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Effect of water on the partial oxidation of propane to acrylic and acetic acids on Mo–V–Sb–Nb mixed oxides

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It is shown that the major effect of water in the oxidation of propane to acrylic and acetic acids on $Mo_1V_{0.3}Sb_{0.25}Nb_{0.08}O_n$ catalysts is to stabilise the active sites and increase the rates of formation of both acids. The usual effect of favoring desorption of the products is considered to be secondary.

KEY WORDS: propane oxidation; water effect; acrylic acid; acetic acid; Mo–V–Sb–Nb mixed oxide catalysts.

1. Introduction

The direct oxidation of propane to oxygenated products, such as acrolein and acrylic acid, has attracted a lot of attention in the past two decades, but until now this process cannot substitute the existing industrial two-step process via propene. It is well documented that addition of water vapor to the reactants feed leads to significant improvement in the selectivities to oxygenates. However, there is no established mechanism explaining how water enhances the yield of acrylic acid. One possibility is that water enhances the desorption of the strongly adsorbed acrylic acid on the catalyst surface and, by doing so, preserves it from overoxidation [1–4]. Still some differences can be noted, probably related to the catalyst. Over Ni–Mo–Te–P–O [3], steam affects essentially only the formation of acrylic acid, whereas on other systems (*e.g.*, V_2O_5–P_2O_5 [1,2] and Ni–Mo–O [4]), a positive effect is also observed in the formation of acetic acid due to hydration of propene to isopropanol, which is further oxidized to acetone and eventually to acetic acid and CO_x.

Catalytic studies of other oxidation processes highlight the effect of water as leading to structural modifications of the catalyst surface. In the oxidative dehydrogenation of isobutyric acid on iron phosphates, it was concluded that water maintains the catalyst surface in a hydrated state and that an oxy-hydroxy phase is the active phase [5]. In a study on selective oxidation of butane over vanadium pyrophosphate (VPO) catalysts, the effect of water addition was attributed to improved crystallinity of the active $(VO)_2P_2O_7$ phase with preferential exposure of (100) surface planes and to a decrease in the ratio between the unselective $V^{V}OPO_4$ and selective $(V^{IV}O)_2P_2O_7$ phases as, well as an increase in the number and strength of acid sites [6].

This publication reports the results of a study of the effect of water addition to propane on the catalytic performance of $Mo_1V_{0.3}Sb_{0.25}Nb_{0.08}O_n$ catalysts in the temperature range 653–713 K.

2. Experimental

The Mo–V–Sb–Nb–O catalyst was prepared according to the patent literature [7] by a slurry method. The slurry contained the salts of four metals (Aldrich): ammonium molybdate, ammonium metavanadate, antimony trioxide and niobium oxalate. Initially the ammonium metavanadate was dissolved in water by heating and stirring, followed by the addition of the antimony trioxide and ammonium molybdate to the metavanadate solution. The suspension was refluxed at 363 K for 12 h and after cooling to room temperature, an aqueous solution of niobium oxalate was added. The slurry obtained was stirred vigorously for 30 min, then concentrated and dried at 393 K. The catalyst precursor of the chemical composition, determined by the atomic absorption technique, $Mo_1V_{0.3}Sb_{0.25}Nb_{0.08}O_n$, was calcined at 873 K under a flow of dry air for 2 h. The sample was further activated in the reactor prior to reaction at 773 K, with a mixture of 20%O_2 in He.

The catalyst was characterized by BET and XRD techniques. The XRD characterization was performed under ambient conditions using a D-5000 Siemens diffractometer with a Co anticathode in the 2θ range of 10–90°.

The reaction was carried out in a continuous-flow, fixed-bed microreactor. Water was produced *in situ* by

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hydrogen combustion at room temperature over a Pt-Al_2O_3 catalyst. The feed comprising propane and oxygen in stoichiometric amounts (for the reaction to acrylic acid), water and helium (10/20/0-60/70-10 vol%, GHSV = 3300 h^{-1}) was then directed to the catalyst bed. The catalyst (0.2 g) ground to a fine powder and diluted with SiC to a total catalyst bed volume of 1.1 ml was packed between two layers of quartz wool; the height of each layer was about 1 cm. Four reaction temperatures of 653, 673, 693 and 713 K were used. The high boiling products (water, acetone, acrolein, allylic alcohol, acetic and acrylic acids) were condensed at room temperature in two successive cold traps, and the rest of the products (CO, CO_2 and propene) as well as unreacted feed were analyzed by on-line GC. The GC analyses were performed with a Varian 3400CX chromatograph, using three columns: Haysep D and MolSieve 13X columns in series, where the on-line detected products and water were analyzed, and an FFAP capillary column for analysis of the condensate. For the water-free reference reactions, all products were analyzed on-line as no condensate of water-soluble oxygenates was generated at the temperature of an ice bath for 3 h of collection.

Propane conversion was calculated as the number of moles of C in all products and the selectivity was taken as the fraction of the moles of C in the product with respect to the total moles of C in all products. Rates of formation represent the moles of oxygenates in the condensate for a given time of collection, normalized to the weight of the catalyst.

3. Results and discussion

3.1. Propane oxidation in the absence of water

Catalytic testing was carried out at short contact time (1.1 s) and therefore low propane conversions (<10%). The results (table 1) show that propane conversion increases with temperature. The selectivity to carbon oxides also increases, with the temperature as expected from the presence of excess oxygen in the feed. The increased CO_x selectivities are at the expense of propene and acetic acid ones. The selectivity to acrylic acid does not change with temperature.

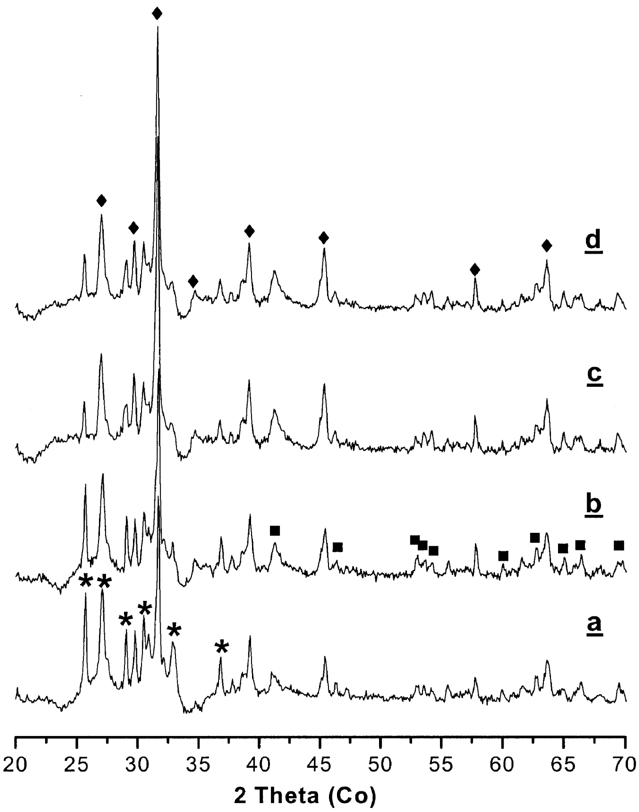

Figure 1. XRD patterns of $Mo_1V_{0.3}Sb_{0.25}Nb_{0.08}O_n$ catalyst before reaction (a), after reaction with 40 vol% water (b), after water-free reaction (c) and after addition of 40 vol% water to the used catalyst from pattern C (d) (*, $(M_yMo_z^{5+}Mo_{1-y-z}^{6+})_5O_{14}$ where M = V and/or Nb, and ◆, $Mo^{6+}O_3$; ■, $SbVO_4$).

Allylic alcohol (acrolein and acrylic acid precursor) is detected in significant amounts and its yield increases with temperature. It will be shown later that this product is not observed when water is added to the feed. This suggests that water addition affects the product distribution by a mechanism that is more than simply facilitating desorption of oxygenated products from the catalyst surface.

This observation is confirmed by BET and XRD analyses of the fresh and used catalysts from water-free reactions (figure 1). BET results show that the surface

Table 1
Results from water-free reference reactions at temperatures between 653 and 713 K ($C_3=$: propene; AA: acrylic acid; AcA: acetic acid; AllylA: allylic alcohol).

Temperature (K)	C_3 conv (%)	Selectivity (mol C%)				
		CO_x	$C_3=$	AA	AcA	AllylA
653	0.9	19.5	55.0	12.3	6.7	6.5
673	1.5	22.3	51.8	12.3	5.8	7.8
693	1.9	27.6	47.5	11.6	4.5	9.2
713	2.7	34.1	39.7	12.4	3.3	10.5

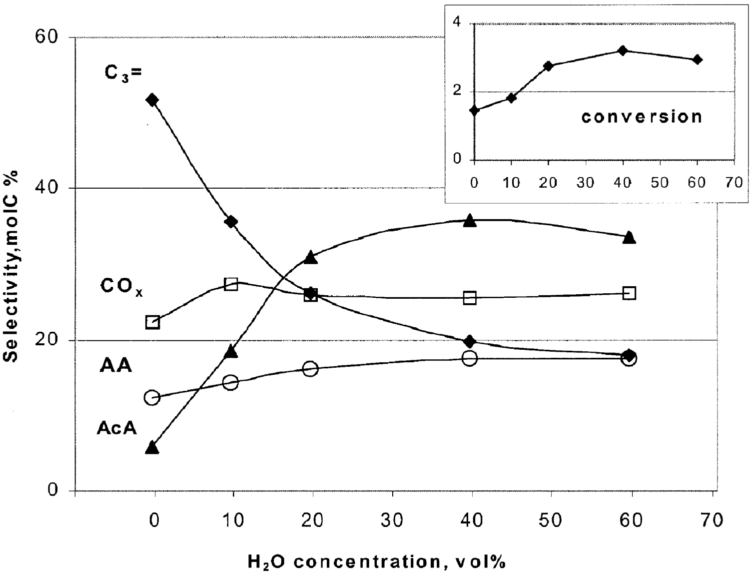

Figure 2. Product selectivities as a function of water concentration (top right: variation in propane conversion with water level) ($C_3H_8:O_2:H_2O:He = 10:20:0–60:70:10$ vol%; GHSV = 3300 h^{-1}; 673 K).

area decreases from 7 to 4 $m^2\,g^{-1}$ during the course of the reaction. The qualitative comparison of the XRD patterns reveals a modification of the crystalline structure of the catalyst (patterns a and c). The peaks assigned to $(M_yMo^{5+}_zMo^{6+}_{1-y-z})_5O_{14}$, *i.e.*, $(V_{0.07}Mo_{0.93})_5O_{14}$ and/or $Nb_{0.09}Mo_{0.91}O_{2.8}$, decrease significantly in the pattern of the used catalyst at the expense of a relative increase in the intensity of peaks belonging to $Mo^{6+}O_3$ (note the main peak at $2\theta = 31.5°$). The $SbVO_4$ phase is unaffected. This shows that under water-free conditions the catalyst surface is more oxidized and that the $(M_yMo^{5+}_zMo^{6+}_{1-y-z})_5O_{14}$ phase, suggested to be active for acrylic acid formation, transforms itself into the unselective $Mo^{6+}O_3$ [8]. Moreover, this reorganization occurs rapidly after the onset of the reaction and is completed after 50 min time on stream.

3.2. *Effect of water addition on catalyst performance at 673 K*

The effect of various water concentrations was studied at a reaction temperature of 673 K. The results from the catalytic tests are presented together with those of the water-free reference reaction (figure 2). Propane conversion increases slightly when water is introduced, but quickly levels off when 20 vol% or more of water is added to the feed.

The major effects appear to be in the formation of acrylic and acetic acids. The rate of formation of acrylic acid increases with the addition of water from 1.6×10^{-4} to 4.3×10^{-4} mol $h^{-1}\,g^{-1}$ (figure 3). The corresponding rate for acetic acid shows a larger increase, more than one order of magnitude, *i.e.*, from 0.8×10^{-4} to 9.7×10^{-4} mol $h^{-1}\,g^{-1}$. Furthermore, acetic acid is produced in higher selectivities than acrylic acid at any positive water concentration. The enhanced production of acrylic and acetic acids is accompanied by a large reduction in propene selectivity from 52 to 18 molC%. The observed rates of formation of these products are actually the difference between their true rate of formation and their rate of consumption by overoxidation. Therefore, an increase in the observed rates of formation can be due to a change in either or both rates.

It is evident from figure 2 that CO_x selectivity is nearly independent of water concentration. This may be expected considering that this Mo–V–Sb–Nb mixed oxide catalyst has very low acidity, the latter being considered as responsible for the strong adsorption and overoxidation of the oxygenated products [8]. Therefore, the enhanced productivity of acrylic and acetic acids is most probably the result of increased true rates of formation by enhanced hydration of propene to isopropanol

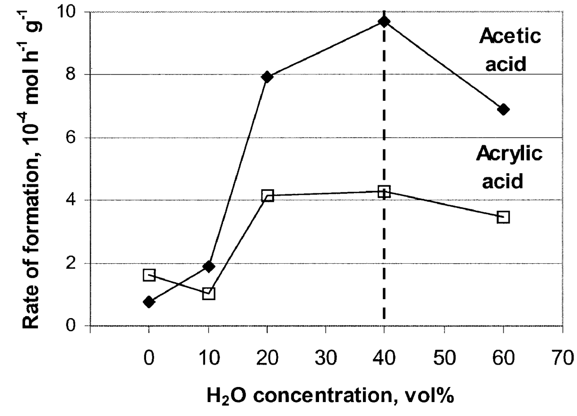

Figure 3. Rates of formation of acrylic (AA) and acetic (AcA) acids as a function of water concentration ($C_3H_8:O_2:H_2O:He = 10:20:0–60:70:10$ vol%; GHSV = 3300 h^{-1}; 673 K).

Table 2
Testing results for fresh and reactivated catalysts used in reactions with 20 and 40 vol% water in the feed.

Water conc.	Catalyst	C_3 conv. (%)	Selectivity* (mol C%)			
			CO_x	$C_3=$	AA	AcA
20%	Fresh	2.8	25.5	26.1	16.2	31.0
	Reactivated	1.2	26.3	47.4	12.6	13.4
40%	Fresh	3.2	21.6	19.7	17.6	35.9
	Reactivated	1.5	22.3	35.5	14.3	26.0

* Traces of acrolein and acetone are the difference between 100% selectivity.

and allyl alcohol oxidation. It should also be noted that the effect of water on the activity towards both acrylic and acetic acids is not linear and that a maximum is observed at 40 vol% water in the feed.

The characterization of the catalyst used in a reaction with feed composition containing 40 vol% water shows no change in the surface area and only small changes in crystalline-phase distribution (figure 1(a) and (b)). This indicates that water is also responsible for maintaining the structure of the active phase(s).

FT-IR and TPO characterization of the catalysts used for 4.5 h in water-free reaction and in a reaction with 40 vol% water in the feed showed no organic material deposition. This indicates that no detectable inhibition or very strong adsorption on the active sites by the products of the reaction occurs.

3.3. *Reactivation of the catalyst after reaction in the absence of water*

Deeper insight into the effect of water was revealed by exposing a catalyst already used in a water-free reaction for 5 h to a water-containing feed. If the effect of water is only to enhance the desorption of intermediate products, it is expected that when a water-containing feed is introduced over the used catalyst, the selectivities to oxygenates should reach immediately those obtained with fresh catalyst under the same conditions. This assumes that changes in the catalyst structure after the water-free reactions are reversible or not important to the catalyst performance.

20 vol% and 40 vol% of water were added to the reaction mixture at 673K. The results indicate only a partial improvement of the catalyst performance (table 2).

In addition, the XRD shows only a slight increase of the $(M_yMo_z^{5+}Mo_{1-y-z}^{6+})_5O_{14}$ phase in the reactivated catalyst (pattern d) compared to the used catalyst (water-free reaction) (c) (figure 1). Two conclusions emerge:

1. Propane conversion and the selectivities to acrylic and acetic acids with reactivated catalyst do not reach the values of those obtained with fresh catalyst at any water level (table 2). However, they increase with increasing water concentration. As mentioned above, the XRD showed only slight recovery of the complex molybdenum oxides doped with vanadium and/or niobium ($(M_yMo_z^{5+}Mo_{1-y-z}^{6+})_5O_{14}$). This leads to the conclusion that these phases have two functions: firstly to activate propane and secondly to transform it into partial oxygenated products, probably involving an Nb-containing phase in the former case and a V-doped one in the latter, as suggested in the literature [9,10].
2. The rates of formation of acrylic and acetic acids are significantly lower than those observed for fresh catalyst at the same water concentration: five times for 20 vol% and three times for 40 vol% of water for both acids (table 3).

3.4. *Effect of water addition on catalyst performance at different temperatures*

Previously, the effect of water was examined at a fixed reaction temperature (673 K). Bearing in mind that

Table 3
Rates of acrylic and acetic acids formation for fresh and reactivated catalysts.

Product	Water concentration (vol%)	Rates of formation (10^{-4} mol h^{-1} g^{-1})		Ratio of rates (fresh : used)
		Fresh catalyst	Reactivated catalyst	
Acrylic acid	20	4.1	0.9	4.6
	40	4.3	1.5	2.9
Acetic acid	20	7.9	1.5	5.3
	40	9.7	2.8	3.5

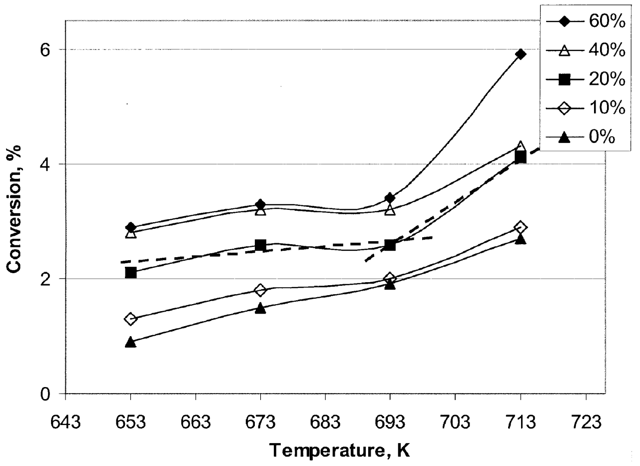

Figure 4. Variation of propane conversion as a function of water concentration and temperature ($C_3H_8:O_2:H_2O:He = 10:20:0–60:70:10$ vol%; GHSV = 3300 h^{-1}).

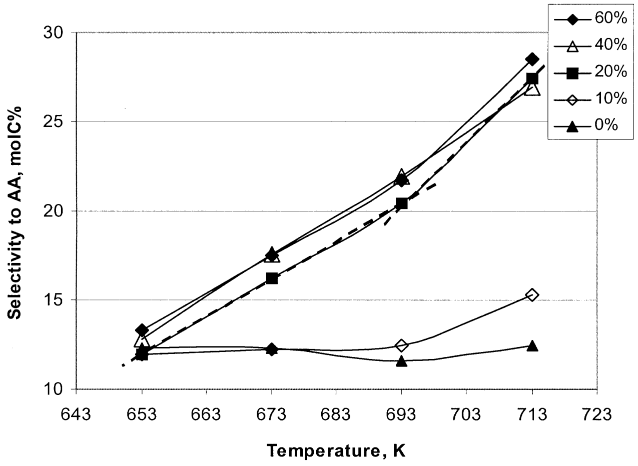

Figure 6. Variation of acrylic acid selectivity as a function of water concentration and temperature ($C_3H_8:O_2:H_2O:He = 10:20:0–60:70:10$ vol%; GHSV = 3300 h^{-1}).

desorption is endothermal, a change in reaction temperature could alter the results significantly.

The conversion of propane as a function of water concentration and temperature is shown in figure 4. As discussed above, propane conversion does not change significantly with an increase in the amount of water in the feed, but it does increase with temperature. It is known indeed that activation of propane is the rate-determining step in the selective oxidation of propane, because of its low reactivity [11,12].

The beneficial effect of water on the selectivity to acetic acid (figure 5) is very pronounced, even at 10 vol% water in the feed. This improvement is not linear and tends to level off with an increase in the water concentration in the same manner, as discussed in section 2. A decrease in acetic acid selectivity is observed when the temperature is increased. It appears that in all cases, the variation of acetic acid selectivity with temperature consists of two regions: one below 673/693 K and another above.

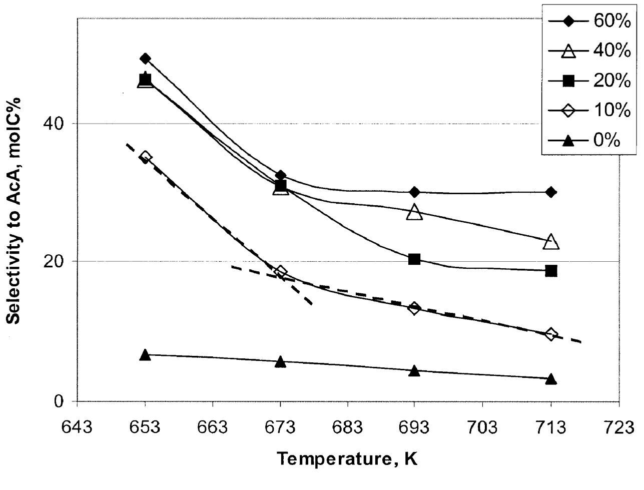

Figure 5. Variation in acetic acid selectivity as a function of water concentration and temperature ($C_3H_8:O_2:H_2O:He = 10:20:0–60:70:10$ vol%; GHSV = 3300 h^{-1}).

Improved selectivity to acrylic acid is observed at all water concentrations and temperatures (figure 6). In this case, the effects of water and temperature are complementary. The positive effect of water addition starts to be significant at water levels above 20 vol%. At 40 and 60 vol% water, the acrylic acid selectivity remains constant. For less than 10 vol% water in the feed, no improvement in the selectivity to acrylic acid is observed below 673 K relative to water-free reference conditions, but when the temperature exceeds 673 K, an increase in the selectivity is observed.

CO_x selectivities remain practically constant with the increase in water concentration and increase only slightly with temperature. Thus, facilitating desorption is again not the major mechanism by which water affects the product distribution.

Opposite trends in the acrylic and acetic acid selectivities with temperature were studied at a fixed water level of 40 vol% (figure 7(a)). This behavior can be explained by the different kinetics of these acid formations. As shown by the Arrhenius plot (figure 7(b)), the apparent activation energy of acrylic acid formation (23 kJ/mol) is much higher than that of acetic acid formation (3 kJ/mol). Thus, temperatures exceeding 683 K are required to obtain higher selectivities to acrylic acid. These values are surprisingly low compared to the common value of 100–150 kJ mol^{-1}. It is known that the apparent activation energy depends on the adsorption enthalpy of the reactant/product. As discussed above, acrylic and acetic acids do not adsorb strongly under the reaction conditions, and, in addition, their order with respect to propane is found to be one and not negative as in the case of catalyst inhibition. The reasons for the observed behavior, therefore, remain unclear.

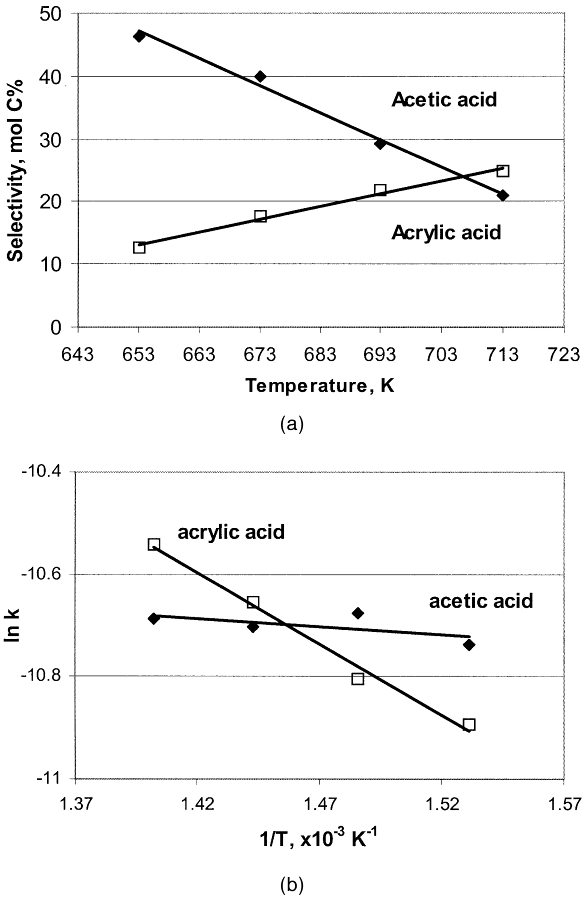

Figure 7. (a) Variation of the selectivities of acrylic and acetic acids as a function of temperature at a fixed water level of 40 vol%; (b) Arrhenius dependence of the rate constants of acrylic and acetic acids.

4. Conclusions

Water has a beneficial effect on the formation of oxygenate products from propane, in particular acrylic and acetic acids. The mechanism by which water affects the formation of these products is not obvious, even though some general features can be highlighted:

1. Water plays a crucial role in preserving the catalyst structure by maintaining the active sites (V- and Nb-doped molybdenum oxides) in a partially reduced oxidation state.
2. Water increases the apparent rates of formation of oxygenates, especially acetic acid, by favoring certain reaction pathways (propene hydration, allyl alcohol oxidation). The highest rates of formation are observed at 40 vol% water in the feed, for both acids.
3. The physical changes of the catalyst that occur under water-free conditions are only partially reversible when water is added to the feed. Only part of the active sites are recovered ($(M_yMo_z^{5+}Mo_{1-y-z}^{6+})_5O_{14}$, M = V and Nb), which results in still lower propane conversion and selectivities to oxygenates.
4. The simultaneous study of the effect of water concentration and reaction temperature shows that improvement in the selectivity to acrylic acid can be achieved at higher water levels and temperatures, whereas the selectivity to acetic acid decreases with temperature.

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