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Research Article

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Construction of a Phosphoric Acid-Based Catalytic System for Efficient Conversion of Mevalonolactone to Isoprene

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Abstract

Isoprene is an important feedstock for the production of synthetic rubber, pharmaceutical intermediates, and fine chemicals. Developing sustainable routes for isoprene production from biomass-derived feedstocks is therefore of considerable interest. In this study, mevalonolactone (MVL) was used as the substrate, and phosphoric-acid-modified Si/Al solid acids were employed as catalysts. The effects of acid type, acid concentration, reaction temperature, reaction time, catalyst dosage, and Si/Al ratio on the catalytic conversion of MVL were systematically investigated. Pyridine-adsorbed infrared spectroscopy (Py-IR) was further employed to characterize the Brønsted and Lewis acid sites on the catalyst surface. The results showed that the H_3PO_4-modified catalysts exhibited substantially higher isoprene selectivity than the H_2SO_4-modified catalyst. Under the optimized reaction conditions, an MVL conversion of 95.9% and an isoprene selectivity of 62.0% were achieved, exceeding the values reported in related studies. The phosphoric acid-based catalytic system also exhibited good recyclability, with an isoprene yield of 61.0% in the first cycle and yields stabilizing at approximately 40% in subsequent cycles. Mechanistic analysis suggested that appropriate regulation of the surface acidity and the Brønsted/Lewis acid sites played an important role in improving isoprene selectivity. This study provides an experimental basis for the chemical production of isoprene from mevalonolactone.

Keywords: Mevalonolactone; Isoprene; Phosphoric acid-based catalytic system; Solid acid catalysis; Biomass conversion

1 Introduction

Isoprene (2-methyl-1,3-butadiene) is an important C_5 platform chemical widely used in the production of polyisoprene rubber, butyl rubber, styrene–isoprene–styrene (SIS) thermoplastic elastomers, and various fine chemicals[1]. Industrial isoprene is currently obtained mainly from C_5 fractions generated during naphtha steam cracking, and its production is therefore strongly dependent on petroleum cracking processes and feedstock composition. In addition, the conventional petrochemical route is associated with fossil-resource consumption and high energy demand. Consequently, the development of alternative isoprene production routes based on renewable resources has attracted increasing attention in green chemistry and biomass catalysis[2, 3]. Current bio-based isoprene production strategies mainly include microbial synthesis and chemical catalytic conversion of biomass-derived platform molecules. Microbial processes can convert renewable carbon sources into isoprene through metabolic pathways such as the mevalonate (MVA) pathway[4]; however, these approaches still face challenges associated with fermentation time, product separation, and large-scale process control. In contrast, the catalytic conversion of stable platform molecules obtained from biological fermentation may combine the renewable nature of biological feedstocks with the high reaction rates of chemical catalysis. Among these molecules, mevalonolactone (MVL) exhibits favorable stability and storage properties and can be converted to isoprene through acid-catalyzed ring opening followed by dehydration and decarboxylation, making it a promising precursor for bio-based isoprene production[5].

Previous studies have shown that Si/Al-based materials can provide Lewis acid sites for MVL conversion and that their catalytic properties can be tuned by varying the Si/Al composition[6]. However, an increase in MVL conversion does not necessarily result in a corresponding increase in isoprene selectivity. Excessively strong or unsuitable acidic environments may also promote secondary reactions, such as cracking, isomerization, or polymerization of the target product[7]. Therefore, regulating the acidic properties of the catalyst to ensure efficient MVL activation while suppressing secondary reactions of isoprene is a key issue for improving the efficiency of this catalytic route.

From the perspective of acid catalysis, Brønsted and Lewis acid sites may play different roles in the conversion of oxygen-containing compounds. Lewis acid sites can activate reactants through coordination with oxygen-containing functional groups, whereas Brønsted acid sites can facilitate bond cleavage and rearrangement through proton transfer[8]. Therefore, introducing an appropriate amount of Brønsted acidity into the Lewis-acidic environment of the Si/Al system may further regulate MVL activation and the subsequent transformation of reaction intermediates. In addition, phosphorylation steps are involved in the biological MVA pathway[9], providing inspiration for the use of phosphorus-containing acidic species to regulate the chemical catalytic system.

Based on these considerations, H_3PO_4 was employed to modify the surface of Si/Al catalysts to construct catalytic environments with different Brønsted/Lewis acid

characteristics. The effects of H_3PO_4 concentration and support Si/Al ratio on catalytic performance were investigated, and the corresponding Brønsted/Lewis acidic properties were analyzed by Py-IR. Reaction temperature, reaction time, and catalyst dosage were subsequently optimized, and the recyclability of the catalyst was evaluated. Particular attention was paid to establishing the relationship among acid modification, Si/Al composition, surface acidity, and catalytic performance, thereby elucidating the role of an appropriate acidic environment in the selective conversion of MVL to isoprene.

2 Experimental

2.1 Materials

Mevalonolactone (MVL, purity ≥98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. SiO_2 and Al_2O_3 were also purchased from Shanghai Macklin Biochemical Co., Ltd. and were mixed at different Si/Al molar ratios to prepare Si/Al materials with Si/Al ratios of 1, 3, 5, 7.6, 9, and 11. Phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4), both of analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd. H_3PO_4 solutions with mass fractions of 30%, 50%, 70%, 85%, and 90% and H_2SO_4 solutions with mass fractions of 30%, 50%, 70%, and 98% were used for catalyst modification. Deionized water was used to prepare the impregnation solutions, and all chemicals were used as received without further purification. High-purity nitrogen (≥99.9%) was supplied by Qingdao Ludong Gas Co., Ltd. and was used as the protective gas during the reaction and as the carrier gas for gas chromatographic analysis. All other reagents were of analytical grade.

2.2 Catalyst Preparation

Phosphoric-acid-modified Si/Al catalysts were prepared by the incipient wetness impregnation method. A given amount of Si/Al support (5.0 g) was first weighed, and H_3PO_4 solutions with concentrations of 30%, 50%, 70%, 85%, and 90% were prepared. According to the predetermined liquid-to-solid ratio, the H_3PO_4 solution was slowly added to the Si/Al support under continuous stirring to ensure uniform impregnation of the support surface. The resulting mixture was allowed to stand at room temperature for 12 h to facilitate sufficient loading of phosphorus-containing species. The impregnated samples were then dried at 110 °C for 12 h to remove water, naturally cooled to room temperature, ground, and sieved through an 80-mesh sieve.

For convenience, the H_3PO_4-modified Si/Al catalysts are denoted as P-x, where P represents H_3PO_4 modification and x represents the mass fraction of H_3PO_4 used for impregnation. Accordingly, the catalysts modified with 30%, 50%, 70%, 85%, and 90% H_3PO_4 are denoted as P-30, P-50, P-70, P-85, and P-90, respectively. H_2SO_4-modified Si/Al catalysts were prepared using the same procedure and are denoted as S-x, where S represents H_2SO_4 modification and x represents the corresponding H_2SO_4 mass fraction; for example, the catalyst modified with 98% H_2SO_4 is denoted as S-98. To investigate the effect of the Si/Al ratio, Si/Al supports with ratios of 1, 3, 5, 7.6, 9, and 11 were modified with 85% H_3PO_4 following the same procedure and subsequently

used for catalytic evaluation.

2.3 Catalyst Characterization

Pyridine-adsorbed Fourier-transform infrared spectroscopy (Py-IR) was employed to characterize the surface acidity of the catalysts and to identify the distribution of Brønsted and Lewis acid sites.

Prior to analysis, the catalyst sample was placed in the IR cell and evacuated at 25 °C for 2 h to remove adsorbed water and surface impurities. Pyridine vapor was subsequently introduced and allowed to adsorb sufficiently on the catalyst acid sites. The sample was then evacuated at 150 °C to remove physically adsorbed pyridine. The infrared spectra of the pyridine-adsorbed catalysts were recorded using a Fourier-transform infrared spectrometer. The absorption bands at approximately 1540 and 1450 cm^{-1} were assigned to pyridine adsorbed on Brønsted and Lewis acid sites, respectively, and were used to qualitatively evaluate the types of surface acid sites[10, 11]. Changes in the corresponding spectral features were further compared among different catalysts to assist in the interpretation of their catalytic performance.

2.4 Catalytic Performance Evaluation

The catalytic conversion of MVL to isoprene was carried out in a high-pressure stainless-steel reactor. In each experiment, 2.0 g of MVL was used as the substrate together with a specified amount of catalyst. To systematically evaluate the catalytic performance, the catalyst type, phosphoric or sulfuric acid concentration, catalyst dosage, reaction temperature, reaction time, and support Si/Al ratio were varied individually while the remaining reaction parameters were kept constant. After each reaction, the reactor was naturally cooled to room temperature, and the liquid products were collected for subsequent gas chromatographic analysis. Each experiment was performed in quintuplicate, and the average values were reported.

Gas chromatographic (GC) analysis was performed using a GC-2010 Pro instrument equipped with a flame ionization detector (FID) and an FFAP column. Isoprene was identified by comparing its retention time with that of an authentic isoprene standard analyzed under identical chromatographic conditions. High-purity nitrogen was used as the carrier gas at a flow rate of 2.7 mL min^{-1}. The injector and detector temperatures were both maintained at 240 °C. The oven temperature was initially held at 50 °C for 7 min, then increased to 240 °C at a heating rate of 10 °C min^{-1} and maintained at 240 °C for 5 min.

After chromatographic separation, individual components were detected by the FID, and peak areas were automatically integrated using the chromatography workstation. Because all samples were analyzed under identical GC conditions, the product distributions were evaluated by a peak-area normalization method for relative quantification. The calculated conversion, selectivity, and yield values were primarily used to compare the catalytic performance under different catalyst and reaction conditions.

The MVL conversion was calculated according to Eq. (1):

$$\text{Conversion (\%)} = (\text{mass of MVL consumed} / \text{initial mass of MVL}) \times 100\% \quad (1)$$

The isoprene selectivity was calculated according to Eq. (2):

Selectivity (%) = (amount of isoprene formed / amount of MVL converted) × 100% (2)

The isoprene yield was calculated according to Eq. (3):

Yield (%) = Conversion × Selectivity / 100 (3)

Experimental data were processed and plotted using Microsoft Excel and Origin. All experimental results were expressed as mean values; when replicate measurements were conducted, the data were reported as mean ± standard deviation. Variations in catalytic performance under different reaction conditions were analyzed in conjunction with the acidic properties of the catalysts.

2.5 Catalyst Stability Test

The recyclability of the catalyst was evaluated using the 85% H_3PO_4-modified Si/Al catalyst as a representative sample under the optimized reaction conditions. Five consecutive reaction cycles were performed. After each cycle, the catalyst was separated from the reaction mixture, washed with ethanol, dried at 110 °C for 12 h, and directly reused in the subsequent cycle. Changes in MVL conversion, isoprene selectivity, and isoprene yield were recorded to evaluate catalyst stability and reusability.

3 Results and Discussion

3.1 Effect of Acid Type and Acid Concentration on the Catalytic Conversion of MVL to Isoprene

To investigate the effect of acid modification on the catalytic performance of Si/Al catalysts, the MVL conversion and isoprene selectivity obtained over unmodified Si/Al and various acid-modified Si/Al catalysts were compared under identical reaction conditions, as shown in Fig. 1.

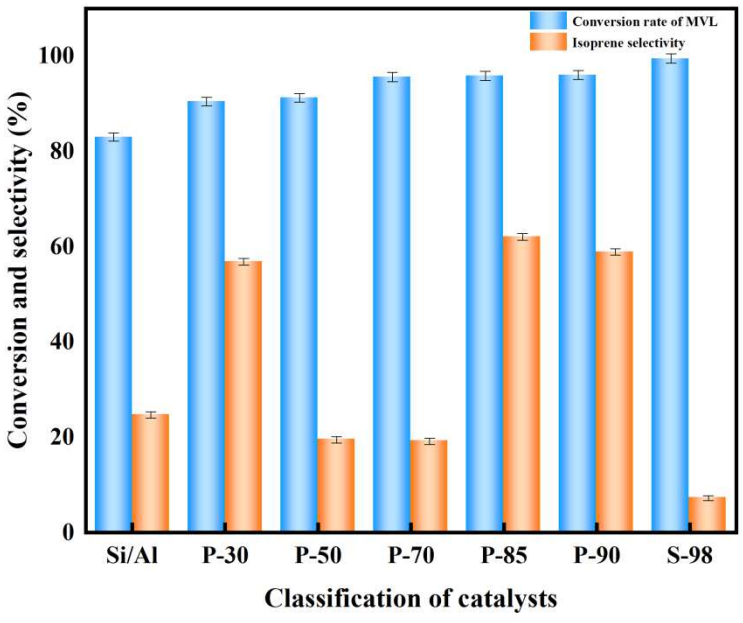


Fig 1. Effect of acid modification on MVL conversion and isoprene selectivity

Reaction conditions: 220 °C, 1 h, 2.0 g MVL, and 0.20 g catalyst.

The unmodified Si/Al catalyst afforded an MVL conversion of 83.0% and an isoprene selectivity of 24.7%, indicating that Si/Al itself was capable of promoting MVL conversion but exhibited relatively low selectivity toward the target product. After H_3PO_4 modification, the MVL conversion increased to above 90% for all catalysts, whereas the isoprene selectivity showed a pronounced non-monotonic dependence on the H_3PO_4 concentration.

At an H_3PO_4 concentration of 30%, the P-30 catalyst exhibited an MVL conversion of 90.5% and an isoprene selectivity of 56.8%. Increasing the H_3PO_4 concentration to 50% and 70% increased the MVL conversion to 91.2% and 95.6%, respectively, whereas the corresponding isoprene selectivities decreased markedly to 19.5% and 19.2%. When the H_3PO_4 concentration was increased to 85%, the P-85 catalyst achieved an MVL conversion of 95.9% and an isoprene selectivity of 62.0%, the highest selectivity among the catalysts examined. A further increase in H_3PO_4 concentration to 90% resulted in only a slight increase in MVL conversion to 96.0%, while the isoprene selectivity decreased to 58.9%.

In contrast, the S-98 catalyst exhibited the highest MVL conversion of 99.5% among the tested catalysts, but its isoprene selectivity was only 7.2%, considerably lower than those obtained over P-30, P-85, and P-90. These results demonstrate that high MVL conversion does not necessarily correspond to high isoprene selectivity. Although H_2SO_4 modification promoted extensive MVL conversion, the resulting acidic environment may also have facilitated undesired side reactions, leading to a pronounced decrease in isoprene selectivity.

Notably, the catalytic performance did not vary linearly with H_3PO_4 concentration. From P-30 to P-70, MVL conversion generally increased, whereas isoprene selectivity initially decreased substantially. When the H_3PO_4 concentration was further increased to 85%, the selectivity increased again to 62.0%. Increasing the concentration to 90% resulted in only a marginal increase in conversion but a decrease in selectivity. These results suggest that catalytic performance is not governed solely by acid concentration or the ability to convert MVL, but may also depend on the relative distribution and balance of Brønsted and Lewis acid sites generated upon H_3PO_4 modification[12, 13].

Considering both MVL conversion and isoprene selectivity, P-85 exhibited a relatively high MVL conversion of 95.9% together with the highest isoprene selectivity of 62.0%, giving the best overall catalytic performance among the tested catalysts. Therefore, subsequent investigations focused on the H_3PO_4-modified system, and Py-IR analysis was further employed to clarify the relationship between H_3PO_4 concentration, surface acidity, and catalytic performance.

To further clarify the origin of the differences in catalytic performance among catalysts modified with different H_3PO_4 concentrations, Py-IR spectroscopy was employed to characterize the surface acid sites, as shown in Fig. 2. The band at approximately 1540 cm^{-1} was mainly assigned to pyridine adsorbed on Brønsted acid sites, whereas the band at approximately 1450 cm^{-1} was attributed primarily to

pyridine coordinated to Lewis acid sites. The band at approximately 1490 cm^{-1} is associated with contributions from both Brønsted- and Lewis-acid-bound pyridine and is therefore referred to here as the B + L band.

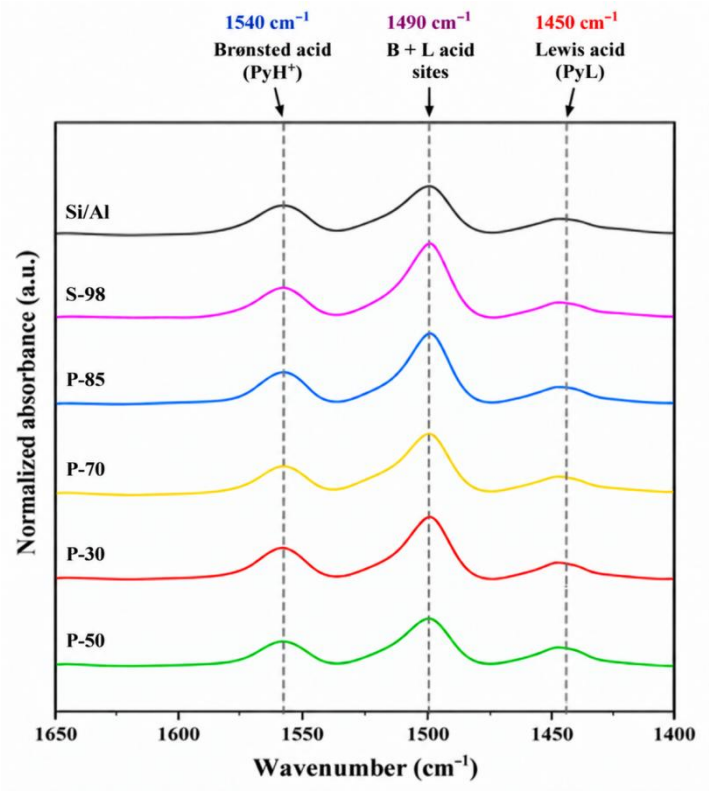


Fig 2. Py-IR spectra of Si/Al catalysts modified with different acids and H_3PO_4 concentrations.

As shown in Fig. 2, changes in H_3PO_4 concentration caused variations in both the Brønsted-acid band at 1540 cm^{-1} and the Lewis-acid band at 1450 cm^{-1}, although the overall differences were relatively limited. In comparison, more pronounced variations were observed for the B/L-associated band at approximately 1490 cm^{-1}, indicating that H_3PO_4 modification significantly influenced the combined acidic characteristics associated with Brønsted and Lewis acid sites. Therefore, the differences in catalytic performance induced by H_3PO_4 concentration may not arise primarily from changes in a single type of acid site, but may instead be closely related to the B/L-associated acidic characteristics reflected by the 1490 cm^{-1} band.

Combining the Py-IR results with the catalytic data in Fig. 1, P-85 exhibited an MVL conversion of 95.9% and an isoprene selectivity of 62.0%, representing favorable overall catalytic performance. At this composition, the relative spectral feature of the B + L band at approximately 1490 cm^{-1} differed from those of the other catalysts. When the H_3PO_4 concentration was further increased to 90%, the MVL conversion increased only slightly, whereas the isoprene selectivity decreased to 58.9%. These observations suggest that selective isoprene formation does not depend solely on the enhancement of either Brønsted or Lewis acidity, but may instead be associated with an appropriate balance between Brønsted and Lewis acidic

characteristics[14]. Such an acidic environment may facilitate both MVL activation and subsequent intermediate transformation while maintaining favorable isoprene selectivity.

3.2 Effect of Si/Al Ratio on Catalytic Performance and Surface Acidity

The Si/Al ratio of the support is an important factor governing both the surface acidity and catalytic performance of the catalyst[15, 16]. To investigate the effect of Si/Al composition on MVL conversion, Si/Al supports with ratios of 1, 3, 5, 7.6, 9, and 11 were modified with 85% H_3PO_4 and evaluated catalytically, as shown in Fig. 3(a).

At a Si/Al ratio of 1, the MVL conversion was 71.4%, while the isoprene selectivity reached 68.7%, the highest value among the samples examined. Increasing the Si/Al ratio to 3 markedly increased the MVL conversion to 97.0%, whereas the isoprene selectivity decreased to 55.4%. At Si/Al ratios of 5, 7.6, 9, and 11, the MVL conversions were 96.7%, 95.9%, 97.4%, and 98.5%, respectively, remaining at consistently high levels, while the corresponding isoprene selectivities were 58.7%, 62.0%, 58.7%, and 49.2%. Notably, the catalyst with a Si/Al ratio of 7.6 maintained a high MVL conversion of 95.9% while achieving an isoprene selectivity of 62.0%, representing the highest target-product selectivity among the high-conversion catalysts with Si/Al ≥ 3.

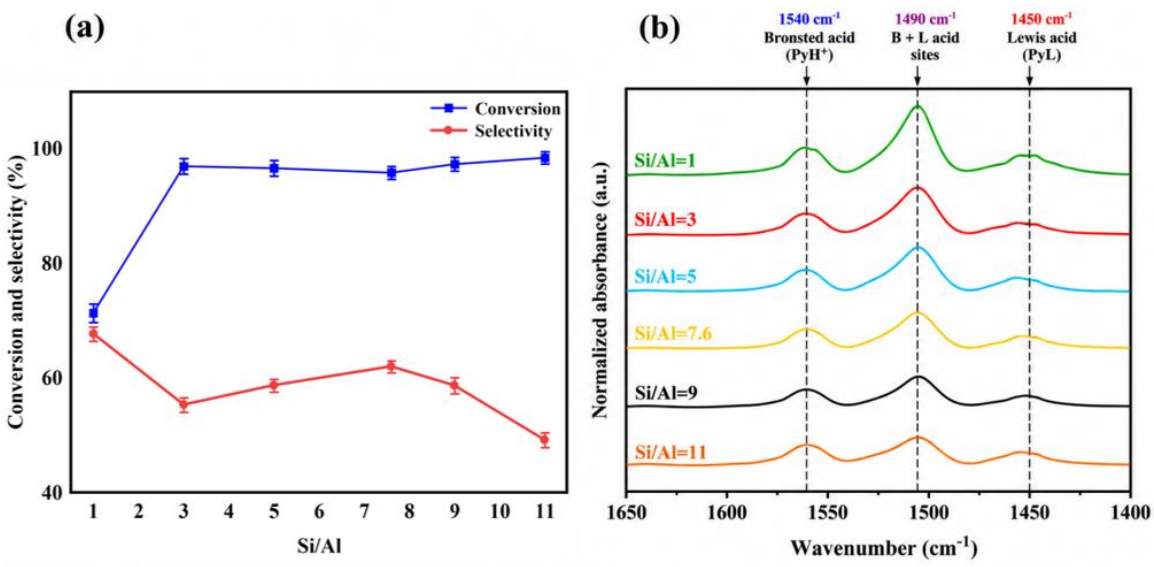


Fig 3. Effect of Si/Al ratio on (a) catalytic performance and (b) acidic sites of the catalysts

Reaction conditions: 220 °C, 1 h, 2.0 g MVL, and 0.20 g catalyst.

These results demonstrate that the effects of the Si/Al ratio on MVL conversion and isoprene selectivity are not parallel. Although the Si/Al = 1 catalyst exhibited the highest isoprene selectivity, its MVL conversion was considerably lower, suggesting

that a relatively low Si/Al ratio favors target-product selectivity but limits overall substrate conversion. Increasing the Si/Al ratio from 1 to 3 substantially enhanced MVL conversion but markedly decreased isoprene selectivity. At higher Si/Al ratios, MVL conversion remained high, whereas isoprene selectivity initially increased and then decreased. Among these samples, Si/Al = 7.6 provided a favorable balance between high conversion and high selectivity. A further increase in the Si/Al ratio to 11 increased MVL conversion to 98.5% but decreased isoprene selectivity to 49.2%, indicating that an excessively high Si/Al ratio is unfavorable for selective isoprene formation.

To further elucidate the effect of the Si/Al ratio on catalytic performance, the surface acidic properties of catalysts with different Si/Al ratios were characterized by Py-IR, as shown in Fig. 3(b). All catalysts exhibited characteristic absorption bands at approximately 1540, 1490, and 1450 cm^{-1}, indicating the coexistence of Brønsted and Lewis acid sites. The relative intensities of these bands varied markedly with the Si/Al ratio, demonstrating that the support composition regulates the acidic environment of the H_3PO_4-modified catalysts. However, these changes did not follow a simple monotonic trend.

Combining the catalytic and Py-IR results suggests that the effects of the Si/Al ratio on MVL conversion and isoprene selectivity cannot be attributed solely to the enhancement of a single type of acid site, but may instead be associated with the relative distribution and cooperative effects of different acidic sites[17]. The acidic environment of the Si/Al = 1 catalyst appears to favor selective isoprene formation but provides relatively limited capability for overall MVL activation. At Si/Al = 7.6, the catalyst maintained a high MVL conversion together with relatively high isoprene selectivity, suggesting that the resulting surface acidic environment may provide a more favorable balance between substrate activation and target-product formation. Further increasing the Si/Al ratio maintained extensive MVL conversion but generally decreased isoprene selectivity, highlighting the importance of an appropriate Si/Al composition in regulating catalyst acidity and product distribution.

3.3 Effect of Reaction Conditions on MVL Conversion

After identifying the H_3PO_4-modified catalytic system, P-85 was selected as the catalyst to further investigate the effects of reaction temperature, reaction time, and catalyst dosage on MVL conversion and isoprene selectivity, as shown in Fig. 4. All three reaction parameters affected MVL conversion and product distribution to varying degrees, with isoprene selectivity being more sensitive to changes in reaction conditions.

As shown in Fig. 4(a), reaction temperature had a pronounced effect on isoprene selectivity. At 210 °C, the MVL conversion was 99.9% and the isoprene selectivity was 38.2%. Increasing the temperature to 220 °C resulted in an MVL conversion of

95.9%, while the isoprene selectivity increased substantially to 62.0%, the highest value within the temperature range investigated. At 230, 240, 250, and 260 °C, the MVL conversions were 99.9%, 96.6%, 99.9%, and 99.8%, respectively, whereas the corresponding isoprene selectivities decreased to 52.6%, 41.9%, 32.5%, and 28.6%. Thus, higher temperatures did not further improve MVL conversion but substantially reduced target-product selectivity, suggesting that excessive temperatures may promote further transformation of isoprene or other competing side reactions[18]. Therefore, 220 °C was considered the most suitable reaction temperature within the range examined.

The effect of reaction time is shown in Fig. 4(b). At 220 °C, an MVL conversion of 98.89% was already achieved after 0.5 h, whereas the isoprene selectivity was only 21.1%. Extending the reaction time to 1 h markedly increased the isoprene selectivity to 62.0%, with a corresponding MVL conversion of 95.9%. When the reaction time was further extended to 1.5 and 2.5 h, the MVL conversion increased to 98.8% and 99.1%, respectively, whereas the isoprene selectivity decreased to 31.8% and 32.6%. These results indicate that high MVL conversion does not necessarily correspond to high isoprene selectivity. A short reaction time may be insufficient for the reaction system to reach conditions favorable for target-product formation, whereas prolonged reaction times may promote secondary reactions of the generated isoprene[19]. Therefore, a reaction time of 1 h provided a favorable balance between MVL conversion and isoprene formation.

Figure 4(c) shows the effect of catalyst dosage on catalytic performance. At catalyst dosages of 0.10, 0.15, and 0.20 g, the MVL conversions were 99.0%, 98.5%, and 95.9%, respectively, while the corresponding isoprene selectivities were 58.9%, 59.0%, and 62.0%. Increasing the catalyst dosage to 0.25 g resulted in an MVL conversion of 99.0%, but the isoprene selectivity decreased to 54.8%. When the catalyst dosage was further increased to 0.30 g, the MVL conversion remained high at 98.9%, whereas the isoprene selectivity decreased sharply to 23.0%. These results indicate that catalyst dosage had a relatively limited influence on MVL conversion within the investigated range but exerted a substantial effect on target-product selectivity. Excess catalyst may increase the number of available acid sites, thereby increasing the probability of further interaction between the generated isoprene and acidic sites and promoting secondary reactions[20].

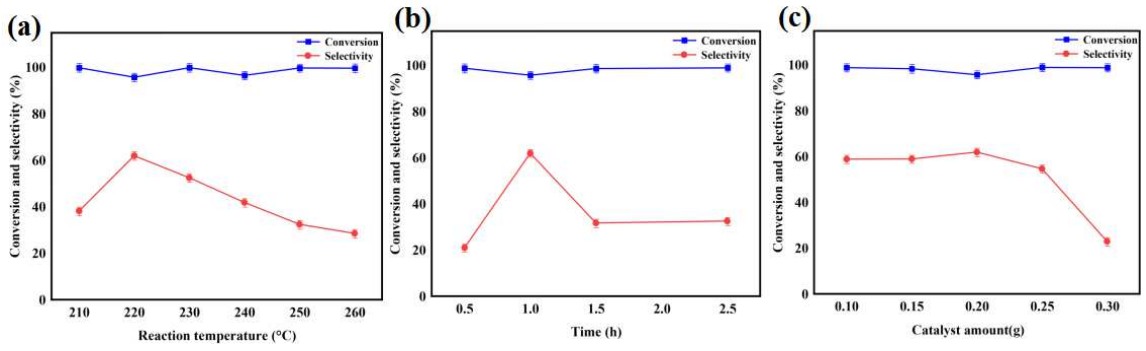


Fig 4. Effects of (a) reaction temperature, (b) reaction time and (c) catalyst dosage on catalytic performance

Considering the combined effects of reaction temperature, reaction time, and catalyst dosage, MVL maintained a relatively high conversion under most of the investigated conditions, whereas isoprene selectivity varied much more significantly. Therefore, optimization of this catalytic system should focus not simply on maximizing MVL conversion but rather on suppressing further reactions of the target product while maintaining efficient substrate conversion. Within the investigated range, the conditions of 220 °C, 1 h, and 0.20 g of P-85 catalyst provided favorable catalytic performance, affording an MVL conversion of 95.9% and an isoprene selectivity of 62.0%.

3.4 Catalyst Recycling Stability

The recyclability of the P-85 catalyst was evaluated over five consecutive reaction cycles under identical reaction conditions, as shown in Fig. 5. In the first cycle, the MVL conversion was 99.9%, the isoprene selectivity was 61.1%, and the corresponding isoprene yield was 61.0%. In the second cycle, the MVL conversion decreased to 77.4%, the isoprene selectivity was 57.5%, and the yield decreased to 44.5%. During the third to fifth cycles, the MVL conversions were 71.0%, 79.1%, and 75.3%, respectively, while the corresponding isoprene selectivities were 61.9%, 53.1%, and 50.7%, giving isoprene yields of 43.9%, 42.0%, and 38.2%, respectively.

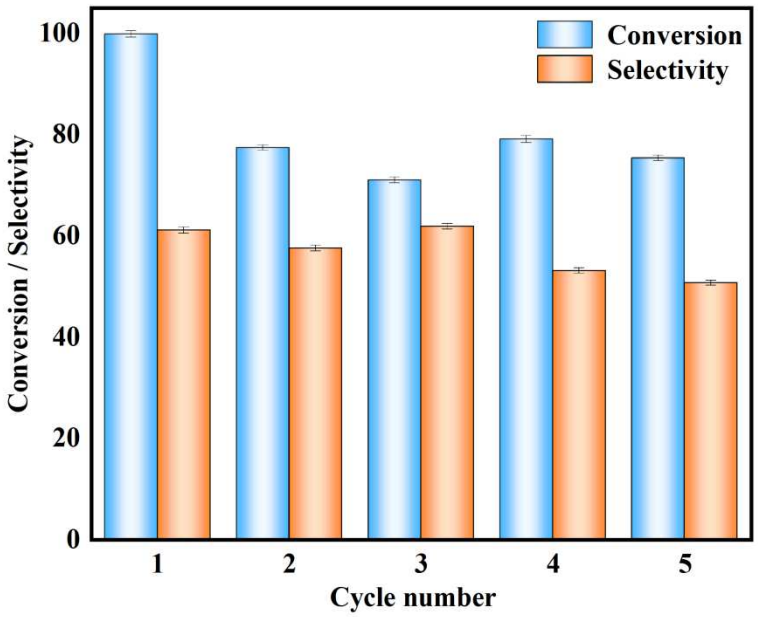


Fig 5. Recycling stability of the catalyst in MVL-to-isoprene reaction

The recycling results indicate that the most pronounced change in catalytic performance occurred between the first and second cycles. After the first cycle, both MVL conversion and isoprene yield decreased markedly. During cycles 2–5, however, the MVL conversion remained generally within approximately 70–80%, while the isoprene selectivity was maintained at approximately 50–62%. This behavior suggests that weakly bound surface phosphorus species may migrate or leach during the first use, resulting in a decrease in catalytic activity, whereas more strongly bound phosphorus species may remain on the catalyst during subsequent cycles, allowing the catalytic performance to become relatively stable[21, 22].

Overall, the H_3PO_4-modified Si/Al catalyst exhibited a certain degree of activity loss after the first reaction cycle but maintained relatively stable MVL conversion and isoprene selectivity over the subsequent cycles, indicating its potential for reuse.

3.5 Proposed Reaction Pathway for the Catalytic Conversion of MVL to Isoprene

Based on previous studies together with the catalytic performance and Py-IR characterization results obtained in this work, a possible pathway for the conversion of MVL to isoprene is proposed, as illustrated in Fig. 6. MVL is initially protonated at Brønsted acid sites, facilitating activation and opening of the lactone ring to form the corresponding oxygen-containing intermediate[23]. The intermediate may subsequently undergo dehydration, decarboxylation, and C=C bond formation at Lewis acid sites, ultimately yielding isoprene[24]. These results suggest that Brønsted acid sites may primarily participate in the initial activation and ring opening of MVL, whereas Lewis acid sites may play an important role in the subsequent transformation of oxygenated intermediates and the formation of isoprene. Accordingly, the overall conversion pathway can be summarized as MVL activation → lactone ring opening → transformation of oxygen-containing intermediates → dehydration/decarboxylation → isoprene formation.

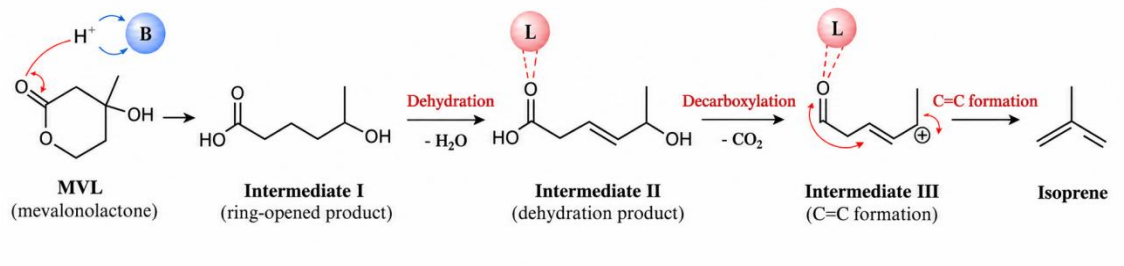


Fig 6. Proposed reaction pathway for MVL catalytic conversion to isoprene over H_3PO_4-modified Si/Al catalyst

4 Conclusion

In this study, isoprene was produced from mevalonolactone (MVL) using H_3PO_4-modified Si/Al solid-acid catalysts. The effects of catalyst preparation parameters and reaction conditions on catalytic performance were systematically investigated, and Py-IR spectroscopy was employed to characterize the Brønsted and Lewis acidic properties of the catalysts and to assist in interpreting the possible reaction mechanism. Based on the catalytic results and acidity characterization, MVL conversion to isoprene was proposed to proceed through substrate activation, lactone ring opening, transformation of oxygen-containing intermediates, and subsequent dehydration/decarboxylation. These results provide an experimental basis for the selective production of bio-based isoprene through regulation of the acidic properties of solid-acid catalysts and offer a potential chemical route for isoprene production.

Declarations

Ethics approval and consent to participate

Not applicable. This study did not involve human participants or animals.

Consent for publication

Not applicable. This manuscript does not contain any individual person's data, images, or videos.

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Availability of data and materials

The datasets generated and/or analyzed during the current study are available from the corresponding authors on reasonable request.

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Not applicable.

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