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Fe and CaO promoted Ni catalyst on gasifier bed material for tar removal from producer gas

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ABSTRACT

A new Ni-based mixed oxide material (Ni-Fe-CaO) for catalyzing Carbo HSP gasifier bed material was prepared and characterized by XRD, TPR, TEM, and SEM techniques. The catalyst performance for tar removal from a simulated producer gas mixture via steam reforming was tested in a laboratory-scale fixed-bed reactor between 700 and 800 °C, using toluene and ethylene as tar surrogates. Ni–Fe–CaO catalysts had significantly higher activity and deactivation resistance for toluene removal compared to either Ni–Fe or Ni catalysts. Keeping CaO loading similar in the catalysts, the Ni:Fe ratio was varied and the optimum tar conversion and highest CO_x selectivity were obtained with ratios of 3:1 and 2:1. The turn over frequency (TOF) on Ni in the Ni–Fe–CaO mixed oxides were higher compared to pure Ni or Ni–CaO combinations and increased with lowering Ni/Fe ratio. High tar removal activity (80% vs 68%) and CO_x selectivity (96% vs 98%) at 750 °C were obtained for 1.6% (Ni45Fe15Ca40)/Carbo HSP and 1.6% (Ni40Fe20Ca40)/Carbo HSP compositions, respectively. Deactivation occurred mainly due to sintering of the 1.6% (Ni45Fe15Ca40) composition reducing conversion efficiency by 17% (from 99.7% to 83%) after 48 h in time-on-stream at 800 °C. After regeneration with a O_2/H_2 sequence, the conversion was reduced from 98% to 80% after 24 h in time-on-stream. Similarly, 1.6% (Ni40Fe20Ca40) composition shows a stable conversion of ~80% at the end of 50 h, which was much superior compared to the 1% (Ni65Fe35)/Carbo HSP catalyst. The individual role of Fe and CaO in promoting Ni for improving catalytic activity and stability in Ni-Fe-CaO was investigated

1. Introduction

Depletion of fossil fuels and associated environmental problems has stimulated the development of alternative renewable energy sources. Biomass resources are a potential source of energy and chemicals. The thermo-chemical processing of biomass results in a producer gas that can be utilized for the production of power, fuels, and chemicals. The producer gas commonly includes H_2, CO, CO_2, H_2O, CH_4, C2–C5 hydrocarbons, tars, NH_3 and H_2S. The tar component is a mixture of aromatic hydrocarbons that are condensable at room temperatures. The tars need to be removed from the producer gas before it enters any downstream processes, as the tars can cause severe fouling and corrosion problems. Nitrogenous and sulphur compound gases are also required to be cleaned depending on the applications.

The dual fluidized-bed (DFB) steam gasification approach is advantageous for the synthesis of a nitrogen-free producer gas with a high heating value [1,2]. Downstream (secondary step) gas-cleaning steps required for subsequent utilization are relatively expensive. The removal of tars by the use of catalyzed bed material inside the gasifier can result in reduced gas-cleaning costs [3]. The uncatalyzed gasifier bed materials like olivine, silica sand, and limestone display only moderate activity for tar removal [4–7]. These minerals have been applied as a support for high performance metal catalyst. Wang et al. [8] tested nickel catalyst on a dolomite substrate and showed 95% conversion of naphthalene as a model tar compound. Ni metal dispersed on Olivine and other supports show higher catalytic activity and selectivity toward tar decomposition [6,9–16]. Although, Ni is low cost and highly active, it can have problems with severe sintering and coke deposition. Moreover, the disposal of the ash waste along with attrited gasifier bed materials from a gasification unit can also be problematic if it contains a high amount of toxic Ni. It is desired therefore, to achieve an acceptable tar removal performance of catalyzed gasifier bed materials with low Ni loading.

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Table 1
Calculated Ni, Fe & CaO based composite catalyst loading on Carbo HSP.

Catalyst on carbo HSP	Catalyst batch prepared(g)	Loading of Ni (g)	Loading of Fe (g)	Loading of CaO (g)	Ni/(Ni + Fe) ratio
1.5% Ni	20	0.3	0.0	0.0	1.0
1.6% (Ni60Ca40)	20	0.19	0.0	0.13	1.0
1.6% (Ni45Fe15Ca40)	20	0.14	0.05	0.13	0.75
1.6% (Ni40Fe20Ca40)	20	0.13	0.07	0.13	0.66
1.6% (Ni35Fe25Ca40)	20	0.11	0.08	0.13	0.58
1.6% (Ni20Fe40Ca40)	20	0.07	0.13	0.13	0.33
1.6% (Fe60Ca40)	20	0.0	0.19	0.13	-
1% (Ni65Fe35)	20	0.13	0.07	0.0	0.65
1% Fe	20	0.0	0.2	0.0	–

Highly active and coke resistance property of noble metals (Pt, Pd etc.) could solve the disposal problem, but due to high price, Ni is selected as the least costly option. To overcome problems with the Ni based catalysts, the stability toward coke resistance as well as sintering can be improved with proper supports, additives oxides, and other metals in the catalyst formulation. Several reports have showed that CeO_2 is a beneficial component for promoting Ni giving higher activity and coking resistance in the steam reforming of tars [16–21]. In a previous investigation, the activity and stability of Ni–CaO–CeO_2 impregnated on gasifier bed material for reforming of producer gas was found to be much superior compared to a pure Ni catalyst [22].

The activity of Ni catalysts can also be improved by using additional metal such as Cu [23], Mo [24], Co [25], and Fe [26,27]. Among these metals, alloying Fe with Ni has been studied extensively [28–32]. Due to higher affinity for oxygen, Fe can enhance the availability of oxygen for coke removal [29,33]. It has been reported that the improved performance in the steam reforming activity of Ni–Fe/Al_2O_3 catalysts is due to the presence of an intimate interaction between Fe and Ni, which results in the formation of a Ni–Fe alloy [29]. In addition, it has been recently reported that the presence of uniform Ni–Fe alloy particles in Ni–Fe/Mg/Al catalysts enables a high catalytic performance in the steam reforming of toluene and phenol [30]. However, a reliable promoter to a Ni–Fe alloy as well as providing stability of the alloy was required. Addition of alkaline earth oxide CaO as a promoter into Ni–Fe [34], Ni–Al_2O_3 [35], Ni–Fe–Al_2O_3 [36] catalysts improved the steam reforming reactions. Ni supported on Mayenite ($Ca_{12}Al_{14}O_{33}$ or $12CaO{\cdot}7Al_2O_3$) phase had remarkable activity and stability [37]. These oxide increase the interfacial distance between the Ni particles and reduces the chance of agglomeration without interacting with them. Moreover, their affinity for CO_2 may be beneficial for coke removal.

In this study a composite Ni–Fe–CaO catalyst for gasifier bed material is investigated for tar removal properties during steam reforming. The role of Fe and CaO in the promotion of Ni loaded catalyst for higher activity and resistivity toward coke deposition is examined.

2. Experimental

2.1. Catalysts preparation & characterization techniques

Using Carbo HSP gasifier bed material as a support, 1 wt% of Ni, Fe and 1.6 wt% of Ni–Fe–CaO were deposited by the wet impregnation method. $Ni(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Ca(NO_3)_2{\cdot}4H_2O$ were used as precursors and the required amounts were dissolved in 5 ml of water to transparent solution. The solution was applied to 20 g of Carbo HSP support mixing with glass rod until it is homogeneously wet. The impregnated mixture was left for 12 h and then kept at 110 °C in an oven for 12 h. The temperature of the furnace was raised by 50°/min up to 800 °C and calcined at this temperature for 12 h. By heating the impregnated nitrate salts, they decompose to the corresponding oxides NiO, Fe_2O_3 and CaO forming composites. A similar loading of CaO content in all the catalysts was maintained while various compositions with different Ni/Fe ratio from 0.0 to 1.0 were prepared. The compositions of the catalysts are referenced as follows: the composite 1.6% (Ni40Fe20Ca40)/Carbo HSP catalyst has Ni, Fe and CaO in weight proportions of 40%, 20% and 40%, respectively. The loading of the active components on the Carbo HSP support is presented in Table 1. As Carbo HSP is common for all the impregnated catalysts, it is not mentioned in the catalyst description in Section 3.

X-ray diffraction (XRD) was performed with an X-ray diffractometer (BRUKER D2 PHASER) equipped with a monochromator for Cu Kα radiation at a voltage of 30 kV, and a current of 100 mA. Samples were crushed to fine powders prior to measurement. During the measurement, samples were scanned from $2\theta = 20$ to 60° at the rate of 0.02°/s. The observed patterns were identified using the International Centre for Diffraction Data (ICDD) database.

Temperature-programmed reduction (TPR) studies of the catalysts were performed to investigate the reduction behavior with a Quantachrome Instrument (ChemBET-3000 TPR/TPD). Typically, a sample of ca. 500 mg was placed in a U-shaped quartz tube, and heated from 40 to 800 °C at 10 °C/min in a gas mixture containing H_2 and N_2. The consumption of H_2 during the reduction was monitored by a thermal conductivity detector (TCD). Prior to a TPR test, the sample was outgassed under inert gas flow at 400 °C for 4 h.

The microstructures of the catalysts were characterized with a scanning electron microscope (SEM, Phillips XL30).

To prepare samples for transmission electron microscopy (TEM, FEI Tecnai Sphera), small amount of impregnated mixed oxides powders were separated from the Carbo HSP support and sampled those powders on Cu grid. The samples were imaged at 200 kV.

2.2. Catalytic test

The schematic diagram and details of a fixed-bed reactor setup used for the steam reforming study has been described previously [33]. Typically, 2000 mg of the catalyst was weighed, and mixed with quartz chips with a ratio of 1:10 (by wt.). The catalyst particles were mixed with sufficient quartz diluent to keep them well separated removing heat transfer limitations. Moreover, steam reforming reactions are endothermic in nature. As the catalyst is impregnated on non-porous Carbo HSP support, the catalytic reactions occur on the easily available surface only, which means mass transfer limitation is almost zero. The catalyst was reduced in situ at 800 °C for 1 h under H_2 flow during the reduction step; the bed temperature was ramped at 10 °C min^{-1} under N_2 flow before it reached the target. The reduction step is necessary to reduce oxides phases into active metallic phases. At the end of reduction, the reactor was cooled down below 650 °C under N_2 flow. For the steam reforming experiments, the bed temperature was increased to 700 °C at a rate of 10° min^{-1}. Experiments were performed at reaction temperatures of 700, 750, and 800 °C, and a total flow rate of 433 sccm including H_2O in gaseous state. Catalyst regeneration