring of the reactor effluent with MS analyzer. The twelve consecutive reduction reoxidation cycles with duration 120 and 40 s, respectively, are compiled in Fig. 5. It is observed that the signals of the products C_3H_6, CO and CO_2 decline with time after switching to propane/He flow indicating the gradual loss of activity due to V reduction. The complete reoxidation is confirmed by the reproducible signals of reactants and products after the exposure to oxygen flow. Tests under varying reoxidation duration from 120 s down to 20 s showed that the latter, very short reoxidation time of 20 s, is enough for the catalyst to fully replenish its activity. The formation of H_2 was not detected in any of the experimental conditions, suggesting that titania supported vanadia catalyst presents negligible dehydrogenation activity. The carbon balance based on gaseous reactants and products was higher than 95%, confirming the absence of dehydrogenation reactions, which are accompanied with heavy carbon deposition. Very low amounts of carbonaceous residues were deposited on the catalyst as deduced from the narrow peak in CO profile during the reoxidation step.

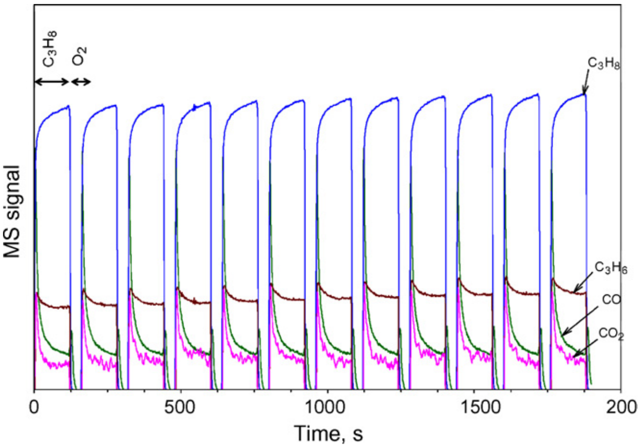

Fig. 5. Repetitive reduction–oxidation cycles over the catalyst VMgTi at 400 °C. Alternate feeds: reduction (5%C_3H_8 in He), oxidation (5%O_2 in He).

Of interest to see in Fig. 5 that while the signals of propene and CO_2 decline continuously with time, at the early stages of the reaction (reduction step) there is an abrupt decrease in the CO signal indicating that "highly active" surface oxygen promotes the oxidation of propane to CO. Depletion of the "highly active" oxygen smoothens the responses to all products. Even though our data are not enough to claim about the nature of this type of oxygen, the presence of adsorbed oxygen on the catalyst surface cannot be excluded as the catalyst sample was pretreated in oxygen environment during the reoxidation step. Literature data support this observation since adsorbed oxygen is considered as the less selective type of oxygen [7,30,31].

Calculations of the theoretical oxygen consumptions based on the integration of the amount of products formed for a time period of 120 s showed that the amount of oxygen removed from the catalyst is 16.3 μmol. The only source for oxygen is the VOx species because neither magnesia nor titania (under these conditions) is reducible. This value corresponds to 5.9% of the total oxygen available in V_2O_5 monolayer. Given that for complete reduction of the available V^{5+} to V^{4+} the amount of oxygen removed is 20%, it is concluded that at the end of each cycle the larger part of vanadia (70%) on the catalyst surface is still on fully oxidized state. Similar values of oxygen depletion after treatment with propane were recorded over VMgO catalyst [15].

The study of the VMgTi catalyst under co-feed and redox decoupling conditions demonstrated that the vanadia species highly dispersed on the TiO_2 surface modified by MgO activate easily propane with the participation of catalyst oxygen forming propene and COx. The similar values of product selectivities obtained in the presence and in the absence of gas phase oxygen, support the conclusion that gas phase oxygen role is limited to catalyst reoxidation.

The experiments presented above were carried out in fixed bed reactors using low amounts of catalyst. Fixed bed reactors operating under realistic industrial conditions are not suited for the oxidative dehydrogenation reaction, since the amount of heat produced, mainly via the deep oxidation route, is quite large especially when operating at high conversions. As mentioned in Section 1, efficient heat removal and maintenance of isothermal conditions in the catalytic bed, thus avoiding the hotspots typical of the fixed beds, can be achieved using fluidized beds. A further advantage of the fluid bed reactor is related to the minimization of the danger associated with the possibility of run away and explosion [1].

To explore the performance of the catalyst under fluid bed conditions, a series of preliminary runs were conducted in a lab scale setup using a quartz fluid bed reactor. The effect of temperature on the VMgTi catalyst reactivity under fluid bed conditions was tested feeding through the distributor a reaction mixture with $C_3H_8/O_2/He = 5/5/90$ composition. Propane

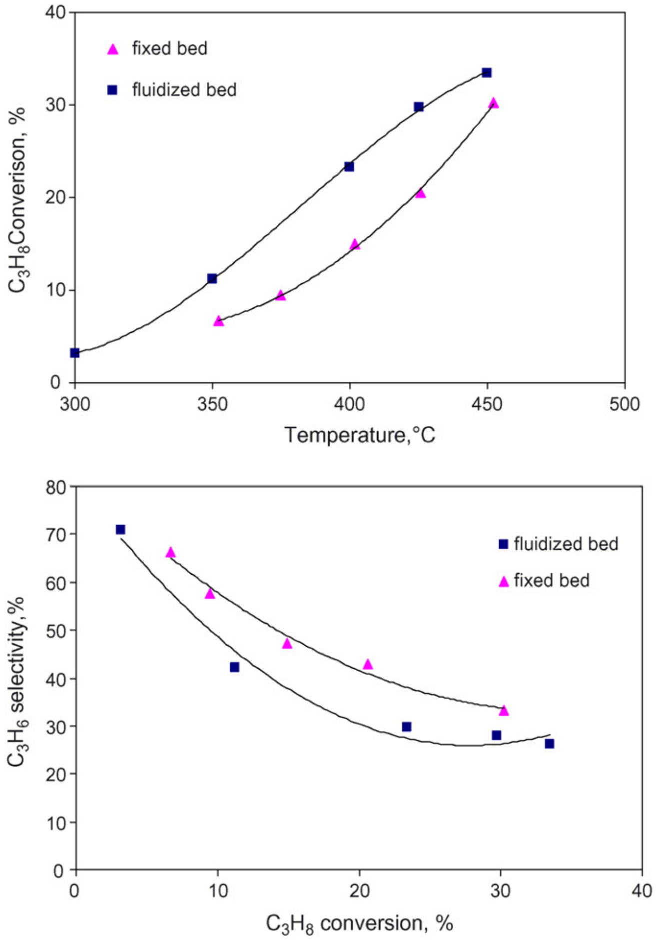

Fig. 6. VMgTi catalyst performance as a function of temperature using fluid bed reactor using premixed feed $C_3H_8/O_2/He = 5/5/90$ (a) conversion of propane and (b) propene selectivities.

conversion and propene selectivity in oxidative dehydrogenation reaction is plotted versus reaction temperature, as shown in Fig. 6(a and b) for the fluidized bed ($u_r = 1.4\ u_{mf}$) and the fixed bed. The higher conversion under fluid bed conditions is attributed to the higher W/F (0.13 g s/cm^3) and longer residence times. The propane conversion at higher than 425 °C, does not increases exponentially with temperature. This deviation is due to the almost complete consumption of oxygen at such conditions. The selectivity to propene decreases with temperature following the same pattern like in fixed bed (Fig. 6b) shifted to lower values. However, the lower selectivity is most probably an effect of the higher conversion attained rather than an intrinsic property of the fluid bed.

The effect of oxygen partial pressure was also tested under fluid bed conditions at temperature 400 °C using propane in the feed with partial pressure 50 mbar (Fig. 7). The conversion of the propane is almost linearly dependent on the oxygen partial pressure and in contrast to the fixed bed conditions, it continues to increase even at the higher than the stoichiometric ratio ($O_2/C_3H_8 = 1/2$). The selectivity to propene as a consequence to the variation in the conversion follows the conventional conversion–selectivity pattern for the VMgTi catalyst with an indication of slightly higher selectivity at lower oxygen partial pressure. The differences observed in the effect of oxygen partial pressure (compare Fig. 2 with Fig. 7) can be explained assuming that gas phase oxygen in fluid bed might have additional role. Apart from re-oxidising the catalyst it is most probable that gas phase oxygen participates to the activation of the alkane and the propene overoxidation reactions. The preliminary results obtained using the conventional fluid bed, imply that the use of fluid bed with distributed reactants feed or even two zone mode of in situ reduction and oxidation might be more effective in terms of selectivity to propene. Worthy to note, that even though the catalyst was not subjected to any special pretreatment, no solid entrainment was observed throughout all the catalyst handling after 8 h of operation.

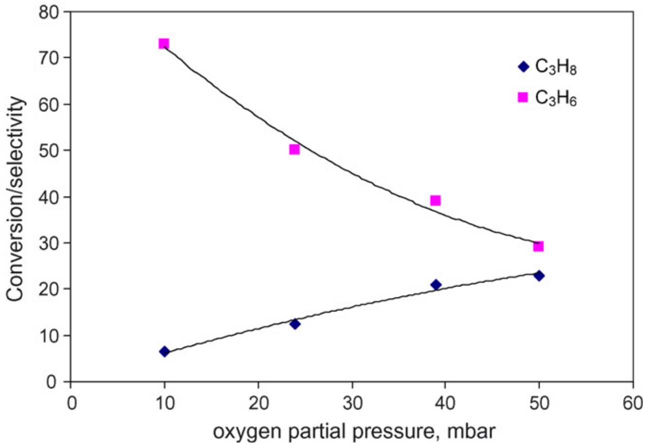

Fig. 7. Effect of oxygen partial pressure on propane conversion and selectivity under fluid bed conditions at 400 °C.

4. Conclusions

The catalyst containing 5 wt%V_2O_5 on TiO_2 promoted with 1.9 wt% MgO exhibits promising catalytic performance in propane oxidative dehydrogenation. The distribution of the products propene and COx mainly depends on the propane conversion with that of propene decreasing due to consecutive oxidation. The beneficial effect of MgO presence in the selectivity is most likely limited to the initial steps of the reaction lowering the extent of propane direct oxidation. Variation of the partial pressure of oxygen does not influence significantly the performance of the catalyst especially for higher than stoichiometric ratios $O_2/C_3H_8 = 1/2$. Even in the absence of gas phase oxygen the catalysts exhibits quite high activity with selectivities not differing from those attained in the presence of gas phase oxygen. Catalyst surface oxygen participates to the propane activation process and product formation with consequent reduction of the surface. Replenishment of the surface and full restoration of the catalyst activity is accomplished after short treatment with oxygen. At the very beginning of the reduction step, high selectivity to COx is ascribed to adsorbed oxygen species which are highly active and unselective. The application of redox decoupling contact mode does not seem to have a positive effect on 5%V_2O_5-1.9%MgO/TiO_2 catalyst. Preliminary testing of the catalyst under fluid bed conditions proved quite promising. The conversion–selectivity relationship shows almost the same dependence on the operating variables like with the fixed bed.

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