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Steam reforming of model gasification tars compounds on nickel based ceria-zirconia catalysts

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ABSTRACT

Gasification tars, leading to various process equipment problems, are undesirable products during coal and biomass gasification; therefore, catalysts for their decomposition are needed. Toluene and 1-methylnapthalene, as a model tar compounds, were tested in steam reforming reaction using ceria-zirconia based Ni catalysts.

1. Introduction

During high- and medium-temperature gasification of coal or biomass, beside H_2 and CO, undesirable products as tar aerosols are formed. Such impurities cause attrition in fluidized bed reactors or chocking, increasing the total cost and decreasing the efficiency of the process [1,2]. Tars are complex mixtures of various hydrocarbons with different reactivities. Their composition depends on the type of gasified materials and gasification conditions. Table 1 reports the compositions of coal and biomass tars [3,4]. Presented constitution of biomass tar is typical for lignocellulosic material, whereas coal tars can have very different properties, even when the samples were obtained from the same manufactured gas plant site. Therefore in Table 1, there is an example composition of coal tar demonstrated.

Tar treatment inside the gasifier by catalytic steam reforming (SR) may eliminate the need for downstream cleanup. Tar steam reforming leads to CO and H_2, enriching gas from biomass or coal gasification in these components [5–7]. Metals (such as Ni, Pt, Pd) supported on ceria-zirconia, have been found to be very promising catalysts in reforming reactions. Ceria-zirconia is known from its high OSC, thermal stability and very good redox properties. The great benefit of $Ce_xZr_{1-x}O_2$ (CZ) is its high resistance for carbon deposition [8–13].

Due to current requests in the field of energetic and the need for renewable energy sources applications, we focused our research on finding active catalysts for biomass and coal tar decomposition. Results of toluene steam reforming on nickel and cobalt based ceria-zirconia catalysts have been presented in our previous paper [14]. The goal of the present work was to compare the activity of Ni(x wt%)/$CeZrO_2$ catalysts in steam reforming reaction of two model tar compounds: toluene and 1-methylnapthalene. Selection of these specified hydrocarbons was based on their occurrence in tars and their different reactivity. We also proposed a kinetic pathway for steam reforming reaction on Ni/CZ catalysts based on our experimental results.

2. Experimental

Preparation, characterization of supported nickel on ceria-zirconia catalysts and methodology of temperature programmed surface reaction (TPSR) of toluene steam reforming were described in our previous paper [14]. TPSR experiments were carried out only for toluene steam reforming reaction, while catalytic tests in stationary conditions were performed for toluene and 1-methylnaphthalene. Both kinds of experiments were carried out at steam to carbon ratio (S/C) equal 2.4, with GHSV of 10,000 h^{-1}, and a total flow rate of 250 mL/min. The temperature programmed regeneration of spent catalyst was carried in 4.2 vol% of O_2 in Ar, with the heating rate of 5 °C/min. In all cases, the catalyst bed of 1 cm high was placed in the quartz reactor of 1.5 cm diameter.

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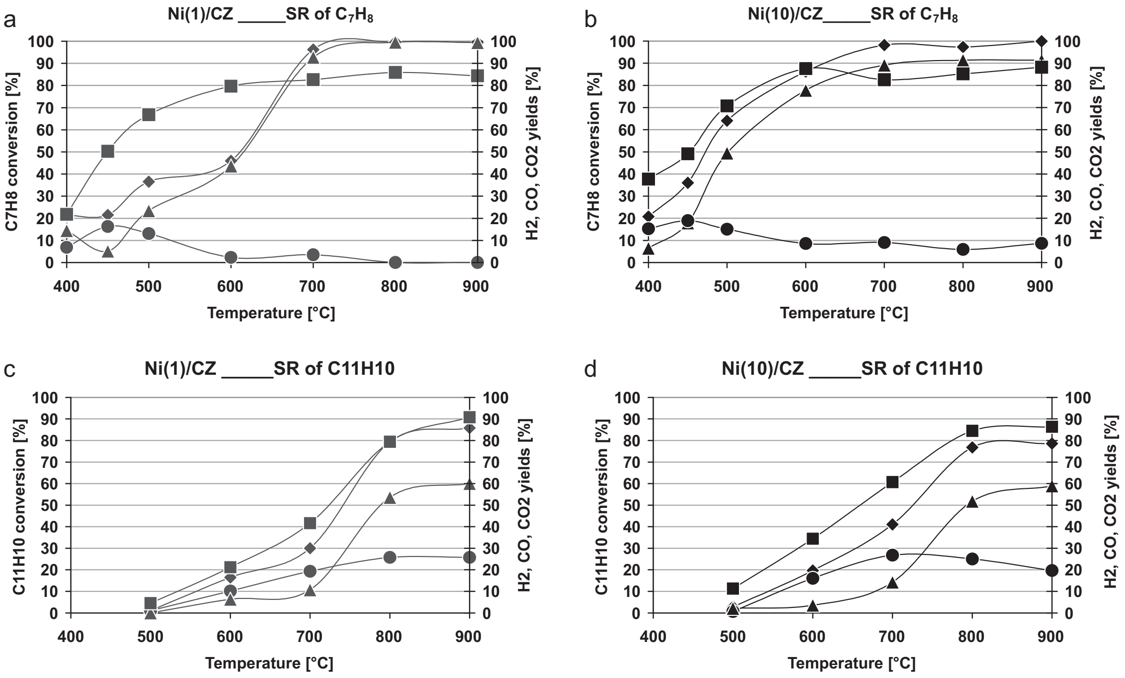

Fig. 1. Hydrocarbon conversion (♦) and yields of the products: H_2 (■), CO (▲) and CO_2 (●) during catalytic runs of toluene (a and b) and 1-methylnapthalene (c and d) steam reforming reaction in stationary conditions, for 1Ni/CZ (a and c) and 10Ni/CZ (b and d).

Table 1
Compositions of biomass and coal tars.

Tars compounds	Biomass [3] (wt%)	Coal [4] (mg/kg)
Benzene	37.9	3390
Toluene	14.3	11900
Other one-ring aromatic hydrocarbons	13.9	1990–7480
Naphthalene	9.6	35700
Other two-ring aromatic hydrocarbons	7.8	1880
Three-ring aromatic hydrocarbons	3.6	4600
Four-ring aromatic hydrocarbons	0.8	5190
Other	12.1	–

The formulas used to calculate conversion of model tar compounds and yields of CO, CO_2 and H_2 are given below. The conversion of toluene and 1-methylnaphthalene was calculated considering only CO and CO_2 concentrations in the outlet of the reactor. For the calculation of hydrogen yield, the total H_2 in the feed (coming from HC and the excess of H_2O) was taken into account.

$$HC_{conversion} = \frac{C_{out}}{C_{in}} \times 100\%$$

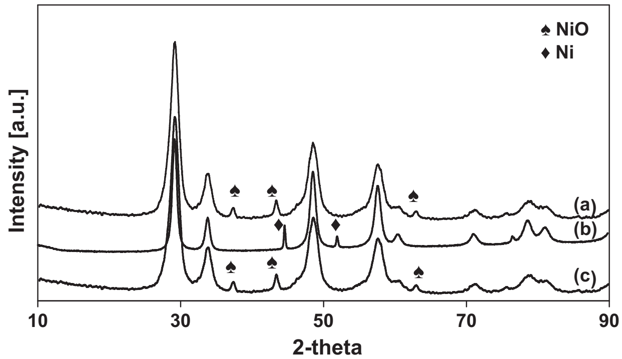

Fig. 2. XRD patterns of 10Ni/CZ: (a) after synthesis; (b) after SR of toluene at 800 °C; (c) after regeneration.

$$CO_{yield} = \frac{CO_{out}}{C_{in}} \times 100\%$$

$$CO_2 = \frac{CO_2}{C_{in}} \times 100\%$$

$$H_2 = \frac{H_2}{H_2} \times 100\%$$

$$C_{in} = n \times [C_nH_m]_{in}$$

$$[H_2]_{in} = [H_2O]_{in} + \frac{m}{2} \times [C_nH_m]_{in}$$

3. Results and discussion

Results of XRD analysis and TPR experiments were presented in our previous paper [14]. XRD characterisation revealed the presence of nickel oxide on ceria-zirconia, whereas H_2-TPR shown two temperature regions for the reduction of NiO to Ni^0.

Temperature programmed surface reaction of steam reforming of toluene enabled us to determine the temperature domain of steam reforming reaction and led us to exclude the less active catalysts. It was noticed that steam reforming of toluene on ceria-zirconia alone started from 550 °C, while it was shifted to lower temperatures by 50 and 100 °C for 1Ni/CZ and 10Ni/CZ, respectively. As observed on CZ, toluene consumption on Ni/CZ was drastic. A detailed description of TPSR experiments was presented in our previous paper [14].

The effects of metal loading and temperature on conversion of model tar compounds and product yields for Ni/CZ are shown in Fig. 1. Conversion of C_7H_8 increases with temperature as expected (Fig. 1a and b). Toluene is almost completely decomposed above 700 °C on both nickel catalysts, but its conversion to CO and CO_2 up to 700 °C is over twice higher for 10Ni/CZ. The difference in activity at low temperatures is determined mainly by CO production, which is much lower for 1Ni/CZ. Nevertheless this catalyst reveals also

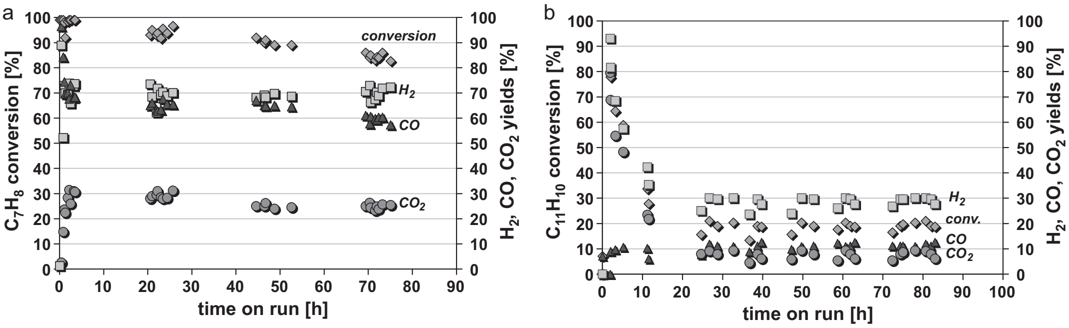

Fig. 3. Durability test of (a) toluene and (b) 1-MN steam reforming on 10Ni/CZ at 700 °C: conversion of HC to CO and CO_2 (♦), H_2 yield (■)), CO yield (▲), CO_2 yield (●).

higher production of CO_2. Hydrogen formation for both nickel catalysts exhibits similar values from 450 °C (50% yield). Above 600 °C its yield remains at a level of 80–85%.

Steam reforming of 1-methylnapthalene starts at 500 °C (Fig. 1c and d). There are no significant differences in $C_{11}H_{10}$ conversion and product yields between 1Ni/CZ and 10Ni/CZ in the whole temperature range but high loaded catalyst is a little bit more active. As a distinct from toluene steam reforming, CO_2 formation is very high at high temperatures. Conversion of 1-MN increases linearly up to 800 °C, and stabilizes at a level of 80%. Supported NiO on ceria-zirconia is reduced to Ni^0 at the beginning of catalytic runs at high temperature (for toluene and 1-MN steam reforming), as shown on XRD patterns after SR runs (Fig. 2a and b).

The major reaction taking place on catalyst surface is steam reforming, according to global reactions (1) and (2):

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \quad (1)$$

$$C_{11}H_{10} + 11H_2O \rightarrow 11CO + 16H_2 \quad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

The H_2/CO ratios for steam reforming reaction of toluene and 1-MN is equal to 1.54 and 1.45 respectively. The higher values of H_2/CO – shown in Table 2 – indicate that a fraction of CO produced by the SR reaction can react with H_2O, according to the water gas shift (WGS) reaction (3), what explains the formation of CO_2 in the gas phase. It was noticed, that in the case of toluene and 1-MN steam reforming, WGS participation was decreasing with the temperature increase (Table 2) due to thermodynamics limitation.

In order to check the good resistance of selected catalysts to carbon deposition, as well as their stability, the most active among tested catalysts—10Ni/CZ, was submitted to a toluene SR in steady state experiment, decreasing the temperature by 100 K from 900 °C to 400 °C. The decreasing of the temperature allows to avoid misinterpretation caused by carbon deposition at low *T* and its gasification at higher *T*, what would enhance product yields. Moreover, starting the reaction of toluene steam reforming between 700 and 900 °C provides almost total decomposition of C_7H_8 and reduction of NiO to Ni^0. For the steady state experiments, two GHSVs were applied: 5,000 and 10,000 h^{-1}. Each isotherm was maintained for over 24 h. In the case of GHSV = 5,000 h^{-1}, no decrease of toluene conversion and H_2 yield was noticed between 500 and 900 °C. The decrease of toluene conversion (by 23 and 51% for GHSV = 5,000 and 10,000 h^{-1} respectively) was observed only at 400 °C. At this temperature, the hydrogen production decreased up to 10 and 20%, respectively, as expected taking into account the ratio of 2 between the two GHSV. Thus, it was found out that 10Ni/CZ is resistant to carbon deposition above 500 °C.

Table 2
H_2/CO ratios during toluene and 1-MN steam reforming on 1Ni/CZ and 10Ni/CZ.

T (°C)	Toluene		1-MN	
	1Ni/CZ	10Ni/CZ	1Ni/CZ	10Ni/CZ
400	4	16.6	–	–
450	28.2	7.9	–	–
500	8.3	4.1	0	15
600	5.3	3.2	7	27.5
700	2.6	2.7	11	12.1
800	2.5	2.7	3.5	4.7
900	2.5	2.8	4.6	4.2

10Ni/CZ was also subjected to the durability tests of steam reforming reaction for toluene and 1-MN. In the case of toluene steam reforming (Fig. 3a) the catalyst revealed slight decrease of hydrocarbon conversion and yields of CO and CO_2. After 75 h or test run, 85% of toluene was decomposed to CO and CO_2. Hydrogen production was almost constant during the whole durability test and averaged 70%. The formation of CO was predominant over CO_2 production, coming from WGS reaction. Thermogravimetric analysis in air revealed 1.5% lose of the sample mass at 530 °C. It was calculated that 0.56×10^{-3} g of carbon was deposited on catalyst surface per 1 g of reacted toluene.

A stability run during 80 h for 1-MN at 700 °C over 10Ni/CZ (Fig. 3b) exhibited a significant decrease of hydrocarbon conversion and syngas production during the first 20 h of run. Let's note that CO_2 formation was constant. Therefore, it can be assumed that some part of active centers has been blocked by carbon deposits resistant to H_2O treatment. Thermogravimetric analysis of such sample in air revealed 16% mass loss at 530 °C, indicating the presence of carbon deposits oxidized to CO_2. It was calculated that during durability test, 1 g of decomposed 1-MN resulted in the deposition of 56.9×10^{-3} g of carbon.

Deactivation by carbon formation on 10Ni/CZ at 800 °C was not so considerable. During 120 h of test run, conversion of 1-MN was decreasing linearly from 95% to 53%. The most probable reactions leading to carbon formation are: Boudouard reaction (4), multi-

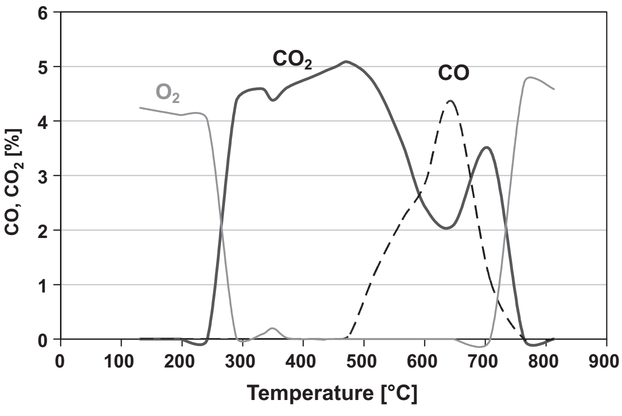

Fig. 4. Temperature programmed regeneration of 10Ni/CZ in flowing 4.2 vol% O_2/Ar.

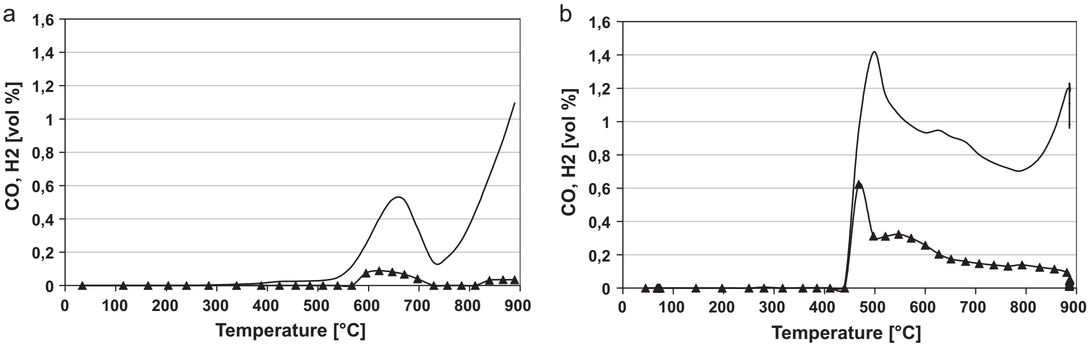

Fig. 5. TPSR of toluene decomposition on ceria-zirconia (a) and 10Ni/CZ (b), carried out in the absence of H_2O (–H_2, ▲CO).

level decomposition of 1-MN (5) and reduction of CO and CO_2 ((6) and (7)). Reaction (5) is privileged at high temperatures, while the other reactions can take place at lower temperatures [15,16]. Carbon deposition can be partially limited by the oxygen (O*) stored in ceria-zirconia (8).

$$2CO \leftrightarrow CO_2 + C \tag{4}$$

$$C_{11}H_{10} = 5H_2 + 11C \tag{5}$$

$$CO + H_2 = H_2O + C \tag{6}$$

$$CO_2 + H_2 = H_2O + C \tag{7}$$

$$C* + O* \rightarrow CO + 2* \tag{8}$$

Temperature programmed regeneration of 10Ni/CZ in 4.2 vol% O_2 in Ar is presented in Fig. 4. The total oxidation of carbon deposits starts at 280 °C and take place up to 470 °C. Then, some part of CO_2 reacts with carbon deposits forming CO. Such regeneration leads to complete re-oxidation of tested catalyst. XRD analysis after regeneration revealed the presence of NiO on catalysts surface (Fig. 2c).

Taking into account previous results, a catalytic sequence of steam reforming of model tar compounds, can be assumed on Ni^0 (symbolized by "*" hereafter). The first step of the SR catalytic sequence is the adsorption and multilevel dehydrogenation of hydrocarbon on Ni^0 active sites ((9) and (10)). It results in active, surface carbon (C*) formation, which is oxidized to CO* by oxygen (O*) (12) coming from H_2O dissociation on Ni^0 (11). After CO desorption to the gas phase (13), the active site "*" is regenerated and able to decompose another HC or H_2O molecule.

The WGS reaction runs in parallel to SR. Some part of CO may react with the active oxygen forming CO_2 (14). Hydrocarbon decomposition and dehydrogenation was proved by TPSR carried out in the absence of H_2O on the support and on 10Ni/CZ (Fig. 5). A high amount of oxygen stored in ceria-zirconia is able to decompose toluene to CO and H_2 from 565 and 460 °C on CZ and 10Ni/CZ respectively. Nevertheless, C_7H_8 dehydrogenation on CZ starts at 500 °C. It indicates that ceria-zirconia has a high ability to decompose toluene, but the addition of nickel significantly improves its activity. Moreover, this experiment reveals, that there are at least two kinds of active sites involved in hydrocarbon decomposition: active site on the support and Ni^0.

The ensemble of main reactions occurring on Ni^0 active sites can be summarized as follows, leading to HC decomposition to *C (active carbon), water dissociation leading to *O, with subsequent H_2 (from HC and water) and CO formations. The kinetic coupling of WGS with SR on *O intermediate species appears through reactions (11) for SR and (14) for WGS.

$$C_nH_m + (n+m)* = nC* + mH* \tag{9}$$

$$H* + H* \rightarrow H_2 + 2* \tag{10}$$

$$H_2O + * \rightarrow O* + H_2 \tag{11}$$

$$C* + O* \rightarrow CO* + * \tag{12}$$

$$CO* \rightarrow CO + * \tag{13}$$

$$CO + O* \rightarrow CO_2 + * \tag{14}$$

4. Conclusions

XRD analysis have shown that NiO is the initial form of supported nickel on ceria-zirconia. During catalytic runs of toluene and 1-MN steam reforming, NiO is reduced to Ni^0. The active sites for SR on Ni/CZ is Ni^0.

TPSR experiments of both model tar compounds revealed very good activity of Ni/CZ for toluene decomposition and poorer for 1-MN. Nevertheless, a simultaneous SR reaction on Ni/CZ for both C_7H_8 and $C_{11}H_{10}$ may proceed above 500 °C.

The optimal temperature for SR of tested hydrocarbons is 800 °C. This temperature prevents deactivation of 10Ni/CZ due to the suppression of carbon deposits by H_2O and CO_2. Running SR process at 800 °C provides 99% conversion of toluene and 80% conversion of 1-MN.

Catalyst regeneration after SR carried in O_2 leads to complete re-oxidation of Ni^0 to NiO. Carbon deposits formed at 400 °C in the case of toluene SR and at 700 °C during SR of 1-MN, are totally oxidized from 280 to 470 °C. Above 470 °C some part of deposited carbon is gasified by CO_2, resulting in CO formation. Analogically, catalysts regeneration in steam leads to CO_2 at lower temperatures and to CO and CO_2 above 400 °C. It is also possible to regenerate catalysts during steam reforming reaction by increasing the temperature up to 800 or 900 °C. The excess of introduced H_2O suppresses carbon deposits and cleans the catalysts surface.

During SR reaction hydrocarbon is dehydrogenated on catalysts active centre leading to active carbon *C and *H ("*" standing for Ni^0 active site). Water also dissociates on Ni^0 leading to *O and *H. Oxidation of C* to CO occurs through reaction with *O.

WGS is a parallel reaction kinetically coupled with SR owing to *O. WGS is due to the excess of H_2O oxidizing CO formed in SR reaction. WGS participation decreases with the temperature increase (thermodynamics equilibrium) and is more significant in the case of steam reforming of 1-MN. Ceria-zirconia is able to decompose tar compounds using oxygen from the lattice but the addition of nickel significantly raises CO and H_2 production.

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