Effects of promoters on biomass gasification using nickel/dolomite catalyst

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Abstract−Metallic nickel has been selected as a catalyst for biomass gasification because of its activity in biomass steam gasification and tar reduction. The effects of types of promoters such as platinum, cobalt, and iron on biomass gasification were evaluated. The area of interest was the effects of preparation methods, which were impregnation and coprecipitation. Catalyst preparation by the impregnation method showed superior performance. The conclusion can be drawn from the experiments that the platinum promoter enhanced the reforming reaction, iron promoted a water-gas shift reaction, and the cobalt promoter favored a methanation reaction. Moreover, the addition of noble metal reduced carbon deposition on Ni/dolomite.

Key words: Promoter, Biomass, Gasification, Ni/Dolomite, Coconut Shell

INTRODUCTION

Gasification is a flexible, reliable, and clean technology that can turn a variety of low-value feedstock into high-value products. It helps to reduce our dependence on foreign oil and natural gas, and provides a clean alternative source of base load electricity, fertilizers, fuels, and chemicals. Gasification is a manufacturing process that converts any material such as coal, petroleum coke (petcoke), or biomass into synthesis gas (syngas). The syngas can be burned to produce electricity or further processed to manufacture chemicals, fertilizers, liquid fuels, substitute natural gas (SNG), or hydrogen. One of the major issues in biomass gasification is how to deal with the tar formed during the process. Tar is a complex mixture of condensable hydrogen which includes single ring to five ring aromatic compounds along with other oxygen-containing hydrocarbons and complex poly aromatic hydrocarbon PAH [1]. Tar can be eliminated by thermal cracking or by the use of a catalyst. The catalytic gasification process is an attractive technological alternative to deal with tar and to produce a high yield of syngas. Many researchers have proved the usefulness and effectiveness of calcined dolomite and nickel-based steam reforming catalysts in decreasing tar yield [1,2]. The catalyst can increase the reaction rate of the steam and can participate in the secondary reactions [3]. Therefore, the catalyst improves the quality of the gas product and reduces tar content in the process [4]. Moreover, adding active bed materials also prevents agglomeration tendencies and subsequent coking of the bed. Nickel and dolomite catalysts have been proven to be very active in terms of tar reduction and show excellent catalytic activity building up resistance to coking and sulfur poisoning in steam gasification of toluene and naphthalene [5,6].

The application of metal catalysts in biomass gasification is an effective method of reducing tar content. In most cases, commercially available, steam reforming Ni catalysts have been applied,

and the problem of catalyst deactivation due to coke deposition has been pointed out [7]. Recently, Asadullah et al. [8] reported the gasification of cellulose and biomass with air using $Rh/CeO_2/SiO_2$. It was found that $Rh/CeO_2/SiO_2$ was a much more effective catalyst for gasification of biomass with air than conventional steam reforming using a Ni catalyst and dolomite. It also showed high resistance to coke deposition and high stability. However, the catalyst has problems of high cost and limited availability originating from the usage of Rh. Metal catalysts have also been developed by the addition of a small amount of noble metal such as Pt, Ru, Rh, or Pd [9]. Noble metals are known to form less coke under reforming reactions and the coke formed differs in nature from that found with the Ni catalyst. Platinum is an interesting metal for use as a catalyst for syngas obtention, due to its good availability and relatively low price in comparison with rhodium [10]. Cobalt catalysts have been reported as an effective catalyst for the steam gasification of wood and biomass, partial oxidation of methane, and steam reforming of ethanol [11]. In summary, the above problems motivated the authors to study the catalytic performance of Ni/dolomite for tar removal in biomass gasification and to investigate catalytic performances of a Ni/dolomite catalyst by adding small amounts of noble metal to a Ni/dolomite catalyst in order to determine its catalytic reactivity for gas production, structural stability and resistance to coking with a reduction of the production costs. We investigated the effects of promoters of transition metal group VIIIB, such as Pt, Co, and Fe, impregnated on a Ni/dolomite catalyst. We also studied the efficiency of a Ni/dolomite catalyst for tar removal and investigated suitable operating parameters of product gas compositions.

MATERIALS AND METHODS

1. Feed Material

Coconut shell (Thailand) was used as the feedstock with a size range of 0.75-1.20 mm. The proximate of biomass was expressed as follows: moisture 5.56%, fixed carbon 19.68%, volatile matter 73.86%, and ash 0.9%, while the ultimate analysis was C 46.02%,

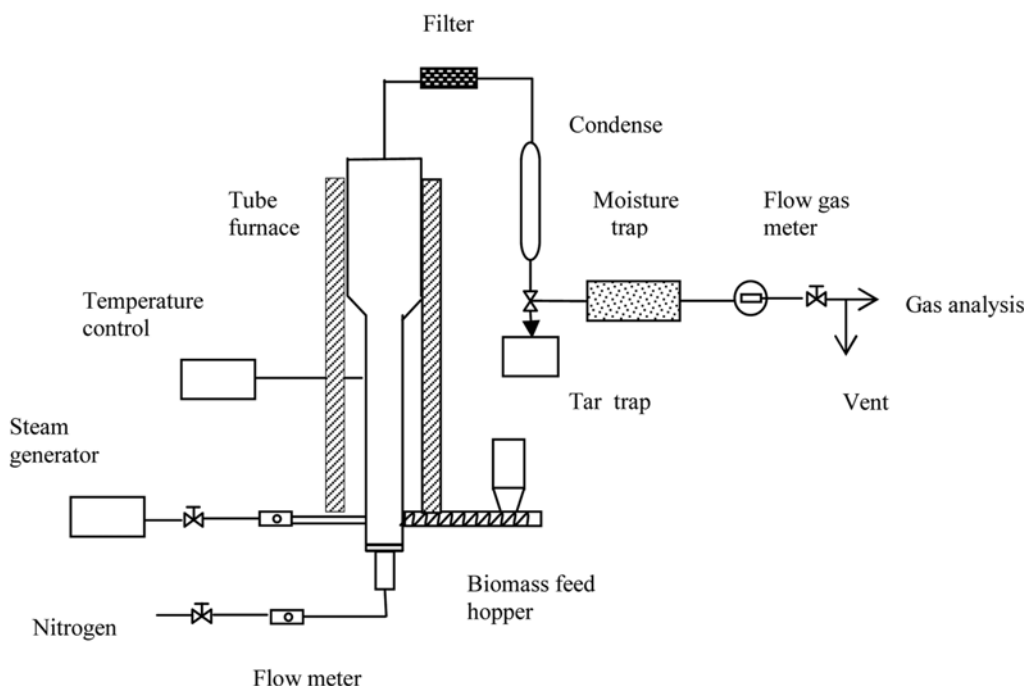†To whom correspondence should be addressed.
E-mail: tharapong.v@chula.ac.th

Fig. 1. Experimental setup for catalytic biomass gasification.

H 6.04%, N 0.18%, and O 47.76%.

2. Apparatus

The experimental setup, shown in Fig. 1, consists of six main parts: (i) a fluidized bed reactor, (ii) biomass feeding section, (iii) steam generator and preheating section, (iv) cooling section, (v) tar collector, and (vi) gas analysis section. Experiments were carried out in a fluidized bed gasifier with a height of 92 cm and diameter of 5 cm. The cylindrical stainless steel reactor is located inside an electric furnace and controlled by an electric heater. During start-up, the reactor was charged with 10 g of Ni/dolomite catalyst as bed material, and a type K thermocouple measured temperature in the catalytic bed. Biomass was continuously fed from the screw feeder with a feed rate of 1.76 g/min. Steam and nitrogen were used as the gasifying medium. Water was pumped into the steam generator and flowed to the reactor entrance through a preheating line at inlet temperature of 200 °C before entering into the heated gasifier. When the bed temperature reached the desired level and become steady, the gas product was analyzed every 3 min. In this experiment, the nitrogen gas was used for fluidization. The minimum fluidization velocity was 0.06 m/s.

3. Gas Analysis

During the reaction, the gaseous product flowed out of the reactor, passed through the cooling section, moisture trap, and finally the gas filter for drying and cleaning. The exit gases were analyzed by an on-line gas chromatograph (Model GC-2010, Zhimadzu, Japan), which is filled with Unibeads C column (3 m×3 mm ID) and TCD detectors with helium as the carrier to detect gases, mainly H_2, CO, CO_2, and CH_4.

4. Catalyst Preparation

The Ni/dolomite was prepared by the method of Srinakruang et al. [5]. The performance of Ni-based catalyst is improved by adding small amounts of promoters containing Pt, Co, and Fe to Ni/dolo-mite catalyst using impregnation and coprecipitation methods, as follows:

4-1. Impregnation Method

The 10 g of Ni/dolomite catalyst was mixed with hexachloro-platinic acid, cobalt nitrate, and ferric chloride. The loading of metal was 1% and expressed in a weight ratio of (Ni+support). The slurry was heated at 80 °C with stirring, and then dried. The catalyst was dried at 120 °C overnight and calcined in air at 600 °C. The catalysts will be referred to as Ni/Pt/DM(Imp), Ni/Co/DM(Imp), and Ni/Fe/DM(Imp) respectively.

4-2. Coprecipitation Method

This catalyst was prepared by precipitating nickel nitrate with aqueous solution containing hexachloroplatinic acid, cobalt nitrate, ferric chloride, and ammonium carbonate in the presence of dispersed dolomite. The slurry was filtered, washed, dried at 120 °C overnight and calcined in air at 600 °C. The catalysts will be referred to as Ni/Pt/DM(Cop), Ni/Co/DM(Cop), and Ni/Fe/DM(Cop).

5. Characterisation of Catalyst

The catalyst surface area was measured by the BET method with N_2. The Ni/dolomite catalyst was analyzed by using the energy dispersive x-ray fluorescence spectrometer and X-ray diffractometer (XRD) at 30 kV, 30 mA Cu Kα radiation, and a scan speed of 0.02°/min.

RESULTS AND DISCUSSION

1. Characteristics of Catalysts

The properties of the Ni/Pt/DM, Ni/Co/DM, and Ni/Fe/DM catalysts prepared by different methods were measured by N_2 absorption and hydrogen chemisorption (Table 1).

Table 1 shows that the catalysts prepared by the impregnation method have higher surface areas of 6.74, 5.76, and 11.18 (m²/g)

Table 1. Properties of catalyst

Catalyst	Preparation method	BET[a] (m^2/g)	Pore volume (cm^3/g)	Metallic surface area[b] (m^2/g)	Active particle diameter[c] (nm)
Ni/Pt/DM	Impregnation	6.74	0.046	0.92	77
Ni/Co/DM	Impregnation	5.76	0.033	0.20	364
Ni/Fe/DM	Impregnation	11.18	0.038	0.03	2671
Ni/Pt/DM	Coprecipitation	5.33	0.038	0.06	166
Ni/Co/DM	Coprecipitation	4.77	0.026	0.05	1532
Ni/Fe/DM	Coprecipitation	8.76	0.028	0.02	2715

[a]Calculated from N_2 adsorption isotherm
[b]Calculated from hydrogen chemisorption
[c]Calculated from chemisorption

for the Ni/Pt/DM, Ni/Co/DM, and Ni/Fe/DM catalysts, respectively. The metallic surface areas of the catalysts prepared by the impregnation method are higher than those of the catalysts prepared by the coprecipitation method. The metallic surface areas resulting from the Ni/Pt/DM, Ni/Co/DM, and Ni/Fe/DM impregnation method are 0.92, 0.2, and 0.03 (m^2/g), respectively. The coprecipitation method resulted in smaller metallic surface areas because metallic active species were transformed to a less active structure. The pore volumes of the catalysts have a similar trend to the surface areas, that is, they depend on the preparation method and type of catalyst loading. The pore volumes of Ni/Pt/DM, Ni/Co/DM, and Ni/Fe/DM obtained by the impregnation method are 0.046, 0.033, and 0.038 (cm^3/g), respectively. Adding promoters created conglomerations of metal particles and increased in crystallite size by the coprecipitation method. Profeti et al. [12] suggested that the addition of noble metal contributed to a decrease in surface area and increase in crystallite size.

2. Catalyst Characterization

The XRD patterns of 10% Ni/dolomite promoted by 1% of Pt, Co, and Fe with two preparation methods are presented in Figs. 2-4. The catalysts were reduced in H_2 at 700 °C. Fig. 2 shows the XRD pattern of Ni/Pt/DM catalysts prepared by two different methods. The two XRD patterns for the preparation methods are almost the same. The peak corresponding to Ni registers a reading of 44.5° and 51.8° on the 2θ horizontal axis, and the Pt peak is at $2\theta=40°$.

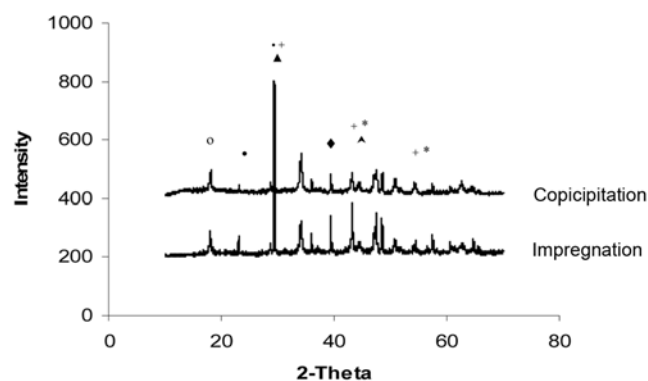Fig. 3 shows the XRD pattern of the Ni/Co/DM catalyst after

reduction of the catalyst under H_2. The two methods of preparation of Ni/Co/DM resulted in the same XRD pattern. Cobalt reaches a peak of 47.5° and nickel reaches 44.5° on the 2θ axis.

Fig. 4 shows XRD patterns of the Ni/Fe/DM catalyst after reduction under H_2. The two methods of preparation of Ni/Fe/DM appeared to have the same XRD pattern. Iron reaches a peak of 44.35° on the 2θ axis, while nickel reaches 44.5°.

3. Effect of Catalyst Preparation

The activity of promoters was studied to compare the effect of the catalyst preparation method on carbon balance as shown in Fig.
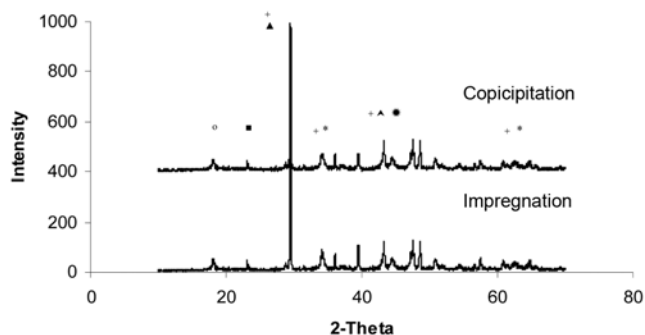

Fig. 3. XRD pattern of the Ni/Co/DM catalyst (+ NiO, * NiMgO₂, ▲ MgO, ▲ Niᵒ, ■ CaO, ○ CaCO₃, ✳ Coᵒ).

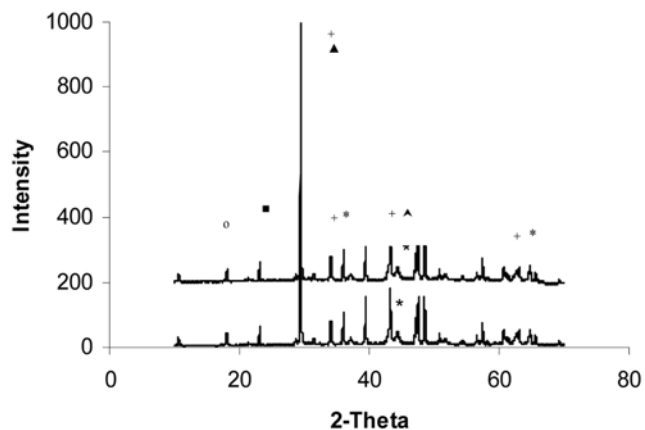Fig. 2. XRD pattern of Ni/Pt/DM catalyst (+ NiO, * NiMgO₂, ▲ MgO, ▲ Niᵒ, ■ CaO, ○ CaCO₃, ◆ Ptᵒ).

Fig. 4. XRD pattern of Ni/Fe/DM catalyst (+ NiO, * NiMgO₂, ▲ MgO, ▲ Niᵒ, ■ CaO, ○ CaCO₃, ✳ Feᵒ).
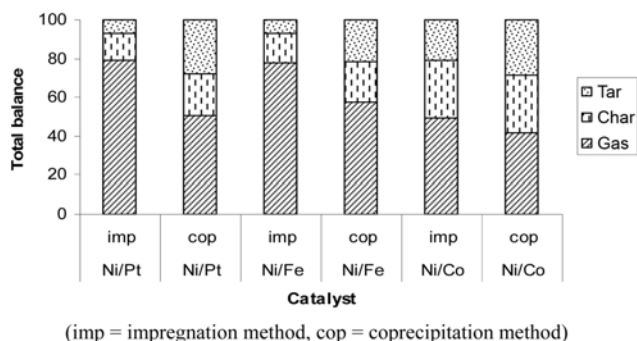
Fig. 5. Effect of catalyst preparation methods on carbon balance (Conditions: temperature 800 °C, (S/C) ratio 0.95, coconut shell feed rate 1.76 g/min).

5. The experiment was performed at a temperature of 800 °C, with an (S/C) ratio of 0.95, coconut shell as a biomass, and feed rate of 1.76 g/min. A comparative study of Ni/Pt/DM, Ni/Fe/DM, and Ni/Co/DM catalysts is presented as a function of the catalyst preparation technique.

Catalyst preparation by the impregnation method yielded higher percentages of carbon conversion to gas. As can be seen from Fig. 5, catalyst prepared by the impregnation method gave C_{conv} to gas of 79.19%, 78.12%, and 49.53% when using Ni/Pt/DM(imp), Ni/Fe/DM(imp), and Ni/Co/DM(imp), respectively. However, in the cases where the catalysts were prepared by the coprecipitation method, the C_{conv} activity was 50.51%, 57.46%, and 41.82% when using Ni/Pt/DM(cop), Ni/Fe/DM(cop), and Ni/Co/DM(cop) as catalysts, respectively.

4. Effect of Promoters on Gas Composition

After the analysis of the effect of preparation method was completed, the effects of promoter types were investigated by considering the effects of the catalytic performance on product gas composition. The experiments were performed at 800 °C and steam to carbon ratio (S/C) of 0.95. This (S/C) ratio of 0.95 was the suitable condition to produce higher gas product by the use of Ni/dolomite catalyst as reported previously [13]. The experiment was carried out by using three types of impregnated catalysts: 10%Ni/1%Pt, 10%Ni1%Fe, and 10%Ni1%Co. The results can be understood through evaluation of the effect of catalyst activity on gas composition and carbon balance.
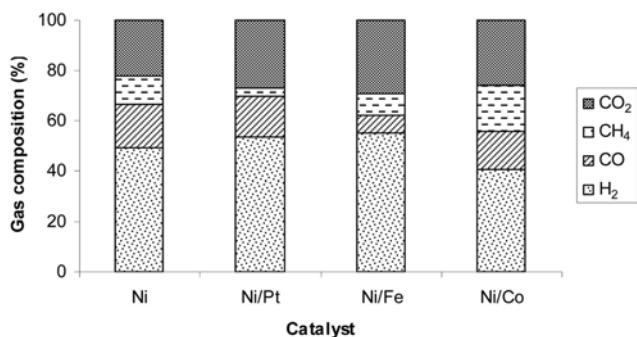

Fig. 6. Effect of promoters on gas composition (Conditions: temperature 800 °C, (S/C) ratio 0.95, coconut shell feed rate 1.76 g/min).
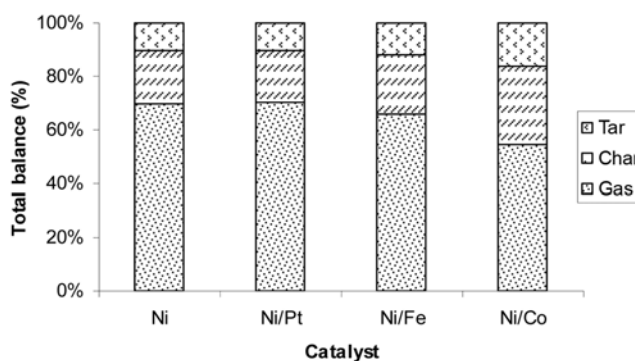
Fig. 7. Effect of promoters on carbon balance (Conditions: temperature 800 °C, (S/C) ratio 0.95, coconut shell feed rate 1.76 g/min).

Figs. 6 and 7 show the effects of promoters on gas composition and carbon balance. The addition of Pt enhances performance of the steam gasification of coconut shell in terms of carbon conversion to gas yield, as shown in Fig. 10. The Ni/Pt/DM catalyst promoted steam reforming and methane reforming and increased H_2, CO, and CO_2 contents. The following equations explain:

$$C+H_2O \rightarrow CO+H_2 \tag{1}$$

$$CO+H_2O \rightarrow CO_2+H_2 \tag{2}$$

$$CH_4+H_2O \rightarrow CO+3H_2 \tag{3}$$

It has been reported that Ni/Pt showed the high performance in steam gasification [9,14]. Addition of Pt to Ni enhanced the catalytic activity [15]. It is indicated that the catalyst with high BET surface area and metallic surface are can provide large contact area for reactants, thus resulting in high reaction activity.

Water-gas shift reaction increased H_2 and CO_2 production by using iron (Ni/Fe/DM) as a catalyst.

$$CO+H_2O \rightarrow CO_2+H_2 \tag{4}$$

The results show trends similar to those observed by Yu et al. [16], who found a significant enhancement of hydrogen production during the gasification of Victorian brown coal in the presence of iron. The Ni/Co/DM catalyst promoted methanation and the reforming of methane resulted in an increasing of the production of CH_4 and CO. This can be seen in the following reactions:

$$C+2H_2 \rightarrow CH_4 \tag{5}$$

$$CH_4+H_2O \rightarrow CO+3H_2 \tag{6}$$
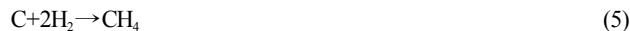
According to the literature, it can be suggested that Ni/Co bimetallic catalyst show excellent stability and high activity for CO_2 reforming of CH_4 [17]. At reaction temperature such as 750 °C, reactions (5) and (6) are thermodynamically favored.

The gaseous products were increased with the use of catalysts in the following order: Ni/Pt/DM (72.34%)>Ni/DM (70.34%)>Ni/Fe/DM (68.12%)>Ni/Co/DM (54%).

5. Coke Formation Analysis

The primary cause of deactivation of the catalyst is the formation of coke deposition on the surface. Thus, it is essential to measure the amount of coke to compare the carbon resistance of the cata-

Table 2. Coke amount measured by thermogravimetric analysis for used catalysts

Catalyst	Coke amount[a] (%)
Ni/DM	16.5
Ni/Pt/DM	6.5
Ni/Fe/DM	8.3
Ni/Co/DM	9.3

[a](g of coke/g of sample)$\times 100$

lysts. The purpose of this section is to design an excellent catalyst which would result in the formation of less coke.

The carbon deposition was analyzed by TGA in air after a test run for 2 h. The weight loss which occurred at 600 °C was a result of carbon being deposited on the surface. From Table 2, it can be seen that the amount of coke formation on the catalysts was in the following order: Ni/Pt/DM<Ni/Fe/DM<Ni/Co/DM<Ni/DM. As reported in a previous study by Chen et al. [15], three kinds of deposited coke have been found in the steam reforming process. Carbon deposition proceeds via the formation of carbide species through the Boudouard reaction ($2CO \rightarrow CO_2+C$) and CH_4 decomposition ($CH_4 \rightarrow 2H_2+C$). The type and nature of the coke formed depend on the metal and in some cases on the support used.

CONCLUSIONS

1. Catalyst preparation significantly changes the values of the BET surface area, pore volume, metallic surface area, crystallite size, and morphology of a catalyst. The impregnation method gave higher BET surface areas and metallic surface areas than the coprecipitation method because of the agglomeration of metal particles, resulting in an increase in crystallite size.

2. Adding a small amount of promoters affects the gas composition. The results implied that different promoters play a significant role in the gasification reaction. The Ni/Pt/DM catalyst promoted steam reforming, a water-gas shift reaction, and increased H_2, CO, and CO_2 contents. The effect of using iron as a catalyst was to catalyze the water-gas shift reaction and increase H_2 and CO_2 production. The Ni/Co/DM catalyst promoted methanation and reforming of methane, which increased the CH_4 and CO_2 content.

3. The effect of noble metals on the stability of coke formation is as follows: Ni/Pt/DM<Ni/Fe/DM<Ni/Co/DM<Ni/DM. The addition of metallic noble metals may help the improvement of metallic dispersion, decrease the sintering, and enhance the improvement of thermal stability.

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