



Molecular level insights to the interaction of toluene with ZrO₂-based biomass gasification gas clean-up catalysts



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ABSTRACT

Gasification of biomass, followed by ZrO₂-catalyzed hot gas clean-up at 600–900 °C for the oxidation of impurities (such as tar), is an environmentally attractive way to produce heat and power or synthesis gas. The interaction of toluene (as a model compound for tar) with ZrO₂-based gasification gas clean-up catalysts was studied by in situ DRIFTS and temperature-programmed gas-phase analysis. Toluene was found to interact in four ways with ZrO₂ surfaces: forming molecularly adsorbed toluene, surface benzoate species, carbonaceous deposits and surface benzyl species. The adsorption of toluene in the absence of gas-phase oxygen at ambient temperature on ZrO₂-based catalysts resulted in weakly adsorbed molecular toluene, while the adsorption of toluene at higher temperatures yielded carbonaceous deposits and surface benzoate species. Combined analysis of infrared and TP data showed that some of the benzoate species decomposed, producing benzene and carbon dioxide. Surface benzyl species, on the other hand, were detected on the surface of ZrO₂-based catalysts only in the presence of gas-phase oxygen at a temperature where toluene and oxygen started to convert. Therefore, it is suggested that benzyl species are the active intermediates from toluene to carbon oxides during the gasification gas cleaning over ZrO₂-based catalysts.

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1. Introduction

Gasification of biomass is a thermochemical process, which converts biomass into syngas (mixture of CO and H₂) [1]. The applications of the product gas include production of energy, H₂, second generation liquid biofuels via Fischer–Tropsch synthesis and several chemicals. However, the product gas also contains impurities such as tar (aromatic hydrocarbons heavier than benzene), and therefore it has to be cleaned before use [2]. Hot-gas cleaning with a catalyst-coated monolith after biomass gasification is a preferable choice for tar decomposition [3]. Since the gas from the gasifier is a complex mixture of compounds, several decomposition and equilibrium reactions take place simultaneously during catalytic gas cleaning. Thus, the determination of tar decomposition reaction rates in the presence of other gas components, such as CO, H₂, CO₂ or H₂O, is challenging [4].

Zirconia-based catalysts have shown to selectively oxidize tar molecules into CO and CO₂ during hot gas clean-up at 600–900 °C when a small amount of oxygen is added to the gas [5]. However, this addition of oxygen changes the tar decomposition

mechanism and makes the determination of tar decomposition reaction rates even more complicated. Furthermore, changes in the composition of the gas along the catalyst-coated monolith have been measured [4,6,7]. At the oxygen-rich zone in the inlet of the monolith, tar molecules preferably use the oxygen available and are oxidized mainly to CO and CO₂. However, near the outlet of the monolith, oxygen is nearly or completely consumed, and therefore other reactions (such as steam and dry reforming, hydrocracking, carbon formation, etc.) might be preferred. The activity of selected ZrO₂-based catalysts in the decomposition of tar from synthetic gasification gas in the presence of oxygen (3 vol%) have been reported to decrease in the order of ZrO₂ > Y₂O₃-ZrO₂ > SiO₂-ZrO₂ [7].

Certain physical and chemical properties have been related to the tar decomposition activity of ZrO₂-based gasification gas clean-up catalysts [5,7]. For example, Juutilainen et al. suggested that increased acidity is not favorable for ZrO₂-based gasification gas cleaning catalyst [5]. In contrast to the high total amount and strength of acidic surface sites, the high total amount and strength of basic surface sites seem to be essential for an active ZrO₂ tar decomposition catalyst [7]. Furthermore, the combination of suitable redox properties of ZrO₂-based gasification gas clean-up catalysts as well as their tendency to generate oxygen vacancies has been related to high activity in tar decomposition [7].

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Table 1
The specific surface areas as well as the amounts of basic and acidic surface sites of the ZrO₂-based catalysts [7].

Catalyst	Specific surface area (m ² /g)	Amount of basic sites (μmol/g)	Amount of acidic sites (μmol/g)
ZrO ₂	24	84	22
Y ₂ O ₃ -ZrO ₂	53	146	36
SiO ₂ -ZrO ₂	92	49	78

Molecular level insight into the ZrO₂-based catalysts under gasification gas conditions offers essential information needed, e.g. when optimizing the catalyst composition. Furthermore, such knowledge combined with the understanding of the influence of gas components on the catalyst performance allows the design and optimization of the cleaning process to ensure high-quality product gas. Since the gasification gas is a complex matrix, a novel approach is needed for overcoming the challenge of finding the tar decomposition mechanism. Our approach is to diminish the complexity by studying simpler subsystems with fewer components and fewer reactions at a time. The first step in this approach is to understand the interaction of a single tar component with ZrO₂-based catalysts. Later the complexity is increased by adding components one by one. By combining in situ spectroscopic methods with temperature-programmed gas-phase analysis, unique knowledge on the relevant surface species and reaction mechanisms is obtained. In this study the adsorption of toluene (as a model compound for tar) is investigated to obtain an insight into toluene decomposition during gasification gas cleaning.

The adsorption of toluene has been studied widely over various reducing and non-reducing oxide catalysts [8–17]. However, the mechanism with which toluene interacts with ZrO₂-based gasification gas clean-up catalysts has not yet been established. Therefore, the adsorption of toluene over selected ZrO₂-based catalysts was studied at temperatures from 30 °C to as high as 600 °C, 600 °C being the relevant temperature for hot-gas cleaning. A reduction pretreatment was applied to the catalysts in order to reduce the amount of surface hydroxyl groups on the catalyst to imitate the reducing conditions of the gasification gas (gasification gas always contains hydrogen and CO). The aim of this study was to discover the relevant surface species formed from toluene in the absence and presence of gas-phase oxygen as well as to estimate the decomposition mechanism of the adsorbed toluene-derived species over ZrO₂, Y₂O₃-ZrO₂ and SiO₂-ZrO₂.

2. Experimental

Pure ZrO₂, 5 mol% Y₂O₃-ZrO₂, and 8 mol% SiO₂-ZrO₂ were provided by MEL Chemicals, where Y₂O₃-ZrO₂ and SiO₂-ZrO₂ were prepared by co-precipitation. The catalysts were calcined in static air at 800 °C for 1 h. The specific surface areas as well as the amounts of basic and acidic surface sites of the catalysts are shown in Table 1. Other previously measured physical and chemical properties of the catalysts have been reported elsewhere [7,18]. Two complementary techniques were used to study the interaction of toluene with ZrO₂-based gasification gas clean-up catalysts: in situ DRIFTS and temperature-programmed gas-phase analysis. Three types of experiments were carried out with both techniques: (1) temperature-programmed desorption of toluene (TPD), (2) temperature-programmed adsorption of toluene (TPA), and (3) temperature-programmed oxidation of adsorbed surface species (TPO). The feed gas compositions and heating rates were matched as close as possible in the DRIFTS and TP gas-phase analysis in order to guarantee accurate comparison between surface species and gas-phase products. This allows surface phenomena to be linked with gas-phase composition. In addition, the interaction of toluene and

oxygen over ZrO₂-based catalysts was studied via the temperature-programmed surface reaction between toluene and oxygen (TPSR) using only in situ DRIFTS. Toluene was chosen as a model compound for tar.

2.1. In situ DRIFTS experiments

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed with a Nicolet Nexus FTIR spectrometer and a Spectra-Tech high temperature/high pressure chamber. The total gas flow through the reaction chamber (passing over the catalyst sample) was kept at 50 cm³/min throughout the experiments. A catalyst sample powder (approx. 30 mg) was pretreated by in situ calcination with 10% O₂/N₂ (synthetic air 99.99%, N₂ 99.999%, AGA) at 600 °C for 2 h followed by N₂ flush for 1 h. In all experiments, the spectrum of an aluminum mirror measured (4 cm⁻¹ resolution, 200 scans) under nitrogen flow was used as the background. After the calcination, the catalyst sample was pre-reduced with 5% H₂/N₂ (H₂ 99.999%, AGA) at 600 °C for 15 min. Spectra were recorded every minute (4 cm⁻¹, 30 scans) for the first 8 min on stream and then after 9 and 12 min (4 cm⁻¹, 100 scans). After the reduction, the catalyst sample was flushed with nitrogen for 30 min while cooling down to the adsorption temperature of toluene.

In the TPD experiments, toluene (750 ppm toluene in He with 1–2 ppm water and even smaller amount of methanol as impurities, AGA) was fed to the sample cell at 30 °C and in the TPA experiments at 100 °C for 30 min. Spectra were collected once every minute (4 cm⁻¹, 30 scans) for the first 5 min, and thereafter once every 5 min (4 cm⁻¹, 100 scans). After the adsorption of toluene, the samples were flushed with nitrogen for 30 min to obtain spectra without the contribution of gas-phase toluene. In the TPD experiments, desorption of the adsorbed species from the samples was followed with increasing temperature stepwise from 30 to 600 °C. During the heating of the sample, spectra (4 cm⁻¹, 100 scans) were collected every 25 °C, i.e. every 4 min. In the TPA experiments, toluene flow was directed back to the sample cell after the nitrogen flush at 100 °C and temperature was increased stepwise from 100 to 200 °C. At 200 °C, the sample cell was flushed with nitrogen for 5 min and a spectrum (4 cm⁻¹, 100 scans) was recorded. In the TPA experiments, spectra (4 cm⁻¹, 100 scans) were collected every 25 °C, i.e. every 5 min under toluene flow and additionally at 100, 200, 300, 400, 500 and 600 °C under nitrogen flow. For comparison, an additional TPA experiment was performed using a calcined ZrO₂ sample, i.e. without hydrogen pre-reduction.

In the TPO experiments, toluene was adsorbed at 600 °C for 30 min and then the sample was flushed with nitrogen while cooling down to 30 °C. Next, the adsorbed species were oxidized (2% O₂/N₂) with increasing temperature stepwise from 30 to 600 °C while spectra (4 cm⁻¹, 100 scans) were collected every 25 °C, i.e. every 5 min.

In the TPSR experiments, 45 cm³/min toluene (750 ppm in He) and 5 cm³/min N₂ (yielding a gas mixture of 675 ppm toluene, 90% He and 10% N₂) was first fed to the sample at 100 °C for 1 h. Thereafter N₂ was replaced by synthetic air, resulting in a gas mixture of 675 ppm toluene, 90% He, 2% oxygen and 8% N₂. The oxygen concentration in the TPSR experiments was kept as low as possible but still resulting in an oxygen surplus, thus matching the oxygen feed composition in the gasification gas cleaning. After a 30-min stabilizing period, the sample cell was heated in the toluene-helium-air mixture from 100 to 600 °C. The spectra (4 cm⁻¹, 100 scans) were collected every 25 °C, i.e. every 5 min. The gas flow from the reactor in the TPSR experiments was followed with a Pfeiffer Vacuum Omnistar mass spectrometer. It should be noted that accurate kinetic data cannot be obtained because there

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