Oxidation of propane to acrylic acid over Mo-V-Sb-La-O$_x$ catalysts: Influence of catalyst preparation and calcination conditions

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Abstract

In the oxidation of propane to acrylic acid over a Mo-V-Sb-La-O$_x$ catalyst, the influence of variables determining solid properties (viz. catalyst preparation methods including calcination conditions) and of process variables (viz. temperature and the C_3H_8/O_2 ratio) on the catalytic performance was studied in the presence of water. The surface and catalytic properties of the Mo-V-Sb-La-O$_x$ catalyst were found to be strongly dependent on the above parameters. The catalyst prepared by a slurry method showed superior catalytic performance compared to the catalyst prepared by co-precipitation and hydrothermal synthesis methods. The presence of water vapour in the reactant feed of propane and oxygen was beneficial for obtaining relatively good selectivity to acrylic acid. The catalyst was highly stable over an extended period of time without losing its activity and selectivity.
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1. Introduction

Presently, acrylic acid is produced commercially by the oxidation of propene through two steps: (i) oxidation of propene to acrolein and (ii) oxidation of acrolein to acrylic acid using transition metal oxide catalysts. During the last decade, interest increased in the potential use of propane for the direct oxidation propane to oxygenates due to the abundant availability of propane and hence, economic reasons. However, activation of the C–H bond in propane is not easy due to its high strength, which requires a high energy of activation. Literature indicates that considerable progress has been made in the oxidation of propane to acrylic acid by molecular gas-phase oxygen. Various catalyst systems such as heteropoly acids [1–8], V-P-O catalysts [9–13] and metal oxide catalysts [14–19] have been studied for the oxidation of propane to acrylic acid. Mo-V-Te-Nb-O$_x$ [20–23] and Mo-V-Sb-Nb-O$_x$ [24–27] mixed oxides are the most active and selective catalysts for this reaction. It was reported that the best catalysts contain well-dispersed V

embedded in a matrix of mixed metal oxides. However, for the preparation of active and selective catalysts, the preparation method and calcination conditions are the crucial factors for the formation of certain crystalline phases, which are responsible for high selectivity to acrylic acid. In the literature, several sources indicate that the catalytic performance strongly depends not only on the chemical composition but also on the catalyst preparation method [28–34]. Recently, it has been reported that Mo-V-Te-Nb-O$_x$ catalysts prepared by hydrothermal synthesis show excellent catalytic performance in the oxidation of propane to acrylic acid [21,35]. Unfortunately, the achievement of the single-step process is not good enough for its commercialization because of the low yields to oxygenates. The acrylic acid can be produced in good yields only at lower reaction temperature; at higher temperatures required for the reaction, the oxygenated products, particularly acrylic acid are converted to unwanted by-products such as carbon oxides (CO and CO_2). Thus, there are limitations on the reaction conditions. Therefore, it is highly desirable to develop a catalyst that is active, selective and stable and operates at lower reaction temperatures. Recently, we found that La-doped Mo-V-Sb-O catalysts show good activity and are able to produce the oxygenates acrylic acid and acetic acid [36]. Thus, the aim of the present work was

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to study this catalyst system in more detail for the oxidation of propane to oxygenates with the following objectives:

(i) preparation of Mo-V-Sb-La oxide catalysts by different catalyst preparation methods (viz. slurry, co-precipitation and hydrothermal synthesis);
(ii) characterization of the catalysts for their properties (viz. surface area and composition, crystal phases);
(iii) evaluation of the catalytic activity and selectivity at different reaction conditions (viz. temperature, C_3H_8/O_2, He/C_3H_8, H_2O/C_3H_8 ratios, etc.).

2. Experimental

2.1. Catalyst preparation

All preparation methods aimed at a Mo-V-Sb-La-O_x catalyst (Mo:V:Sb:La = 1.0:0.4:0.25:0.2). Under the slurry method, typically the required amount of ammonium molybdate, ammonium metavanadate, antimony chloride ($SbCl_5$) and lanthanum nitrate with desired atomic ratios were mixed in deionized water at 90 °C to form slurry. The water was then evaporated at 90 °C with constant stirring until a thick paste was obtained. The thick slurry was then dried at 120 °C for 12 h.

In co-precipitation the desired amounts of ammonium molybdate, ammonium metavanadate, antimony nitrate and lanthanum nitrate were dissolved in deionized water at 90 °C to form slurry. A precipitate was then obtained by the addition of an aqueous ammonia solution (pH ≥ 8.0), being afterwards left during 30 min for ageing. Subsequently, the precipitate was filtered and washed with deionized water and finally dried at 120 °C for 12 h.

In hydrothermal synthesis the desired amounts of ammonium molybdate, ammonium metavanadate, antimony chloride ($SbCl_5$) and lanthanum nitrate were dissolved in deionized water at 90 °C to form slurry. The gel was kept in Teflon-lined stainless steel autoclaves at 175 °C for 48 h. The resulting precipitate was filtered, washed and dried at 120 °C for 12 h.

In all cases the dried catalyst masses were calcined at 600 °C for 2–8 h in a flow of nitrogen. After calcination, the catalysts were pressed binder-free and crushed to 20–30 mesh sized particles.

2.2. Catalyst characterization

The surface area of the catalyst was determined by a five-point BET method by adsorption of N_2 using an ASAP 2010 surface analyzer.

The crystalline phases of the catalysts were determined by X-ray powder diffraction with a STOE Transmission Diffractometer using Cu Kα_1 radiation. XPS measurements were done using an ESCALAB 220 iXL (Fisons).

2.3. Oxidation of propane

The catalytic experiments were carried out in a fixed-bed tubular reactor made of quartz (i.d. 8 mm, o.d. 10 mm and length 200 mm) at atmospheric pressure. The catalyst samples (particle size: 22–30 mesh) were located within the reactor between two layers of quartz chips (size, 850–1180 nm). Before the reaction, the catalysts were pretreated at 450 °C for 2 h in a flow of helium (20 cm^3 min^{-1}). The feed consisted of a mixture of pure propane, oxygen, helium and water vapour. The reaction was performed at different temperatures (400–500 °C), C_3H_8/O_2 ratios (0.33–2.0), H_2O/C_3H_8 ratios (0.9–6.0) and He/C_3H_8 ratios (2.0–20) and at a constant gas hourly space velocity (GHSV) (840 cm^3 g^{-1} h^{-1}). Gaseous reactants and products were analyzed by on-line micro-gas chromatography (Varian-Chrompack CP-2002) with a thermal conductivity detector (TCD) using two columns (Porapak-Q for the separation of CO_2 and hydrocarbons and molecular sieve for the separation of He, O_2 and CO). The liquid oxygenated products were analyzed off-line also by gas chromatography (Shimadzu GC 14a) with a Porapak-Q capillary column and a flame ionization detector (FID). The effluent gases from the reactor were passed through a cold trap (0 °C) for the condensation of water and to remove all the water-soluble oxygenated compounds before analyzing the gases in a micro-GC. A mass spectrometer was mounted in front of the cold trap to assess the presence of oxygenated products in the reaction. The carbon balance was always above 95%. The selectivities were calculated based on C_3H_8 converted.

3. Results and discussion

3.1. Catalyst characterization

The BET surface area and XRD analysis data of the differently prepared Mo-V-Sb-La-O_x catalysts, which were calcined for 2 and 8 h, respectively, are presented in Table 1. The results show that the surface area is slightly higher for the catalysts prepared by co-precipitation than the catalysts prepared by the slurry- or hydrothermal synthesis methods (calcined at 600 °C for 8 h). Furthermore, the surface area decreased by increasing the time of catalyst calcination from 2 to 8 h.

The XRD data for the differently prepared catalysts showed the presence of crystalline phases as well as amorphous ones. For the catalysts prepared by the slurry method and calcined different times (2 and 8 h), similar crystalline phases (MoO_3, La_2O_3, VO_2, $VSbO_4$ and La_2MoO_6) were observed. In addition, $LaVO_4$ and molybdenum–vanadium-oxide phases were observed for the catalyst calcined for 8 h. Similar crystalline phases were obtained for the catalysts calcined for 4 and 8 h. Besides crystalline $LaVO_4$ phase (which was only present in the catalyst prepared by the slurry method), all the other crystalline phases were similarly observed for the catalysts prepared by both the slurry and hydrothermal synthesis methods, whereas the catalyst prepared by co-precipitation showed only the presence of crystalline La_2O_3, $VSbO_4$, $LaVO_4$, VO_2, Sb_2O_5 phases but no MoO_3 and lanthanum–molybdenum-oxide phases. Comparison of Table 1 (crystalline phases) and Table 2 (surface composition) indicates the surface enrichment of vanadium and lanthanum for the catalyst prepared by the co-precipitation method. This may be the reason for the few different crystalline phases observed for the catalysts prepared

Table 1
Surface area and XRD analysis data of Mo_1-$V_{0.4}$-$Sb_{0.25}$-$La_{0.2}$-O_x catalysts prepared by different methods and calcination conditions

Catalyst preparation method[a]	Surface area ($m^2\,g^{-1}$)	Crystalline phases							
Slurry[b]	5.19	La_2O_3	MoO_3	VO_2	$VSbO_4$	$La_2(MoO_6)$			
Slurry[c]	3.24	La_2O_3	MoO_3	VO_2	$VSbO_4$	$La_2(MoO_6)$	$VMoO_2$	$LaVO_4$	$La_4Mo_2O_{11}$
Slurry	1.78	La_2O_3	MoO_3	VO_2	$VSbO_4$	$La_2(MoO_6)$	$VMoO_2$	$LaVO_4$	$La_4Mo_2O_{11}$
Co-precipitation	2.90	La_2O_3	MoO_2	VO_2	$VSbO_4$	$LaVO_4$	Sb_2O_5		
Hydrothermal synthesis	2.19	La_2O_3	MoO_3	VO_2	$VSbO_4$	$La_2(MoO_6)$	MoV_2O_8	La_6MoO_{12}	$MoO_3 \cdot OH$

[a] Calcined at 600 °C for 8 h.
[b] Calcined at 600 °C for 2 h.
[c] Calcined at 600 °C for 4 h.

Table 2
XPS analysis data of Mo-V-Sb-La-O_x (composition calculated from preparation Mo:V:Sb:La = 1.0:0.4:0.25:0.2) catalysts prepared by different methods and calcination conditions

Catalyst preparation method[a]	XPS composition				Binding energy (eV)			
	Mo	V	Sb	La	Mo 3d	V $2p_{3/2}$	Sb $3d_3$	La 3d
Slurry[b]	1.0	0.52	0.78	0.25	233.3	517.5	540.7	835, 838.4, 855
Slurry	1.0	0.61	0.44	0.97	233.0	518.8	541.5	839.9, 843.5, 860.1
Co-precipitation	1.0	17.0	7.5	29.0	231.6	517.7	542.1	836.7, 840.4, 856.9
Hydrothermal	1.0	0.33	0.63	0.64	233.0	517.4	540.6	835.6, 839.3, 856.0

[a] Calcined at 600 °C for 8 h.
[b] Calcined at 600 °C for 2 h.

by the co-precipitation method compared to the catalysts prepared by the slurry and hydrothermal synthesis methods.

The XPS analysis data for the various Mo-V-Sb-La-O_x catalysts (Mo:V:Sb:La = 1:0.4:0.25:0.2) are shown in Table 2. The surface and near-surface compositions are different for all the catalysts of the same composition but prepared by different preparation methods (viz. slurry, co-precipitation and hydrothermal synthesis). For all the calcined catalysts the surface concentration of V, Sb and La is higher than the bulk metal concentration resulting from the preparation with the exception of V, which is lower in case of the catalyst prepared by the hydrothermal synthesis method. The co-precipitated catalyst mainly contains La, V and Sb in the near-surface area whereas Mo exists only in trace amounts. In this catalyst, the peak for Mo is also shifted to lower binding energies.

3.2. Oxidation of propane

The effect of temperature on catalytic activity and product selectivity in the oxidation of propane over the Mo-V-Sb-La-O_x catalyst, prepared by the slurry method, is presented in Fig. 1. The major oxygenated products obtained over this catalyst were acetic acid and acrylic acid. Acrolein, 2-propanol and acetone were obtained in only minor amounts. Propane conversion increased as expected with an increase in temperature as the selectivities for CO and CO_2, whereas the propylene selectivity decreased to a large extent. The selectivity to acetic acid and acrylic acid passed through a maximum with increasing temperature. It seems that the increase in selectivity to acetic acid and acrylic acid is related to the loss of selectivity to propylene. Normally, the selectivity to acrylic acid decreases with increasing temperature but for the chosen catalyst and reaction conditions,

an increase in acrylic acid selectivity was observed on increasing the temperature from 400 to 450 °C. A further increase in temperature caused a decrease in the selectivity. At higher temperatures, the oxygenated compounds are oxidized to carbon oxides and hence, the selectivity to oxygenates decreased.

The catalyst prepared by the slurry method was highly stable for a long period of operation (i.e., about 80 h) without losing its activity and selectivity.
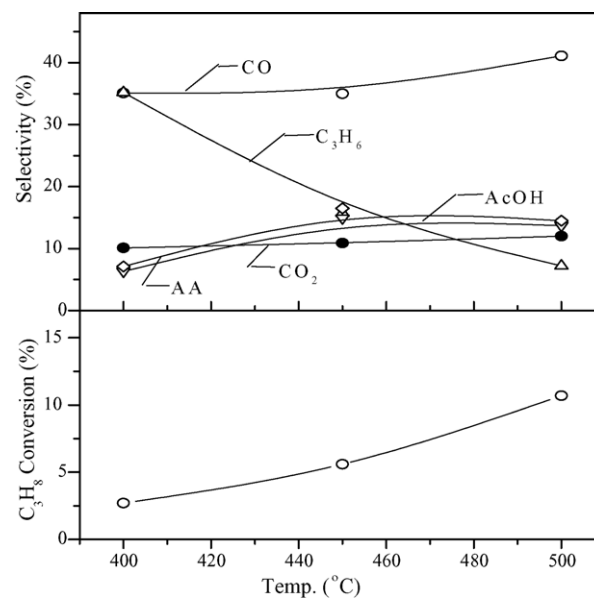

Fig. 1. Effect of temperature on the catalytic performance in oxidation of propane over Mo-V-Sb-La-O_x catalyst prepared by the slurry method (C_3H_8:O_2:He:H_2O = 1:1.5:4:1.5, GHSV = 840 $cm^3\,g^{-1}\,h^{-1}$ and calcination time = 8 h).
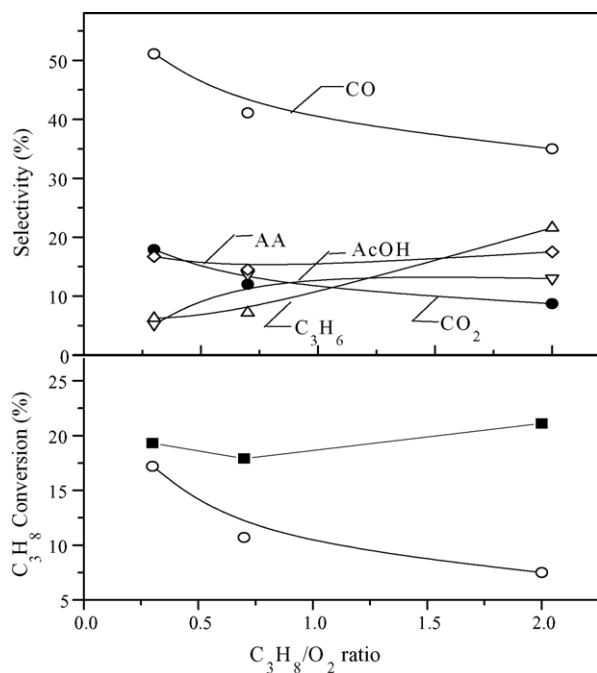
Fig. 2. Effect of C_3H_8/O_2 on the catalytic performance in oxidation of propane over Mo-V-Sb-La-O_x catalyst prepared by slurry method (temperature = 500 °C, GHSV = 840 cm^3 g^{-1} h^{-1} and calcination time = 8 h).

Fig. 3. Effect of catalyst calcination time on the catalytic performance in oxidation of propane over Mo-V-Sb-La-O_x catalyst prepared by slurry method (temperature = 500 °C, C_3H_8:O_2:He:O_2 = 1:1.5:4:1.5 and GHSV = 840 cm^3 g^{-1} h^{-1}).

The influence of the C_3H_8/O_2 ratio on propane conversion and product selectivity is shown in Fig. 2. The propane conversion is decreased with increasing propane-to-oxygen ratio in the feed. However, the conversion of O_2 is not influenced significantly by a change in the C_3H_8/O_2 ratio. The selectivities for CO and CO_2 decreased to a small extent but selectivity to propylene increased with increasing C_3H_8/O_2 ratio. The selectivity to acrylic acid was not much affected but the selectivity to acetic acid increased with increasing C_3H_8/O_2 ratio in the feed.

The effect of calcination time on the catalytic performance over the Mo-V-Sb-La-O_x catalysts, prepared by the slurry method, is presented in Fig. 3. The propane conversion decreased with increasing calcination time from 2 to 4 h but a further increase in calcination time causes only a marginal decrease in conversion. This is in agreement with a loss of specific surface area with increased calcinations time (see Table 1). The catalyst calcined for 2 h showed high selectivity to carbon oxides (i.e., CO and CO_2), and moreover, the formation of propylene, acrylic acid, acetic acid, and other oxygenated products such as 2-propanol, acetone and acetic acid was also observed. When the calcination time increased to 4 h the selectivities to CO and CO_2 are decreased but that to acrylic acid and acetic acid is increased. The propane conversion and selectivity to oxygenated products are not much affected when the calcination time is further increased from 4 to 8 h. However, the selectivity to propylene varies with calcination time. It is interesting to note that the selectivities to acrylic acid and acetic acid are increased greatly when the calcination time increases from 2 to 4 h but a further increase in calcination time did not affect selectivity. The variation in the conversion and selectivity pattern suggests that the catalyst was not in a stable form when a short calcination time
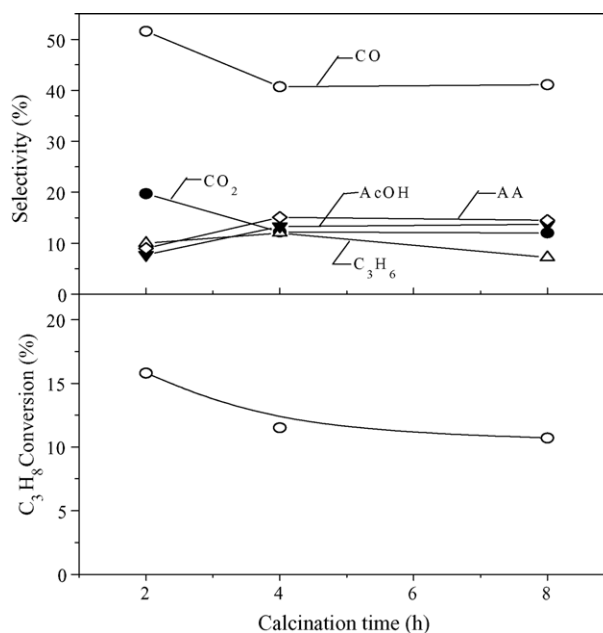
(2 h) was applied, and hence, a low selectivity was obtained for the oxygenated products. This may be due to the fact that the active sites being responsible for the formation of oxygenated products may not be formed at the lower calcination time and hence, an excess formation of CO and CO_2 was observed.

To study the effect of the various preparation methods on the catalytic performance and the surface properties of the catalysts, a detailed investigation was carried out over the Mo-V-Sb-La-O_x catalyst. The results of this study are presented in Table 3. The following important conclusions were drawn:

- Catalysts prepared by different methods (viz. slurry, co-precipitation and hydrothermal synthesis) exhibit different catalytic performance that depends very much on catalyst preparation and calcination conditions.
- The catalyst prepared by the slurry method shows good selectivity to acetic acid and acrylic acid.
- A significant increase in propane conversion, i.e., activity, was observed for the catalyst prepared by hydrothermal synthesis compared to the slurry method. For this catalyst, CO and CO_2 selectivities are markedly high, especially the selectivity to CO, but the selectivities for acetic acid and acrylic acid are low.
- The catalyst prepared by co-precipitation shows a totally different catalytic performance from the other ones, i.e., its activity was highest. The selectivity to oxygenated products, however, was totally suppressed. The catalysts showed preferentially the formation of CO and CO_2 but very little formation of propylene.

The above discussion reveals that the catalyst prepared by the co-precipitation method was totally inactive towards oxy-

Table 3
Effect of catalyst (Mo_1-$V_{0.4}$-$Sb_{0.25}$-$La_{0.2}$-O_x) preparation methods on the catalytic performance in oxidation of propane at 500 °C (reaction conditions: C_3H_8:O_2:He:H_2O = 1.0:1.5:4.0:1.5 and GHSV, 840 $cm^3\,g^{-1}\,h^{-1}$)

Catalyst preparation method[a]	Surface area ($m^2\,g^{-1}$)	C_3H_8 conversion (%)	Selectivity (%)					Σ_{oxy}
			CO	CO_2	C_3H_6	AcOH	AA	
Slurry[b]	5.42	30.9	68.3	17.2	7.8	4.0	1.9	5.9
Slurry[c]	5.19	15.8	51.6	19.7	10.0	7.7	9.0	18.2
Slurry	1.78	10.7	41.1	12.0	7.2	13.7	14.5	30.9
Hydrothermal	2.19	22.9	55.8	18.7	5.9	6.0	8.2	15.7
Co-precipitation	2.90	39.2	50.9	37.6	11.5	0.2	0.3	0.8

AA: acrylic acid and AcOH: acetic acid.
[a] Calcined at 600 °C for 8 h.
[b] Catalyst, Mo-V-Sb (1:0.4:0.25), reaction temperature = 450 °C.
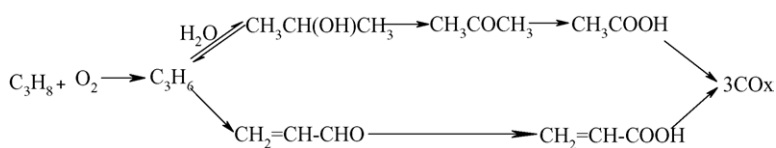[c] Calcined at 600 °C for 2 h.

Fig. 4. Oxidation pathways over Mo-V-Sb-La-O_x catalyst.

genated products. It shows very high selectivity (about 90%) to carbon oxides. This may be due to the following reasons. As discussed earlier in the context of the XRD analysis, no MoO_3 and lanthanum–molybdenum-oxide phases were observed for the co-precipitation catalyst (Table 1); after calcination a number of high intensity phases (between 30° and 55°) are observed. The XRD data indicate the presence of an Sb_2O_5 phase; that is, Sb_2O_5 is not fully consumed for compound formation. XPS data also show that Mo exists only in trace amounts in the catalyst surface (Table 2).

For the catalysts prepared by slurry and hydrothermal synthesis methods, most of the crystalline phases observed were similar except for the additional $LaVO_4$ phase observed in the catalyst prepared by the slurry method.

It seems that the active sites, which are responsible for the formation of oxygenates, particularly acrylic acid and acetic acid, were not formed on the surface of the catalyst prepared by co-precipitation and thus the catalyst became totally unselective towards the oxygenated products.

The catalysts studied did not show satisfactory oxygenates selectivities (acrylic acid S_{max} = 14.5%; acetic acid S_{max} = 13.7%) at a propane conversion of approximately 11%. The results showed, however, a significant effect of catalyst preparation procedures on selectivity and activity; this may serve as a support in further catalyst development.

In the literature, the reaction pathways of the oxidation of propane to oxygenates over V-P-O [37], Te-P/NiMoO [38], Mo-V-Te-Nb-O [33,39] and V-OH beta zeolite [33] catalysts have been reported. For the present Mo-V-Sb-La-O_x catalyst system, the proposed oxidation pathways comprising all the partial oxidation products lead to the reaction scheme given in Fig. 4. The products obtained in the present study were acrolein, acetone, 2-propanol, acetic acid, acrylic acid, CO, CO_2 and C_3H_6. In the proposed reaction scheme, two major pathways have been pro-

posed. In the first route, the acrolein formation mainly occurs via propene, which is formed by the oxidation of propane. The acrolein is then further oxidized to acrylic acid in the presence of molecular oxygen. As stated earlier, the products such as acetone, 2-propanol and acetic acid were also obtained in this catalyst system in oxidative conversion of propane; therefore, the formation of acetic acid via acetone as an intermediate has been proposed. Acetone is formed by the oxidation of 2-propanol, which in turn results from water addition to propene, whereas direct formation of propane cannot be ruled out. A similar parallel reaction pathway for oxidation of propane with oxygen to 2-propanol and acetone has already been proposed as minor pathways on mixed oxide catalysts containing Mo and V metals [25,27,33,37,39,40].

It seems that the majority of the reaction proceeds through the first route, i.e., acrylic acid formation occurs via acrolein as an intermediate. The oxygenated products particularly acrolein and acrylic acid have low stability on the surface of the catalyst and hence they are further oxidized to carbon oxides and thus the selectivity to acrylic acid is decreased.

4. Conclusions

In the oxidation of propane the catalytic activity and selectivity of the Mo-V-Sb-La-O_x catalysts depend strongly on the catalyst preparation method including the calcination time and process conditions (viz. temperature, C_3H_8/O_2 ratio, space velocity, etc.). The catalyst prepared by the slurry method gives a good catalytic performance compared to the catalysts prepared by hydrothermal synthesis or co-precipitation. The catalytic activity and selectivity remains unchanged when the reaction was continued for up to 80 h; this indicates that a high stability of the catalyst may exist.

Acknowledgements

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