



The steam reforming of naphthalene over a nickel–dolomite cracking catalyst

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Received 20 November 2002; received in revised form 11 September 2003; accepted 9 November 2004

Available online 28 January 2005

Abstract

With naphthalene as a model compound, catalytic cracking experiments on biomass tar were made on Ni–dolomite catalysts. The performance of catalyst preparation, activity, coke formation and regeneration were analysed. The results showed that the ratio of the one-step conversion of naphthalene was 95% at space velocity 0.81 h^{-1} and $700 \text{ }^\circ\text{C}$; with saturated wet air as regeneration gas, the regeneration time was within 0.5 h; compared with thermal cracking at the same reaction temperature, the catalytic cracking was propitious to deep cracking of naphthalene.

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Keywords: Biomass; Tar; Naphthalene; Ni–dolomite catalyst; Catalytic cracking

1. Introduction

As a source of renewable energy, biomass has several environmental advantages. It is a possible alternative to the direct use of fossil fuel energy. Biomass, a CO_2 neutral source of renewable fuel, can contribute to the demand for heat, electricity and synthesis gas. However, gas cleaning is still the bottleneck in advanced gas utilization that limits the development of the use of biomass for electricity generation, indirect liquefaction and other specific applications. Biomass gasification

involves partial oxidation of the raw material to obtain a mixture of hydrogen, carbon oxides, water, nitrogen and small amounts of methane and higher hydrocarbons. The product gas also contains variable amounts of ash particles, volatile alkali metals and tar, which is a complex mixture of aromatics that includes a significant fraction of polycyclic aromatic hydrocarbons [1]. Current trends for gas cleaning were based on the hot-gas conditioning. The fundamental idea was to process the raw gas at high temperature (above $600 \text{ }^\circ\text{C}$) using a catalyst to destroy tar components. Three groups of catalysts have been evaluated for the elimination of biomass tar [2–5]. These three groups of catalysts are dolomite, alkali metals, and nickel. The first two types of catalysts are

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cheaper, but do not reach the low levels of tar for most gas applications. Nickel-based catalysts, on the other hand, almost completely removed tar, but they are deactivated by coke formation and are more expensive [4–10]. Roberto Coll et al. [1] investigated five types of model compounds of biomass tar (benzene, toluene, naphthalene, anthracene, and pyrene). The results showed that naphthalene was the most difficult compound to reform. In petroleum refinery industries, the performance on cracking of aromatic compounds is that at a temperature of 300–500 °C, the benzene ring cannot be cracked and cracking reaction occurs only at side chains. The selectivity of petroleum cracking catalysts is emphasized on the aim of obtaining certain oil products, not for gas products. So the reaction temperature is not above 550 °C. The aim of biomass tar cracking is different from that of petroleum. The gas products (H₂, CO, etc.) are the final products. For this reason, higher reaction temperature and higher selectivity catalysts are needed. The catalysts also should be stable at the high reaction temperature (>700 °C) [11–13]. In this paper, we have studied the reformation of naphthalene using Ni–dolomite catalysts which were cheap and prepared by using metallic nickel as an active phase grafted on dolomite.

2. Experimental

2.1. Preparation of catalysts

The Ni–dolomite catalysts have been prepared by using metallic nickel as an active phase grafted on dolomite. Nickel nitrate was dissolved into distilled water. The origin, composition, and physical properties of the as-received dolomite are indicated in Table 1. Dolomite was crushed to pass a 1 mm screen. For 10 g of support, a solution obtained with 2.5 g of Ni (NO₃)₂·6H₂O in 40 ml water was used. Bonding agent (525R silicate cement, 5 wt%) and molding agent (LG35-99 medium-carbon graphite, 3 wt%) were added into the mixture. After 15 minutes of stirring, catalysts were dried, molded, calcined, crushed and shifted to 20–40 mesh. The element

Table 1

Physical and chemical properties of the as-received dolomite

Item	Properties
Origin	Guangdong, China
Composition (%)	
CaO	31.3
MgO	19.8
CO ₂	43.7
SiO ₂	1.3
Fe ₂ O ₃	0.7
Al ₂ O ₃	0.5
ρ (g/cm ³)	
Before calcining	2.58
Calcined	1.24
BET surface (m ² /g)	
Before calcining	0.3
Calcined	11.6

Table 2

Metal element analysis of catalyst

Item	Content (ppm)
Cu	0.13
Ni	494.67
Si	11.01
Mg	11914.73
Fe	784.05
Ca	583498.07

analysis of the catalyst is shown in Table 2. The pressure of catalyst molding markedly affected the hole size distribution. The higher the pressure, the bigger the percentage of small size hole. The experiments showed that the optimal pressure was 15 MPa.

2.2. Techniques for characterization of the nickel–dolomite samples

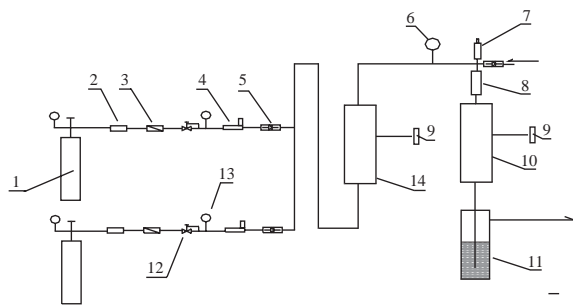
The Ni–dolomite samples have been characterized by elementary analysis performed on THERMO ISIR1000, by powder X-ray diffraction (XRD) on a Siemens D500TT diffractometer using Cu K α radiation, by scanning electron microscopy (SEM) on a Topcon EM 002B apparatus coupled to energy dispersive X-ray spectroscopy, by thermal analysis on A&D HM-200.

2.3. Catalytic tests of the nickel–dolomite catalysts

In order to determine the catalytic activity and stability of the various catalysts on the conditions of biomass gasification, the reactions of reforming of naphthalene ($C_{10}H_8$, >98%, CAS [91-20-3] obtained from a Russian source) have been studied. The schematic diagram of experimental apparatus is shown in Fig. 1.

The operating conditions were the following: fixed bed quartz reactor (8 mm ID); inlet temperature: 700 °C; total feed flow rate: 1.5 Nl h^{-1} ; weight of catalysts: 2.5 g; particle size of the catalysts: 20–40 mesh.

The outlet gas was analyzed by a Shimadzu GC-2010 gas chromatogram equipped with a thermal conductivity detector. The carrier gas, column temperature, and pressure were, respectively, argon, 338 K, and 0.2 MPa. Two packed columns, molecular sieve $13 \times 60/80$ mesh and Porapak Q, were used. The reaction temperature program was composed of two different steps without catalyst reducing treatment. During the initial step (40 °C/min from room temperature to 700 °C), a little yellow smoke from the catalyst bed was observed for each catalytic test. During the second step (700 °C), on-line gas chromatographic analyses for gas composition and catalyst aging study were performed.



1–gas resource 2–purifier 3–filter 4–mass flowmeter 5–valve
6–manometer 7–relief valve 8–mixed box 9–temperature controller
10–reactor 11–scour 12–pressure stabilizer 13–manometer
14–evaporator

Fig. 1. Schematic diagram of experimental apparatus.

3. Results and discussion

3.1. Optimization of catalyst preparation

The thermal analysis of fresh catalyst is shown in Fig. 2. The curve of DTA shows an endothermic peak at 450 °C indicating that $CaCO_3$ decomposition reaction happened. The slope of TG curve decreased as the temperature increased. But it was constant when temperature was above 800 °C. Thus, no decomposition was observed for the catalyst at high temperature (>800 °C). The cracking of biomass tar takes place at high temperature (>700 °C). It was suggested that the catalyst should be calcined at high temperature (>900 °C) for 4 h and packed hermitically before using.

3.2. Characterization of the nickel–dolomite initial interaction

The XRD diagrams of catalyst calcined at 900 °C are presented in Fig. 3. It showed that the dolomite phase was maintained as two phases with a slight shift compared, respectively, to the JCPDS file of the CaO and $Ca(OH)_2$ references. The most particular area was situated at 2θ between 37.5° and 43.5°, characteristic of the cubic NiO phase (JCPDS 22-1189).

The SEM of the Ni–dolomite catalyst (Fig. 4) showed porosity of this support (hole diameters ranging from 1 to 5 μm) and a deposit of almost spherical uniform grains (probably NiO) with size between 0.2 and 0.3 μm can be observed and this hides the surface of the support completely. After

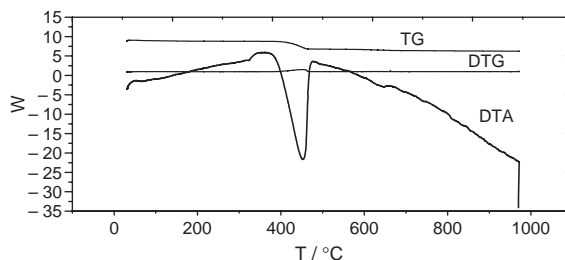


Fig. 2. Thermal analysis of fresh catalyst. Ambience: dry air, sample 9.5 mg, TG scale 10 mg, DTA sensitivity 100 μV , DTG scale 10 mV/min , ratio of heating 10 K/min , air flow 29 ml/min .

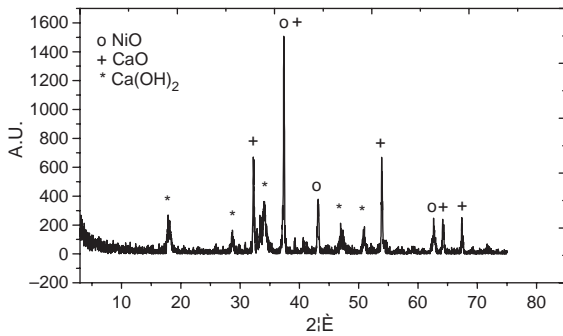


Fig. 3. X-ray diffractograms of Ni-dolomite calcined at 900 °C. References CaO (37-1497 JCPDS file), Ca(OH)₂ (4-0733 JCPDS file), NiO (22-1189 JCPDS file).

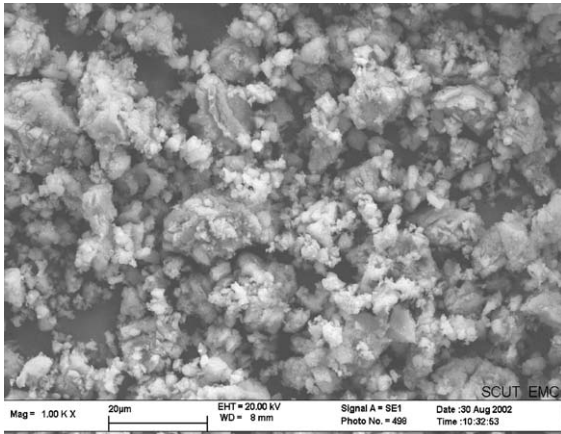


Fig. 4. Scanning electron micrographs of Ni-dolomite calcined at 900 °C.

being calcined at 1100 °C, the porosity observed on Ni-dolomite catalyst disappeared, and more compact grains were formed and the local crystallinity was increased. The element distribution is presented in Table 3.

3.3. Coke formation of catalyst

Regarding Naphthalene as a feed sample, the cracking experiment was carried out at 700 °C. Thermal analysis of catalyst after coke deposition is presented in Fig. 5. Two obvious exothermic peaks were observed. One was located at 400–500 °C, and the other was located at

Table 3
Element distribution of catalyst

Element	wt%	at%
C	0.67	1.27
O	47.87	68.22
Na	2.06	2.04
Mg	1.53	1.43
Al	0.43	0.36
Si	1.98	1.60
Ca	41.09	23.38
Ni	4.38	1.70
Total	100.00	100.00

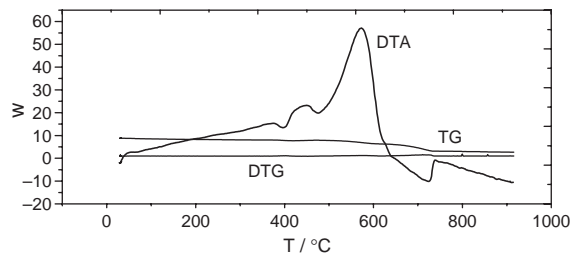


Fig. 5. Thermal analysis of catalyst after coke deposition. Ambience: dry air, sample 9.8 mg, TG scale 10 mg, DTA sensitivity 100 uv, DTG scale 10 mv/min, Ratio of heating 10 K/min, air flow 28 ml/min.

500–600 °C. The reaction included several steps. The first one was that naphthalene was absorbed on the surface of catalyst, and then decomposed and aggregated. Finally, coke was formed. The coke was distributed on the surface of catalyst and incumbent on active centre. So the catalytic activity decreased. Because both nickel and dolomite had a catalytic effect on naphthalene [4,6–7], using the Ni-dolomite double-function catalyst, may be there exist two forms of coke formation. The former may be the coking on the surface of nickel, and the latter may be the coking on the surface of dolomite. On comparison with the area of two exothermic peaks, it was indicated that the coke formation on dolomite was primary. The curve of bed resistance vs. reaction time is presented in Fig. 6. Several authors think that the whisker-type carbon is easily formed on the nickel catalyst on this reaction condition [14–16]. So the

inter-particle void space was lost to the passage of gas. The longer the reaction time, the higher the reaction bed resistance. Catalyst regeneration experiment was carried out at 700 °C with saturated wet air as regeneration fluid. The activity of the catalyst was regained within 0.5 h.

3.4. Cracking performance of nickel–dolomite

The cracking performance of Ni–dolomite was evaluated by calculating the carbon balance. From Table 4, Figs. 7 and 8, we could see that the fresh catalyst had very high catalytic activity, but its cracking activity decreased rapidly within 10 h and then decreased slowly from 10 to 35 h; the one-step conversion ratio decreased linearly when the cracking temperature decreased. When the cracking temperature was at 500 °C, the one-step conversion ratio was approximately the same as that of thermal cracking at 700 °C. The earliest coke formation on the surface of catalyst had a key effect on cracking activity. The coke covered

the centre of activity, so the one-step conversion ratio decreased. The more serious the coke formation, the lower the conversion ratio, but the content of H₂ in the produced gases increased appreciably and the content of CO₂ in the produced gases decreased appreciably. It was predicted that at high reaction temperature (700 °C), the coke reacted with H₂O and CO₂. Compared with thermal cracking at the same temperature, the composition of product gas was different, namely, the gas produced by catalytic cracking had a high content of H₂ and a low content of CH₄, C₂H₄, C₂H₆, but the gas produced by thermal cracking was opposite. The principle of these two cracking methods was different. In order to obtain high content of H₂ and CO by thermal cracking, higher reaction temperature (above 1100 °C) was needed.

Aromatic compounds were stable to heat. In the process of thermal cracking, polymerization reaction was primary. The longer the polymerization

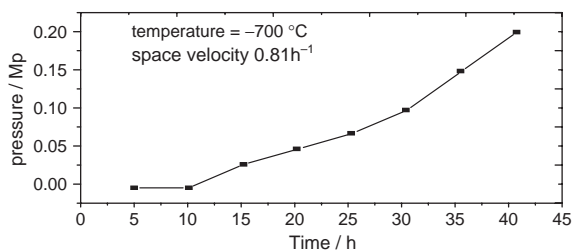


Fig. 6. Bed resistance vs. reaction time.

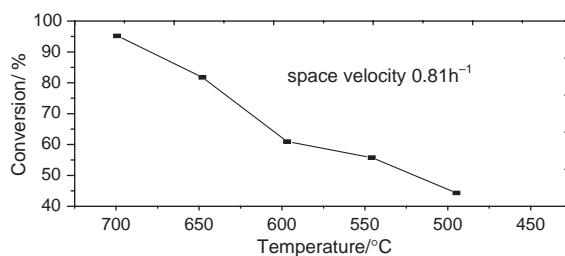


Fig. 7. Conversion ratio vs. temperature.

Table 4
Composition of product gas

Catalytic cracking	Gas composition (%)						Conversion (%)
	H ₂	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	
1 h	50.1	32.5	8.3	6.4	0.4	0.1	94.8
5 h	51.5	31.7	11.6	3.3	0.4	0.2	84.3
10 h	56.7	30.1	11.4	1.4	0.2	0.2	63.7
15 h	56.6	29.4	12.0	1.5	0.4	0.1	61.6
20 h	54.8	28.4	15.5	1.0	0.3	0.1	57.4
Thermal cracking	35.4	29.1	20.2	2.0	12.5	0.8	40.4

Catalytic cracking reaction condition: 700 °C, 0.81 h⁻¹, Ni–dolomite catalyst packed. Thermal cracking reaction condition: 700 °C, 0.81 h⁻¹, ceramic rings packed.

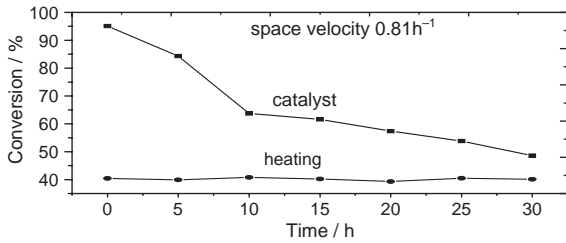


Fig. 8. Conversion ratio vs. reaction time.

reaction time, the greater the weight of molecule. Finally, coke was formed. It was predicted that the process of catalytic cracking included two steps. The first step was that the earliest polymer was formed, and the second step was that steam conversion reaction took place between the earliest polymer and steam under the condition of catalysts. But the former was rapid and the latter was slow. So the latter was the control step, and a better method should be researched to improve the second reaction velocity.

4. Conclusions

In order to make the catalyst stable for long time at high reaction temperature (700 °C), bond (cement) and mold (medium-carbon graphite) agents were added. It was suggested that the catalyst should be calcined at 900 °C for 4 h, then hermetically packed.

Coke formation was the primary cause to decrease the catalytic activity and to increase the reaction bed resistance. The catalytic activity decreased rapidly from 0 to 10 h and slowly from 10 to 35 h. With saturated wet air as regeneration fluid, the catalytic activity was regained within 0.5 h at 700 °C.

The principle of catalytic cracking was different from that of thermal cracking. When the one-step conversion ratio based on carbon balance calculation was same, the composition of the produced gas was different. Compared with thermal cracking, catalytic cracking was propitious to the production of H₂ and CO at the same reaction temperature.

Acknowledgement

Financial support from the “One-hundred-scientist Program” of the Chinese Academy of Sciences to J. Chang is gratefully acknowledged.

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