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Toluene oxidation over ZrO_2-based gasification gas clean-up catalysts: Part A. Effect of oxygen and temperature on the product distribution

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ABSTRACT

Biomass gasification combined with effective gas cleaning is an interesting way to produce energy or syngas for numerous applications. ZrO_2-based catalysts have been proven to remove the undesired tar molecules when a convenient oxygen amount is added. The oxidation of toluene (a tar model compound) was addressed in this work by applying temperature-programmed surface reaction (TPSR) experiments with a continuous feed of toluene and oxygen. Complete toluene conversions were achieved over all zirconia-based catalysts (ZrO_2, Y_2O_3-ZrO_2 and SiO_2-ZrO_2) in toluene oxidation above 550 °C (toluene WHSV 0.06-0.07 1/h). Toluene was oxidized into four products (CO_2, H_2O, CO and H_2). The formation of incomplete oxidation products (CO and H_2) suggests that these catalysts are able to convert undesired tar molecules also into valuable synthesis gas components. Increasing the oxygen amount increased the product ratio of CO_2 and CO. Over pure ZrO_2, the formation of CO and H_2 was detected at 600 °C even with the highest feed ratio of O_2/TOL (≈ 3.5 x theoretical toluene total oxidation ratio), while over the doped zirconias the formation of CO and H_2 approached zero with increasing temperature and over-stoichiometric feeds. Separate CO oxidation experiments confirmed different but appreciable activities of different zirconia materials for that reaction. However, a very minor water-gas shift activity in the presence of oxygen was detected only over pure ZrO_2 at the studied temperature range. The collected multiresponse reaction data was subsequently subjected to transient kinetic modeling established on hypotheses of surface reaction mechanisms (Part B: Kinetic modeling).

1. Introduction

Gasification of biomass is an attractive way to produce energy, liquid biofuels via Fischer–Tropsch synthesis as well as numerous chemicals [1]. The main components of gasification gas are CO, H_2 and CO_2 [1]. In addition, the product gas also contains impurities such as ammonia and tar (aromatic hydrocarbons heavier than benzene), and therefore it has to be cleaned before use [2]. One of the most advantageous technologies to decompose the tar molecules is catalytic hot gas cleaning downstream of the gasifier [3,4]. Hence, the activities of several catalysts have been studied in catalytic hot gas cleaning. In a review by Sutton et al., three main types of reforming catalysts for the elimination of tar are listed: dolomite ($MgCO_3 \cdot CaCO_3$), alkali metals and nickel [2].

Over ZrO_2-based catalysts, successful tar decomposition results are obtained when a small oxygen amount is added to the gas, i.e. by selectively oxidizing tar molecules within the gasification gas (e.g. [5–7]). Reactions involved in the biomass gasification gas cleaning are numerous as equilibrium reactions between the main gas components and hydrocarbon decomposition reactions take place simultaneously, and the addition of oxygen increases the number of possible reactions even further. For this reason, the presence of other gas components (CO, H_2, CO_2, H_2O, etc.) has an effect on the tar oxidation activity of a catalyst [8].

Due to the complexity of the gasification gas mixture, a novel approach was introduced in our previous contribution; the system was simplified to subsystems with fewer components at a time, resulting in an adsorption/oxidation study of a single tar compound (toluene) [9]. In this study, it was discovered by in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) and mass spectrometry that the oxidation