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ChemComm
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Effect of water on the catalytic behaviour of VPO in the selective oxidation of propane to acrylic acid

G. Landi,*[a] L. Lisi[b] and J. C. Volta[c]
[a] *Dipartimento di Ingegneria Chimica, Università "Federico II", P. le Tecchio, 80–80125 Napoli, Italy. E-mail: landi@unina.it*
[b] *Istituto di Ricerche sulla Combustione, CNR, Napoli, Italy*
[c] *Institut de Recherches sur la Catalyse, CNRS, Villeurbanne, France*

Received (in Cambridge, UK) 22nd November 2002, Accepted 13th January 2003

The role of water in propane oxidation to acrylic acid is associated to slow structural modifications of VPO enhancing catalytic performances.

Olefins and oxygenated compounds represent the basic molecules for production of many industrial products and are currently obtained through very expensive multi-step processes with a high environmental impact. Nevertheless, in the last decades the abundance of light paraffins has addressed the research towards the development of more environmentally friendly routes for the transformation of alkanes into more valuable chemicals.[1] A catalyst is generally required to direct the reaction towards the desired product preventing the further oxidation of the intermediate. Nowadays, acrylic acid (AA) is produced through a double-step process starting from propylene.[2] The first step is the production of acrolein which is further oxidised to the acid in a different reactor. Provided that AA yields were close to those required for industrial applications a single step process using propane as feedstock would significantly reduce both costs and pollution. Vanadyl pyrophosphate (VPO) is one of the catalysts giving the best performances among those proposed for this reaction although AA selectivity and yields are still low.[2–5] Therefore, improvement of both catalyst features and operating conditions are the main objective of the research. In particular, determination of the role of water vapour in the formation of AA, inhibited under anhydrous conditions,[2,6] is a key step for the comprehension of this reaction.

In this paper the effect of addition of water to the reaction mixture has been investigated by carrying out dynamic catalytic tests, effecting cycles in its presence and in its absence, and exploring a wide range of water vapour concentrations in the reaction mixture analysing the response of the catalyst to different reaction atmospheres. Furthermore, the effect of water vapour in the activation mixture on the transformation from the precursor to the catalyst was also studied.

VPO catalyst was prepared by refluxing V_2O_5 and H_3PO_4 in isobutyl alcohol in the presence of acetic acid (HAc/V = 0.02) for 16 h. After filtration and washing, the precursor (vanadyl acid phosphate hemihydrate) was dried at 110 °C. Activation was carried out in a fixed bed reactor (0.4 g h l^{-1} contact time) feeding 1.6% C_3H_8 and 17.8% O_2 in N_2 at 430 °C for 17 h, then lowering the temperature to 400 °C and, after 2.5 h, introducing 20% H_2O for 20 h. Activation procedures without introducing water and under pure N_2 were also performed under the same temperature conditions of the standard activation.

XRD analysis showed that precursor is a well crystallised single phase $VOHPO_4{\cdot}0.5H_2O$. After each activation a transition to the pure $(VO)_2P_2O_7$ phase occurred, however, introduction of water results in a better crystallised material whereas broader peaks present in XRD patterns of VPO activated without water and under N_2, respectively (Fig. 1) suggest that addition of water promotes crystallisation of the sample. A detectable improvement of crystallisation, compared to that of the sample activated under pure N_2, was observed even under a C_3H_8–O_2–N_2 mixture since the catalyst was contacted with the water produced by propane oxidation. TG analysis carried out on the precursor under the same conditions used for activating the samples showed that the transformation hemihydrate–pyrophosphate occurs more rapidly under an inert atmosphere thus explaining the production of less crystallised materials.

During the activation, CO and CO_2 were the only products of propane oxidation at 430 °C. On the other hand, a low amount of propylene and traces of ethane and ethylene were detected when the temperature was lowered to 400 °C, while propane conversion decreased. Introduction of 20% water at this temperature resulted in disappearance of these hydrocarbon intermediates and in a significant formation of AA and, in lower amounts, of acetic acid, while propane conversion further decreased.

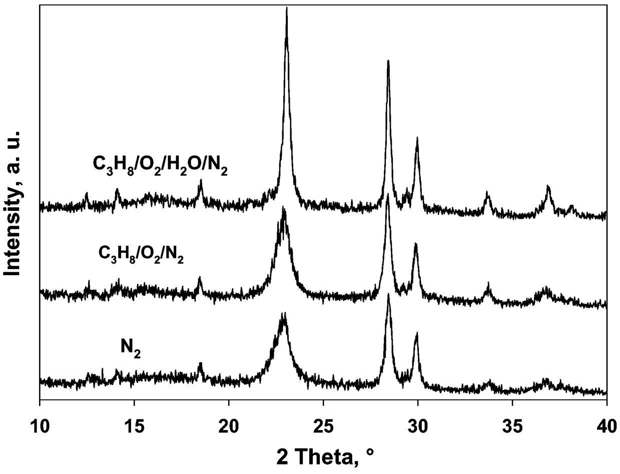

Fig. 1 Cu-Kα XRD patterns of VPO catalysts activated under different gas mixtures showing characteristic lines.

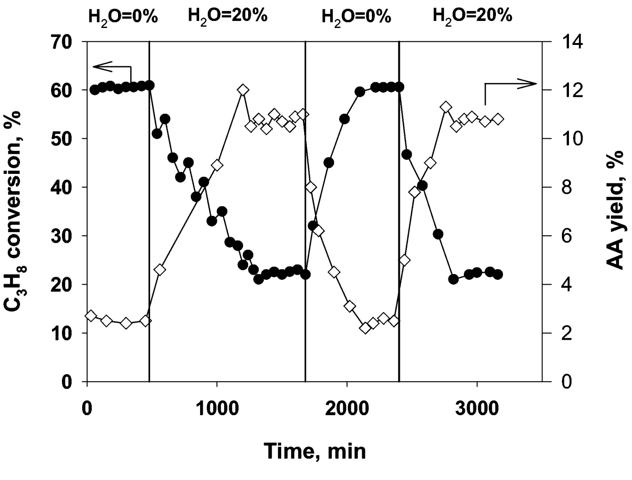

Fig. 2 C_3H_8 conversion and AA yield as a function of addition or removal of 20% H_2O to reaction mixture.

DOI: 10.1039/b211619g

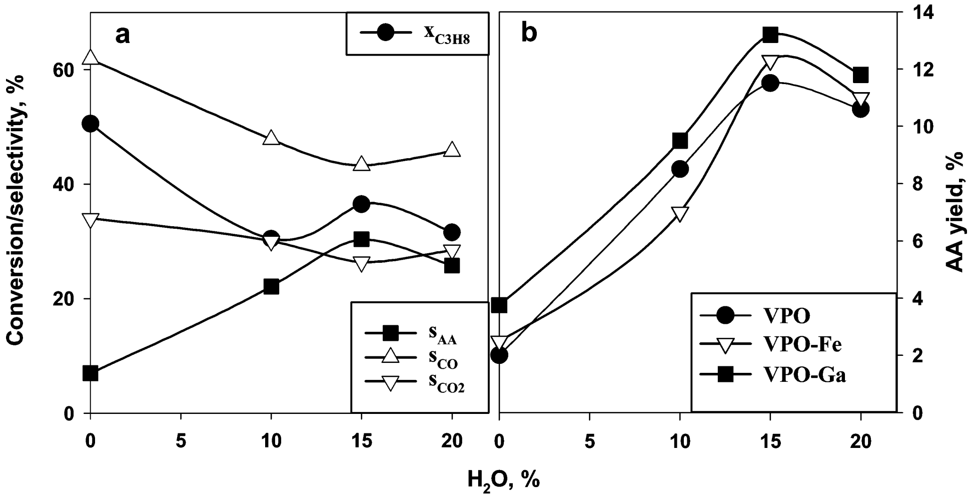

Fig. 3 Propane conversion ($x_{C_3H_8}$) and AA (s_{AA}), CO (s_{CO}) and CO_2 (s_{CO_2}) selectivity as a function of H_2O volume concentration in the reaction mixture at 400 °C for a VPO catalyst (a) and AA yield for pure and doped VPO catalysts (b).

The enhancement of AA selectivity was mainly balanced by the decrease of CO selectivity whereas production of CO_2 was almost unaffected by the reaction conditions.

Dynamic catalytic tests on the sample activated according the standard procedure were carried out at 400 °C in the same experimental plant used for the activation feeding 1.6% C_3H_8 and 17.8% O_2 in N_2. A stable propane conversion of 60% and production of CO_x were observed under these conditions (Fig. 2).

Introduction of 20% H_2O resulted in a slow (about 13 h) reduction of propane conversion to 22–23% and in the simultaneous increase of AA yield to 10–12% from about 2%. The length of the time required to reach stable conditions excludes that the 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. Initial values of both propane conversion and AA yield are restored upon removal of water vapour from the gas mixture showing that the phenomenon is completely reversible. Return to 22–23% propane conversion upon re-introduction of water occurs in a shorter time compared to the first cycle suggesting that modification of the catalyst leading to these results became faster after 35–40 h time on stream.

The effect of water vapour concentration was investigated performing tests at 400 °C on the sample activated according to the standard procedure increasing the H_2O concentration in the reaction mixture from 0 to 20% while keeping the C_3H_8 and O_2 concentration constant (1.6 and 17.8%, respectively). A decrease of C_3H_8 conversion and, at the same time, increase of AA selectivity were observed up to 10% H_2O. Increasing the water vapour concentration up to 15% gives rise to a partial restoring of propane conversion although the AA selectivity still increases. A further increase of water vapour concentration (20%) produces a reduction of both conversion and selectivity thus determining a maximum of AA yield at 15% H_2O (Fig. 3(a)).

The same behaviour was found on catalysts synthesised without adding acetic acid in the solution or catalysts doped with 1% Fe or Ga (Fig. 3(b)). The presence of a maximum of AA yield, not observed previously due to the limited values of H_2O concentration investigated, suggests that water induces modification 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.

Table 1 Results of catalytic tests carried out on catalysts activated under different gas mixtures

Activation mixture composition	C_3H_8 conversion (%)	CO selectivity (%)	CO_2 selectivity (%)	AA selectivity (%)
C_3H_8–O_2–H_2O–N_2	39.2	43.4	30.1	26.5
C_3H_8–O_2–N_2	35.1	46.5	29.5	24.0
N_2	31.2	44.2	29.4	25.4

Finally, the effect of water in the activation mixture was investigated carrying out standard catalytic tests (1.6% C_3H_8, 17.8% O_2 and 15% H_2O, respectively) on samples activated under different gas mixture as described above. Results are reported in Table 1.

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 a component of the reaction mixture or as a 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 conclusion, VPO catalysts are very sensitive to both activation and the reaction gas mixture. In particular, the presence of water vapour induces structural modifications, probably associated with sample crystallinity, which improves catalytic performances leading to better AA yields.

Notes and references

1 F. Cavani and F. Trifirò, *Catal. Today*, 1999, **51**, 561.
2 M. M. Lin, *Appl. Catal. A*, 2001, **207**, 1.
3 M. Ai, *J. Catal.*, 1986, **101**, 389.
4 M. Ai, *Catal. Today*, 1998, **42**, 297.
5 Y. F. Han, H. M. Wang, H. Cheng and J. F. Deng, *Chem. Commun.*, 1999, 521.
6 E. M. O'Keeffe, F. C. Meunier and J. R. H. Ross, *Proceedings of 12th ICC*, Granada, 2000.