



Equilibrium potassium coverage and its effect on a Ni tar reforming catalyst in alkali- and sulfur-laden biomass gasification gases



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ABSTRACT

Biomass conversion to syngas via gasification produces certain levels of gaseous by-products, such as tar and inorganic impurities (sulfur, potassium, phosphorus etc.). Nickel, a commonly used catalyst for hydrocarbon steam reforming, suffers reduced reforming activity by small amounts of sulfur (S) or potassium (K), while resistance against deleterious carbon whisker formation increases. Nevertheless, the combined effect of biomass derived gas phase alkali at varying concentrations together with sulfur on tar reforming catalyst performance under realistic steady-state conditions is largely unknown. Prior to this study, a methodology to monitor these effects by precise K dosing as well as K co-dosing with S was successfully developed. A setup consisting of a 5 kW biomass fed atmospheric bubbling fluidized bed gasifier, a high temperature hot gas ceramic filter, and a catalytic reactor operating at 800 °C were used in the experiments. Within the current study, two test periods were conducted, including 30 h with 1 ppmv potassium chloride (KCl) dosing followed by 6 h without KCl dosing. Besides an essentially carbon-free operation, it can be concluded that although K, above a certain threshold surface concentration, is known to block active Ni sites and decrease activity in traditional steam reforming, it appears to lower the surface S coverage (θ_s) at active Ni sites. This reduction in θ_s increases the conversion of methane and aromatics in tar reforming application, which is most likely related to K-induced softening of the S–Ni bond. The K-modified support surface may also contribute to the significant increase in reactivity towards tar molecules. In addition, previously unknown relevant concentrations of K during realistic operating conditions on typical Ni-based reforming catalysts are extrapolated to lie below 100 $\mu\text{g K/m}^2$, a conclusion based on the 10–40 $\mu\text{g K/m}^2$ equilibrium coverages observed for the Ni/MgAl₂O₄ catalyst in the present study.

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1. Introduction

Biomass utilization is recognized as one realizable solution with high potential for the future to meet our current energy and environmental challenges [1–3]. The main drivers for the increased interest towards biomass are related to sustainable energy issues, as well as to its abundance and the potential of reducing the emission of greenhouse gases [1,2,4,5]. Among different thermochemical pathways for biomass conversion, gasification has attracted the most attention due to its high conversion efficiency and its versatility in accepting a wide range of biomass feedstocks

to produce an intermediate syngas suitable for further upgrading to various high-value end products [4,6,7].

The producer gas or fuel gas produced must be cleaned and suitable for downstream devices [8,9]. High content of tar, *i.e.* polycyclic aromatic hydrocarbon byproducts from the biomass gasification, can lead to many operational difficulties such as condensation at temperatures below 350–400 °C, plugging and corrosion of pipes and equipment, as well as formation of carbon deposits on catalysts in downstream processing [3,10]. The level of tar, produced in a gasification process, is dependent on the type of gasifier. According to Milne et al. [11], a very crude generalization of tar level for different gasifiers is in the range of 1–100 g/Nm³, where in general terms, downdraft gasifiers are considered as the cleanest, updraft gasifiers the dirtiest and fluidized bed gasifiers are in the lower intermediate range [11]. For a given gasifier, the level of tar is dependent on the process conditions, such as the biomass type and its particle size

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distribution, and on the operating conditions of the reactor, including temperature, gasifying agent (air, steam, steam-O₂), and other parameters related to the selected technology. Hot gas conditioning methods for tar elimination are usually preferred compared to other methods, since they eliminate tars by converting them into useful permanent gas components and thus retaining the chemical energy in the product gas, as well as avoiding treatment of an additional waste stream, as for wet methods [12]. An attractive option, among hot gas conditioning methods, is catalytic steam reforming using a nickel-based catalyst. This method offers several advantages, such as high tar conversion, thus also increased syngas yield, and thermal integration of the process to the gasifier exit temperature [3,12,13]. Several different types of Ni-based catalysts have been tested and found to be cost-effective for tar reforming application in comparison to other types of catalyst [3,13–17].

In tar reforming applications, a Ni-based catalyst is exposed to a number of inorganic trace components such as alkali, sulfur, phosphor and chloride species, as well as other trace elements [8,15,18,19]. The level of these inorganic impurities in the biomass gasification gas depends on several parameters such as the gasification technology employed, the process conditions of the given gasifier, the type of biomass and the choice of technology for gas cleaning upstream of the catalytic reactor such as if a hot gas filter being used for particulate removal [8,20,21]. The impurity level of S, Cl, and N compounds in the gas phase seems to be well correlated with the biomass composition and gasification conditions. The levels are in general between 20 and 200 ppmv (ppmv) on dry gas basis (db) for both S (mainly H₂S) and Cl (mainly HCl) compounds [15,18], and 500–3000 ppmv (db) for NH₃, in case of woody biomass [22]. The large part of the alkali is retained in the gasifier ash, and in case of fluid bed gasifiers, also in the bed solids. Typical gas phase K-species levels are around 0.01–5 ppmv (db), with one case reported as high as 25–30 ppmv [8,18,23–25].

Small amounts of sulfur and potassium influence the activity of the catalyst. For instance, as previously shown [26,27], the potassium in K-promoted nickel catalysts increases the resistance to carbon formation. However, it is also shown that potassium, above a certain threshold concentration, decreases the steam reforming activity [26,28] as well as the hydrogenation activity [29]. Sulfur, a known and severe poison for Ni steam reforming catalyst, tends to retard the formation of whisker carbon above certain coverages, due to blockage of C nucleation sites [26,28,30,31]. Optimally, a catalyst promoted with sulfur and potassium will just have enough additives to block coke formation and still proceed at sufficient reaction rates [32]. Cl and NH₃ do not seem to affect the reforming performance of the Ni catalyst [33,34].

Co-adsorption of K and S on Ni has been investigated in several surface science related studies. For instance, in a study performed by Chen and Shiue [35], it was proposed that the adsorbing ability of sulfur compound on nickel surfaces decreases for the potassium promoted nickel, as the surface concentration of potassium increases. They hypothesized this to be the result of electron transfer to nickel by adsorbed K, inhibiting the formation of nickel sulfide. Politano et al. [36] observed a Ni–O bond weakening, during co-adsorption of K and O, in studies of the related K–O/Ni system. As it would also be expected for the similar K–S/Ni system, it was argued that electron donation from K to the O/Ni system results in a filling of Ni–O anti-bonding states. The observed Ni–O bond weakening, upon K co-adsorption, confirmed prior DFT results regarding K co-adsorption induced metal-oxygen bond weakening [37]. In another study by Ferrandon et al. [38] on Rh/La–Al₂O₃ for hydrogenation of benzene, it was suggested that besides inhibition of coke formation, the improvement in sulfur tolerance of the catalyst could be related to alkali blocking part of the catalyst and thus hindering the adsorption of H₂S and thiophene [38]. Papageorgopoulos et al. [39], established that K interacted strongly with S

at a Ni surface. The formation of a KS compound was observed for high S coverages, *i.e.* S coverages higher than 0.5 monolayer (ML), and was taken as evidence for a K-induced S–Ni bond weakening. Similarly, in studies by Blaszczyzyn et al. [40,41], pre-deposited S on a Ni (100) surface was found to drastically increase the binding energy of potassium. They speculated that the increased K binding energy could be due to an increase in the work function of the clean nickel by sulfur, enhancing the ionic adsorption of potassium on the S/Ni surface.

Evidently, both negative and positive sulfur and potassium adsorption effects have been documented. The combined effect of potassium and sulfur on a Ni-based catalyst under steady-state tar (steam) reforming process conditions has not yet been clarified. There are only very few studies of the effect of alkali on tar reforming catalysts [34,42–44]. A limitation in all these studies is the method used to investigate the influence of K on the catalyst, which is different from actual mechanisms of potassium transport, deposition and equilibration on the catalyst [34]. In addition, few of these studies were performed under exposure to real producer gas from biomass [44], as well as none were investigated under realistic steady-state conditions [34,42–44]. In a study by Li et al. [42], pre-exposure of alkali salt vapors to a monolithic Ni-based catalyst, resulted in loss of surface area and deactivation of the reforming reaction. Albertazzi et al. [44] and Einvall et al. [43] observed a recovered or only a minor loss in reforming activity after pre-deposition of K species on the Ni catalysts. The reason for both phenomena was related to a cleaning effect of steam (alkali volatilization) during activity tests and under reforming condition of a real producer gas.

In our previous study [45], we developed a methodology to enable the investigation of combined effects of biomass-derived impurities in gas phase under realistic steady-state conditions on a typical tar (steam) reforming catalyst. Aging of the catalyst resulted in stable BET and nickel surface areas. Pre-sulfidation of the catalyst caused an isolation of K effects on catalyst performance by removing the transient in activity of the catalyst due to change in S coverage. The pretreated catalyst exposure tests were carried out with real producer gas. However, since time on stream was rather short, the results were inconclusive as to whether K has any impact on catalyst activity. Another observation was a significant slowdown in K uptake with increased hydrogen sulfide concentration in the gas, an effect discussed in terms of K preferential adsorption sites and possible spill-over phenomena. In the present study, we continue with a longer exposure time to determine the K equilibrium coverages on the catalyst, as well as its effect on the catalyst performance. The K and S concentration profile in the catalytic bed is also investigated to study the effect of K on the S–Ni system. In addition, the early stage of alkali removal from the catalytic bed and its effect on reforming activity, while reducing the alkali content in the gas phase were investigated.

2. Experimental

2.1. Experimental setup

All experiments were performed in a gasification system, consisting of a 5 kW pine pellet fed atmospheric bubbling fluidized bed gasifier, a high temperature hot gas ceramic filter, a fixed bed catalytic reactor, a cleaning section, an analytic section and an aerosol generator setup. The hot gas filter is used to remove particulates. Alkali metal compounds were produced and dosed into the dust-free raw producer gas through a setup consisting of two main parts: an aerosol generator (Constant Output Atomizer model 3076, TSI Inc.) and a homemade diffusion dryer (similar to model 3063, TSI Inc.). Fig. 1 shows the schematic of the experimental setup used in

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