Oxidative Dehydrogenation of Ethane over MoVTeNbO Catalyst Prepared by a Slurry Method

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The oxidative dehydrogenation (ODH) of ethane to ethene has attracted much attention in recent years. López Nieto et al. [1] reported that MoVTeNbO catalysts prepared by hydrothermal synthesis show high activity and selectivity for ODH of ethane, and an ethene yield of 75% was obtained at 400 °C on the best catalysts. In ethane oxidation, the catalytic behavior of MoVTeNbO catalysts can be mainly related to the presence of the multifunctional Te2M2O57 orthorhombic phase in cooperation with the (V, Nb)-containing Mo3O12-type phase [2,3].

In this paper, we report the preparation of the MoVTeNbO catalyst by a slurry method, its characterization and the influence of the calcination atmosphere on the catalytic performance for the ODH of ethane.

The MoVTeNbO catalyst was prepared by a slurry method. Ammonium heptamolybdate, ammonium metavanadate and telluric acid were dissolved upon heating to 80 °C in a flask, and niobium oxalate was dissolved in another flask. The atomic ratio of Mo: V: Te: Nb was 1: 0.3: 0.23: 0.1. The aqueous solution of niobium oxalate was added to the first flask to result in a slurry. The water in this slurry was removed by a rotary evaporator to obtain the precursor solid. After it was dried at 80 °C for 10 h, the precursor solid was calcined at 600 °C for 2 h in a N2 stream (the sample is denoted as SL-N). For comparison, the same precursor solid was calcined at 600 °C for 2 h in air (denoted as SL-A).

The catalytic performance of the MoVTeNbO catalyst for the ODH of ethane was tested in a fixed-bed quartz tubular reactor at atmospheric pressure. The result is shown in Table 1. SL-N showed good catalytic performance for the ODH of ethane to ethene at reaction temperatures above 400 °C, and ethene was formed as the main product. The ethene conversion increased and the selectivity for ethene decreased with increasing temperature. A maximum ethene yield of 80.9% was achieved at 440 °C on SL-N. However, on SL-A almost no activity for the ODH of ethane was detected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t/ °C</th>
<th>X/ %</th>
<th>C2H4</th>
<th>CO</th>
<th>CO2</th>
<th>Y/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>440</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SL-N</td>
<td>400</td>
<td>59.0</td>
<td>95.4</td>
<td>0.8</td>
<td>3.8</td>
<td>56.3</td>
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<tr>
<td></td>
<td>420</td>
<td>75.5</td>
<td>93.6</td>
<td>1.4</td>
<td>5.0</td>
<td>70.7</td>
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<tr>
<td></td>
<td>440</td>
<td>89.6</td>
<td>90.3</td>
<td>1.5</td>
<td>8.2</td>
<td>80.9</td>
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<tr>
<td></td>
<td>460</td>
<td>95.8</td>
<td>83.4</td>
<td>3.9</td>
<td>12.8</td>
<td>79.9</td>
</tr>
<tr>
<td>SL-A</td>
<td>440</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: 500 mg catalyst, total flow rate 10 ml/min, feed composition 30%C2H630%O240%N2.

XRD patterns of the MoVTeNbO catalyst are shown in Fig 1. SL-A was primarily composed of the MoO3 phase but no MoO5 was observed in the pattern of SL-N. SL-N gave peaks at 2θ = 7.7°, 9.0°, 22.1°, 26.2°, 26.8°, 27.3°, 29.2° and 35.4°, which were mainly related to an orthorhombic Te2M2O57 (M = Mo, V and Nb) phase, while peaks

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at 7.7°, 8.7°, 14.0°, 22.1°, 23.3°, 24.9°, 29.7°, 31.5°, 32.4° and 33.5° were attributed to (Mo_{0.93}V_{0.07})_2O_{14} \quad [\text{JCPDS, 31-1437}] \quad \text{and/or} \quad \text{Nb}_{0.99}\text{Mo}_{0.01}\text{O}_{2.80} \quad [\text{JCPDS, 27-1310}] \quad \text{or} \quad \text{Mo}_{5.1}\cdot(\text{V/Nb})_0.9_{14}\text{-like phases. The peaks at 22.1°, 28.2°, 36.2°, 45.2° and 50.0° were assigned to the}\n\text{Te}_{0.33}\text{Mo}_{1.01}(\text{M} = \text{Mo}, \text{V}, \text{and} \text{Nb}) \quad \text{phase}[3, 4].}

![XRD patterns of solid MoVTeNbO catalyst samples](image1)

**Fig 1**: XRD patterns of solid MoVTeNbO catalyst samples

(1) SL-N, (2) SL-A

The difference in the surface morphology of the two samples was revealed by SEM, as shown in Fig. 2. SL-A has plate-like structure with fairly smooth surfaces, while SL-N has a porous surface morphology with some fine structure, which was in good agreement with the surface area measurements. The BET specific surface area of SL-N was 6.92 m²/g, while that of SL-A was only 0.31 m²/g. This result also agreed with the finding by Watanabe et al.[5] that a higher surface area of the catalyst correlated well with a higher catalytic activity.

In conclusion, the MoVTeNbO catalyst prepared by the slurry method and calcined at 600 °C in a N₂ stream exhibits an ethane conversion of 90% and an ethene selectivity of 90% at 440 °C. A highly crystalline MoVTeNbO catalyst may be one of the most effective catalysts for ethene production using low cost ethane.

**References**