Effects of water on the catalytic performances of MoVTeNbO catalyst in the oxidation of propane to acrylic acid have been investigated at different reaction temperatures and different steam contents. Obtained results show that both catalytic performances and catalyst structure are very sensitive to the presence of water vapor in the reaction feed. Presence of water induces some structural modifications: improvement the crystallinity, decreasing production of non-selective sites and enhanced presence of the orthorhombic (M1) phase leading to better acrylic acid selectivity. Moreover, the number as well as strength of the acid sites detected after reaction in water-present condition is lower than those of the used one in dry condition.

**Keywords**: Selective oxidation of propane, Acrylic acid, MoVTeNbO catalyst, Role of water.

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 [1-4]. In particular, selective oxidation of propane to acrylic acid has been intensively studied [5-9]. By now, three classes of catalyst systems, VPO-type catalysts [10], heteropoly compounds catalysts (HPC) [4,11] and mixed metal oxides catalysts (MMO) [5-9] have been studied for the selective oxidation of propane to acrylic acid (Scheme 1).

The first group comprises catalysts which have been successfully used in the industrial process of n-butane oxidation to maleic anhydride. The second group type is known for its dehydrogenation activity. The third group is widely used in the propane oxidation to acrolein and further to acrylic acid and is efficient in propane ammoxidation [8]. The major advantage of the HPC type of compounds over the VPO or other metal oxide catalysts is their well-defined cage type of structures, which allow well controlled structural modifications, such as the partial substitution of the protons in heteropolyacid with metal cations, and the control of surface acidity. While, one major disadvantage of HPC type of catalysts is their general lack of thermal stability. In general, MMOs do not have a well-defined primary structure as HPC do. Rather, MMOs contain a mix of multiple crystal and amorphous phases. MMOs are generally prepared through calcination at high temperatures and thus have excellent thermal stability. It is noted that the main efforts to increase the performance of the catalyst had been concentrated on MMOs [8].

The nature of active and selective sites in the MoVTeNbO catalysts is still under discussion. According to the well-documented literature [12-15], the efficient MoVTeNbO catalysts have crystalline phases called M1 and M2. The M1 phase with \([\text{TeO}]_{2-x}(\text{Te}_2\text{O})_{x}\text{Mo}_5\text{O}_{36}\) formula is the most active and selective phase for propane oxidation to acrylic acid and it crystallizes in the orthorhombic system. The M2 phase with \([\text{TeO}]_{8-x}\text{Mo}_x\text{O}_8\) formula is inactive to propane but synergism effects between M1 and M2 phases could improve the catalytic performance.

The oxidation of propane takes place via several different reaction pathways, leading to the formation of many partial oxidation products such as propene, acrolein, acetone, acrylic, propionic, and acetic acids as well as carbon oxides and water. The reaction networks and product distributions are very sensitive...
Besides the intrinsic characteristics of the catalysts, the reaction conditions such as: reaction temperature, space velocity, feed composition especially water presence are the important factors influencing the catalytic performance of propane oxidation [17-20]. It is worth indicating that water plays a significant role in this oxidation reaction. According to well-documented literature, the presence of water should be beneficial, detrimental, or both to the desired valuable products (acrylic acid and acrolein) in many systems of propane oxidation [21-23]. There are many speculations about how water affects the catalyst performance and product distribution, such as by facilitating oxygenates desorption from the catalyst surface [24], modifying the catalyst structure [10,19] and varying the rate of selected reactions [21], but none of them has been completely confirmed.

The aim of this work is investigating of the role of water vapor in the production of the acrylic acid by propane oxidation on MoVTeNbO catalyst.

Mo1V0.3Te0.23Nb0.12Ox catalyst was produced by slurry method [25]. Ammonium paramolybdate (Merck), ammonium metavanadate (Merck) and telluric acid (Fluka) with the molar ratio of Mo/V/Te:1/0.3/0.23 were dissolved in 100 mL of water at 60 °C to obtain a uniform aqueous solution. 0.5 h later, the solution was cooled to 30 °C, and then 41.1 mL of an aqueous solution of niobium oxalate having niobium concentration of Mo/Nb:1/0.12 was mixed to obtain a slurry. The nominal metal ratio of the Mo–V–Te–Nb–O catalyst formed from such a solution should be Mo1V0.3Te0.23Nb0.12Ox. Rotated continuously for 2 h, the water of this slurry was removed via heat evaporation at a bath temperature of about 60 °C. Solid precursor of the catalyst was calcined in a nitrogen flow environment at 600 °C. The oven was heated at a rate of 5 °C/min up to 600 °C and held at that temperature for 2 h.

2.2. Catalyst characterization

XRD was performed with an X-pert Philips diffractometer using an X'Pert HighScore Plus software for evaluation of peak parameters. Temperature programmed desorption of ammonia (NH3-TPD) was performed using a NanoSORD analyzer equipped with a TC detector. After a pre-treatment at 300 °C under argon flow, to desorb the physisorbed water, the sample was saturated with ammonia at 100 °C. After purging, NH3 was desorbed during heating at constant rate (10 °C/min) up to 600 °C in an argon stream of 100 mL/min. Scanning electron microscopy (SEM) was performed on a Tescan microscope.

2.3. Catalytic test

The catalytic performance of Mo1V0.3Te0.23Nb0.12Ox catalyst was evaluated for the selective oxidation of propane to acrylic acid in a continuous-flow fixed-bed reactor at atmospheric pressure. The reactor was made of quartz tube, 100 cm long and 0.6 cm i.d., mounted vertically. An electrical heater was used for heating and controlled by an external temperature controller (PID). A K-type thermocouple, inserted just above the catalyst bed, permitted temperature measurements. A mixture of propane, oxygen and nitrogen was fed in from the top of the reactor. Water with specified flow rate was sent to the reactor with a syringe pump and converted to steam before entering into the reactor. The off-gas was condensed and the liquid phase separated from the gas phase in a cold trap. The gas phase and condensed liquid (water, acrylic acid and propionic acid) were analyzed with online GC and offline HPLC, respectively. The detailed process was discussed in previous paper [25].

3. Results and Discussion

3.1. XRD pattern of the prepared catalyst

Fig. 1 shows XRD pattern of the prepared Mo1V0.3Te0.23Nb0.12Ox catalyst after the heat treatment at 600 °C in nitrogen. Based on the literature [26], diffraction lines with 2θ= 6.6°, 7.7°, 9.0°, 22.1°, 26.6°, 27.2°, 45.2° assigned to the orthorhombic M1 phase and 2θ= 22.1°, 28.2°, 36.2°, 44.7°, 50° to the hexagonal M2 phase. All the characteristic peaks exist in the pattern which indicates that Mo1V0.3Te0.23Nb0.12Ox catalyst has been formed effectively.
3.2. SEM image of the catalyst

SEM image of the prepared catalyst is shown in Fig. 2. Aggregates of small cylinder-shaped crystallites with a length of about 200-500 nm are observed. Such kind of morphology of the MoVTeNbO catalyst was already reported [26, 27].

3.3. Effect of reaction temperature

The effect of reaction temperature was studied in propane selective oxidation over MoVTeNbO catalyst at water-free conditions and reactions in the presence of water vapor. The results are shown in Fig. 3. Acrylic acid, propylene and COx are major products and propionic acid is produced in a small amount.

It can be seen from Fig. 3 that temperature has great effect on the catalytic performance and products distribution. As temperature is elevated, the propane conversion increases in both dry and wet conditions (Fig. 3a). Acrylic acid selectivity reduces strongly by elevating temperature in the absence of water. Meanwhile, in wet conditions, acrylic acid selectivity passes through a slight maximum at 440 °C (Fig. 3b).

Oh et al. [17] have also reported a maximum in acrylic acid selectivity at 400 °C as temperature is elevating from 370 to 520 °C. Propane is a saturated hydrocarbon and has low reactivity at low reaction temperatures [18]; consequently, the conversion of propane is higher at higher temperatures, which lead to over oxidation of acrylic acid, propylene and other intermediate to COx (Fig. 3d) and decrease of acrylic acid and propylene selectivity (Fig. 3c).

From the results of Fig. 3, acrylic acid is produced even in water free reactions. But, it is clear that acrylic acid selectivity increases rapidly when water vapor is introduced (Fig. 3b). On the other hand, the formation of propionic acid is unaffected by the introduction of water vapor in the feed (Fig. 3e). It is worth indicating that different active sites were involved in propane oxidation to propionic acid and acrylic acid.

3.4. Effect of steam concentration

Catalytic performance of MoVTeNbO catalyst in partial oxidation of propane was studied as a function of steam concentration. The results are shown in Fig. 4. The major effects of water introduction appear to be in...
the formation of acrylic acid and CO\textsubscript{x}. The selectivity to acrylic acid increases rapidly from 7.2% to 36% when steam of (steam)/(C\textsubscript{3}H\textsubscript{8}) = 5 was introduced into the feeds (Fig. 4b). The variation of selectivity to CO\textsubscript{x} is just opposite to that of the selectivity to acrylic acid and decreases rapidly from 66.8% to 33% when steam of (steam)/(C\textsubscript{3}H\textsubscript{8}) = 5 was introduced (Fig. 4d). It is evident from Figs. 4a and 4c that introduction of water vapor has little effects on propane conversion and propene selectivity.

On the other hand, when (steam)/(C\textsubscript{3}H\textsubscript{8}) ratio is elevated from 5 to 7.5 propane conversion and acrylic acid selectivity increase a little accompanied by decreasing formation of propene and CO\textsubscript{x} slightly. Obtained results suggest that steam concentration has little effects on catalytic performance; denoting that water do not participate directly in propane conversion (Scheme 1). Novakova et al. [21] observed the rates of propane and oxygen conversions are zero order against the water concentration over MoVSbNbO catalyst.

3.5. Effect of water vapor on catalyst structure

In order to evaluate the effects of water vapor on the catalyst structure, XRD patterns of the Mo\textsubscript{1}V\textsubscript{0.3}Te\textsubscript{0.23}Nb\textsubscript{0.12}O\textsubscript{x} catalysts a) after calcination, b) after reaction in dry condition and c) after reaction in wet condition are shown in Fig. 5. Fig. 5 clearly indicates that reaction in the absence of water led to the formation of some new species; MoO\textsubscript{3} (2\textdegree = 14.9\textdegree, 27.1\textdegree, 29\textdegree, 31.5\textdegree, 39.4\textdegree, JCPDS:35-0609) and Mo\textsubscript{6}O\textsubscript{23} (2\textdegree = 25.5\textdegree, 29.8\textdegree, 30.3\textdegree, 34.6\textdegree, 38.6\textdegree, 54.9\textdegree, JCPDS: 05-0339). It is well known [28] that MoO\textsubscript{3} forms oxygen defect shear structures with the general formula Mo\textsubscript{2}O\textsubscript{3n-m}, where n = 4, 5, 8, 9 and m= 1 corresponding
Fig. 4. Effect of steam content on catalytic performance. \((\text{O}_2/\text{C}_3\text{H}_8)=2, \text{GHSV}=3000 \text{ ml/(min gcat)}, \text{T}=440 ^\circ \text{C})

Fig. 5. XRD patterns of a) Fresh catalyst; b) Used catalyst in dry conditions \((\text{O}_2)/(\text{C}_3\text{H}_8)=2\); c) Used catalyst in wet conditions \((\text{O}_2)/(\text{C}_3\text{H}_8)=2, \text{(steam)/(C}_3\text{H}_8)=7.5\). (Reaction temperature=440 ^\circ \text{C}, \text{GHSV= 3000 ml/(h gcat)})

to the stoichiometries Mo\text{O}_{11}, \text{MoO}_{14}, \text{Mo\text{O}_{23}}, \text{MoO}_{26}. \text{Mestl et al. [29,30] tested some of these sub-oxides in various oxidation reactions. They concluded that MoO}_3 \text{ is a non-selective catalyst. Therefore, it is possible to predict that the presence of MoO}_3 \text{ after reaction in dry-condition will result in less selective reaction, i.e. higher CO}_x \text{ formation compared to the reaction in wet-condition. In general, heat treatment at high temperature may lead to the formation of MoO}_3. But literature results clearly}
show that the heat treatment atmosphere, whether containing air or an inert atmosphere plays a very critical role. Lin has shown [31] the MoO$_3$ phase did not appear to exist in the resulting Mo$_1$V$_{0.3}$Te$_{0.23}$Nb$_{0.12}$O$_{x}$ oxides when the calcination was carried out under an inert atmosphere. While, indexing with standard XRD references reveals that the major diffraction peaks of the air-calcined samples are consistent with the characteristic peaks of MoO$_3$. Therefore, it is not surprising that MoO$_3$ crystal phase has not been detected in the XRD pattern of as-calcined catalyst in nitrogen flow at 600 °C (Fig. 5a). All the characteristic peaks exist in the XRD pattern of the used catalyst in wet condition indicating that the crystalline structure is kept after reaction in the presence of water. On the other word, the characteristics of MoO$_3$ do not appear in the XRD patterns of the used one in wet condition. While, reaction in the absence of water led to the formation of MoO$_3$. Based on the well-documented literature, water may take away the heat produced during the reaction to avoid the hot spots on the catalyst surface [4]. Therefore, formation of MoO$_3$ in the absence of water due to the hot spots on the catalyst surface is expectable.

Furthermore, the diffraction peaks of the sample obtained after reaction in wet condition appear more intense compared to those of the fresh catalyst and used one in dry condition. The area of the three strongest peaks at 7.9°, 22.1° and 28.3° are presented in Table 1. Obviously, the peaks area for the fresh sample in the wet condition increases significantly. It means that under water-present condition, greater amount of the crystalline (M1 and M2) phases are produced. The crystallization degree improvement after water addition has also been reported by Landi et al. [10,19] in selective oxidation of propane over VPO catalyst.

Using results from the literature [26], the ratios of the peak area at 7.9° for the M1 phase and at 28.3° for the M2 phase to the peak area at 22.1° were used to calculate their relative quantities. The results are presented in Table 1, clearly shown that the relative quantities of M1 phase increases considerably with reaction in the presence of water.

In order to investigate the possible effect of the water on the catalyst acidity, NH$_3$-TPD tests were carried out on the used catalyst after reaction in the presence and absence of water. The NH$_3$-TPD results are summarized in Table 1, while the NH$_3$-TPD profiles are shown in Fig. 6. According to these results, a reduction of the number of acid sites can be inferred in the case of samples obtained after reaction in wet condition. Introduction of water in the reaction mixture promoted the shift of TPD peak toward the lower temperature. For the NH$_3$-TPD profile of the used sample in dry condition, one peak with maximum at 210 °C and a shoulder at about 400 °C are recognized. While, the used sample in wet condition has one quiet well-defined peak with maximum at 180 °C. This means that the acid sites of the used one in dry condition are more strength than those of the used one in wet condition.

According to these results, water presence in the feed decreases the number as well as the strength of the acid sites. By comparison of these results with catalytic performances, it can be concluded that, although the presence of water is necessary to produce acrylic acid, its selectivity increases with enhancing the order of crystalline structure and decreasing the surface acidity.

Therefore, formation of acrylic acid from propane requires a well-crystallized MoVTeNbO catalyst with a low acidity. The reduction of the total acidity related to the increase of selectivity to partial oxidation products has been found also by different authors [6,10,32]. Martin et al. [32] that have studied toluene oxidation to benzaldehyde on VPO catalysts have shown that the blockage of non-selective Brønsted acid sites allowed the increase of benzaldehyde selectivity. All of these observations suggest that although the presence of acid sites is fundamental for activity, reducing the acidity of the catalyst has relative benefit on selectivity.

In recent years, many investigations have been conducted on the intrinsic activity and the role of each M1 and M2 phases in propane oxidation. It was shown that the active M1 phase has all the sites needed to transform propane to acrylic acid and it is also very efficient at oxidizing propylene to acrylic acid [5-7]. Lintz et al. [8] have shown that synergism effects between M1 and M2 phases could improve the catalytic performance. These synergetic effects have been described as different as bifunctional catalysis, solid state reaction affecting the bulk phases, surface chemical interaction (migration, contamination), formation of coherent interface and supporting effects. Therefore, positive effect of crystallization degree improvement on catalytic performances is expectable.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak area</th>
<th>Relative intensities</th>
<th>Acid sites (µmol NH$<em>3$/g$</em>{cat}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.9°</td>
<td>22.1°</td>
<td>28.3°</td>
</tr>
<tr>
<td>Fresh</td>
<td>6.7</td>
<td>32.0</td>
<td>28.2</td>
</tr>
<tr>
<td>Used one in wet condition</td>
<td>28.7</td>
<td>82.8</td>
<td>54.7</td>
</tr>
<tr>
<td>Used one in dry condition</td>
<td>7.1</td>
<td>39.8</td>
<td>37.7</td>
</tr>
</tbody>
</table>
4. Conclusions

An effective Mo V0.3Te0.23Nb0.12Ox catalyst for the selective oxidation of propane to acrylic acid was synthesized using slurry procedure. The prepared catalyst was characterized by XRD and SEM techniques and shown to contain effective crystalline phases called M1 and M2 as the major phases. The effects of water vapor were investigated on the catalytic performance in partial propane oxidation. Obtained results showed that presence of water affects on the catalyst structure leading to increase acrylic acid selectivity accompanied by decreasing CO x selectivity. NH3-TPD and XRD analysis of the used catalysts in dry and wet condition proposed that water introduction into the reaction feed can give rise to: a) decreasing production of non-selective sites, b) improvement the crystallization degree, c) enhanced presence of the orthorhombic (M1) phase, d) decreasing the number as well as strength of surface acidity.

References