Effect of potassium doping on the catalytic behavior of Mo–V–Sb mixed oxide catalysts in the oxidation of propane to acrylic acid

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Small addition of potassium to a Mo–V–Sb mixed oxide catalyst (previously prepared by hydrothermal synthesis) strongly modifies its catalytic behavior. Thus, while acetic acid is mainly observed in the K-free catalysts, acrylic acid is selectively obtained in K-doped catalysts. In this case, a selectivity to acrylic acid of about 30% is achieved at propane conversions of 30%. This catalytic behavior is apparently not due to modification of the crystalline phases in the K-doped catalysts but to the elimination of the acid sites of the undoped Mo–V–Sb mixed oxide catalyst.

KEY WORDS: propane oxidation; acrylic acid; acetic acid; molybdenum; vanadium; antimony; potassium; hydrothermal synthesis; Lewis and Bronsted acid sites.

1. Introduction

The investigation of new catalytic systems for the gas-phase selective oxidation of propane to acrylic acid has special interest from both industrial and fundamental point of view. In this way, Mo–V–Te–Nb–O catalysts seem to be the most active and selective at relatively moderate temperatures [1,2].

Mo–V–Sb–O mixed oxide catalysts have been proposed as active and selective in the oxidation of propane to acrylic acid [3]. Despite this interest, relatively few fundamental studies on the nature of Mo–V–Sb-based catalysts and their catalytic behavior [4–7] have been published. Recently, it has been proposed that the calcination conditions strongly influence the catalytic behavior of Mo–V–Sb–Nb–O catalysts [4], but relatively low selectivities to acrylic acid were reported [4–6].

Hydrothermal synthesis has also been proposed as an interesting alternative synthetic route in the preparation of Mo–V–Sb–O-based catalysts [7]. At this moment, low selectivities to acrylic acid (ca. 6%) have been reported over hydrothermally synthesized Mo–V–Sb–O catalysts, although the selectivity to acrylic acid was increased from 6 to 20% by grinding the samples before the calcination step [7].

In this paper, we present how the incorporation of potassium to Mo–V–Sb–O catalysts (previously synthesized by a hydrothermal synthesis) has a promoter effect on their catalytic performance for the selective oxidation of propane. In addition, the characterization results suggest that the higher selectivity to acrylic acid observed in K-doped catalysts could be related to elimination of acid sites on the catalyst surface, which could favor a higher formation of propylene and/or a selective transformation of propylene to acrylic acid.

2. Experimental

2.1. Catalyst preparation

Mo–V–Sb mixed oxide catalyst has been prepared by a hydrothermal method. The catalyst was prepared using vanadyl sulphate, antimony (III) sulphate, ammonium heptamolybdate and water with a Mo/V/Sb atomic ratio of 1/0.18/0.15. The gel was autoclaved in teflon-lined stainless-steel autoclaves at 448 K for 48 h. The resulting precursor was filtered, washed, dried at 353 K for 16 h and heat-treated at 873 K during 2 h in N\textsubscript{2} stream. It was named MVS sample. K-doped catalysts (with K/Mo atomic ratios of 0.005 and 0.02) have been prepared by “wet” impregnation of the MVS sample with an aqueous solution of potassium nitrate with the corresponding K/Mo atomic ratio. The resulting powders were dried overnight at 373 K and finally heat-treated at 773 K for 1 h in a N\textsubscript{2} stream. The samples were named K-x, in which x is the K/Mo atomic ratio.

From a comparative purpose, the MVS sample was also treated with water in the same way as that described for K-x samples and with a final heat-treatment at 773 K for 1 h in a N\textsubscript{2} stream. This sample was named MVS-m. The characteristics of catalysts are shown in table 1.

2.2. Catalyst characterization

X-ray diffraction patterns (XRD) were collected using a Philips X\textsuperscript{P}ert diffractometer equipped with a...
graphite monochromator, operating at 40 kV and 45 mA and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm). Infrared spectra of the solid catalysts have been recorded with a BioRad instrument using KBr pellets containing a 1 wt% catalyst (total weight of pellet, 120 mg). Infrared spectra of adsorbed $\text{NH}_3$ on catalyst surfaces have been recorded using conventional IR cells connected to a vacuum-dosing system. The catalytic experiments were carried out in a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure [8,9]. The feed consisted of a mixture of propane/oxygen/water/helium with a molar ratio of 4/8/30/58. Experiments were carried out in the 613–693 K temperature interval in order to achieve the highest selectivity to partial oxidation products. Reactants and reaction products were analyzed by on-line gas chromatography using two Hewlett-Packard apparatus equipped with three columns: (i) 23% SP-1700 Chromosorb PAW (30 m × 1/8 in) to separate hydrocarbons and $\text{CO}_2$; (ii) Carbosieve-S (8 m × 1/8 in) to separate $\text{O}_2$ and $\text{CO}$; (iii) Porapak Q (3.0 m × 1/8 in) to separate oxygenated products. Blank runs showed that under the experimental conditions used in this work, the homogeneous reaction could be neglected.

### 2.3. Catalytic tests

The catalytic experiments were carried out in a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure [8,9]. The feed consisted of a mixture of propane/oxygen/water/helium with a molar ratio of 4/8/30/58. Experiments were carried out in the 613–693 K temperature interval in order to achieve the highest selectivity to partial oxidation products. Reactants and reaction products were analyzed by on-line gas chromatography using two Hewlett-Packard apparatus equipped with three columns: (i) 23% SP-1700 Chromosorb PAW (30 m × 1/8 in) to separate hydrocarbons and $\text{CO}_2$; (ii) Carbosieve-S (8 m × 1/8 in) to separate $\text{O}_2$ and $\text{CO}$; (iii) Porapak Q (3.0 m × 1/8 in) to separate oxygenated products. Blank runs showed that under the experimental conditions used in this work, the homogeneous reaction could be neglected.

### 3. Results and discussion

The propane oxidation results at 653 K are shown in table 1. Partial oxidation products, i.e., propylene, acrylic acid, acrolein, acetone and acetic acid and carbon oxides, have been observed. The MVS sample presents a very low selectivity to acrylic acid but an important selectivity to acetic acid. A relatively higher selectivity to acids (acrylic and acetic acids) was obtained over the MVS-m without apparent changes in the propane conversion. These results are similar to those reported by Ueda et al. [7], in which the selectivity to acrylic acid was increased from 6 to 20% by grinding the samples before the calcination step.

The catalytic behavior is completely modified after the incorporation of potassium on the surface of the catalyst. The incorporation of small amounts of potassium (K/Mo atomic ratio of 0.005) notably increases the selectivity to acrylic acid, decreasing the selectivity to both acetic acid and carbon oxides. Although the propane conversion decreases when the K-content increases, the sum of organic acids initially increases with the K-content (figure 1). Thus, and at the same reaction conditions, the yield of acrylic acid obtained on K-doped catalysts is higher than that of undoped Mo–V–Sb samples (figure 1). We must inform that the yield of acrylic acid obtained here is also higher than those previously reported in literature on Mo–V–Sb–O [7] or on Mo–V–Sb–Nb–O [4–6] catalysts.

Higher amount of potassium has a negative effect on the propane conversion, indicating a probable interaction between the active sites for propane oxidation and the potassium ions.

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>K/Mo atomic ratio</th>
<th>$S_{\text{BET}}$ (m$^2$/g$^{-1}$)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)$^b$</th>
<th>AA</th>
<th>$\text{C}_3\text{H}_6$</th>
<th>ACRO</th>
<th>ACET</th>
<th>AcOH</th>
<th>CO</th>
<th>$\text{CO}_2$</th>
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<tr>
<td>MVS</td>
<td>0</td>
<td>8.4</td>
<td>18.1$^a$</td>
<td>8.6</td>
<td>11.3</td>
<td>–</td>
<td>1.9</td>
<td>17.7</td>
<td>22.1</td>
<td>38.4</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>39.7</td>
<td>2.0</td>
<td>3.6</td>
<td>–</td>
<td>1.4</td>
<td>17.7</td>
<td>24.7</td>
<td>50.7</td>
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</tr>
<tr>
<td>MVS-m</td>
<td>0.005</td>
<td>8.2</td>
<td>13.5$^d$</td>
<td>34.4</td>
<td>27.1</td>
<td>0.1</td>
<td>2.1</td>
<td>5.1</td>
<td>11.0</td>
<td>20.3</td>
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<tr>
<td>K–0.02</td>
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<td>8.0</td>
<td>19.7</td>
<td>30.8</td>
<td>9.1</td>
<td>0.1</td>
<td>1.1</td>
<td>11.3</td>
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<td></td>
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<td>33.2</td>
<td>13.0</td>
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<td>1.8</td>
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<td>10.5</td>
<td>14.9</td>
<td>26.4</td>
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</tbody>
</table>

$^a$Reaction conditions: $\text{C}_3\text{H}_8/O_2/H_2O/\text{He}$ molar ratio of 4/8/30/58; Contact time, W/F = 500 gcat h$^{-1}$ (moleC$_3$H$_8$)$^{-1}$.

$^b$Chemical analysis was obtained by atomic absorption spectroscopy. In all cases, the heat-treated samples presented a Mo/V/Sb atomic ratio of 1/0.18/0.15.

$^c$Acrylic acid (AA); propylene ($\text{C}_3\text{H}_6$); acrolein (ACRO); acetone (ACET); acetic acid (AcOH), and carbon oxides (CO and $\text{CO}_2$); t = traces.

$^d$Contact time, W/F = 250 gcat h$^{-1}$ (moleC$_3$H$_8$)$^{-1}$.