



Full Length Article

The impact of components of synthesis gas from coal gasification on conversion of model tar compounds over Ni/CeZrO₂ catalyst

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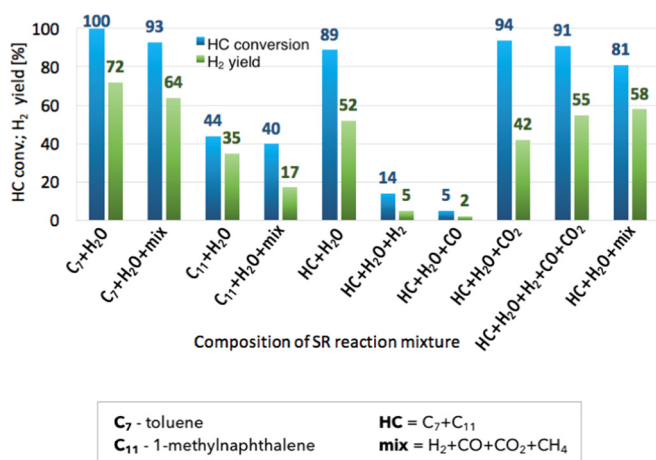
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GRAPHICAL ABSTRACT

The influence of components of raw gas from coal gasification on conversion of model tar compounds and H₂ yield during steam reforming reaction.



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ABSTRACT

Coal gasification is accompanied with formation of tars that cause equipment problems and have to be removed from the raw gas. Our previous studies proved that nickel supported ceria-zirconia catalyst (Ni/CZ) reveals high activity towards decomposition of toluene and 1-methylnaphthalene (1-MN) via steam reforming reaction (SR). However, the components of the raw gas from coal gasification (i.e. H₂, CO, CO₂ and CH₄) may influence the performance of Ni/CZ catalyst. The influence of particular components of the raw gas on catalyst performance during SR of model tar compounds have been studied and discussed in this paper. It has been found that H₂ and CO addition to the steam reforming feed drastically decreases the activity of Ni/CZ catalyst, whereas CO₂ presence enhances conversion of toluene and 1-MN mixture owing to the occurrence of dry reforming reaction (DR). It has also been observed that methane, which is present in the raw gas from coal gasification consumes partly both the H₂O and CO₂, causing some decrease in conversion of model tar compounds. The influence of contact time (t_c) on hydrocarbons conversion and the participation of (DR) have been examined. As was observed, lower contact times lead to decrease in hydrocarbons conversion in SR, making the same participation of DR more pronounced than for higher t_c values. This work proves that Ni/CZ catalyst can be used for removal of tarry compounds via the catalytic hot gas cleaning of the raw gas from coal gasification.

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1. Introduction

Fossil fuels, i.e. the natural gas, petroleum and coal play a key role in global energy supply now and in the near-medium term future. According to almost every forecast of world energy use, they will continue to remain essential components in power generation sector. Unlike petroleum and natural gas, coal is abundant and inexpensive resource; however, it is also the major source of anthropogenic CO₂ emissions. Many European countries have already taken action to reduce CO₂ emissions and prevent climate change. These actions include not only exploitation of renewable energy sources but also application of alternative technologies allowing coal conversion into energy, including CO₂ capture technologies. Coal gasification is the one of the most promising future technologies for power generation. It is also one of the ways to produce hydrogen on a large scale (about 19% of the worldwide H₂ production comes from coal [1]).

Conventional coal gasification process requires steam and/or oxygen as reactants and temperatures higher than 800 °C. The composition of gaseous product depends on the type of coal, gasification process and operating conditions, but generally, it is a mixture of H₂, CO, CO₂, CH₄ and other minor gases. For example, gas produced from Lurgi dry ash gasifier at 1000 °C is composed in 38–39% of H₂, 15–18% of CO, 10–12% of CH₄ and in 31–32% of CO₂ [2]. In general, the composition of the producer gas depends on reactions of carbon with air, steam and hydrogen (Eqs. (S1)–(S12)). These reactions do not take place individually, but their occurrence arises from the parameters of gasification process. The process of coal gasification also produces some amounts of tars [3,4]; however, in most gasification processes, especially those carried out in fluidized and fixed bed, it still remains an unsolved problem.

Gasification tar is a complex mixture of hydrocarbons of different reactivity and it originates from volatiles present in gasified material. Tars may consist of over a hundred different components but only about 20 species are present in significant quantities [5]. These are e.g. toluene, naphthalene, methyl-naphthalenes, phenols, indene, xylenes, styrene and multi-ring (4–6) PAH's [6]. The composition and concentration of tar in raw gas from coal gasification depends not only on the feedstock but also on the type of gasifier. The highest amount of tars is formed in the fixed bed, and much lower when gasification is carried out in the entrained bed at temperatures as high as 1200–1500 °C. Using fluidized bed reactor that runs at approximately 900 °C allows to decrease tar formation owing to good mixing of solid and gaseous reagents; and therefore, better heat and mass exchange. In addition, gas obtained in high-temperature dispersive reactors is almost free from tar contaminants [7]. Tar can condense or polymerize into more complex structures in the pipes, filters or heat exchangers, causing equipment problems, decreasing total efficiency of the process and increasing its cost [8–12]. Moreover, processing of tars from coal gasification usually results in formation of substantial amounts of coal deposits [13]. The concentration of tars in the synthesis gas produced during coal gasification is also important from the point of view of its further utilization. For example, the synthesis gas directed to gas turbine should contain less than 5 mg/m³ of tars, and must be free from tar contaminants when is to be used in chemical syntheses [14,15]. In contrary, there are almost no restrictions on the gas quality concerning tars if the product gas from coal gasification is to be utilized as a fuel for heat production. However, even such gas should be cleaned from tars because the final combustion exhaust must meet the emission regulations imposed by the authorities. Hence, it is obvious that tar disposal becomes one of the most urgent problems during coal gasification process.

There are several methods for tar elimination [9], including non-catalytic and catalytic high temperature cleaning of the raw gas [16,17]. The addition of the catalyst directly to the gasifier may decrease the temperature of the cleaning process even to 550–700 °C. The most popular catalyst for tar removal are calcined limestone, dolomite or olivine. These materials are inexpensive but require temperatures of

above 800 °C. Moreover, the mechanical properties of the two former are unsatisfactory. Olivine is less active but more resistance to attrition [14,18]. Nickel is the most applicable catalyst for tar removal since it is extensively used for high-temperature steam reforming reactions of hydrocarbons in chemical industry. However, the typical reforming catalysts, which is Ni/Al₂O₃, is vulnerable to deactivation due to coke deposition and poisoning with hydrogen sulfide [19,20]. Formation of carbon deposits over nickel based monolith during hot gas cleaning was observed by Corella et al. [21–23]. Nickel substitution with noble metals (Pt, Rh, Ru) prevents soot formation but increases significantly the cost of catalyst [24]. Cerium oxide (CeO₂) has been also used as a promoter in nickel based catalysts. Owing to high oxygen storage capacity (OSC) and very good redox properties, CeO₂ improves Ni resistance to coke formation during steam reforming reactions. The performance of CeO₂ can be upgraded by the addition of zirconium, which positively effects its OSC and thermal stability [25,26]. Ceria-zirconia supported nickel catalysts (Ni/CeZrO₂) of different Ce/Zr ratio have been successfully used in methane reforming and partial oxidation reactions. The best performance and the highest resistance to carbon deposition revealed the catalyst with Ce/Zr = 3:1 [27,28]. In general, ceria-zirconia supported metal catalysts are very promising for reforming reactions, water gas shift and partial oxidation of hydrocarbons, which allows to merge these processes into the autothermal one. Another advantage of these catalysts is their resistance to poisoning with sulfur compounds and possibility of ammonium decomposition [20].

In recent years many papers have been published on catalytic decomposition of model tar compounds, such as toluene, naphthalene, methyl-naphthalene or hexadecane [21,29–34]. The majority of these studies are conducted in laboratory scale using model compounds, while conditions occurring in the industrial scale installations can be substantially different. Nevertheless, the importance of tests in laboratory scale with the use of model compounds or mixtures arises from its cost effectiveness and allows better understanding of the process. In this paper, we demonstrate the performance of ceria-zirconia supported nickel catalyst (Ni/CeZrO₂) that was formed in pastilles to be then used for tars removal in a semi-pilot scale. We show the impact of particular components of the raw gas from coal gasification (as well as the model mixture of such a gas) on conversion of two model tar compounds: more reactive toluene and less reactive 1-methylnaphthalene. Moreover, taking into account results of our previous research on steam reforming of model tar compounds, we determine whether the formation process influenced the activity of Ni/CeZrO₂. The results of presented in this paper research allowed to propose parameters of the process of tarry compounds removal from the raw gas from coal gasification in a semi-pilot scale. The results of these tests (including the impact of H₂S and ash) will be presented in our next paper, that will also demonstrate the possibility of practical use of our catalyst.

2. Experimental

2.1. Catalyst preparation

The Ni/CeZrO₂ catalyst, denoted Ni/CZ, was obtained by the wetness incipient impregnation of commercial CeZrO₂ (ACTALYS 921, Rhodia) being a solid solution containing 67–72% of Ce and 28–33% of Zr. Prior to impregnation with the aqueous solution of nickel nitrate (Ni(NO₃)₂·6H₂O), the CeZrO₂ was formed in the shape of pastilles (5 mm × 4 mm; diameter × height) and calcined at 500 °C for 5 h. The CeZrO₂ pastilles were tested for moisture absorption in order to determine the exact amount of water required for preparation of Ni(NO₃)₂ solution. After impregnation, the CeZrO₂ pastilles were dried at room temperature overnight and then at 120 °C for 12 h. Next, dried pastilles were calcined in flowing air at 750 °C for 2 h.

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