Selective oxidation of isobutane on V–Mo–O mixed oxide catalysts

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Abstract: Four V–Mo–O mixed metal oxides were prepared, characterized and tested for the selective oxidation of isobutane in the temperature range 350–550 °C, at atmospheric pressure. Isobutane was mainly oxidized to iso-butene and carbon oxides. The systems with low vanadium contents showed low activities but high isobutene selectivities, while the systems with high vanadium contents showed high activities with high carbon oxides selectivities. The effects of temperature, contact time and the molar ratio iso-butane to oxygen on the conversion of isobutane and the selectivity of the oxidation were studied.

Keywords: vanadium molybdenum oxides; iso-butane oxidation; iso-butene.

INTRODUCTION

Selective oxidation of light alkanes is one of the most challenging topics for study because of the difficulty in stopping the oxidation at intermediate stages corresponding to olefin or oxygenates formation.

The development of more active and selective catalysts for the partial oxidation of alkanes has been extensively pursued in both industrial and academic research.1,2

In the literature,3−8 several catalysts with different contents of V2O5 and MoO3 have been studied for the selective oxidation of isobutane in order to determine the catalytically active phases. Thus, different oxide species were reported to be part of the active phase system in these catalysts. Andrushkevich3 revealed MoO3 and V2O4 as the major components of V–Mo–O catalysts and reported that the catalytic activity is related to the content of V4+. Tichy et al.4 identified VMo3O11, whereas Werner et al.5 proposed VMo4O14 as the active phase. Both mixed oxides build layered structures, belonging to shear structures.

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Werner et al.\(^5\) explained that these structures are able to integrate and remove oxygen by a transition from corner-linked octahedra into edge sharing regions.

A key aspect towards the application of this type of catalysts is the exploration of how to control the operating conditions in order to maximize the catalytic performance (temperature, isobutane-to-oxygen molar ratio, hourly space volume velocity). It is commonly accepted that highly specific, local electronic structures of the active metal sites are essential for the catalytic performance.\(^9\) The catalyst composition, as well as the conventional optimization of the microstructure by optimizing the synthesis procedure could result in further improvement of the catalytic performance. Hoang et al.\(^10\) showed that alumina-supported vanadia exhibits low (15\%) selectivity to isobutene. An olefin selectivity of about 50\% was achieved at isobutane conversions of 10–15\% over vanadium-containing MCM-41 mesoporous catalysts.\(^11,12\)

Good results for the oxidative dehydrogenation of isobutane were also obtained with heteropoly compounds\(^13–17\) and pyrophosphates.\(^18,19\)

The aim of this work was to study ways of enhancing the catalytic performance of V–Mo–O mixed oxide catalysts in the isobutane oxidation process, by adjusting the operating conditions and the catalyst composition. Thus, the influence of temperature, space velocity and feed composition on the catalytic performance of four V–Mo–O systems were investigated.

**EXPERIMENTAL**

**Preparation and characterization of the catalysts**

Mo–V–O-based catalysts, with the calculated compositions listed in Table I, were prepared from (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)·4H\(_2\)O (99.8\%) and NH\(_4\)VO\(_3\) precursors using the same method as reported by Ueda et al.\(^20\)

The (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)·4H\(_2\)O (99.8\%) and NH\(_4\)VO\(_3\) precursors were dissolved separately in distilled water and the (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)·4H\(_2\)O solution was added to the NH\(_4\)VO\(_3\) solution. For all the samples, the obtained mixture was heated at 90 °C to evaporate the water and then the remaining solid was dried at 120 °C for 15 h and calcined at 200 °C for 2 h, 400 °C for 2 h and 600 °C for 4 h, to obtain the final catalyst. For all the preparations, the same method and the same calcination temperatures were employed knowing that the preparation method and the calcination temperature influence the phase composition of Mo–V-oxides.\(^21–23\)

The symbols used to denote the prepared catalysts are listed in Table I.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calculated catalyst composition</th>
</tr>
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<tbody>
<tr>
<td>C(_1)</td>
<td>10 % V(_2)O(_5)–90 % MoO(_3)</td>
</tr>
<tr>
<td>C(_2)</td>
<td>30 % V(_2)O(_5)–70 % MoO(_3)</td>
</tr>
<tr>
<td>C(_3)</td>
<td>50 % V(_2)O(_5)–50 % MoO(_3)</td>
</tr>
<tr>
<td>C(_4)</td>
<td>90 % V(_2)O(_5)–10 % MoO(_3)</td>
</tr>
</tbody>
</table>

The surface areas of the catalysts were measured from the adsorption isotherms of N\(_2\) at 77 K using the BET method with an ASAP 2000 sorptometer. The crystal structures of the
samples were controlled by X-ray diffraction using a PW 3710 diffractometer with CuKα radiation for Bragg's angles (2θ) from 4 to 70°.

Catalytic reactions

The selective oxidation of isobutane was carried out in a fixed bed, quartz tube, down-flow reactor operating at atmospheric pressure. The internal diameter of the reactor tube was 20 mm. The catalyst was supported by quartz wool. Normally, 2 cm³ (1.7 g) catalyst was used. The axial temperature profile was measured using a chromel–alumel thermocouple placed in a thermowell centered in the catalyst bed. The reactor temperature was controlled using a chromel–alumel thermocouple attached to the exterior of reactor. Quartz chips were used to fill the dead volumes below and above the catalyst bed to minimize potential gas-phase pyrolysis reactions at higher reaction temperatures. The reaction mixture, consisting of isobutane and air, was passed through the catalyst bed at a volume hourly space velocity (VHSV) of 1000–2500 h⁻¹. The influence of the isobutane to oxygen ratio was studied by varying this ratio in the range 0.5–2.0. The flow rates were controlled by fine needle valves and were measured using capillary flow meters. The catalyst was activated in air at 550 °C for 2 h before the reaction. Each run was carried out over a period of 3 h. In all studies, the reactor effluent passed through a condenser to remove water and liquid oxygenated products. The gas phase reactants and products were analysed as follows: a flame ionization detector and a GC-alumina column for the hydrocarbons and a thermal conductivity detector with a CTR-1 column for air, methane and carbon oxides. The condensate was analyzed with a Thermo Finnigan chromatograph using a DB-5 column and a flame ionization detector. Isobutene, CO, CO₂ were the major products formed under the employed reaction conditions; minor amounts of the liquid oxygenated products, acetic acid, methacrolein and unknowns were detected. The carbon balance was within 95–105 % for all of the reactions.

RESULTS AND DISCUSSION

Catalysts characterization

The XRD patterns of the prepared catalysts are shown in Fig. 1 and the observed phases are listed in Table II.

Examination of the powder diffraction patterns reveals the formation of multi-phase materials. Thus, in the 10 % V₂O₅–MoO₃ catalyst (C₁), three phases were observed, the MoO₃ phase being the predominant one. In the 30 % V₂O₅–MoO₃ catalyst (C₂), four phases were observed, the V₂MoO₈ phase being the predominant one. It should be noted that a V₂O₅ phase was not observed in these catalysts. In the catalyst with 50 % V₂O₅–MoO₃ (C₃), with four phases, the intensities corresponding to the V₂MoO₈ phase decreased and a V₂O₅ phase appeared. In the 90 % V₂O₅–MoO₃ (C₄) catalyst, with only two phases, the intensities of the V₂O₅ were the most dominant, while a MoO₃ phase was not observed.

The specific surface areas of the catalysts, obtained using the BET method, are presented in Table II. It can be observed that surface areas of all four catalysts were low, under 3 m² g⁻¹.

Catalytic properties

The four catalysts were tested in the selective oxidation of isobutane using an isobutane-to-oxygen ratio of 1. The conversion obtained and the distribution
of the products are listed in Table III. From the results shown in Table III, it can be seen that the C1 and C2 catalysts revealed a similar activity for the conversion of isobutane. The same behavior was observed for the C3 and C4 catalysts. The catalysts containing the V2O5 phase, namely C3 and C4, were more active but less selective for isobutene. In these cases, higher quantities of COx were formed.

Fig. 1. X-Ray diffraction patterns of V–Mo mixed oxide catalysts.

TABLE II. The main crystalline phases determined by XRD and the specific surface areas of the V–Mo–O catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SSA / m² g⁻¹</th>
<th>Crystalline phase identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.81</td>
<td>MoO3 V₂MoO₈ VO₂ – –</td>
</tr>
<tr>
<td>C2</td>
<td>1.63</td>
<td>MoO3 V₂MoO₈ VO₂ Mo₆V₉O₄₀</td>
</tr>
<tr>
<td>C3</td>
<td>0.94</td>
<td>MoO3 V₂MoO₈ VO₂ V₂O₅ – –</td>
</tr>
<tr>
<td>C4</td>
<td>2.66</td>
<td>– V₂MoO₈ V₂O₅ – –</td>
</tr>
</tbody>
</table>

The selectivity of conversion to iso-butene for the C1 and C2 catalysts was appreciably higher than that for the C3 and C4 catalysts and the main over oxidation products were CO and CO₂. Oxygenated compounds were detected in a fairly low amount with the C3 and C4 catalysts and only traces at higher temperatures were found with the C2 catalyst. These two different ranges observed for iso-butene selectivity are probably related to the prevalence of two different catalytic sites on the surface. The most selective catalysts (C1 and C2) have isobutene
selectivities that were about five times higher than the less selective one (the C3 catalyst). Finally, it should be noted that cracking products were observed only with the C1 catalyst and only at temperatures as high as 450 °C for space velocity of 2000 h⁻¹, or at temperatures higher than 490 °C with a space velocity of 2500 h⁻¹.

**TABLE III.** Catalytic performance of the V–Mo catalysts in the oxidation of isobutane (molar ratio i-C₄H₁₀:O₂ = 1:1)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>VHSV×10⁻³ h⁻¹</th>
<th>t / °C</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
<th>Ratea mol kg⁻¹ h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>i-C₄H₁₀</td>
<td>i-C₄H₈</td>
<td>Oxogenated compounds</td>
</tr>
<tr>
<td>C₁</td>
<td>2.00</td>
<td>400</td>
<td>2.7</td>
<td>84.7</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>450</td>
<td>5.2b</td>
<td>65.9</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>400</td>
<td>1.7</td>
<td>85.3</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>450</td>
<td>3.2</td>
<td>85.4</td>
<td>–</td>
</tr>
<tr>
<td>C₂</td>
<td>2.00</td>
<td>400</td>
<td>2.6</td>
<td>80.8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>450</td>
<td>3.2</td>
<td>62.9</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>400</td>
<td>2.4</td>
<td>78.4</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>450</td>
<td>2.9</td>
<td>57.0</td>
<td>2.4</td>
</tr>
<tr>
<td>C₃</td>
<td>2.00</td>
<td>400</td>
<td>9.2</td>
<td>18.3</td>
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<tr>
<td></td>
<td>2.00</td>
<td>450</td>
<td>13.9</td>
<td>21.4</td>
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</tr>
<tr>
<td></td>
<td>2.50</td>
<td>400</td>
<td>8.1</td>
<td>14.1</td>
<td>2.3</td>
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<tr>
<td></td>
<td>2.50</td>
<td>450</td>
<td>11.3</td>
<td>16.2</td>
<td>2.1</td>
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<tr>
<td>C₄</td>
<td>2.00</td>
<td>400</td>
<td>7.2</td>
<td>22.2</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>450</td>
<td>9.6</td>
<td>25.4</td>
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</tr>
<tr>
<td></td>
<td>2.50</td>
<td>400</td>
<td>6.8</td>
<td>16.0</td>
<td>4.0</td>
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<tr>
<td></td>
<td>2.50</td>
<td>450</td>
<td>8.5</td>
<td>38.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*aReaction rate of isobutane; bselectivity to cracking products 13.1 %

The conversion of isobutane for the four catalysts as a function of reaction temperature is shown in Fig. 2. The conversion of *iso*-butane increased with increasing reaction temperature for all catalysts. The systems with a higher vanadium content (C₃ and C₄) were more active than the other two, over all the considered temperature range. Moreover, the V₂O₅ phase appeared only in these two catalytic systems and it is considered that this phase is responsible for the enhanced catalytic activity. No correlation was observed between the activity and the specific surface area of these catalysts.

The effect of the reaction temperature on the selectivities for *iso*-butene, COₓ and oxygenated products is shown in Fig. 3. Isobutene selectivity decreased with the temperature on the C₁ and C₂ catalysts, while, interesting, it increased for the C₃ and C₄ catalysts with increasing temperature. The latter phenomenon was also observed by Pless *et al.* ²⁴ in the oxidative dehydrogenation of propane at tempe-
ratures higher than 400 °C and was related to the complete depletion of O₂ from the reactant stream, i.e., when depletion of O₂ in the reactant stream occurs and as the temperature increases, a more efficient utilization of oxygen is realized, leading to an increase in selectivity. In the present case, the oxygen is far from completely depleted (Table III) which means that other factors must also be considered for explaining this phenomenon. The oxidative dehydrogenation of iso-butane to isobutene is more important over the C₁ and C₂ catalysts which contain mainly MoO₃ and V₂MoO₈ phases and do not contain a V₂O₅ phase. The selectivity for COₓ increased with increasing temperature on the C₁ and C₂ catalysts, while for the C₃ and C₄, the COₓ selectivity decreased with increasing temperature. The oxygenate compounds were detected in a fairly low amounts with the C₃ and C₄ catalysts and only traces were evidenced at higher temperature with the C₂ catalyst.

Fig. 2. Variation of the isobutane conversion with the reaction temperature over V–Mo–O catalysts (VHSV = 1500 h⁻¹, molar ratio \( i-C_4H_{10}:O_2 = 1:1 \)); ▲ – C₁; ■ – C₂; ● – C₃; ◆ – C₄.

Fig. 3. Selectivity to: a) isobutene, b) COₓ and c) oxygenated products as function of temperature (VHSV = 1500 h⁻¹, molar ratio \( i-C_4H_{10}:O_2 = 1:1 \)); × – C₁; ▲ – C₂; ■ – C₃; ◆ – C₄.
The variations of isobutane conversion and product selectivities as a function of the \(i\text{-C}_4\text{H}_{10}:\text{O}_2\) molar ratio on the C\(_1\) and C\(_3\) catalysts at 400 °C are shown in Fig. 4. On the C\(_1\) catalyst, the isobutane conversion was only slightly influenced by the \(i\text{-C}_4\text{H}_{10}:\text{O}_2\) molar ratio and the isobutene selectivity passed through a maximum for the molar ratio 1:1. This maximum corresponds to a minimum of CO\(_x\) selectivity. For the C\(_3\) catalyst, the isobutane conversion decreased clearly with the \(i\text{-C}_4\text{H}_{10}:\text{O}_2\) molar ratio and the isobutene selectivity increased reaching a plateau at a ratio of around one. The CO\(_x\) selectivity decreased while the selectivity of oxygenates increased when the \(i\text{-C}_4\text{H}_{10}:\text{O}_2\) molar ratio was increased. These results indicate that, with the C\(_3\) catalyst, as the amount of oxygen was higher, the excess oxygen could oxidize a specific hydrocarbon species (adsorbed on the catalyst surface) to overoxidation products, such as CO and CO\(_2\).

The influence of the contact time on the conversion of isobutane and the isobutene and CO\(_x\) selectivities is shown in Fig. 5 for the C\(_1\) catalyst at 450 °C. The conversion increased with increasing contact time, while the isobutene selectivity decreased. As expected, the operation at shorter contact time decreased the selectivity for overoxidation products and thus increased the selectivity to isobutene.
Finally, the apparent activation energies corresponding to the conversion of isobutane on the different catalysts under the same conditions (VHSV = 1500 h⁻¹; isobutane/oxygen = 1, t = 350–550 °C) were calculated and Arrhenius plots obtained, presented in Fig. 6. The activation energies on the C₁ and C₂ catalysts were 79 and 67 kJ mol⁻¹, respectively. The activation energies on the C₃ and C₄ catalysts were 38 and 50 kJ mol⁻¹, respectively. It can be observed that the activation energies on the catalysts containing a V₂O₅ phase were lower than those measured on the catalysts without a V₂O₅. The lowest apparent activation energy was observed on the C₃ system, which contained both V₂O₅ and MoO₃ phases. All these values are comparable with those presented in the literature for the same reaction over vanadia based catalysts²⁵ and other oxide-based catalysts.²⁶

**CONCLUSIONS**

Four Mo–V–O based catalysts were examined for the selective oxidation of isobutane. A relationship between the phase composition of the catalysts and their oxidation of isobutane activity was evidenced. No correlation was observed between the activity and the specific surface area of these catalysts. The activity of the four studied catalysts increased with increasing content of vanadium. The C₃ and C₄ catalysts, containing a V₂O₅ phase, were more active but less selective, while the C₁ and C₂ catalysts were less active but more selective to iso-butene. On the C₃ and C₄ catalysts, total oxidation products (COₓ) were predominantly obtained.

The oxygenates (acetic acid and methacrolein) were detected in a fairly low amount with the C₃ and C₄ catalysts and for the C₂ catalyst, only at high temperatures.

The conversion of isobutane increased with increasing reaction temperature for all catalysts and the isobutene selectivity decreased with the temperature on the C₁ and C₂ catalysts, while, interesting, for the C₃ and C₄ catalysts, it increased.
with increasing temperature. The \(i\text{-C}_4\text{H}_{10}\)-to-\(O_2\) molar ratio was found to be optimum around a value of one. Operation at shorter contact time decreased the selectivity for the overoxidation products and thus increases the selectivity to isobutene.

The apparent activation energies for the transformation of isobutane were in the range 38–79 kJ mol\(^{-1}\).

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