Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 93–95 (2004) 229–234

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effects of reaction conditions on the selective oxidation of propane to acrylic acid on Mo–V–Te–Nb oxides

Baichun Zhu, Hongbo Li, Weishen Yang*, Liwu Lin

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China

Available online 8 July 2004

Abstract

An effective $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalysts for the selective oxidation of propane to acrylic acid was successfully prepared by using rotavap method. The catalyst was characterized by XRD and shown to contain $(V_{0.07}Mo_{0.93})_5O_{14}$, $(Nb_{0.09}Mo_{0.91})O_{2.8}$, $3MoO_2{\cdot}Nb_2O_5$, Mo_5TeO_{16} and/or $TeMo_4O_{13}$, $Te_4Nb_2O_{13}$ and a new TeMO (TeVMoO or TeVNbMoO; M = Mo, V and Nb) crystalline phase as the major phase. Regardless of the intrinsic catalytic characteristics of the catalyst, the external reaction conditions would have strong effects on the catalytic performance for propane oxidation. So in this paper, the effects of reaction conditions were investigated and discussed, including temperature, space velocity, $V(\text{air})/V(C_3H_8)$ ratio and $V(\text{steam})/V(C_3H_8)$ ratio. A stability test was also carried out on $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst. The experimental run was performed during 100 h under the optimized reaction conditions. During the 100 h of operation, propane conversion and acrylic acid selectivity remained at about 59 and 64%, respectively.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Propane; Selective oxidation; Acrylic acid; Mo–V–Te–Nb oxide catalysts

1. Introduction

The direct oxidation of propane to acrylic acid using molecular oxygen as an oxidant has recently attracted great attention in both academia and industry. By now, three classes of catalyst systems, VPO-type catalysts [1,2], heteropoly compounds catalysts (HPC) [3,4] and multi-component metal oxides catalysts (MMO) [5–10], have been studied for the selective oxidation of propane to acrylic acid. MMO catalysts are commonly considered to have a possibility to substitute the traditional catalysts in the existing industrial two-step process via propylene. Among those catalyst systems, Mo–V–Te–Nb oxide catalyst is the most promising one [7–10]. An appropriate MoVTeNb metal ratio is critical to the formation of catalyst active phase, according to the two patents of Ushikubo and Lin [7,8], the catalysts with metal ratio of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ have excellent catalytic performance for selective oxidation of propane to acrylic acid. In this paper, $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ was used as the catalyst for propane oxidation to acrylic acid.

The excellent performance of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst for propane oxidation is mainly due to its the intrinsic characteristics. Each of the constituent elements Mo, V, Te and Nb was shown to be necessary for both high conversion of propane and high selectivity to acrylic acid [11–13]. In addition, the morphology or the grain size of the catalyst and the oxidation state of the metals also greatly affect their catalytic performance, these factors can be controlled by the grinding or the pretreatment conditions [14]. Based on these latest results, one can conclude that not only the composition of the catalysts, but also some specific structures of the resulting catalysts are closely related to their catalytic performance.

Besides the intrinsic characteristics of the catalysts, the reaction conditions are the important factors influencing the catalytic performance of propane oxidation. Ai [1] has ever reported that on Te-modified VPO catalyst higher concentrations of oxygen and steam, a lower concentration of propane, and a lower reaction temperature are favorable for propane selective oxidation to acrylic acid.

The relationship between the intrinsic characteristics of the catalysts and the catalytic performance for propane oxidation will be discussed in detail in our another paper. This paper will focus on discussing the effects of external

---

* Corresponding author. Tel.: +86 411 4379073; fax: +86 411 4379073.
E-mail address: yangws@dicp.ac.cn (W. Yang).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.045

reaction conditions on the catalytic performance and the catalyst stability under the optimized reaction conditions.

2. Experimental

2.1. Catalyst preparation

6.4 g ammonium paramolybdate (Aldrich), 1.3 g ammonium metavanadate (Aldrich) and 1.9 g telluric acid (Aldrich) were dissolved in 105 mL of water at 353 K in a flask to obtain a uniform aqueous solution. 0.5 h later, the solution was cooled to 303 K, and then 41.1 mL of an aqueous solution of niobium oxalate having niobium concentration of 9.8 mg/mL was mixed thereto to obtain a slurry. The nominal metal ratio of the Mo–V–Te–Nb–O catalyst formed from such a solution should be $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$. Rotated continuously for 2 h, the water of this slurry was removed via a rotary evaporator at a bath temperature of about 313–333 K and at a reduced pressure of 10–40 mmHg to obtain 11 g of precursor solid. Five grams of the catalyst precursor solid was calcined in a covered small quartz tube pre-purged with nitrogen, non-flow environment at 873 K for 2 h. The oven had previously been heated to 473 K at a rate of 3 °C/min and held at that temperature for 1 h, then ramped to 873 K at a rate of 3 °C/min and held at that temperature for 2 h. During the calcination, the covered quartz tube was placed in a large quartz tube with a nitrogen flow rate of 1 mL/min. Because of the covered tube, the nitrogen did not flow over the precursor surface, but served to ensure that the atmosphere outside the covered tube was nitrogen. The atmosphere inside the covered tube remained nitrogen and off gasses from the catalyst. Then the material was ground, pressed and sieved to 20–30-mesh granules. Before reaction, the granules was activated by a series of chemical and physical methods. The detailed process will be discussed in another paper. After activation, the final $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst was thus obtained.

2.2. Catalyst characterization

The crystalline structure of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst was characterized by XRD technique, which was performed under ambient temperature and pressure using a Rigaku D/MAX-RB diffractometer with a Cu anticathode in the 2θ range of 10–80°.

2.3. Catalyst evaluation

The catalytic performance of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst was evaluated for the selective oxidation of propane to acrylic acid in a continuous-flow fixed-bed microreactor at atmospheric pressure. The reactor was made of quartz tube, 40 cm long and 0.8 cm i.d., mounted vertically and heated with an electric furnace. A mixture of propane–air-steam was fed in from the top of the reactor. The off-gas was condensed and the liquid phase separated from the gas phase in a cold trap. Both the gas and liquid phases of the product streams were analyzed with GC to determine the values of propane conversion, AA yield and the distribution of other products. They are defined as below:

$$\text{Conversion (\%)} = \frac{\frac{1}{3}\sum niNi}{\text{propane fed}} \times 100$$

$$\text{Selectivity (\%)} = \frac{niNi}{\sum niNi} \times 100$$

$$\text{Yield (\%)} = \frac{\frac{1}{3}niNi}{\text{propane fed}} \times 100$$

where Ni represents the moles of carbon-containing products and ni represents the number of C atoms in carbon-containing products.

3. Results and discussion

3.1. The crystalline structure of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst

It has been known [7,8] that the effective Mo–V–Te–Nb–O catalyst for the selective oxidation of propane to acrylic acid should have X-ray diffraction peaks at diffraction angles of $2\theta = 22.1°$, 28.2°, 36.2°, 45.1° and 50.0°. Fig. 1 shows the XRD pattern of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst. Apparently, all the five characteristic peaks exit in the pattern, which indicates that an effective catalyst is formed in our experiment.

By using PCPDFWin software, the peak at $2\theta = 22.1°$ can be related to the presence of several Mo-containing phases, i.e., $(V_{0.07}Mo_{0.93})_5O_{14}$ (peaks at $2\theta = 16.5°$, 22.3°,

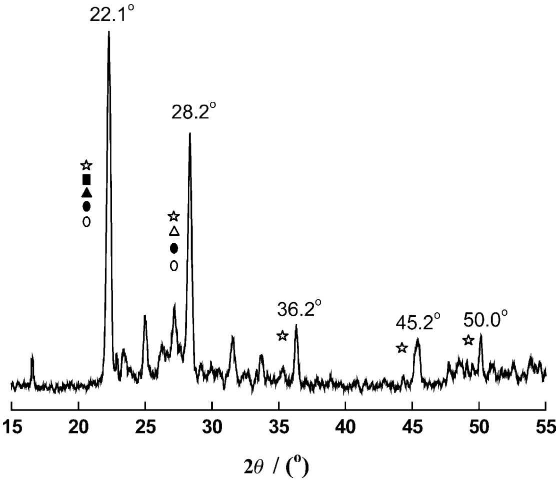

Fig. 1. XRD patterns of the Mo–V–Te–Nb–O catalyst: (○) $(V_{0.07}Mo_{0.93})_5O_{14}$, (●) $(Nb_{0.09}Mo_{0.91})O_{2.8}$, (▲) $3MoO_2{\cdot}Nb_2O_5$, (■) Mo_5TeO_{16} and/or $TeMo_4O_{13}$, (△), $Te_4Nb_2O_{13}$ (☆) TeMO (TeVMoO and/or TeVNbMoO) crystalline.

23.3°, 24.9°, 28.2°, 31.5° and 33.7°) (JCPDS: 31-1437), $(Nb_{0.09}Mo_{0.91})O_{2.8}$ (peaks at $2\theta = 16.5°$, 22.1°, 23.3°, 24.9° 26.1°, 27.6°, 28.1°, 31.3°, 31.5°, 32.4° and 33.5°) (JCPDS: 27-1310), $3MoO_2{\cdot}Nb_2O_5$ (peaks at $2\theta = 16.3°$, 22.2°, 23.1°, 24.6°, 31.2°, 33.4° and 38.6°) (JCPDS: 18-0840), Mo_5TeO_{16} (JCPDS: 31-0874) and/or $TeMo_4O_{13}$ (JCPDS: 34-0622) (peaks at $2\theta = 21.8°$, 24.7°, 26.2°, 26.7° and 30.5°).

The peak at $2\theta = 28.2°$ can be related to $(V_{0.07}Mo_{0.93})_5O_{14}$, $(Nb_{0.09}Mo_{0.91})O_{2.8}$ and $Te_4Nb_2O_{13}$ (peaks at $2\theta = 23.5°$, 24.9°, 27.2°, 28.0, 28.4°, 31.6° and 37.2°) (JCPDS: 36-1175).

However, by using PCPDFWin software, none of the compounds formed by two or three metal elements among Mo, V, Te and Nb could correspond to the other three peaks at $2\theta = 36.2°$, 45.2° and 50.0°. In a recent published literature [15], the five characteristic peaks at $2\theta = 22.1°$, 28.2°, 36.2°, 45.1° and 50.0° were assigned to a new TeMO (TeVMoO or TeVNbMoO; M = Mo, V and Nb) crystalline phase. Aouine et al. [16] considered that the new TeMO crystalline phase could correspond to the phase $Te_{0.33}MO_3$ (M = Mo, V, and Nb). While Baca et al. [12] considered that the new TeMO crystalline phase could be related to two major phases M1 $[(Te_2O)M_{20}O_{56}]$ and M2 $[(TeO)M_3O_9]$ (M = Mo, V) having orthorhombic and hexagonal structure, respectively, and the orthorhombic M1 phase is the most active and selective phase for propane oxidation, a synergism due to cooperation between M1 and M2 phases improves the catalyst performance.

3.2. Effect of reaction temperature on catalytic performance

The effect of reaction temperatures was studied in a range 643–703 K. The results are shown in Fig. 2. In the reaction, acrylic acid and CO_x are major products; acetic acid and propylene are by-products in a small amount. Meanwhile, acetone, acrolein and propionic acid are also formed in a trace amount. It is clear that the reaction temperatures have strong effects on the products distribution. As the temperature is elevated from 643 to 703 K, the conversion of propane increases from 39 to 74%, and the selectivity to acrylic acid decreases from 74 to 42% at the expense of a relative increase of the selectivity to CO_x from 13 to 55%. The selectivities to propylene, acetic acid and the trace products also decrease slightly.

As a saturated hydrocarbon, propane has low reactivity under lower reaction temperatures. Higher temperatures are benefit to propane activation, so the conversion of propane increases with the temperature increasing.

While according to Lin's results on Mo–V–Te–Nb–O catalyst [17], the order of relative reactivity of reactants was propane ≪ acetic acid = acrylic acid < propylene < acetone < acrolein = isopropanol. That is, acrylic acid is more reactive than propane. So, increasing temperatures would accelerate the overoxidation of acrylic acid and other intermediate to CO_x, which leads to a decrease in the selectivities to them and a rapid increase in the selectivity to CO_x.

Due to the opposite contribution of reaction temperatures to acrylic acid selectivity and propane conversion, the yield of acrylic acid reaches at a maximum at 683 K. Considering the selectivity to acrylic acid, the suitable reaction temperature is in the range 663–683 K.

3.3. Effect of space velocity on catalytic performance

The effect of various space velocities was studied at a reaction temperature of 673 K. The results are shown in Fig. 3. The results had been obtained by changing the amount of catalysts used from 1.73 to 2.88 g. As the space velocity is elevated from 600 to 1000 mL/(g_{cat} h), the conversion of propane decreases from 68 to 49%. Meanwhile, the selectivity to acrylic acid increases from 57 to 66% and the selectivity to CO_x decreases from 36 to 25%. And the selectivities to other intermediate also increase slightly with the space velocity increasing.

Literature results [17,18] suggest that propane oxidative dehydrogenation to propylene is the first step of the

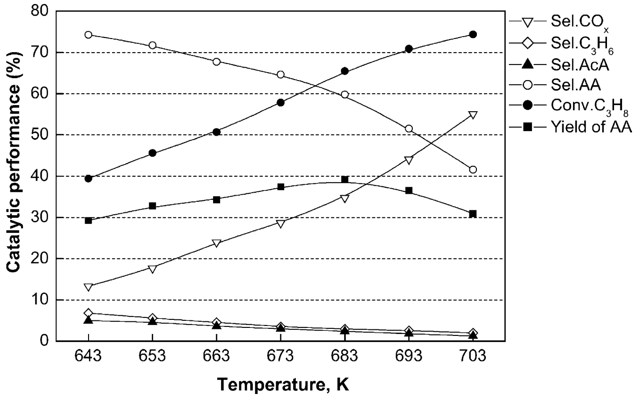

Fig. 2. Effect of reaction temperatures on catalytic performance $V(C_3H_8)/V(air)/V(steam) = 1/15/12$, GHSV = 800 mL/($g_{cat}$ h), catalyst loading = 2.14 g.

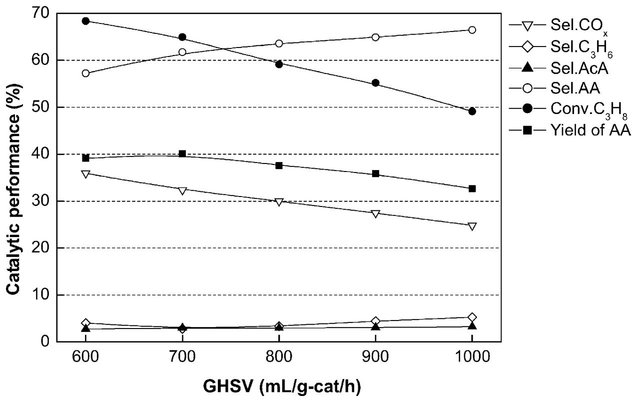

Fig. 3. Effect of space velocity on catalytic performance flow rate of propane:1.0 mL/min, $V(C_3H_8)/V(air)/V(steam) = 1/15/12$, $T = 673$ K.

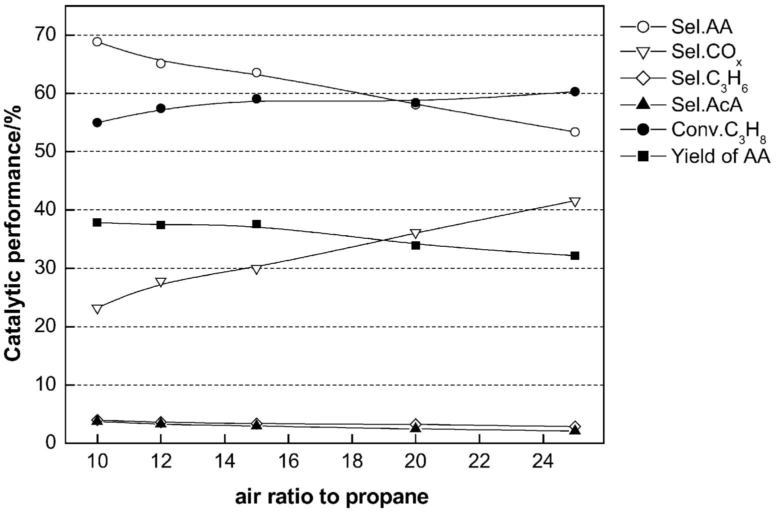

Fig. 4. Effect of V(air)/V(C_3H_8) ratio on catalytic performance flow rate of propane: 1.0 mL/min, V(C_3H_8)/V(air)/V(steam) = 1/10–25/12, GHSV = 800 mL/(g_{cat} h), T = 673 K.

reaction. From the results in Fig. 3, the concentrations of the primary product propylene in tail gases are relatively low during the whole range, approximately 3–5%, which suggests the $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst has high reactivity to propylene oxidation, propylene is quickly consumed in the next steps of the reaction as soon as it is produced. With the space velocity increasing, the contact time of propane and propylene with the catalyst becomes short, part of them leave the catalyst surface without reacting. So propane conversion decreases and the concentration of propylene in tail gases increases with the space velocity increasing. At the same time, the contact time of acrylic acid and other intermediate with the catalyst also becomes short, which prevents them from staying longer on the catalyst surface, thus decrease the chance of being further oxidized to CO_x. So the selectivities to acrylic and acetic acid increase with increasing space velocity.

The observed yield of acrylic acid is a product of propane conversion and acrylic acid selectivity, while the effect of space velocity on them is opposite. So the higher acrylic acid yield could be obtained in the range 600–800 mL/(g_{cat} h).

3.4. Effect of V(air)/V(C_3H_8) ratio on catalytic performance

The reaction was conducted by fixing propane flow rate at 1.0 mL/min, and changing air flow rate from 10 to 25 mL/min. Then the corresponding V(air)/V(C_3H_8) ratio varied from 10 to 25. The space velocity was maintained at 800 mL/(g_{cat} h) by changing the amount of the catalyst used in the reaction. Fig. 4 shows the catalytic performance at 673 K under different V(air)/V(C_3H_8) ratios.

With V(air)/V(C_3H_8) ratio increasing from 10 to 15, the conversion of propane increases from 55 to 59%, and then levels off when V(air)/V(C_3H_8) ratio is more than 15. The selectivity to acrylic acid decreases steadily from 69 to 53% with V(air)/V(C_3H_8) ratio increasing while the selectivity to CO_x increase from 23 to 42%. And the selectivities to propylene and acetic acid, etc. also decrease slightly.

In the reaction of propane selective oxidation to acrylic acid, the theoretical V(O_2)/V(C_3H_8) ratio equals to 2, so the theoretical V(air)/V(C_3H_8) ratio should equal to 10. That means higher oxygen concentration is favourable for propane activation. So propane conversion increases with the V(air)/V(C_3H_8) ratio increasing. When the oxygen concentration gets to a certain degree, propane conversion does not increase any longer. While acrylic acid and other intermediates, including propylene and acetic acid, are prone to be overoxidized to CO_x under higher oxygen concentration. So, with the V(air)/V(C_3H_8) ratio increasing, the selectivities to acrylic acid, propylene and acetic acid decrease while the selectivity to CO_x increases.

The higher yield of acrylic acid (>37%) is obtained when the V(air)/V(C_3H_8) ratio is in the range 10–15.

3.5. Effect of steam ratio in the feed on catalytic performance

The reaction was conducted by fixing propane flow rate at 1.0 mL/min, and changing the steam ratio in the feed gas V(C_3H_8)/V(air)/V(steam) =1/15/0–24. The space velocity was maintained at 800 mL/(g_{cat} h) by changing the amount of the catalyst used in the reaction. Fig. 5 shows the catalyst performance at 673 K under different steam ratios, with the steam-free reaction as reference.

It is evident that propane conversion increases from 51 to 57% when steam of V(steam)/V(C_3H_8) = 6 is introduced, but quickly levels off when more steam is added to the

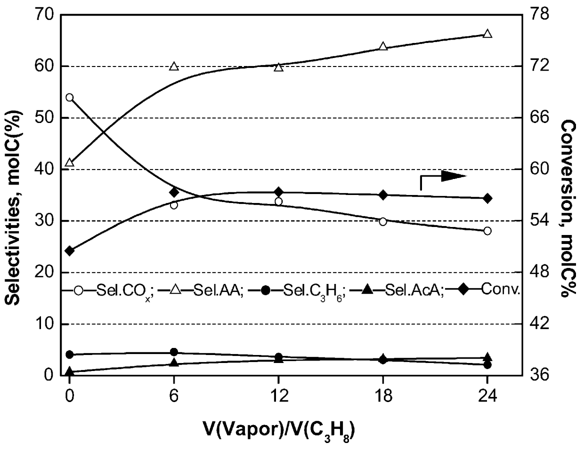

Fig. 5. Effect of steam ratio in the feed on catalytic performance flow rate to propane: 1.0 mL/min, $V(C_3H_8)/V(air)/V(steam) = 1/15/0–24$; GHSV = 800 mL/($g_{cat}$ h); $T = 673$ K.

feed. The major effects appear to be in the formation of acrylic acid and CO_x. The selectivity to acrylic acid increases rapidly from 41 to 60% when steam of $V(steam)/V(C_3H_8) = 6$ was introduced into the feeds, then increases slightly to 66% when more steam is introduced. The variation of selectivity to CO_x is just opposite to that of the selectivity to acrylic acid. The selectivity to CO_x decreases rapidly from 54 to 33% when steam of $V(steam)/V(C_3H_8) = 6$ was introduced into the feeds, then decreases slightly to 28% when more steam is introduced.

From the results in Fig. 5, it can be seen that acrylic acid has already been formed even in steam-free condition, which indicates that steam is important but not the indispensable for the formation of acrylic acid. The most possible reason for the positive effect is that steam enhances the desorption of the strongly adsorbed acrylic acid on the catalyst surface to prevent it from overoxidation to CO_x [5,19,20].

The higher yield of acrylic acid can be obtained when $V(steam)/V(C_3H_8)$ ratio is in the range 12–24.

3.6. The stability of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst under optimized reaction conditions

The stability of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst is another important point to be considered. It was performed for 100 h under the optimized reaction conditions, $V(C_3H_8)/V(air)/V(steam)$ ratio of 1/15/12, space velocity of 800 mL/(g_{cat} h), catalyst loading of 2.14 g and reaction temperature of 673 K (see Fig. 6).

During the 100 h of operation, the conversion of propane maintains at 57–59%, the selectivities to acrylic acid and CO_x maintain at 63–65 and 27–30%, respectively. This suggests that the $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst not only have a good performance for the selective oxidation of propane to acrylic acid, but also have good reaction stability. It is worthy of mention that the catalyst reaches a steady state just as the reaction start.

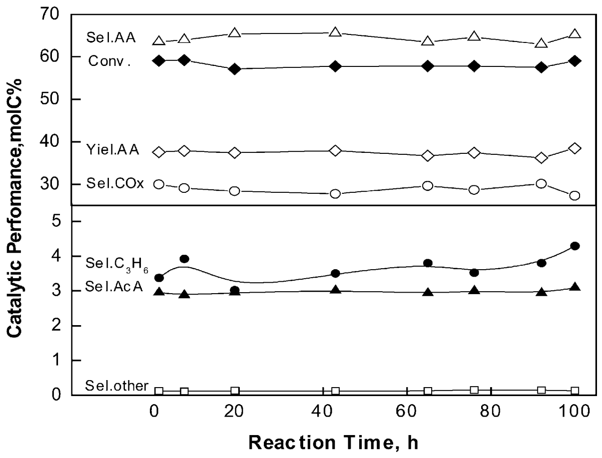

Fig. 6. The long-term test of the Mo–V–Te–Nb–O catalyst $V(C_3H_8)/V(air)/V(steam) = 1/15/12$, GHSV = 800 mL/($g_{cat}$ h), catalyst loading = 2.14 g. $T = 673$ K.

4. Conclusion

The $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst prepared by using rotavap method is an effective catalyst for the selective oxidation of propane to acrylic acid. XRD results indicates that the effective catalyst has five characteristic peaks at $2\theta = 22.1°, 28.2°, 36.2°, 45.1°$ and $50.0°$. It contains $(V_{0.07}Mo_{0.93})_5O_{14}$, $(Nb_{0.09}Mo_{0.91})O_{2.8}$, $3MoO_2{\cdot}Nb_2O_5$, Mo_5TeO_{16} and/or $TeMo_4O_{13}$, $Te_4Nb_2O_{13}$ and a new *Te*MO (TeVMoO or TeVNbMoO; M = Mo, V and Nb) crystalline phase as the major phase. On $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst, the catalytic performance of propane selective oxidation to acrylic acid is greatly influenced by the reaction conditions. The temperature of 663–683 K, the space velocity of 600–800 mL/(g_{cat} h), the $V(air)/V(C_3H_8)$ ratio of 10–15 and the $V(steam)/V(C_3H_8)$ ratio of 12–24 are suitable for acrylic acid production. The main role of steam is to enhance the desorption of acrylic acid from the catalyst surface to prevent it from being overoxidized to CO_x. The stability of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst under the optimized reaction conditions was examined. During the 100 h of operation, propane conversion and acrylic acid selectivity remained at about 59 and 64%, respectively.

Acknowledgements

The authors gratefully acknowledge financial supports from the Ministry of Science and Technology of China (Grant No. G1999022401).

References

[1] M. Ai, J. Catal. 101 (1986) 389.
[2] B. Kerler, A. Martin, M.M. Pohl, M. Baerns, Catal. Lett. 78 (2002) 259.

[3] N. Mizuno, M. Tateishi, M. Iwamoto, Appl. Catal. A 128 (1995) 165.
[4] W. Ueda, Y. Suzuki, Chem. Lett. 7 (1995) 541.
[5] A.C. Kaddouri, C. Mazzocchia, E. Tempesti, Appl. Catal. A 180 (1999) 271.
[6] E.K. Novakova, J.C. Védrine, E.G. Derouane, J. Catal. 211 (2002) 226.
[7] T. Ushikubo, H.Nakamura, Y. Koyasu, S. Wajiki, EP 0,608,838,A2 (1994).
[8] M. Lin, M. Linsen, EP 0,962,253,A2 (1999).
[9] H. Watanabe, Y. Koyasu, Appl. Catal. A 194–195 (2000) 479.
[10] P. Botella, M. López Nieto, B. Solsona, A. Mifsud, F. Márquez, J. Catal. 209 (2002) 445.
[11] R.K. Grasselli, Top. Catal. 15 (2001) 93.
[12] M. Baca, A. Pigamo, J.L. Dubois, J.M.M. Millet, Top. Catal. 23 (2003) 39.
[13] M.M. Lin, Appl. Catal. A 250 (2003) 305.
[14] K. Oshihara, T. Hisano, W. Ueda, Top. Catal. 15 (2001) 153.
[15] P. Botella, J.M. López Nieto, B. Solsona, Catal. Lett. 78 (2002) 383.
[16] M. Aouine, J.L. Dubois, J.M.M. Millet, Chem. Commun. (2001) 1180.
[17] M.H. Lin, T.B. Desai, F.W. Kaiser, P.D. Klugherz, Catal. Today 61 (2000) 223.
[18] E.K. Novakova, J.C. Védrine, E.G. Derouane, J. Catal. 211 (2002) 235.
[19] M. Ai, Catal. Today 42 (1998) 297.
[20] J. Barrault, C. Batiot, L. Magaud, M. Ganne, Stud. Surf. Sci. Catal. 110 (1997) 375.