Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Catalysis Today 91–92 (2004) 275–279

CATALYSIS TODAY
www.elsevier.com/locate/cattod

Role of water in the partial oxidation of propane to acrylic acid

G. Landi [a,*], L. Lisi [b], J.-C. Volta [c]

[a] Dip. di Ing. Chimica, Univ. di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy
[b] Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125 Napoli, Italy
[c] Institut des Recherches sur la Catalyse, CNRS, 2 Av. Einstein, 69626 Villeurbanne, France

Abstract

Effect of water on the catalytic performances of VPO catalyst in the oxidation of propane to acrylic acid has been investigated at 400 °C carrying out both stationary and dynamic tests at different water vapour concentrations. Presence of water, necessary to obtain a detectable formation of acrylic acid, affects, in addition to the catalytic performances, both crystallinity and surface acidity of VPO leading to slow and reversible modifications of the material as shown by XRD and NH_3 TPD analysis. A maximum acrylic acid yield was obtained in correspondence of 15% H_2O. Under this condition, the sample shows the best crystallinity and the highest surface acidity among catalysts operated under wet conditions. A linear correlation between kinetic constant of acrylic acid formation and acid sites was found.

Keywords: Propane oxidation; Acrylic acid; Vanadyl pyrophosphate; Water effect

1. Introduction

The interest in paraffin partial oxidation reactions for production of light oxygenated compounds has grown during last years, due to the possibility of obtaining the desired product through less expensive processes with a lower environmental impact [1]. Most of processes based on paraffin partial oxidation are at research stage, industrial application being limited to few cases, like production of maleic anhydride starting from *n*-butane. Partial oxidation of propane to acrylic acid (AA), although promising, is not widely studied [2]. This compound, representing an important intermediate for the chemical industry, is obtained by two-step oxidation of propylene, having acrolein as intermediate product, catalysed by two different mixed multi-component metal oxides, containing Mo, Fe, Co, V and Cu with an overall theoretical yield higher than 85% [2]. Direct propane oxidation to AA, according to the reaction $C_3H_8 + 2O_2 \rightarrow CH_2{=}CH\text{–}COOH + 2H_2O$, should allow formation of the desired product through a one-step process. From a general point of view, an effective catalyst for the partial oxidation is a redox and acid solid. In fact, the first feature is necessary for the oxygen insertion, while an acid surface allows the adsorption of the intermediates, usually alkenes, moderately basic, and the desorption of the product, which generally possess an acid function [3]. For acrylic acid production from propane, three catalysts have been claimed [2]: vanadyl pyrophosphate (VPO), heteropolyacids and their derived salts and mixed multi-component metal oxides. Their common features are the presence of vanadium, the redox character and the acidity. Vanadyl pyrophosphate is industrially used for *n*-butane oxidation to maleic anhydride since 1970s, but the interest as a catalyst for propane oxidation started in 1980s after the first studies of Ai [4], who proposed the following reaction path: after propane dehydrogenation, supposed oxidative, the propylene is, on one side, oxidised 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 combustion of the acids generates CO_x. Several efforts have been done to enhance VPO performances by doping [2,4–8], in analogy to what has been done for *n*-butane oxidation [9–11]. Nevertheless, very few doped materials showed higher performances than undoped VPO [2,4,8]. In a previous work of ours [19], we found comparable catalytic properties of doped (Fe, Ga) and undoped VPO. On the contrary, the feed composition, particularly the presence of water vapour, plays an important role. Water has a double

---

[*] Corresponding author. Fax: +39-08-1593-6936.
E-mail address: landi@unima.it (G. Landi).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.03.043

effect [2,13,14]: increasing selectivity to acrylic acid, negligible under dry conditions, and decreasing propane conversion. An increment of surface hydroxyl groups related to the presence of H_2O has been evidenced by O'Keeffe et al. [14], using a DRIFT in situ analysis. Different hypotheses [12,14–17] 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, and change of surface acidity), but none of them has been completely confirmed. The aim of this work is to investigate the role of water vapour in the production of the acrylic acid by propane oxidation on a VPO-based catalyst and relate the catalytic activity under wet conditions to structural and acid properties of the material.

2. Experimental

2.1. Preparation of precursor

VPO catalyst was prepared by Exxon organic method [12]. V_2O_5 (11.8 g) and H_3PO_4 (9.7 cm^3, 85%) were added to isobutanol (250 cm^3). This mixture was heated up to isobutanol boiling point (105 °C) and refluxed for 16 h under an inert atmosphere. A condensator provides recovering of isobutanol vapours in order to keep the suspension volume constant. After 16 h refluxing, the suspension is light blue; the solid is separated from the liquid by filtration and washed with isobutanol and ethanol. The resulting solid is refluxed in hot water (9 cm^3 H_2O/g_{solid}), filtered and dried in air at 110 °C for 16 h. The vanadyl acid phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) obtained is the precursor of the vanadyl pyrophosphate.

2.2. Catalyst activation

An activation was carried out to transform the precursor in the active catalyst, according to the procedure developed by Gribot Perrin [13]. Precursor was placed in a fixed-bed microreactor under a gas flow mixture ($W/F = 0.4\,g\,h\,dm^{-3}$) 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 ($C_3H_8/O_2/H_2O/N_2 = 1.6/17.8/20/60.6$ vol.%), without changing the total flow rate. After 20 h under wet conditions the catalyst is considered activated. Alternatively the activation has been carried out without introducing water vapour or under nitrogen at 430 °C for 12 h.

2.3. Catalytic tests

Catalytic tests were carried out in the same microreactor used for the activation. All of them were performed at 400 °C, at the same contact time ($W/F = 0.4\,g\,h\,dm^{-3}$). Water concentration was changed in the range 0–25 vol.% without changing propane and oxygen content (1.6 and 17.8%, respectively); nitrogen was used as carrier in balance concentration.

2.4. Characterisation of materials

XRD was performed with a Siemens D500 diffractometer using Cu Kα at 35 kV and 30 mA, using a Diffractoplus Eva software for evaluation of peak parameters. Temperature programmed desorption of ammonia (NH_3 TPD) was performed using a Micromeretics TPD/TPR 2900 analyser equipped with a TC detector and coupled with a Hiden HPR 20 mass spectrometer. After a pre-treatment at 200 °C under helium flow, to desorb the physisorbed water, the sample was saturated with ammonia at 100 °C. After purging at 100 °C, NH_3 was desorbed heating at constant rate (10 °C/min) up to 620 °C. Masses of ammonia and other products, possibly produced or desorbed during the experiment, like water, nitrogen and its oxides, were followed with the mass spectrometer. In our experiments only ammonia was detected.

3. Results

XRD analysis, reported in Fig. 1, showed that precursor is well crystallised single-phase $VOHPO_4{\cdot}0.5H_2O$. In fact, intense and narrow peaks appear at about 15.6 and 30.4°, corresponding to the main planes, whose indexes are (0 0 1) and (2 2 0), respectively; in order to avoid superposition among the different spectra in Fig. 1, XRD pattern of the precursor has been scaled by a factor 10. In the same figure spectra recorded after the different activations have been reported. All activations give rise to transformation of precursor into pure $(VO)_2P_2O_7$, whose principal reflections are at about 23° ((2 0 0) plane), 28.4° ((0 2 4) plane) and 29.8° ((0 3 2) plane) [18]. However, peaks appear broader and less intense, compared to those of precursor indicating that

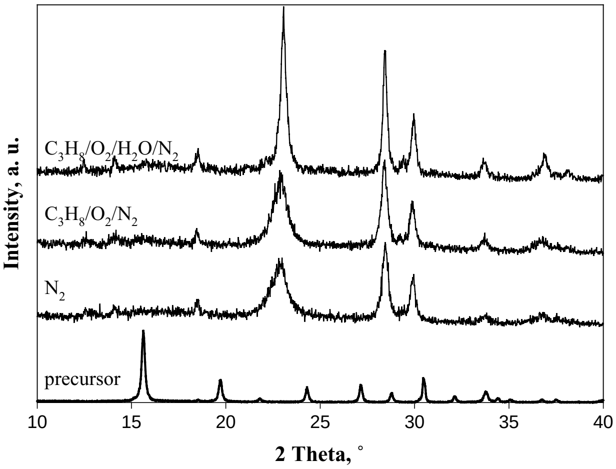

Fig. 1. XRD spectra of VPO precursor and samples activated under different gas mixtures.

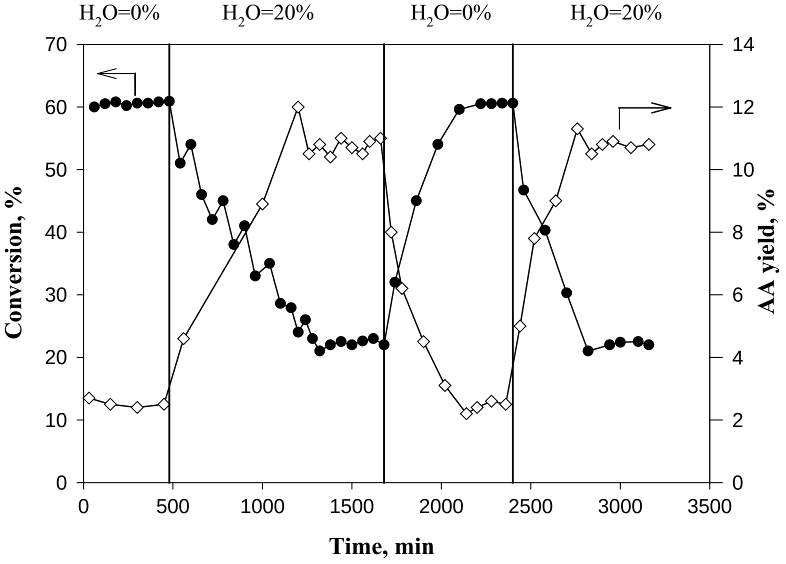

Fig. 2. C_3H_8 conversion and AA yield during dynamic catalytic test on standard activated VPO.

after the activation the samples are much less crystalline and, at the same time, the typical crystallite dimension is reduced. Moreover, differences can be noticed among samples activated under different activation environments: the crystallisation degree increases with water content in the gas stream. As matter of fact, sample activated under nitrogen is the least crystalline, while the most crystalline is the one activated under 20% H_2O-containing mixture; in the last case (activation under propane–oxygen–nitrogen) a non-zero water partial pressure is generated by propane catalytic combustion. This behaviour is probably due to a slower precursor transformation into VPO in the presence of water, as it has been verified through TG analysis performed on the precursor under the same condition used for activation. The experiments have been carried out heating from room temperature to 430 °C (i.e. the activation temperature) at 10 °C/min under nitrogen or under propane–oxygen–nitrogen (1.6/17.8/80.6 vol.%) mixture and keeping constant the temperature for 16 h. Under nitrogen the transformation is completed at 400 °C and no further weight losses were detected. Under $C_3H_8/O_2/N_2$ mixture, the transformation occurred very slowly and was completed only after a night at 430 °C. The final weight loss is slightly different in the two cases; under nitrogen it is somewhat lower (11.3%) than under propane–oxygen-containing mixture (about 12%). This behaviour is probably due to different final oxidation states reached after the activation under various environments. This aspect is still under study. Dynamic catalytic tests on the sample activated according to the standard procedure were carried out at 400 °C feeding 1.6% C_3H_8 and 17.8% O_2 in N_2 ($W/F = 0.4\,\mathrm{g\,h\,dm^{-3}}$). In the absence of water the AA yield is negligible (Fig. 2); introduction of 20% H_2O resulted in a slow reduction of propane conversion and in the simultaneous increase of AA yield, related to a strong enhancement of selectivity. Removal and subsequent re-introduction of the water vapour restore the values of the propane conversion and AA yield measured during the previous cycle, which is, therefore, completely reversible. The length of the time period required to reach stable conditions excludes that role of water vapour is limited to avoid hot spots on the catalyst surface since a much less short time should be expected in this case. Catalytic tests changing H_2O (0–25%) concentration and keeping constant O_2 (17.8%) and C_3H_8 (1.6%) concentration were carried out on the same sample in order to study the effect of water partial pressure on VPO performances. Catalytic results are reported in Table 1. A maximum yield has been found at 15% H_2O in the feed; among the wet

Table 1
Catalytic results on differently activated VPO samples at different H_2O partial pressures

Activation mixture	H_2O in the catalytic test mixture (%)	$x_{C_3H_8}$ (%)	s_{CO} (%)	s_{CO_2} (%)	s_{AA} (%)	y_{AA} (%)
C_3H_8–O_2–H_2O–N_2	0	63.1	61.3	35.0	3.7	2.3
C_3H_8–O_2–H_2O–N_2	10	40.1	49.0	33.1	17.9	7.2
C_3H_8–O_2–H_2O–N_2	15	43.6	44.3	26.8	28.9	12.6
C_3H_8–O_2–H_2O–N_2	20	36.3	44.6	28.0	27.4	9.9
C_3H_8–O_2–H_2O–N_2	25	33.2	44.8	28.6	26.6	8.8
C_3H_8–O_2–N_2	15	35.1	46.5	29.5	24.0	8.4
N_2	15	31.2	44.6	29.7	25.7	8.0

reaction conditions a relative maximum of conversion was found at the same water concentration. The presence of a maximum of AA yield, never observed before due to the limited values of H_2O concentration explored, suggests that water induces modifications of the catalyst and/or of the reaction mechanism favouring AA production, likely through the formation of new acid sites, but that excess water (>15%) inhibits the reaction leading to AA probably due to an overadsorption on the catalyst surface. Finally, effect of water in the activation mixture was investigated carrying out standard catalytic tests (1.6% C_3H_8, 17.8% O_2, 15% H_2O, balance N_2) on samples activated under different gas mixture as described above. The catalytic results are reported in Table 1, too. The best performances, as concerns both propane conversion and acrylic acid selectivity, were obtained with the sample activated in the presence of water whereas when water is absent, either as component of reaction mixture or as product of propane oxidation, a reduction of catalytic activity was observed. This result suggests that better crystallised samples show superior catalytic performances in propane oxidation to AA. In order to investigate the possible effect of the acidity on catalytic performances, after reaction tests TPD of NH_3 were carried on catalysts activated according to the different procedures described before just after catalytic test under conditions reported in Table 1. When stable conditions were reached in the catalytic test, catalyst was rapidly quenched and a TPD experiment was performed. A simple reaction model was used to calculate the kinetic constant of propane oxidation to AA (k_{AA}), according to the following parallel and independent reactions network:

$$C_3H_8 + 2O_2 \rightarrow CH_2{=}CH\text{–}COOH + 2H_2O \qquad (1)$$

$$C_3H_8 + 3.5O_2 \rightarrow 3CO + 4H_2O \qquad (2)$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (3)$$

Since the mixture is very oxygen-rich and oxygen conversion never exceed about 11%, a constant oxygen concentration can be considered. A first-order kinetics with respect to propane was hypothesised. In Fig. 3 the kinetic constant evaluated for each catalyst is reported as a function of the ammonia amount desorbed during the TPD. Excluding the sample operated under dry conditions, showing a very low value of k_{AA} but a high concentration of acid sites (1.3 mmol NH_3/g), likely related to acid centres with different nature, a quite good linear correlation was found between k_{AA} and NH_3 desorbed during TPD. The reduction of the total acidity related to an increase of selectivity to partial oxidation products on VPO catalysts has been found also by Martin et al. [17] studying toluene oxidation to benzaldehyde. In that case the blockage of non-selective Brønsted acid sites allowed the increase of benzaldehyde selectivity. The same reaction is catalysed by alkali-promoted vanadium catalysts [19], whose acidity is reduced by potassium; although the authors underlined that the presence of acid sites is fundamental for activity and selectivity, a relative benefit on selectivity has been observed reducing the acidity of the sample.

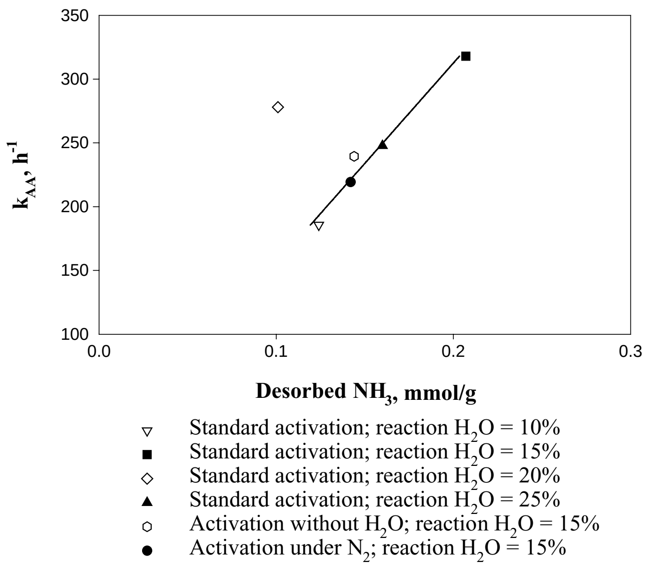

Fig. 3. Kinetic constant of AA production vs. NH_3 amount desorbed during TPD measures for different reaction conditions and differently activated samples.

According to the hypothesis that adsorption of ammonia occurs on the same type of site and that sites are all similar, it can be concluded that each site possesses the same turnover frequency (TOF), i.e. the same reaction rate. Under these hypotheses, the kinetic constant for an active site can be calculated as following:

$$\dot{k} = \frac{\bar{k}}{\bar{n}N} = 2.6 \times 10^{-18}\,\mathrm{g\,site^{-1}\,h^{-1}}$$

where $\dot{k}$ is the kinetic constant per site, $\bar{k}$ the mean value of the kinetic constants calculated for the different reaction conditions (excluding the dry condition), $\bar{n}$ the mean value of the NH_3 amounts desorbed during the TPD (excluding the dry condition) and N the Avogadro number.

4. Conclusions

In conclusion, both structure and catalytic performances of VPO catalyst for mild oxidation of propane are very sensitive both to the activation and to the composition of the reaction gas mixture. In particular, the presence of water vapour induces structural modifications and particularly an improvement of the crystallinity of the VPO material, which improves catalytic performances leading to better AA yields. Moreover, acid sites detected after water treatments appear directly related to AA production. The control of the number of these sites is possible by varying the water partial pressure in the feed.

References

[1] F. Cavani, F. Trifirò, Catal. Today 51 (1999) 561.
[2] M.M. Lin, Appl. Catal. A: Gen. 207 (2001) 1.
[3] M. Ai, Catal. Today 42 (1998) 297.
[4] M. Ai, J. Catal. 101 (1986) 389.
[5] M. Ai, Catal. Today 13 (1992) 679.
[6] M. Ai, J. Mol. Catal. A: Chem. 114 (1996) 3.
[7] Z. Wang, W. Wie, G. Liu, G. Mao, D. Kuang, Acta Petrol. Sinica 14 (1998) 21.
[8] Y. Han, H. Wang, H. Cheng, J. Deng, Chem. Commun. (1999) 521.
[9] F.B. Abdelouahab, R. Olier, M. Ziyad, J.C. Volta, J. Catal. 157 (1995) 687.
[10] G.J. Hutchings, Appl. Catal. A: Gen. 72 (1991) 1.
[11] C. Carrara, S. Irusta, E. Lombardo, L. Cornaglia, Appl. Catal. A: Gen. 217 (2001) 275.
[12] G. Landi, L. Lisi, J.-C. Volta, Chem. Commun. (2003) 492.
[13] N. Gribot Perrin, Ph.D. Thesis, Université Claude Bernard, Lyon 1, 1995.
[14] E.M. O'Keeffe, F.C. Meunier, J.R.H. Ross, in: Proceedings of Twelfth ICC, Granada, 2000.
[15] R.M. Contractor, H.S. Horowitz, G.M. Sisler, E. Bordes, Catal. Today 37 (1997) 51.
[16] E.W. Arnold III, S. Sundaresan, Appl. Catal. 41 (1988) 225.
[17] A. Martin, U. Bentrup, B. Lücke, A. Brückener, Chem. Commun. (1999) 1169.
[18] S.A. Linde, Yu.E. Gorbunova, A.V. Lavrov, V.G. Kuznetsov, Dokl. Akad. Nauk SSSR 245 (1979) 584.
[19] M. Ponzi, C. Duschatzky, A. Carrascull, E. Ponzi, Appl. Catal. A: Gen. 169 (1998) 373.