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Effect of gasification gas components on naphthalene decomposition over ZrO_2

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ABSTRACT

One of the main challenges for biomass gasification is to remove the produced tar from the product gas. Cleaning of the gasification gas is essential, because tar may cause operational problems in downstream processes. In this study naphthalene was used as a tar model compound. The effects of the main components of the gasification gas on the naphthalene decomposition activity of ZrO_2 were studied. Without O_2 in the gasification gas feed the conversion of naphthalene was below 10% at the studied temperature range (600–900 °C), indicating that the main reactions in naphthalene decomposition on ZrO_2 are oxidations. Furthermore, the higher the O_2 concentration in the feed, the higher was the naphthalene conversion. Moreover, naphthalene conversion was higher when only O_2 and naphthalene (with CO_2 as a carrier gas) was fed into the reactor compared to the gasification gas feed. Thus, the presence of the gasification gas components lowers the oxidation of naphthalene. Especially water (at 700 °C) but also hydrogen and carbon monoxide (at 800–900 °C) were found to inhibit the naphthalene oxidation reactions, whereas ammonia had no discernible effect on the naphthalene conversion. The reactions of naphthalene at the studied conditions are occurring not only catalytically but thermal reactions have a significant role at temperatures above 700 °C.

1. Introduction

Gasification of biomass is an efficient alternative for liquid fuel production via the FT-synthesis or for power and heat production [1]. Cleaning of the gasification gas is essential, because e.g. tar may cause operational problems in downstream processes by blocking the particulate filters and engine suction channels.

Extensive literature exists of catalysts that can be used to eliminate tar with e.g. nickel based catalysts [2] and alkali metals (reviewed by Sutton et al. [3]). Recently ZrO_2 and doped ZrO_2 catalysts have also been shown to be active and sulfur resistant in tar decomposition [4–7]. Monolith type of catalysts are suitable for clean-up of the product gas from fluidised bed gasifier since the plugging problems caused by dust can be reduced [8]. Moreover, the monolith based gas cleanup concept, consisting of the Novel fixed bed gasifier, a catalytic reformer followed by a filter and a gas scrubber/cooler, is considered to be suitable for use in modern turbo charged engines (Fig. 1). The gas produced in this way is reported to have very low tar ($<100\,mg/m_n^3$), ammonia (<50 ppm) and particulate ($<5\,mg/m_n^3$) contents [9–11].

ZrO_2 is a metal oxide with acidic, basic, oxidizing and reducing properties [12] and the high thermal stability makes it attractive material both as a catalyst and as a support [13]. Pure ZrO_2 has three stable crystal structures at atmospheric pressure: cubic above 2370 °C, tetragonal above 1170 °C and monoclinic below 1000 °C [14]. Tar decomposition over ZrO_2 in the conditions of complex mixture of gasification gas is suggested to occur via oxidation reactions [4–7]. The biomass gasification gas mainly composes of H_2O, CO_2, H_2, CO, with low quantities of CH_4 and other light hydrocarbons together with the impurities such as tar, sulfur and ammonia. Each of the components can have an influence on the tar decomposition. Several studies have been made on the effect of individual gas components or gas mixtures on tar decomposition over olivine [15], dolomite [16,17] and nickel [17,18] catalysts. In order to solve the challenges on tar decomposition the effect of the major gas components must be understood. Furthermore, since the gas matrix is very complex, one of the most challenging tasks is to determine the kinetic parameters and the reaction network for tar decomposition. The reaction network consists of several competitive and parallel reactions. The main tar decomposition reaction over ZrO_2-based catalysts has been proposed by Juutilainen et al. [4] to be a two-step oxidation mechanism (written for naphthalene in Eqs. (1) and (2)). In addition to oxidation of carbon monoxide (Eq. (2)),

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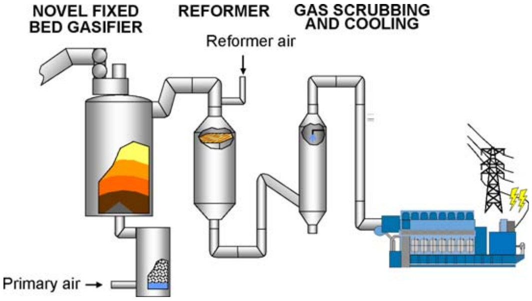

Fig. 1. Layout of the Novel combined heat and power plant.

hydrogen can be oxidized into water (Eq. (3)):

$$C_{10}H_8 + 7O_2 \rightarrow 10CO + 4H_2O, \quad \Delta H(600\,^{\circ}C) = -2230\,kJ \tag{1}$$

$$CO + (1/2)O_2 \rightarrow CO_2, \quad \Delta H(600\,^{\circ}C) = -283\,kJ \tag{2}$$

$$H_2 + (1/2)O_2 \rightarrow H_2O, \quad \Delta H(600\,^{\circ}C) = -247\,kJ \tag{3}$$

Other possible hydrocarbon decomposition reactions besides oxidation include steam and dry reforming of hydrocarbons, steam dealkylation, hydrocracking, hydrodealkylation, thermal cracking and carbon formation [17]. In addition to the hydrocarbon decomposition reactions, several equilibrium reactions may occur between the main gas components including e.g. water–gas shift (Eq. (4)), methanation reactions (Eqs. (5) and (6)), water–gas reactions (Eqs. (7) and (8)), Boudouard reaction (Eq. (9)) and ammonia synthesis (Eq. (10)):

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H(600\,^{\circ}C) = -36\,kJ \tag{4}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O, \quad \Delta H(600\,^{\circ}C) = -223\,kJ \tag{5}$$

$$C + 2H_2 \leftrightarrow CH_4, \quad \Delta H(600\,^{\circ}C) = -88\,kJ \tag{6}$$

$$H_2O + C \leftrightarrow CO + H_2, \quad \Delta H(600\,^{\circ}C) = 136\,kJ \tag{7}$$

$$2H_2O + C \leftrightarrow CO_2 + 2H_2, \quad \Delta H(600\,^{\circ}C) = 99\,kJ \tag{8}$$

$$CO_2 + C \leftrightarrow 2CO, \quad \Delta H(600\,^{\circ}C) = 172\,kJ \tag{9}$$

$$N_2 + 3H_2 \leftrightarrow 2NH_3, \quad \Delta H(600\,^{\circ}C) = -108\,kJ \tag{10}$$

The aim of this study was to understand the effects of the main components of the gasification gas on the naphthalene decomposition activity of ZrO_2. Since naphthalene is one of the most stable of tar components and thus, difficult to decompose [15], naphthalene was chosen as a model compound for tar. This study was performed on powder catalysts to reduce the temperature gradients along the catalyst bed. Nevertheless, in larger scale monolithic honeycomb reactors are used [8–11].

2. Experimental

Naphthalene decomposition experiments under various gas compositions were carried out in a fixed-bed quartz reactor with a temperature range of 600–900 °C under atmospheric pressure. The reactor was packed with 0.2 g of calcined ZrO_2 powder (MEL Chemicals, ECO 100, with BET area of 39.4 m^2/g) and placed in a three-zone furnace. Prior the experiments, the ZrO_2 powder was calcined at 1000 °C for one hour in air and sieved to particle size 0.212–0.313 mm. The reaction zone consisted of the zirconia bed supported on a quartz grid. The reactor was equipped with a thermocouple pocket in the center of the catalyst bed in order to measure the temperature profile. The K-type thermal element was drawn downwards at 1 mm intervals inside the thermocouple pocket to measure the temperature profile. The gas feed rate was adjusted to 2 $dm^3\,min^{-1}$ and the gases were mixed using mass flow controllers (gases supplied by AGA Ltd.). The effect of gas components on naphthalene conversion was investigated by varying the individual gas components and keeping the other parameters constant. Total feed gas was kept constant by using nitrogen to compensate the change in the gas volume. The gas compositions utilized at the experiments are listed in Table 1. The thermal decomposition reactions of naphthalene were studied by making blank run with an empty reactor with the oxygen concentrations of 0.4 and 1.2 vol.% using the basic gasification gas feed (see Table 1).

Water was fed through HPLC pump and vaporized before mixing into the gas stream. Naphthalene vapor was carried into the reactor by CO_2 flow which passed through the liquid naphthalene. The naphthalene feeding system was uniformly heated to 80 °C. CO_2 flow was used as carrier for the naphthalene, since CO_2 is always present at the gasification gas and being at the product side of the oxidation reactions it was expected to have the lowest reactivity with naphthalene. All the gas lines were heated to 200 °C to avoid condensation. The volumetric compositions of inlet and outlet gases were analyzed with a Gasmet FTIR gas analyzer after which the condensable compounds were removed by a cold trap consisting of isopropanol and water in series in an ice bath. An online gas chromatograph (HP 5890) was used for the tar analysis. The collected samples from the gas flow were analyzed with a HP PLOT-Q (20 m × 0.53 mm ID, 40 μm + TRAP) column and FID. The flow rate and temperature of the dried gas were measured and the gas was directed to separate Sick Maihak-type S710 on-line gas analyzers to measure the volumetric composition of the dry gas in terms of the various component gases (CO, CO_2, CH_4, O_2 and H_2). Conversions of naphthalene, ammonia, oxygen and other gas compounds were calculated from the reactor mass balances based

Table 1
Composition of the gas mixtures used (wet gas). In each case N_2 was used to balance.

Gas mixture	CO (vol.%)	CO_2 (vol.%)	H_2 (vol.%)	H_2O (vol.%)	O_2 (vol.%)	NH_3 (ppm_v)	$C_{10}H_8$ (ppm_v)	T range (°C)
Gasification gas[a]	14.9	8.4	20.9	38.7	0.4–1.8	1200	190	600–900
Without O_2	14.9	8.4	20.9	38.7	0	1200	190	600, 900
Without H_2	14.9	8.4	0	38.7	0.4	1200	190	600–900
Without CO	0	8.4	20.9	38.7	0.4	1200	190	600–900
Without NH_3	14.9	8.4	20.9	38.7	0.4	0	190	600–900
Oxidation[b]	0	3.6	0	0	0.4; 1.2; 1.8	0	190	600–900
Without $C_{10}H_8$	14.9	8.4	20.9	38.7	0.4; 1.2	1200	0	600–900
Without CO, H_2	0	8.4	0	38.7	1,2	1200	190	700
Without H_2O	14.9	8.4	20.9	0	1.2	1200	190	700
N_2 and CO_2	0	3.6	0	0	0	0	190	700

[a] Light hydrocarbons of gasification gas (CH_4, C_2H_4) were not included in this study in order to observe clearly the reactions of naphthalene.
[b] CO_2 was used as the carrier gas for naphthalene feeding into the reactor.

on molar flows at steady state according to Eq. (11):

$$X_i = \frac{F_{i,\mathrm{in}} - F_{i,\mathrm{out}}}{F_{i,\mathrm{in}}} \times 100\% \qquad (11)$$

where X_i is the conversion of compound i, $F_{i,\mathrm{in}}$ and $F_{i,\mathrm{out}}$, are the molar flows of compound i at the inlet and outlet, respectively. Conversions are presented as a function of the mean catalyst bed temperature calculated from the measured temperature profile along the catalyst bed. However, in the text the temperatures refer to the set point temperatures to gain clarity. Thermodynamic equilibria to the gasification feed with 0.4 vol.% O_2 at 700 and 900 °C were calculated with the HSC Chemistry 5.11 program based on the minimization of Gibbs energy

3. Results and discussion

3.1. Effect of various main gas components

The feed gas composition had a significant effect on naphthalene and oxygen conversions. The effect of the absence of various reactants on the naphthalene conversion was studied at temperature range 600–900 °C over calcined ZrO_2. The experimental results for naphthalene and oxygen conversion under various reaction media as a function of the mean catalysts temperature are shown in Fig. 2. In Fig. 2. gasification refers to basic gasification gas composition.

Under a gasification gas environment naphthalene conversion increased with temperature to above 30% at 900 °C. Without oxygen, the conversions remained below 10% even at 900 °C. Without hydrogen the naphthalene conversion was higher compared to gasification feed when temperature was higher than 700 °C whereas at 700 °C lower conversions were measured. Furthermore, without CO in the gas feed, the naphthalene conversion was higher compared to the gasification feed when temperature was higher than 700 °C. Nevertheless, removing ammonia from the gasification gas had no discernible effect on the naphthalene conversion. The conversion levels for naphthalene with all the tested gasification mixtures were always lower than those obtained in oxidation (only oxygen and the additive CO_2 from naphthalene feed) with an exception of the measuring point of 900 °C, where the hydrogen removal from the gasification gas, resulted in comparable, around 80% naphthalene conversion with the oxidation gas feed. In the blank experiment at 600 and 700 °C the thermal reactions had only small effect on the naphthalene conversion. However, at temperatures of 800 and 900 °C the thermal reactions seem to have a significant role in naphthalene decomposition at the applied conditions.

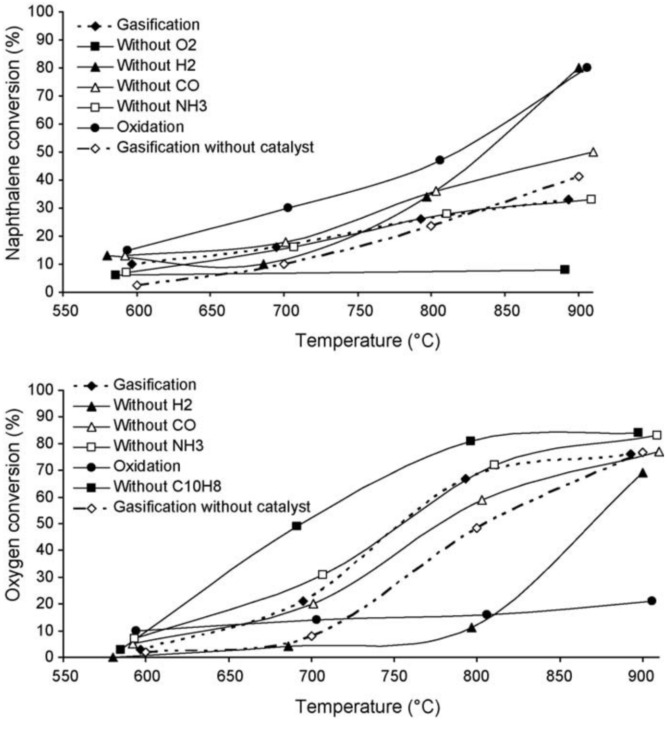

Fig. 2. Effect of gas composition on naphthalene (upper) and oxygen (lower) conversion as a function of the mean catalyst bed temperature over ZrO_2.

The ammonia conversion (not shown) over ZrO_2 was low and similar with all the gas feeds with an exception of gas feed without H_2 when the highest, 6% NH_3 conversion was measured at 900 °C. Without oxygen in the feed and without naphthalene in the feed, the ammonia conversion was zero with the measuring accuracy. These results indicate that the ammonia oxidation (Eq. (12)) is much slower on ZrO_2 compared to naphthalene oxidation (Eq. (1)):

$$2NH_3 + 1.5O_2 \rightarrow N_2 + 3H_2O, \quad \Delta H(600\,^{\circ}\mathrm{C}) = -632\,\mathrm{kJ} \qquad (12)$$

The oxygen conversion with the basic gasification gas feed increased with temperature to around 80% at 900 °C (Fig. 2). The oxygen conversion increased when naphthalene was not with the feed whereas the oxygen conversion decreased remarkably without hydrogen in the gas, and less without CO. Without ammonia in the gas the oxygen conversions were slightly higher compared to the gasification gas feed. However, the oxygen conversion remained under 25% when only naphthalene oxidation (with the possible effect of the additive CO_2 from naphthalene feed) occurred. When only naphthalene was oxidized, the observed conversion rise of oxygen as a function of temperature (Fig. 2) was not high because naphthalene was in ppm levels compared to the excess of oxygen (being 0.4 vol.%). In the blank run with the gasification gas, the oxygen conversion remained below 10% between 600 and 700 °C and increased remarkably at higher temperatures.

When H_2 or naphthalene was not in the feed the measured bed temperatures were lower than with the gasification gas below the set point of 800 and higher at 800–900 °C (Table 2). Without CO, NH_3 and in oxidation the average bed temperature was lower than with gasification feed at set point of 600 °C and somewhat higher above it. Without catalyst and without oxygen the temperatures were always lower than with the gasification feed.

The naphthalene decomposition over ZrO_2 requires oxygen. And the oxidation reactions of naphthalene are decreased by the other gas components within the gas. Especially H_2 and CO seem to have an inhibiting effect on the naphthalene oxidation reactions. However, at 700 °C the absence of H_2 in the feed lowered the naphthalene conversions compared to that of basic gasification gas. This might be due to the lower temperatures of the bed especially at 700 °C (e.g. without H_2 686 °C at the set point 700 °C) compared to the basic gasification gas (695 °C), which might have resulted from the fact that less heat was produced in exothermic H_2 oxidations when H_2 was not within the feed. This seems to have an influence at 700 °C, whereas above 700 °C the naphthalene oxidation is not that sensitive to small changes in temperature.

The out/in ratio was calculated for the main gases (CO, CO_2, H_2, O_2 and H_2O) at 600–900 °C (Table 2). Values greater than 1 indicate formation of the component and below 1 indicate consumption. Thus, values equal to 1 indicate that in complex overall reactions the gas was neither consumed nor produced. It has to be borne in mind, however, that the main gases are in percents compared to the ppm levels of naphthalene and ammonia and thus, the changes in these gases because of naphthalene or ammonia decomposition

Table 2

The out/in ratios of the main gases as a function of the mean catalyst bed temperature with various gas feeds over ZrO_2. F denotes for slight formation of the component.

Measured T (°C)	Gasification				Measured T (°C)	Without NH_3			
	597	695	793	893		593	707	811	909
CO	1.00	1.00	1.00	0.99	CO	1.00	1.00	1.00	1.00
CO_2	1.00	1.00	1.01	1.02	CO_2	1.00	1.01	1.01	1.02
H_2	1.00	1.00	0.99	0.99	H_2	1.00	1.00	0.99	1.00
O_2	0.97	0.80	0.33	0.24	O_2	0.93	0.69	0.28	0.17
H_2O	1.00	1.00	1.01	1.01	H_2O	1.00	1.00	1.01	1.01
Measured T (°C)	Without H_2				Measured T (°C)	Without $C_{10}H_8$			
	580	686	797	n.a.		585	691	796	898
CO	1.00	1.00	0.99	0.92	CO	1.00	1.00	0.99	0.99
CO_2	1.00	1.01	1.02	1.10	CO_2	1.00	1.01	1.02	1.02
H_2				*F*	H_2	1.00	0.99	0.99	0.99
O_2	1.00	0.96	0.89	0.37	O_2	0.96	0.51	0.19	0.16
H_2O	1.00	1.00	1.00	0.99	H_2O	1.00	1.01	1.01	1.01
Measured T (°C)	Without CO				Measured T (°C)	Gasification without catalyst			
	592	701	803	910		561	672	778	877
CO			*F*	*F*	CO	1.00	1.00	1.00	0.99
CO_2	1.00	1.00	1.00	1.00	CO_2	1.00	1.00	1.01	1.02
H_2	1.00	0.97	0.96	0.98	H_2	1.00	1.00	1.00	0.99
O_2	0.94	0.81	0.41	0.23	O_2	0.99	0.92	0.52	0.23
H_2O	1.00	1.00	1.01	1.01	H_2O	1.00	1.01	1.01	1.01

n.a.: not available.

are not high. Furthermore, since the measuring accuracy of the FTIR analysis, the values in Table 1 are considered to be only indicative. With the basic gasification gas, H_2 was consumed and H_2O and CO_2 formed at the set points of 800–900 °C and CO consumed at 900 °C. When H_2 was removed from the gas feed CO was consumed already at 800 °C and above and CO_2 formed above 600 °C. Some H_2 was formed and H_2O slightly consumed only at 900 °C. Interestingly, without CO in the feed, CO was slightly formed at 800–900 °C and CO_2 was not formed at any temperature, whereas H_2 was converted more than with basic gasification gas already at 700 °C and above. Similarly H_2O was formed above 700 °C. When NH_3 was removed from the gas, CO_2 was formed already at 700 °C and CO and H_2 were not consumed at 900 °C as compared to the basic gasification gas feed. Without catalyst the gas composition was similar to that with the catalyst with an exception of oxygen which was consumed less without the catalyst below 900 °C, in accordance with the lower naphthalene conversion. Finally, in the oxidation (not shown) some CO was formed at all temperatures and some CO_2 was formed at 700 °C and above.

These results indicate that naphthalene but especially the H_2 and CO oxidations are occurring also thermally particularly at 800 °C and above at the studied conditions. However, the main reactions at the studied conditions seem to be the oxidation reactions (1), (2) and (3). When H_2 or CO is removed the conversion of CO or H_2 is increased, respectively.

Zirconia is studied in the various hydrocarbon oxidations. For example Labaki et al. [19] suggested that toluene and propene oxidation over ZrO_2 occurs in the oxygen vacancies. Moreover, the Mars–van Krevelen reduction–oxidation mechanism was used by Zhu et al. [20] to describe methane oxidation over ZrO_2 and Y_2O_3–ZrO_2. Similar mechanism of naphthalene oxidation was suggested also over $Ce_{0.75}Zr_{0.25}O_2$ [21]. According to this mechanism e.g. methane is selectively oxidized by surface lattice oxygen, leaving oxygen vacancy which is differently replenished over ZrO_2 and over Y_2O_3–ZrO_2 which has enhanced number and different types of oxygen vacancies. The active site of methane [22] and tar oxidation [7] is suggested to be the surface lattice oxygen coordinated with Zr^{4+}-ion. Moreover, since the CO_2 and H_2O were formed it seems that the naphthalene decomposition over zirconia, at the studied conditions, does not occur via steam and dry reforming reactions as suggested for nickel and dolomite [16,17]. It is also noted by Zhu [22] that the steam and dry reforming activity of methane over Y_2O_3–ZrO_2 is low below 1000 °C.

In addition to the hydrocarbon decomposition reactions, several equilibrium reactions may occur between the main gas components. Without naphthalene in the gas, CO and H_2 were consumed and CO_2 and H_2O were formed at lower temperatures than with the basic gasification feed (Table 2). This explains the higher measured oxygen conversions than with the basic gasification feed. Without oxygen (not shown) the out/in ratios of the gases were 1 at 600 as well as at 900 °C indicating that the main reactions were occurring only with oxygen within the feed. Thus, at the studied conditions the main reactions between the gas components were also oxidations. The equilibrium composition was calculated to the basic gasification feed with 0.4 vol.% oxygen at 700 and 900 °C. According to calculations the system was not in equilibrium neither at 700 nor at 900 °C.

Among the listed main gas components, other compounds were also detected in the GC analysis. Unfortunately, the compounds with molar masses higher than naphthalene could not detected with the analysis methods utilized for tar. However, it is known that when toluene and naphthalene mixture is used as tar model compound, also other aromatic hydrocarbons such as benzonitrile are formed over ZrO_2 [6]. Since the mass balances for carbon had always over 95% accuracy, these compounds were not expected to be formed that much. Over the basic gasification gas feed, methane, ethylene/acetylene (not separable in the GC analysis) and benzene were formed (all in concentrations below 30 ppm) at 800–900 °C. Toluene was detected at all temperatures in very low concentration, being 2 ppm. When H_2 was removed from the gas, traces of benzene and toluene were detected at all temperatures. Methane was formed without H_2 in the gas feed (33 ppm) only at 900 °C together with some ethylene/acetylene. Without CO and without NH_3 methane, ethylene/acetylene, benzene and traces of toluene were formed at 800–900 °C. In the oxidation, ethylene/acetylene was formed at 700 °C and above, increasing with temperature to 79 ppm at 900 °C, and the other compounds were traces of benzene and toluene (below 5 ppm). Without oxygen, only traces of toluene

(2 ppm) were detected among the naphthalene. Without catalyst, more methane and benzene were formed compared to with catalyst at 900 °C. Moreover, some formation of ethylene was also detected without catalyst. These results indicate that among the main reactions (1), (2) and (3), the naphthalene decomposition may occur via other reactions such as:

$$C_{10}H_8 + 5O_2 \rightarrow C_2H_4 + 8CO + 2H_2O, \quad \Delta H(600\,^{\circ}C) = -1474\,kJ \tag{13}$$

$$C_{10}H_8 + 5.5O_2 \rightarrow CH_4 + 9CO + 2H_2O, \quad \Delta H(600\,^{\circ}C) = -1712\,kJ \tag{14}$$

$$C_{10}H_8 + O_2 + H_2 \rightarrow C_2H_4 + C_6H_6 + 2CO, \quad \Delta H(600\,^{\circ}C) = -116\,kJ \tag{15}$$

$$C_{10}H_8 + O_2 + 3H_2 \rightarrow 2CH_4 + C_6H_6 + 2CO, \quad \Delta H(600\,^{\circ}C) = -331\,kJ \tag{16}$$

Since more methane, benzene and ethylene were formed without catalyst at 900 °C, these reactions seem to be at least partly thermal instead of catalytic at the applied conditions. Furthermore, the traces of toluene and benzene were probably resulting from thermal cracking reactions (Eq. (17)):

$$nC_{10}H_8 \rightarrow mC_xH_y + pH_2 \tag{17}$$

3.2. Effect of oxygen concentration

Since oxygen was the most critical parameter on the conversion of naphthalene, the effect of oxygen concentration on the naphthalene and oxygen conversion was studied by making experiments with various oxygen concentrations with the gasification gas feed (see Table 1). The results are shown in Fig. 3. Naphthalene and oxygen conversion increased with increasing temperature and oxygen concentration. At 600 °C the naphthalene as well as oxygen conversion increased with oxygen concentrations below 0.4 vol.%, after which they remained at 10% for naphthalene and 5% for oxygen, regardless of oxygen concentration. At temperatures of 700 °C and higher the conversion of naphthalene and oxygen increased with increasing oxygen concentration. However, when oxygen concentration was higher than 0.8 vol.%, the naphthalene and oxygen conversions at 800 and 900 °C had no discernible distinction between each other. These results are in good agreement with studies of Bampenrat et al. who noted that the rate of the oxidation of naphthalene increases with increasing oxygen concentration over $Ce_{0.75}Zr_{0.25}O_2$ [21].

The actual measured temperature was not clearly influenced by higher oxygen concentration at the set points of 600 and 700 °C (Fig. 3). However, at 800–900 °C the measured catalyst bed temperature increased with oxygen concentration, suggesting that the higher conversions at higher oxygen concentrations at 800–900 °C might be partly due to the temperature differences and not only because of higher oxygen content.

The effect of oxygen concentration and temperature had an influence also on the other gas components. The ammonia conversions were always below 5% and had no clear trend with increasing oxygen concentration or temperature. Some CO was converted at 800 °C and above when oxygen feed was ≥0.4 vol.%. At 1.8 vol.% oxygen feed (3 vol.% at the dry gas) the CO conversion was at highest, being ~2% at 900 °C. The conversion of H_2 increased with temperature and oxygen concentration above 600 °C, where no clear conversion occurred. The highest conversion of H_2 was ~12% at 900 °C and with 1.8 vol.% oxygen feed. H_2O and CO_2 were formed above 600 °C and over 0.3 vol.% oxygen concentrations. The formation of both water and CO_2 increased with temperature and oxygen concentration. These results indicate that H_2 is oxidized faster than CO and when more oxygen is available it is preferably used in reaction (3) than in reaction (2).

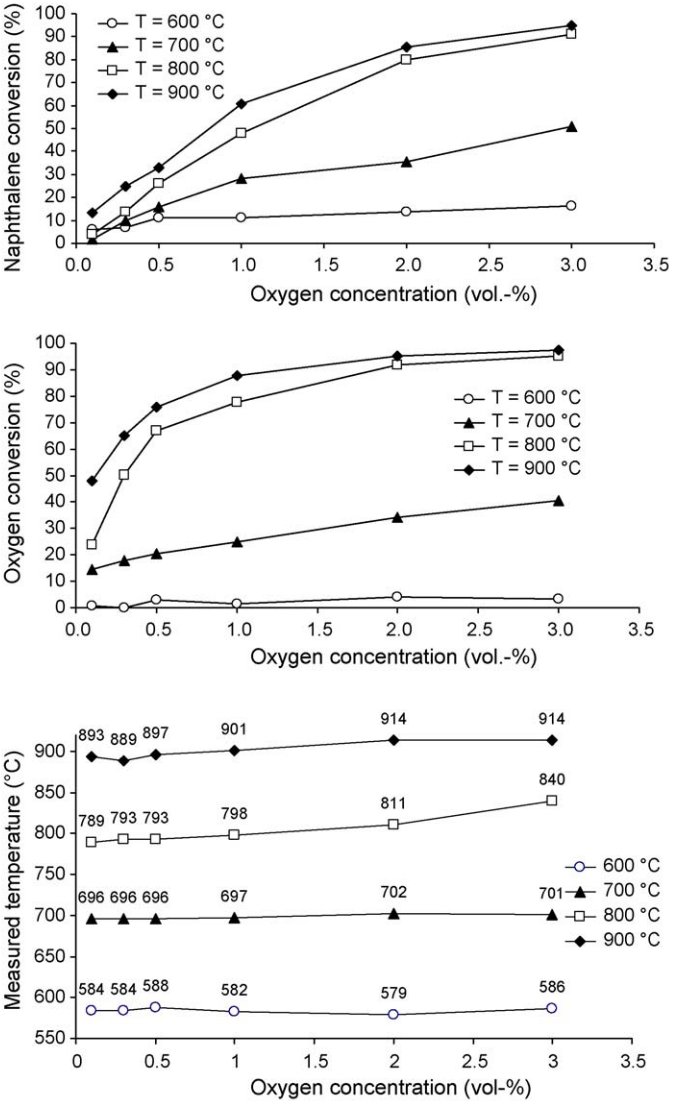

Fig. 3. Effect of oxygen concentration (dry gas basis) on the naphthalene (upper) and oxygen conversion (middle) over ZrO_2 at the set points of 600–900 °C with gasification feed and the measured bed temperatures at the each set point temperature (lower).

3.3. Effect of various main gas components at 700 °C

Since the conversion levels for naphthalene with all the tested gasification mixtures were lower than those obtained in oxidation, the effect of various gas components were studied in detail at 700 °C where thermal reactions are not taking place abundantly. The oxygen concentration in these experiments was 1.2 vol.% in order to achieve high enough conversion levels to detect the differences more clearly between the gas matrixes (Fig. 4). When temperature was kept constant and the gas matrixes were varied, the measured temperature of the catalyst bed changed (Fig. 4). In pure oxidation feed (with the additive CO_2 from naphthalene feed) the naphthalene conversions was 54% and oxygen conversion 7% and temperature of the bed was 696 °C being similar with that obtained without oxygen feed when only N_2 and the naphthalene (with the additive CO_2 from naphthalene feed) was fed. With the

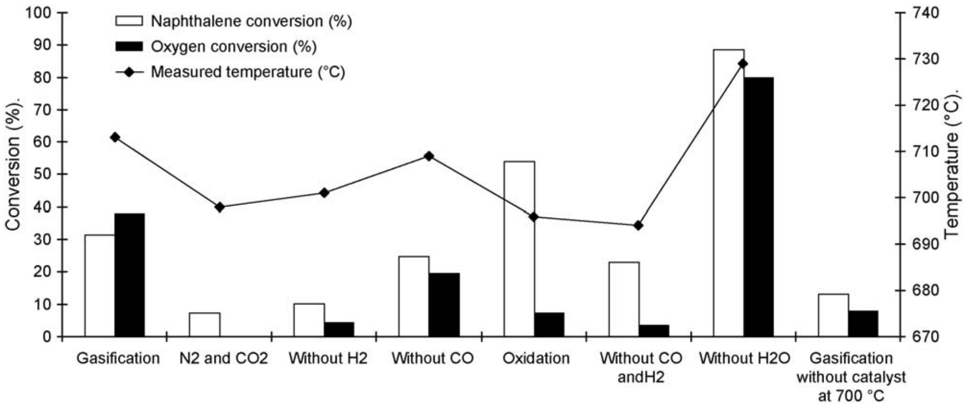

Fig. 4. Naphthalene and oxygen conversions and measured bed temperatures at the set point of 700 °C over various gas feeds. Gasification refers to basic gasification gas feed, N_2 and CO_2 only those and naphthalene in the gas feed and oxidation only O_2, CO_2 and naphthalene in the gas feed.

basic gasification gas feed, the conversion of naphthalene was lower and temperature (713 °C) and oxygen conversion higher than with oxidation feed. When H_2 was not with the feed, the temperature (701 °C) as well as naphthalene and oxygen conversion were lower than with gasification feed. Similar but less significant effect was observed when CO was removed from the gas feed. However, when both the H_2 and CO were removed from the gas the naphthalene conversion was between those obtained without H_2 and without CO whereas the temperature (694 °C) was lower than without H_2 or CO in the gas and oxygen conversion was similar to that without H_2 addition. Interestingly, the highest conversions and temperatures (729 °C) were measured when H_2O was removed from the gas feed. When only H_2 was not in the feed the ammonia conversion increased to 12% and without water to 21% from around 2–3% with the other gas feeds.

The out/in ratio was calculated for the main gases at 700 °C (Table 3). With all the examined gas feeds (when H_2 was with the gas) O_2 and H_2 were consumed and CO, CO_2 (with and exception when CO was not within the gas) as well as H_2O were formed. The order of O_2 consumption was feed without water > basic gasification gas feed > without CO > oxidation gas feed > without without CO and H_2 ~ without H_2. Without H_2 and CO as well as without CO and in oxidation some CO formation was also observed, indicating occurrence of the reaction (1). H_2 was not formed when it was not within the feed. This means that if H_2 is produced in oxidation reactions such as (18), the formed H_2 is oxidized quickly further in reaction (3):

$$C_{10}H_8 + 5O_2 \rightarrow 10CO + 4H_2, \quad \Delta H(600\,^{\circ}C) = -1242\,kJ \tag{18}$$

H_2 was consumed more when water was not in the feed than with gasification feed, whereas without CO the H_2 consumption was comparable to that measured over the gasification feed. These results indicate that water would but CO would not remarkably inhibit H_2 oxidation. Some H_2O was generally formed; however H_2O was not formed in discernible amounts when H_2 was not within the feed and with the oxidation feed. The water formation in oxidation is not observed probably since naphthalene is in ppm levels and thus, the formation is small compared to that formed in H_2 oxidation which is in percent level in the gas. With the empty reactor the values were 1 for other gases than oxygen, which was converted. Without water in the feed, at 700 °C and with 1.2 vol.% oxygen feed a significant formation of methane (over 300 ppm) was observed. Other compounds formed without water were benzene (34 ppm) and some ethylene/acetylene and ethane around 8 ppm both.

Without water, the measured catalyst bed temperature as well as the O_2, H_2 and NH_3 conversions were higher compared to the basic gasification feed. Thus, H_2O seems to have a strong inhibiting effect on the naphthalene as well as ammonia and other conversions. The naphthalene conversions measured when water was removed were higher than in the oxidation (with the CO_2 feed for naphthalene). This is probably due to the higher temperature of the catalyst bed compared to the oxidation which resulted from e.g. H_2 oxidation. The inhibiting effect of H_2 and CO seem not to be as strong as that of water at 700 °C and at the low temperatures the lower naphthalene conversions measured compared to gasification gas feed seem to be connected with the lowering of the temperature of the catalyst bed when either H_2 or CO are removed from the gas. Since CO_2 was used as a carrier, and since H_2O seem to have a significant effect on the naphthalene oxidation, the effects of CO_2 and H_2O need to be studied in detail in the future. Furthermore, the effect of thermal reactions needs to be studied to gain more understanding of the reactions at the studied conditions.

4. Conclusions

In conclusion, the naphthalene and ammonia decomposition over ZrO_2 requires oxygen. Moreover, the higher the oxygen concentration the higher the naphthalene conversion with the gasification feed. The main gases of the gasification gas have a significant influence on the naphthalene conversion although they are not very reactive as such. Especially water (at 700 °C) but also

Table 3
The out/in ratios and the measured mean catalyst bed temperatures of the main gases at 700 °C with various gas feeds over ZrO_2. *F* denotes for slight formation of the component.

Gas mixture	Gasification	Without H_2 and CO	Without H_2	Without CO	Oxidation	Without H_2O	Gasification without catalyst
Measured temperature (°C)	713	694	701	709	696	729	Set point 700
CO	1.01	*F*	1.00	*F*	*F*	1.01	1.00
CO_2	1.02	0.99	1.01	1.00	*F*	1.03	1.00
H_2	0.98			0.98		0.94	1.00
O_2	0.64	0.96	0.96	0.80	0.93	0.19	0.98
H_2O	1.02	1.02	1.00	1.01		*F*	1.00

hydrogen and carbon monoxide (at 800–900 °C) are inhibiting the naphthalene oxidation reactions whereas ammonia has no discernible effect on the naphthalene conversion. The reactions of naphthalene are occurring not only catalytically and thermal reactions have significant role in the reactions at temperatures higher than 700 °C.

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