Enhancement of the catalytic performance of V_2O_5/γ-Al_2O_3 catalysts in the oxidehydrogenation of propane to propylene by the use of a monolith-type reactor

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The catalytic performance of a γ-Al_2O_3-supported vanadium oxide catalyst in the oxidehydrogenation of propane to propylene was compared when the catalyst was used in the form of granules (packed fixed-bed reactor), and when the V_2O_5/γ-Al_2O_3 was coated in the form of a thin layer over a cylindrical ceramic support (monolith-type reactor configuration). A considerable enhancement of the catalytic performance was achieved in the latter case, because the consecutive reaction of propylene overoxidation, responsible for a remarkable decrease in selectivity at high conversions in packed-bed reactors, was minimized.

Keywords: oxidehydrogenation of propane; monolith reactor; packed-bed reactor; alumina-supported vanadium oxide

1. Introduction

The synthesis of light olefins for the petrochemical industry is mainly carried out through the well known processes of steam cracking and FCC of natural gas or oil fractions, as well as by paraffin dehydrogenation. Dehydrogenation allows specific olefins to be obtained for use in the polymer and intermediates industry. An important example is given by the synthesis of isobutene by dehydrogenation of isobutane, the production of which has been growing in recent years due to the demand for this olefin for MTBE synthesis [1,2].

However, dehydrogenation suffers from some constraints, being an endothermic reaction, favoured at high temperature and thermodynamically limited by equilibrium. High energy costs are associated with the furnishing of heat at high reaction temperatures (600–700°C). In addition, coke is favoured under such conditions, and the catalysts need frequent regeneration. Alternative processes are (i) the exothermic oxidation of hydrogen generated by the reaction, in order to internally supply the heat for dehydrogenation, and (ii) oxidative dehydrogenation [3–6]. The latter is an exothermic process, not limited by equilibrium, the main drawbacks of which are the loss of the valuable coproduct hydrogen, which is transformed to water, and the low selectivity which is generally achieved, due to the preferred formation of carbon oxides. An advantage in the case of propylene synthesis by oxidehydrogenation, is the possibility to integrate directly the first oxidative step with the downstream reactor for propylene conversion, i.e. to acrylic acid or to acrylonitrile, without the intermediate separation of hydrogen and propylene from the unconverted propane.

Most literature results for propane, *n*-butane and isobutane oxidative dehydrogenation indicate the possibility of achieving good selectivities at low conversion; however, as soon as the conversion is increased, the selectivity rapidly decreases [3–12]. Significant improvements in different oxidation reactions in monolith-type reactors have been recently claimed by Schmidt and coworkers [13–16]. These authors used a noble metal catalyst to activate selectively saturated organic substrates and convert them to olefins or to oxygenated compounds, under very low residence time and high temperature, conditions which allowed the system to operate auto-thermally.

In this work, we present the results obtained using a monolith-type reactor, with a catalyst based on a component typically used in the selective oxidative activation of hydrocarbons, i.e. vanadium oxide. We compared the catalytic performance of an alumina-supported vanadium oxide catalyst in the oxidehydrogenation of propane, when this system is used in a conventional packed fixed-bed reactor, and when the same active compound is spread forming a thin layer coated over a tubular ceramic monolith.

2. Experimental

Catalysts were prepared by deposition of vanadium oxide over a γ-Al_2O_3 powder characterized by a surface area of 150 m^2/g, and an average pore diameter of approximately 5 nm. The same alumina (0.2 wt% γ-Al_2O_3) was deposited in the form of a thin layer (2 or 3.5 μm thick) on the inside of a multilayered α-Al_2O_3 membrane (US-Filter SCT) with tubular configuration (length 150 mm, internal diameter 7 mm, external diameter 11 mm).

Two kinds of reactor configurations were used for the catalytic tests:

(1) *Packed, fixed-bed reactor:* the reactor (internal diameter 10 mm) was made in stainless steel and operated at atmospheric pressure. For the catalytic tests 2 ml of catalyst were loaded. The catalyst, in the form of grains 0.3–0.5 mm in diameter, was prepared by pelletization of the γ-alumina powder upon which vanadium oxide had been previously deposited, and then calcined at 450°C for 6 h. In addition, the catalyst was diluted with 2 ml of inert material (steatite), in order to minimize local overheating due to the exothermic reactions. The residence time was calculated in reference to the volume of the catalyst only. The absence of homogeneous reactions was checked by operating at reaction conditions, in the presence of only the inert material. No propane conversion was obtained up to 500°C. In addition, catalytic tests were made in the presence of pure γ-Al_2O_3 particles only, without deposition of the vanadium oxide. The alumina was completely inactive for the title reaction over the entire range of experimental conditions used for the catalytic tests. Only at temperatures higher than 500°C did cracking reactions, catalyzed by the surface acidity of the alumina, occur which led to the formation of ethane, ethylene and methane.

(2) *Monolith-type reactor:* the catalyst was prepared by deposition of the vanadium oxide onto the γ-Al_2O_3 layer (2 μm thick in the device used for catalysts prepared by ion exchange, 3.5 μm thick for catalysts prepared by impregnation). The reactor (internal diameter 16 mm) was made in stainless steel and operated at atmospheric pressure. The ceramic tube was inserted in the reactor; the external wall of the ceramic tube did not fit the internal wall of the reactor, and a void space was left around the outside of the ceramic tube itself. Graphite o-rings provided seals at the head and bottom of the reactor between the reactor wall and the ceramic monolith. All reactants were made to flow past the core side of the ceramic monolith, where the catalytically active component was deposited. Since the monolith is porous, and since the internal wall of the reactor did not fit the external wall of the monolith itself, diffusion and back diffusion of the reactants or products through the ceramic wall cannot be excluded. The absence of active components in the macropores of the ceramic tube (as will be shown in the Results section), however, makes the diffusion and back diffusion through the monolith wall a non-significant phenomenon, unless either homogeneous reactions or reactions catalyzed by the α-Al_2O_3 (which constitutes the skeleton of the ceramic monolith) were present under the conditions used for propane oxidehydrogenation. In order to verify the absence of these phenomena, the reaction was carried out over the monolith, but without deposition of the vanadium oxide. No conversion of propane was detected throughout the entire range of experimental conditions employed for the catalytic tests.

Products were analyzed by means of gas chromatography. Propane and propylene were separated using a 2 m long Porapak QS packed column, in a gas chromatograph equipped with a FID detector. Oxygenate products (acrolein, acrylic acid, acetic acid, propionic acid) were analyzed with a SP 1200-10% H_3PO_4 supported on Chromosorb WAW packed column, and a FID detector. Carbon oxides and oxygen were separated in a Carbosieve S column, with TCD and oven temperature programmed from 40 to 220°C.

Atomic absorption measurements were carried out with a Varian Spectra A/300 Zeeman instrument, equipped with a graphite furnace.

SEM analysis was made with a Stereoscan Laike Cambridge 440S instrument, equipped with a Link Oxford EDX device for microanalysis.

3. Results and discussion

3.1. Catalyst preparation and characterization

The catalysts were prepared by two different techniques: (i) ion exchange and (ii) multiple impregnation.

Ion exchange was achieved by suspension of 0.1 g of the γ-Al_2O_3 powder in 20 ml of an aqueous solution, containing increasing amounts of NH_4VO_3 (from 0.9×10^{-3} to 3.3×10^{-3} M); the pH of the solution was 7.0. Lower values of pH were tried by addition of HCl, but the amount of resulting vanadium exchanged was lower. The suspension was left under stirring at room temperature for 24 h. The maximum amount of vanadium ion loading achieved with this technique was 1.5–1.55 wt% V. The amount of vanadium was determined by two methods: (i) titration of residual V^{5+} in the aqueous solution, and (ii) dissolution of the final sample in HNO_3/HCl, followed by atomic absorption analysis. The values of vanadium loading determined by the two techniques were very similar. The solid was then filtered from the suspension, dried at 140°C overnight and calcined at 450°C for 6 h. The surface area of the γ-Al_2O_3 was unchanged with respect to the sample before deposition of vanadium oxide.

The deposition of vanadium onto the γ-Al_2O_3 deposited on the tubular ceramic device was achieved with the same procedure, by immersing it in a suitable volume of aqueous solution of NH_4VO_3 for 24 h.

The impregnation technique was used to deposit a higher amount of vanadium ion on the surface of the monolith device. An aqueous solution containing

NH_4VO_3 (0.2 M) was prepared and maintained at 70°C, in order to avoid precipitation of the NH_4VO_3. The ceramic tube was dried at 200°C, then dropped into 200 ml of the hot solution for approximately 0.5 min, then washed with cold water, and finally dried at 200°C for 2 h. The procedure was repeated three times, in order to reach a high vanadia loading. With this technique, it was possible to load 16 wt% V, as determined by atomic absorption analysis. The impregnated system was finally calcined at 450°C for 6 h. This procedure led to a decrease in the surface area from 150 m^2/g (for the pure γ-Al_2O_3) to 135 m^2/g for the impregnated γ-Al_2O_3.

Reported in fig. 1 is the amount of vanadium along the depth of the γ-Al_2O_3 layer, as determined by SEM-EDX analysis, for the exchanged (γ-Al_2O_3 layer thickness 2 μm) and for the impregnated (γ-Al_2O_3 layer thickness 3.5 μm) systems, respectively. For the exchanged sample, the amount of vanadium ranged from 1 to 1.5 wt% in the first 1.5 μm of depth, which corresponds well to the amounts determined by chemical analysis and by atomic absorption on the alumina powder. The amount of vanadium decreases rapidly with increasing depth, and is very low at a depth of 2 μm. In the case of the impregnated membrane, the amount of vanadium was around 16 wt%, and rapidly decreased after 3.5 μm in depth (which corresponds to the γ-Al_2O_3 skin depth).

3.2. Catalytic tests

Catalytic tests of propane oxidative dehydrogenation were carried out with the two different reactor configurations (see experimental for description). For each configuration, two different conditions were used:

(i) a propane-to-oxygen ratio allowing operation at the fuel-rich side, with respect to the flammability zone for the propane/oxygen/inert system; under such conditions, the limiting reactant is oxygen, while the conversion of propane never exceeds 6–8%;

(ii) a propane-to-oxygen ratio allowing operation at the fuel-lean side; under these conditions the hydrocarbon is the limiting reactant, and higher paraffin conversions can be obtained, since oxygen is in considerable excess with respect to the stoichiometric ratio.

3.2.1. Packed fixed-bed reactor: exchanged catalyst

Shown in figs. 2 and 3 are the propane and oxygen conversions and the selectivity to propylene and carbon oxides for the exchanged catalyst. Data were collected by varying the residence time, at the temperature of 450°C, and at two different feedstock compositions: (a) 9.2 mol% propane, 1.6 mol% oxygen (molar ratio C_3H_8/O_2 5.8), balance helium (fig. 2); (b) 2 mol% propane, 20 mol% oxygen (molar ratio 0.1), balance helium (fig. 3). In all cases, the only products obtained were propylene and carbon oxides; no oxygenate product could be found.

The conversion of propane and of oxygen increased over the entire range of residence time examined, allowing us to exclude that diffusion phenomena may condition the rate of reaction. In all cases the selectivity decreased with increasing propane conversion. The decrease in selectivity was more pronounced when the lower hydrocarbon-to-oxygen ratio was used. These data agree with data from the literature, which indicate that the selectivity to the olefin is a function of the propane conversion [3–12]. This is due to the presence of a consecutive reaction of propylene combustion to carbon oxides.

Amongst carbon oxides, CO and CO_2 were obtained in almost equimolar amounts (with a slight prevalence of CO) at a propane-to-oxygen ratio of 5.8. Both products increased in correspondence to the decrease in selectivity

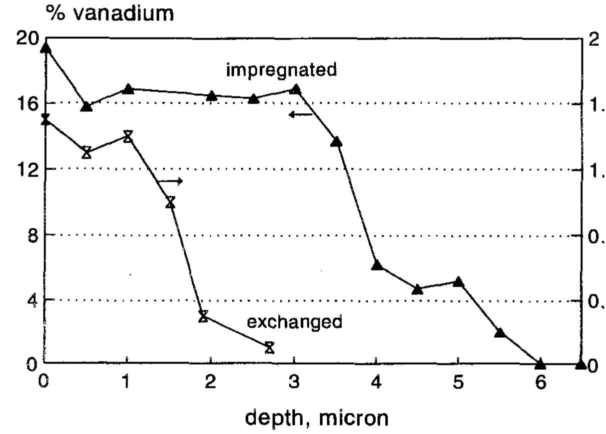

Fig. 1. Amount of vanadium along the depth of the γ-Al_2O_3 over the ceramic monolith as determined by SEM-EDX in samples prepared by ion exchange and by multiple impregnation.

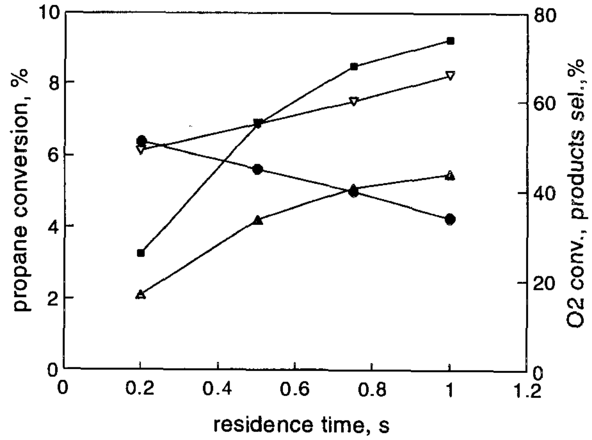

Fig. 2. Propane conversion (△), oxygen conversion (■), selectivity to propylene (●) and selectivity to carbon oxides (▽) with the V_2O_5/γ-Al_2O_3 catalyst prepared by ion exchange in the packed-bed reactor as functions of residence time. $T = 450°C$, propane in feed 9.2 mol%, oxygen 1.6%.

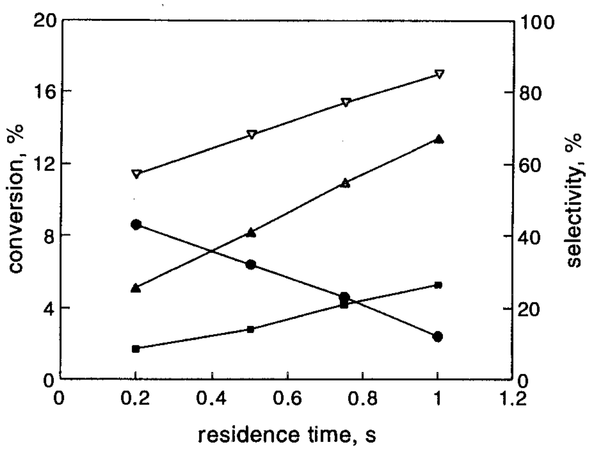

Fig. 3. Catalytic performance of the V_2O_5/γ-Al_2O_3 catalyst prepared by ion exchange in the packed-bed reactor as a function of residence time. $T = 450°C$, propane in feed 2 mol%, oxygen 20%. Symbols as in fig. 2.

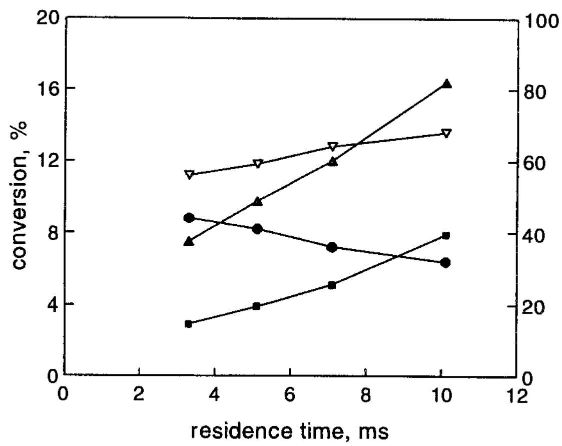

Fig. 5. Catalytic performance of the V_2O_5/γ-Al_2O_3 catalyst prepared by ion exchange in the monolith-type reactor as a function of residence time. $T = 450°C$, propane in feed 2 mol%, oxygen 20%. Symbols as in fig. 2.

to propylene. In the other case, CO_2 prevailed over CO, and the former was the prevailing product formed in correspondence to the consecutive combustion of propylene.

3.2.2. *Monolith-type reactor: exchanged catalyst*

The results obtained in the monolith-type reactor, under the same conditions used in the packed-bed reactor, are reported in figs. 4 (temperature 450°C, propane-to-oxygen ratio 5.8) and 5 (temperature 450°C, propane-to-oxygen ratio 0.1). The flow rate was adapted in order to reach the same levels of conversion that were achieved in the packed-bed reactor. With reference only to the volume of the V_2O_5/γ-Al_2O_3 skin in the monolith, in this case residence times corresponding to a few milliseconds are enough to obtain the same conversion levels as those obtained in the packed-bed reactor.

The most striking difference between the two reactor configurations is the trend of propylene selectivity, which is practically constant under the conditions of fig. 4, thus under fuel-rich conditions, and only slightly declines in the case of fuel-lean conditions (fig. 5). A comparison between the two reactor configurations shows that while the selectivity to propylene is comparable at low conversion (around 55–60%), the difference becomes remarkable at higher conversion of propane. This indicates that the contribution of the consecutive reaction of propylene combustion is substantially less in the monolith-type configuration. This effect can be easily explained by taking into account that the diffusion of propylene into the pores of the catalyst grains, in the case of the packed-bed reactor, is responsible for the consecutive reactions of olefin combustion. By contrast, this effect is nil in the monolith-type reactor configuration, since the catalyst is in the form of a very thin layer.

The effect of the reaction temperature on the catalytic

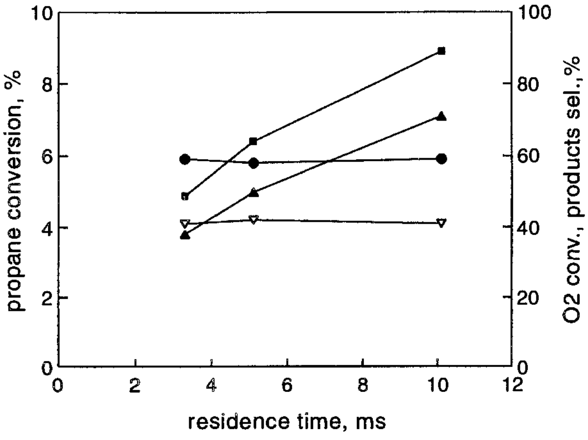

Fig. 4. Catalytic performance of the V_2O_5/γ-Al_2O_3 catalyst prepared by ion exchange in the monolith-type reactor as a function of residence time. $T = 450°C$, propane in feed 9.2 mol%, oxygen 1.6%. Symbols as in fig. 2.

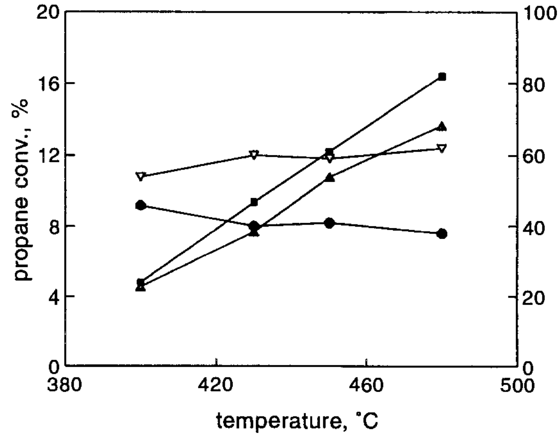

Fig. 6. Catalytic performance of the V_2O_5/γ-Al_2O_3 catalyst prepared by ion exchange in the monolith-type reactor as a function of reaction temperature. Residence time 10.1×10^{-3} s, propane in feed 9.2 mol%, oxygen 4.5%. Symbols as in fig. 2.

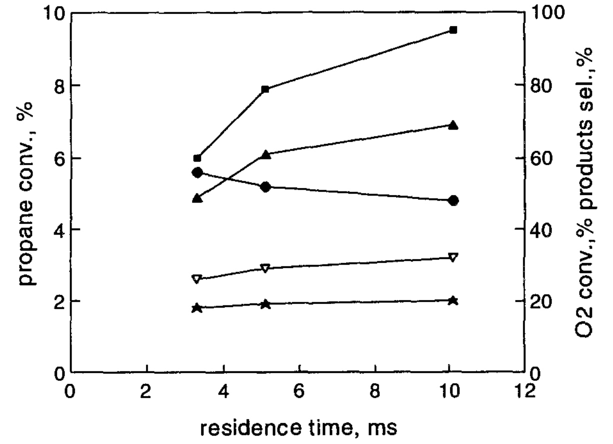

Fig. 7. Propane conversion (△), oxygen conversion (■), selectivity to propylene (●), selectivity to CO (▽) and selectivity to CO_2 (★) with the V_2O_5/γ-Al_2O_3 catalyst prepared by multiple impregnation in the monolith-type reactor as a function of residence time. $T = 400$°C, propane in feed 9.2 mol%, oxygen 1.6%.

performance is examined in fig. 6. Also in this case the selectivity to propylene was maintained high even at total oxygen conversion, and the products distribution was not affected by the temperature. This effect confirms the improvements achieved with this reactor configuration, since the literature data for packed-bed reactors show a decrease in selectivity to the olefin when the reaction temperature is increased. Only at temperatures higher than 500–550°C, at which homogeneous processes favour the oxidative transformation of radical intermediates to the olefin [3], the selectivity to propylene is increased also in packed-bed reactors. In our case, however, homogeneous phenomena can be excluded, since temperatures higher than 500°C were not used.

3.2.3. Monolith-type reactor: impregnated catalyst

The catalytic performance of the impregnated system as a function of the residence time is shown in fig. 7 (molar ratio C_3H_8/O_2 5.8, temperature 400°C). This catalyst turned out to be much more active than the exchanged catalyst, and higher levels of propane conversion were achieved. However, the selectivity to propylene was lower in the case of the impregnated catalyst, and in addition it decreased as the paraffin conversion increased. The amount of CO was relevant, and much higher than CO_2. This effect can be related to the presence of bulk V_2O_5, since it is known that crystalline vanadia in supported catalysts negatively affects the selectivity to the olefin in paraffin oxidehydrogenation [4,17]. Characterization of fresh and spent catalyst by FT-IR spectroscopy demonstrated the presence of aggregates of crystalline V_2O_5, which, by contrast, were not present in the case of the exchanged catalyst.

These data therefore indicate that the significant improvements achieved with the monolith-type reactor are better exploited if a catalyst is prepared which contains a low loading of vanadium oxide.

4. Conclusions

The oxidehydrogenation of propane to propylene can be carried out with monolith-type reactors where the catalytically active component (in the present case V_2O_5/γ-Al_2O_3) is coated in the form of a thin layer over the ceramic support. This configuration allows a better catalytic performance to be obtained with respect to conventional packed-bed reactors. In fact, besides the usual advantages of such reactor configurations (i.e., lower pressure drop), a further advantage derives from the overcoming of diffusional effects that are associated with the use of catalyst formed in grains or pellets. Diffusion phenomena are responsible for the decrease of the selectivity to the product of partial oxidation (in the present case propylene) because of the consecutive reaction of combustion. The use of a thin layer (a few microns) of active component allows a more rapid desorption and diffusion of propylene towards the gas phase.

The amount of vanadium loading is also an important parameter. Higher vanadium loadings make it possible to reach higher levels of propane conversion, but the improvements gained with the use of the monolith-type reactor configuration are in part lost, due to the high activity of bulk V_2O_5 in the combustion of propylene.

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