

## Article

# Catalytic Pyrolysis of Naomaohu Coal Using Combined CaO and Ni/Olivine Catalysts for Simultaneously Improving the Tar and Gas Quality

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**Abstract:** Catalytic pyrolysis of low-rank coal is currently an effective method for producing high-quality tar and gas. In this study, catalytic upgrading of volatiles from Naomaohu (NMH) coal pyrolysis has been conducted in a two-stage fixed-bed reactor using combined CaO and Ni/olivine (Ni-loaded olivine) catalysts. The effect of catalyst distribution modes and catalytic temperature on the tar and gas quality has been investigated. Simulated distillation and GC-MS analysis have been used to investigate the distribution of tar components. The results indicated that the light oil fraction in tar dramatically increased due to the combination of CaO and Ni/olivine. The CaO-Ni/olivine mode is especially better compared to the layouts of the Ni/olivine-CaO mode and the mixed mode. The CaO-Ni/olivine mode ensures a higher light fraction in tar at 69.3% and a light oil fraction at 29.8% at a catalytic temperature of 450 °C, while the heavy tar fraction decreased to 30.7%. Meanwhile, the contents of benzene (heteroatomic substituents) in tar significantly increased from 2.55% to 6.45% compared with the blank test. In this scenario, CaO breaks down macromolecular compounds in tar and cleaves long-chain esters to produce aliphatic hydrocarbons. These hydrocarbons are then dehydrogenated to produce lighter aromatic hydrocarbons over the CaO surface. Subsequently, the volatiles pass through the Ni/olivine catalysis, where ether compounds are produced by means of dehydration reactions. In addition, the CaO absorbs the CO<sub>2</sub> in the pyrolysis gas, leading to an elevation of CH<sub>4</sub> and H<sub>2</sub> concentration. Particularly, the concentration of H<sub>2</sub> significantly increased from 16.2% to 30.37%, while the concentration of CO<sub>2</sub> significantly decreased from 37.9% to 10.57%. These findings suggest that the usage of combined CaO and Ni/olivine catalysts is beneficial for improving both the tar and gas quality.

**Keywords:** CaO; Naomaohu coal pyrolysis; volatile upgrading; Ni/olivine



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## 1. Introduction

The pyrolysis-based staged conversion technology for low-rank coal is a thermochemical process that transforms coal into gas, tar, and char. The objective of this process is to achieve clean and efficient usage of low-rank coal [1–3]. However, the conventional pyrolysis process often generates a notable quantity of heavy tars with boiling points exceeding 360 °C and also produces CO<sub>2</sub> as a by-product [4,5]. Over 50% of the total tar consists of heavy components characterized as highly viscous and corrosive [6]. These properties can result in clogs in downstream equipment and compromise the stability of

the pyrolysis process [7]. Higher concentrations of CO<sub>2</sub> hinder the further utilization of pyrolysis gas from low-rank coal. This limitation imposes restrictions on the industrial application of pyrolysis products. Hence, it is of utmost importance to minimize the formation of heavy components and enhance the gas components to advance the development of the pyrolysis process.

Numerous studies have demonstrated that catalytic cracking technology holds great potential for improving tar quality [8]. The selection of an appropriate catalyst is crucial for the successful implementation of catalytic cracking technology. Currently, transition metals (Fe, Ni, and Mo) and alkali and alkaline earth metals (K and Ca) have been widely used as upgrading catalysts in recent studies [9–11]. Metal catalysts play a significant role in the catalytic upgrading of coal pyrolysis volatiles due to their higher activity [12,13]. Among the various metal catalysts, transition metals have received more attention in comparison to noble metals due to their relatively lower cost for industrial applications [14]. For instance, Han et al. [15,16] reported the catalytic cracking of bituminous coal using Ni-char-based and Ce-Ni-based catalysts, resulting in a significant increase in the fraction of light tar by 69% and 75%, respectively. Le et al. [17] investigated the catalytic cracking process of Shenmu coal pyrolysis using USY zeolite, CaO, and K<sub>2</sub>CO<sub>3</sub> as catalysts and found that an increase has been shown in the light tar yield from 9.5 to 11.1% on coal by adding 1% USY zeolite.

In recent years, extensive research has been conducted on the use of synthetically created or modified naturally occurring minerals for catalytic pyrolysis due to their abundant availability and wide distribution. Olivine ((Mg, Fe)<sub>2</sub>SiO<sub>4</sub>)-based catalyst has gained attention due to its high catalytic activity and mechanical strength [18]. It has been found that the catalytic activity of olivine is mainly attributed to its iron content [19]. However, the catalytic activity of olivine alone is still not sufficient for tar catalytic cracking. In previous studies, a Ni/olivine (Ni-loaded olivine) catalyst was developed to enhance tar catalytic cracking activity [20,21]. Currently, there is limited literature available on the use of a Ni/olivine catalyst for improving the quality of tar from low-rank coal pyrolysis. Ni/olivine appears to be a promising catalyst material due to its high mechanical strength and superior tar catalytic activity.

Although Ni/olivine catalysts have shown improvements in tar quality, they are still insufficient to efficiently improve gas quality. Due to its intrinsic properties, CaO is expected to significantly influence the process of CO<sub>2</sub> release in the gaseous products. This presents an opportunity to effectively control the distribution and regulation of pyrolysis gaseous products in the early stages by separating and absorbing CO<sub>2</sub> and producing hydrogen-rich and methane-rich gases. The presence of a hydrogen-rich and methane-rich gas atmosphere promotes the catalytic upgrading reaction by increasing the H/C molar ratio in the tar. This environment enhances the content and yield of light tar while minimizing the decrease in tar yield. CaO also plays a specific role in the cracking of tar macromolecules, facilitating the transformation of large molecules into smaller ones [22]. It also aids in the breaking of C-C, C-OH, and C-COOH bonds in aromatic compounds, leading to a reduction in heavy components in the tar [23]. To date, there have been no studies on the catalytic pyrolysis of low-rank coal using a combination of CaO and Ni/olivine catalysts. Therefore, it is crucial to investigate the pyrolysis characteristics and mechanisms of low-rank coal using combined CaO and Ni/olivine catalysts.

This study aimed to investigate the catalytic pyrolysis of Naomaohu coal using a combination of CaO and Ni/olivine catalysts in order to improve the quality of tar and gas products. Specifically, three different catalytic modes were studied: CaO-Ni/olivine mode, Ni/olivine-CaO mode, and mixed mode. The impact of catalytic temperature on the yields and distribution of pyrolytic products was also examined. The study delved into the different catalytic reaction mechanisms involved in the catalytic upgrading of coal pyrolysis volatiles under the three catalytic pyrolysis modes.

## 2. Experimental

### 2.1. Materials

The low-rank coal used in this study was obtained from Naomaohu (NMH) in Xinjiang, China. Pure CaO was sourced from Shanghai Myriad Corporation, Shanghai, China. Both the coal sample and CaO underwent milling and sieving processes to achieve a particle size of 0.25–0.425 mm before the test. The coal sample was dried in an oven at 105 °C for 8 h prior to the experiment. Table 1 provides the proximate and ultimate analyses of the NMH coal.

**Table 1.** Proximate and ultimate analyses of NMH coal.

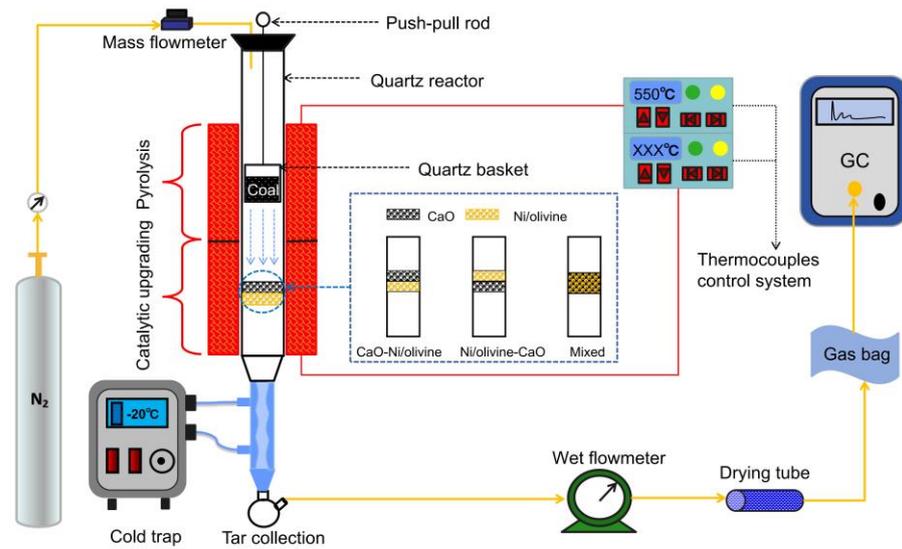
| Proximate Analysis (wt.%, ad) |       |          |                | Ultimate Analysis (wt.%, daf) |      |       |      |      |
|-------------------------------|-------|----------|----------------|-------------------------------|------|-------|------|------|
| Moisture                      | Ash   | Volatile | Fixed Carbon * | C                             | H    | O *   | N    | S    |
| 4.88                          | 12.77 | 48.52    | 33.83          | 68.40                         | 3.55 | 24.86 | 2.77 | 0.42 |

\* By difference.

The natural olivine used in this study was obtained from Yichang, China. Prior to the test, it was sieved to achieve a particle size range of 0.25–0.425 mm and calcined in air for 4 h at a temperature of 900 °C. X-ray fluorescence (XRF) analysis revealed that the olivine predominantly consisted of 42.9% MgO, 44.8% SiO<sub>2</sub>, 9.6% Fe<sub>2</sub>O<sub>3</sub>, 1.1% CaO, and 1.0% Al<sub>2</sub>O<sub>3</sub>. An olivine-supported 5% Ni catalyst (Ni/olivine) was synthesized by wet impregnation of the calcined olivine with nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O). Before commencing the tests, the Ni/olivine catalyst was reduced at 800 °C by passing a mixture of 50% H<sub>2</sub> and 50% N<sub>2</sub> through the reactor at a rate of 100 mL/min for 2 h.

### 2.2. Experimental Apparatus and Procedure

The experiments were conducted using a two-stage fixed-bed reactor, as shown in Figure 1. The apparatus consisted of a gas supply system, a quartz tube fixed bed, a temperature-controlling part, a volatiles condensation part, and a pyrolysis gas sampling system. The quartz tube reactor had an inner diameter of 24 mm and a length of 970 mm. In the pyrolysis stage of the reactor, coal was subjected to fast pyrolysis. The resulting pyrolysis volatiles then passed through the lower stage, where catalytic upgrading took place. Prior to each test, 5 g of coal sample was placed in a quartz basket suspended at the top of the reactor (unheated area) with the help of a push–pull rod. In the catalytic upgrading stage, 2.5 g of CaO and 1 g of Ni/olivine catalysts were placed using three different distribution modes: CaO-Ni/olivine, Ni/olivine-CaO, and mixed mode. In the case of the blank test, quartz sand was used as the bed material. High-purity N<sub>2</sub> was employed as the carrier gas, maintaining a constant flow rate of 200 mL/min regulated by a mass flow meter throughout the reactor. The temperature of the pyrolysis stage was consistently set at 550 °C for all experiments, while the temperature of the catalytic upgrading stage varied between 400 °C and 650 °C. Both the pyrolysis and catalytic upgrading stage temperatures were increased from ambient conditions at a rate of 10 °C/min to reach the desired temperature. To conduct coal fast pyrolysis, the quartz basket containing the coal sample located in the top reactor was swiftly lowered to the pyrolysis stage using a push–pull rod. The coal was subjected to a pyrolysis temperature of 550 °C for 30 min, during which the pyrolysis volatiles were passed through the connected catalytic upgrading stages by the carrier gas. The resulting volatiles from the catalytic upgrading stage were then directed into a cooling system, where the condensable fraction was collected in a cold trap set at −20 °C. The non-condensable gases were measured using a wet flowmeter and collected in a gas bag for subsequent analysis via gas chromatography. The liquid product was separated into tar and water according to ASTM D95-05e1 (2005) [24], with toluene used to determine the tar yield through subtraction.



**Figure 1.** Schematic diagram of the two-stage fixed-bed reactor.

### 2.3. Analysis of Pyrolysis Products

The distribution of tar according to the boiling point was conducted by simulated distillation (Agilent Technologies 7890B, Santa Clara, CA, USA) equipped with a flame-ionization detector (FID). Based on ASTM D2887 standards [25], the boiling point distribution test technique for tar was used. Pitch (>360 °C), light oil (<170 °C), phenolic oil (170~210 °C), naphthalene oil (210~230 °C), washing oil (230~300 °C), and anthracene oil (300~360 °C) were the categories into which tar was separated based on its boiling point. A fraction of boiling point lower than 360 °C was designated as light tar, while a boiling point higher than 360 °C was designated as heavy tar [26]. The tar composition was determined by the GC-MS system (PerkinElmer, Waltham, MA, USA). High-purity helium was used as carrier gas. The injector and detector temperatures were 250 °C and 270 °C, respectively. The oven temperature was kept at 50 °C for 5 min, then the temperature increased to 270 °C for 8 °C/min, and finally, it was kept at 270 °C for 20 min. The contents of pyrolysis gases, including H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>, were analyzed by a GC (INFICON, Bad Ragaz, Switzerland, Micro GC Fusion) with a thermal conductivity detector (TCD). For convenience, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>, were denoted as C<sub>2</sub>-C<sub>3</sub>. The char yield ( $Y_{char}$ ), tar yield ( $Y_{tar}$ ), water yield ( $Y_{water}$ ), gas yield ( $Y_{gas}$ ), gas concentrations ( $C_{i,gas}$ ), and CO<sub>2</sub> absorption ratio were calculated by the following formulas:

$$Y_{tar} = \frac{M_{tar}}{M_{coal}} \times 100\%$$

$$Y_{water} = \frac{M_{water}}{M_{coal}} \times 100\%$$

$$Y_{char} = \frac{M_{char}}{M_{coal}} \times 100\%$$

$$Y_{gas} = \frac{\sum M_i V_i / 1000 V_m}{M_{coal}} \times 100\%$$

$$C_{i,gas} (\%) = \frac{V_i}{V_m} \times 100\%$$

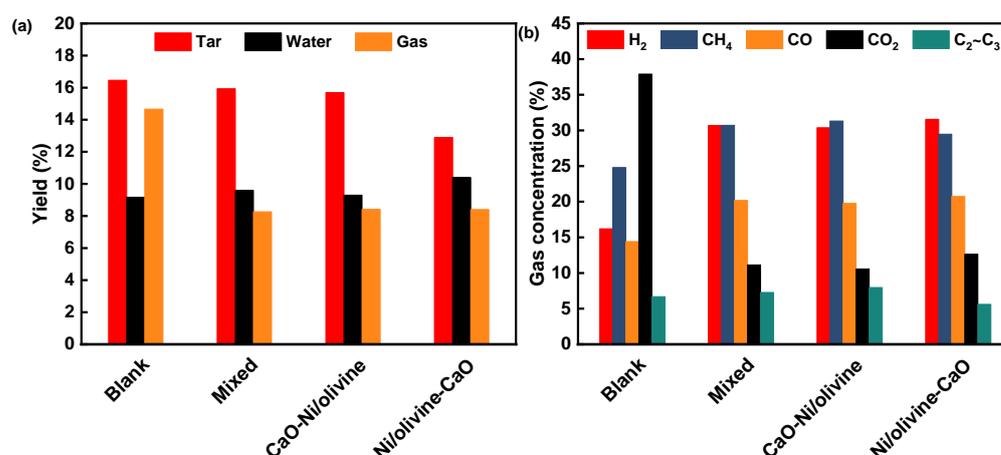
where  $M_{char}$ ,  $M_{tar}$ , and  $M_{water}$  are the weights of char, tar, and water.  $M_{coal}$  represents the weight of the coal sample, and  $M_i$  (g/mol) is the molar mass of the non-condensable pyrolysis gas component of  $i$  under standard conditions (0 °C, 1 atm).  $C_{i,gas}$  represents the concentrations of the pyrolysis gas.  $V_i$ ,  $i$  was used to quantify the main gaseous species

by GC. Ni/olivine was separated from the catalysis mixture by a magnet, and the CO<sub>2</sub> adsorption properties of CaO have been investigated based on XRD analysis.

### 3. Results and Discussion

#### 3.1. Pyrolysis Product Distribution at Different Catalytic Modes and Temperatures

The effect of catalytic modes has been evaluated at a catalytic temperature of 450 °C. Figure 2a presents the pyrolysis product yields of coal at different catalytic modes. For all the tests, the char yield remained stable at  $59 \pm 0.5\%$  due to consistent pyrolysis conditions; the upper reactor temperature was maintained at 550 °C without any contact with the catalyst. In the case of the blank test, the tar, water, and pyrolysis gas yields were measured at 16.46%, 9.17%, and 14.66%, respectively. In contrast to coal alone, the tar yield of pyrolysis coal with catalysts decreases. The tar yield for the different catalyst distribution modes follows the order of mixed > CaO-Ni/olivine > Ni/olivine-CaO, which is closely related to the catalyst's capacity for secondary cracking of volatiles. CaO has a weaker cracking effect on the volatile components compared with Ni/olivine. The use of the Ni/olivine-CaO mode results in the lowest tar yield (12.9%), which can be attributed to the strong cracking for volatiles of Ni/olivine. Compared with other modes, the CaO-Ni/olivine mode shows a higher tar yield (15.69%), indicating that in the CaO-Ni/olivine mode catalysis, the volatiles over CaO reduce the possibility of the secondary cracking reaction among macromolecular compounds over the Ni/olivine, which increases the tar yield. The change in gas yield is caused by the absorption of CO<sub>2</sub> in pyrolysis gas by CaO on the one hand, and the change in the reaction process of functional groups in coal pyrolysis is induced by a catalyst on the other hand.

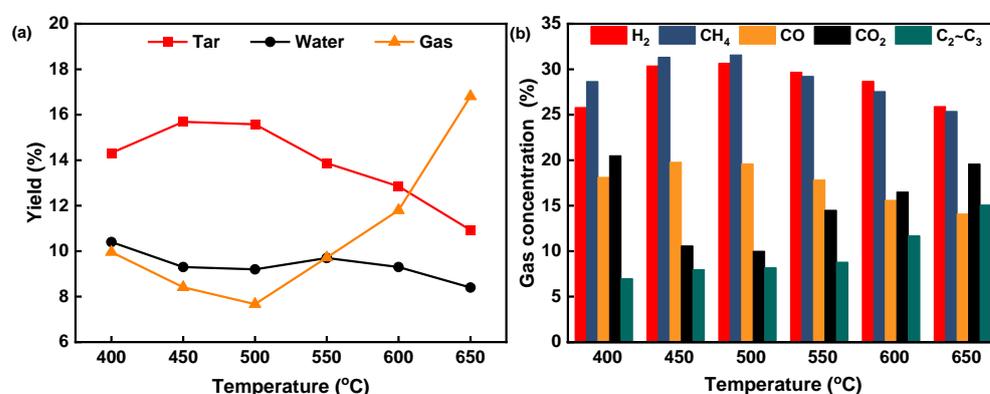


**Figure 2.** Product distribution at different catalytic modes at 450 °C: (a) tar, water, and gas yields; (b) gas concentrations.

Figure 2b illustrates the effect of catalytic modes on the components of non-condensable pyrolysis gases. In the case of the blank test, the coal pyrolysis gas was dominated by CO<sub>2</sub> (37.9%), which can be attributed to the low coalification of the low-rank coal [27]. It was followed by CH<sub>4</sub> (24.79%), H<sub>2</sub> (16.2%), CO (14.41%), and C<sub>2</sub>-C<sub>3</sub> (6.69%). The catalytic modes order of H<sub>2</sub> components after catalytic upgrading is Ni/olivine-CaO > CaO-Ni/olivine > mixed, which is closely related to the cracking of long-chain hydrocarbons and the reactions of polymerization, cyclization, and aromatization over Ni/olivine. In addition, the concentration of CO<sub>2</sub> decreased significantly to 10.57% due to the absorption of CaO. It is generally acknowledged that CO<sub>2</sub> comes from the decomposition of oxygen-containing functional groups such as carboxyl groups, carbonyl groups, ether bonds, and other oxygen-containing heterocycles in coal [4]. The addition of Ni/olivine results in a slight decrease in the CO<sub>2</sub> concentration. Moreover, the difference in concentration of CO<sub>2</sub> for Ni/olivine-CaO, CaO-Ni/olivine, and mixed is small. It can be seen that the

Ni/olivine catalyst can inhibit the decomposition of oxygen-containing functional groups in the pyrolysis tar.

The effect of catalytic temperatures has been evaluated at the catalytic mode of CaO-Ni/olivine. Figure 3a presents the pyrolysis product yields of coal at different catalytic temperatures. The tar yield increased and then decreased with increasing catalytic temperature. A maximum value of 15.69% was obtained at a temperature of 450 °C. In contrast, the gas yield exhibits a decreasing trend followed by an increasing trend as the catalytic temperature increases. It reaches a minimum of 7.67% at a temperature of 500 °C. It is generally acknowledged that the coking processes of tar, which convert volatile materials into solid carbonaceous compounds, cause tar yields below the maximum value at lower temperatures. Additionally, subsequent gas-phase cracking processes of tar are responsible for tar yields that are below the maximum value at higher temperatures. At lower temperatures, between 400 and 500 °C, the absorption of CO<sub>2</sub> by CaO is responsible for the drop in gas output. The desorption of CO<sub>2</sub> by CaO and the breakdown of oxygen-containing functional groups at temperatures between 500 and 650 °C are the main causes of the rise in gas output.



**Figure 3.** Product distribution at different catalytic bed temperatures in the mode of CaO-Ni/olivine: (a) tar, water, and gas yields; (b) gas concentrations.

Figure 3b presents the effect of the catalytic temperature on the components of non-condensable pyrolysis gases. It is evident that the pyrolysis gas components undergo significant changes with an increase in temperature. The concentrations of H<sub>2</sub> and CH<sub>4</sub> increased and then decreased as the catalytic temperature increased. Maximum values of 30.66% and 31.58% were obtained at a temperature of 500 °C. However, the concentrations of CO<sub>2</sub> decreased and then increased as the catalytic temperature increased. A minimum value of 9.99% was obtained at a catalytic temperature of 500 °C. The concentration of C<sub>2</sub>~C<sub>3</sub> increases continuously with the catalytic temperature increases. This suggests that the capacity of nickel to split aliphatic hydrocarbons is amplified as the temperature increases.

### 3.2. Simulated Distillation Analysis of the Tar

Figure 4 illustrates the tar fractions and yields over the catalyst at different catalytic modes, as determined by the simulated distillation method. In the blank test, the pitch content fraction of the tar was 35.6%, while the light tar fraction was 64.4%, of which the light oil fraction was only 20.5%. The order of light tar fraction is CaO-Ni/olivine > Ni/olivine-CaO > mixed after catalytic upgrading of different catalytic modes catalysts. Compared with other catalytic modes, the use of the CaO-Ni/olivine mode results in the highest fraction of light tar (69.3%) and light oil (29.8%), which can be attributed to the strong cracking for the secondary cracking of pitch over the Ni/olivine catalysts. The pyrolytic volatile undergoes selective cracking and de-hetero-atomization effects on the conversion of macromolecular compounds to pre-cracked precursors over the CaO-catalyzed stage. When these precursors pass through the Ni/olivine-catalyzed stage, they are broken down into smaller molecules by the strong cracking action of Ni/olivine. This

process reduces the pitch content in the tar, indicating that the CaO-Ni/olivine mode has a positive effect on tar yield during volatiles upgrading.

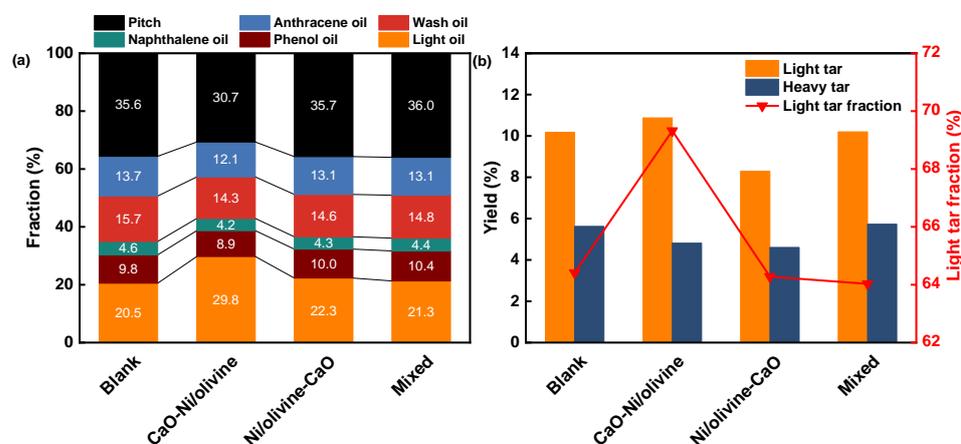


Figure 4. The fraction distribution (a) and yield (b) of tar over the different catalytic modes at 450 °C.

Figure 5 illustrates the tar fractions and yields over the catalyst at different catalytic temperatures. In the blank test, the light yield was 10.18%, and the heavy tar yield was 5.62%. At the same temperature of 450 °C and using CaO-Ni/olivine as the catalyst bed, the yield of heavy tar decreased to 4.81%, while the yield of light tar increased to 10.87%. Additionally, the lowest heavy tar fraction of 30.7% was obtained. The light oil fraction of tar increased and then decreased with increasing temperature. It reaches a maximum of 29.8% at a temperature of 450 °C. The data demonstrate that temperature has a significant impact on Ni/olivine's ability to selectively crack compounds in tar. The results demonstrate that CaO has the ability to selectively crack pitch fraction in tar, resulting in the preservation and improvement of the light oil content. However, Ni/olivine exhibits a strong ability to crack both light and heavy tars. Thus, the heavy tar is reduced while light tar is maintained and improved simultaneously when using the CaO-Ni/olivine catalytic mode.

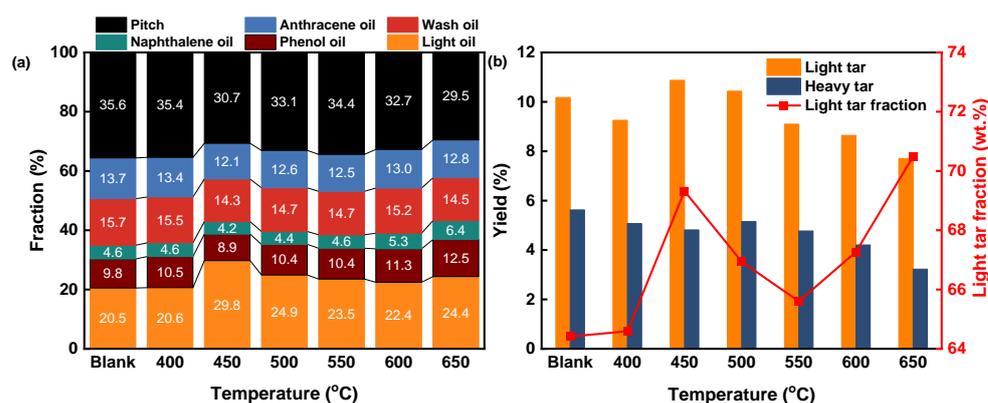
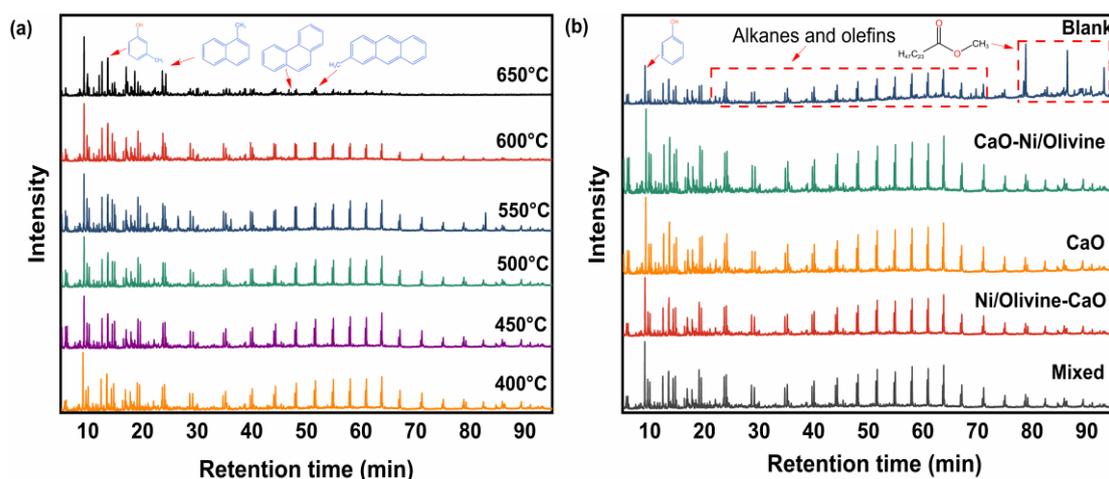


Figure 5. The fraction distribution (a) and yield (b) of tar over the different temperatures in the mode of CaO-Ni/olivine.

### 3.3. GC-MS Analysis of the Tar

This section discusses the changes in representative compounds that occur during the catalytic upgrading process and provides a detailed analysis of the role of catalysts in tar upgrading. Figure 6 shows that the composition of tar compounds undergoes significant changes after catalytic upgrading. The main tar peaks prior to catalysis are predominantly located in the region of longer retention time, such as tetracosanoic acid, methyl ester (78.823 min), hexacosanoic acid, methyl ester (86.421 min), and octacosanoic acid, methyl ester (93.145 min). However, the spectral intensities of the main peaks and the area ratio of

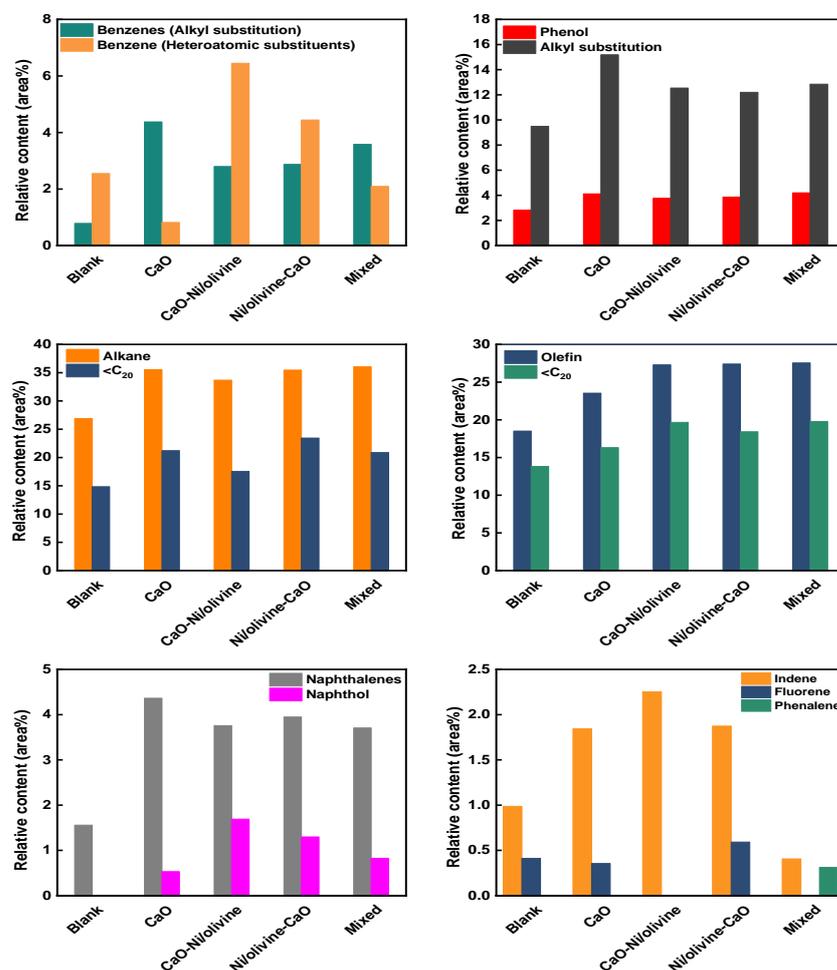
the characteristic peak decreased by 24.4% due to the CaO exhibiting selective cleavage of long-chain esters. The spectral intensities of alkanes and olefins obtained with the use of three different catalytic modes are enhanced compared to the blank test. Compared with CaO, the spectral intensities of naphthalene and phenol and their alkyl-substituted homologs in upgraded tar over CaO-Ni/olivine increase, which suggests that Ni/olivine has better performance for heavy tar cracking. Furthermore, the spectral intensities of alkanes and olefins in tar decrease while the spectral intensities of two-ring and three-ring aromatics and their alkyl-substituted homologs increase with temperature increase. Thus, the relay catalytic upgrading of pyrolysis volatiles via CaO-Ni/olivine catalysts is an effective method for tar upgrading at lower temperatures.



**Figure 6.** GC-MS spectra of the tar (a) at different temperatures over the mode of CaO-Ni/olivine and (b) with different catalyst distribution modes at 450 °C.

Figure 7 displays the distribution of coal pyrolysis tar over the catalyst at different catalytic modes. In the case of the blank test, the contents of typical two-ring compounds, naphthalene, and single-ring compounds, benzenes and phenols, are insignificant. The contents of alkane and olefin are 26.51% and 16.88%, respectively, while the contents of <C<sub>20</sub> compounds are only 14.85% and 13.82%, respectively. In the case of CaO as a catalytic bed, the contents of these components increased significantly after catalytic upgrading. The contents of benzenes, phenols, and naphthalene were increased to 4.38%, 4.12%, and 4.36%, respectively. In contrast, the benzene (heteroatomic substituents) content decreased from 2.55% to 0.82%. Additionally, the contents of alkane and olefin increased significantly to 35.54% and 23.54% due to the selective cleavage of long-chain esters by CaO. It is suggested that CaO promotes the transformation of oxygen-containing compounds into hydrocarbons during the initial stage of the pre-cracking reaction [28]. During the second stage of catalytic cracking, CaO acts as a catalyst to break C-C bonds in long-chain hydrocarbons, resulting in the transformation of long-chain alkanes and olefins into various short-chain aliphatic hydrocarbons and smaller compounds. Furthermore, CaO facilitates the processes of cyclization, aromatization, and dehydrogenation. This results in the conversion of short-chain aliphatic hydrocarbons into aromatics [17,29], leading to an increase in the levels of benzenes, phenols, and naphthalene. The introduction of Ni/olivine resulted in a decrease in the levels of naphthalene, phenol, and benzene. Compared to the single use of a CaO catalyst, the lowest benzene contents of 2.8% are achieved when using the CaO-Ni/olivine mode, while the benzene (heteroatomic substituents) content significantly increases from 0.82% to 6.45%. As important chemicals, the content of benzene (heteroatomic substituents) in tar is in the order of CaO-Ni/olivine > Ni/olivine-CaO > mixed. Ni/olivine catalysts are closely related to the ability to precatalyze secondary reactions of precursors. In addition, there is an insignificant change in the contents of naphthalene and phenols after three modes of catalytic upgrading. These results demonstrate that Ni/olivine has better selectivity

for cleaving alkyl substituents of aromatic side chains and promotes the formation of the structure of aromatic ether carbon.

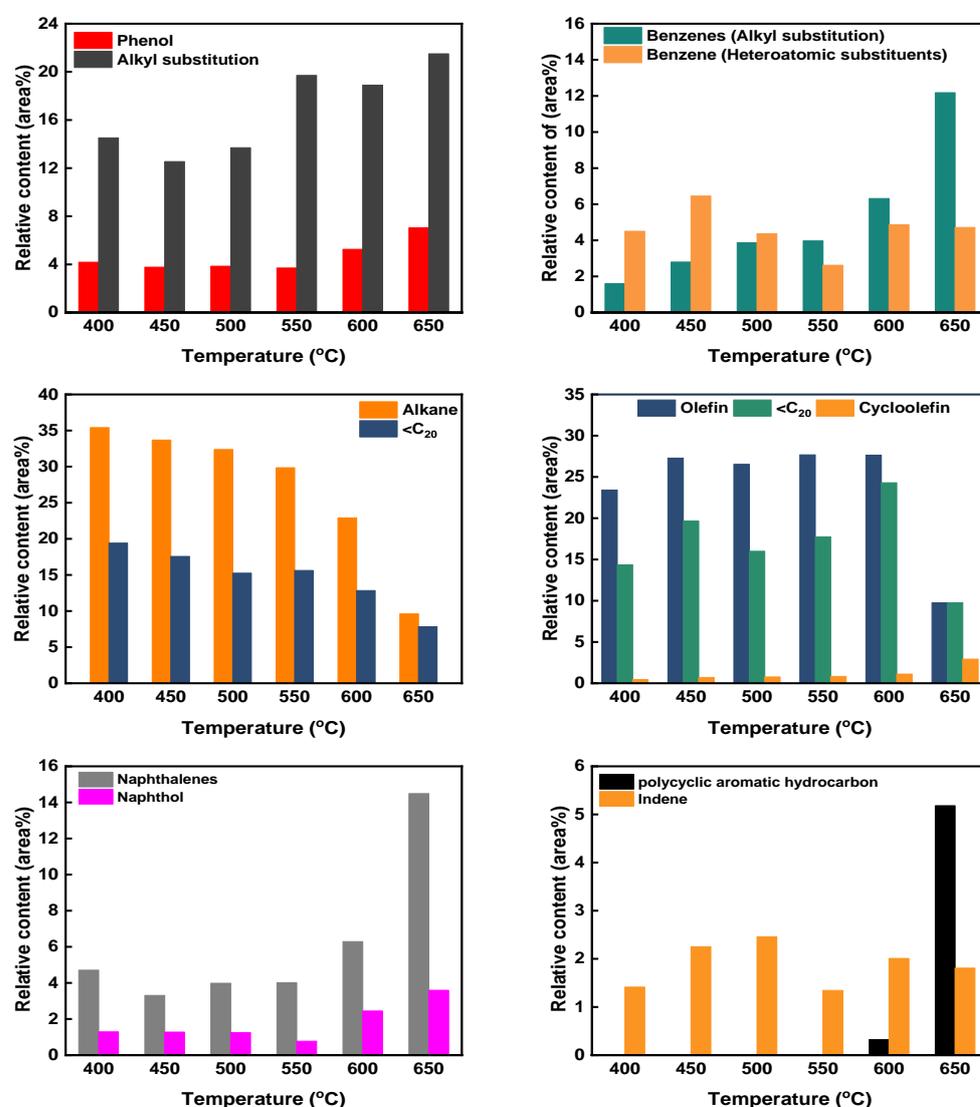


**Figure 7.** Composition distributions of tar obtained from coal pyrolysis over the catalyst with different catalytic modes at 450 °C.

The CaO catalyst facilitates the cleavage of the aromatic oxygen–carbon bond in the macromolecular structure of tar, resulting in the formation of C-O radicals containing aromatic rings when the pyrolytic volatile fraction passes through the CaO bed. Active hydrogen radicals provided by the environment will bind to the C-O radicals, producing phenols that remain in the aromatic side chain. This is consistent with the view of Le et al. [17]. As the phenols pass through the Ni/olivine bed, the Ni/olivine cleaves the alkyl substituents of the phenols side chains and promotes the formation of aromatic ether bonds through dehydration reactions between neighboring phenols molecules. Alternatively, it induces C-O bonds to attach to the benzene ring by cleaving oxygenated bonds in long-chain oxygenated compounds, which then recombine with free radicals in the environment to produce new aromatic ether bonds. These results suggest that the catalytic upgrading of pyrolysis volatiles using the CaO-Ni/olivine catalyst is an effective method for upgrading volatiles.

Figure 8 displays the distribution of coal pyrolysis tar over the catalyst at various temperatures. The content of typical compounds in the coal tar varies with the catalytic temperature. The content shows an increase in the typical two-ring compounds, naphthalene, and single-ring compounds, benzenes and phenols, as the temperature increases. At a temperature of 650 °C, it reaches the maximum values of 14.49%, 12.18%, and 7.04%, respectively. However, the alkane content decreased while the olefin content increased with temperature in the tar. The presence of CaO may facilitate the conversion of saturated

aliphatic hydrocarbons to unsaturated aliphatic hydrocarbons [30,31], which is a crucial step in the transformation of aliphatic hydrocarbons into aromatic intermediates. Passing unsaturated aliphatic hydrocarbons through the catalytic bed of Ni/olivine causes a strong cleavage, decreasing the  $>C_{20}$  compound in saturated aliphatic hydrocarbons and producing more small molecules. This is a factor in the increase in  $<C_{20}$  compounds in olefins. Previous studies have shown that phenolic compounds are emitted during coal pyrolysis due to the cracking of C-O structures, such as aromatic ether bonds. This is one pathway for the generation of phenolic precursors rather than the escape of phenols that already exist in the raw coal [32]. CaO can generate free radical fragments by promoting aromatic side chain C-O breakage and generates a large amount of phenoxy radical. The broken -O- is stabilized by H-rich radicals to produce -OH to form phenolics [29,33]. The mode of CaO-Ni/olivine cleaves the side chain groups of the phenolic compounds generated in the CaO phase. This process dehydrates the two -OH groups, forming a new ether bond or causing the -OH to break and re-inducing the broken alkyl radical fragments to combine with the phenoxy group created by the break to create an ether bond. It has been demonstrated that lower temperature (400~450 °C) promotes this process.



**Figure 8.** Composition distributions of tar obtained from coal pyrolysis over the catalyst with different temperatures in the mode of CaO-Ni/olivine.

### 3.4. XRD Analysis

Figure 9 shows the XRD patterns of fresh and used CaO catalysts. The diffraction peaks of fresh CaO are  $32.17^\circ$ ,  $37.31^\circ$ ,  $53.86^\circ$ ,  $64.15^\circ$ , and  $67.36^\circ$ . Compared to the fresh CaO, the peaks were reduced at  $32.17^\circ$ ,  $37.31^\circ$ , and  $53.86^\circ$  for the used CaO catalyst significantly, while the diffraction peaks of  $\text{CaCO}_3$  were detected at  $29.3^\circ$ . It is suggested that CaO can absorb  $\text{CO}_2$  from pyrolyzed volatiles in all three catalytic modes during the catalytic upgrading of volatile fractions, leading to the production of  $\text{CaCO}_3$ . Improving pyrolysis gas products is crucial, particularly when using the catalytic mode of CaO-Ni/olivine. In this mode, volatiles play a role in pre-cracking and  $\text{CO}_2$  uptake in the CaO catalytic bed. The pre-cracked precursors are then supplied to the catalytic bed of Ni/olivine in a hydrogen-rich and methane-rich atmosphere. Ni/olivine performs a secondary cracking of the pre-cracked precursors in this atmosphere, which improves the tar quality while delaying the tar cracking.

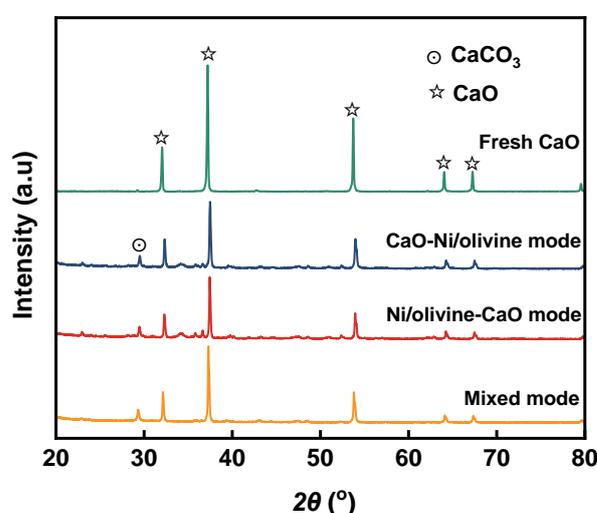
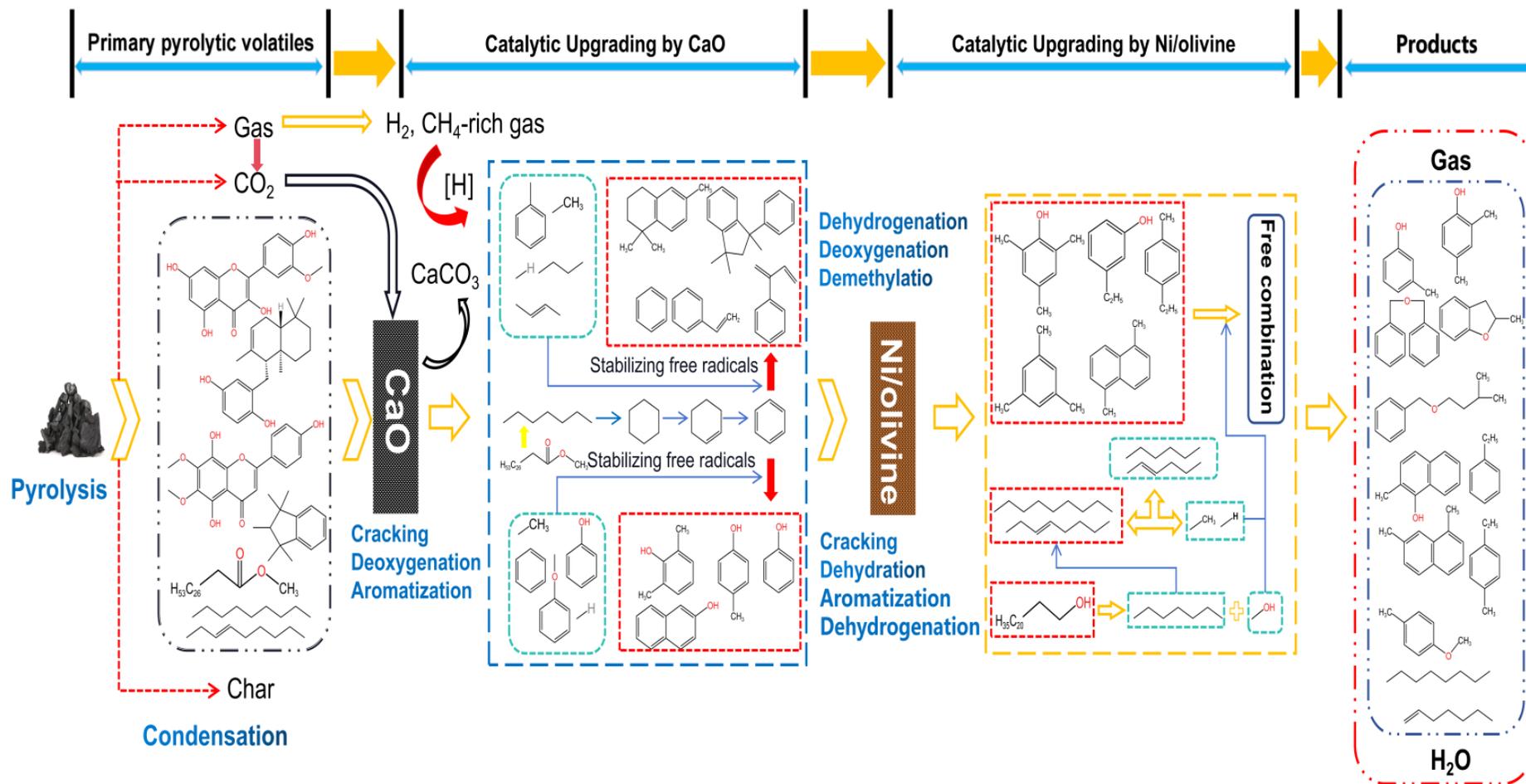


Figure 9. XRD patterns of CaO with different catalytic modes.

### 3.5. Proposed Mechanism for Catalytic Upgrading

Figure 10 illustrates the proposed reaction mechanism for the upgrading of NHM coal pyrolysis volatiles over CaO-Ni/olivine catalytic mode catalysts based on the detailed production distribution. The pyrolysis process of NHM coal produces primary volatiles such as tar, water, and gas. These volatiles then pass through the CaO catalyst stage. CaO absorbs the  $\text{CO}_2$  present in the gas products and converts it to  $\text{CaCO}_3$ . This process enhances the  $\text{H}_2$  and  $\text{CH}_4$  content of the pyrolysis gas, creating a hydrogen- and methane-rich environment for subsequent reactions that provide hydrogen-rich radicals to the catalytic upgrading. The tar is primarily composed of long-chain ester compounds, aliphatic hydrocarbons, aromatic hydrocarbons, phenols, and large molecules (quercetin 3'-methyl ether, etc.) compounds. As these substances pass through the catalytic stage of CaO, the large molecules are broken down into smaller ones. The CaO causes de-isomerization of long-chain esters, converting them into alkanes. The process of deoxygenating and aromatizing alkanes produces aromatic precursors. These precursors then stabilize the small molecules and free radical fragments that result from cracking, ultimately leading to the production of catalytic intermediates.



**Figure 10.** Proposed mechanism for catalytic upgrading of coal pyrolysis volatiles over CaO-Ni/olivine.

When the substance produced in the CaO stage enters the Ni/olivine stage, the Ni/olivine cleaves the side chain alkyl groups of benzene and phenols, inducing the ether bond produced by the dehydration reaction between the hydroxyl groups of phenols. Alternatively, the fragments of oxygen-containing functional groups generated by cleavage can react with the hydroxyl groups of the side chain of the benzene ring to generate ether bonds and remain on the benzene. As a result, the production of monocyclic compounds increases. This results in the upgrading of coal pyrolysis volatile.

#### 4. Conclusions

The catalytic pyrolysis experiments of NMH coal were conducted using combined CaO and Ni/olivine catalysts to improve both tar and gas quality. The CaO-Ni/olivine mode is better in terms of tar quality compared to layouts of the Ni/olivine-CaO mode and the mixed mode. The heavy tar fraction decreased from 35.6 to 30.7%, while the light tar fraction increased from 64.4% to 69.3% at a catalytic temperature of 450 °C. The use of combined CaO and Ni/olivine catalysts can convert long-chain esters and polycyclic aromatic hydrocarbons in tar into single-ring aromatic compounds. After catalysis, the contents of long ester chain compounds decreased by 24.4%, and the benzene (heteroatomic substituents) content significantly increased from 2.55% to 6.45%. The content of naphthalene, benzenes, and phenols increased with the increasing catalytic bed temperature up to maximum values of 14.49%, 12.18%, and 7.04% at a catalytic temperature of 650 °C, respectively. The concentrations of H<sub>2</sub> and CH<sub>4</sub> increased in the pyrolysis gas due to the absorption of CO<sub>2</sub> by CaO. The concentration of CO<sub>2</sub> significantly decreased from 37.9% to 10.57% compared to without the catalyst, while the concentrations of H<sub>2</sub> increased up to 31.32%. Therefore, high-quality tar and H<sub>2</sub>- and CH<sub>4</sub>-rich gas can be obtained with the help of dual CaO and Ni/olivine catalysts through volatile upgrading.

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