

Catalytic reforming of jet fuels over Rh/Al₂O₃

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Introduction

The conversion of logistic fuels via catalytic partial oxidation (CPOX) on Rh/Al₂O₃ is generally accepted as an efficient method for generating hydrogen-rich synthesis gas. Some recently investigated fuels are ethanol [1-2] and gasoline [2-3]. In the aircraft sector, the catalytic reforming of kerosene-based jet fuels to synthesis gas for the operation of APUs (auxiliary power units) [4-6] is an opportunity to reduce the fuel consumption in the ground operation of airplanes. Due to the highly varying hydrocarbon composition, the content of hundreds of different hydrocarbons and a significant amount of sulfur in a logistic fuel like JET A1, no conclusions can be drawn regarding the influence of the various compounds on the synthesis gas yield. Therefore, it is essential to replace the jet fuel with a model fuel with two chemically different components representing the main catalytic properties, such as product yields. Hence, surrogates with a varying paraffin-to-aromatic ratio are tested in the catalytic partial oxidation on Rh/Al₂O₃. Additionally, the influence of sulfur on the catalyst deactivation and its impact on the product yield is investigated, as it is uneconomic to use fully desulfurized kerosene as a jet fuel. For the investigations, a two-component blend consisting of 1,2,4-trimethylbenzene and n-dodecane was chosen. Also, a technical kerosene sample was investigated under similar conditions.

Materials and Methods

All experiments were carried out for varying molar C/O ratios (C/O = 1.0 – 0.65) at atmospheric pressure, and under quasi-autothermal conditions. A total volume flow of 5 SLPM (standard liters per minute) with a fixed oxygen concentration of 10 vol-% was chosen. A honeycomb monolith, coated with Rh/Al₂O₃-washcoat and a cell density of 900 cpsi (channels per square inch), was used throughout all experiments. The fuel is sprayed directly into the quartz tube reactor by a two-substance spray nozzle with nitrogen as carrier gas. The product composition was analyzed simultaneously by FTIR, H-Sense and Magnos Oxygen Analyzer. 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 K/min, 15 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 an addition of dibenzothiophene were investigated. Additionally, one unmodified kerosene sample representing a low-sulfur jet fuel, provided by Petrobras, was used for this investigation. The exact composition of the investigated fuels is given in Table 1.

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

Content	Su1	Su2	Su3	Su2_25	Su2_50	Su2_100	JF
Aromatics	9.0	17.0	25.0	17.0	17.0	17.0	19.8
Paraffins	91.0	83.0	75.0	83.0	83.0	83.0	80.2
Sulfur	0	0	0	25	50	100	36

Results and Discussion

Figure 1 shows the main product yield for a selection of surrogate fuels (Su1 and Su3), as well as for the unmodified jet fuel (JF).

For C/O values ≥ 0.75 , the product distribution is shifted towards the products of the catalytic partial oxidation. Furthermore, for C/O > 0.8, an increasing rate of catalyst deactivation was observed. At a C/O ratio < 0.75, however, the yields of the products of total oxidation are more dominant. As the product distribution is highly dependent on the C/H-ratio of the hydrocarbons in the surrogate, less hydrogen and more CO are produced for components with higher aromatic content, such as Su2 compared to Su1 and JF, respectively. For the jet fuel, despite of the sulfur content of 36 ppm (weight), a loss in synthesis gas yield of around 5% was observed after a reaction time of 5 hours.

Additionally, the catalyst was only affected through reversible deactivation by sulfur and coke, as the same catalytic activity was reached after each temperature programmed oxidation. The product distribution for low C/O-ratios of the unmodified jet fuel is reproducible by using a two-component surrogate. Therefore, the application of surrogates with and without sulfur can be employed for displaying the product yields for CPOX of jet fuels on Rh/Al₂O₃-catalysts.

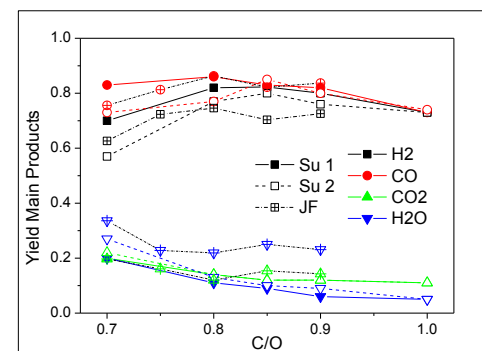


Figure 1. Yield of main products of two surrogates and one kerosene samples as a function of the C/O-ratio.

Significance

The investigation of a two-component surrogate with a sulfur-containing additive extends the understanding about the CPOX of a paraffin/aromatic blend and the probable deactivation of the catalyst due to sulfur derivatives in the fuel. The surrogates can represent the chemical properties of a multi-component fuel such as a jet fuel in a CPOX reactor with good accuracy.

References

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