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Short Communication

Development of a bimetallic dolomite based tar cracking catalyst

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ABSTRACT

In this study a bimetallic dolomite based tar cracking catalyst was developed and tested. It was enriched in Ni and Fe with BET surface area of 12.31 m^2/g. The catalytic characterizations were tested with tar simulated by naphthalene, and with tar produced by biomass and coal co-pyrolysis. 93% naphthalene was decomposed at 950 °C. A first order apparent kinetic model was developed. Activation energy of 63.96 kJ/mol and pre-exponential factor of 396.2/s were calculated. Furthermore, reduction in char yield by 7%, when the catalyst was used in the biomass–coal co-pyrolysis, was observed.

1. Introduction

Recently, biomass gasification is regarded as one of widest utilizations of biomass conversion technology. However, a bottleneck problem in biomass gasification that should not be overlooked is the high molecular weight organic compounds (tar) that are found along with the producer gas. Tar is very complex in nature containing more than 10,000 species, just like those showed in Table 1, and most of which are aromatic [1].

Nowadays, several methods for tar reduction have been proposed, but catalytic cracking is considered the most promising and effective route by most researchers [2–5]. The main groups of purification catalysts for gasification gas include dolomite [6–8], alkali metals [5,9], and nickel based catalysts [10–12]. Dolomite and Ni-based catalysts have been proven to be very active in terms of tar reduction. The research of dolomite attracts much attention, since it is a cheap disposable catalyst that can significantly reduce the tar content of the product gas from a gasifier. But dolomite is softer and thus gets eroded leading to an increased carryover of solids from the bed. Ni-based catalysts also have been investigated extensively for their effectiveness in terms of tar removal [13–15]. The main limitation of using Ni-based catalysts is that these are expensive and experience rapid deactivation. In addition, several researchers found that the iron oxide contents in the catalyst seemed to be an important factor for tar decomposition [2,7]. Orio et al. [7] investigated four different dolomites which contain different iron oxide contents for oxygen steam gasification of wood in a downstream catalytic reactor. They found that the higher activity dolomites may be accounted for by their higher iron oxide contents and their larger pore diameters. Fe-based catalysts have been investigated for tar decomposition [16,17]. Metallic iron is known to be an active species for aromatic hydrocarbon decomposition (C−C and C−H bond cleavage), Mirella Virginie et al. [18] indicated that a high percentage of metallic iron in Fe/olivine catalyst is maintained leading to C−C and C−H bond cleavage. Thus, a new catalyst, which can combine the advantages of the dolomite, Ni- and Fe-based tar cracking catalysts, should be promising. This may lead to a catalyst with high catalytic activity, high hardness and low cost.

This paper will address the preparation and performance of a bimetallic dolomite based catalyst for tar cracking. Performance of the catalyst is assessed by tests using naphthalene as model compound which has been reported as the most difficult to be cracked and reformed. Furthermore, catalyst performance on tar cracking from co-pyrolysis is assessed and finally a first order kinetic model is applied to determine the apparent kinetic parameters.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst comprises a binder (A), dolomite and Fe_2O_3 support (B). The mixture which was obtained by α-Al_2O_3 powder (BET

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Table 1
Typical composition of biomass gasification.

Compound	Percentage weight (wt.%)	Compound	Percentage weight (wt.%)
Benzene	37.9	Three-ring aromatic hydrocarbons	3.6
Toluene	14.3	Four-ring aromatic hydrocarbons	0.8
Other one-ring aromatic hydrocarbons	13.9	Phenolic compounds	4.6
Naphthalene	9.6	Heterocyclic compounds	6.5
Other two-ring aromatic hydrocarbons	7.8	Others	1.0

surface area: 1.4228 m^2/g, pore volume: 0.001708 cm^3/g) solute in Ni $(NO_3)_2 \cdot 6H_2O$ (the weight of Ni is 15% of Al_2O_3's) after being calcinated in air at 700 °C for 2 h was used as the binder (A). Fe_2O_3 (5 wt.%) and calcinated dolomite powder were mechanically mixed (B). A (2 wt.%) and B were molded, dried and calcinated in air at 900 °C for 2 h. The molded mixture was called support C. The bimetallic dolomite based catalyst was prepared by impregnation method. Support C was put into 1 mol/L Ni $(NO_3)_2 \cdot 6H_2O$ solution, stirring for 2 h, aged overnight, dried and calcinated at 400 °C for 2 h. At last, the catalyst was sieved to obtain particle sizes between 18 and 40 ASTM meshes (0.425–1.00 mm).

The BET surface area of fresh catalyst was obtained by means of nitrogen adsorption at 77 K using a Micromeritics ASAP2020 instrument. Catalyst elemental composition was determined by ICP-OES method using OPTIMA 7000 apparatus. The X-ray diffraction (XRD) pattern of calcinated dolomite and bimetallic dolomite based catalyst is taken with D8 FOCUS XRD apparatus with Ni-filtered CuKα radiation. The acceleration voltage was 40 kV and the acceleration current was 40 mA. The hardness was tested by an activated carbon hardness device according to ASTM D3802-2010.

2.2. Experimental setup

The setup consisted of a naphthalene vaporization unit and catalytic bed reactor. The temperature of naphthalene vaporization unit was 100 °C using a controlled electric oven. The reactor was consisting of a quartz tube (i.d. 25 mm) which was straightly placed in a tube furnace equipped with K-type thermocouples. Typically, 7.5 g of catalyst sample was packed between quartz wool layers. An adsorption bottle filled with 200 mL picric acid located at the reactor outlet was used to adsorb the unreacted naphthalene. The exposed parts, including the part between naphthalene vaporization and catalytic bed reactor and the part between catalytic bed reactor and adsorption bottle, were maintained at 300 °C by heating tapes. Before the activity test, the catalyst bed temperature reached the activity test temperature 650–950 °C flowing at 50 NmL/min N_2. The feed gases were allowed to pass through the catalyst bed at a rate of 100–800 NmL/min. The naphthalene vapors into the reactor were varied by changing the flow rate of nitrogen.

2.3. Catalytic tests of the bimetallic dolomite based catalysts

2.3.1. Naphthalene catalytic cracking reaction

Toluene, benzene, phenol, 1-methyl-naphthalene and naphthalene are the most studied model biomass tar compounds. Among them, naphthalene is one of the most tar aromatic compounds, and it is stable and difficult to decompose [4,19,20]. L. Devi et al. [4] found that naphthalene contributes a major part of the total tar even after severe catalytic treatment with dolomite and olivine at a high temperature of 900 °C. And decomposition of higher tars (higher than naphthalene) leads to the formation of naphthalene [21]. So in this work the naphthalene will be the tar modeling compound for the aim of testing the catalyst characterizations.

The content of naphthalene before or after the catalytic bed was determined by the method of GB 12209.1-90 (the National Standard of the People's Republic of China "Determination of naphthalene of gas in urban area—picric acid method"). The naphthalene conversion ratio can be defined as:

$$\alpha(\%) = \frac{C_{naph,in} - C_{naph,out}}{C_{naph,in}} \times 100\%.$$

$C_{naph,in}$ and $C_{naph,out}$ represent the naphthalene flow rate at the inlet and outlet lines, mg/min, respectively, and α is the conversion rate (%).

2.3.2. Biomass and coal catalytic co-pyrolysis reaction

10% (wt.%) bimetallic dolomite based catalyst blended into the poplar sawdust and bituminous coal mixture whose B/C was 1:1. The mixture was placed in the catalytic cracking reactor. The product gas was swept by 100 NmL/min N_2, and tar was collected by ice trap. The collected tar was analyzed by GC–MS (Agilent 6890N/5973N). The TGs (Netzsch 409PC) of co-pyrolysis with and without catalyst were also carried out.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET analysis

Brief overview of BET surface area catalyst which includes the component of Ni, dolomite and Fe_2O_3 in the literature is presented in Table 2. It can be seen that the catalyst produced in this study has higher BET surface area than the reported values.

The molecular diameter of all organics in tar is very large. The calculated Van der Waals dimensions of modeling compound naphthalene are as follows: length is 9.1 Å, width is 7.3 Å and thickness is 5.4 Å [22]. Fig. 1 shows that in the bimetallic dolomite based catalyst, the Cumulative Pore Volume of pore diameter less than 50 Å accounts for very small percentage, and most pore diameters were larger than 50 Å. It can be concluded that mainly the pore diameter of the catalyst is far larger than naphthalene.

3.1.2. Catalyst elemental composition

The elemental composition of calcinated dolomite and freshly developed catalyst is presented in Table 3. It can be found that the developed catalyst contains more Fe and Ni than calcinated dolomite.

3.1.3. X-ray (XRD) diffraction and scanning electron microscopic (SEM) analysis

According to Reference [23] the peaks at 43.8 and 62.4 for 2θ in Fig. 2 are identified as MgO, but in Reference [24] they thought the

Table 2
Comparison of BET surface area of catalyst in this study and literatures, in m^2/g.

Ni-base	Dolomite	Fe_2O_3 series	This study
2.5 [19]	9.1178 [4]	7.4 [2]	12.31
11.6 [29]	8.8 [30] (the support of this study)		
5.09 [31]	7.3 [30]		
2.31 [32]			