Production of Acetic Acid by Catalytic Oxidation of Butene*

by Katsumi Kaneko**, Takeo Koyama** and Shozo Wada**

Summary: Catalytic oxidation of 1-butene over a vanadium oxide system for producing acetic acid has been studied. The reaction was carried out in the presence of steam in a temperature range from 200 to 300°C by using one, two or three component oxide/SiO₂ catalyst containing vanadium.

A binary system such as V-Sn, V-W or V-Ti and a ternary system such as V-Sn-W or V-Sn-Ti exhibited high activity for acetic acid formation, while V₂O₅ itself showed low activity. The reaction was promoted by addition of steam, and a higher selectivity was obtained in a lower temperature range. Over a V-Sn-W (1:1:0.5)/SiO₂ catalyst, acetic acid was produced with selectivity of about 50% at 225°C. The main products were acetic acid and carbon oxides which were considered to be formed by different reactions occurring in parallel.

It is concluded that activities of both isomerization and oxidation at lower temperatures are indispensable for the selective formation of acetic acid which seems to be formed from 2-butenes by oxidation at its double bond.

1 Introduction

It has been generally accepted that a number of partial oxidation reactions of olefins over transition metal oxides often proceed through an allylic intermediate formed by hydrogen abstraction at the C-H bond adjacent to the double bond of an olefin. This type of oxidation is referred to as allylic oxidation1). However, oxidation of olefins to saturated aldehydes and acids with a smaller carbon number than that of the starting olefins is also known2),3) and, it has been explained without having investigated in details as resulting from side reactions of allylic oxidation4). Recently, production of acetic acid was proposed by vapor phase oxidation of propylene5),6) or butene7)9), which is considered as belonging to the latter class of oxidation. This direct synthesis of acetic acid is noteworthy from the view point of C₃ and C₄ utilization and as a new promising acetic acid production process10,11). Although most of the patents recommend mixing of vanadium pentoxide with other metal oxides, their claims are vague due to a lack of systematic explanation, and no detailed studies on the reactions have been published until recently.

Thus the authors have performed oxidation of butenes over several oxide catalysts containing vanadium to obtain some detailed information on effective catalysts and reaction conditions for synthesizing acetic acid. The results obtained are reported in this paper12).

2 Experimental

2.1 Preparation of Catalysts

Ammonium metavanadate was dissolved in hot water together with oxalic acid and mixed with commercially available silica sol (Nissan Chem. Co., Snowtex-30), then evaporated at 80°C. The dried residue was powdered in a ball mill, and it was formed into cylindrical pellets (3 mm x 5 mm), followed by calcination in a furnace at 500°C for 8 hrs. Various V₂O₅/SiO₂ catalysts with different V₂O₅ contents were thus prepared. Binary and ternary oxide catalysts supported on silica were also prepared by mixing an aqueous solution of the respective metal salts and the silica sol by the same method described above. As starting reagents, GR grade of (NH₄)₆Mo₇O₂₄·4H₂O, 5(NH₄)O·12WO₃·5H₂O, Al(NO₃)₃·9H₂O, KNO₃, H₃PO₄, Sb₂O₃, SnCl₂·2H₂O and Ti(CH₃)(CH₂)₃O₄, supplied by Koso Chem. Co., were used. As for SnCl₂·2H₂O, Sn(OH)₂ gel obtained by adding an aqueous ammonia solution to a SnCl₂·2H₂O solution was used after it was filtered and washed sufficiently with water. The V₂O₅ content of a catalyst was determined by oxidation-reduction titration using diphenylamine as an indicator, and the surface area of a catalyst was determined by BET method, using nitrogen at -196°C.

2.2 Apparatus, Procedure and Analysis

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Reactions were conducted in a conventional flow system under atmospheric pressure using a stainless steel U type reactor (15 mmØ) immersed in a salt or an oil bath. Experimental runs were carried out at the following flow rate: 20 ml/min of 1-butene, 1,000 ml/min of air and 9.0 g/hr of H2O (molar ratio of 1-butene: H2O: air=1:10:50). 1-Butene was supplied by Takachiho Chem. Ind. Co., and its purity was above 99%. The amount of catalyst charged was 50 ml unless otherwise stated, and the contact time was indicated by the volume of a catalyst (ml) per total flow rate (ml/sec). After introducing a reaction gas for a few hours, the catalytic activity became constant at which the experimental data were obtained. Both gaseous and liquid products were analyzed by means of gas chromatography (propylene carbonate+glutaronitrile column for air, CO2 and butenes; molecular sieve 13X column for N2, O2 and CO; dioctylsebacate+sebacic acid column for liquid products). Total acid was determined by alkali titration and maleic anhydride by the precipitation method13). Conversion and selectivity with respect to a specific product and isomerization of butenes were calculated from the following equations:

\[
\text{Conversion (mol\%) = } 100 \times \left(1 - \frac{\text{moles of } n\text{-butenes in exit gas}}{\text{moles of } 1\text{-butene fed}}\right)
\]

\[
\text{Selectivity to product A (carbon \%) = } 100 \times \frac{\text{moles of product A}}{\text{carbon number of product A}} \times \frac{4}{\text{moles of } n\text{-butenes consumed}}
\]

\[
\text{Isomerization of butenes (mol\%) = } 100 \times \frac{\text{moles of 2-butenes}}{\text{moles of } n\text{-butenes}} \text{ in exit gas.}
\]

In this study, the amount of butene isomers formed is not included in the conversion.

3 Results and Discussion

3.1 V2O5/SiO2 Catalyst

Vanadium pentoxide is thought to be one of the effective catalysts for vapor phase oxidation of hydrocarbons. But this oxide is usually used as a component of a binary or ternary metal oxide, and therefore a satisfactory catalyst for 1-butene oxidation to acetic acid is expected to be a multicomponent catalyst. However, in order to obtain basic information on V2O5 catalysts, authors have investigated the V2O5/SiO2 catalyst system initially.

Effects of reaction temperature were examined in the range of 200~300°C (Fig. 1). Conversion and selectivity to carbon oxides increased with increase in temperature, while a reverse tendency was observed for selectivity to acetic acid and acetaldehyde. A small amount of acrolein, maleic anhydride and butadiene which were allylic oxidation products were also detected. The composition of butene isomers formed attained equilibrium at above 250°C14) that suggested that the rate of butene isomerization was greater than that of oxidation and, therefore, acetic acid and acetaldehyde seemed to have been produced from 2-butenes. Formation of acetic acid and that of acetaldehyde from 2-butenes have already been reported in connection with their oxidation over V oxide16), Mo-Co oxide16) and fused alumina17). Thus, V2O5/SiO2 catalyst presumably is effective for both isomerization and oxidation.

Data for oxidation over V2O5/SiO2 catalysts with varying V2O5 contents are shown in Fig. 2. Conversion was proportional to the specific surface area of the catalysts, and almost no catalytic activity was observed over the catalysts with a V2O5 content of less than 5 wt%. On the other
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Catalyst; V2O5/SiO2, 50ml, Reaction temperature; 250°C, Contact time; 2.5 sec

Fig. 2 Effect of V2O5 Content of V2O5/SiO2 Catalyst on 1-Butene Oxidation

hand, with a catalyst of V2O5 content greater than 5 wt%, the composition after reaction of butene isomers had reached the equilibrium at a reaction temperature of 250°C, and the values of selectivity to acetic acid and acetaldehyde were almost constant regardless of the extent of conversion. These results show that acetic acid can be produced by oxidation of 1-butene at lower reaction temperatures over V2O5/SiO2 catalysts of greater than 20 wt% V2O5 content. However, since selectivity to acetic acid was not necessarily satisfactory, and the oxidation activity of V2O5/SiO2 was relatively low, the authors investigated a series of binary oxide catalysts containing V2O5.

3.2 Binary Oxide Catalyst

Oxidation of 1-butene was conducted at 250°C over several binary oxides supported on SiO2 (symbolized as V-X/SiO2, X=P, Mo, W, Sn, Sb, Ti, Al or K). The results obtained are shown in Table 1. A remarkable decrease in the activity was observed with a catalyst containing P, Mo or K. The decrease seems to be attributable to a decrease in the specific surface area of the catalyst and chemical retardation of the oxidation activity of V2O5 as reported in the case of P addition18),19). Addition of Ti increased the activity, and the conversion per surface area was the greatest among the catalysts tested. However, a steady state of activity was not obtained over the V-Ti(1:1)/SiO2 oxide catalyst because of the temperature control difficulty. Almost no oxidation was observed over TiO2/SiO2 (wt ratio 1/1) catalyst under the same reaction conditions. Conversion over V2O5/SiO2 catalyst (34.8 wt% of V2O5) was lower than that over V-Ti(1:0.5)/SiO2 catalyst although the V2O5 content in both catalysts was almost the same. These facts suggested that new active species were formed by interaction of V and Ti.

Over the binary oxide catalysts containing W, Sn, Sb and Al, a steady state of activity was obtained, and high activity and selectivity to acetic acid were observed over V-Sn(1:1)/SiO2 catalyst. The increase in the oxidation activity of V2O5 by addition of SnO2 was previously reported by many worker concerned with oxidation of CO19), benzene20), naphthalene21) and benzaldehyde22). The activity increase was considered to be effective for butene oxidation to acetic acid, because the increase in the oxidation activity caused the reaction at a lower temperature which resulted in a higher selectivity to acetic acid.

Effects of atomic ratio of Sn/V were then investigated (Fig. 3). While the specific surface area was independent of an atomic ratio, con-

Table 1 Effect of X Component of V-X(1-x)/SiO2 Catalyst in the 1-Butene Oxidation

<table>
<thead>
<tr>
<th>X</th>
<th>x</th>
<th>V2O5 (wt%)</th>
<th>Specific Surface Area (m²/g)</th>
<th>Weight (g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Isomerization (%)</th>
<th>( \times 10^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO4+CO</td>
<td>AcH</td>
<td>AcOH</td>
<td>TAO</td>
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<td>-----</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>20.1</td>
<td>52.1</td>
<td>29</td>
<td>42.1</td>
<td>41.6</td>
<td>12.0</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>46.3</td>
<td>8.6</td>
<td>36</td>
<td>9.6</td>
<td>12.4</td>
<td>8.2</td>
<td>14.6</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>27.9</td>
<td>15.5</td>
<td>34</td>
<td>6.4</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>P</td>
<td>1.0</td>
<td>19.4</td>
<td>45.8</td>
<td>35</td>
<td>24.8</td>
<td>16.6</td>
<td>9.9</td>
<td>30.2</td>
</tr>
<tr>
<td>Mo</td>
<td>1.0</td>
<td>16.5</td>
<td>58.0</td>
<td>43</td>
<td>60.0</td>
<td>37.0</td>
<td>9.1</td>
<td>23.7</td>
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<td>W</td>
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<td>18.9</td>
<td>43.0</td>
<td>40</td>
<td>36.9</td>
<td>35.7</td>
<td>5.3</td>
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<td>Sn</td>
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<td>63.2</td>
<td>31</td>
<td>43.2</td>
<td>42.9</td>
<td>2.8</td>
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<td>Ti</td>
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<td>32.0</td>
<td>56.6</td>
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<td>30.9</td>
<td>26.7</td>
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<td>31.4</td>
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<tr>
<td>Al</td>
<td>1.0</td>
<td>47.0</td>
<td>10.2</td>
<td>35</td>
<td>1.6</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

a) Temperature: 250°C, Catalyst: 50 ml, Contact time: 2.5 sec.
b) Acetaldehyde, c) Acetic acid, d) Total acid, e) Conversion/surface area.

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Table 2 Effect of X Component of V-Sn-X(1 : 1 : x)/SiO₂ Catalyst in the 1-Butene Oxidation

<table>
<thead>
<tr>
<th>X</th>
<th>VₓOₓ (wt%)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Isomerization (%)</th>
<th>γ × 10⁴ (％/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Specific Surface Area (m²/g)</td>
<td>CO₂ + CO</td>
<td>AcH</td>
<td>AcOH</td>
</tr>
<tr>
<td>P</td>
<td>0.1</td>
<td>18.3</td>
<td>43.0</td>
<td>56.9</td>
<td>33.7</td>
</tr>
<tr>
<td>P</td>
<td>0.5</td>
<td>18.3</td>
<td>43.0</td>
<td>56.9</td>
<td>33.7</td>
</tr>
<tr>
<td>Mo</td>
<td>0.5</td>
<td>14.5</td>
<td>44.2</td>
<td>56.0</td>
<td>32.5</td>
</tr>
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<td>W</td>
<td>0.5</td>
<td>12.7</td>
<td>67.2</td>
<td>61.1</td>
<td>32.5</td>
</tr>
<tr>
<td>Sb</td>
<td>0.5</td>
<td>14.4</td>
<td>105</td>
<td>52.5</td>
<td>45.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.5</td>
<td>16.4</td>
<td>42.9</td>
<td>55.9</td>
<td>44.4</td>
</tr>
<tr>
<td>Al</td>
<td>0.5</td>
<td>17.1</td>
<td>36.7</td>
<td>54.6</td>
<td>44.9</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>18.3</td>
<td>72.2</td>
<td>18.4</td>
<td>40.8</td>
</tr>
</tbody>
</table>

a) Temperature: 250°C, Catalyst: 50 ml (38~41 g), Contact time: 2.5 sec.
b) Maleic anhydride.

conversion and selectivity to acetic acid became maximum at Sn/V=1. The formation of carbon oxides was promoted by the increase in atomic ratio of Sn/V.

3.3 Ternary Oxide Catalyst

Effects of adding P, Mo, W, Sb, Ti, Al or K as a third component to V-Sn(1 : 1)/SiO₂ catalyst were further examined (Table 2). The activity of a catalyst containing P or K was low in spite of its large specific surface area, indicating the chemical retardation effects of P and K. Addition of P or Mo promoted the formation of maleic anhydride, while a reverse tendency was observed with a catalyst containing W, Sb or Ti, and in this case acetic acid was obtained with about 40% selectivity. However, over a catalyst containing Sb, Ti, Al or K, isomerization was less than 70%, and the formation of carbon oxides was prominent. Only with V-Sn-W/SiO₂ catalysts, relatively high values of conversion, isomerization and selectivity to acetic acid were obtained. Since both oxidation and isomerization activities seemed to be indispensable for the selective formation of acetic acid, further studies were made with V-Sn-W/SiO₂ catalysts in detail.

3.4 V-Sn-W/SiO₂ Catalysts

3.4.1 Effects of W Content

The results of oxidation over V-Sn-W(1 : 1 : x)/SiO₂ catalysts (x=0~1.5, 50 wt% of SiO₂) are presented in Fig. 4. In spite of the different contents of W, these ternary oxide catalysts have almost the same specific surface area which is about 1.5 times that of V-Sn(1 : 1)/SiO₂ catalyst, while a maximum conversion was shown at an atomic ratio of W/V=1. As for the product distribution, acetic acid and carbon oxides increased and acetaldehyde decreased by addition.
of W. In the oxidation over the catalyst of W/V=1.5, both activity and selectivity to acetic acid decreased due to a lower content of V₂O₅.

In another experiment, only slight oxidation and isomerization activities were observed over Sn-W(1:1)/SiO₂ (50 wt% of SiO₂) catalyst containing no V₂O₅.

Thus, the addition of W to V-Sn(1:1)/SiO₂ catalyst increased its surface area, which reflected in increasing the oxidation activity and in promoting a conversion of acetaldehyde to acetic acid.

### 3.4.2 Effects of Catalyst Supports

Effects of silica contents in the catalysts were investigated under a constant atomic ratio of V/Sn/W=1/1/0.5 (Table 3). The specific surface area increased with increase in SiO₂ content, and a reverse tendency was observed in bulk density. The catalyst having 33.7 wt% of SiO₂ showed a maximum activity per volume of the catalyst, whereas the maximum activity per surface area was shown with a catalyst containing 23.2 wt% of SiO₂. Selectivity to acetic acid was about 45%, independent of conversion and silica content. This fact may be explained by considering that the silica contributes to effective dispersion of metal oxides.

Thus, various kinds of supports were also examined (Table 3). The direct dependency of the specific surface area on the activity was not observed, and the highest yield for acetic acid was obtained over a catalyst prepared with silica sol. A catalyst prepared with silica gel, having a large specific surface area, showed a relatively high conversion of butenes, but low selectivity for acetic acid formation. Other catalysts prepared with alumina or silica-alumina exhibited lower oxidation activity and selectivity to acetic acid than those prepared with silica.

### 3.4.3 Effects of Reaction Conditions

1) Addition of Steam

Effects of addition of steam on oxidation over V-Sn-W(1 : 1 : 0.5)/SiO₂ catalyst (prepared with silica sol) are shown in Fig. 5. Conversion increased with the increase in steam up to a molar ratio of steam/1-butene=10 and it was almost constant in the range of the ratio greater than 10. The product distribution was remarkably dependent on the amount of steam added, and the selectivity to acetic acid increased from 23.8% (without steam) to 51.0% (steam/1-butene=10). The formation of acetaldehyde also increased by addition of steam, whereas the selectivity to MEK showed a constant value of 0.5%. On the other hand, the formation of

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**Table 3 Effect of Supports of V-Sn-W(1 : 1 : 0.5) Catalyst in the 1-Butene Oxidation**

<table>
<thead>
<tr>
<th>Support Kind</th>
<th>V₂O₅ (wt%)</th>
<th>SiO₂ (wt%)</th>
<th>Specific Surface Area (m²/g)</th>
<th>Weight (g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Isomerization (%)</th>
<th>γX10² (%/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ sol</td>
<td>20.2</td>
<td>25.5</td>
<td>20.0</td>
<td>69</td>
<td>61.3</td>
<td>30.3</td>
<td>33.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Al₂O₃ sol</td>
<td>67.0</td>
<td>4.8</td>
<td>96.7</td>
<td>35</td>
<td>13.2</td>
<td>29.4</td>
<td>3.3</td>
<td>48.7</td>
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<tr>
<td>SiO₂-Al₂O₃</td>
<td>33.7</td>
<td>16.9</td>
<td>24.1</td>
<td>56</td>
<td>49.3</td>
<td>36.0</td>
<td>1.6</td>
<td>30.8</td>
</tr>
<tr>
<td>SiO₂ gel</td>
<td>33.7</td>
<td>16.9</td>
<td>61.3</td>
<td>52</td>
<td>45.5</td>
<td>33.5</td>
<td>1.7</td>
<td>35.6</td>
</tr>
<tr>
<td>SiO₂ gel</td>
<td>33.7</td>
<td>16.9</td>
<td>76.3</td>
<td>53</td>
<td>58.0</td>
<td>43.0</td>
<td>1.2</td>
<td>34.1</td>
</tr>
</tbody>
</table>

**Note:**

- Temperature: 250°C, Catalyst: 50 ml, Contact time: 2.5 sec.
- **Temperature:** 225°C, **Contact time:** 2.2~2.9 sec
- **Catalyst:** V-Sn-W(1 : 1 : 0.5) SiO₂ (SiO₂/Al₂O₃=80/20, Nikki Chem.) and SiO₂ (Nikki Chem.) were used in place of SiO₂ sol.
- **Alumina sol-200** (Nissan Chem.)

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**Fig. 5 Effect of Steam Addition**

Temperature: 225°C, Contact time: 2.2~2.9 sec

Catalyst: V-Sn-W(1 : 1 : 0.5)/SiO₂ (SiO₂ 33.7 wt %, 50 ml)

Feed: butene : steam : air = 1 : 16 : 50

**: Selectivity to acrolein, : Selectivity to MEK

Other symbols are the same as shown in Fig. 1

Fig. 5 Effect of Steam Addition
acrolein and maleic anhydride, "allylic oxidation products", decreased with addition of steam. These results suggest that steam increases the oxidation activity of the catalyst and retards the allylic oxidation reactions that result in promotion of the formation of acetaldehyde and acetic acid. Isomerization of butenes also increased by addition of steam in the range of steam/1-butene up to 5 and the composition of the isomers approached to an equilibrium value in the range greater than 5 at 250°C.

2) Reaction Temperature and Contact Time

Effects of reaction temperature on oxidation of 1-butene and decomposition of acetic acid over V-Sn-W (1:1:0.5)/SiO₂ catalyst (33.7 wt% of SiO₂) in the range of 200~275°C are shown in Fig. 6. Oxidation of 1-butene gave a tendency almost similar to that over V₂O₅/SiO₂ catalyst as shown in Fig. 6; however, a greater conversion and higher selectivity to acetic acid were obtained at the same reaction temperature.

Decomposition of acetic acid under the same reaction conditions as those in the 1-butene oxidation increased with temperature; but below 250°C, the degree of decomposition was very small in comparison with the formation of acetic acid in the 1-butene oxidation. Therefore, decomposition of the acetic acid produced in the
Table 4 Oxidation of Butene Isomers over V-Sn-W/SiO₂ Catalysta)

<table>
<thead>
<tr>
<th>Butene</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>CO₂+CO (%)</th>
<th>AcH (%)</th>
<th>Acrolein (%)</th>
<th>Acetone (%)</th>
<th>MEK (%)</th>
<th>AcOH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>225</td>
<td>43.4</td>
<td>85.6</td>
<td>1.0</td>
<td>0.2</td>
<td>47.6</td>
<td>0.6</td>
<td>43.2</td>
</tr>
<tr>
<td>23</td>
<td>250</td>
<td>47.4</td>
<td>84.8</td>
<td>1.2</td>
<td>0.2</td>
<td>45.0</td>
<td>0.4</td>
<td>51.8</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>225</td>
<td>40.8</td>
<td>83.0</td>
<td>3.2</td>
<td>0.2</td>
<td>47.5</td>
<td>0.6</td>
<td>49.3</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>250</td>
<td>41.0</td>
<td>84.8</td>
<td>1.2</td>
<td>0.2</td>
<td>17.1</td>
<td>0.6</td>
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<tr>
<td>Isobutene</td>
<td>250</td>
<td>41.0</td>
<td>84.4</td>
<td>1.2</td>
<td>0.2</td>
<td>17.1</td>
<td>0.6</td>
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</tr>
<tr>
<td>n-Butane</td>
<td>250</td>
<td>35.8</td>
<td>83.0</td>
<td>1.2</td>
<td>0.2</td>
<td>17.1</td>
<td>0.6</td>
<td>17.1</td>
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<tr>
<td>Mixed Butenesb)</td>
<td>250</td>
<td>75.1</td>
<td>74.2</td>
<td>1.8</td>
<td>0.2</td>
<td>17.1</td>
<td>0.6</td>
<td>17.1</td>
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</table>

a) Catalyst: V-Sn-W (1 : 1 : 0.5)/SiO₂ (SiO₂ 33.7 wt%), 50 ml, Contact time: 2.5 sec.
b) 1-Butene 53.4, trans-2-Butene 15.8, cis-2-Butene 10.8, n-Butane 16.3, Isobutane 2.7, Isobutene 0.3 and 1, 3-Butadiene 0.7 (vol %).
c) Methacrolein.

The oxidation reaction seems negligible in a temperature range below 250°C.

Effects of contact time were investigated at 200, 225 and 250°C as shown in Figs. 7, 8. The selectivity to acetic acid was dependent only on the reaction temperature, but not on conversion and contact time; and acetic acid was obtained with selectivities 47, 53 and 60% at 250, 225 and 200°C, respectively.

At a fixed reaction temperature of 225°C, the formation of acetaldehyde, maleic anhydride and acrolein decreased with increase in contact time, whereas the selectivity to acetic acid was almost constant regardless of the change in contact time (Fig. 9).

From these results, oxidation of 1-butene seems to consist mainly of two parallel reactions, the formation of acetic acid and that of carbon oxides.

**3.4.4 Oxidation of Butene Isomers**

Table 4 shows the results of oxidation of butene isomers over V-Sn-W/SiO₂ catalyst. In the reactions of 1-butene, trans-2-butenes and cis-2-butenes, nearly similar results were observed both in reactivity and selectivity. Even in the oxidation of n-butene mixtures containing a small quantity of n-butane, similar results were also obtained in spite of the greater conversion due to the lower concentration of n-butene in the reaction gas. n-Butane was not oxidized, showing its inertness under these reaction conditions. Formic acid, propionic acid and maleic anhydride were also detected as substances produced from n-butenes other than those listed.

Isobutene showed a lower reactivity in comparison with n-butenes, and a poorer selectivity to acetic acid was obtained which might be expected from its carbon skeleton. Methacrolein and acetone were detected as substances produced from isobutene. These facts support a hypothesis that acetic acid is produced by oxidation at the double bond of 2-butenes. Moreover, by considering the fact that both 1-butene and 2-butenes showed similar results in conversion and selectivity, acetic acid is produced presumably from the same reaction intermediate.

**Literatures**

9) Kuraray, Japan 47-10,692~5 (1972).