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Article

Biocatalytic optimization: Performance and mechanism of molecular sieve composite aluminum-calcium oxides in tobacco biomass pyrolysis

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Abstract: In recent years, China has faced challenges such as energy shortages and environmental pollution. Metal oxides, as biocatalysts, offer promising solutions for biomass energy conversion by enhancing biochemical reaction rates, reducing energy consumption, and improving biomass conversion product quality. This study focuses on using metal-based biocatalysts in the pyrolysis of tobacco, a key cash crop. We prepared aluminum/calcium composite molecular sieves through extraction, calcination, and acid leaching of metal ores. These biocatalysts optimized the tobacco pyrolysis process, improving the composition of bioactive components in the products. Results showed that metal oxide composites effectively facilitated the cleavage and reorganization of tobacco biomolecules, influencing the structure and composition of pyrolysis gases. The presence of alkali metals led to earlier cleavage of tobacco at lower temperatures and increased pyrolysis gas concentration. Specifically, calcium or aluminum increased total weight loss in the 100–300 °C range while decreasing maximum weight loss, leading to higher concentrations of low-temperature pyrolysis gases. The optimal catalyst-to-tobacco mass ratio was 2:1 at 500 °C, maximizing nicotine content, reducing ester formation, and enhancing hydrocarbon biosynthesis. This low-temperature pyrolysis method efficiently releases aroma substances and improves smoke concentration. It offers a practical approach for biomass energy conversion and bioactive substance extraction, providing new insights into metal-based biocatalysts' role in complex biomass systems.

Keywords: tobacco pyrolysis; metal catalytic conversion; pyrolysis efficiency; metal oxide catalysts; low-temperature pyrolysis; bioactive compound extraction

1. Introduction

Biocatalysts have important applications in the field of biomass energy conversion. These catalysts are widely used in various reactions such as catalytic cracking, catalytic reforming, catalytic hydrogenation and so on. The application of biocatalysts in pyrolysis catalysis and energy engineering of biomass is of significant value. There is a close connection between these two fields. Therefore, evaluating the catalytic properties of biocatalysts in biomass pyrolysis provides important insights to optimize the biomass energy conversion process.

The manufacturing process of tobacco has been the focus of research. Different processing methods produce cigarettes with different flavors due to the extraction of different aromatic and beneficial components during the manufacturing process. In current tobacco pyrolysis processes, biocatalysts are used to reduce toxicity or modulate pyrolysis products through targeted and effective mechanisms [1–3]. Typically, zeolites are placed in cigarette filters or attached to tobacco fibers at the microscopic level to infer the composition of combustion smoke [4–6]. Theoretically, zeolite molecular catalysts can convert steam pyrolysis products into hydrocarbons (e.g., olefins and aromatic hydrocarbons) and COX. Due to their large pore size (2–49 nm), mesoporous catalysts are widely used to adsorb molecules and macromolecules to their active sites. Mesoporous technology can reduce unwanted macromolecular PAHs in tobacco pyrolysis smoke and remove substances such as nitrosamines from the main smoke mixture. The addition of SBA-15 (mesoporous material) reduces the toxicity of pyrolysis smoke and improves pyrolysis efficiency [7]. These catalysts facilitate the generation of desired products by targeting olefins and aromatics. Different pyrolysis and catalytic temperatures produce different products. Specific temperatures greatly affect the aromatic and olefinic compositions, thus the use of catalysts is crucial. Catalysts maximize the reaction rate and lower the reaction energy barrier. Their presence allows the reaction to take place under mild conditions, consuming the least amount of energy [8]. By using appropriate catalysts, we can enable pyrolysis to release aromatics at low temperatures. Zeolites and mesoporous materials are widely used in pyrolysis. Emilio and Antonio [7] used SBA-15 mesoporous silica as catalyst for pyrolysis. The catalyst was mixed with tobacco at 5%, 15% and 50%. The results showed that the addition of catalyst had no significant effect on pyrolysis under inert atmosphere and high temperature conditions. However, the generation of pyrolysis products was significantly reduced under oxidizing atmosphere and low temperature conditions. The concentration of the catalyst affects the formation of selective pyrolysis products. 5% catalyst concentration is sufficient to obtain significant results. In addition, the pore size of the catalyst is an important feature affecting the performance, which influences the contact area of the active sites of the reaction. For example, catalysts with larger pore sizes allow more contact of reactants with the active sites. As a result, pyrolysis efficiency is improved and toxicity is reduced. Since mesoporous catalysts have large pore sizes, Yong et al. [9] and Xu et al. [10] utilized these properties to select catalysts. The selected catalysts can reduce unwanted macromolecules and aromatics and remove toxic substances, such as nitrosamines, from the exhaust gas.

Biocatalysts and alkali/alkaline earth metals showed significant activity during high temperature and rapid pyrolysis of biomass resources. The injection of Zr^{4+} into CeO_2 to form $CexZr^{1-x}$ solid solution and with doped Al to form a catalyst with excellent oxygen storage capacity is a promising option, which provides a large Al_2O_3 surface area and excellent oxygen storage capacity [11]. As catalysts, biocatalysts have a wide range of applications in tobacco pyrolysis [12–15]. Li et al. [16] used four types of catalysts for pyrolysis including organosodium salts, potassium, magnesium and calcium. The results showed that the temperature required to reach the maximum mass loss rate for tobacco pyrolysis was significantly reduced by 36 °C with the addition of the alkali metals—Na or K as catalysts. In contrast, with the addition of the alkaline earth metals—Mg or Ca as catalysts, the maximum mass loss rate was only slightly reduced in the range of 100 °C to 300 °C. In their study, K significantly facilitated the pyrolysis process in the conventional cigarette process and improved combustion performance [17]. Other studies have shown that both organic and inorganic potassium salts are effective in reducing the maximum pyrolysis temperature of hydrocarbons and other compounds. In addition, organic potassium salts can significantly inhibit the release of CO and CO_2 [18]. During tobacco pyrolysis, potassium salts can change the pyrolysis temperature and gas distribution of tobacco biomass. Thus, catalytic pyrolysis of heated tobacco leaves can occur at low temperatures. Ca-based catalysts have similar effects. In addition to K, other alkali/alkaline earth metals such as Mg and Ca show strong activity in tobacco biomass pyrolysis. $MgCl_2$-assisted rapid pyrolysis of tobacco leaves under the atmosphere at 500–700 °C greatly increased the amount of furan and acetic acid in the gas phase products [19]. Catalyzed by alkaline earth metals, more furans and lipid compounds were produced, indicating that alkali metal catalysts can accelerate the low-temperature pyrolysis of heated tobacco. As a result, the concentration of pyrolysis gases and aromatics increased. These studies provide new insights into flavor enhancement and aromatics production in cigarette manufacturing. However, catalysts tend to fail during pyrolysis due to carbon buildup. Therefore, it is necessary to introduce molecular sieves to separate molecules based on their size and shape. Gu [20] used HZSM-5 as a silica-alumina source and employed a post-synthesis method to grow mesoporous catalytic structures (MCM-41) on its surface. The composite molecular sieves he produced were used in pyrolysis experiments. In the experiments, the mass ratio of biomass feedstock to catalyst was 1:2. The relative content of hydrocarbons in the pyrolysis product catalyzed by HZSM-5 was 48.41%. In contrast, the relative content increased to 64.43% with the addition of the prepared composite molecular sieves, which was 16.02% higher than that catalyzed by HZSM-5 only. In the final product, monocyclic aromatic substances accounted for 44.39% of the total while polycyclic aromatic hydrocarbons accounted for 15.36%. Similarly, Lei [21] found that post-treatment desilication increased the number of mesopores in molecular sieves while maintaining the microporous structure under different alkaline conditions. The use of porous molecular sieve HZSM-5 resulted in a slight increase in the yield of liquid products from lignin pyrolysis, while the selectivity of oxygenated compounds decreased from 27% to 5%. This approach significantly improved the deoxygenation process of pyrolysis. Kaliappan and Karthick [22] stated that the yield of bio-oil was increased by up to 16.95% during catalytic pyrolysis due to Ca-enriched waste. In particular, alkali and alkaline earth metals in eggshells may positively influence the decomposition of biomass materials. Therefore, mesoporous materials, biometals/alkali metals [23] and molecular sieves [24] are widely used as catalysts for tobacco pyrolysis and other biomasses.

Currently, the main environmental challenges facing tobacco pyrolysis include high energy consumption at high temperatures, generation of large amounts of pollutants and inefficient biomass conversion. The high energy consumption and pollutant generation of conventional pyrolysis processes put pressure on energy resources and the environment. By applying metal oxide composite molecular sieve catalysts, this study aims to reduce the operating temperature of tobacco pyrolysis, thereby reducing energy consumption and pollutant emissions. The optimized catalyst not only promoted effective cleavage and recombination of tobacco biomolecules and increased gas concentration at low temperatures, but also improved the bioactive composition of the product. This improved pyrolysis method effectively enhances conversion efficiency and product quality while reducing negative environmental impacts, providing a new solution for clean and sustainable energy conversion of tobacco and other biomass.

In this study, the catalytic properties of alkali metal/alkaline earth metal Al and Ca compounds were investigated when mixed with molecular sieve HZSM-5. In the experiment, the molecular sieve was used for pyrolysis of tobacco leaves. After the experiment, we used the data to determine the thermal properties and gas products of tobacco leaves at different temperatures. We also analyzed the gas product distribution of tobacco leaves at different temperatures. Different model compounds were selected in order to investigate possible catalytic mechanisms. The aim of this study was to investigate the potential application of alkali metals/alkaline earth metals in low-temperature catalytic pyrolysis of heated tobacco leaves. The results of the study will be used to improve tobacco flavor, smoke concentration and aromatic yield. In addition, the performance of biocatalysts in biomass energy conversion is discussed.

2. Materials and methods

2.1. Experimental plan

The design of the experiment is as follows: before the experiment, molecular sieves were prepared. (HZSM-5 molecular sieve, known for its good acid and heat resistance, excellent selective cracking, and isomerization performance, is widely used in biomass catalytic pyrolysis to produce aromatic hydrocarbon) Kaolin and limestone were also prepared to be backup materials.

The main components of the tobacco samples used are determined as follows **Table 1**:

Table 1. The main components of tobacco.

Composition	Water	Propylene Glycol	Glycerin	Nicotine	Cellulose	Lignin
Content	11.18%	9.71%	18.58%	7.89%	35.79%	14.85%

The preparation of the catalysts and the design of the experiment are outlined as follows:

(1) The preparation of metal oxides:

Aluminum Oxide Preparation: After the extraction of aluminum from kaolin through leaching process, we carry out the precipitation of aluminum hydroxide through the hydrolysis method. The obtained aluminum hydroxide is calcined to produce aluminum oxide powder. Next, kaolin is ground to powder to increase its surface area. Then, it is mixed with acidic solutions such as dilute sulfuric acid or hydrofluoric acid for acid leaching. During this process, the aluminum oxide in kaolin reacts with the acid to produce aluminum salts. The solution that contains aluminum salts is filtered to remove impurities and residues from the filtrate. After adding the aluminum salt solution to the alkaline solution of sodium hydroxide, the aluminum hydroxide precipitates. The reaction equation is: $Al^{3+} + 3OH^{-} \rightarrow Al(OH)3 \downarrow$. The precipitated aluminum hydroxide is filtered and washed to remove residual alkaline solution and impurities. Then, it is dried to obtain aluminum hydroxide powder.

Calcium Oxide Preparation: First, limestone (chemical formula $CaCO_3$) is placed into a calcination furnace and heated to high temperatures (usually between 800 ℃ and 1000 ℃) for limestone calcination. During this process, calcium carbonate decomposes into calcium oxide and carbon dioxide. The reaction equation is: $CaCO_3 \rightarrow CaO + CO_2$. Subsequently, calcium oxide powder is filtered from the carbon dioxide gas.

Lastly, metal oxides are solidified. Aluminum oxide and calcium oxide are placed in a muffle furnace with an initial temperature of 200 °C. The heating rate is 2 °C/min, which is programmed to rise to 500 °C. The temperature is maintained at 500 °C for 2 h to achieve complete curing until the properties of the metal oxides (aluminum oxide and calcium oxide) become stable.

(2) Design of the experiment:

The ratio of tobacco raw materials to catalyst materials is 1:2. The experimental conditions include: molecular sieve alone, molecular sieve combined with prepared aluminum oxide (denoted as H-Al), and molecular sieve combined with prepared calcium oxide (denoted as H-Ca).

(3) Pyrolysis temperature and product analysis:

The pyrolysis temperature ranges from 300 °C to 600 °C, with intervals of 50 °C for comparative experiments. After the pyrolysis, the reaction products are condensed and store. Then, we begin to analyze the products' distribution and catalytic conversion under various catalyst conditions. It is noted that the microporous nature of HZSM-5 molecular sieve may limit the diffusion of large-molecule oxygen-containing volatiles, resulting in a higher coking rate. As the coke keeps deposits on the surface of catalyst, the catalyst may be deactivated. Thus, this experiment also tests the catalyst's ability to properly handle carbon buildup on its surface.

(4) Thermal stability analysis of catalysts:

The change in catalytic activity after multiple uses is analyzed to evaluate their thermal stability. The process is divided into the stage of pyrolysis and the catalytic stages. H represents molecular sieve alone; H-Al indicates the condition in which the molecular sieve is combined with aluminum oxide; and H-Ca stands for the combination of molecular sieve and calcium oxide. Before pyrolysis, tobacco is dried to remove the moisture. The gas from the pyrolysis furnace is transported through pipelines to a cooling crucible. After 24 h of condensation, the condensed pyrolysis liquid is obtained.

2.2. Preparation and characterization catalytic parameters

HZSM-5 molecular sieves were first synthesized using a mixture of a silicon source and an aluminum source in a molar ratio of 40:1 and left to crystallize at 80 °C for 48 h, followed by calcination at 550 °C for 6 h. Then, the synthesized HZSM-5 molecular sieves were mixed with aluminum oxides or calcium oxides in a 1:1 mass ratio and heated up to 500 °C at 200 °C and kept for 2 h to complete the curing. Finally, the physicochemical properties of the composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption to determine the specific surface area. These steps ensured the stability and reproducibility of the materials and provided a reliable basis for subsequent experiments.

This experiment selects molecular sieves as carriers. Metal oxides that contain Al and Ca serve as catalysts attaching to the carriers. Acidic metal salts (aluminum nitrate and calcium nitrate) are used to obtain metal oxides (aluminum oxide and calcium oxide) or low-valence metal salts. They are placed in a muffle furnace with an initial temperature of 200 °C. The heating rate is set to be 2 °C/min and programmed to rise to 500 °C. The temperature is maintained at 500 °C for 2 h. The obtained oxides and metal salts (which are reprocessed to obtain oxides) are uniformly activated. Finally, molecular sieves, aluminum oxide, and calcium oxide are mechanically mixed and cured under a nitrogen atmosphere to study the surface area and pore size of the catalysts.

This experiment adopts a field-emission transmission electron microscope and a scanning electron microscope to observe the morphological characteristics of the samples. X-ray diffraction (XRD) is conducted on the samples, with a scanning range of 8° to 92°, a scan step width of 0.04°, a scan rate of 8°/min, and X-ray voltage and current of 60 kV and 60 mA. The slit width is 0.5 mm. X-ray photoelectron spectroscopy (XPS) are measured at room temperature using a Kα X-ray photoelectron spectrometer. The X-ray beam is 120 W with a diameter of 300 mm. The laser scanning area is 4 mm × 0.3 mm. Thermogravimetric analysis is performed at a heating rate of 20 K/min from 50 °C to 800 °C under a nitrogen atmosphere. The gas flow rate is 40 mL/min and the sample size is approximately 20.0 mg. Li et al. [16] investigated the low-temperature catalytic pyrolysis performance of alkali metals/alkaline earth metals on heated tobacco leaves using TG-FT-IR and Py-GC-MS. They used alkaline earth metal catalysts in their experiments and studied thermal weight loss and products at different stages. The detection techniques are similar to those mentioned in this paper on compound catalysts, thus showing a similar trend in catalytic and tobacco pyrolysis detection technologies as Li et al.

3. Results and discussion

3.1. Characterization of catalysts by SEM, XRD, and pore structure properties

According to the SEM images, the prepared aluminum oxide and calcium oxide have a cubic structure. The aluminum oxide displays a multi-faceted structure, which facilitates its thorough contact with reactants. Under the conditions of H-Al, H-Ca, and H-Al-Ca composite, the particle size increases and specific surface area slightly increases. The crystal sizes are non-uniform, and the structures have multi-faceted characteristics. The particle morphology of the oxide catalysts compounded with molecular sieves is like that of the oxides. Most particles have a cubic shape (ranging from 20 to 45 μm), but the shape is not fixed (**Figures 1** and **2**).

In the XRD experiment, diffraction peaks are obtained by changing the incident angle and detection angle. Each diffraction peak corresponds to a set of crystal planes in the crystal, so their positions and intensities indicate the crystal structure. The crystal structure of the aluminum oxide (Al_2O_3) is hexagonal, with diffraction peaks including (012), (104), and (110). The crystal structure of calcium oxide (CaO) is cubic, with diffraction peaks including (200), (111), and (220).

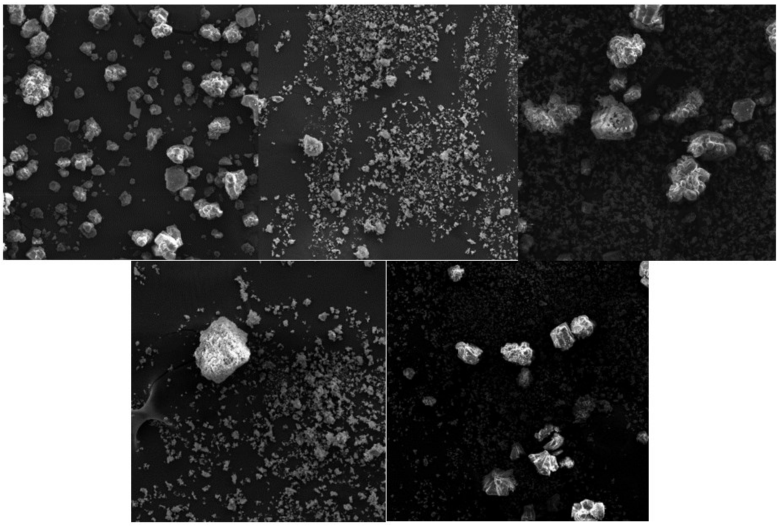

Figure 1. SEM characterization of five catalysts at 100 µm. (Upper left alumina, upper middle calcium oxide, upper right H-Al, lower left H-Ca, lower right H-Al-Ca).

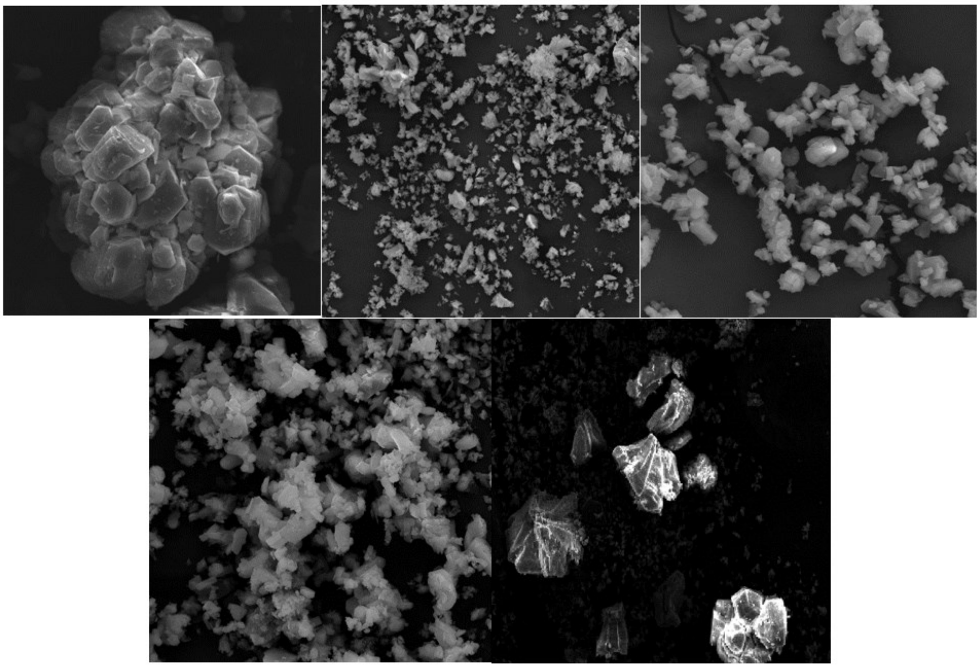

Figure 2. SEM characterization of five catalysts at 20 µm. (Upper left alumina, upper middle calcium oxide, upper right H-Al, lower left H-Ca, lower right H-Al-Ca).

In the XRD pattern of aluminum oxide, multiple sharp peaks are observed, corresponding to diffractions from different crystal planes in the crystal. Strong peaks appear at around $2\theta = 45°$, 66°, and 67°, corresponding to diffractions from the (200), (220), and (311) crystal planes, respectively. In contrast, the XRD spectrum of calcium oxide shows fewer peaks, with strong peaks appearing at around $2\theta = 53°$ and 64°, corresponding to diffractions from the (220) and (311) crystal planes, respectively.

Given the specifications and structures, the prepared H, H-Al, and H-Ca catalysts will be used in the pyrolysis experiments (**Figures 3** and **4**).

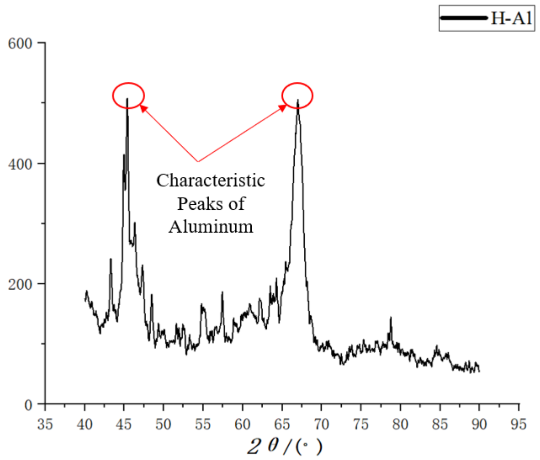

Figure 3. XRD characterization of H-Al.

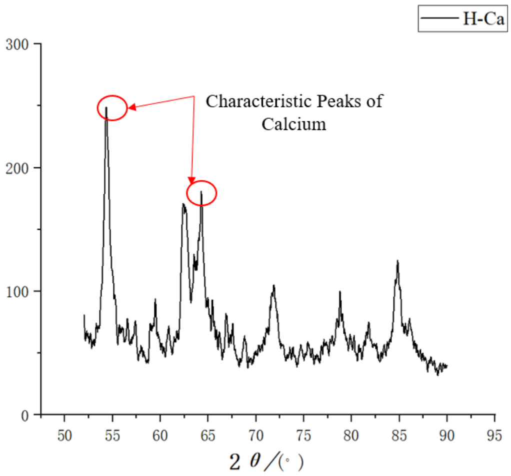

Figure 4. XRD characterization of H-Ca.

As shown in **Table 2**, the specific surface area (50.2 m^2/g) and pore volume (0.0779 cm^3/g) of H-Ca catalyst are relatively small, with a noticeable microporous structure. Compared with H-Ca, H-Al-Ca catalyst shows minimal changes in specific surface area and average pore diameter. On the other hand, the specific surface area and cumulative pore volume of the H-Al catalyst group significant increase due to the addition of Al atoms. The average pore diameter slightly decreases. This trend is similar to findings of Tong et al. [25] about the introduction of Al atoms in catalysts.

Table 2. Catalyst pore size parameters.

Catalyst	**Specific surface area/$m^2 \cdot g^{-1}$**	**Micropore area/$m^2 \cdot g^{-1}$**	**Pore volume/$cm^3 \cdot g^{-1}$**	**Average pore diameter/nm**
H-Al	72.8	1.45	0.1025	5.02
H-Ca	50.2	1.22	0.0779	5.66
H-Al-Ca	50.36	1.20	0.0726	5.52

3.2. TG/DTG analysis of tobacco raw materials

Figure 5 shows the TG and DTG analysis of tobacco raw materials. The pyrolysis process can be divided into six stages: (i) 60–150 °C, (ii) 150–200 °C, (iii) 200–240 °C, (iv) 240–290 °C, (v) 290–380 °C, and (vi) 380–580 °C. They are labeled as S1-S6. The peak in the first stage (i) is due to the evaporation of crystalline water from the surface of the tobacco stems. This results in a 6% mass loss. Stages (ii) and (iii) are the initial phase of pyrolysis, with a 20% mass loss. This is due to the release of small molecular compounds, including glucose, fructose, nicotine, and some volatile substances, as well as the decomposition of hemicellulose and partial cellulose. The mass loss peak in stages (iv) to (vi) reaches a maximum of 52% and has the widest temperature range. This is due to the decomposition of cellulose, hemicellulose, sugars, lignin, and pectin. The selected pyrolysis and catalysis temperatures for the tobacco stems range from 500 °C to 550 °C.

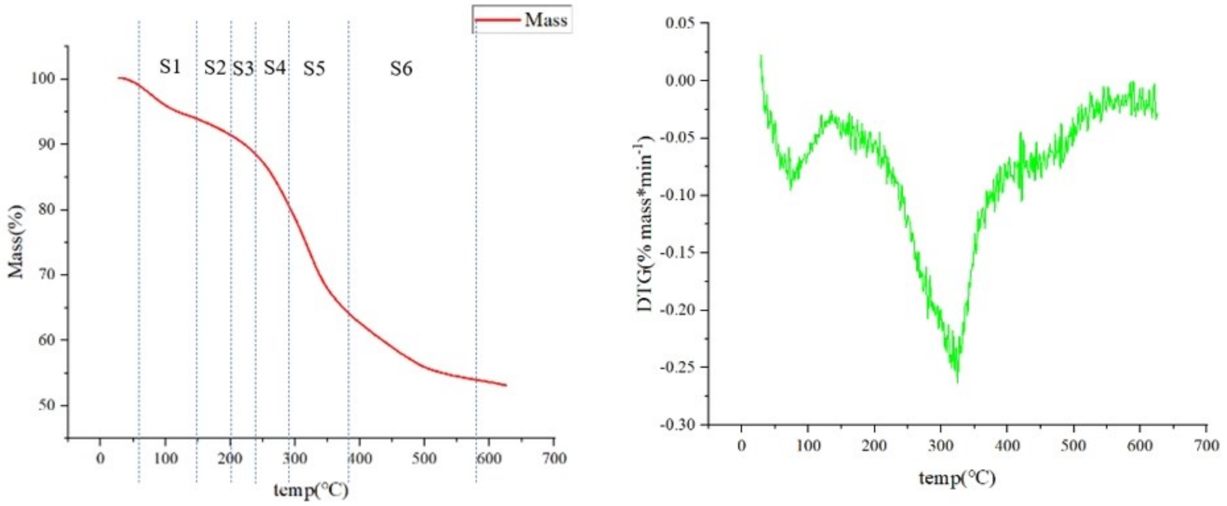

Figure 5. TG and DTG curves of tobacco pyrolysis.

3.3. Analysis of nicotine in catalytic products

The ratio of catalyst to tobacco is another important factor that affects the distribution of pyrolysis products. **Figure 6** shows the yield and peak area percentage of nicotine at 550 °C pyrolysis temperature under different catalysts (H-Al and H-Ca) to tobacco ratios (0, 0.25, 0.5, 1, 2, and 4). When the ratio of catalyst to tobacco increases, nicotine’s yield and peak area percentage first initial increase and then decrease. When the ratio of catalyst to tobacco is 2, the maximum yield of nicotine is 3.42 wt%, with a peak area percentage of 35.13%.

According to **Figure 7**, the use of catalysts significantly affects the pyrolysis of nicotine. Under the influence of H-Al, there is a certain increase in the pyrolysis content of nicotine. When the temperature is around 500 °C, the enhancement is the maximum, approximately 0.7 wt%. At a lower temperature around 300 °C and under the influence of H-Ca, there is a significant increase followed by a similar trend to the H-Al group at subsequent temperatures.

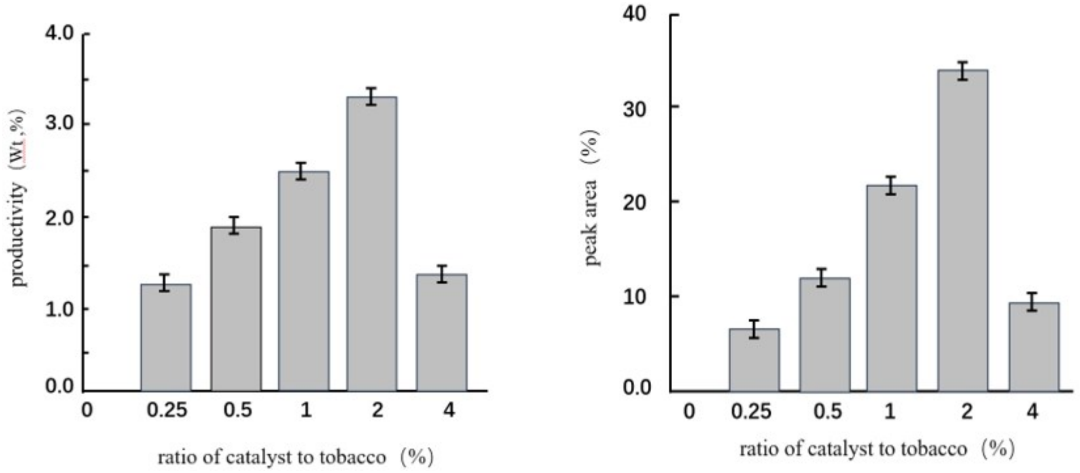

Figure 6. Nicotinic pyrolysis yield and peak area under different catalyst-to-tobacco ratios. (At different ratios of tobacco catalysts, the upper and lower highest nicotine contents and their peak areas of the data obtained after multiple trials were within 5% of each other).

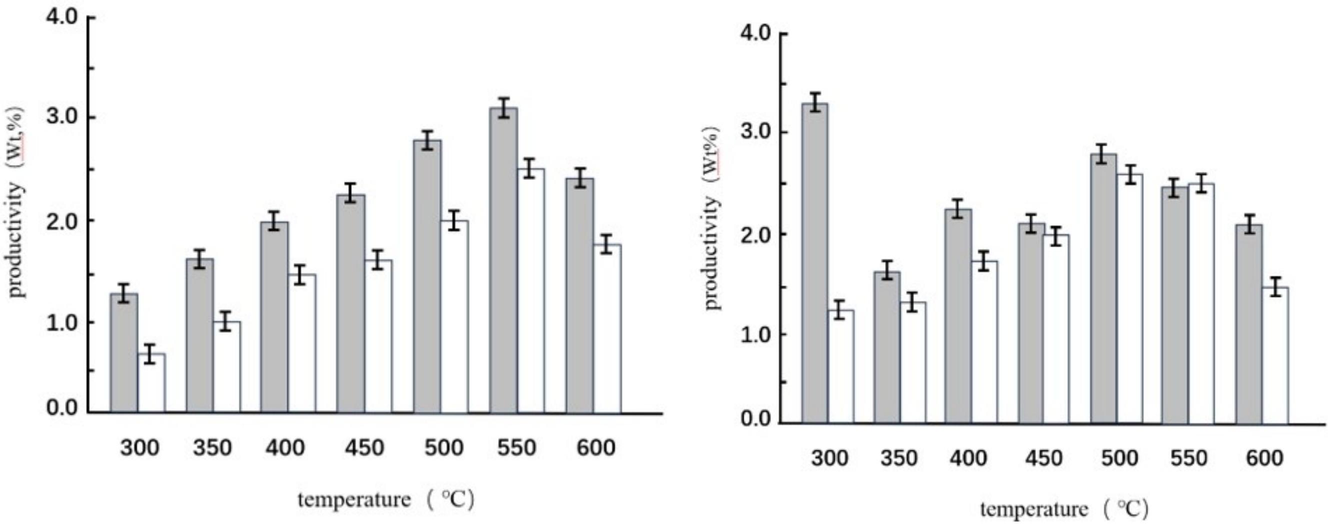

Figure 7. Pyrolysis results under the two catalysts (H-Al on the left, H-Ca on the right, and control group on the blank). (At different pyrolysis temperatures, the confidence intervals indicating the yield of nicotine under different catalysts catalyzed by different catalysts, the results of this experiment are 95% confidence intervals, indicating that the probability of the true value is higher in this range).

3.4. Analysis of aroma compounds in catalytic products

Comparative experiments were carried out under different conditions to study aroma compounds in the pyrolysis stage. Since aroma compounds are composed of aromatic hydrocarbons, and the breaking of chemical bonds will affect the formation of aromatic hydrocarbons during the thermal decomposition of compounds, especially furan compounds. Therefore, the content of compounds after catalytic pyrolysis are measured and the results are shown in **Figure 8**:

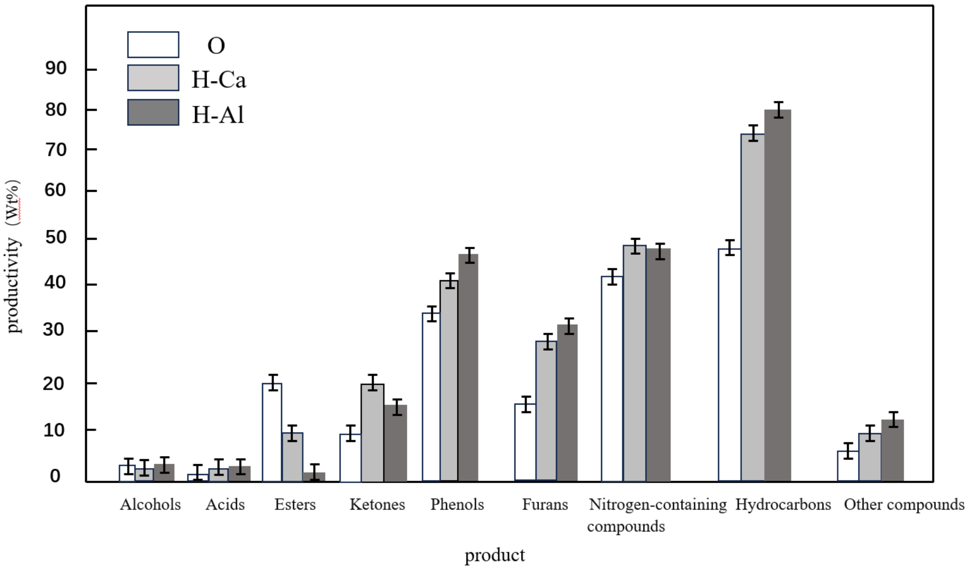

Figure 8. Content of catalytic pyrolysis products. (Indicating the margin of error of various organic production under the experimental conditions of the two catalysts as well as the blank control group can reflect the possible systematic or random errors in the experimental process and help to assess the reliability of the experiments.).

The pyrolysis and catalytic temperatures for the tobacco stalks were set at 500 °C, with a mass ratio of raw material to catalyst of 1:2. Then we observed the distribution of catalytic conversion products under different conditions and categorized detected compounds into the following nine classes: alcohols, acids, esters, ketones, phenols, furans, nitrogen-containing compounds, hydrocarbons, and others. The addition of catalysts suppressed the formation of ester compounds, especially under H-Al catalysis, where ester compounds nearly disappeared. This could be attributed to the rapid transfer rate of active oxygen on the surface of the H-Al catalyst, which hindered the formation of ester substances. After adding catalysts, more hydrocarbons were generated, which mainly included alkanes, alkenes, and aromatic hydrocarbons, with aromatic hydrocarbons comprising the largest proportion. Light aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene can be obtained through biomass-directed catalytic pyrolysis. HZSM-5 molecular sieves have excellent acid and heat resistance, as well as outstanding selectivity for cracking and isomerization. They are suitable for the preparation of aromatic hydrocarbons in biomass catalytic pyrolysis.

We also compared our analysis with the results of several recent studies, some of which are summarized below. When comparing our research with previous studies, several distinctions and similarities emerge. Smith and Zhang [26] focused on transition metal oxides and their effects on carbon yield and VOC production, while our work specifically emphasizes the role of aluminum/calcium composites and their direct impact on tobacco biomolecules and enzyme activity. Johnson and Kim [27] highlighted the benefits of alkali and alkaline earth metals in enhancing gas yield by promoting earlier degradation, paralleling our findings on the effect of calcium and aluminum in lowering cleavage temperatures but focusing directly on tobacco's unique properties. Liu and Wang [28] explored metal-organic frameworks (MOFs) and their potential for tailored catalytic properties; however, our research offers practical insights into the efficiency of simpler aluminum/calcium composites, which may be more accessible for widespread application in biomass pyrolysis.

Lastly, Chen and Zhao [29] directly analyzed various biocatalysts in tobacco pyrolysis, confirming that aluminum-based catalysts optimize nicotine content. This aligns with our findings of maximizing nicotine retention and hydrocarbon biosynthesis at an optimal catalyst mass ratio, reinforcing the advantage of specific biocatalyst selection in pyrolysis processes. Overall, our study contributes to the growing body of literature by providing a detailed analysis of composite metal oxides and their significant impact on tobacco pyrolysis, addressing practical improvements in biomass energy conversion and bioactive substance extraction.

3.5. Mechanistic analysis of metal oxides in catalytic pyrolysis

The biocatalyst-mediated catalytic cleavage of tobacco involves the breaking and reorganization of chemical bonds. Specifically, the following types of bond breaking and reorganization may occur. Regarding C-C bond breaking and reorganization, the organic matter in tobacco is mainly composed of carbon and hydrogen. Biocatalysts can promote the breaking of C-C bonds and the formation of new C-C bonds during the reaction. In terms of C-H bond breaking and reorganization, biocatalysts promote the breaking of C-H bonds in tobacco and participate in the reorganization of new C-H bonds, thus driving the reaction. It is due to these microstructural changes that the desired products are reassembled.

During tobacco pyrolysis, the interaction between the catalyst and tobacco molecules significantly affects the efficiency of the reaction and the distribution of the products through several mechanisms. First, van der Waals forces, a weak intermolecular attraction, enable the adsorption of small molecules from tobacco, such as carbon monoxide and small hydrocarbons, on the catalyst surface. Although this adsorption is physical, it is capable of directing small molecules to the vicinity of the catalytically active site, thereby accelerating the subsequent chemical reaction. Second, hydrogen bonding is a strong intermolecular interaction that may be formed especially when compounds containing hydroxyl or amino groups in tobacco constituents approach the catalyst surface. The phenolic compounds in tobacco in this experiment can interact with the oxygen groups on the catalyst surface through hydrogen bonding, and this interaction not only enhances the stability of the molecules, but also changes the energy path of the reaction and reduces the activation energy of the reaction, thus increasing the reaction rate. In addition, π-π interactions occur between molecules containing aromatic rings. This interaction with PAHs in tobacco may occur when the catalyst has an aromatic ring structure or its surface is modified with aromatic groups. This interaction not only contributes to the adsorption of the molecules, but also affects the selectivity of the reaction and the distribution of the final products by changing the distribution of the electron density between the molecules, which is the most important aspect of this experiment in which the addition of the catalyst has an effect on the pyrolysis products. There are also electrostatic interactions, which are also an important mechanism. When charged or polar molecules are present in a tobacco composition, electrostatic attraction occurs when these molecules approach a catalyst with an oppositely charged or polar surface. For example, a positively charged metal catalyst surface may attract anions or negatively charged polar groups in tobacco. This interaction helps to localize reactants near the active site of the catalyst, thereby enhancing the catalytic effect. Finally, interactions between catalysts and tobacco components are not limited to physical adsorption; sometimes catalysts can form direct chemical bonds with tobacco components, causing rearrangement or cleavage of the molecular structure. For example, metal catalysts may form coordination bonds with double or triple bonds in tobacco by leading to the activation of these bonds, which in turn triggers a series of chemical reactions such as hydrogenation, oxidation or cleavage reactions. Together, these complex interactions significantly affect the reaction mechanisms and product properties during tobacco pyrolysis.

In summary, biocatalysts are able to promote pyrolysis of tobacco by participating in the breaking and reorganization of chemical bonds. This affects the combustion of tobacco and the formation of chemicals. In this experiment, the catalyst played a key role in tobacco cracking by accelerating the reaction rate, lowering the reaction temperature, and improving product selectivity. During the cracking process, most of the target products such as nicotine and aroma compounds contain nitrogen compounds. They contain nitrogen atoms (with a large atomic mass) in their molecular structure. Under the catalytic action of a biocatalyst with a large surface area, the nitrogen content atoms can bind to the catalyst surface. This provides additional binding sites for free chemical bonding and facilitates the generation of the target product.

For example, during the formation of nicotine, the breaking of C-C and C-H bonds exposes more available binding sites in the cleavage. In addition, nitrogen atoms are mixed with nicotine. Due to their relatively large atomic mass, they are more easily attached to the catalyst surface. As the contact space increases, free binding chemical bonds become easier, yielding more target products.

3.6. Study on the reusability of catalysts

The tobacco pyrolysis catalysts can be reused through the following approach: After the tobacco pyrolysis is completed, devices and methods are designed to recover the catalyst. Based on the differences in pore size, filtration and precipitation are used to separate the catalyst from the tobacco pyrolysis products. The recovered catalyst is subjected to regeneration treatment by calcination to remove the carbon deposition and impurities attached to its surface, thereby restoring its activity and characteristics.

Performance evaluation is conducted on the regenerated catalyst to determine whether its activity, selectivity, and stability meet the requirements. Effective catalysis will be reused in tobacco pyrolysis reaction. The XRD characterization of the catalyst used for three cycles, denoted as non-synthesized H-Al-Ca, as shown in **Figure 9**. The characterization results indicate that the used catalyst still shows characteristic diffraction peaks of the two oxides, with minimal surface carbon deposition effects, thus achieving the desired reusability. Since catalysts are compounds formed by metal ions, there are specialized methods for their treatment. Metal ions will affect the ecosystem during processing. For example, it causes soil pollution and disrupts the natural ecological balance, especially in regions already affected by environmental pollution due to energy use. This plays a protective role [30]. Therefore, repeated use of catalysts can reduce their emissions.

In this way, the tobacco pyrolysis catalysts can be reused. As the consumption of catalyst decreases, both the production costs and damage to the environment are reduced.

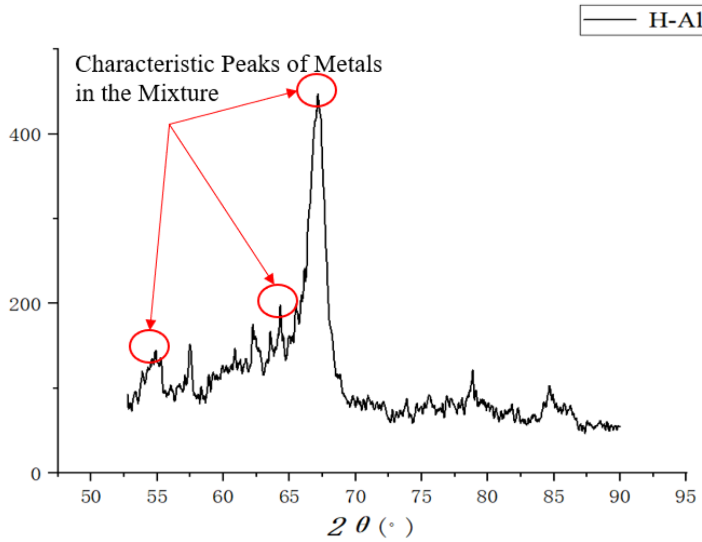

Figure 9. Comprehensive XRD characterization results of H-Al-Ca.

Scaling up the process of metal oxide catalysts for biomass energy conversion involves multiple cost and benefit considerations. First, the production cost of catalysts may rise, as the synthesis of high-purity metal oxides and the preparation of composite molecular sieves require expensive raw materials and complex processes. However, these costs can be effectively controlled and reduced by optimizing the production process and achieving economies of scale. Secondly, scaled-up production is expected to significantly improve energy efficiency and reduce the need for high-temperature, long-duration reactions, which in turn reduces overall energy consumption and production costs, as well as the impact on the environment. In addition, scaling up the process can also improve product quality and consistency, further enhancing market competitiveness and added value. Although the initial investment is large, in the long run, the expansion of the process scale will bring considerable economic and environmental benefits through improved production efficiency, energy saving and consumption reduction, as well as product quality improvement.

4. Conclusions

(1) After the metal salt is heated in the muffle furnace and combined with molecular sieves, the specific surface area slightly enlarges, with uneven crystal particle size and a multi-faceted structure. The particle morphology of the oxide catalysts combined with molecular sieves resembles that of the oxides. The shape of most particles is cubic.

(2) With the auxiliary effect of alkaline metals Ca or Al, the maximum rate of weight loss temperature of the heated tobacco slices decreases. The total weight loss increases from 100 to 300 ℃, resulting in a higher concentration of low-temperature

pyrolysis gases. Across the six stages of thermogravimetric analysis, the mass loss peak in stages (iv) to (vi) reaches a maximum of 52%, with the widest temperature range. This is due to the decomposition of cellulose, hemicellulose, sugars, lignin, and pectin.

(3) After loading alkaline metals, the predominant compounds in the products of tobacco pyrolysis are phenols, furans, nitrogen-containing compounds, and hydrocarbons. Hydrocarbons account for 38.2%, followed by 36.1% nitrogen-containing compounds. The use of catalysts significantly suppresses the formation of esters and alcohols. More aromatic hydrocarbons are generated.

This study demonstrates that alkali metal catalysts can achieve low-temperature pyrolysis of heated tobacco. Metal-catalyzed pyrolysis has proven to be an effective method for enhancing the aroma and smoke concentration of heated tobacco. The research highlights the significant contribution of understanding catalytic mechanisms in complex biomass systems to the fields of biomass energy and bioactive substance extraction. The application of catalysts not only improves the efficiency of biomass pyrolysis but also optimizes the extraction process of bioactive compounds. In the biomass energy sector, metal catalysts can enhance the selectivity and efficiency of the pyrolysis process; in the bioactive substance extraction field, they can improve the yield and purity of target compounds. This study provides new catalyst options for biomass energy and bioactive substance extraction, with excellent acid-base resistance and high-temperature stability.

The results of this study significantly contribute to the reduction of the environmental impact of tobacco processing. Firstly, the application of metal oxide catalysts directly reduces the emission of harmful gases during tobacco pyrolysis, and reduces the production of greenhouse gases such as carbon dioxide, carbon monoxide and other harmful gases by increasing the catalytic efficiency, thus reducing the negative impact on air quality. Secondly, the efficient performance of the catalyst also brings indirect environmental benefits. The optimized pyrolysis process improves energy efficiency and reduces energy consumption, which in turn reduces dependence on conventional energy sources and the associated carbon footprint. In addition, by reducing energy demand, greenhouse gas emissions from tobacco processing are reduced, thereby reducing the overall environmental impact. Together, these direct and indirect environmental benefits drive a green transformation of the tobacco processing process and contribute positively to reducing the environmental burden of the tobacco industry.

Future research could be further expanded in several areas: firstly, the performance of metal oxide composite molecular sieve catalysts could be explored in different types of biomass, including agricultural waste, wood and seaweed. This will help assess the catalyst’s universality and applicability, and optimize the pyrolysis process of different biomasses for a wider range of energy conversion and waste utilization. Secondly, it is crucial to study the long-term stability and regeneration ability of catalysts. Understanding the durability and failure mechanisms of catalysts will help to improve their service life and economics, making them more viable for practical applications. Finally, the effect of linking metal oxide catalysts with other green technologies (e.g., photocatalysis, electrocatalysis, or biocatalysis) can be explored, and by combining different catalytic technologies, the efficiency of the biomass pyrolysis process may be further enhanced, environmental impacts may be reduced, and optimization of multiple objectives may be achieved. These studies will deepen the understanding of the mechanisms involved in the application of metal-based catalysts in biomass energy conversion and promote their practical use in a wider range of environmental and energy applications.

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