Selective Oxidation of \( n \)-Butane over VPO Catalyst Modified by Different Additives

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Abstract: A series of vanadyl pyrophosphate catalyst (VPO) modified by different additives have been prepared with the aim to study the performance for selective conversion of \( n \)-butane to maleic anhydride (MA). The addition of various promoters improved the catalytic performance remarkably on both activity and selectivity. The correlation of activity and selectivity of the catalysts with their structure has been discussed. The increase in BET surface areas and surface redox sites leads to an enhanced activity. However, good selectivity can only be obtained on those surfaces with suitable surface acid sites.

Key words: vanadyl pyrophosphate, catalyst, additives, selective oxidation, maleic anhydride

1. Introduction

The \( n \)-butane to maleic anhydride reaction is a fascinating and complex system. This catalytic system performs a 14-electron oxidation involving the abstraction of 8 hydrogen atoms and insertion of 3 oxygen atoms. The productivity from \( n \)-butane is quite low due to the lower selectivity to maleic anhydride at higher conversions and the low feed concentration (less than 2mol\%) used to avoid combustion of the process streams. Various modified VPO catalysts have been extensively investigated for the oxidation from \( n \)-butane to maleic anhydride (MA). The nature of the active sites of the VPO catalysts for \( n \)-butane oxidation to MA has been widely discussed [1–3]. The studies on the reaction mechanism, kinetic analysis and some other important aspects provide better understanding of \( n \)-butane oxidation on a molecular scale [4–6], and the active and selective phase is identified as \((\text{VO})_2\text{P}_2\text{O}_7\). But an obvious deficiency to be resolved is that research work has failed to identify the factors which would allow the production of industrial VPO catalysts with high selectivity. In this work, a series of promoted VPO catalysts have been synthesized and catalytic reactions have been performed. The aim of this research was to obtain a further understanding of the factors that would affect the catalyst performance.

2. Experimental

2.1. Preparation and characterization of catalysts

VPO catalyst was prepared according to the method described in the literature [7]. The promoted VPO catalysts were obtained with the above preparation procedure, with the addition of Me (Me=Zr, Ce, La, Fe, Co, Cu), the atomic content of the additives was 5\%, \( \text{i.e.} \) Me/V=1/19. The prepared catalysts were activated in a flow of a mixture of 2\%\( n \)-butane and air at 673 K.

The BET surface area was measured by classical continuous flow method, with nitrogen as ad-
sorbent. The number of surface V=O species was determined by using the NO-NH$_3$ rectangular pulse technique (NARP) as given in the literature[8,9]. Most experiments were carried out under the following conditions: catalyst weight =0.02 g; flow rate of carrier gas (He)=150 cm$^3$/min; concentration of NO=4.86×10$^{-8}$mol/cm$^3$; concentration of NH$_3$=9.25×10$^{-7}$mol/cm$^3$; pulse width=60 sec.; reaction temperature=550–580 K. The catalyst was pre-oxidized in flowing O$_2$ at 773 K for 30 min in advance to the introduction of each rectangular pulse of NO-NH$_3$ mixture. On the basis of surface active sites (V=O) measured by NARP, the Turnover Frequency can be calculated according to the following equation.

\[
\text{TOF} = \frac{\text{mole of products}}{\text{mole of active sites}}.
\]

2.2. Catalytic activity and selectivity measurements

The oxidation of n-butane was carried out by using a continuous flow reactor at atmospheric pressure. The catalyst was placed in a pyrex glass tube (10 mm i.d.) and formed a bed ca. 20 mm long with SiO$_2$ (3.5 g) as a diluent. At the center of the catalyst bed, a pyrex glass tube with o.d. 4 mm was installed to house the thermocouple. Reactions were carried out under the following conditions: reaction temperature 573–673 K, total pressure 1 atm (101.3 kPa), space velocity 5660 ml/(g·h). The composition of the feed gas was as follows: n-butane 2.0%, oxygen 18.8% and nitrogen 79.2%. The last was used as the carrier gas and internal standard. The products were analyzed by on-line gas chromatography. The outlet stainless tube from the reactor was kept at 463 K to prevent condensation of products, and led into the sampling valve (3.0 cm$^3$ capacity) mounted in the oven held at 463 K. Products were separated on a gas chromatograph mounted with a 2 m column of porapak QS. He at 50 cm$^3$/min was used as a carrier gas, and sensed by a flame-ionization detector. The exit steam passed an ice-water trap at 273 K to remove condensable products and led into a gas chromatograph with thermal conductivity detector. Oxygen, nitrogen and carbon oxides were measured.

3. Results and discussion

3.1. Effect of various promoters on activity

Figure 1 demonstrates that the reaction rate of n-butane increases with the reaction temperature. As shown in Figure 1, the activities of all promoted VPO catalysts have been improved significantly by the impregnation of a third component that is the various promoter. However, different promoters improve the activities in different degrees. The promoting effects of various promoters are in the order: Zr>Ce>La≈Fe>Co≈Cu>VPO.

3.2. Effect of various promoters for selectivity

Similar to the activity, the selectivity of various promoted VPO catalysts on n-butane oxidation to maleic anhydride has also improved significantly by the incorporation of a promoter, as indicated in Figure 2. The promoting effects on selectivity are in a different order: Co>Ce>Cu>Fe>La>Zr>VPO.
Generally, the selectivity decreases slowly with the increase of reaction temperature, as shown in Figure 2. In most cases, the selectivity decreases slowly with the increase in conversion. However, the selectivity decreases markedly with increasing conversion on some catalysts. Their low-conversion selectivity is quite high, but the high-conversion selectivity is not desirable.

The catalytic performances of all promoted VPO catalysts have been improved significantly as demonstrated by the results of n-butane oxidation. It is quite easy to see the increase in activity, that is the increase in reaction rate of n-butane. According to the Table 1, the BET surface area of all promoted VPO catalysts has increased remarkably. So, the increase in activity of all promoted VPO catalysts is the result of the increase of the BET surface area.

Table 1. Surface areas of various promoted catalysts

<table>
<thead>
<tr>
<th>Promoter</th>
<th>$A_{BET}$(m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>19.6</td>
</tr>
<tr>
<td>Zr</td>
<td>50.8</td>
</tr>
<tr>
<td>Ce</td>
<td>33.6</td>
</tr>
<tr>
<td>La</td>
<td>37.6</td>
</tr>
<tr>
<td>Fe</td>
<td>45.1</td>
</tr>
<tr>
<td>Co</td>
<td>42.6</td>
</tr>
<tr>
<td>Cu</td>
<td>36.3</td>
</tr>
</tbody>
</table>

The selectivity of promoted catalysts has been found to be improved. The promoting effects on selectivity are different from those on activity, since the highest active catalyst did not have the highest selectivity.

3.3. Effect of various promoters for Turnover Frequency

On the basis of surface active sites (V=O) measured by NARP, the Turnover Frequency can be calculated. These results are shown in Figure 3. Turnover Frequency on maleic anhydride (TOF$_{MA}$) of various promoted catalysts is different from type to type. The TOF$_{MA}$ of all promoted catalysts is higher than that of VPO. The situation for Turnover Frequency on the product of deep oxidation (CO$_x$) (TOF$_{CO_x}$) is quite different. In most cases, the promoted catalysts nearly have the same value of TOF$_{CO_x}$ as on VPO catalyst at various reaction temperatures. However, the Zr and Fe promoted VPO catalysts have higher TOF$_{CO_x}$ values, as shown in Figure 4.

![Figure 3. Effect of additives on MA Turnover Frequency at various temperatures](image1)

![Figure 4. Effect of additives on CO$_x$ Turnover Frequency at various temperatures](image2)

From the results, we found the Turnover Frequency (TOF) of maleic anhydride was improved by various promoters in different degrees, and in some cases the TOF$_{MA}$ values were very high while in some cases are not so high.

Comparing Figure 3 and Figure 4, Zr and Fe promoted catalysts have higher TOF$_{MA}$ and TOF$_{CO_x}$ values, they have higher activity but lower selectivity. Co and Ce promoted catalysts have higher TOF$_{MA}$, but their TOF$_{CO_x}$ values are nearly the same as VPO. Those catalysts have higher activity and higher selectivity. In conclusion, the addition of promoters increased the Turnover Frequency of maleic anhydride but not that of Turnover Frequency of CO$_x$, and the selectivity of the catalysts was improved significantly.
4. Conclusions

From the results and discussion above, we can conclude as follows: (1) The catalytic performances of all promoted VPO catalysts were improved significantly, and the promoting effect on activity is the result of the increase in BET surface areas. (2) The addition of promoters increased the Turnover Frequency of maleic anhydride but not that of Turnover Frequency of CO\textsubscript{2}, and the selectivity of the catalysts was improved significantly.

References