Impact of Sulfur on Catalytic Partial Oxidation of Kerosene-Based Surrogates on Rh/Al₂O₃

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Introduction

The conversion of logistic fuels via catalytic partial oxidation (CPOX) on Rh/Al₂O₃ at short contact times is an efficient method for generating hydrogen-rich synthesis gas. Some recently investigated fuels are e.g. ethanol [1-2], gasoline [2-3], and jet fuel [4-5]. Logistic fuels contain hundreds of different hydrocarbons and a significant amount of sulfur. The composition was reported to influence the product gas yield significantly [3, 6]. However, the hydrocarbon composition and sulfur content vary depending on distributor, season, and refinement. Therefore, little is known on the influence of the various compounds on the synthesis gas yield and the impact of sulfur on the product yield. To unravel the influence of the main compounds, surrogates with a varying paraffin-to-aromatic ratio are tested in the catalytic partial oxidation on a Rh/Al₂O₃ model catalyst. In this study, we chose n-dodecane and 1,2,4-trimethylbenzene as representative components of alkanes and aromatics, respectively. Additionally, for a fixed paraffin-to-aromatic ratio, dibenzothiophene was added as a sulfur component in three different concentrations.

Materials and Methods

All experiments were carried out for varying molar C/O ratios (C/O = 0.65 – 1) at atmospheric pressure, and under quasi-autothermal conditions. A total volume flow of 5 SLPM (standard liters per minute) with an oxygen concentration of 10 vol-% was chosen. A honeycomb monolith (diameter: 2 cm, length: 1 cm) with a cell density of 900 cpsi (channels per square inch) and coated with Rh/Al₂O₃ was used throughout all experiments. The fuel is sprayed directly into the quartz tube reactor by a two-substance spray nozzle with N₂ as carrier gas. The product composition was analyzed simultaneously by FTIR, and MS. To guarantee repeatability for each measurement, a temperature-programmed oxidation was carried out before each experiment (2 SLPM, 10 % O₂, rest N₂, 700 °C, 10 °C/min) in order to restore catalyst activity. As fuels, several surrogates consisting of a blend of 1,2,4-trimethylbenzene and n-dodecane, with and without addition of dibenzothiophene, were investigated. The exact composition of the investigated fuels is given in Table 1.

Table 1. Composition of investigated surrogates (Su) in [vol-%] (for aromatics and paraffins) and in [mg sulfur atoms /kg fuel] (for sulfur)

<table>
<thead>
<tr>
<th>Content</th>
<th>Su 9</th>
<th>Su 17</th>
<th>Su 25</th>
<th>Su 17_10</th>
<th>Su 17_50</th>
<th>Su 17_200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>9.0</td>
<td>17.0</td>
<td>25.0</td>
<td>17.0</td>
<td>17.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Paraffins</td>
<td>91.0</td>
<td>83.0</td>
<td>75.0</td>
<td>83.0</td>
<td>83.0</td>
<td>83.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>50</td>
<td>200</td>
</tr>
</tbody>
</table>

Results and Discussion

In Figure 1, the selectivity of H-atoms, available in the reactant mixture, as a function of the C/O-ratio and the time on stream is displayed. For C/O ≥ 0.75, the product distribution is shifted towards hydrogen for all fuels. At a C/O ratio < 0.75, however, the yields of the products of total oxidation are more dominant, whereas for the surrogate with low aromatic content – Su 9 – the hydrogen selectivity remains at approx. 80 %, compared to approx. 70 % for the other fuels at a C/O-ratio of 0.67. The addition of sulfur in the fuel leads to a decrease in conversion by up to 6 % (for Su17_200) and an increase in C1 and C2 by-product formation (not shown) by an order of magnitude with rising amount of sulfur. The hydrogen main product distribution is shifted towards more water formation for C/O = 0.75, whereas the carbon main product distribution is nearly unaffected by sulfur addition (not shown). These effects increase with increasing sulfur content in the fuel. The rising amount of water and hydrocarbon by-product formation indicate that steam reforming downstream the catalyst may be hindered by sulfur, blocking active sites. For C/O > 0.8, an increasing rate of catalyst deactivation was observed for the sulfur-free surrogates. Despite a maximum sulfur content of 200 ppm (weight) in Su 17_200, a loss in H-selectivity for hydrogen of less than 3% was observed after a total reaction time of 4 hours. Nevertheless, a catalyst deactivation over time, probably due to coke formation, was observed, indicated by a significant formation of ethylene (not shown). The catalyst activity could be regenerated entirely in all cases through temperature-programmed oxidation.

Figure 1. H-selectivity of main products: a) as function of C/O-ratio for fuels with various compositions; b) as function of time on stream for Su 17 with increasing S-content.

Significance

The impact of sulfur-containing components on the reaction sequence and on the deactivation process of CPOX on Rh/Al₂O₃ coated monoliths was studied. The results help to understand the reforming process of sulfur-containing logistic fuels like kerosene. This gained knowledge can be used to identify requirements for logistic fuels in mobile applications based on CPOX and to optimize the overall system efficiency.

References