KINETIC EVALUATION OF Pd ALUMINA SUPPORTED CATALYST FOR THE REACTION OF OXIDATIVE DEHYDROGENATION OF PROPANE

Hugo Zea[1] and L. M. Carballo[2]
[1]Departamento de Ingeniería Química y Ambiental, Facultad de Ingeniería, Universidad Nacional de Colombia,
Carrera Numero Edificio, of. Bogotá, Colombia
[2]Durham, NC, USA
E-Mail: hrzear@unal.edu.co

ABSTRACT

Monometallic catalysts of Pd supported on gamma-Al_2O_3 were prepared using wet impregnation, pretreated under oxidative conditions and tested for catalytic activity for the reaction of oxidative dehydrogenation of propane (ODHP). Propane conversion and selectivity to propylene on Pd supported catalyst was evaluated as function of feed ratio (W/Feed C_3H_8), ratio of oxygen/propane (U) and temperature, showed a strong effect of the oxygen/propane ratio both on conversion and selectivity. Higher concentration of oxygen in the reactor feed increases propane conversion, but reduces propylene selectivity; the best performance of selectivity as a function of the ratio of oxygen/propane (U) was at the stoichiometric condition (U=1). Propane conversion increases as the feed ratio (W/Feed C_3H_8) increases, on the contrary propylene selectivity decreases as the feed ratio (W/Feed C_3H_8) increases; both behaviours are properly adjusted by a Simplified Eley-Rideal (SEM) mechanism.

Keywords: Pd catalyst, propane reactions, oxidative dehydrogenation.

INTRODUCTION

Important economic incentives exist for the development of catalysts able to activate the selective conversion of alkanes, especially propane. The conversion of light and saturated hydrocarbons to unsaturated ones is a challenging technical endeavour, is necessary to develop active and selective catalysts that would allow meeting an increasing demand for olefins. The oxidative dehydrogenation of propane to propylene (ODHP) has been proposed as a thermodynamically favourable route for the production of propylene from propane (equation (1)).

$$C_3H_8 + 0.5O_2 \leftrightarrow C_3H_6 + H_2O \qquad (1)$$
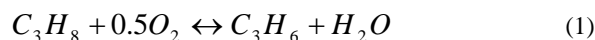
In a previous study [1] the performance of Pd supported in gamma-alumina catalysts for the ODPH reaction has been evaluated, this catalyst presented high activity for the conversion of propane but low selectivity to the formation of propylene, the selectivity was dominated by the formation of CO_x species.

A kinetic model is the basic step for the mathematica1modeling of chemica1 reactions; kinetic models can provide a comprehensive quantitative description of the reaction systems and became fundamentals for the development and optimization of the industrial processes. Several studies have been reported the kinetics of ODHP based on catalysts containing vanadium [2-4] Other catalytic systems such as nickel molybdates [5-7], oxides, mixed oxides, spinels and graphene oxide [7-9] have received less attention. In this study a Simplified Eley-Rideal mechanism (SER) was used to describe the kinetics mechanism of the ODHP reaction over a wide range of compositions, temperatures and flow conditions.

MATERIALS AND METHODS

Catalysts synthesis

Monometallic 1.25% on weight Pd supported on gamma-alumina (1.25Pd) catalysts were prepared by wet impregnation. The support (alumina, Alpha-Aesar, gamma-phase > 99.97 %, surface area; 79 m^2/g, pore volume: 0.31 cm^3/g) was impregnated with an aqueous solutions of palladium chloride ($PdCl_2$) with the proper concentrations to generate the proposed metallic loads as described in detail elsewhere [1].

An oxidative pretreatment consisting of a heating temperature ramp of 5ºC/min from room temperature to 450ºC in dry air atmosphere with a total flow of 70 ml/min (STP) was applied to all the catalysts prepared. These conditions were kept during 120 minutes and then the temperature was increased to 600ºC (5ºC/min), kept at this temperature for 240 minutes and then natural cooling was allowed; catalysts were stored in an inert atmosphere (He) to avoid its degradation.

Catalytic activity

ODHP catalytic activity on 1.25Pd catalyst was measured in a fixed bed flow stainless steel reactor (6.3 mm internal diameter) containing 100 mg of oxidized catalyst sample (particle size between 200 - 250 microns) and coupled directly to a gas chromatograph. Propylene, carbon monoxide and dioxide were found to be the main reaction products. The flow rate of the reaction mixture was controlled with a mass flow meter Bronkhorst High-Tech series F-200 and F201. Preliminary experiments indicated the absence of mass transfer restrictions for the reaction conditions. The reaction was a mixture of 100 ml/min containing propane, oxygen and helium as balance gas.

The catalytic activity was evaluated calculating conversion of propane (X) and selectivity to propylene (S) at three temperatures (400, 450 and 500ºC), varying the ratio of oxygen/propane (U) in the feed to evaluate catalytic activity in the stoichiometric condition (U=1), below stoichiometric condition (U=0.5) and above stoichiometric condition (U=2) as a function of the feed ratio W/Feed C_3H_8 (grams of catalyst/C_3H_8 moles).

RESULTS AND DISCUSSION

Results of the catalytic activity data for the monometallic 1.25Pd catalyst are presented in Figures 1, 2 and 3. Figure-1 shows the variation of propane conversion (X) and selectivity to Propylene (S) as a function of feed ratio (W/Feed C_3H_8) for various oxygen/propane (U) ratios at 400 ºC experiments. It can be observed the reduction tendency in selectivity as the reaction conversion increases. The experiment done below stoichiometric and at stoichiometric conditions (U=0.5 and U=1, respectively) shown overlapping similar profiles of the conversion as the feed ratio increases. Conversion data obtained for feed ratio above stoichiometric condition (U=2) has a stronger increment when compared with U=0.5 and U=1 experiments, with values up to 1.42 times higher. Figure-1 also shows the important effect the feed ratio has on the reaction selectivity; the selectivity profiles for the case of the conditions (U=2 and U=0.5) are substantially lower than the values obtained for U=1 condition, being in average 1.76 and 2.19 times higher than the values obtained for the non-stoichiometric conditions, respectively.
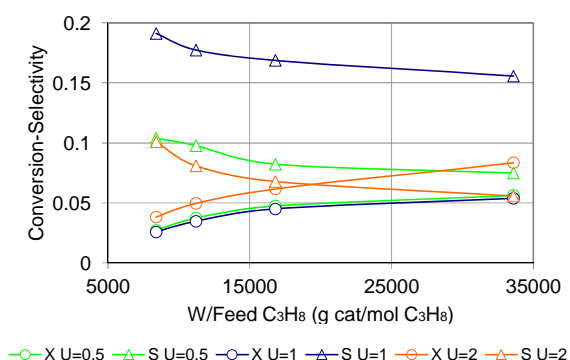

Figure-1. Conversion and selectivity as function of feed ratio (W/Feed C_3H_8) and the ratio of oxygen/propane (U) at 400ºC.

Figure-2 shows the variation of propane conversion (X) and selectivity to Propylene (S) as a function of feed ratio (W/Feed C_3H_8) for various oxygen/propane (U) ratios at 450ºC experiments. In these set of experiments the tendency of selectivity reduction as conversion increases is still observed; conversion values reported for the 450ºC are higher than the obtained for the 400ºC experiments; on the contrary, the selectivity values reported for the 450ºC are lower than the one obtained for

the 400ºC experiments. Conversion profiles for the U= 1 and U=0.5 conditions have not any longer the overlapping profiles observed on the experiments performed at 400ºC; both profiles have the same initial conversion values close to 0.06 at feed ratio (W/FeedC_3H_8) of 7553; however the profile for the U= 0.5 show a higher slope, departing form the conversion profile of the U=1 ending at values of conversion around 0.13.
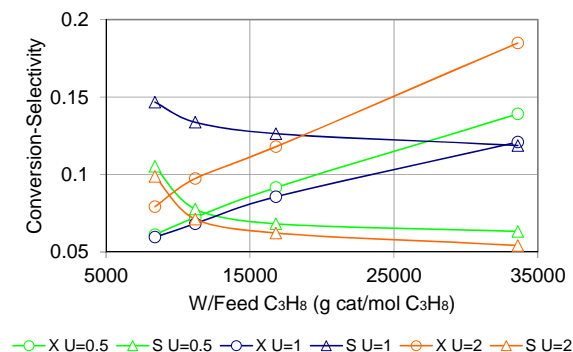

Figure-2. Conversion and Selectivity as function of feed ratio (W/Feed C_3H_8) and the ratio of oxygen/propane (U) at 450ºC.

Selectivity is still higher for the U=1 conditions as observed for the 400ºC experiments; selectivity of the U=1 condition is in average 1.46 and 2.06 higher than the selectivity obtained for the U= 2 and U= 0.5 respectively, this factor are smaller than the ones calculated for the 400ºC experiment.

Figure-3 shows the variation of propane conversion (X) the selectivity to Propylene (S) as a function of feed ratio (W/Feed C_3H_8) for different values of oxygen/propane (U) ratios at 500ºC experiments. The opposed profile behaviours of selectivity and conversion continued; conversion of the U=1 condition shows higher values than the obtained for the U= 2 and U= 0.5 conditions, this behaviour is different when compared to the conversion data at 400 and 450ºC experiments were the conversion values of the U=1 condition were always below the U=2 and U=0.5 conditions.
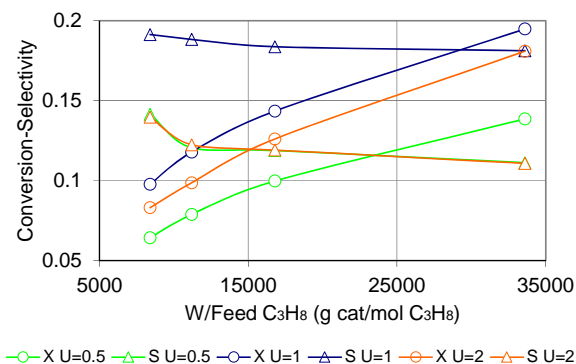
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Figure-3. Conversion and selectivity as function of feed ratio (W/Feed C_3H_8) and the ratio of oxygen/propane (U) at 500ºC.

In term of selectivity changes, the catalyst continue having the best behaviour for the U=1 condition. The U=2 and U=0.5 selectivity profiles overlap following a closing tendency observed both in the 400ºC and 450ºC experiments. The U=1 selectivity is a lot higher than the selectivity for the condition U=2 and U=0.5; this strong dependency of catalysts selectivity as a function of the Oxygen/Propane ratio in the reactor feed is a clear indication that the reaction selectivity is strongly dependent of the amount of oxygen available in the reaction mixture. The selectivity of the U=1 is in average 1.3 and 1.65 times higher than the values obtained at the U=2 and U=0.5 conditions.

The 1.25Pd catalyst was subjected before the catalytic test to an oxidative pretreatment with the purpose of ensuring the catalyst surface to be populated by PdO species [1]. The capacity of O_2 adsorption on PdO is small due to the tendency PdO to reduce when exposed to mixtures of oxygen-propane[10, 11]. A simplified reaction mechanism involves the propane adsorption on the PdO species and the direct reaction between the adsorbed propane on the catalyst surface with oxygen presented in the homogeneous phase. A schematic representation of the mechanism is shown:

$$A + X \leftrightarrow AX \tag{2}$$

$$AX + B \leftrightarrow X + R + S \tag{3}$$

Where A corresponds to propane, B to oxygen, R to propylene and S water to molecules; X corresponds the active sites of the catalysts surface and AX corresponds to the surface specie formed by the adsorption of propane on the active site. Equation (2) represents propane adsorption on an active site, meanwhile equation (3) represents the direct reaction of the adsorbed propane with oxygen from the homogenous phase to produce propylene that desorbs and leave an available active site.

Two kinetic rate equations can be proposed applying the concept of controlling step (41, 64, 65);

equation (4) and (5) correspond to the cases in which propane adsorption is the controlling step and the case where the superficial reaction is the controlling step, respectively.

$$R_A = \frac{k_A \left(Y_A - Y_R * Y_S\right) \Big/ \left(K * Y_B^{1/2}\right)}{\left(1 + K_A * Y_R * Y_S \Big/ K * Y_B^{1/2}\right)} \tag{4}$$

$$R_A = \frac{k_{sr} * K_A * \left(Y_A * Y_B^{1/2} - Y_R * Y_S \Big/ K\right)}{\left(1 + K_A * Y_A\right)^2} \tag{5}$$

Where k_A is the kinetic constant of adsorption of the specie A, k_{sr} is the surface reaction kinetic constant, K_A is the adsorption equilibrium constants for specie A and K is the reaction equilibrium constant.

Propane conversion data as function of the feed ratio (W/Feed C_3H_8) shows the reactors behaves as a differential reactor, the activity catalytic data obtained are adjusted by means of error minimization methods to the reaction kinetic equations (4) and (5)[2, 12-16].

The kinetic rate equation with the best fitting to experimental data for the monometallic catalyst corresponds to one with the propane adsorption as controlling step, equation (4). The results of the experimental kinetics values and the values calculated from the fitted equation are show in Figures 4, 5 and 6 for the 400, 450 and 500ºC temperatures.
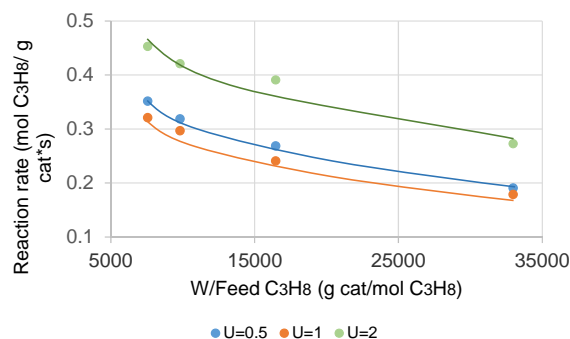

Figure-4. Reaction rate as function of feed ratio (W/Feed C_3H_8) and the ratio of oxygen/propane (U) at 400ºC.

Continuous lines in Figures 4, 5 and 6 represents the reaction rate calculated form the adjusted equation, average error form experimental and calculated date is below 3%. Kinetics and equilibrium constants, adsorption enthalpy, and heat of adsorption are obtained from Vant Hoff equation

$$k_A = 2.26 \times 10^7 e^{\left(-9145.61 \Big/ T\right)} \tag{6}$$

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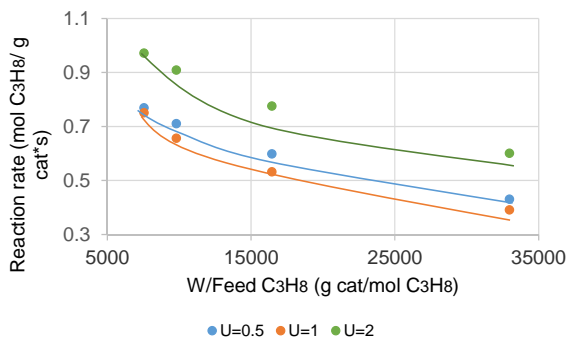$$K_A = 5.013 \times 10^{13} e\left(12635.38 \middle/ T\right) \qquad (7)$$

Figure-5. Reaction rate as function of feed ratio (W/Feed C_3H_8) and the ratio of oxygen/propane (U) at 450ºC.
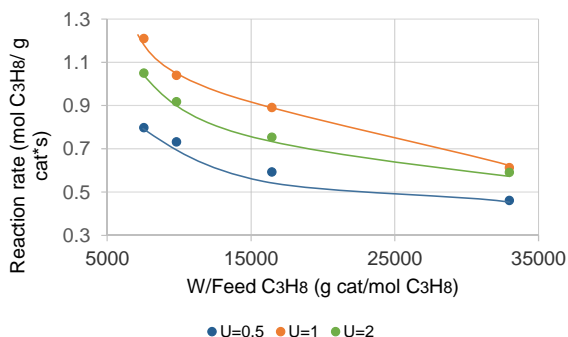

Figure-6. Reaction rate as function of feed ratio (W/Feed C_3H_8) and the ratio of oxygen/propane (U) at 500ºC.

The standard enthalpy change of the adsorption of propane on the active site is -105 kj/adsorbed mol. ODHP reaction enthalpy is (ΔH^o at 420ºC is 2116.7 kJ/mol], is also a irreversible process (ΔG^o at 420ºC is 2176.1 kJ/mol) where the selectivity to propylene is limited by the oxidative process leading to thermodynamically stable CO_x species. Accordingly to the Eley-Rideal mechanism a higher coverage of the adsorbed propane on the catalyst surface and a higher pressure of oxygen on the homogenous phase would be beneficial to yields a higher reaction rate, this trend is well describe for all the reaction temperatures, (W/Feed C3H8) feed ratios and the (U) oxygen/propane ratios, except for the U=2 condition at 500 ºC; a higher U ratio implies more Oxygen molecules available in the homogeneous phase to react with the adsorbed propane, as the temperature reaction increases also the thermodynamically tendency to the production of CO_x also increases.

From the kinetic point of view, the ODHP reaction is generally described by a set of parallel-consecutive reaction system, where both the selective reaction to propylene and its oxidation to CO_x species and the parallel direct formation of COx species are included. Many literature data report that COx is formed mainly by consecutive oxidation of propylene and to a lesser extent on parallel path by direct oxidation of propane [17-19].

CONCLUSIONS

Propane conversion and selectivity to propylene on Pd supported catalyst was evaluated as function of feed ratio (W/Feed C_3H_8), ratio of oxygen/propane (U) and temperature shows a strong effect of the oxygen/propane ratio both conversion and selectivity. Higher concentration of oxygen in the reactor feed increases propane conversion, but reduces propylene selectivity, the best performance of selectivity as a function of the ratio of oxygen/propane (U) was at the stoichiometric condition (U=1).

Propane conversion increases as the feed ratio (W/Feed C_3H_8) increases, on the contrary propylene selectivity decreases as the feed ratio (W/Feed C_3H_8) increases; both behaviors are properly adjusted by a Simplified Eley-Rideal (SEM) mechanism where higher coverage of the adsorbed propane on the catalyst surface and a higher pressure of oxygen on the homogenous phase would be beneficial to yields a higher reaction rate, this trend is well describe for all the reaction temperatures, (W/Feed C_3H_8) feed ratios and the (U) oxygen/propane ratios, except for the U=2 condition at 500 ºC; a higher U ratio implies more Oxygen molecules available in the homogeneous phase to react with the adsorbed propane, as the temperature reaction increases also the thermodynamically tendency to the production of COx also increases.

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