

## Article

# Catalytic Rearrangement of $\beta$ -Pinene Epoxide to Perillyl Alcohol on Ammonium Phosphomolybdate Anchored to N-Basylous AC: Solvent Effect and Kinetic Characteristics

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## Abstract

Perillyl alcohol, a rare monoterpene, can be widely used in chemical, agriculture, and food industries and shows promise in medicine as an anticancer agent. The artificial synthesis of perillyl alcohol from  $\beta$ -pinene epoxide using inexpensive and abundant turpentine is chosen for improving its pharmaceutical and industrial applications. This work presents a green and sustainable catalytic process for the rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol. A novel ammonium phosphomolybdate solid acid (AC-COIMI-NH<sub>4</sub>PMo) was built via phosphomolybdic acid chemisorption onto an N-basylous site of imidazolized activated carbon followed by ammonia fumigation, which exhibits outstanding catalytic performance in the rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol in nitromethane under mild conditions. At 80 °C over 80 min, nearly complete conversion of the epoxide is achieved with a perillyl alcohol selectivity of 77.3%. Moreover, the used catalyst can be readily recycled after washing with hot nitromethane. The favorable proton-donating capacity of nitromethane for the rearrangement and the comparison of adsorption energies between substrates and main products on ammonium phosphomolybdate are revealed through DFT calculation. Kinetic analysis based on the Langmuir adsorption model indicates that the surface reaction of strongly adsorbed  $\beta$ -pinene epoxide is a rate-determining step and follows a zero-order reaction process; the activation energy is 29.64 kJ/mol within the temperature range of 50–80 °C. Finally, a parallel catalytic rearrangement mechanism is proposed, and an eight-step reaction pathway toward perillyl alcohol is elaborated for  $\beta$ -pinene epoxide conversion on AC-COIMI-NH<sub>4</sub>PMo.

**Keywords:**  $\beta$ -pinene epoxide; perillyl alcohol; catalytic rearrangement; ammonium phosphomolybdate; activated carbon



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## 1. Introduction

Thanks to its volatile property, perillyl alcohol can be delivered intranasally to lower systemic toxic risks and reduce adverse side effects during tumor chemotherapy.

Perillyl alcohol is a monocyclic terpenoid alcohol with a unique odor similar to linalool and turpentine alcohol. Beyond its application in flavors and fragrances, perillyl alcohol has been found to possess multi-purpose biomedical activity [1,2]. As cancer has become

one of the killers threatening human health, the anticancer effects of perillyl alcohol have motivated its use in extensive investigations for the clinical treatment of lung cancer [3,4], skin cancer [5], pancreatic cancer [6,7], breast cancer [8–10], prostate cancer [11], glioblastoma [12,13], etc. Due to its volatility, perillyl alcohol has the advantage of allowing drug delivery through the nasal cavity, to improve systemic hazards and greatly reduce side effects in cancer treatment [14]. Nasal administration allows a sufficiently long retention time in the brain lesion tissue, and it is also used for the therapy of brain tumors [15], recurrent malignant gliomas [16], glioma [17], glioblastoma [18], and so on, which shows up-and-coming efficiency in treating different tumor cells. As a phytomedicinal, perillyl alcohol possesses the potential to cope with Parkinson's Disease [19], as well as rheumatoid arthritis [20], imiquimod-induced psoriasis-like skin inflammation [21], ulcerative colitis [22], and antiparasitic and antifungal drug research [23–25]. Patent authorization of pharmaceutical compositions comprising perillyl alcohol derivatives is obtained by Chen et al. [26]. It can be expected that the industrial demand for perillyl alcohol will significantly increase.

As an essential oil, perillyl alcohol is usually produced from a variety of plants by hydrodistillation or extraction with organic solvent, but the process cost is expensive because its content in the plant is very low. For example, the extraction yield of perillyl alcohol was 0.18–0.35% from different parts of perillyl leaves with selected different solvents from Ahmed's recent report [27]. Solid–liquid extraction was applied to flavedos by Andrea Salvo et al. [28] using n-hexane as the solvent; the yield of the extract was about 1.16%, in which the content of perillyl alcohol was only 0.32%. Additionally, flavedos were ground into a blender and then treated with water and n-hexane; the yield of the extract was determined as 2%, with perillyl alcohol lowered to 0.29%. Therefore, the exploration of artificial/synthetic routes for perillyl alcohol is particularly important [29].

From the perspective of molecular structure, perillyl alcohol seems to belong to a mono-oxygen derivative of limonene; that is, the primary hydroxyl group  $\text{CH}_2\text{-OH}$  is formed by inserting oxygen on  $\text{CH}_2\text{-H}$  in the methyl group linked by the six-membered ring of limonene. There are expectations for the biocatalytic conversion of limonene as a strategy to gather perillyl alcohol [30]. Qin's results [31] have shown that it is possible to convert limonene into hydroxylated perillyl alcohol using bio-enzyme cytochrome P450 alkane hydroxylase as a catalyst in *Escherichia coli*; however, the content of required perillyl alcohol is only about 50 ppm in the final reaction solution, which is less than in some natural plants.

Scholars from academia and industry have been researching the production of biomedical functional chemicals using turpentine as raw material, which has the competitive advantage of low price and large supply with an annual global output of hundreds of thousands of tons of turpentine [32,33]. Due to the high toxicity of heavy metal oxidants, the chemical oxidation method has been limited to industrial licenses for the preparation of perillyl alcohol from pinene in turpentine. The two-step process of perillyl alcohol through the epoxidation of  $\beta$ -pinene and the rearrangement of its epoxide has the technological advantage of short reaction steps, benign conditions, and simpler operation, and should become a preferred way to produce perillyl alcohol from abundant turpentine.

In compliance with the advancement of green sustainable chemical processes, substantial efforts have been devoted to develop solid acid for the rearrangement of  $\beta$ -pinene epoxide. Due to the poor thermal stability of monoterpene-based substrate and products, liquid–solid catalytic systems have become an optimal choice under mild conditions. In the past decade or so, several heterogeneous catalytic materials have been found that may suit the rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol, such as inorganic Colombian natural zeolite [34], Sn-modified zeolites [35], dendritic ZSM-5 zeolites [36], Fe-modified

zeolite beta [37], Cu- or Fe-supported MCM-41 and SBA15 mesoporous zeolites [38]. Researchers have also explored organic composite solid acids with favorable substrate affinity, such as Lewis acids supported in ionic liquid catalysts (SILCAs) [39] or pentatetramidazole nitrate [40]. In addition, the solvent in the reaction process drastically alters the product distribution in the rearrangement of  $\beta$ -pinene epoxide. Using polar basic solvent, Vyskočilová E et al. observed perillyl alcohol as a main product over Sn-MCM-41 [41]; over Fe-modified zeolite, high perillyl alcohol selectivity was achieved by adding nitric acid in dimethyl sulfoxide (DMSO) as solvent [37], which means that the catalytic performance of solvents for the rearrangement of  $\beta$ -pinene epoxide depends on the intrinsic physicochemical property of specific catalytic material. Hence, efficient heterogeneous catalytic systems for highly selective perillyl alcohol synthesis from  $\beta$ -pinene epoxide under mild conditions remain urgently required for industrial and academic exploitation.

In our previous contributions on highly stable supported heteropolyacid catalysts from activated carbon, we presented a facile preparation strategy involving phosphotungstic acid bonded to an imidazole basic site on activated carbon as a reusable catalyst, successfully applied for the aqueous  $\text{H}_2\text{O}_2$ -mediated oxidation of alcohols [42] and epoxidation-hydration of  $\alpha$ -pinene to sobrerol [43], as well as for selective catalytic isomerization of  $\alpha$ -pinene epoxide to carveol in the absence of moisture [44]. Building upon these foundations, this work will present catalyst structural features, solvent-dependent catalytic behavior and kinetic investigation for heterogeneous  $\beta$ -pinene epoxide rearrangement on novel catalyst ammonium phosphomolybdate immobilized on N-basylous imidazolized activated carbon (AC-COIMI- $\text{NH}_4\text{PMo}$ ).

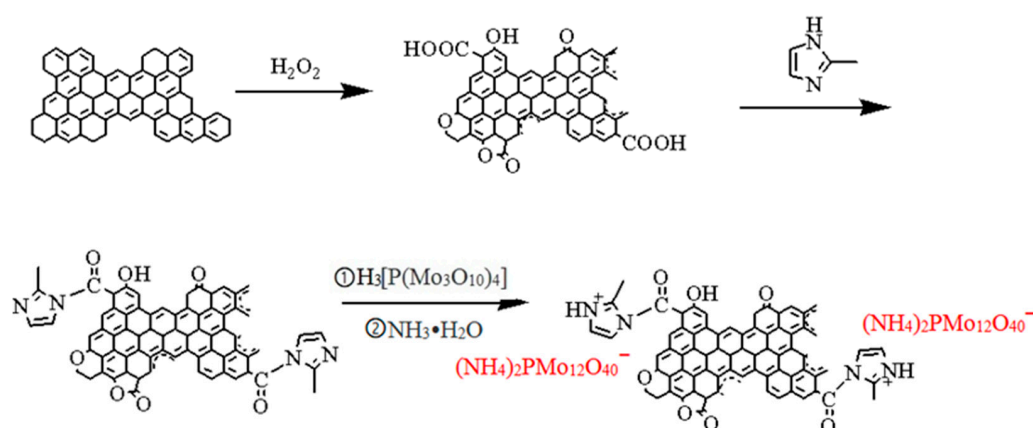
## 2. Materials and Methods

### 2.1. Materials and Reagents

$\beta$ -Pinene epoxide (85%) was kindly supplied by Yongzhou Lihao Technology Co., Ltd. (Yongzhou, China) and was fractionally distilled before use to obtain a purity of at least 96% (Including cis- and trans-isomers). All of the other reagents (AR-grade) were commercially supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), which were directly used without any future purification or treatment in the experiment.

### 2.2. Catalyst Preparation

According to the previous preparation procedure of the supported phosphotungstic acid catalyst from activated carbon in our group [43], the preparation of phosphomolybdic acid supported on imidazoline activated carbon AC-COIMI- $\text{NH}_4\text{PMo}$  catalyst is shown in Figure 1.



**Figure 1.** The illustration for the preparation procedure of AC-COIMI- $\text{NH}_4\text{PMo}$ .

The acyl imidazolized activated carbon AC-COIMI [43] was used as a support for AC-COIMI-NH<sub>4</sub>PMo. A precise quantity of HPMo was dissolved in ultrapure water, resulting in a 0.1 mol·L<sup>−1</sup> HPMo standard solutions. Subsequently, 1.00 g of AC-COIMI was immersed in the respective solution and allowed to stand for 24 h. The supernatant was separated through centrifugation and washed repeatedly with ultrapure water until the absence of phosphomolybdic acid was confirmed by UV-vis spectrometry. The obtained wet material was then vacuum-dried at 50 °C overnight, leading to the formation of the AC-COIMI-HPMo catalyst. To prevent contamination by volatile ammonia gas, concentrated ammonia was introduced into a beaker placed inside an empty desiccator. The AC-COIMI-HPMo sample was placed on the separator of the desiccator, covered, and left for 24 h at room temperature. Subsequently, the catalytic material was removed from the H<sup>+</sup> acidic site to NH<sub>4</sub><sup>+</sup> on AC-COIMI-HPMo through ammonia fumigation, and vacuum-dried at room temperature overnight; the collected ammonium phosphomolybdate bonded to imidazolylated activated carbon catalyst was marked as AC-COIMI-NH<sub>4</sub>PMo.

### 2.3. Catalyst Characterization

FT-IR of the catalyst samples was collected by the KBr pellet technique at room temperature on a Nicolet 370 infrared spectrophotometer in the range of 500–4000 cm<sup>−1</sup>. XRD patterns of the sample were recorded by a Bruker diffractometer (Bruker, Billerica, MA, USA) with Cu Kα radiation and diffraction angle (2θ) ranging from 5° to 80°. XPS of the materials was recorded by a Thermo Scientific K-Alpha+ spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) within 0–1200 eV. The UV-Vis spectrum of washing liquid in the preparation of supported heteropoly acid was measured by Shimadzu UV-2450 (Shimadzu, Kyoto, Japan) in 190–900 nm. The BET surface area, total pore volume and pore size distribution of the catalyst sample were measured, employing the Brunauer–Emmett–Teller (BET) equation and the Horvath–Kawazoe (H-K) model, by the adsorption of nitrogen with the Micromeritics ASAP 2460 surface area analyzer (Micromeritics, Norcross, GA, USA) at 77.3 K, P/P<sub>0</sub> = 0.000~0.994. The surface acidity and ICP measurement of phosphomolybdate in the catalytic materials were similar to our previous work [42].

### 2.4. Catalytic Performance Test

The weighed catalyst and measured solvent were added to the two-neck flask containing the reaction, stirred electromagnetically, heated in an oil bath, and raised to the reaction temperature for 15 min to activate the catalyst, and we then added β-pinene epoxide to operate the reaction. The general reaction conditions: 10 mmol β-pinene epoxide, catalyst dosage 5%, solvent 10 mL, 80 °C, 80 min, stirring 400 rpm. After the reaction was terminated, the flask was naturally cooled to room temperature; the catalyst particles were centrifuged in a high-speed centrifuge and the supernatant was reserved for component analysis of the product. The qualitative structural confirmation of components was carried out by a Shimadzu GCMS-QP2010 (Shimadzu, Kyoto, Japan) capillary gas chromatograph-mass spectrometer, and the conformity of the product components with the standard samples was above 95% by using the instrument's mass spectrometry database search and comparison, e.g., perillyl alcohol (152, M<sup>+</sup>; 131, CH<sub>3</sub>CH<sub>2</sub>CC<sub>6</sub>H<sub>8</sub><sup>+</sup>, 100%; 79, C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 82%). The quantitative content of components was analyzed by an internal standard method with a Shimadzu GC-2010 capillary gas chromatograph, and phenylethanol was used as the internal standard.

Following Vyskočilová E et al. [37], the conversion of β-pinene epoxide was simplified as follows:

$$\text{Conv.(\%)} = \frac{(\text{moles of } \beta\text{-pinene epoxide in raw material} - \text{moles of } \beta\text{-pinene epoxide in the product})}{\text{moles of } \beta\text{-pinene epoxide in raw material}} \times 100\%$$

The selectivity of component  $i$  in the product of  $\beta$ -pinene epoxide rearrangement is calculated as follows:

$$Sel_i (\%) = \frac{\text{moles of component } i \text{ in the product}}{(\text{moles of } \beta\text{-pinene epoxide in raw material} - \text{moles of } \beta\text{-pinene epoxide in the product})} \times 100\%$$

## 2.5. DFT Calculation

Relevant auxiliary software was used for density functional theory (DFT) calculations [45]. The exchange-correlation functional utilized was the Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [46]. Additionally, DFT-D corrections were applied using the Grimme method to account for dispersion effects [47]. The structural optimizations were carried out using the self-consistent field (SCF) method, with the convergence threshold set to  $1 \times 10^{-6}$  au for both energy and electron density. The energy convergence criterion was set to  $1 \times 10^{-5}$  Ha, the force convergence criterion to  $0.002 \text{ Ha}/\text{\AA}$ , and the electron displacement criterion to  $0.005 \text{ \AA}$ . The global orbital cutoff distance was set to  $4.1 \text{ \AA}$ , ensuring the accuracy and reliability of the calculations. The adsorption energy ( $E_{\text{ads}}$ ) of the substrates (EL and IPA) is calculated according to the following expression:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{sub}} - E_{\text{cat}}$$

where  $E_{\text{tot}}$  represents the energy of the substrate adsorbed onto the catalyst system,  $E_{\text{sub}}$  denotes the energy of the substrate, and  $E_{\text{cat}}$  refers to the energy of the catalyst.

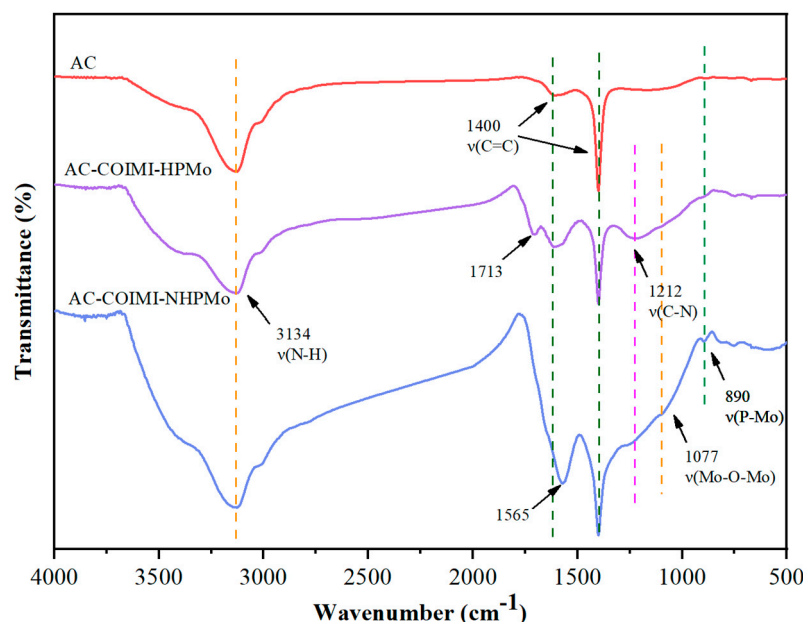
## 3. Results and Discussion

### 3.1. Characterizations

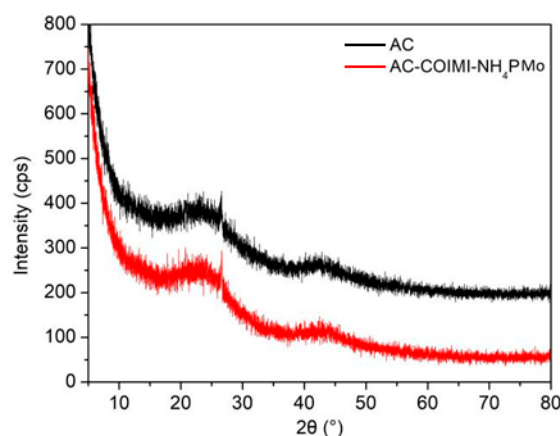
The FT-IR spectra of three catalytic materials are shown in Figure 2, which provides chemical bonding information derived from bulk-compatible surfaces. The peaks at  $1608 \text{ cm}^{-1}$  and  $1400 \text{ cm}^{-1}$  belong to the C=C stretching vibration absorption of the thick aromatic skeleton in the activated carbon, and the absorption in the range of  $3134\text{--}3400 \text{ cm}^{-1}$  can be provided by the stretching characteristics of OH on the surface of activated carbon [47,48]. Compared with AC, FT-IR spectra of AC-COIMI-HPMo and AC-COIMI-NH<sub>4</sub>PMo show the HPMo adsorbed on -NH- in the imidazole group of AC-COIMI, and the conversion of H<sup>+</sup> of AC-COIMI-HPMo into NH<sub>4</sub><sup>+</sup> after adsorption of NH<sub>3</sub>. Between  $3000$  and  $3360 \text{ cm}^{-1}$ , almost overlapping with the stretching of OH, N-H symmetric and asymmetric stretching vibration of NH<sub>4</sub><sup>+</sup> in AC-COIMI-NH<sub>4</sub>PMo is broadly absorbed and enhanced. The absorption characteristic peak of C-N appears at  $1713 \text{ cm}^{-1}$  and  $1212 \text{ cm}^{-1}$  [48,49], and the characteristic peaks of Mo-O appear at  $890 \text{ cm}^{-1}$  and  $1077 \text{ cm}^{-1}$  [50]. In addition, the absorption at  $1565 \text{ cm}^{-1}$  was significantly enhanced, because the increased peak of C=O by the oxidation coincided with the absorption of the carbon skeleton, and the peak exhibited blue shift [49], indicating that HPMo is chemically connected to the surface basic site of imidazolized activated carbon. No HPMo absorption peak of crystalline structure emerged in the catalyst, which confirmed that the chemisorbed ammonium phosphomolybdate was evenly dispersed, and also consistent with XRD results (Figure 3).

The wide-angle X-ray diffraction curves of support and catalyst are presented in Figure 3. The figure only shows the diffraction characteristics of amorphous AC and AC-COIMI-NH<sub>4</sub>PMo, and the crystal diffraction peak of ammonium phosphomolybdate does not exist, similar to the reported results of ammonium phosphotungstate immobilized on the imidazolized activated carbon AC-COIMI-NH<sub>4</sub>PW [43]. This is because ammonium molybdate phosphate is adsorbed on each alkaline imidazole site by single HPMo molecule

chemisorption on AC-COIMI, in which the average surface area occupied by each HPMo molecule may be  $4 \text{ nm}^2$  from the N-base density of  $103 \text{ } \mu\text{mol/g}$  from the titration and ICP method used before [42], so there would be no diffraction peak of ordered crystal phase ammonium phosphomolybdate at all in AC-COIMI- $\text{NH}_4\text{PMo}$ . In other words, the catalytic site species has been unimolecularly highly self-dispersed to the surface basic site of imidazolized activated carbon through acid–base interactions.



**Figure 2.** FT-IR of AC, AC-COIMI-HPMo, and AC-COIMI- $\text{NH}_4\text{PMo}$ .



**Figure 3.** XRD of AC and AC-COIMI- $\text{NH}_4\text{PMo}$ .

We can clearly observe the obvious XPS intensity of P and Mo after loading HPMo on imidazolized activated carbon AC-COIMI, and ammoniated AC-COIMI-HPMo from Figure 4. In the phosphomolybdate anion on AC-COIMI- $\text{NH}_4\text{PMo}$ , P is in the central position, Mo is connected by an oxygen bridge,  $\text{H}^+$  is converted into  $\text{NH}_4^{4+}$ , and it may be difficult to significantly affect the core electronic structure of P and Mo. Therefore, the absorption of XPS associated with P and Mo in AC-COIMI-HPMo and AC-COIMI- $\text{NH}_4\text{PMo}$  is almost the same. As  $\text{NH}_4^{4+}$  is formed by  $\text{NH}_3$  with  $\text{H}^+$  in AC-COIMI-HPMo during the ammonification process, the N 1s in the XPS is significantly enhanced from the contribution of  $\text{NH}_4^{4+}$  on the AC-COIMI- $\text{NH}_4\text{PMo}$ . The binding of  $\text{NH}_3$  increases the nitrogen content in the catalyst.

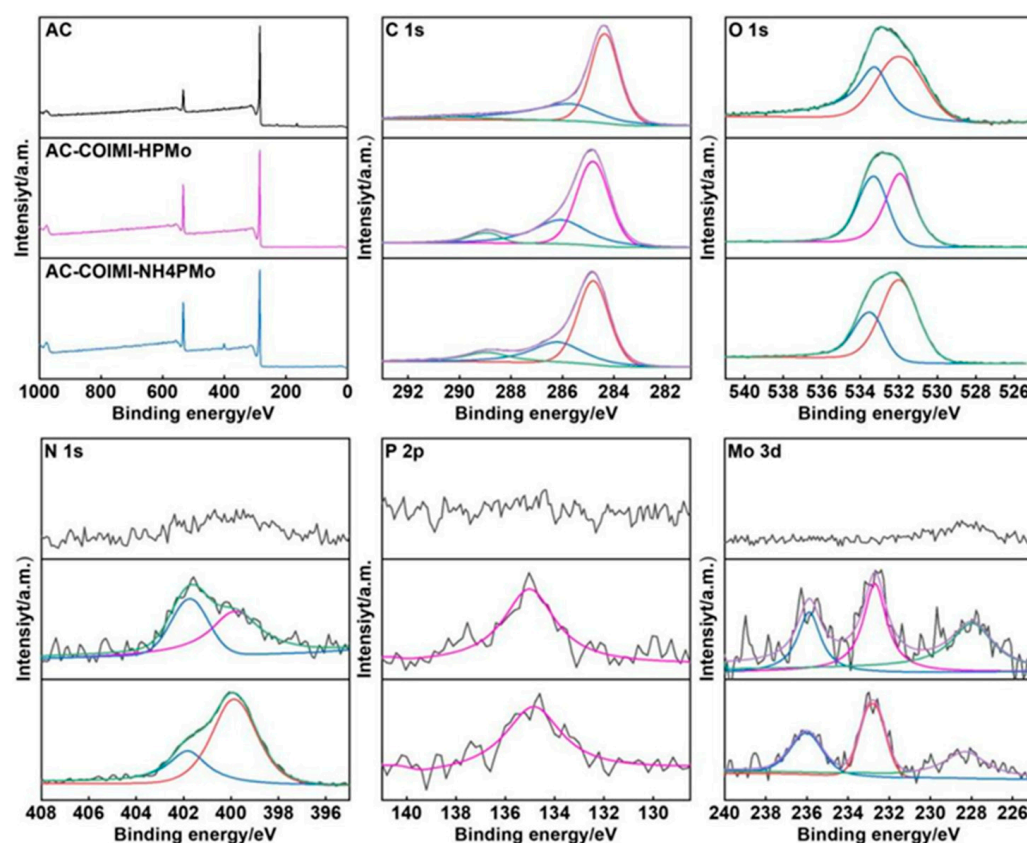
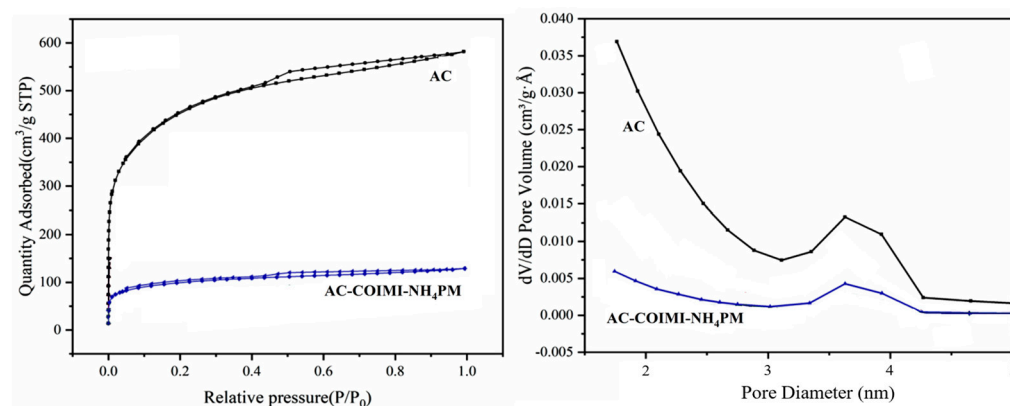


Figure 4. XPS intensity vs. binding energy plots for three materials.

The adsorption isotherms of both AC and AC-COIMI-NH<sub>4</sub>PMo exhibit type IV behavior in Figure 5 (left), which indicates the presence of mesoporous structures in the materials. The specific surface area, total pore volume, acidity, and P and Mo content of AC and AC-COIMI-NH<sub>4</sub>PMo are shown in Table 1; it is indicated that after oxidized, imidazolized, and chemically adsorbed modifications, the texture of the activated carbon-based catalytic material changed with a significant decrease in pore volume and specific surface area; after deducting 15 wt% ammonium phosphomolybdate adsorbed by single molecules that are ineffective in pore formation, the specific surface area of the remaining porous carbon is also about 300 m<sup>2</sup>/g. However, the average pore size was expanded from 2.57 nm to 2.97 nm, similar to the preparation of AC-COIMI-NH<sub>4</sub>PW [43], which is also more conducive to the diffusion of larger volume  $\beta$ -pinene epoxide substrates (estimated kinetic diameter ~0.6 nm) and products in the catalytic process. From the pore distribution in Figure 5 (right), it is evident that the changes in these texture parameters are due to the significant elimination of micropores in AC during these modification processes; once ammonium phosphomolybdate with a molecular diameter greater than 1 nm is adsorbed on the pores of the corresponding micropores, it becomes difficult for the adsorbate molecule nitrogen to enter the closed micropores, so the pore volume and specific surface area are significantly reduced. The adsorption capacity of ammonium phosphomolybdate decreases from the potential N(imidazole)-base density 103  $\mu$ mol/g to only an actual 77  $\mu$ mol/g (Table 1), which also proves its own gate-closing effect.



**Figure 5.** Adsorption isotherm (left) and pore distribution (right) of AC and AC-COIMI-NH<sub>4</sub>PMo.

**Table 1.** Texture and surface properties of catalytic materials.

| Materials                                 | Sg (m <sup>2</sup> /g) | Vg (cm <sup>3</sup> /g) <sup>b</sup> | Groups (μmol/g)                     | P (μmol/g) | Mo (μmol/g) |
|-------------------------------------------|------------------------|--------------------------------------|-------------------------------------|------------|-------------|
| AC                                        | 1025                   | 0.66 (2.57)                          | 11 (–COOH)                          | –          | –           |
| AC-COIMI-NH <sub>4</sub> PMo <sup>a</sup> | 253                    | 0.12 (2.97)                          | 233 (NH <sub>4</sub> <sup>+</sup> ) | 77         | 922         |
| Used-AC-COIMI-NH <sub>4</sub> PMo         | –                      | –                                    | 229 (NH <sub>4</sub> <sup>+</sup> ) | 76         | 918         |

<sup>a</sup>: The N-base density of imidazolized activated carbon AC-COIMI is 103 μmol/g; <sup>b</sup>: average pore size (nm).

### 3.2. Influence of Catalytic Site on $\beta$ -Pinene Epoxide Rearrangement

The results of  $\beta$ -pinene epoxide rearrangement on some catalysts are listed in Table 2. The catalytic rearrangement mainly proceeds along two pathways in this process. One route is the ‘epoxide ring-opening and hydrogen transfer’ of  $\beta$ -pinene epoxide to form two bicyclic products, myrtenol (M-ol) and myrtenal (M-al). Another is the formation of expected single-ring perillyl alcohol (PA), through ‘epoxide ring opening, quaternary ring cleavage and hydrogen transfer’ of the epoxide. All by-products are classified as others in the rearrangement. It can be seen that the  $\beta$ -pinene epoxide rearrangement occurs to a certain extent with 8.6% catalyst-free conversion in nitromethane. When using oxidated active carbon AC-O as the catalyst, the conversion of  $\beta$ -pinene epoxide is increased to 19.6% relative to the blank reaction of nitromethane, which indicates that the oxidation of activated carbon improves its acid catalysis in the rearrangement.

**Table 2.** Catalytic rearrangement of  $\beta$ -pinene epoxide on different materials.

| Catalyst                            | Conv. (%) | Sel. (%) |      |      |        |
|-------------------------------------|-----------|----------|------|------|--------|
|                                     |           | M-al     | M-ol | PA   | Others |
| –                                   | 8.6       | 28.0     | 31.0 | 37.0 | 4.0    |
| AC-CO                               | 19.6      | 24.7     | 22.4 | 43.6 | 9.3    |
| AC-COIMI-NH <sub>4</sub> PW         | 87.3      | 5.8      | 15.0 | 61.4 | 17.8   |
| AC-COIMI-HPMo                       | 100       | 0.4      | 0.6  | 27.7 | 72.3   |
| AC-COIMI-NH <sub>4</sub> PMo        | 97.5      | 5.8      | 0.6  | 77.3 | 16.3   |
| (NH <sub>4</sub> ) <sub>3</sub> PMo | 90.8      | 4.8      | 1.5  | 71.2 | 22.5   |
| NH <sub>4</sub> NO <sub>3</sub>     | 83.9      | 5.3      | 17.3 | 59.2 | 18.2   |
| AC-COIMI-HNO <sub>3</sub>           | 94.5      | 5.6      | 5.1  | 62.3 | 27.0   |

Through HPMo bonded to the imidazole nitrogen-doped activated carbon (AC-COIMI), which came from acylation of 2-methylimidazole with carboxyl groups on the surface of oxidized activated carbon [43], AC-COIMI-HPMo presented a significant catalytic activity for the complete transformation of  $\beta$ -pinene epoxide in nitromethane. Comparing the catalytic performance between ammoniated AC-COIMI-NH<sub>4</sub>PMo with AC-COIMI-HPMo

in Table 2, the conversion of  $\beta$ -pinene epoxide is almost identical on AC-COIMI-NH<sub>4</sub>PMo, but the main product of the rearrangement is perillyl alcohol, in which the selectivity of perillyl alcohol is significantly increased from 27.7% to 77.3%. When AC-COIMI-HPMo is used as the catalyst in  $\beta$ -pinene epoxide rearrangement, behind epoxy-bond ring-opening in the adsorbed epoxide, cracking of quaternary rings more easily occurs on strong acid H<sup>+</sup> sites in HPM, so the total selectivity of myrtenol and myrtenal is also about 1%. The adsorbed epoxide and primary products are consecutively converted into other by-products by dehydration, hydrogen transfer reaction, oligomerization, and so on.

When unsupported (NH<sub>4</sub>)<sub>3</sub>Mo<sub>12</sub>O<sub>40</sub>P was directly used as catalyst, its catalytic activity and the selectivity of perillyl alcohol are both lower than on AC-COIMI-NH<sub>4</sub>PMo, but the selectivity of perillyl alcohol is still 43% higher than on AC-COIMI-HPMo as catalyst, indicating that weaker NH<sub>4</sub><sup>+</sup> is a suitable catalytic active site for the rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol. In other words, the appropriate acid strength and acidic species bonded to the catalytic site are the key factors in regulating the fine catalytic performance for this rearrangement in the development of future catalysts.

Compared with using ammonium nitrate as the catalyst in industrial perillyl alcohol production for the rearrangement of  $\beta$ -pinene epoxide, which involves hidden risks of explosion and environmental hazards, AC-COIMI-NH<sub>4</sub>PMo provides higher catalytic activity to increase the conversion of  $\beta$ -pinene epoxide by 13% and the selectivity of perillyl alcohol by 19% than NH<sub>4</sub>NO<sub>3</sub> in the same reaction conditions. It is interesting that AC-COIMI-HNO<sub>3</sub>, nitric acid adsorbed on imidazolated activated carbon AC-COIMI, presents better catalytic performance, both catalytic activity and selectivity, than NH<sub>4</sub>NO<sub>3</sub>, which indicates that the ammonium ion acid site constructed on the basic position of the imidazole ring on AC-COIMI has excellent catalytic function for the rearrangement of  $\beta$ -pinene epoxide, but the conjugated base of the corresponding anion can provide a modifying effect on the performance.

### 3.3. Solvent Effect on Catalytic Rearrangement

As is well known, solvents have the potential to modulate the rate and direction of organic reactions. In the liquid–solid rearrangement of  $\beta$ -pinene epoxide on a novel catalyst, the optimal choice of solvent is usually obtained through systematic comparison [29,34,36,37,40,41]. The effects of different solvents on the catalytic rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol over AC-COIMI-NH<sub>4</sub>PMo are listed in Table 3. The results show that although the catalytic activity of COIMI-NH<sub>4</sub>PMo in the reaction medium is the lowest with non-polar cyclohexane as solvent, which is the best choice on Mo/SBA-15 [29], the selectivity of myrtenol is 46.5%, which exceeds perillyl alcohol, and the selectivity of myrtenal is less than 1%. It indicates that in the presence of cyclohexane, polar  $\beta$ -pinene epoxide rearrangement struggles to generate perillyl alcohol at the catalytic active site. In toluene, another non-polar solvent, the conversion rate of  $\beta$ -pinene epoxide reached 62%, but more unknown products were produced.

Although chloroform, ethyl acetate, and acetone are polar solvents in the reaction medium, the conversion of  $\beta$ -pinene epoxide remained around 25%, which is consistent with the above non-polar cyclohexane system, and the selectivity of perillyl alcohol did not exceed 12%. It might be that these solvent molecules in the reaction medium struggle to form an effective composite catalytic species or catalytic active site with NH<sub>4</sub><sup>+</sup> and phosphomolybdate anions through solvation on AC-COIMI-NH<sub>4</sub>PMo, so the activation of the substrate is hindered, and the reaction rate slows down accordingly. When the reaction medium is constructed with a protonic strong polar solvent such as methanol, the substrate is basically transformed completely, but the selectivity of the target product is still very small, and the etherification product is the main component from the addition of methanol

with  $\beta$ -pinene epoxide, which could provide a path to synthesize ether derivatives using alcohols and  $\beta$ -pinene epoxide as substrate.

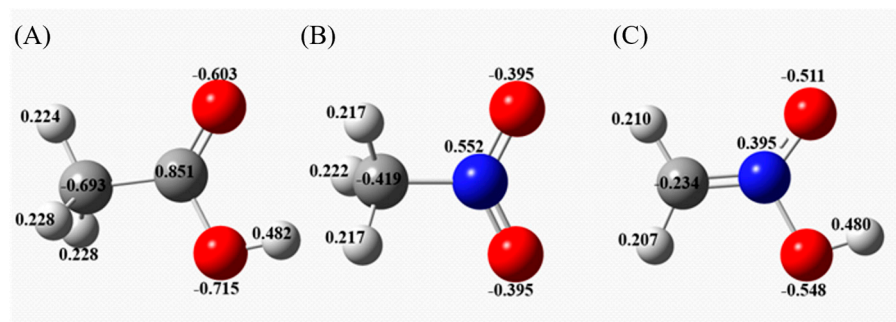
**Table 3.** Effect of different solvents on  $\beta$ -pinene epoxide rearrangement.

| Solvent                         | Conv. (%) | Sel. (%) |      |      |        |
|---------------------------------|-----------|----------|------|------|--------|
|                                 |           | M-al     | M-ol | PA   | Others |
| Cyclohexane <sup>a</sup>        | 21.4      | 0.3      | 46.5 | 29.0 | 24.2   |
| Toluene                         | 51.8      | 0.4      | 24.6 | 11.6 | 63.4   |
| Trichloromethane <sup>a</sup>   | 22.5      | 1.3      | 18.5 | 9.8  | 70.4   |
| Ethyl acetate <sup>a</sup>      | 29.2      | 1.8      | 18.1 | 10.6 | 69.5   |
| Acetone <sup>a</sup>            | 23.3      | 1.9      | 15.0 | 9.2  | 73.9   |
| Methanol <sup>a</sup>           | 99.9      | 14.0     | 9.4  | 11.2 | 65.4   |
| Dimethyl sulfoxide              | 98.0      | 15.8     | 18.6 | 47.3 | 18.3   |
| Nitromethane                    | 97.5      | 5.8      | 0.6  | 77.3 | 16.3   |
| Nitromethane (0.1) <sup>b</sup> | 92.1      | 5.5      | 0.5  | 65.2 | 28.8   |
| Nitromethane (0.2) <sup>b</sup> | 88.7      | 5.3      | 0.5  | 56.7 | 37.5   |
| Nitromethane <sup>c</sup>       | 96.8      | 5.2      | 0.6  | 77.1 | 17.1   |

<sup>a</sup>: Reaction at reflux temperature ( $\leq 80$  °C); <sup>b</sup>: the content of water in nitromethane (wt%); <sup>c</sup>: fourth reuse by washing catalyst with hot nitromethane.

Unlike the synthesis of perillyl alcohol catalyzed by pentaertetramidazole nitrate in our laboratory [40] and Fe-modified zeolite beta in Vyskočilová E's group [37], when AC-COIMI-NH<sub>4</sub>PMo was used as a catalyst to construct the reaction system with strong polarity and weak alkaline solvent DMSO,  $\beta$ -pinene epoxide was quickly rearranged; however, the perillyl alcohol selectivity was less than 50% through 'epoxy-bond ring-opening, quaternary ring cracking, and hydrogen transfer'. The total selectivity of myrtenal and myrtenol reached 34.4%. When  $\beta$ -pinene epoxide liquid phase catalytic rearrangement was used to synthesize perillyl alcohol, there were individual differences in the medium system required for the optimal catalytic performance of different catalysts, which may be determined by the difference of catalytic active sites.

It is pleasantly surprising to announce in Table 3 that when nitromethane is used as the solvent to form the reaction medium for the rearrangement of  $\beta$ -pinene epoxide, AC-COIMI-NH<sub>4</sub>PMo not only presents high catalytic activity but also significantly improves the selectivity of perillyl alcohol, which is raised to 77.3%. By comparing the rearrangement of the blank experiment without a catalyst,  $\beta$ -pinene epoxide also showed obvious conversion (8.6%) in nitromethane, as listed in Table 2, which means that nitromethane can provide acid catalytic function to a certain extent for the rearrangement. Based on the fact that nitromethane can be used as an adduct in Michael addition [48], it can be inferred that its deductive isomer methylene nitrate may provide acidic protons. By means of using the 6-311 + G (d, p) basis set and Gaussian 09 W to operate the DFT calculations [31], the atomic charges in three molecules of nitromethane, methylene nitrate and acetic acid were described by the natural bond orbital (NBO) charge distribution (Figure 6). It is revealed that the positive charge of proton in the hydroxyl of methylene nitrate (C) is equal to that in the hydroxyl of acetic acid (A), but the negative charge of oxygen atoms in the hydroxyl of methylene nitrate is less than in acetic acid, meaning that the acid strength of nitromethane as a solvent would be weaker than that of acetic acid. Therefore, the strong protonation ability of nitromethane causes self-catalysis in the conversion of  $\beta$ -pinene epoxide and improves the catalytic rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol by interacting with protons in ammonium ions at the active site of AC-COIMI-NH<sub>4</sub>PMo, so finding ways to obtain relevant energy data may have important scientific implications.

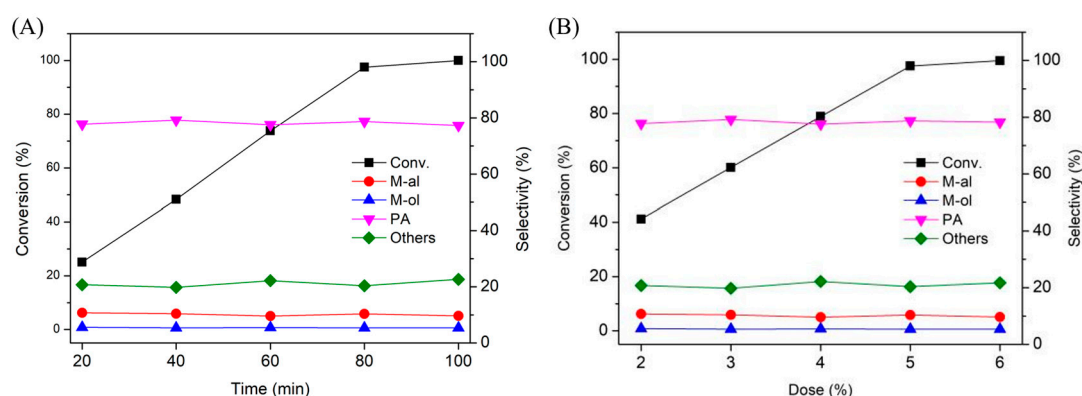


**Figure 6.** NBO charge distribution of acetic acid (A), nitromethane (B) and methylene nitrate (C).

It is noted that nitromethane has strong water absorption in industrial processes as a solvent, so the influence of water on the catalysis of AC-COIMI-NH<sub>4</sub>PMo in the rearrangement of  $\beta$ -pinene epoxide was investigated. The result in Table 3 indicates that both activity and perillyl alcohol selectivity of AC-COIMI-NH<sub>4</sub>PMo are decreased in the presence of trace amounts of water in nitromethane. A possible reason could be that the equation of NH<sub>4</sub><sup>+</sup> or H<sup>+</sup> at the acidic site hinders the adsorption of oleophilic  $\beta$ -pinene epoxide, leading to a decrease in catalytic activity. The decrease in the selectivity of perillyl alcohol may be due to the addition of water to the carbocation intermediate of  $\beta$ -pinene epoxide adsorbed at the acidic catalytic site, which generates other by-products. In the rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol, removing the moisture from the solvent may have a wide adaptability to ensure the intrinsic catalytic performance of acidic materials.

### 3.4. Kinetic Characteristics

The effect of reaction time on the catalytic rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol by AC-COIMI-NH<sub>4</sub>PMo is shown in Figure 7A. As the reaction time increases, the conversion of  $\beta$ -pinene epoxide continues to increase until the reaction time is extended to 100 min, at which the substrate  $\beta$ -pinene epoxide can be completely converted, in which the conversion of  $\beta$ -pinene epoxide is linearly increased to 97.5% with the time from 20 to 80 min. The selectivity of the target product perillyl alcohol also decreases from the highest value, 77.3%, at 80 min to 75.8%. Continuing to extend the time, there is no significant change in the selectivity of products, which exhibits the characteristic of parallel reactions.

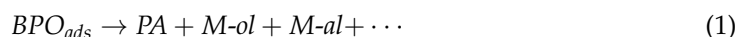


**Figure 7.** Effect of reaction time (A) and catalyst dose (B) on  $\beta$ -pinene epoxide rearrangement.

As can be seen from Figure 7B, while the mass of the catalyst used accounted for 2–5% of the substrate  $\beta$ -pinene epoxide, the conversion of  $\beta$ -pinene epoxide increased with the increase in the amount of catalyst, and it was proportional to the increase in catalyst dosage,

which was similar to that of the extension of reaction time. When the dosage of the catalyst was 5%, the conversion of  $\beta$ -pinene epoxide reached 97.5%. Also, the AC-COIMI-NH<sub>4</sub>PMo catalyst dosage had little effect on the selectivity of  $\beta$ -pinene epoxide rearrangement, and several products were formed by parallel reaction.

According to the data from the phenomenon in Figure 7A,B, it can be inferred that the reaction rate of  $\beta$ -pinene epoxide catalyzed by AC-COIMI-NH<sub>4</sub>PMo seems unrelated to concentration, showing the characteristics of a zero-order reaction. Obviously,  $\beta$ -pinene epoxide (BPO) rearrangement on the surface of AC-COIMI-NH<sub>4</sub>PMo catalyst is a single-molecule reaction. If the surface reaction of adsorbed  $\beta$ -pinene epoxide ( $BPO_{ads}$ ) on the NH<sup>4+</sup> acid site is the rate-determining step,



Its surface reaction rate  $r_{BPO}$  is

$$r_{BPO} = k_{s+} \cdot \theta_{BPO} \quad (2)$$

where  $k_{s+}$  is the reaction rate constant of adsorbed  $\beta$ -pinene epoxide on the surface, and  $\theta_{BPO}$  is the coverage of adsorbed  $\beta$ -pinene epoxide  $BPO_{ads}$  on the catalytic site of the surface.

According to the uniform behavior of the heteropolyacid adsorption site on AC-COIMI [45] and acid on the active site with oxygen lone pair electrons in ether bonds to form pseudo salt, the Langmuir adsorption isotherm equation, which was recently used by Luis A. Gallego-Villada's group for BPO rearrangement on dendritic ZSM-5 zeolites in 2026 [36], is adopted to describe the adsorption behavior of  $\beta$ -pinene epoxide on the surface catalytic site of AC-COIMI-NH<sub>4</sub>PMo as follows:

$$\theta_{BPO} = \frac{A_{BPO} \cdot C_{BPO}}{1 + A_{BPO} \cdot C_{BPO} + \dots} \quad (3)$$

where  $C_{BPO}$  is the equilibrium concentration of  $\beta$ -pinene epoxide, and  $A_{BPO}$  is the Langmuir adsorption equilibrium constant or adsorption coefficient. The epoxy bond in  $\beta$ -pinene epoxide has Lewis alkalinity from its lone pair electrons and has been adsorbed on the NH<sup>4+</sup> acidic active site on the surface of AC-COIMI-NH<sub>4</sub>PMo. If the adsorption equilibrium constant of  $\beta$ -pinene epoxide is large enough to make  $A_{BPO} \cdot C_{BPO}$  much greater than sum of 1 and other adsorption items, then

$$(1 + A_{BPO} \cdot C_{BPO} + \dots) \approx A_{BPO} \cdot C_{BPO} \quad (4)$$

In this way, substituting into the denominator of Equation (3), the adsorption of  $\beta$ -pinene epoxide on the acid active site reaches saturation:

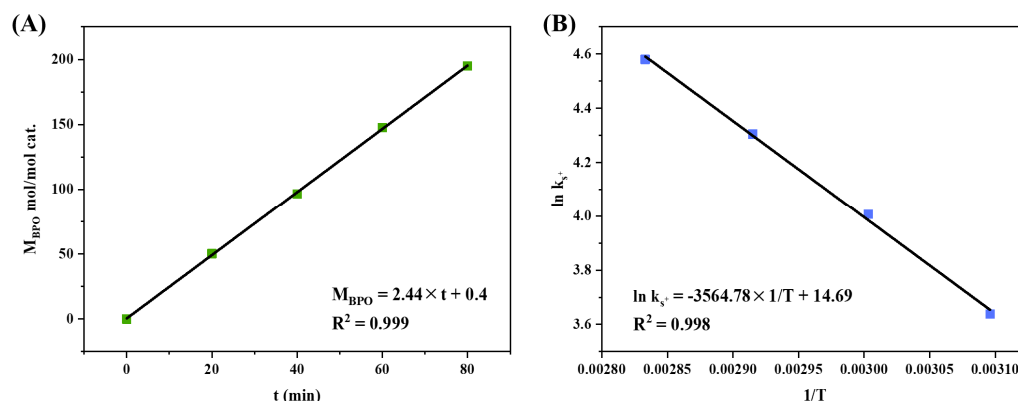
$$\theta_{BPO} = 1 \quad (5)$$

The surface reaction rate is  $k_{s+}$ :

$$r_{BPO} = k_{s+} \cdot \theta_{BPO} = k_{s+} \quad (6)$$

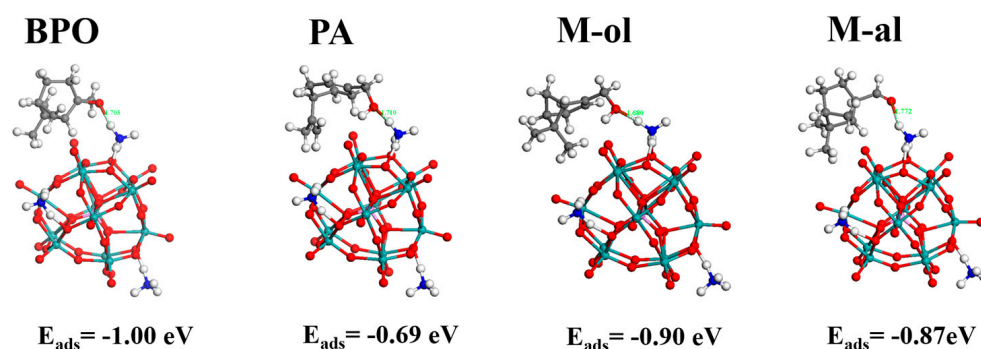
Therefore, the conversion of  $\beta$ -pinene epoxide is linearly increased to 97.5% with reaction time prolonging to 80 min based on the reaction rate being constant. As shown in Figure 7A, the linear regression correlation between the conversion of BPO and reaction time at 80 °C (Figure 8A) has a very high coefficient of determination ( $R^2 = 0.999$ ), so it is illustrated that the zero-order reaction kinetic equation (Equation (6)) obtained from the

assumption of (4) is highly consistent with the experimental results from the conversion of  $\beta$ -pinene epoxide on AC-COIMI-NH<sub>4</sub>PMo.



**Figure 8.** The correlation between the conversion of BPO and time at 80 °C (A); Arrhenius relationship of apparent rate constants of BPO in the range of 50–80 °C (B).

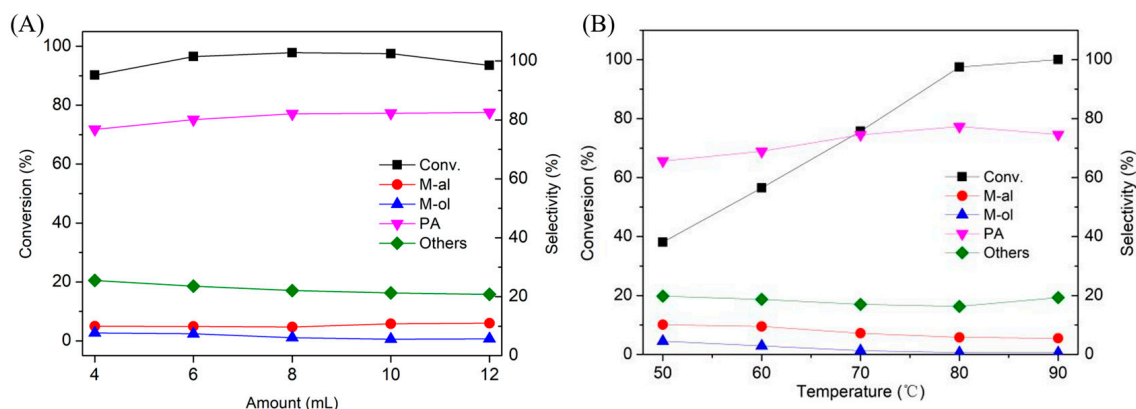
Essentially, the catalytic site on surface AC-COIMI-NH<sub>4</sub>PMo is a single ammonium molybdate molecule, and DFT calculations were performed to investigate the adsorption of the substrate BPO and three main products on it. The calculated adsorption energies reveal that BPO adsorbs more strongly on ammonium phosphomolybdate than the corresponding products (Figure 9). The adsorption energy of  $\beta$ -pinene epoxide is  $-1.00$  eV, which is more negative than that of perillyl alcohol (PA), myrtenol (M-ol), and myrtenal (M-al). This stronger adsorption can be attributed to the interaction between the hydrogen atoms in NH<sub>4</sub><sup>+</sup> on the catalytic site ammonium molybdate and the oxygen atom of the epoxide group. Such an interaction favors substrate adsorption and epoxide activation by polarizing the C–O bond. In contrast, the products show weaker adsorption on the catalytic site. In particular, PA exhibits the weakest adsorption energy of  $-0.69$  eV, suggesting that it can readily desorb from the active sites after formation. This adsorption behavior indicates that ammonium phosphomolybdate can efficiently activate BPO while avoiding strong retention of the target product, resulting in an apparent zero-order reaction in the rate-determining step of the surface reaction. Therefore, the stronger adsorption of the substrate and the weaker adsorption of PA are favorable for active-site regeneration and may suppress product inhibition and secondary transformations.



**Figure 9.** Optimized adsorption configurations and energies of BPO and three products on (NH<sub>4</sub>)<sub>3</sub>Mo<sub>12</sub>O<sub>40</sub>P catalytic site.

During the rearrangement of  $\beta$ -pinene epoxide on AC-COIMI-NH<sub>4</sub>PMo, the effect of solvent nitromethane dosage, equivalent to different concentrations of  $\beta$ -pinene epoxide, on the reaction is shown in Figure 10A. It can be found that the catalytic rearrangement rate is almost not changed with the concentration of  $\beta$ -pinene epoxide within a certain

range, which further confirms that the process on AC-COIMI-NH<sub>4</sub>PMo in nitromethane is a zero-order reaction (Equation (6)).



**Figure 10.** Effect of nitromethane dosage (A) and temperature (B) on the rearrangement.

The effect of reaction temperature on the rearrangement of  $\beta$ -pinene epoxide catalyzed by AC-COIMI-NH<sub>4</sub>PMo is listed in Figure 10B. The results showed that the conversion of  $\beta$ -pinene epoxide increased with the increase in reaction temperature. When the temperature increased to 80 °C, the conversion of  $\beta$ -pinene epoxide was almost fully completed. The selectivity of perillyl alcohol increased from 65.6% at 50 °C to 77.3% at 80 °C. The selectivity of myrtenal and myrtenol did not change when the reaction temperature was further increased to 90 °C, but the selectivity of perillyl alcohol decreased, and the other heavy products increased. It can be seen that 80 °C is the optimum temperature for  $\beta$ -pinene epoxide rearrangement to perillyl alcohol with nitromethane as solvent by AC-COIMI-NH<sub>4</sub>PMo.

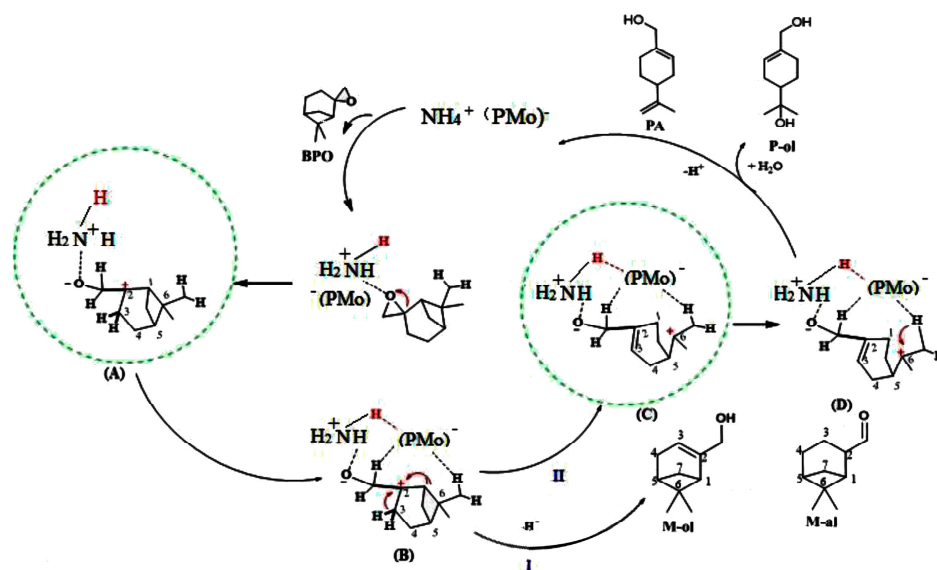
Based on Figure 7A and the reaction kinetic equation (Equation (6)), the apparent surface reaction rate constant  $k_{s+}$  between 50 and 80 °C is very convenient to obtain, from Figure 10B. Apparent rate constants at varied temperatures (50–80 °C) fit the Arrhenius equation excellently ( $R^2 = 0.998$ , Figure 8B), delivering calculated apparent activation energy of 29.64 kJ mol<sup>−1</sup>, far lower than the previously reported 62.0 kJ mol<sup>−1</sup> over dendritic ZSM-5 zeolite catalyst [36], demonstrating superior intrinsic catalytic efficiency of AC-COIMI-NH<sub>4</sub>PMo.

### 3.5. Plausible Reaction Pathway

Based on the general principle of carbocation and the discussions about the relative reaction mechanism in the literature [29,40,41], the catalytic pathway of molecular transformation during the rearrangement of  $\beta$ -pinene epoxide (BPO) on the acid site of AC-COIMI-NH<sub>4</sub>PMo was proposed (Figure 11). At first, the epoxy bond of BPO is broken into a transient state (A) through the attack of ammonium ion NH<sub>4</sub><sup>+</sup> on the acidic side of AC-COIMI-NH<sub>4</sub>PMo, and the adsorbed carbonium ion species (B) of BPO is formed in coordination with the phosphomolybdate anion on the site.

Then, the adsorbed BPO species (B) could be converted into bicyclic allyl myrtenol (M-ol) by hydrogen transfer at the C3 position, and to myrtenal (M-al) by hydrogen transfer at the C10 position. Another method of BPO rearrangement is the  $\beta$ -cleavage of the four-member-ring C-C single bond between C1 and C7 in the adsorbed BPO species (B), to form the adsorbed carbonium ion species (D) through transient state (C), then desorption into a single six-member-ring product perillyl alcohol (PA) by eliminating the hydrogen proton in the C8 or C9 methyl group. If the reaction system contains water, the water molecules participate in the cleavage transition state carbocation or addition reaction on C6 to produce

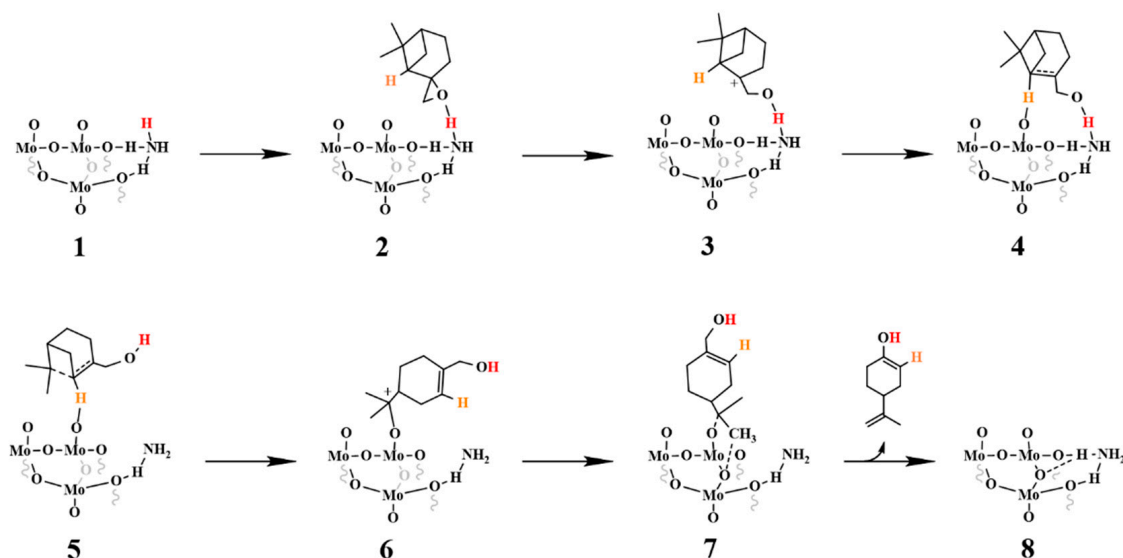
a small amount of  $\beta$ -hydrated pinene epoxide (P-ol) or  $\beta$ -pinole hydrate. Then, the catalytic active acid sites are restored by the desorption of products.



**Figure 11.** Proposed catalytic pathway of  $\beta$ -epoxane rearrangement on AC-COIMI-NH<sub>4</sub>PMo.

Based on DFT calculations of acidic ammonium ions and some adsorbed states on AC-COIMI-NH<sub>4</sub>PMo (Figure 9), a theoretical mechanism for the conversion of  $\beta$ -pinene oxide to the main product perillyl alcohol over ammonium phosphomolybdate is further proposed through an eight-step pathway, as shown in Figure 12. Initially, the ammonium hydrogen in ammonium phosphomolybdate interacts with the oxygen atom of the substrate's epoxide group, forming adsorption configuration state 2. The calculated adsorption energy for this process is  $-1.00$  eV. Subsequently, the epoxide ring opens to generate a carbocation intermediate of  $\beta$ -pinene oxide, corresponding to state 3. To stabilize the structure, an oxygen atom in ammonium phosphomolybdate further adsorbs a hydrogen atom, forming state 4. Following the loss of a hydrogen atom from the ammonium group, its interaction with the phosphomolybdate framework weakens, while a hydroxyl group forms in the transitional intermediate, corresponding to state 5. Due to the electron-deficient nature and steric hindrance of the tertiary carbon center, a C–C bond cleavage of four rings occurs, generating a new carbocation intermediate, state 6. Then, the terminal methyl group interacts with the oxygen atom of ammonium phosphomolybdate, state 7, losing a hydrogen atom and forming a C=C double bond, yielding the target product perillyl alcohol. The catalyst, after accepting the hydrogen atom, state 8, regenerates ammonium phosphomolybdate and enters next new catalytic cycle.

Based on the previously described excellent selectivity of catalytic sites, as well as coupling of ammonium ions and phosphomolybdate anchored on imidazole sites in the rearrangement of  $\beta$ -pinene epoxide to perillyl alcohol on AC-COIMI-NH<sub>4</sub>PMo, it can be expected that the proposed reaction pathways and catalytic models will provide theoretical references for optimizing the design of catalytic active sites for the development of the rearrangement at the molecular scale using computational chemistry and molecular simulation methods, thus providing new perspectives for the preparation of new industrial catalysts.



**Figure 12.** Detailed eight-step catalytic cycle for  $\beta$ -pinene epoxide into perillyl alcohol on ammonium phosphomolybdate active site.

### 3.6. Catalytic Stability

Table 4 systematically benchmarks our catalytic system against state-of-the-art heterogeneous catalysts documented globally over the past decade. The highest literature PA selectivity (66%) was achieved over Sn-MCM-41 with DMSO solvent, yet catalyst regeneration required energy-intensive calcination at 550 °C in the mixture  $\text{O}_2:\text{N}_2 = 30:70$  for 8 h after each run [41]. By contrast, AC-COIMI- $\text{NH}_4\text{PMo}$  delivers outstanding 77.3% PA selectivity under mild nitromethane medium and convenient catalyst recovery via centrifugation followed by simple hot nitromethane rinsing. Recyclability tests verify slight activity decline for second and third cycles originating from trace oligomeric carbon deposition blocking partial active sites without altering intrinsic  $\text{NH}_4^+$  active-site structure; hot anhydrous nitromethane washing fully recovers initial catalytic performance in the fourth reuse with PA selectivity maintained at  $\sim 77\%$  (Table 3), which is verified in the pilot test. Such facile regeneration and superior catalytic performance endow AC-COIMI- $\text{NH}_4\text{PMo}$  with promising industrial application prospects.

**Table 4.** Heterogeneous catalysts reported for rearrangement of  $\beta$ -pinene epoxide.

| Catalyst                      | Condition                             | Conv. (%) | PA Sel. (%) | Test for Reuse                   | Ref. |
|-------------------------------|---------------------------------------|-----------|-------------|----------------------------------|------|
| Mo/SBA-15                     | Hexane, 80 °C, 1 h                    | 100       | 63          | six times without apparent loss  | [29] |
| Colombian natural zeolite     | toluene, 70 °C, 2.5 h                 | 97        | 47          | five times without apparent loss | [34] |
| Sn-modified zeolite           | toluene, 70 °C, 30 min                | 72        | 64          | without test                     | [35] |
| ZSM-5 zeolite                 | ethyl acetate, 70 °C, 60 min          | 94        | 22          | declining in reuse               | [36] |
| Fe-modified zeolite beta      | DMSO- $\text{HNO}_3$ , 70 °C, 180 min | >99       | 63          | without test                     | [37] |
| Fe-SBA-15                     | toluene, 70 °C, 24 h                  | 60        | 0           | without test                     | [38] |
| $\text{ZnCl}_2/\text{SILCAs}$ | Hexane, 70 °C, 3 h                    | 92        | 18          | four times without apparent loss | [39] |

Table 4. Cont.

| Catalyst                     | Condition                   | Conv. (%) | PA Sel. (%) | Test for Reuse                                         | Ref.      |
|------------------------------|-----------------------------|-----------|-------------|--------------------------------------------------------|-----------|
| Tetraimidazolium nitrate     | DMSO, 40 °C, 80 min         | 100       | 47          | six times without apparent loss                        | [40]      |
| Sn-MCM-41                    | DMSO, 70 °C, 4 h            | 93        | 66          | without loss after each run calcined at 550 °C for 8 h | [41]      |
| AC-COIMI-NH <sub>4</sub> PMo | nitromethane, 80 °C, 80 min | 100       | 77          | no loss after each run with washing by nitromethane    | This work |

#### 4. Conclusions

A recyclable ammonium phosphomolybdate solid acid catalyst (AC-COIMI-NH<sub>4</sub>PMo) is successfully constructed via chemisorption of phosphomolybdic acid onto imidazole-grafted activated carbon followed by ammonia fumigation. Under optimized anhydrous nitromethane solvent at 80 °C, nearly full conversion of  $\beta$ -pinene epoxide is realized alongside significantly high perillyl alcohol selectivity of 77.3%. Trace water contamination in nitromethane severely deteriorates catalytic performance by competitive site occupation and intermediate hydration to generate extra by-products. Kinetic study reveals that the rearrangement follows apparent zero-order kinetics governed by saturated substrate adsorption on NH<sub>4</sub><sup>+</sup> active sites. DFT calculations confirm stronger adsorption of  $\beta$ -pinene epoxide ( $E_{\text{ads}} = -1.00$  eV) versus perillyl alcohol ( $E_{\text{ads}} = -0.69$  eV), which accounts for high perillyl alcohol selectivity by facilitating rapid desorption. A parallel dual-path carbocation rearrangement mechanism is proposed to interpret product distribution, and a detailed eight-step molecular catalytic cycle is established combining DFT theoretical results. The catalyst can be conveniently regenerated by hot nitromethane washing without calcination, displaying great potential for green industrial perillyl alcohol production from renewable turpentine-derived feedstock. Further molecular-scale theoretical and experimental research will accelerate targeted development of advanced heteropolyacid solid acid catalysts for terpenoid fine chemical synthesis.

**Author Contributions:** Conceptualization, M.Z., Z.X. and D.Y.; data curation, M.Z. and J.W.; formal analysis, M.Z., X.L. and D.Y.; funding acquisition, D.Y.; investigation, M.Z., Y.X. and J.W.; methodology, M.Z., Y.X. and J.W.; project administration, X.L.; resources, X.L. and D.Y.; software, M.Z. and Y.X.; supervision, X.L. and D.Y.; validation, Y.X. and J.W.; visualization, M.Z. and J.W.; writing—original draft, M.Z.; writing—review and editing, M.Z., Z.X., Y.X. and D.Y. All authors have read and agreed to the published version of the manuscript.

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