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Catalytic tar removal from bio syngas—Catalyst development and kinetic studies

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ABSTRACT

One of the most demanding areas of current energy research is related to the production, use and integration of fuels from renewable, i.e. CO_2 neutral, primary energy sources. The generation of biofuels of the second generation requires the gasification of biomass. Thereby considerable amounts of tar are formed in the crude gas. These impurities must be removed before further processing via Fischer–Tropsch or methanol synthesis [1]. For energy efficiency reasons of the whole process, the catalytic hot-gas-cleaning is a promising method. The operating temperature range from 450 to 700 °C results from the outlet temperature of the gasification process and the working temperature of the following synthesis steps. By means of selective, oxidative tar removal on Mo/V/W-mixed oxide catalysts tar compounds can be removed systematically, without converting the synthesis gas components hydrogen and carbon monoxide [2,3].

Therefore, stationary and transient kinetic experiments were performed with naphthalene as tar model compound on Mo/V/W-catalysts [4]. In the temperature range of interest Mo/V/W-mixed oxides show the required performance [5]. That way the total conversion of 2500 ppm naphthalene with an oxygen-feed of 3% ($L\,L^{-1}$) is already obtained at 425 °C. At the same time no conversion of CO and H_2, and, therefore no disturbance of the synthesis gas yield takes place. It turned out that the selective oxidation of the tar ingredients in crude synthesis gas on mixed oxide catalysts is a promising alternative for the tar removal in the required temperature range.

1. Introduction

In the near future the production of pure bio synthesis gas made out of biomass will be very important, since the availability and price of fossil raw materials (crude oil and gasoline) become more and more uncertain. This gas, produced from renewable energy sources, is applicable in various ways and therefore of great interest. That way it can be converted into hydrocarbons via Fischer–Tropsch:

$$CO + 2H_2 \rightarrow -(CH_2)- + H_2O$$

or into basic chemicals like methanol:

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O.$$

Bio synthesis gas is produced out of dry biomass, like straw or wood. With the help of pyrolysis, that means the thermal conversion in the absence of oxygen, a bio crude oil with a 20 times higher energy density is produced in the first step. Afterwards this liquid can be converted into crude bio synthesis gas via gasification. Thereby the exact gas composition depends on the process conditions (temperature, pressure), the gasification agent, the feedstock composition and the gasification technology (e.g. fluidized bed, fixed bed or circulating fluidized bed) [6]. However, this bio synthesis gas contains several impurities like nitrogen, halogens and sulfur components, as well as particles and tar. Tar mainly consists out of polycyclic aromatic components with a high boiling point. An efficient removal of these side products is essential, because tar condenses on moving parts, like gas turbines, so that they might block, break down and interrupt the continuous production. In addition to that tar leads to a catalyst deactivation by forming a coke layer on the catalyst surface [7]. For this reason the tar concentration is limited to special values. The present state of the art distinguishes between three tar removal strategies: physical, thermal and catalytic methods [2,8,9].

Physical methods involve filters and scrubbers, where the tar is separated in a condensed form. However, a great disadvantage of this strategy is that the crude synthesis gas needs to be cooled down before the final separation. Furthermore a huge amount of waste water is produced. In addition to that tar can be removed thermally. Thereby temperature from over 1000 °C is required to remove the undesired components completely.

From an economic and technical point of view the catalytic process therefore is a promising alternative. Great advantage of this

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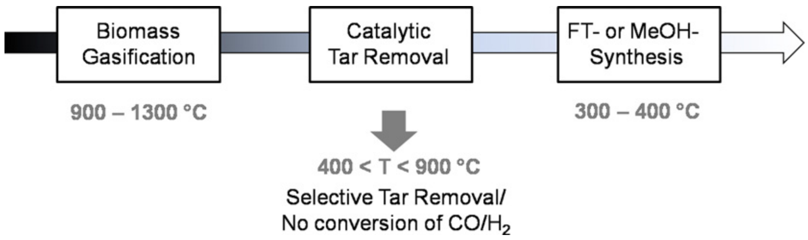

Fig. 1. Catalytic tar removal strategy.

strategy is that a high degree of purity can be achieved at low temperature and simultaneous increase of the fuel value. Depending on the experimental conditions, catalytic methods can be classified into reforming, cracking, hydrogenation and selective oxidation.

To meet the demands of an energy efficient process, a tar removal strategy in the temperature range from 350 to 700 °C is desirable. This temperature-range results from both, the outlet temperature of the gasification process (900–1300 °C) and the operating temperature of the following steps, like Fischer–Tropsch (300–400 °C), in a way that the strategies for tar removal strategies are highly restricted. A tar removal strategy without the already mentioned problems which fulfills the requirements is the catalytic partial oxidation [2]. The addition of a small amount of oxygen (stoichiometric towards tar) causes an efficient tar reduction to a fuel gas based on CO/H_2. A special challenge is indeed the choice of the catalyst, since the tar needs to be removed without oxidizing the synthesis gas components. The general strategy is shown in Fig. 1.

One main topic of our research group is the partial oxidation of aldehydes to carboxylic acids on transition metal mixed oxides [10]. Especially spray-dried Mo/V/W-mixed oxides are qualified for the selective oxidation since they operate like a sponge for molecular oxygen: Oxygen is stored in the bulk and remains available for the selective oxidation of organic substrates. Focusing on the main components of the catalyst (Mo/V/W) the system is very complex and needs to be reduced to understand the entire catalytic process. For the oxidation of acrolein to acrylic acid, MoO_3 has proved to be inactive, V_2O_5 is active but unselective and WO_3 is inert [11]. Mixed metal oxides based on both elements V and Mo show activity and selectivity. In this context structure types like Mo_3Vo_{11} and Mo_4VO_{11} are discussed to be the active and selective phases [12,13].

It is known that amorphous and defect parts are essential for the partial oxidation which can be influenced by the formal metal ratio, the preparation, drying and calcinations process. This has extensively been described in previous work [10]. In a ternary V-Mo mixed oxide, the metastable structures are not stable at higher temperatures. Calcination leads to phase transitions and amorphous parts are converted into crystalline parts. The addition of W, even in small amounts has a establishing influence, in a way that amorphous parts are not converted into crystalline parts during calcination [11]. Therefore the mixed oxide catalyst retains its activity.

This industrially used mixed metal oxide catalyst offers excellent activity and selectivity for the partial oxidation of acrolein. On the other hand, referring to the biomass gasification, the synthesis gas components CO/H_2 are hardly oxidized in the presence of oxygen. The application of this knowledge to our problem turned out to be a full success. In previous work it turned out that these mixed oxide catalysts affect acrolein 10 times stronger than CO and H_2 in temperature programmed reactions [16].

2. Proceeding

With the help of the tar model component naphthalene the general applicability of mixed oxides as tar removal catalysts was examined. To exclude the undesired oxidation of the synthesis gas components experiments with CO/H_2 were conducted in a TG/DTA-apparatus. In addition to that quantitative, transient and stationary kinetic experiments were performed in a tubular reactor. Objective of these analysis were the detailed description of the surface reactions. Besides the total oxidation these reactions also include the partial oxidation of naphthalene (NA) to naphthochinone, phthalic acid (PAA) and maleic acid anhydride (MAA) which are shown in the following scheme (Fig. 2).

Naphthalene is supposed to undergo several reactions on the mixed oxide catalyst. Possible pathways are the total oxidation directly to CO_2 and H_2O or the oxidation to intermediate oxygenates.

3. Experimental

All experiments were performed under continuous flow (overall volume flow 100 mL min^{-1}, standard conditions) and at ambient pressure. The reaction gas mixtures were balanced with argon. As model reactions the oxidation of hydrogen to water and carbon monoxide to carbon dioxide and the total oxidation of naphthalene were investigated. Previous to each TP-reaction a pre-treatment was carried out with the intent to bring the catalyst to a definite starting point. After pre-treatment, TP-reactions were realized in a temperature range from 100 to 580 °C.

The experimental set-ups consist of three main parts: a gas dosing unit, the reactor (TG/DTA-apparatus or tubular reactor) and the analytical apparatus. The gas dosing was carried out by mass flow controllers (Bronkhorst) and two-stage saturators for the addition of liquid and solid components.

3.1. TG/DTA analyzer

Thermal analysis is conducted in a thermal gravimetric analyzer (Netzsch, STA 449 C) coupled with a mass spectrometer. During thermal analysis, where mass changes (TG-signal) as well as the activity (DTA-signal) of the catalyst could be measured, educts and products are determined directly via MS. A schematic picture of

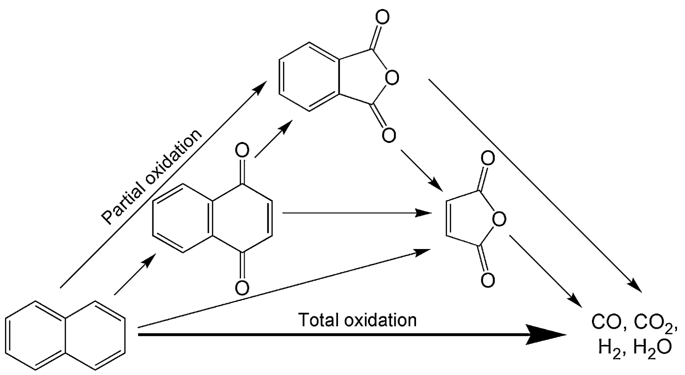

Fig. 2. Schematic description of the reaction scheme of the naphthalene oxidation.

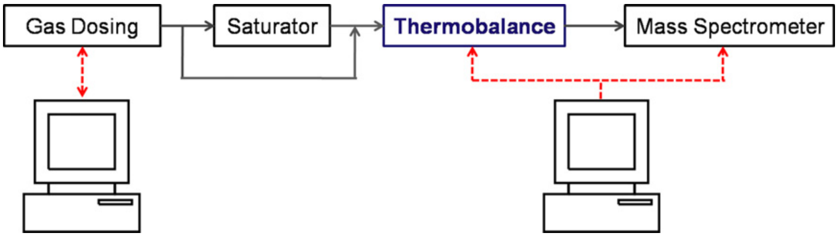

Fig. 3. Scheme of the TG/DTA set-up including the gas unit, the micro balance and the analytics.

every single unit of the TG/DTA set-up is shown in Fig. 3. A detailed description of the apparatus has been described in previous work [14].

The micro balance forms the analytic part of the set-up. 50 mg of the catalyst was placed in an aluminum crucible (5 mm diameter, 2.5 mm depth) which was set on the sample holder. The gas stream that flows through the micro balance can be analyzed with a quadrupole mass spectrometer (InProcess Instruments, GAM 400) afterwards. The control of both the thermo balance and the mass spectrometer as well as the recording of the data is implemented in a software routine.

3.2. Tubular reactor

The measurements were carried out on an apparatus (Fig. 4), which allows fully automatic changes in the applied gas mixtures of quantitative stationary and transient experiments during the naphthalene oxidation on mixed oxide catalysts. The set-up consists of several parts. The gas dosing system, an arrangement of several mass flow controllers and two-stage gas saturators, allows a flexible dosing of gaseous, liquid and solid components. A quartz tube serves as reactor in which the catalyst is fixed between two stoppers of quartz wool. On-line analysis of the gaseous components at the reactor outlet has been performed by a quadrupole mass spectrometer (Pfeiffer Vakuum Typ Omnistar GSD 301 O_2). Before the actual measurement an extensive calibration with each component has been carried out. The calibration itself is based on a complex matrix involving the dependencies between the ion currents and the gas concentrations as well as the fact that some components have peaks at the same mass number.

The reactor (see Fig. 5) consists of a replaceable tube, narrowed at the end and made out of quartz glass (external diameter 10 mm, inner diameter 8 mm). In this reactor the catalyst is retained by quartz wool. The sample thermo-couple was placed marginally above the catalyst. The reactor is placed in a copper heating block. This heating block can be separated vertically into two halves and heating cartridges (Type S/HS/T-10/130/400/230-C, Heinz Stegmeier) with integrated K-type thermo couples can be inserted. The supplementary isolation of this heating unit is made out of ceramic material (Gossler Thermal Ceramics).

With the help of the tube fitting, shown in Fig. 5 the gas-tight connection between the reactor and the 1/8 in. stainless steel pipe is provided.

Educts (NA, PAA, MAA, O_2) and inert gas (Ar) are supplied into the reactor by mass flow controllers (Bronkhorst). Two identical saturators, arranged in series (Fig. 6), enable reproducible load of the inert gas flow with liquid (MAA, PAA, H_2O) and solid (naphthalene) components.

Saturator systems consist of multiple-walled, temperature controlled glass vessels (hold-up = 100 mL). Inert gas is passed into the glass vessels which contain the liquid by means of a 1/8 in. glass tube that reaches nearly to the bottom. To facilitate the dispersion of the bubbles, so that smaller bubbles are formed, the liquid is stirred with the help of a magnetic stirrer (Fa. IKA Typ Color Squid). Thereby the exchange at the gas/liquid interface increase both on the bubbles and on the liquid film. The first vessel operates at a higher temperature, enriching the gas phase with the desired component. The concentration is adjustable with the aid of the vapor pressure curve by varying the lower temperature in the second vessel. In order to avoid undesired condensation effects all supply and exhausting tubes are heated electrically (160 °C).

3.3. Catalyst

3.3.1. Preparation

The following catalyst with the general formula $Mo_8V_2W_1O_x$ was prepared following the preparation strategy developed by Kunert. Details have been described in previous works [15,16]. An aqueous solution containing ammonium heptamolybdate, metavanadate and metatungstate, according to the desired metal ratio of the solid catalyst, is boiled under reflux for 90 min. The solution is directly used for spray-drying. Spray-drying was performed in a self-constructed apparatus. In this way a dry powder catalyst precursor is continuously produced that fulfills high quality demands concerning reproducibility, particle size distribution and homogeneity. The spray dried precursors are subjected to a calcination procedure under nitrogen. This is conducted in a self-constructed calcination station (muffle furnace, Heraeus).

3.3.2. Characterization

XRD: X-ray measurements were recorded by Bragg-Brentano geometry (Siemens, D500), equipped with a scintillation counter detector. Monochromatic (graphite secondary monochromator) Cu Kα radiation was used.

SEM: SEM was conducted with a high-resolution microscope, Philips XL 30 FEG. It features a SE and BSE, as well as an EDX-detector for element analysis.

Detailed information, as well as XRD pattern and SEM images were already presented in previous work [14].

XRD pattern shows that spray dried Mo/V/W-mixed oxides are X-ray amorphous precursor materials. This structure shaping mainly influences the activity of this precursor compared to crystalline samples. SEM images confirm these observations and exemplify that spray-drying leads to spherical, smooth particles where no distinct surface features can be seen. Furthermore, the powder is characterized by narrow particle size distribution. The mean diameter is about 1 μm. In addition to that BET experiments revealed that spray dried particles exhibit a small specific surface area of about 2 $m^2 g^{-1}$.

3.4. TP-reactions

Temperature programmed reactions are suitable to characterize the catalyst performance [15]. Conversion, selectivity and yield were calculated starting from the measured volume fractions. 50 mg (TG/DTA-apparature) to 1.5 g (tubular reactor) mixed

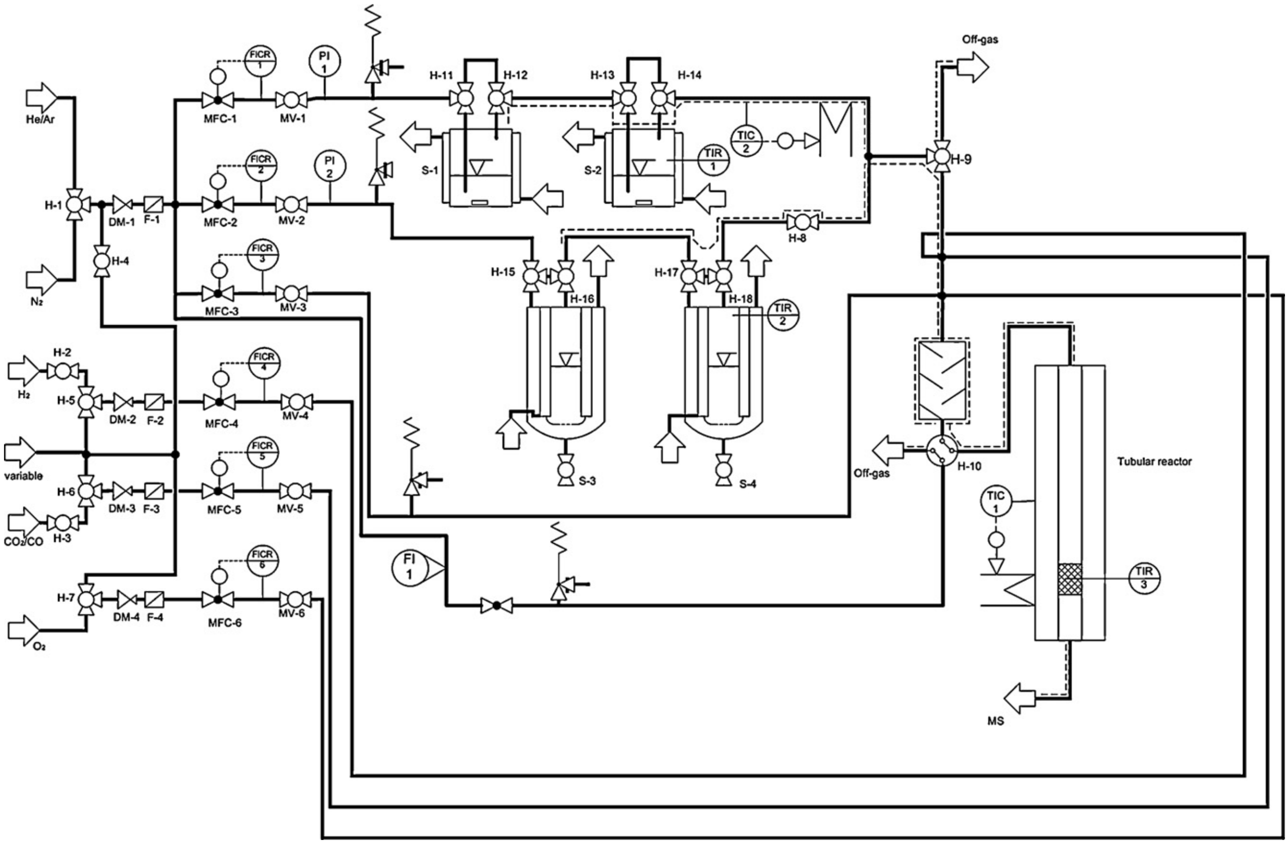

Fig. 4. Flow sheet of the aperture including the gas unit and the reactor.

oxide powder was employed. The calcined catalyst undergoes an oxidative pre-treatment (400 °C, 5% oxygen ($L\,L^{-1}$) in Ar, 60 min). Subsequently, several consecutive temperature programmed reactions, each followed by a re-oxidation were carried out. In the case of the TP-reduction in the TG/DTA-apparatus two cycles and during TP-reactions in the tubular reactor three cycles were conducted.

In TP-reactions with naphthalene oxygen was used in stoichiometric amounts, since we expect full conversion of the tar model compound to CO/H_2. Besides the residual time, as well as the feed concentration needs to be published in further works.

Fig. 7 shows the characteristics of such a temperature programmed experiment. Repeating the procedure like this, allows judging the activating and deactivating processes as well as long-term stability. Alternatively a long-term stationary pre-treatment under reaction gas atmosphere at constant temperature would be necessary.

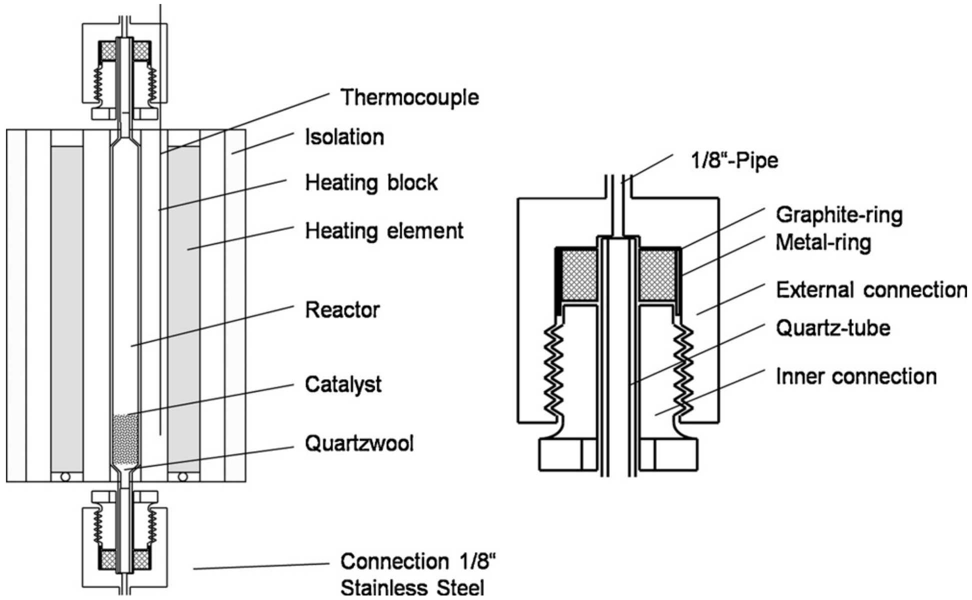

Fig. 5. Schematic drawing of the tubular reactor for the investigation of the oxidation of naphthalene via TP-reactions and the tube fitting.

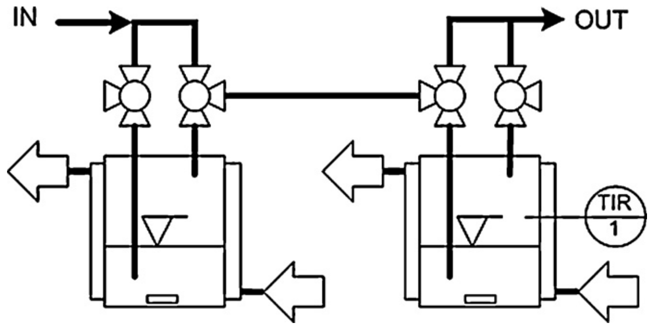

Fig. 6. Two-stage saturator for naphthalene. The volume fraction of naphthalene is adjusted by the temperature in the 2nd stage.

4. Results

4.1. Temperature programmed reduction of $Mo_8V_2W_1O_x$ through H_2, CO and $C_{10}H_8$

The differential thermal gravimetric analyzer was used as a reactor to investigate the activity of the synthesis gas components hydrogen, carbon monoxide and the tar model compound naphthalene on $Mo_8V_2W_1O_x$ to get information about the potential of this mixed oxide to be used as tar removal catalyst. While connecting the reactor directly to the mass spectrometer it is possible to detect the volume fraction of every single. In order to see if significant deactivation processes, caused by the removal and insertion of oxygen take place, two cycles consisting of oxidation and reduction are performed.

As one can see in Fig. 8 the reduction of the mixed oxide in the presence of the synthesis gas component hydrogen starts at 250 °C. At 580 °C the mass loss is about 1.8%. A comparison with CO shows that no mass change caused by reduction takes place. Also the corresponding DTA-signal shows no heat of reaction, in a way that significant reduction processes on the catalyst can be excluded.

During the temperature programmed reduction with naphthalene as reducing agent a significant reduction of the mixed oxides takes place. Beginning at 250 °C the catalyst is already reduced to a small extent. At around 450 °C the reduction starts to accelerate significantly and flatten again at 515 °C. At the end of the temperature range the mass loss is about 8.4%. As one see at both, the TG- and the DTA-signal, there is no overlapping of reduction processes. A comparison of these results with the reduction activity of CO/H_2 towards the Mo/V/W-oxides shows, that naphthalene is a much stronger reduction agent, even though the concentration of the synthesis gas components is 20 times higher.

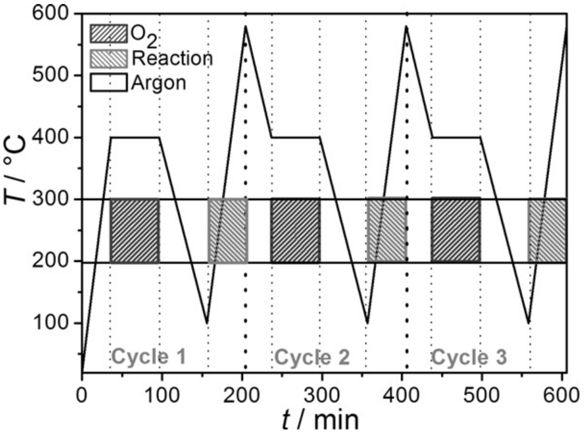

Fig. 7. Schematic diagram of the temperature program and the gas composition during TP-measurements.

Summing up it should be pointed out, that the Mo/V/W-mixed oxide is a proper catalyst for the investigation of the selective, catalytic oxidation of tar components, because:It is reduced to a much higher extent through the tar component naphthalene than through the synthesis gas components CO/H_2.No irreversible structure changes, caused by the release of oxygen, occur in such a way that no deactivation processes on the catalyst take place.Regarding the temperature programmed reduction of Mo/V/W-mixed oxides by the use of naphthalene no loss in activity is observed during the process. After activating the catalyst in the first cycle (Fig. 7) the mixed oxide remains its starting activity.

4.2. Temperature programmed reaction of hydrogen, carbon monoxide and naphthalene with oxygen on $Mo_8V_2W_1O_x$ in the tubular reactor

With the help of blind measurements that means in the absence of catalyst it was first investigated if in the temperature range of interest a non-catalytic oxidation of the synthesis gas components or naphthalene takes place (Fig. 9). These results help to explain the characteristics of the following experiments on the mixed-oxides in a way that new effects can only be referred to the catalytic process.

Regarding Fig. 9 it turns out, that hydrogen and carbon monoxide are not oxidized in the regarded temperature range (a) and (b). Starting at 480 °C, in the presence of naphthalene, carbon dioxide is formed to a small degree (c). While dosing a mixture of these three components, besides carbon monoxide, water is detected as well at about 400 °C. However, the hydrogen concentration does not change. Summing up, these experiments point out that in the relevant temperature range no oxidation of the synthesis gas components and naphthalene takes place. Only a thermal decomposition of the tar model compound is detected, but no stoichiometric reaction.

For a quantitative description of the applicability of Mo/V/W-mixed oxide in the catalytic tar removal process it should be first investigated to what extent these components (CO, H_2 and $C_{10}H_6$) are converted in the presence of oxygen on this catalyst. Fig. 10 shows the X(T)-diagram of the oxidation of the synthesis gas components on different amounts of $Mo_8V_2W_1O_x$.

In both cases the oxidation of the synthesis gas components starts at about 425 °C and increase significantly with higher temperature. At 560 °C and 1 g catalyst about 11% hydrogen and 2% carbon monoxide are converted on the mixed oxide. Increasing the catalyst weight leads to a proportional increase in conversion as it could also be seen in Fig. 10. Based on these experiments it turned out that carbon monoxide is oxidized significantly less, compared to hydrogen. To avoid the interaction of the synthesis gas composition with regard to CO/H_2, it is therefore necessary to restrict the temperature of the tar removal process below 500 °C when 1.5 g of catalyst is used. In this range the hydrogen conversion remains below 5% so that the previously mentioned requirements for the catalytic tar removal strategy are adhered.

The analysis of the reaction behavior of the mixed oxides in the catalytic oxidation of naphthalene as tar model compound are carried out according to the already discussed oxidation of the syntheses gas components in the tubular reactor. The volume fractions of every single compound are shown in Fig. 11.

Looking at the spectra of the temperature programmed reaction it can be noticed that the oxidation of naphthalene starts slightly at around 250 °C. Total conversion is achieved at 415 °C. At the same time the formation of MA reaches its maxima at 450 °C and remains almost constant until 530 °C. Starting at this temperature the volume-fractions of the intermediate anhydrides begin to decrease slightly. However, this observation cannot be referred

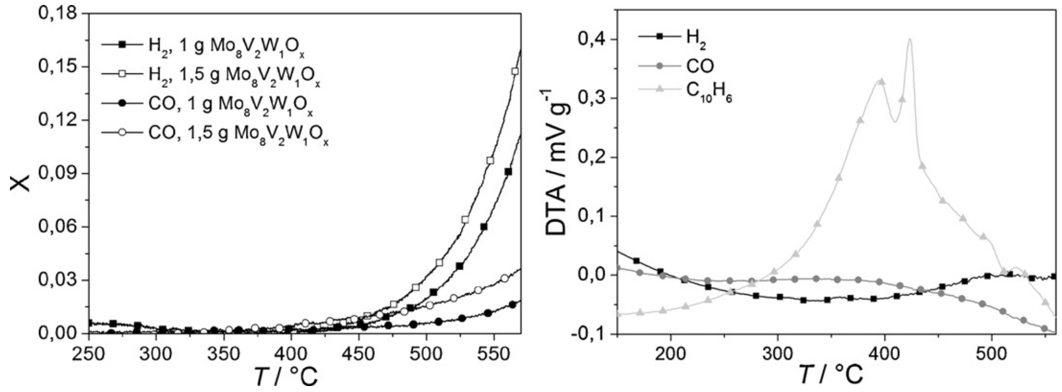

Fig. 8. Temperature programmed reduction on $Mo_8V_2W_1O_x$, weight of catalyst: 30 mg, volume-flow 100 mL min^{-1}, 5% (L L^{-1}) H_2,CO, 0.25 (L L^{-1}) % $C_{10}H_8$ in Ar; heating rate: 10 K min^{-1}.

to the onset of the total oxidation, because the volume-fractions of the total oxidation products CO_2 and H_2O, as well as the oxygen uptake, do not change in the expected, stoichiometric extend. So these characteristics rather indicate a thermal decomposition or a coking process, than a catalytic oxidation of the acidic anhydrides. This can be confirmed by the oxidation of MAA in an empty tube, see Fig. 12.

Referring to this experiment it turned out that MA tend towards coking, because the formation of carbon dioxide starts to decrease at around 370 °C, while simultaneously the oxygen uptake remains at a constant level. In addition to that an even in acetone hardly soluble residue is formed on the reactor wall. Consequently the previous discussed observations (Fig. 11) can be referred to a coking process instead of a catalytic oxidation of the adsorbed species.

These just mentioned characteristics, the total oxidation of naphthalene and the formation of intermediate products are also detected in stationary experiments. Fig. 13 shows the conversion of H_2 and NA and the selectivity towards PAA during the catalytic tar removal in presence of the synthesis gas components.Based on this stationary experiment the reaction process can be divided into three parts:

- From 150 to 400 °C (part I) naphthalene is converted partially.
- Mainly full conversion is achieved in the second division at 420 °C. However, at the same time a remarkable selectivity of around 40% towards the undesired intermediate PAA is observed. Hydrogen conversion starts to a low extend at about 470 °C.

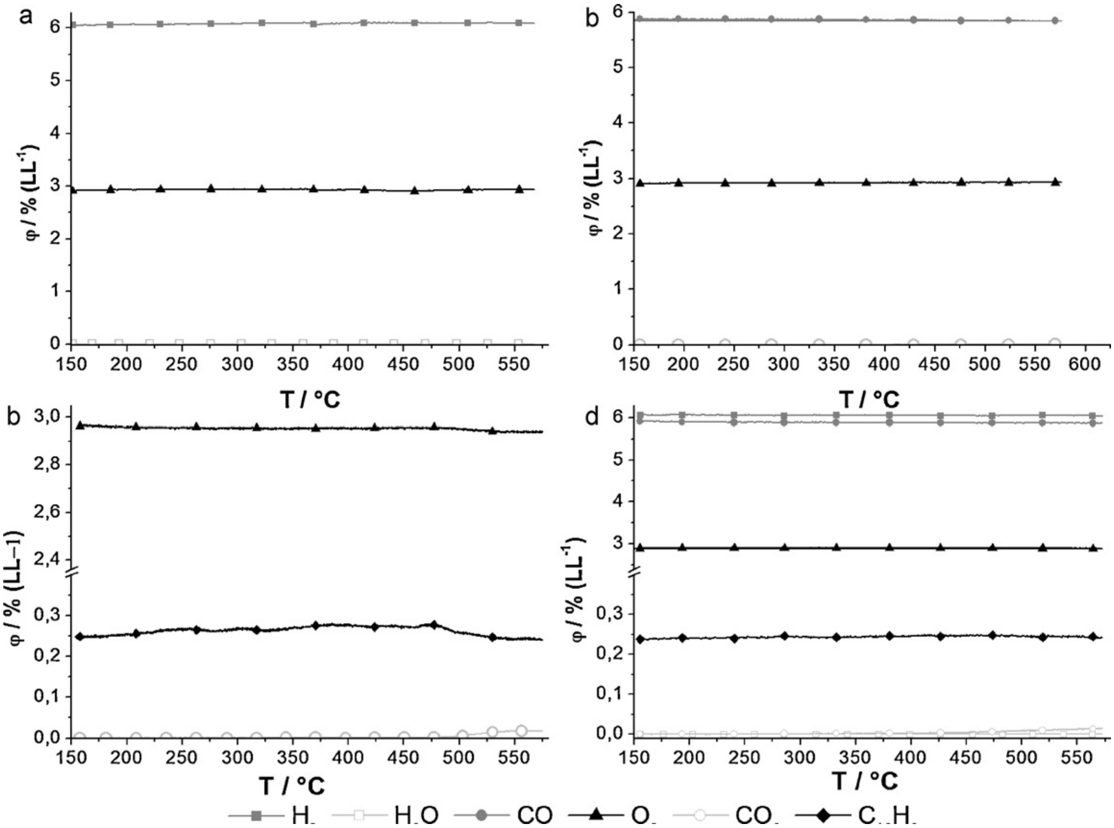

Fig. 9. Empty tube experiments, volume-flow 100 mL min^{-1}, 3% (L L^{-1}) O_2 and (a) 6% (L L^{-1}) H_2, (b) 6% (L L^{-1}) CO, (c) 0.25% (L L^{-1}) $C_{10}H_8$, (d) 6% (L L^{-1}) H_2, 6% (L L^{-1}) CO and 0.25% (L L^{-1}) $C_{10}H_8$ in Ar, heating rate: 10 K min^{-1}.

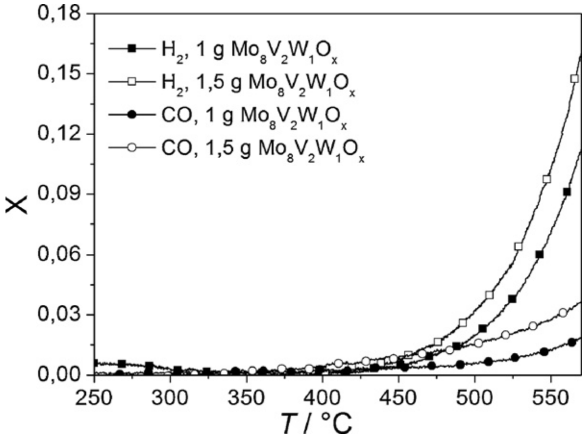

Fig. 10. Conversion-degree of H_2/CO depending on the amount of catalyst, 1 g and 1.5 g $Mo_8V_2W_1O_x$, volume-flow 100 mL min^{-1}, 6% CO, 3% O_2 in Ar, heating rate: 5 K min^{-1}.

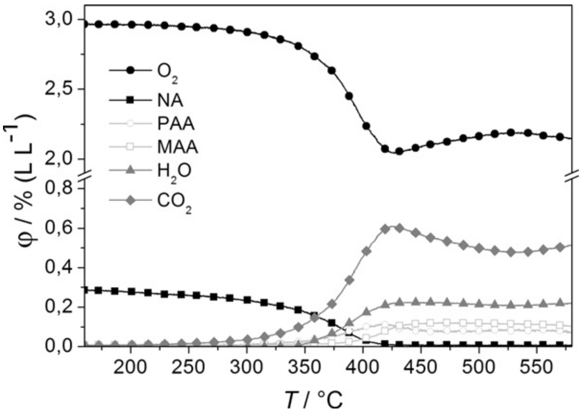

Fig. 11. Temperature programmed reaction of naphthalene and O_2 on $Mo_8V_2W_1O_x$, weight of catalyst: 1.5 g, volume-flow 100 mL min^{-1}, 3% (L L^{-1}) O_2, 0.25% (L L^{-1}) $C_{10}H_8$ in Ar, heating rate: 5 K min^{-1}.

- In section III, at about 500 °C, the selectivity towards PA decreases. However, the conversion of hydrogen increases strongly, in a way that the requirements for the catalytic tar removal are not fulfilled.

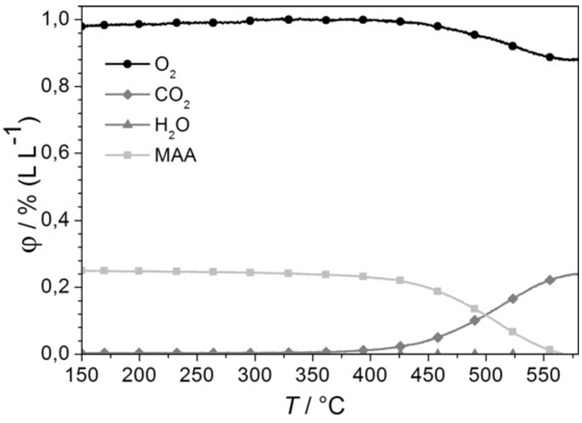

Fig. 12. Empty tube experiments with maleic acid anhydride, volume flow 100 mL min^{-1}, 0.25% (L L^{-1}) MAA, 1% (L L^{-1}) O_2 in Ar, heating rate: 10 K min^{-1}.

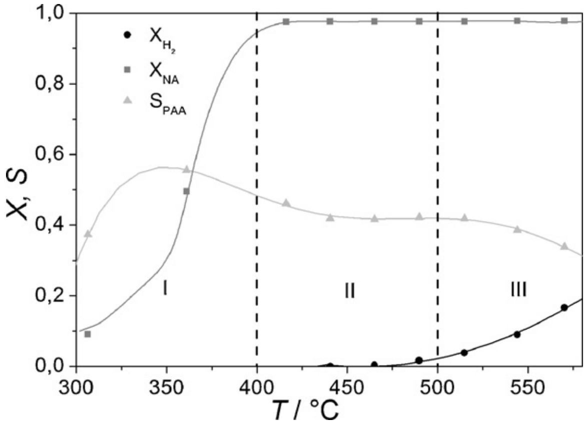

Fig. 13. Conversion of $C_{10}H_8$ and H_2 as well as the selectivity towards PAA in presence of H_2 and CO on $Mo_8V_2W_1O_x$, weight of catalyst: 1.5 g, stationary reaction conditions, volume-flow 100 mL min^{-1}, 0.25% (L L^{-1}) $C_{10}H_8$, 3% (L L^{-1}) O_2, 6% (L L^{-1}) CO, 6% (L L^{-1}) H_2 in Ar, heating rate: 5 K min^{-1}.

5. Conclusions

The focus of this work is the investigation of the tar removal from bio synthesis gas through catalytic oxidation on Mo/V/W-mixed oxides in the temperature range from 250 to 700 °C.

Referring to the TG/DTA-experiments it could be proofed that the Mo/V/W-catalyst shows different activities towards the reduction with CO/H_2 and the tar model compound. During the temperature programmed reaction with CO no detectable mass loss occurs and only an increase of 1.8% in the presence of hydrogen at 580 °C is detected. In contrast to that, the degree of reduction while using naphthalene as reducing agent is about 4.7 times higher. So we can point out, that the Mo/V/W-mixed oxide is generally applicable for the catalytic tar removal in synthesis gas atmosphere, because naphthalene shows a much higher activity than the synthesis gas components towards $Mo_8V_2W_1O_x$.

Based on these results a quantitative analysis of the catalytic performance is conducted in the tubular reactor. These experiments allow specifying the temperature range, appropriate for the tar removal. It turned out, that the catalytic tar removal in synthesis gas atmosphere should be limited to a temperature below 500 °C, so that CO and H_2 are not converted.

Regarding the oxidation of naphthalene, full conversion is achieved at a temperature from about 410 °C. However, not only the products of the total oxidation CO_2 and H_2O, but also the intermediate oxygenates PAA and MAA, are formed.

For this reason Mo/V/W-mixed oxides can generally be used for the catalytic tar removal via oxidation in synthesis gas atmosphere, because until 500 °C naphthalene is fully converted. At the same time the conversion of CO and H_2 is negligible. However, the product distribution of the catalytic naphthalene oxidation needs to be optimized, because the intermediates PAA and MAA desorb from the catalyst surface and are existent in gaseous phase as stable products.

Consequently a modification should be considered, with the objective to prevent desorption of the intermediate anhydrides, so that the oxidation of these compounds is facilitated. A promising modification could be the application of basic centers on the catalyst surface, in a way that this variation might prevent desorption of PAA and MAA, because of the strong acid–base interaction. The acidic intermediate is supposed to stay adsorbed on the catalyst, so that the oxidation is facilitated significantly, since it is less stable than the anhydride. This approach will be approved in further works.

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