

Oxidation of propane and propylene to acrylic acid over vanadyl pyrophosphate

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Abstract

The single and combined effect of operating parameters, as water and oxygen concentration, temperature and contact time on the catalytic activity of a VPO catalyst in the oxidation of propane and propylene to acrylic acid has been investigated in a fixed bed reactor. The results indicate that acrylic acid is formed by propylene produced by propane dehydrogenation and that carbon oxides are mainly produced by hydrocarbons oxidation up to 400 °C, acrylic acid oxidation becoming significant only at higher temperatures. Water concentrations >7.5% provide a strong increase of selectivity to acrylic acid at each value of the other operating parameters investigated. Acrylic acid yields can be improved, up to 400 °C, by increasing contact time due to the enhancement of propane conversion coupled with quite constant acrylic acid selectivity.

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1. Introduction

The availability of great amounts of light alkanes has increased the interest in partial oxidation processes for the production of olefins, oxygenates and nitriles allowing the reduction of the environmental impact, replacing olefins and aromatics currently used as raw materials. Nevertheless, most of them are at the research stage, because effective catalysts have not yet been found [1].

The catalytic oxidation of propane to produce propylene and oxygenates, not widely studied up to the end of '90s, has recently received an increasing interest [2–17]. Particularly, three types of catalysts have been claimed [2] for acrylic acid (AA) production from propane: vanadyl pyrophosphate (VPO), heteropolyacids and their derived salts, mixed multi-component metal oxides. Their common features are the presence of vanadium, the redox character and the acidity.

Ai [5] proposed the subsequent reaction path activated by the above-mentioned catalysts (Fig. 1) [2,14]: after propane dehydrogenation, supposed oxidative, the propylene is, on one side, oxidized to acrolein and then to acrylic acid and, on the other side, hydrolysed by water to give 2-propanol, later on dehydrogenated to acetone, whose oxidation produces acetic acid. The oxidation of the acids generates CO_x. Nevertheless, it has been reported [2] that direct oxidation of propane and propylene to CO_x can also occur. Several studies on the reaction pathway activated by mixed oxides have been published [12,14,18]. Védrine et al. [18] proposed that the two main paths reported in Fig. 1 are controlled by the nature of the surface phase of the MoNbSbV oxide catalyst and that acrylic and acetic acid can be formed also through anti-Markonikov and Markonikov water addition to propylene, respectively. A simplified reaction network has been proposed by Lopez Nieto and co-workers [12,14] for MoVTenb oxide catalysts, also including the oxidation of both acids and of propylene to CO_x.

The presence of water strongly affects the catalyst behaviour. For MoVSbNb-mixed oxides [19] it increases

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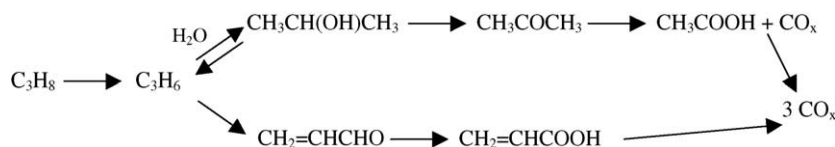


Fig. 1. Reaction scheme of propane mild oxidation to acrylic acid reported by Ai [4].

both propane conversion and acrylic acid selectivity up to 40% with respect to dry conditions, preserving the crystalline structure of the active phase which is partially modified in the absence of water.

Otherwise, propane conversion is strongly depressed by water addition for VPO catalyst whereas selectivity to acrylic acid significantly increases [2,8]. Different hypotheses [8,20–23] have been made to explain the effect of the water (influence on the residence time of the intermediates, prevention of overheating of catalyst surface and oxidation of adsorbed species), but none of them has been completely confirmed. Recently [24], we have demonstrated that water increases the crystallinity of VPO and suppresses a significant fraction of the surface acid sites. An increment of surface hydroxyl groups related to the presence of H_2O has been evidenced by O’Keeffe et al. [20], using DRIFT in situ analysis. The presence of water has been found fundamental also for the formation of acrolein and acrylic acid from propylene on a Pd/SDB catalyst [25].

No papers are devoted to the effect of temperature on VPO whereas, this effect has been studied for mixed oxides catalysts [19] both in the absence and in the presence of water. It has been found that temperature affects in a opposite way acrylic acid and acetic acid selectivity, the former increasing and the latter decreasing with temperature due to the different activation energy of the two parallel reactions.

In order to determine the parameters mainly affecting the acrylic acid yield from propane over a VPO catalyst, in this paper the effect of oxygen and water partial pressure, contact time and temperature was investigated. The occurrence and the prevailing of one or more of the different steps of the reaction pathway were studied by exploring a wide range of operation conditions. Furthermore, in order to evaluate the activity of the catalyst towards the steps following that of formation of propylene, supposed to be the main reaction intermediate, additional catalytic tests were carried out feeding C_3H_6 instead of C_3H_8 .

2. Experimental

2.1. Preparation of the catalyst

VPO catalyst was prepared by Exxon organic method, as described in [8]. An activation was carried out to transform the precursor into the active catalyst, according to the following procedure [8,23]: the precursor was placed in a fixed bed microreactor under a gas flow mix-

ture ($W/F = 0.4 \text{ g h dm}^{-3}$) containing propane, oxygen and nitrogen (1.6/17.8/80.6 vol.%) and heated up to 430°C . After 16 h the temperature was lowered down to 400°C and 2.5 h later water vapour was introduced in the mixture ($\text{C}_3\text{H}_8/\text{O}_2/\text{H}_2\text{O}/\text{N}_2 = 1.6/17.8/20/60.6 \text{ vol.}\%$), without changing the total flow rate. After 20 h under wet conditions the catalyst is considered activated. This procedure provides a structurally and catalytically stable catalyst [24].

2.2. Catalytic tests

Catalytic tests were carried out on activated catalysts in the same quartz microreactor used for the activation. C_3H_8 , O_2 and N_2 flows were controlled by Brooks mass-flow controllers. Water was fed using a Gilson Minipuls 3 pump heating the line from the pump to the reactor at 170°C in order to keep water as vapour phase. Propane and propylene concentrations were measured using a Hewlett–Packard series II 5890 gas chromatograph equipped with a FID. CO , CO_2 and O_2 concentrations were continuously measured with a on-line Hartmann & Braun URAS 10E specific analyzer. Oxygenated products as acrylic acid, acetic acid, iso-propanol, acrolein and maleic anhydride possibly formed during the process, were solubilized into water bubbling the gas stream into two series cylinders and the solution was analyzed with a Waters Breeze HPLC system equipped with a UV detector. AA concentration absorbed in the water during a known time interval is related to its gas concentration through the following equation:

$$Wc_1 = \int_{t_1}^{t_2} F(c_g(t) - c_g^{\text{out}}) dt$$

where W is the amount of water, c_1 , the AA concentration in the water (measurable by HPLC analysis), F , the total flow rate of gases, $c_g(t)$ and c_g^{out} , the AA concentration in the gas phase at the inlet and the outlet of cylinders, respectively, and dt is the differential time integrated in the range t_1 – t_2 , (t_1 and t_2 represent the times of two consecutive measurements, generally $(t_2 - t_1)$ does not exceed 30 min). Due to low gas phase concentration and high solubility of acrylic acid, c_g^{out} is zero. At steady state conditions, AA concentration in the gas phase is constant and time independent. So c_g can be calculated from a simple equation:

$$Wc_1 = Fc_g \Delta t$$

where Δt is $(t_2 - t_1)$.

The effect of oxygen was investigated carrying out catalytic tests at three different O_2 partial pressures (10, 17.8 and

25 vol.%). At each oxygen concentration water concentration was changed in the range 0–25 vol.% without changing propane concentration (1.6 vol.%). The tests were carried out at two contact times, 0.2 and 0.4 g h dm⁻³, while the reaction temperature was changed in the range 300–450 °C. In the catalytic tests with propylene the same concentration (1.6 vol.%) of hydrocarbon was used while contact time ranged from 0.1 to 0.4 g h dm⁻³. All reaction mixtures were out of the flammability limits at 25 °C.

All results reported are related to steady state conditions reached after about 12 h and each experimental point has been confirmed by at least three measurements. Under each condition, the main detected products were CO, CO₂, acrylic acid and unconverted reactants. In propane oxidation only little amounts of propylene, acetic acid and maleic anhydride were detected (oxygenated products having been detected in the oxidation of propylene as well), whose selectivities did not reach 3% in any case. So in the following they will not be reported.

Carbon balance was closed within ±3% error in all experiments.

3. Results and discussion

A more complete catalyst characterization is reported elsewhere [24]. Surface area of activated VPO, measured by BET method, is 12 m²/g, while the only phase detected by XRD and ³¹P NMR is the vanadyl pyrophosphate. SEM analysis revealed that the sample has a lamellar structure, with lamellae generally overlapped and mainly orientated along the same direction.

3.1. Blank tests

Reaction tests in the absence of the catalyst were carried out to verify the occurrence of homogeneous reactions. A

gas mixture containing the hydrocarbon (1.6 vol.%), oxygen (17.8 vol.%) and nitrogen (balance) was fed into a microreactor containing quartz particles with the same dimension of catalyst particles. The hydrocarbon conversion was found negligible up to 450 °C for both propane and propylene, so it can be concluded that results reported below are only catalytic or catalytically induced.

3.2. Oxidation of propane

It was preliminarily verified that no detectable propane conversion takes place under the reaction conditions investigated. Fig. 2 shows propane conversion and selectivity to acrylic acid, CO and CO₂ at 400 °C and $W/F = 0.4 \text{ g h dm}^{-3}$. Propane conversion diminishes decreasing oxygen and increasing water concentration (Fig. 2a). The presence of water reduces the catalytic activity at each oxygen concentration up to 20% H₂O, while oxygen promotes the conversion of propane as expected on the basis previous results reported by Ai [4] and by the authors themselves [8,23]. Selectivity to AA (Fig. 2a) is quite negligible (4–7%) up to 7.5% H₂O for all O₂ concentrations, whereas a significant increase was obtained further enhancing water vapour concentration. CO is the most abundant by-product during the oxidation of propane. Its selectivity (Fig. 2b) does not change introducing water in the feed mixture but decreases significantly at 10% H₂O mainly compensating changes of AA selectivity. The trend of selectivity to CO₂ (Fig. 2b), produced in lower amounts, is similar to that of CO selectivity.

The effect of water has been reported by Novakova et al. [19] for MoVSbNb-mixed oxide catalyst exploring a wide range of concentrations. The opposite effect on propane conversion and the significant formation of AA also in the absence of water found in that work suggest that a completely different mechanism is activated by VPO, further confirmed by the negligible formation of acetic acid representing, on the other hand, one of the main products for mixed oxides cat-

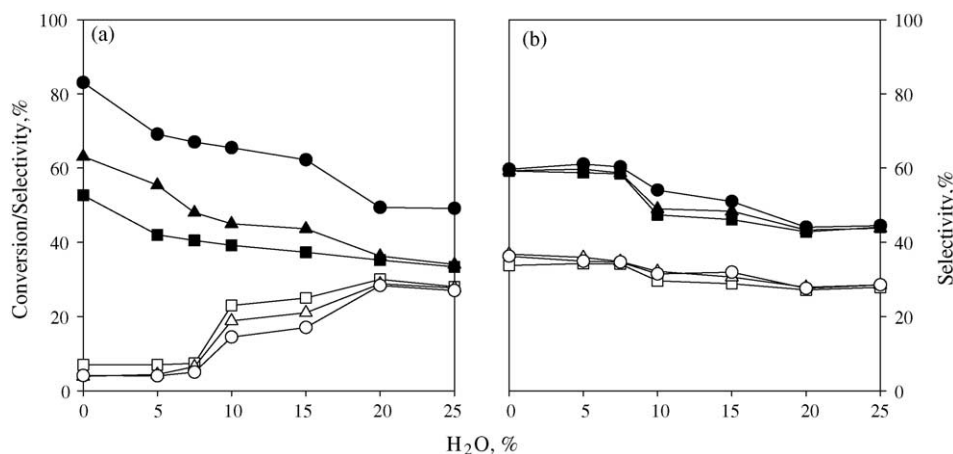


Fig. 2. Catalytic performances in propane oxidation at different water vapour concentrations: $T = 400 \text{ °C}$; $W/F = 0.4 \text{ g h dm}^{-3}$. Curves are parametric in oxygen concentration: 10 vol.% (\square); 17.8 vol.% (Δ); 25 vol.% (\circ). (a) Propane conversion (full symbols), selectivity to acrylic acid (empty symbols); (b) selectivity to CO (full symbols) and to CO₂ (empty symbols).

alysts. O’Keeffe et al. [20] explored the range 0–30% H₂O for the acrolein formation from propane over a VPO catalyst. They found that propane conversion reduces by increasing H₂O concentration, whereas, formation of acrolein, negligible in the absence of water, increases up to 20% H₂O. At 30% H₂O, due to the active sites blocking by water molecules, production of acrolein decreases. These results are in good agreement with our findings suggesting that formation of AA in the presence of water takes place through formation of acrolein.

The effect of water and oxygen concentration is qualitatively the same at lower contact time (0.2 g h dm⁻³). Fig. 3 shows the comparison between conversion and selectivity to AA obtained at the two different contact times investigated at the same O₂ concentration. As expected, conversion increases enhancing the contact time, however, the selectivity to AA does not decrease, as it should be expected by the further oxidation of AA according to a series reactions scheme, on the contrary, slightly increases at each water and oxygen concentration explored. As a consequence, these results suggest that under the reaction conditions investigated, the oxidation of acrylic acid to carbon oxides is negligible, CO_x being likely produced by the parallel oxidation of propane or of some reaction intermediate. This led to obtained AA yields as high as 14%, in comparison with 3–5% yields obtained at $W/F=0.2\text{ g h dm}^{-3}$, just doubling the contact time. An improvement of AA yield with contact time was also found for MoVTeNb catalyst [12], although due to a marked increase of propane conversion not balanced by the slight decrease of AA selectivity.

The effect of reaction temperature was investigated at $W/F=0.4\text{ g h dm}^{-3}$ and 17.8 vol.% O₂ concentration. The catalytic results obtained changing reaction temperature in

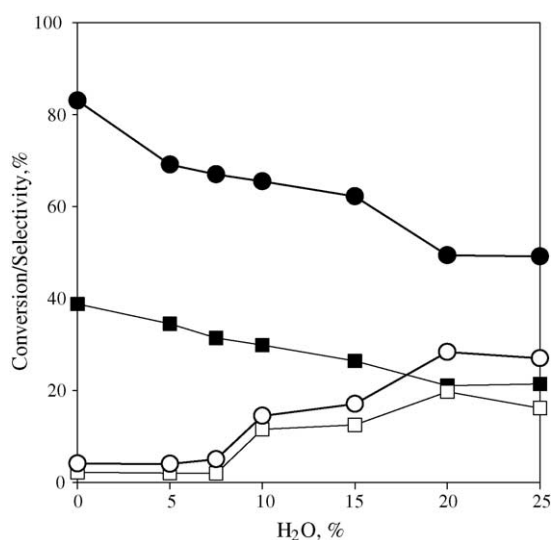


Fig. 3. Propane conversion (full symbols) and selectivity to acrylic acid (empty symbols) in propane oxidation at $T=400\text{ }^{\circ}\text{C}$ and 25 vol.% O₂ at different W/F (0.2 g h dm⁻³ (□) and 0.4 g h dm⁻³ (○)) as a function of water vapour concentration.

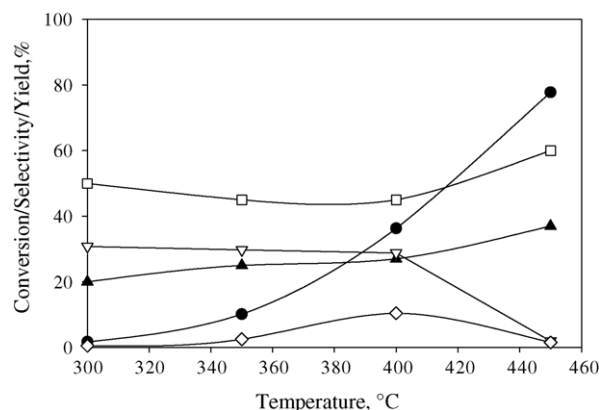


Fig. 4. Conversion (●), selectivity to CO (□), CO₂ (▲), AA (▽) and yield to AA (◇) as a function of the reaction temperature in propane oxidation: $W/F=0.4\text{ g h dm}^{-3}$; $\text{C}_3\text{H}_8/\text{O}_2/\text{H}_2\text{O}/\text{N}_2=1.6/17.8/20/60.6\text{ vol.}\%$

the range 300–450 °C are shown in Fig. 4. Conversion is low at 300 °C and grows rapidly up to 78% at 450 °C. On the contrary, AA selectivity is nearly constant up to 400 °C, i.e. in a wide range of conversion, and then dramatically reduces down to about 2% at 450 °C. A decrease of acrolein selectivity was also observed by O’Keeffe et al. [20] at $T>500\text{ }^{\circ}\text{C}$ for VPO catalyst. The behaviour observed supports the hypothesis that CO_x and AA formation occurs in parallel at temperatures $\leq 400\text{ }^{\circ}\text{C}$, while at temperatures $>400\text{ }^{\circ}\text{C}$ AA oxidation is activated, dramatically reducing the selectivity to the desired product. The acid nature of active sites [2] likely promotes a rapid desorption of AA preventing its overoxidation which, due to a greater activation energy, takes place at higher temperature, probably homogeneously.

These results confirm the activation of a different reaction network by VPO and mixed oxide catalyst. In fact, Novakova et al. [19] found a poor effect of temperature on propane conversion up to 420 °C whereas selectivity to AA markedly increases in the whole range of temperature explored, provided that H₂O concentration exceeds 10%.

A simple reaction model, based on the parallel formation of AA and CO_x from propane, was used to calculate the kinetic constants (k and k_{AA} , respectively) of these two reactions (data for k_{AA} limited at temperatures $\leq 400\text{ }^{\circ}\text{C}$). Since the mixture was very oxygen-rich and oxygen conversion never exceeds 20%, a constant O₂ concentration was supposed. A first-order kinetics with respect to propane concentration and a PFR model for the reactor were hypothesized. Fig. 5 shows the Arrhenius plots for the kinetic constants k and k_{AA} . The quite good linear correlation obtained for both constant validates the hypotheses reported above and confirms our previous results concerning the reaction order with respect to propane and oxygen [23]. Moreover, it shows that the reaction regime is kinetic in the whole range of temperatures investigated, thus mass transfer from gas phase is not limitative. The slope of the Arrhenius plots of k_{AA} and k is the same thus leading to the evaluation of a common value of activation energy of 24 kcal/mol for both reactions.

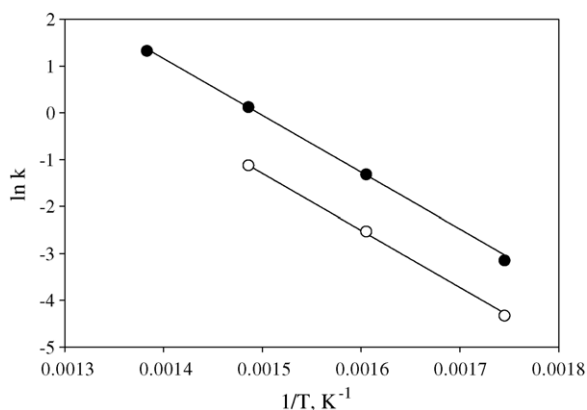


Fig. 5. Arrhenius plots for kinetic constants of propane oxidation: overall (full symbols) and to AA (open symbols).

The combined effect of reaction temperature and water concentration was also studied; the range of temperature investigated was limited to 400 °C in order to avoid conditions promoting the AA oxidation. The results are shown in Fig. 6 for three different reaction temperatures. As expected, conversion increases with temperature and decreases with water concentration at each temperature. The selectivity to AA shows a very similar trend for the three temperatures investigated and is much less affected by this parameter with respect to conversion. As a consequence, the effect of the temperature on AA yield in the range 300–400 °C is positive, i.e. yield increases increasing temperature. The CO/CO₂ ratio decreases increasing temperature, particularly in the region where acrylic acid formation is negligible (water concentration <10 vol.%), indicating that higher temperatures favour CO oxidation to CO₂.

In conclusion, the best operating temperature is 400 °C; as a matter of fact, at lower temperatures propane conversion is too low and not balanced by a significant increase of selec-

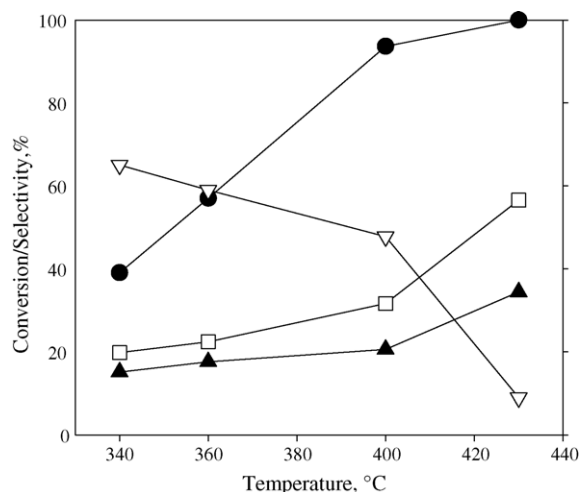


Fig. 7. Conversion (●), selectivity to CO (□), CO₂ (▲) and AA (▽) as a function of the temperature in propylene oxidation at $T=400$ °C, $W/F=0.2$ g h dm⁻³ and O₂ concentration, 17.8 vol.%

tivity to AA, while at higher temperatures selectivity to AA is negligible due to its overoxidation.

3.3. Oxidation of propylene

Propylene conversion and selectivity to the main products are reported as a function of reaction temperature at $W/F=0.2$ g h dm⁻³ in Fig. 7. As expected, propylene is much more active than propane, as shown by C₃H₆ conversion reaching 100% at 420 °C. The contact time does not influence significantly the products distribution but total propylene conversion is reached already at 400 °C for $W/F=0.4$ g h dm⁻³. For both values of W/F explored acrylic acid is the most abundant product up to 400 °C whereas CO is produced in higher amounts with respect to CO₂, as also observed for propane oxidation. This provided a AA yield approaching 50% for

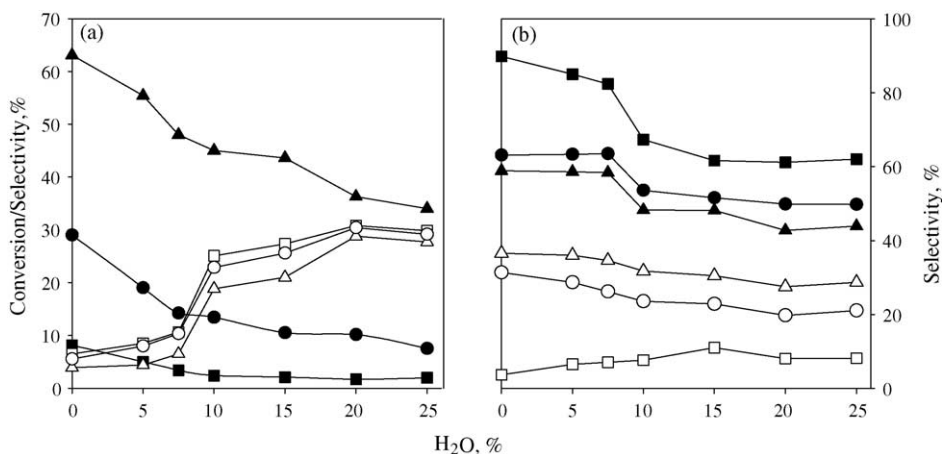


Fig. 6. Catalytic performance in propane oxidation at different water vapour concentrations: O₂ concentration, 17.8 vol.%; $W/F=0.4$ g h dm⁻³. Curves are parametric in the reaction temperature: 300 °C (□); 350 °C (○); 400 °C (Δ). (a) Propane conversion (full symbols), selectivity to acrylic acid (empty symbols); (b) selectivity to CO (full symbols) and to CO₂ (empty symbols).

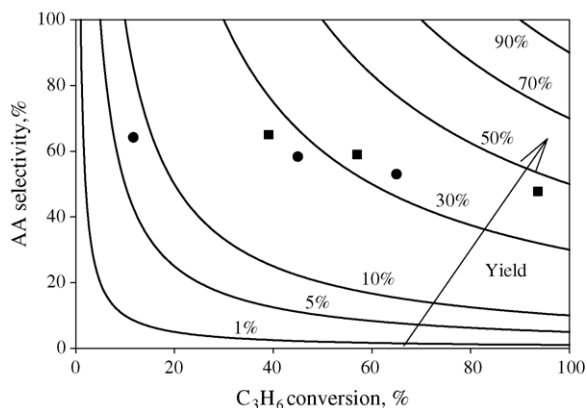


Fig. 8. C_3H_6 conversion as a function of AA selectivity at different temperatures ($C_3H_6/O_2/H_2O/N_2 = 1.6/17.8/15/65.6$ vol.%). (■) $W/F = 0.2$ $g\ h\ dm^{-3}$; (●) $W/F = 0.4$ $g\ h\ dm^{-3}$ (iso-yields curves are reported).

the higher contact time, as shown in Fig. 8, related to the very weak negative slope, typical of a series reaction path, in the wide range of conversion investigated. Therefore, these results suggest that acrylic acid is formed by propylene and when the propane is fed as hydrocarbon reactant, the reaction is limited by the formation of the olefin by oxidative dehydrogenation of propane.

The combined effect of oxygen and water partial pressures was studied also for propylene oxidation at $400^\circ C$. In order to limit propylene conversion, the contact time used in these experiments was $0.1\ g\ h\ dm^{-3}$. Fig. 9a shows propylene conversion and selectivity to AA at different water vapour and oxygen concentrations. As for propane oxidation, introduction of water results in a decrease of hydrocarbon conversion, although this effect is very weak at the lowest O_2 concentration. Moreover, in contrast with propane oxidation, further addition of water does not affect the alkene conversion. Nevertheless, the main difference with the oxidation of the corresponding paraffin is that AA is produced in quite high amounts also in the absence of water vapour (Fig. 9b).

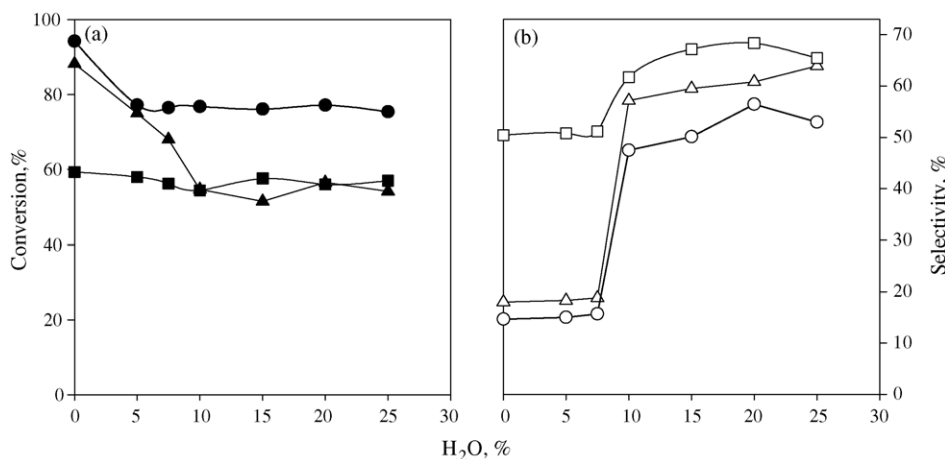


Fig. 9. Propylene conversion (a) and selectivity to acrylic acid (b) at different water vapour concentrations. Curves are parametric in the oxygen concentration: 10 vol.% (□); 17.8 vol.% (△); 25 vol.% (○); $W/F = 0.1\ g\ h\ dm^{-3}$.

Table 1

AA yields for propane ($W/F = 0.4\ g\ h\ dm^{-3}$) and propylene ($W/F = 0.1\ g\ h\ dm^{-3}$) oxidation at $400^\circ C$ at different O_2 and H_2O concentrations

AA yield (%)						
H_2O conc. (vol.%)	C_3H_8			C_3H_6		
	10 ^a	17.8 ^a	25 ^a	10 ^a	17.8 ^a	25 ^a
0	3.7	2.5	3.4	29.9	15.9	13.8
5.0	2.9	2.4	2.8	29.5	13.7	11.6
7.5	3.0	3.1	3.4	28.8	12.8	12.0
10	9.0	8.5	9.5	33.6	31.2	36.5
15	9.3	9.2	10.6	38.7	30.7	38.1
20	10.6	10.5	14.0	38.3	34.4	43.6
25	9.4	9.4	13.3	37.3	34.6	39.9

^a O_2 conc. (vol.%).

Introduction of 10% H_2O resulted in a marked increase of AA selectivity for each value of O_2 partial pressure, its value approaching 70% at 10% O_2 .

Quite different results were found by Xie et al. [25] for the oxidation of propylene to AA on a Pd based catalyst. They observed a minimum value of C_3H_6 conversion at about 43% H_2O ; for higher water concentrations, conversion increased and, at the same time, AA yield increased from a quite negligible value up to 8–12% at 60–80% H_2O .

The effect of oxygen partial pressure is, as expected, to lower AA selectivity at each H_2O concentration. Selectivity to CO and CO_2 (not reported) balances, as also observed in the other experiments, the AA selectivity, CO formation slightly prevailing on CO_2 formation.

AA yields obtained in both propane and propylene oxidation tests at different O_2 and H_2O concentrations are reported in Table 1. A step increase of AA yield was observed by increasing H_2O concentration from 7.5 to 10 vol.% for all values of O_2 partial pressure and in the whole range of temperatures explored. A similar behaviour of AA selectivity was observed for MoVSbNb catalyst [19] between 10 and 20% H_2O which the authors explained with the prevention of molybdenum oxide active phase under H_2O rich conditions.

Likewise, for VPO catalyst this result could indicate that production of AA probably requires the formation of specific active sites promoted by a minimum value of water vapour partial pressure. In a previous paper [23] we showed that surface acidity of VPO is strongly depressed by addition of water by carrying out NH_3 TPD experiments on catalysts operated at 400 °C under reaction mixtures with different partial pressures of water vapour. The largest reduction of the number of acid sites was detected between catalysts operated with 0 and 10 vol.% H_2O , respectively, further increasing H_2O concentration only slightly lowering surface acidity. This supports the hypothesis that a significant modification of the catalyst surface occurs for H_2O concentration higher than 7.5 vol.%, related to the AA formation. Moreover, the large number of acid sites present on VPO surface in the absence of water can be responsible of the high deep oxidation activity found under these conditions. Further increasing water partial pressure, although still reducing C_3H_8 conversion, does not influence the AA yield suggesting that active centres on the catalyst surface have reached stable conditions, as confirmed by TPD experiments. However, it should be noticed that, although low, a certain number of sites active for AA formation should be present also for H_2O concentration $\leq 7.5\%$ since AA is produced also under these conditions, both for propane and propylene oxidation (in poor amounts for propane oxidation likely due to the low concentration of propylene produced).

Results reported by O’Keeffe et al. [20] on acrolein formation from propane at different H_2O concentrations are in qualitative agreement with those reported in this paper. In fact, selectivity to acrolein, well below 5% in the absence of water, increases up to 8–20%, depending on the temperature, when 10% H_2O is introduced. Moreover, comparison of our results with those reported in [20] suggest that acrolein, although detected only in trace amounts under conditions used in the present work, represents an intermediate for AA formation.

The effect of O_2 partial pressure is mainly to improve the hydrocarbons conversion favouring the total oxidation reactions. It does not influence the AA formation, as shown by the about constant yields obtained at different values of O_2 concentrations, in agreement with that reported in [4]. Therefore, the formation of carbon oxides can be limited both decreasing O_2 concentration and enhancing water vapour concentration.

Xie et al. [25] proposed for propylene oxidation over Pd/SDB catalyst that the π -allyl intermediate, formed by propylene adsorption, can react either with oxygen and with water leading to CO_2 or to partial oxidation products, respectively. Addition of H_2O significantly suppresses propylene combustion resulting in a lower global propylene conversion. This competitive reaction scheme is likely activated also by VPO.

At 10% O_2 concentration, for propylene oxidation tests, propylene conversion does not change significantly in the whole range of H_2O concentration (0% included), suggesting a lower contribution of propylene total oxidation, confirmed by the very high selectivity to AA in the range 0–7.5% H_2O ,

probably related to the minor competition of partial oxidation of propylene with its total oxidation, requiring larger amount of O_2 . The step increase of AA selectivity, although less marked, was observed also at 10% O_2 suggesting that generation of additional active sites, or significant suppression of those leading to complete oxidation, occurs also in this case.

4. Conclusions

The study of the single and combined effect of the operating parameters on the acrylic acid formation allowed the determination of the reaction pathway, activated by VPO catalyst, in the mild oxidation of propane. Comparison with other catalysts reported in literature suggests that the prevailing of one or more path of the reaction network is strongly dependent on the nature of the material. Over VPO catalyst in the temperature range 300–400 °C and O_2 concentration between 10 and 25%, acrylic acid is formed by propylene, obtained by propane, whereas CO_x are produced by direct oxidation of hydrocarbons. Oxidation of acrylic acid to CO_x takes place significantly at $T > 400$ °C while formation of acetic acid is negligible in the whole range of experimental conditions explored, in contrast with mixed oxides catalysts greatly favouring this reaction.

Water vapour concentrations exceeding 10% likely generate a large number of active sites for acrylic acid formation and simultaneously suppress those promoting total oxidation. At lower values of H_2O concentration, the total oxidation of propane prevails. The activation of VPO in the presence of at least 10% H_2O has been related to the strong modification of surface acidity observed with NH_3 TPD experiments, previously reported, taking place for VPO operated at an H_2O concentration value $\geq 10\%$ with respect to the same catalyst operated under dry conditions.

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