



Effect of gas phase alkali species on tar reforming catalyst performance: Initial characterization and method development



Pouya H. Moud^{a,*}, Klas J. Andersson^b, Roberto Lanza^a, Jan B.C. Pettersson^c, Klas Engvall^a

^a Department of Chemical Engineering and Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

^b Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kongens Lyngby, Denmark

^c Department of Chemistry and Molecular Biology, Atmospheric Science, University of Gothenburg, SE-412 96 Gothenburg, Sweden

HIGHLIGHTS

- A method to study gas alkali–catalyst interactions in real conditions is developed.
- Initial K uptake at low θ_K is approximately linearly proportional to time on stream.
- Indications of a slow approach to K equilibration on the catalyst were observed.
- Different KCl levels in the gas phase demonstrate different initial uptake of K.
- K adsorption suppression by sulfur was observed.

ARTICLE INFO

Article history:

Received 5 December 2014

Received in revised form 6 February 2015

Accepted 12 March 2015

Available online 23 March 2015

Keywords:

Tar reforming

Ni catalyst

Biomass gasification

Alkali

Sulfur

Potassium

ABSTRACT

In thermochemical conversion of biomass to synthesis gas and biofuels, the effect of varying gas phase alkali concentrations on tar reforming catalyst performance in combination with gas phase sulfur and chlorine is largely unknown. The current study demonstrates a new methodology for investigating gas phase alkali adsorption and presents results for early stage adsorption on a Ni-based catalyst under realistic industrial conditions. The experiments were carried out using pine pellets as feedstock in a setup consisting of a 5 kW atmospheric bubbling fluidized bed gasifier, a high temperature hot gas filter and a catalytic reactor – all operating at 850 °C. A potassium chloride solution was atomized with an aerosol generator, and the produced submicrometer KCl particles were continuously introduced to the catalytic reactor where they rapidly evaporated to form KCl (g). The accurate dosing of gas-phase alkali was combined with elimination of transient effects in catalytic performance due to catalyst sintering and S adsorption, and results for K uptake in relation to sulfur uptake were obtained. Different KCl levels in the gas phase demonstrates different initial uptake of K on the catalyst surface, which at low K coverage (θ_K) is approximately linearly proportional to time on stream. The results also show a clear suppressing effect of sulfur adsorption on potassium uptake. Indications of a slow approach to K equilibration on the catalyst were observed. The potential of the developed methodology for detailed studies under close to industrial conditions is discussed.

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1. Introduction

The majority of the world's energy use is supplied by carbon-based fossil fuels, such as oil, coal and natural gas. The fossil resources are not endless and also not regarded as sustainable from an environmental point of view. A versatile renewable resource, receiving increased attention, is biomass [1,2]. One of the routes to utilize biomass is gasification, converting the biomass feedstock

into energy carriers for direct use or further upgrading in industry and society. The product gas, from biomass gasification, contains in general major components, such as CO, H₂, CO₂, CH₄, H₂O and in some cases N₂ as well. In addition, byproducts such as light and heavy organic compounds [3], as well as inorganic impurities, e.g. H₂S, HCl, NH₃, P-, As- Si-, and alkali compounds, are also present in the product gas [4–6].

The formation of heavy hydrocarbons (tar) and its removal has in general been declared one of the greatest technical challenges to overcome before large scale commercialization of biomass gasification becomes viable [1]. The term “tar” does not have a generally accepted definition [2,3], but it often refers to the condensable

* Corresponding author. Tel.: +46 8 790 82 36.

E-mail address: pouyahm@kth.se (P.H. Moud).

fractions of organic compounds from gasification products with a molecular weight higher than 78 g/mol (benzene) [2,3]. Issues related to tar are condensation at temperatures below 350–400 °C, plugging and corrosion of pipes and equipment, and formation of carbon deposits on catalysts in downstream processing [1,7].

There are several tar mitigation techniques, including scrubbing, catalytic tar steam reforming, thermal cracking (e.g. via partial oxidation), and plasma treatment [1,3,4,8]. Tar reforming was early on recognized to be one of the most efficient mitigation methods [1] improving carbon efficiency by conversion of tar to syngas components, and thus also significantly reducing waste water treatment requirements. Typical biomass gasification temperatures are about 800–900 °C [2]. Importantly, catalytic steam reforming of hydrocarbons is well-suited for this temperature range [9–14], allowing for a tar mitigation technology operating at temperatures close to that of the gasifier exit temperature, and thus with lower heat penalties compared to low-temperature scrubbing, high-temperature cracking or plasma technologies.

Several different catalysts exist for catalytic tar conversion; synthetic as well as mineral-based [1,2,4,8,15,16]. Transition metals are considered good catalysts for steam and dry reforming of methane and hydrocarbons. Although Rh-, Ru-, Pd- and Pt-based reforming catalysts outperform Ni in terms of activity, due to its favorable cost-to-activity ratio Ni-based catalysts continue to be the most frequently studied materials for steam reforming downstream of biomass gasifiers [1,2,4,8,15,16].

During realistic operation conditions, besides tar, the catalyst is also exposed to significant levels of inorganic impurities. The level of inorganic impurities in the biomass gasification gas depends on a number of parameters, such as the type of biomass (e.g. wood, straw, miscanthus), the use of gasifier bed materials or additives (e.g. dolomite, olivine, kaolin) and the gasification technology employed. Furthermore, if a hot gas filter is used to remove particulates the impurity levels will also depend on the filtration conditions including the temperature, as well as the chemical and physical properties of the dust particles collected in the filter cake [5,17,18]. Depending on the conditions, alkali metal compounds can be present either in gaseous form, condensed on ash particles or as submicrometer aerosol particles that may be enriched in the fine fraction penetrating the hot gas filter [19]. According to thermodynamic calculations, potassium in the gas phase will be distributed between KOH, KCl, and to a minor degree elemental K. The actual ratios will depend on the composition of the biomass and the gasification conditions [20].

The impurity levels in biomass producer gas are generally between 20 and 200 ppm volumetric (ppmv) on dry gas basis (db) for both S (mainly H₂S) and Cl (mainly HCl) compounds [4]. Torres et al. [4] also provided a range of 1000–14,000 ppmv (db) for NH₃, while NH₃-values of 500–3000 ppmv (db) are more representative when woody biomass is used [21]. Whereas the sulfur, chlorine, and nitrogen compound content in the gas phase appear well correlated with the composition of the biomass and gasification conditions [4,6], the greater part of fuel alkali is retained in gasifier ash and bed solids. Typical gas-phase K-levels of around 0.01–5 ppmv (db) have been reported [5,6,22–24], although in one case, as high as 25–30 ppmv was observed [6].

Deactivation of catalysts can be classified into chemical, mechanical or thermal depending on the nature of the deterioration [25]. Reduced reforming activity due to thermal sintering of Ni, S and K adsorption, but also increased resistance against deleterious carbon whisker formation by S and K adsorption, are fairly well studied phenomena [10,26–28]. However, the effects of gas-phase alkali at varying concentrations in combination with biomass-derived gas-phase sulfur and chlorine are still largely unknown, in particular the influence of alkali on catalyst activity

and carbon lay-down when alkali is equilibrated and co-adsorbed with sulfur on the Ni catalyst surface.

There are only very few studies of the effect of alkali on tar reforming catalysts and none of them were carried out under realistic steady-state operating conditions, where the catalyst was continuously exposed to a controlled gas phase alkali content. Li et al. [14], exposed a monolithic Ni-based catalyst to alkali salt vapors (KCl, K₂SO₄, K₂CO₃) and subsequently observed a general deactivation of the reforming reaction. Physical characterization revealed severe loss of surface area of the catalyst. The most deleterious effect was reported for K₂SO₄, which could be expected due to the additional sulfur dosing. Einvall et al. [13], exposed reforming catalysts to species in fly ash, as well as aerosol particles containing K₂SO₄. The effect of the alkali addition was reported to be a loss in surface area and available metal area, but the corresponding loss in activity was not severe, probably due to a cleaning (volatilization-induced) effect of the steam during subsequent activity testing. In another study, Albertazzi et al. [29] investigated Ni-based catalyst samples and observed a loss in reforming activity when K₂SO₄ and ash were deposited on the surface prior to the exposure to gas from a lab-scale gasifier. The activity was regained during the reforming process, implying that the alkali salt was volatilized from the catalyst surface under reaction conditions. The amount of deposited alkali salt, decreased after 8 h of reaction in all the tested samples, thus highlighting the importance of alkali volatilization under reaction conditions. However, the surface area also decreased during reaction, which may be due to catalyst carrier and Ni particle sintering and clogging of wider pores [29].

As previously stated, and reaffirmed by the few alkali related studies above, there is limited information regarding the effect of gas-phase alkali on tar reforming catalyst performance under realistic conditions, including alkali uptake/removal rates and equilibrium alkali coverages at different concentration levels. Whereas small amounts of S and K separately influence catalyst steam reforming activity (negatively) and carbon whisker coking resistance (positively), [10,25,26], Cl and NH₃ do not affect the catalyst performance in any significant way [30]. However, the combined effect of alkali and sulfur remains largely unknown. The current study presents findings from experiment and investigations with the main aim of investigating the early stages of gas phase alkali adsorption and interaction with a Ni-based catalyst under simulated industrial conditions. As a first step, we describe a method to characterize and validate the interaction. By introducing an atomized alkali salt solution and following the K uptake, we investigate the early stages before the establishment of equilibrium K coverages by simulating the effect of K at different KCl (g) concentrations. Furthermore, the sulfur chemical potential is tailored via adjusted partial pressures of H₂S and H₂ in a way to equilibrate the surface of the catalyst with realistic sulfur concentrations.

2. Experimental

2.1. Experimental setup

The experiments were performed in a testing rig including a 5 kW bubbling fluidized bed (BFB) gasifier, a filter, an alkali aerosol generator, a reforming reactor, a cleaning unit and an analytic section. The cleaning unit consists of impinger bottles, a phosphorous pentoxide column and a cooling trap. A schematic view of the system is shown in Fig. 1. The reactor consists of a fluidized bed (inner diameter of 50 mm and a height of 300 mm) and a freeboard (diameter of 100 mm and height of 0.45 m). The freeboard lowers the gas velocity, which allows the bed particles in the gas to fall back into the bed. The total volume of the reactor is 5.1 L. The reactor is externally heated and has a maximum operating temperature

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