Effect of Temperature on the Deactivation of a Pd-Fe/α-Al₂O₃ Catalyst for CO Coupling to Diethyl Oxalate

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Abstract: Destructive tests of the catalyst was carried out to study the effect of temperature on the catalytic activity of CO coupling to diethyl oxalate (DEO) over a Pd-Fe/Al₂O₃ catalyst. It was found that a temperature jump could cause the deactivation of the Pd-Fe/α-Al₂O₃ catalyst. The catalyst deactivated at different temperatures has different characteristics. After deactivation the crystal structure of α-Al₂O₃ did not change, but the Pd particle size was enlarged. Most of the Pd⁰ were oxidized to Pd²⁺, and Fe²⁺ was oxidized to Fe³⁺ on the surface of the deactivated catalyst. The catalyst could be regenerated, but its original activity could not be recovered completely.

Key words: accelerating deactivation test, diethyl oxalate, palladium, carbon monoxide

1. Introduction

Oxalate and oxalic acid are important chemical products which are widely used in industry. However, traditional processes for the production of oxalate and oxalic acid are facing serious problems of pollution, high cost and high energy consumption. A new method for the synthesis of diethyl oxalate from CO and ethanol has attracted more and more attention [1–6]. In fact, the main reactions can be described as follows:

1. The coupling reaction of CO with RONO

2CO + 2RONO → 2NO + (COOR)₂

2. The regeneration reaction of RONO

2ROH + 1/2O₂ + 2NO → 2RONO + H₂O

3. The total reaction is

2CO + 2ROH + 1/2O₂ → (COOR)₂ + H₂O

In previous studies Pd-Fe/α-Al₂O₃ has been found to be the best catalyst for the CO coupling reaction, and suitable reaction conditions have been proposed [4-9]. The catalyst has performed well in a continuous 1000 hours’ scale-up test. To scale-up this process to industrial production, it is necessary to study the deactivation of the catalyst caused by temperature and other factors. The effects of certain impurities such as H₂, NH₃ and O₂ on deactivation of the catalyst have been studied [7-9]. In this paper, the effects of high temperature on the catalytic performance have been studied in accelerating deactivation tests. Temperature jump occurred when the reaction temperature was too high, and the catalyst would lose its activity. The deactivated catalysts were characterized by XRD, XPS and other methods.

2. Experimental

2.1. CO coupling reaction and accelerating deactivation test

The catalyst was prepared as described in reference [5]. The CO coupling reaction was carried out in a fixed bed quartz reactor (i.d. 20×200 mm). The tube was electrically heated, and the temperature was
controlled by an XCT191 temperature controller with a ZK50 voltage adjuster. A thin wall-sheathed K-type thermocouple was placed in the middle of the catalyst bed. The reaction gas mixture of CO/C$_2$H$_5$ONO/N$_2$ with a mole ratio of 1:1:3 was fed from the top of the reactor to the 3 ml catalyst bed at a flow rate of 100 ml/min. The inlet and outlet gases were analyzed by a SP-2305 gas chromatograph, and the liquid products were analyzed by a GC-3700 gas chromatograph.

The accelerating deactivation tests on the catalyst were carried out in the same reaction system. When the coupling reaction became stable at 393 K for 3 h, the temperature was increased manually to a higher level, and then temperature jump occurred in the reactor. The reaction temperature after the temperature jump was kept for 1 h, and the test for the degree of catalyst deactivation was conducted. The processes were carried out three times and the temperatures after the temperature jumps reached to about 673 K (#1 catalyst), 873 K (#2 catalyst) and 1073 K (#3 catalyst) respectively. The regeneration of the deactivated catalysts was conducted by a H$_2$ reduction.

2.2. Characterization of catalysts

CHEMBET-3000 was used to measure the specific surface area of the catalysts at partial pressures of N$_2$ of 0.1, 0.2 and 0.3 in a N$_2$ and He mixture. Before each measurement, the sample was degassed at 473 K for 1 h. The XRD data were acquired by using a D/Max-2500 X-ray instrument, with graphite monochromatized Cu K$_\alpha$ as the radiation source, and operated at 100 mA and 40 kV. Powder diffractions of the samples were recorded over a range of 2θ from 20° to 80° at a step size 0.04. Palladium particle size was estimated using the Scherrer's equation:

$$D_{hkl}=\frac{0.89\lambda}{B\cos(\theta_B)}$$

$D_{hkl}$ was the diameter of the Pd particle, $\lambda$ was the wave length and $B$ the half peak width at $2\theta=\theta_B$.

XPS measurements were performed on a multi-pass analyzer (PHI 5600) with Mg K$_\alpha$ (1253.6 eV) as the X-ray source. The catalysts were fixed on a sample holder and evacuated to $2\times10^{-7}$ Pa before the measurement.

3. Results and discussion

3.1. Performance of the catalysts

The space-time yield of DEO of the fresh catalyst, the deactivated catalysts and the regenerated catalyst are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1. The activities of fresh, deactivated and regenerated catalysts</th>
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<tbody>
<tr>
<td>Catalyst</td>
</tr>
<tr>
<td>373 K</td>
</tr>
<tr>
<td>Fresh catalyst</td>
</tr>
<tr>
<td>#1 regenerated catalyst</td>
</tr>
<tr>
<td>#2 regenerated catalyst</td>
</tr>
<tr>
<td>#3 regenerated catalyst</td>
</tr>
<tr>
<td>#2 deactivated catalyst</td>
</tr>
</tbody>
</table>

Since the #1 and #3 deactivated catalysts have lost their activities completely, so that their performances are not presented in Table 1. The activity of the fresh catalyst, the #2 deactivated catalysts and the regenerated catalysts at different temperatures are determined, as shown in Table 1. The #2 deactivated catalyst remained slightly active. After the regeneration, the activity of the #2 catalyst could be recovered to the original level at both reaction temperatures of 393 K and 403 K. As for the #1 and #3 catalysts, only partial activities were recovered. At a lower reaction temperature the activities of all catalysts could not be recovered to those of the fresh catalyst after the regeneration, which shows that the activation of the catalyst in lower reaction temperatures is difficult. The reason why the three deactivated catalysts had different performance is given below. The deactivation test of the #1 catalyst was carried out at 673 K, and the reactions were quite complex at this temperature. During the reaction, the active sites on the catalyst could be covered with the formed organic products, so that the catalyst lost its activity completely. During the regeneration process, not only the organic products but also some Pd particles might
have been removed so that the regenerated catalyst regained a part of its original activity.

At 873 K, the C$_2$H$_5$ONO in the gas reactants will decompose completely before it reaches the catalyst surface, rendering less C$_2$H$_5$ONO available for the CO coupling reaction, and thus results in a decrease in the DEO formation. When the temperature is raised to 1073 K, more carbon is generated by the decomposition of CO and C$_2$H$_5$ONO. At the same time catalyst sintering occurs at this temperature, which results in the deactivation of the catalyst as well as make it difficult to regenerate the deactivated catalyst.

### 3.2. Changes in the catalyst surface

Specific surface areas of the catalysts are shown in Table 2. All deactivated catalysts have smaller specific surface area than that of the fresh catalyst. Comparatively the #1 deactivated catalyst has the least specific surface. This is because organic compounds with higher boiling points have covered the catalyst surface, which results in the decrease of the specific surface area. When the catalyst is covered with the formed organics, it will lose activity completely. After regeneration, the organics were removed and the specific surface area was recovered to its original value. The #2 deactivated and regenerated catalyst has little change in specific surface area. The specific surface area of the #3 deactivated catalyst has decreased to 4.20 m$^2$/g, and could not be recovered after regeneration.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>7.643</td>
<td>7.8</td>
</tr>
<tr>
<td>Deactivated catalyst</td>
<td>3.26</td>
<td>13.6</td>
</tr>
<tr>
<td>Regenerated catalyst</td>
<td>9.78</td>
<td>6.4</td>
</tr>
</tbody>
</table>

### 3.3. XRD studies

The XRD patterns of the fresh catalyst and all of the deactivated catalysts are shown in Figure 1. Because the metal loading on the catalysts is quite low, the main features of the XRD patterns are related to the $\alpha$-$\text{Al}_2\text{O}_3$. All the features of the $\alpha$-$\text{Al}_2\text{O}_3$ did not change, which shows that the crystal structure of the $\alpha$-$\text{Al}_2\text{O}_3$ remained stable in the accelerating deactivation tests. The peak at $2\theta=40.12$ is assigned to Pd. The Pd particle sizes are estimated from the data and are shown in Table 2. The result shows that the Pd particle sizes of the deactivated catalysts become bigger. After regeneration, the particle size had recovered to its original value. Previous studies have proved that the element Fe on the catalyst exists as Fe$^{2+}$ [10]. However, no peak corresponding to Fe or iron oxide exists in the XRD patterns for the fresh catalyst and the #1 deactivated catalyst, since Fe is highly dispersed on the catalysts. The signal of Fe$_2$O$_3$ (peaks at $2\theta=33.2$) appears in the XRD patterns of the #2 and #3 deactivated catalysts. The reason is that Fe$^{2+}$ was oxidized into Fe$^{3+}$, which transformed into Fe$_2$O$_3$ particles at a higher temperature. Fe$^{2+}$ ions can easily contribute electrons as a donor, and it appears to affect the valence state regulation of the active species [2]. The oxidization of Fe$^{2+}$ would affect the activities of the catalysts.

### 3.4. XPS results

The XPS spectra for Pd of the fresh catalyst and the deactivated catalyst are presented in Figure 2.
The 3d$_{5/2}$ signal peak at 335.1 eV is attributed to Pd$^0$, and the 3d$_{5/2}$ peak at 337.9 eV corresponds to Pd$^{2+}$ [11]. It can be seen that the Pd on the fresh catalyst mainly exists in the form of Pd$^0$. After the accelerating deactivation test, most of the Pd$^0$ on the deactivated catalyst is oxidized to Pd$^{2+}$. In the CO coupling reaction the oxidation of Pd to Pd$^{2+}$ is an intermediate step for the formation of DEO, and our previous work illustrated that Pd was partially oxidized during the reaction [2].

Therefore, the oxidation of Pd$^0$ to Pd$^{2+}$ is believed to be responsible for the deactivation of the catalyst. The peaks corresponding to PdO could not be found in the XRD patterns of the deactivated catalysts. It implies that the oxidation of Pd only takes place on the surface of the Pd particles.

4. Conclusions

Temperature jump will cause the deactivation of the Pd-Fe/$\alpha$-Al$_2$O$_3$ catalyst. The catalysts deactivated at different temperatures have different characteristics. After the deactivation, the crystal structure of $\alpha$-Al$_2$O$_3$ did not change, but the Pd particle size was enlarged. Most of the Pd$^0$ among the Pd particles were oxidized to Pd$^{2+}$, and Fe$^{2+}$ was oxidized to Fe$^{3+}$ on the surface of the deactivated catalyst. For the #1 and #3 catalysts, they could be regenerated partially, while for the #2 catalyst, completely regeneration could be achieved.

References