Mechanistic study of NO\textsubscript{x} storage and reduction behavior over Pt/alkali metal nitrate nanocomposite catalysts supported on TiO\textsubscript{2}

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Introduction

Since the pioneering work of NO\textsubscript{x} storage-reduction (NSR) catalysts by Toyota’s research group, many studies have been reported on the mechanism of NSR reaction over Pt-BaO/Al\textsubscript{2}O\textsubscript{3} catalysts. The generally accepted mechanism on this reaction is “NO\textsubscript{x} transfer from Pt to BaO forming Ba(NO\textsubscript{3})\textsubscript{2} surface layers. Recently, we have found that K-titanate-nanobelt (KTN: K\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}) supported Pt/KNO\textsubscript{x} NSR catalyst exhibited high NO\textsubscript{x} storage capacity and excellent redox behavior, and proposed a novel “K- transfer mechanism” from and back to K rich titanate surface layers\textsuperscript{[1]}. In the present study, we have employed different crystalline structure TiO\textsubscript{2}’s (P-25, ST-01, MT-150A) with various loading amounts of Pt (0.5-5 wt%) and KNO\textsubscript{x}(10-41 wt%) to study the activity and selectivity controlling factors for NSR process.

Materials and Methods

The K-titanate nanobelt (K\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} : KTN) was prepared by hydrothermal treatment, using TiO\textsubscript{2} (P-25) and KOH. Various amounts (x = 0, 20, 26, 33, 41 wt%) of KNO\textsubscript{x} and 1.5 wt% Pt were supported on KTN, ST-01 (Anatase:270nm\textsuperscript{1}), MT150A(Rutile;100nm\textsuperscript{2}) and P-25(A/R=0.8, 50nm\textsuperscript{3}) supports by a conventional impregnation method. After reduction of a catalyst (0.2g) at 350°C, a NO\textsubscript{x} storage process (lean; 80ml/min of 930ppm NO/7%O\textsubscript{2}/He) was performed on a gas flow system and the output gas was analyzed by mass spectroscopy, followed by a rich process of 80ml/min of 4%H\textsubscript{2}/He flow. The lean-rich cycle experiments were carried out using an interval of 6 min of NO\textsubscript{x} (930ppm) and 4 min of H\textsubscript{2} (4%) with 80ml/min flow (catalyst: 0.1g).

Results and Discussion

Fig.1 shows the dependence of the NO\textsubscript{x} storage capacity upon the added amount of KNO\textsubscript{x} on various supported catalysts. In the case of KTN and ST-01 catalysts, the highest storage capacity of 2.3-2.4 mmol/g was achieved when 33 wt%KNO\textsubscript{x} was loaded. In the case of KTN catalysts, TEM images showed that the nanobelt structure was completely maintained even after the redox cycle, when the amount of modified KNO\textsubscript{x} was lower than 26 wt%. P-25 and MT-150A supported catalysts exhibited similar dependency although the maximum stored amounts were less than former ones. From these results we can conclude that NO\textsubscript{x} storage capacity is mainly determined by the loaded amount of KNO\textsubscript{x} with no direct relation to the crystalline structure of the support.

Table 1. Full trapping period & amounts of stored NO and desorbed N\textsubscript{2} over various catalysts

<table>
<thead>
<tr>
<th>Catalysts\textsuperscript{1} (TiO\textsubscript{2} crystallinity)</th>
<th>Surf. area (m\textsuperscript{2}/g)</th>
<th>Pt size determ. by CO ads.\textsuperscript{2} (&amp; TEM)</th>
<th>Full trapping period\textsuperscript{3} (min)</th>
<th>NO stored\textsuperscript{4} (mmol/g)</th>
<th>N\textsubscript{2} desorb.\textsuperscript{5} (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-01(Anatase)</td>
<td>71.6</td>
<td>2.9nm (2.5nm)</td>
<td>18</td>
<td>2.25</td>
<td>1.11</td>
</tr>
<tr>
<td>MT150A(Rutile)</td>
<td>15.4</td>
<td>4.1nm (5.2mm)</td>
<td>1</td>
<td>1.25</td>
<td>0.66</td>
</tr>
<tr>
<td>P-25(A/R=0.7)</td>
<td>14.9</td>
<td>3.7nm (3.5mm)</td>
<td>8</td>
<td>1.28</td>
<td>0.57</td>
</tr>
<tr>
<td>KTN</td>
<td>108</td>
<td>2.1nm (1.5mm)</td>
<td>25</td>
<td>2.36</td>
<td>1.15</td>
</tr>
</tbody>
</table>

1) 1.5wt%Pt-33wt%KNO\textsubscript{x} 0.1g, 2)Lean:80ml/min-930ppmNO/7%O\textsubscript{2}/He, 3)Rich:80ml/min-4%H\textsubscript{2}/He

Fig. 2 NO\textsubscript{x} storage-reduction cycles at 350°C over (a) KTN and (b) ST-01 supported catalysts

Significance

Excellent NO\textsubscript{x} storage properties were realized by adding KNO\textsubscript{x} to Pt/KTN catalysts. Maintaining the nanobelt structure and optimizing the amount of KNO\textsubscript{x} were the key factors to obtain high NO\textsubscript{x} storage capacity. The segregation of K\textsuperscript{+} from and back to the lattice of nanobelt wall may be the NO\textsubscript{x} storage and reduction mechanism of these materials.

References