

Article

$(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4\text{Pd}^0$ Olivine: Influence of Lewis Acids on Heterogeneous Heck–Mizoroki Catalysis

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Abstract

This study investigates the influence of Lewis acids on a novel stratified $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4\text{Pd}^0$ olivine catalyst for the Heck–Mizoroki coupling of iodobenzene and methyl acrylate. Comprehensive characterization (ICP-OES, Raman, P-XRD, XPS) confirms the successful synthesis of a material with surface-incorporated Pd^{2+} and bulk Pd^0 nanoparticles within a Co_2SiO_4 matrix. The promoter-free system with triethylamine base achieved the highest initial rate of $3.92 \times 10^{-7} \text{ mol.s}^{-1}$ with an average rate of $1.18 \times 10^{-7} \text{ mol.s}^{-1}$, despite a 30 min induction period. However, ZnCl_2 , the weakest acid, showed the most substrate activation and lowered the induction period to 10 min, while AlCl_3 also reduced the induction period to 20 min. FeCl_3 showed the poorest performance, attributed to redox-mediated site poisoning rather than hydrolysis. Selectivity over the catalyst was maintained at >99 mol% towards methyl cinnamate irrespective of the Lewis acid or base used. However, recycling of the catalyst led to a gradual decrease in selectivity toward methyl cinnamate from >99 mol% to ~94.6 mol% over three cycles, while conversion remained consistently high at >99 mol% across all cycles, indicating that the catalyst's primary activity was largely preserved despite surface evolution toward side-product formation. Lewis acids were found to function primarily as surface modifiers and/or productive substrate activators, with stronger Lewis acids also targeting the olivine framework, as seen from the preferential leaching of Co relative to Pd.

Keywords: bimetallic olivine catalyst; Heck–Mizoroki reaction; sol–gel synthesis; Lewis acid promoters; leaching tests; recyclability; Hg^0 poisoning resistance

1. Introduction

The Heck reaction is an important and widely used method for the formation of carbon–carbon bonds in organic chemistry [1–3]. This palladium-catalyzed coupling reaction has changed the landscape of synthetic organic chemistry by providing a versatile and efficient method for the synthesis of complex organic molecules. The Heck reaction has found broad applications in the synthesis of pharmaceuticals, agrochemicals, natural products, and materials due to its ability to forge C–C bonds selectively and with high functional group compatibility [3,4]. It has become a pivotal tool for synthetic chemists seeking to create new carbon frameworks and introduce valuable functional groups into organic molecules. The Heck reaction can be conducted under homogeneous or heterogeneous catalytic conditions, providing flexibility in catalyst design and application [5–10]. Over the years, various strategies have been explored to enhance the reactivity and selectivity of Heck reactions,



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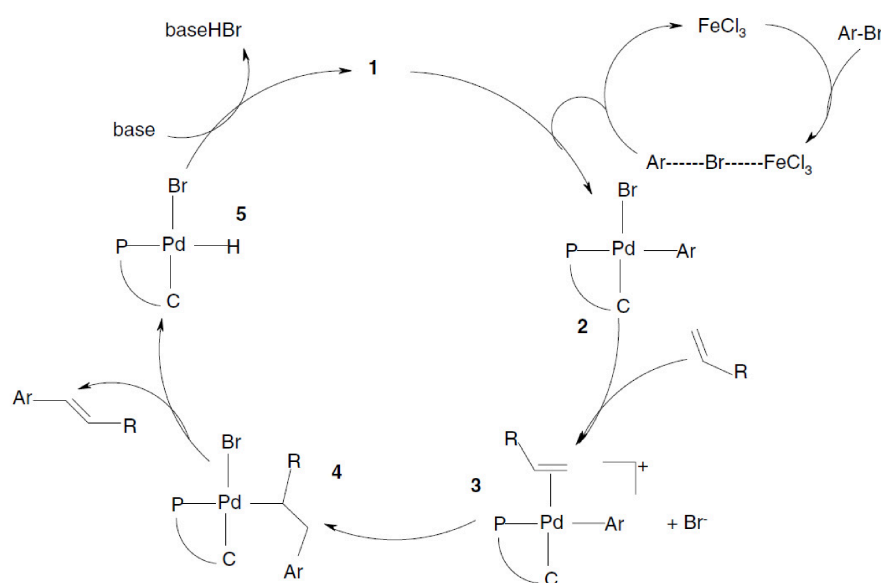
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especially in heterogeneous catalysts [11]. Recent advances in heterogeneous palladium catalysis have explored various support materials, including magnetic nanoparticles, to enhance catalyst recovery and recyclability. These systems have demonstrated good activity for the Mizoroki–Heck reaction under green conditions, achieving high selectivity for aryl iodides and bromides with low metal leaching [12].

A further approach involves the use of Lewis acids, which play a crucial role in modulating the reaction outcome. When combined with palladium catalysts in Heck reactions, Lewis acids can exert a profound impact on the reaction efficiency and selectivity [10,13–15]. Combined with the relative abundance and the low cost of these Lewis acids, this is an attractive approach.

In the traditional Heck reaction, a palladium catalyst facilitates the oxidative addition of an aryl or vinyl halide to generate a reactive organopalladium intermediate [16,17]. The subsequent migratory insertion and reductive elimination steps lead to the formation of a new C–C bond. However, the introduction of a Lewis acid in the reaction system introduces additional complexity and control over the reaction pathway [13,14]. The coordination of a Lewis acid to the palladium catalyst can influence the rates of the oxidative addition, transmetalation, and reductive elimination steps. The Lewis acid can interact with the palladium complex, altering its electronic and steric properties, thereby impacting the selectivity and efficiency of the C–C bond formation. Additionally, Lewis acids can facilitate the activation of substrates, promote desired migratory insertion, or modulate the regioselectivity of the reaction. The choice of Lewis acid in Heck reactions is critical and depends on the specific reaction requirements and desired outcomes. Various Lewis acids, such as boron, aluminum, tin, and zinc compounds, have been explored in conjunction with palladium catalysts. These Lewis acids exhibit different reactivities and coordination abilities, allowing for fine-tuning of the reaction conditions and controlling the reaction outcome [13,18]. This influence then manifests as an enhancement in the reaction rate, improved yield, influence on regioselectivity, and expanded substrate scope. Lewis acids can facilitate substrate activation, promote the formation of reactive intermediates, and stabilize key transition states. Moreover, the use of Lewis acids can enable the activation of challenging substrates that are otherwise unreactive in traditional Heck reactions. Sud et al. postulated a reaction mechanism where the Lewis acid functions as a promoter and provides a pre-activated aryl halide that can then undergo oxidative addition [13]. This is shown in Scheme 1 [11].



Scheme 1. Heck–Mizoroki reaction mechanisms with Lewis acid contribution.

Scheme 1 shows how the Lewis acid is speculated to activate the aryl or vinyl halide by coordinating with the halogen atom and polarizing the carbon–halogen bond. This polarization can increase the electrophilicity of the halide and facilitate its oxidative addition to the palladium catalyst. Thus, it functions more as a promoter than a catalyst. Therefore, Lewis acids have the potential to activate electrophilic substrates, typically aryl or vinyl halides, by coordinating with the halogen atom. This coordination polarizes the carbon–halogen bond, increasing its electrophilicity and facilitating its reaction with the palladium catalyst [13,19].

However, the two primary limitations of using Lewis acids in Heck reactions are the possibility of unwanted side reactions and catalyst deactivation, resulting in lower yields [20,21]. The Lewis acid, in some cases, can coordinate with the palladium catalyst, forming stable complexes, or it can react with the active species or functional groups of the homogeneous catalyst. These new complexes may be inactive, result in the decomposition of the catalyst, hinder the oxidative addition step, or impede the desired migratory insertion and reductive elimination processes, limiting the activity and lifespan of the catalyst. Furthermore, Lewis acids, especially strong ones, can promote undesired side reactions by overreacting with substrates instead of acting as a promoter. These side reactions can lead to the formation of unwanted by-products, reducing the selectivity of the desired reaction. Controlling and suppressing these side reactions can be challenging [22]. In this work, a Pd-substituted Co_2SiO_4 heterogeneous catalyst is explored in conjunction with the use of Lewis acids. The olivine framework (M_2SiO_4) was selected for this study due to its ability to accommodate divalent transition metals in two distinct octahedral sites (M1 and M2), providing a structurally robust matrix that can stabilize Pd^{2+} ions while allowing formation of Pd^0 nanoparticles upon thermal reduction. This structural flexibility offers a unique platform for studying metal-support interactions in Heck catalysis, with the silicate framework potentially modulating the electronic properties of incorporated metals. Prior studies on Ni-Co olivines in this reaction [23] showed promising activity, motivating the exploration of Pd-substituted Co olivines. Co-only catalyst systems have been explored in the literature, and preliminary screening showed that Co_2SiO_4 alone exhibited promising activity under these conditions, and the Pd-substituted material was hypothesized to show significantly enhanced performance [23]. It was observed that Co alone allows for a redox Heck–Mizoroki type reaction, but in a bimetallic system with Ni, selectivity was improved at the expense of the kinetic rate. Additional studies have demonstrated that heterogeneous catalysts incorporating mixed-valence metal centers can exhibit enhanced catalytic performance through synergistic redox interactions between different oxidation states [24].

Furthermore, leaching in heterogeneous catalysts is often attributed to the oxidation–addition step as the palladium attempts to activate the C–X bond. The use of a Lewis acid is postulated to limit the amount of catalyst leached by providing preactivated aryl halides.

2. Materials and Methods

2.1. Synthesis

All chemicals and reagents were purchased from Merck (Merck, Darmstadt, Germany) and used as is, unless otherwise stated.

Synthesis procedure of the $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ material: Molar compositions of (90Co:10Pd) of metal nitrate salts (Merck, Darmstadt, Germany) were dissolved in water in a 50 mL round-bottomed flask with 1 mL of acetic acid (ACE chemicals, Johannesburg, South Africa) and stirred. In an addition funnel, 2 mL of TEOS (triethylorthosilicate) (Merck, Darmstadt, Germany) was mixed with 2 mL of ethanol (Merck, Darmstadt, Germany) and added to the mixed metal nitrate solution dropwise. The solution was allowed to stir for

4 h, then transferred into a beaker and left in the dark overnight until a gel formed. The gel was then evaporated at 80 °C in an oven for 12 h and transferred into an alumina crucible for calcination. The dried gel was introduced into a furnace at room temperature in an alumina boat, and the temperature was ramped to 1000 °C at a rate of 4 °C min⁻¹ and allowed to calcine for 5 h. The resultant material was ground upon cooling using a mortar and pestle and characterized.

2.2. Activity Testing Procedure

In total, 0.5 mmol of iodobenzene and 1.5 mole equiv. of methylacrylate, 2 mole equiv. of triethylamine or sodium carbonate, 2 mL of DMF (Alfa Aesar, Heysham, UK) and 26 mg of catalyst were added into a 50 mL pear-shaped flask and refluxed at the boiling point of the solvent. Aliquots were sampled at 10 min intervals. For Lewis acid screening, 10 mol% of Lewis acid relative to iodobenzene was added to the mixture prior to heating. The progress of the reaction was monitored via GC-FID (Perkin Elmer, Hopkinton, MA, USA) and gas chromatography-mass spectrometry (GC-MS) (Shimadzu, Kyoto, Japan).

2.3. Leaching Tests

A total of 0.5 mmol of iodobenzene and 1.5 mole equiv. of methylacrylate, 2 mole equiv. of triethylamine, 2 mL of DMF, and 26 mg of catalyst were added into a 50 mL pear-shaped flask and refluxed at the boiling point of the solvent for 4 h and then centrifuged at 2700 rpm. The solution was then decanted and refluxed until completion. The progress of the reaction was monitored via GC-FID (Perkin Elmer, Hopkinton, MA, USA) and gas chromatography-mass spectrometry (GC-MS) (Shimadzu, Kyoto, Japan).

2.4. Conversion Profile of Quantitative Recycling

The reaction was monitored at one-hour intervals via gas chromatography-mass spectrometry (GC-MS) (Shimadzu, Kyoto, Japan) until completion. The reaction medium was then centrifuged at 5000 rpm for 30 min, and the supernatant liquid was decanted to separate the catalyst. The catalyst was then dried and weighed once more for subsequent reactions. The procedure was repeated for three consecutive reactions. The selectivity was determined at >99 mol% conversion.

2.5. Mercury Poisoning Test Procedure

The reaction was allowed to stir under reflux for 20 min to initiate the reaction and monitored via GC-FID to ensure conversion. The solution was then centrifuged for 30 min at 5000 rpm. The supernatant liquid was then decanted into a clean 50 mL pear-shaped flask, and 150 mmol of mercury (300 mol equiv.) were added. The solution was then refluxed to reaction completion and monitored every hour via gas chromatography-mass spectrometry (GC-MS) (Shimadzu, Kyoto, Japan). A selectivity profile was based on the products found and was plotted at >99 mol% conversion.

2.6. Instrumentation Details

ICP-OES analysis was conducted using a Perkin Elmer 2100 Optima instrument (Perkin Elmer, Hopkinton, MA, USA) and cobalt, palladium, and silicon standards were purchased from CC Imelmann (Johannesnurg, South Africa). A mass of 0.05 g of sample was weighed out into a beaker with 10 mL of H₂SO₄. The solution in the beaker was then swirled to ensure adequate contact between the sample and acid. In a fume hood, the solution of the sample and acid was then placed on a hot plate and covered with a watch glass for digestion. Once the boiling of the acid had ceased, 10 mL portions of water were added dropwise into the acid solution and the solution was left to further digest until ~5 mL of acid solution remained. An additional 5 mL of double-distilled water was added to transfer

the acid solution into a 25 mL volumetric flask, which was made up to the mark with double-distilled water. For the 20-fold dilution, 5 mL of the original sample was pipetted into a 100 mL volumetric flask and made up to the mark with double-distilled water. The sample was finally filtered through a 0.45 μm filter and sent for ICP analysis.

Preparation of standards for ICP:

Multi-element standards with Pd, Co, and Si were prepared for ICP analysis to determine the metal content of the prepared material. Multi-element standards were prepared for a 20–160 mg/L calibration range. In total, 0.05 g of catalyst was digested in 7 mL HF, 3 mL of aqua regia, and left standing for a week.

FTIR

For FTIR spectroscopy, a sample was placed on a sample plate, and a force gauge was applied. An average from 5 spectra was obtained with a resolution of 3 from a Perkin-Elmer Spectrum 100 Series (Perkin Elmer, Hopkinton, MA, USA). The data were processed on PerkinElmer Spectrum IR Assist software (Perkin Elmer, Hopkinton, MA, USA) v6.1.0.

Raman Spectroscopy:

A sample was placed on a slide after the instrument was calibrated with a Si standard. The sample was focused with a 20 $\times$ objective lens at a wavelength of 514 nm. The spectra were then acquired at a 30 s exposure time on 10% laser power for an average of 2 scans on a Renishaw inVia Raman microscope (Gloucestershire, United Kingdom England). For Raman spectroscopy, a sample was placed on a slide after the instrument was calibrated with a Si standard. The sample was focused using a 20 $\times$ objective lens at a wavelength of 514 nm. The spectrum was then acquired at 30 s with an exposure time of 10% Laser power for an average of 2 scans.

Powder X-ray Diffraction (P-XRD)

PXRD was performed at iThemba Labs (Cape Town, South Africa). The materials were ground into a fine powder using a mortar and pestle. A portion of the final amount was transferred into a sample holder and pressed hard and flat. The sample was then loaded into a Bruker (Karlsruhe, Germany) AXS D8 Advance diffractometer and a Cu-K α radiation source. The sample was run at a continuous θ -scan in locked coupled mode, using a LynxEye detector (Bruker, Karlsruhe, Germany) and processed using the ICDD:PDF database 1999 and EVA software (ver. 3) from Bruker (Karlsruhe, Germany).

X-ray Photoemission Spectroscopy (XPS)

XPS spectra were obtained on a Thermo Scientific™ K-Alpha™ X-ray photoelectron spectrometer (Agawam, MA, USA), equipped with a hemispherical analyzer and Al K α ($h\nu = 1486.7$ eV) as an excitation source. Survey spectra were collected from a 0.7×0.4 mm analysis area with a pass energy of 160 eV and a step size of 1 eV. Peaks for all the expected elements in the samples were identified in the survey spectra.

Chromatograms were obtained using a Shimadzu GC-2010 Plus (Kyoto, Japan) with a GC_MS-QP2010 Ultra instrument with Shimadzu Lab solutions (Kyoto, Japan) software. The method is detailed in Appendix A in the Calibration standards (reactants, product, and benzophenone as the internal standard) were prepared and re-run every 13 samples to calculate response factors (RF), which were then used to determine the concentrations of the analytes. Conversion was calculated by monitoring the disappearance of iodobenzene via peak area integration relative to the internal standard. All reactions were performed in triplicate. For kinetic profiling, aliquots were sampled at 10 min intervals.

3. Results and Discussion

3.1. ICP-OES Analysis

The $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ material was prepared by sol–gel synthesis. Its BET surface area of $2 \text{ m}^2/\text{g}$ was low, as expected from the very high synthesis temperature. The exact metal compositions of the materials were quantified using ICP-OES. Table 1 compares the mol% of the intended and the actual loading that was achieved using this synthesis method.

Table 1. ICP-OES relative transition-metal loading of the prepared catalysts in mol %.

Metal	Nominal mol%	Actual mol%
Co	90	93
Pd	10	7

The actual cobalt content is higher than the intended value, while that of Pd is lower than intended. This is attributed to the synthesis process, such as incomplete Pd precursor conversion, loss during drying, and tolerance of the olivine framework to incorporation of Pd into the olivine framework.

3.2. Raman Analysis

Raman analysis was performed to determine the structural integrity of the olivine structure after the introduction of palladium atoms into the olivine network. Figure 1 shows the vibrational modes observed for the material.

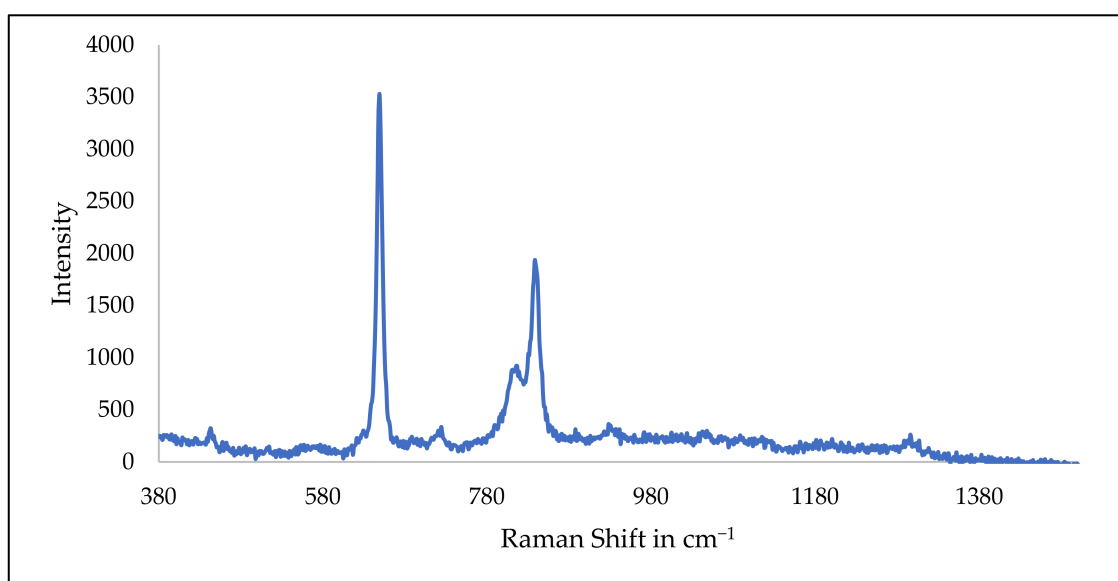


Figure 1. Raman spectrum of (93:7) $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$.

The Raman spectrum in Figure 1 shows the characteristic olivine doublet at 819 cm^{-1} (κ_1) and 842 cm^{-1} (κ_2) corresponding to Si–O–M symmetric stretching vibrations of SiO_4 tetrahedra [23,25–29]. The κ_1 peak at 819 cm^{-1} is typically the M1-sensitive peak and κ_2 the M2-sensitive peak. The characteristic profile of the Co_2SiO_4 doublet shows a less intense κ_1 and a corresponding intense κ_2 peak, as observed in Figure 1, suggesting that the olivine was formed. Notably, there is a shift in wavenumbers of κ_2 relative to the peak in pure Co_2SiO_4 , indicating structural perturbation of the larger M2 octahedral site that we attribute to Pd^{2+} substitution [23]. A distinct peak at 648 cm^{-1} in the spectrum is observed from the B_{1g} Pd–O vibrational mode [30]. This feature can only have two sources of origin, namely, an isolated Pd–O or Pd^{2+} incorporated into the olivine lattice. However,

the absence of additional Pd–O peaks of the A_{1g} and E_g shoulder suggests that Pd primarily incorporates into the lattice rather than forming separate Pd–O clusters. Thus, successful incorporation of Pd^{2+} into the M2 site of the Co_2SiO_4 olivine structure, while maintaining the overall framework integrity, is implied. Figure 2 shows the P-XRD of the material.

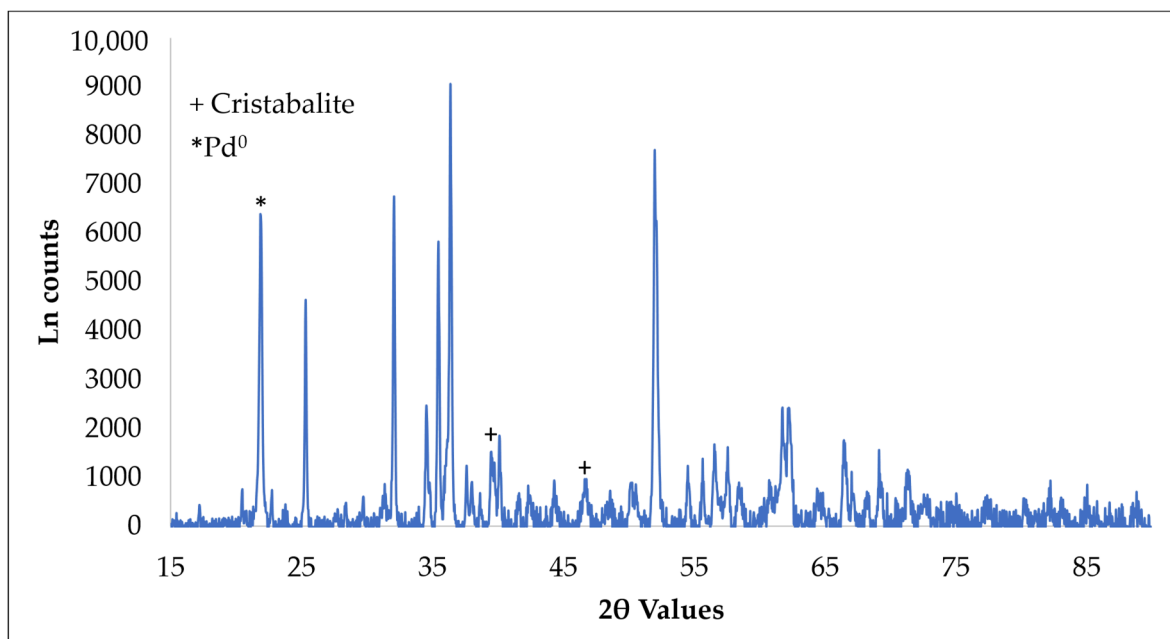


Figure 2. P-XRD of (93:7) $(Co^{2+}, Pd^{2+})_2SiO_4$.

3.3. P-XRD Analysis

Figure 2 confirms the dominant Co_2SiO_4 olivine phase (JCPDS 01-078-1501) alongside cristobalite impurities (JCPDS 00-046-1043 at $\sim 21^\circ$ 2θ) [23,31–34]. This comes from unreacted silica at the 1000 °C synthesis temperature transforming into cristobalite [23,35–37]. Additional reflections at ~ 40 and 47° 2θ values, suggesting the presence of metallic Pd (PDF #46-1043), are also observed [38–40]. The absence of olivine peak shifts relative to Co_2SiO_4 indicates negligible bulk lattice parameter change [17,41].

This is contrary to the information from the Raman spectra, where the κ_2 peak shift observed revealed localized M2 site distortion near the surface of the material. This suggests that bulk Pd exists as Pd^0 in the olivine framework, formed through high-temperature reduction of Pd^{2+} [42]. The coexistence of these phases suggests a synthesis-driven redox gradient where surface Pd remains oxidized, while bulk Pd aggregates into metallic nanoparticles due to thermal reduction, hence, the absence of peak shifts in P-XRD. This indicates minimal long-range lattice strain from interstitial or substitutional defects. This results in spatial heterogeneity where Pd exists as both incorporated surface oxide and bulk metal within the same material framework. Figure 3 shows the XPS of the material.

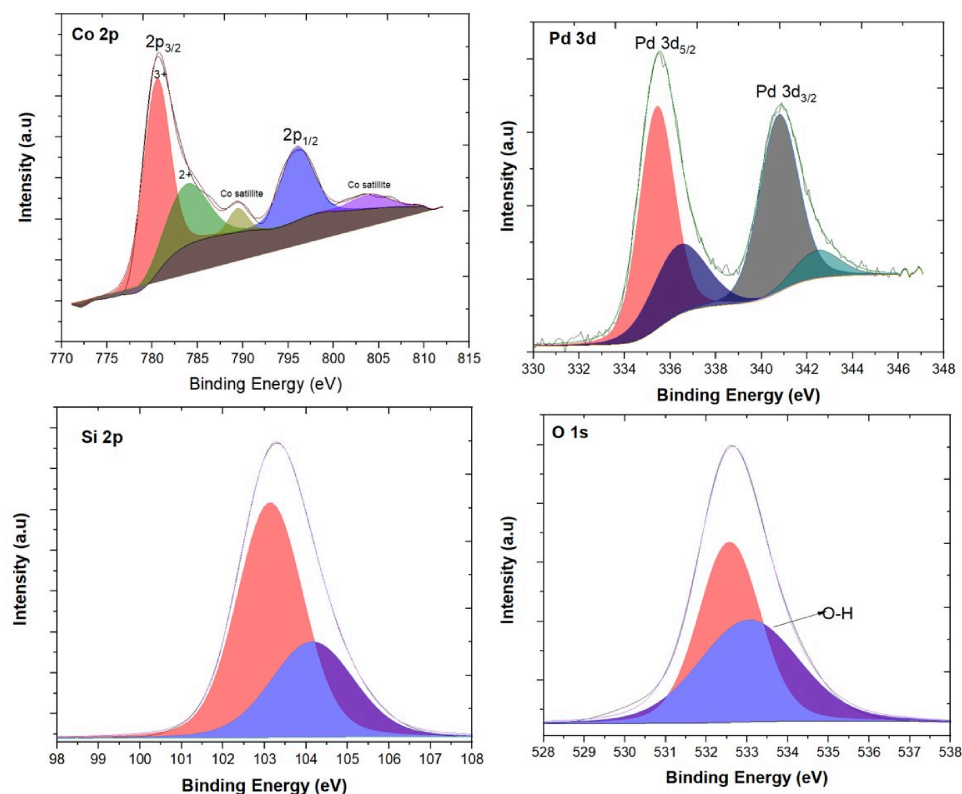


Figure 3. XPS analysis of (93:7) $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$. Colours show the deconvolution.

3.4. XPS Analysis

The Co 2p spectrum of the (93:7) $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ material, depicted in Figure 3, shows the main peaks at 780 eV, 779 eV, 785 eV, and 788 eV due to $2p_{3/2}$. The peak at 780 eV contributes to the main component of the Co species with a corresponding satellite at 779 eV of similar intensity [23,43]. The two satellites at 785 eV and 788 eV are at lower intensity with a ΔE of 5–8 eV from the main peak, suggesting that these are shake-up peaks [43,44]. The ΔE of 15 eV between the $2p_{3/2}$ and $2p_{1/2}$ suggests the presence of octahedral sites, typically observed in olivine materials. Finally, a peak at 803 eV is also observed with a ΔE of 8 eV shift from the main peak, which is typical of the shake-up region [23,43,44]. Thus, the main peaks show a Co^{2+} spectrum with shake-up peaks and satellites of equal or similar intensity that are characteristic of Co^{2+} [23,33,43,45,46]. No evidence of Co^{3+} is observed, suggesting Pd incorporation occurs without oxidizing the host matrix.

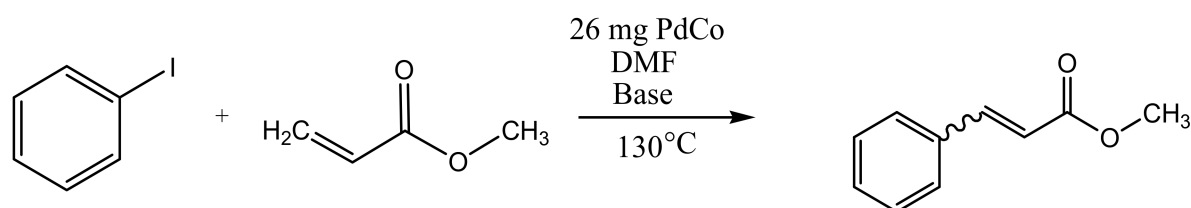
Based on the Pd 3d spectrum, the deconvolution shows two Pd chemical states, with the dominant doublet at approximately 335.5 eV (Pd $3d_{5/2}$) and 340.8 eV (Pd $3d_{3/2}$), characteristic of metallic Pd^0 . In addition, weaker higher-binding-energy components at around 336.5 eV (Pd $3d_{5/2}$) and 342.0 eV (Pd $3d_{3/2}$) indicate the presence of oxidized Pd species (Pd^{2+}), suggesting partial surface oxidation of the Pd nanoparticles [47–50]. The coexistence of Pd^0 and Pd^{2+} states confirms the successful incorporation of palladium, while highlighting strong metal-support interactions and the formation of Pd–O surface bonds. The observed spin–orbit splitting of approximately 5.3 eV between the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ levels is consistent with reported values for palladium species, confirming the preservation of the Pd electronic structure despite variations in the local coordination environment. The relatively higher contribution of the Pd^0 component indicates that metallic palladium remains the predominant species, in agreement with the crystalline Pd phase identified by P-XRD analysis. The coexistence of multiple oxidation states in

heterogeneous catalysts, as confirmed by XPS analysis, has been shown to play a crucial role in catalytic activity through redox synergy [24].

Olivine formation is further supported by the Si (c) and O (d) spectra with peaks at 103 eV and 532 eV. The binding energy of Si in silicate species is typically in the 103 eV region. The peaks deconvolute to the two Si environments found in the olivine, one associated with Si–O–M [1] and the other with Si–O–Si. The cristobalite impurity phase observed in Figure 2 appears chemically inert in these redox processes, as no Si⁰ or modified silicate species were detected by XPS. Therefore, surface regions maintain Pd²⁺ in the olivine lattice while intermediate depths contain Pd⁰ nanoparticles, and the interface shows evidence of charge-transfer stabilization through the observed M2 site distortion. O^{2−} in silicate materials is typically in the 532 eV region, and the two deconvoluted peaks are attributed to the two distinctive oxygen environments of the Si–O–Si bridge and the Si–O–Co [23,50–52].

3.5. Catalytic Testing

The catalyst was tested for the Heck reaction following Scheme 2, which also illustrates the reaction conditions. Iodobenzene and methyl acrylate were used as starting materials, and dimethylformamide (DMF) was used as a solvent at 130 °C for the model reaction. The base was varied between triethylamine and sodium carbonate to investigate the effect of an inorganic base. The selection of a soluble base is aimed at promoting better catalytic efficiency and interaction between the catalyst and the reactants. Both bases were added at 1.5 mol equivalents to iodobenzene in the reaction media. Table 2 lists the conditions and results.



where DMF = Dimethylformamide

Base = Triethylamine or Na₂CO₃

Scheme 2. Heck–Mizoroki reaction conditions with substrates.

Table 2. Kinetic parameters for the Heck–Mizoroki reaction under triethylamine (TEA) and sodium carbonate (Na₂CO₃).

Base	Time (min)	Induction Period (min)	^a Initial Rate, r_0 (mol.s ^{−1})	^b Mass-Normalized r_0 (mol.s ^{−1} mg ^{−1})	^c Avg. Rate (mol.s ^{−1})
TEA	70	30	3.92×10^{-7}	1.51×10^{-8}	1.18×10^{-7}
Na ₂ CO ₃	80	10	2.58×10^{-7}	9.94×10^{-9}	1.03×10^{-7}

^a Initial Rate—Calculated post-induction period from reactant consumption between 30 and 40 min for TEA and 10–20 min for Na₂CO₃ using a linear fit to initial data points. ^b Mass normalized rate—Calculation from initial rates with catalyst mass of 26 mg. ^c Avg Rate—Calculated as 99 mol/time to completion with catalyst mass of 26 mg, iodobenzene 0.5 mmols.

To establish the baseline catalytic performance of the catalyst, kinetic experiments were performed and summarized in Table 2. Initial, average, and mass normalized rates were calculated for both bases.

It should be noted that the ‘initial rate’ reported in Table 2 refers to the post-induction rate calculated immediately after the induction period (30–40 min for TEA; 10–20 min for Na₂CO₃). This approach allows for meaningful comparison of intrinsic catalytic activity between systems with different induction periods, as the rates reflect steady-state catalytic

turnover once the catalyst is fully activated. The induction period itself represents catalyst activation rather than catalytic conversion, and no conversion is observed during this period. The conversion time data in Table 2 show that the PdCo olivine catalyst demonstrates high reactivity with both bases, achieving complete conversion in 70 min for TEA and 80 min for Na_2CO_3 . This performance aligns with established base functions in Heck catalysis, where the base facilitates multiple critical steps, namely the deprotonation of the aryl halide to generate a nucleophilic aryl anion, assistance in beta-hydride elimination to form the final olefin product and potentially activating the heterogeneous catalyst through reduction of palladium species [5,16,17,53]. Despite TEA having a longer induction period, suggesting prolonged activation requirements, TEA compensates with a higher initial rate and average rate during the active catalytic phase, of 3.92×10^{-7} compared to $1.18 \times 10^{-7} \text{ mol.s}^{-1}$ of the carbonate and corresponding mass-normalized efficiency. This results in the shorter reaction time observed for TEA. The shorter reaction time with TEA can be attributed to its stronger basicity ($\text{pK}_a = 10.75$) and better coordinating ability, which likely effectively stabilize reactive intermediates and promote faster oxidative addition steps. Noteworthy is the effectiveness of Na_2CO_3 , despite its weaker basicity of $\text{pK}_a = 10.33$ [17]. This was likely facilitated by several factors, such as the use of DMF as a solvent, which provides excellent solubility for both organic and inorganic substrates, compensating for solubility limitations [54]. Additionally, the olivine catalyst likely provides additional activation pathways that reduce base requirements, and the milder conditions associated with Na_2CO_3 may actually prevent catalyst deactivation pathways that occur with stronger bases [54]. Nevertheless, the average rates show similar reactivity since the carbonate system is not delayed by an induction period. Thus, the contrasting kinetic profiles suggest distinct mechanistic pathways. TEA likely follows a transformation pathway involving initial complex formation followed by generation of highly active species, while Na_2CO_3 may function through more direct base assistance in deprotonation and substrate activation steps. Figure 4 further explores the kinetic dynamics of both reactions to establish whether there are other periods of high or low reactivity during the reaction.

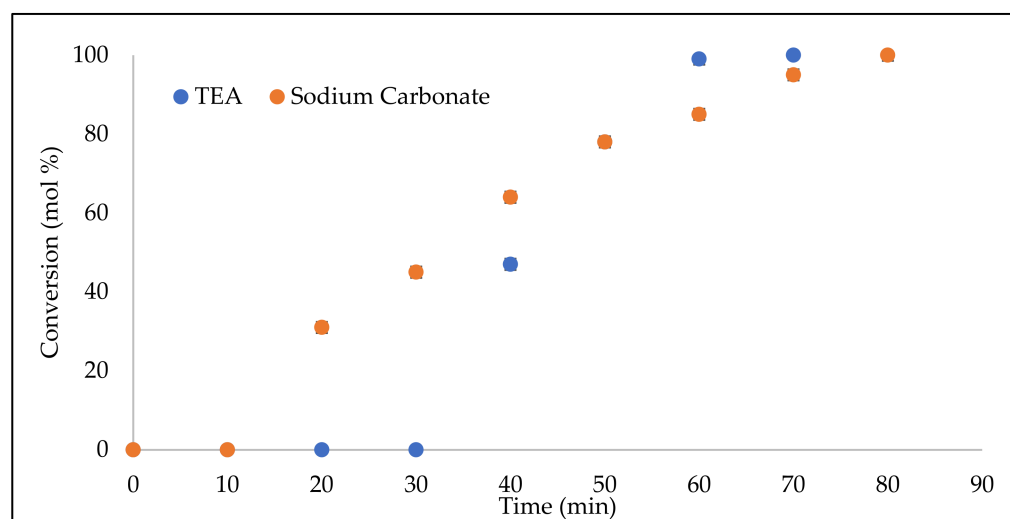


Figure 4. Reaction profile of the model Heck reaction over (93:7) $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ with triethylamine and Na_2CO_3 as bases.

The TEA system exhibits a profile with two distinct trends, beginning with a 30 min induction period of zero activity, followed by a period of high conversion between 30 and 60 min, where conversion increases from 0 mol% to 99 mol% in 30 min. This sharp transition suggests a threshold activation mechanism where once sufficient reactive intermediates accumulate or TEA transforms into active species, catalysis proceeds with

high efficiency. Interestingly, even within this acceleration phase, the rate is not constant; the 30–40 min interval shows a ~47 mol% conversion, while the subsequent 40–50 min interval shows ~31 mol% increase, and the final 50–60 min interval shows ~21 mol% increase, indicating gradually decelerating kinetics as the reaction approaches completion. This pattern suggests either substrate depletion effects or potential product inhibition as methyl cinnamate accumulates.

The Na_2CO_3 system presents a more complex profile with three distinct trends with subtle reactivity modulations. After a brief 10 min induction, the system enters a high-reactivity phase between 10 and 30 min, achieving 45 mol% conversion. However, between 30 and 50 min, the system enters a moderate-reactivity phase where conversion increases from ~45 mol% to ~78 mol%. This deceleration may indicate changing rate-limiting steps as the reaction progresses or evolving catalyst surface conditions. The final phase 50–80 min shows further deceleration to ~0.73 mol% per minute as the system approaches completion, consistent with typical kinetics for reactions nearing equilibrium or experiencing diffusion limitations at high conversion.

Notably, both systems converge at 50 min with identical 78 mol% conversion, despite following different pathways to reach this point. This convergence suggests that while the bases affect the kinetic trajectory, the underlying catalytic capacity of the Pd-Co olivine system remains consistent. After this convergence point, TEA shows better activity in the final stages, reaching >99 mol% in 60 min compared to ~85 mol% for Na_2CO_3 at the same time point. The final approach to completion also differs: TEA achieves the last 1 mol% conversion between 60 and 70 min, while Na_2CO_3 requires 20 min 80–100 min for the final 5 mol%, suggesting different sensitivities to product inhibition or mass transfer limitations at high conversion. Figure 5 shows the selectivity of both basic systems.

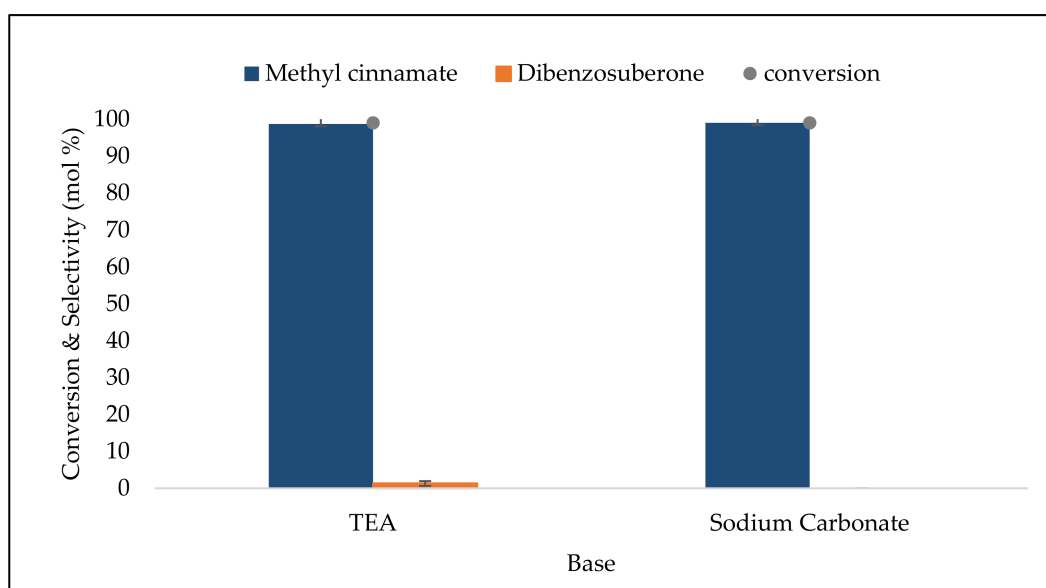


Figure 5. The product selectivity graphs of the model Heck reactions with triethylamine and Na_2CO_3 , as bases, respectively.

The selectivities for both TEA and Na_2CO_3 show direct Heck reaction over the Pd-Co olivine catalyst exclusively toward the desired methyl cinnamate product, achieving 100 mol% selectivity with >99 mol% conversion. Notable is the high conversion and selectivity with Na_2CO_3 , given that Na_2CO_3 is a weaker base with a pKa of 10.33 compared to TEA with a pKa of 10.75. This is despite the difference in reaction pathways and kinetics. Thus, the olivine framework, with its stratified $\text{Pd}^{2+}/\text{Pd}^0$ sites, provides a sufficiently activated environment even in the presence of milder base and can efficiently drive the

reaction to completion without alternative side reactions. Triethylamine was selected as the base for Lewis acid screening studies due to its established coordination chemistry with palladium centers, which provides a sensitive kinetic profile, as seen from Figure 4. Figure 6 shows the product selectivity of the heterogeneity tests performed, namely recyclability and Hg^0 poisoning.

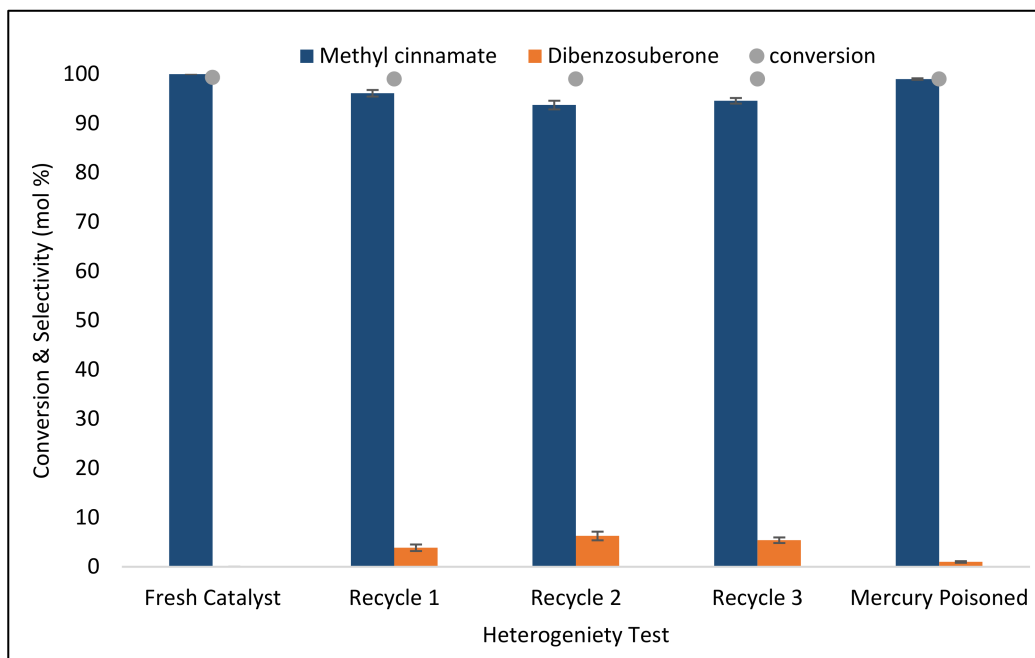
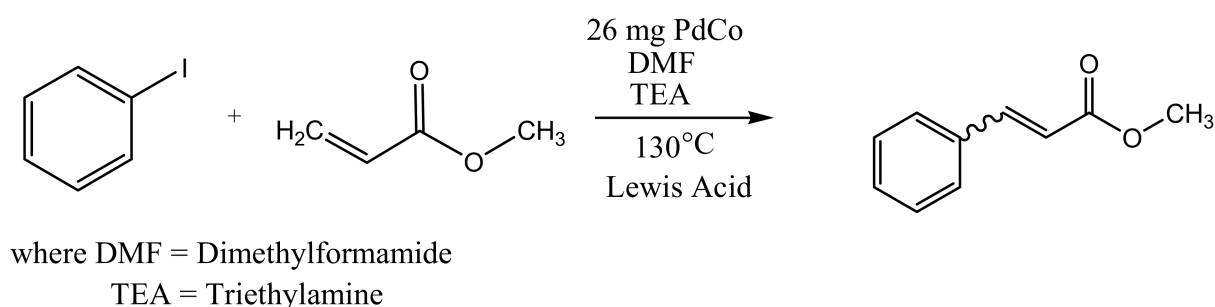


Figure 6. Conversion at >99 mol% and product selectivity over the solid catalyst after recycling and Hg^0 tests.

The fresh catalyst shows high selectivity toward methyl cinnamate of ~100 mol% at >99 mol% conversion. However, upon recycling, selectivity towards methyl cinnamate decreases to ~96.1 mol% in the first recycle, ~93.7 in the second, and stabilizes at approximately 94.6 mol% in the third cycle. Dibenzosuberone formation increases correspondingly from 0 mol% to ~3.9 mol%, then ~6.3 mol%, and finally ~5.4 mol% with each cycle. This progressive enhancement of aldol condensation pathways suggests dynamic restructuring of the catalyst surface during recycling, likely involving several concurrent processes. The increasing dibenzosuberone formation with catalyst recycling indicates a gradual transformation of surface sites toward configurations that promote secondary condensation reactions. This evolution may result from several factors, such as selective leaching of surface species that originally suppressed side reactions, structural reorganization exposing new active sites with different catalytic properties, or accumulation of organic residues that modify surface chemistry. The stabilization of selectivity patterns by the third cycle at ~94.6 mol% methyl cinnamate and 5.4 mol% dibenzosuberone suggests that the catalyst reaches a steady-state surface configuration after initial restructuring, with the olivine framework providing sufficient stability to maintain consistent activity. The maintained high conversion across all cycles confirms the robust heterogeneous nature of the catalyst, with the olivine framework preserving structural integrity and active site accessibility despite minor selectivity changes. The primary Heck coupling mechanism remains functional while secondary reaction pathways become increasingly accessible. Following catalyst filtration after 45 min of reaction, the introduction of 150 mmol Hg^0 to the filtrate did not completely quench catalytic activity, with the leached species giving >99 mol% conversion after 3 h. The continued activity despite substantial Hg^0 addition indicates that not all catalytically active species in solution are susceptible to mercury poisoning through amal-

gamation. Hg^0 selectively poisons homogeneous Pd^0 species by forming Pd-Hg alloys, but this process requires accessible, zerovalent palladium in appropriate chemical form. The persistence of activity suggests that the leached species may include Pd^{2+} complexes or Pd species in coordination environments resistant to amalgamation. The >99 mol% conversion after Hg^0 addition, with maintained selectivity, suggests that while leached species are active, their concentration and behavior differ from the performance of the solid catalyst, which was faster, supporting the presence of soluble Pd^{2+} species like those observed in a “release-and-capture” mechanism. This aligns with the characterization findings of the $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ stratified architecture that established the presence of surface-incorporated Pd^{2+} that could leach as Pd^{2+} amine or Pd^{2+} -silicate complexes that do not readily reduce to an amalgam-forming Pd^0 under these conditions. Similar recyclability and structural stability have been reported for other heterogeneous catalyst systems, where performance remained >95% over multiple cycles [12,24]. The high selectivity of >99 mol% toward methyl cinnamate of these leached species further confirms the preservation of the Heck coupling pathway as the heterogeneous catalyst, indicating mechanistic continuity between heterogeneous and leached-phase catalysis. The slower conversion in the filtrate indicates that while leached species are active, they exhibit lower efficiency than the heterogeneous catalyst. This efficiency gap likely stems from several factors, such as lower concentration of active species in solution, different coordination environments that modify catalytic rates, or absence of synergistic effects present in the solid catalyst's $\text{Pd}^{2+}/\text{Pd}^0/\text{Co}^{2+}$ framework. The addition of Lewis acids as promoters has been investigated under the conditions summarized in Scheme 3.



Scheme 3. The model Heck–Mizoroki reaction with reaction conditions.

Scheme 3 illustrates the reaction conditions for the Lewis acid screening experiments using triethylamine and DMF as the solvent. Triethylamine was chosen as the base as it gave a higher average reaction rate. Table 3 summarizes the kinetic rates observed with the use of each Lewis acid of varying acidity.

Table 3. Kinetic parameters of reactions with Lewis acids.

System	Time (min)	Induction Period (min)	^a Initial Rate, r_0 (mol.s ^{−1})	^b Mass-Normalized r_0 (mol.s ^{−1} mg ^{−1})	^c Avg. Rate (mol.s ^{−1})
TEA	70	30	3.92×10^{-7}	1.51×10^{-8}	1.19×10^{-7}
ZnCl ₂	90	10	3.83×10^{-7}	1.47×10^{-8}	9.26×10^{-8}
AlCl ₃	100	20	5.00×10^{-8}	1.92×10^{-9}	8.33×10^{-8}
^d SnCl ₄	>100	30	2.08×10^{-7}	8.01×10^{-9}	$<7.25 \times 10^{-8}$
^d FeCl ₃	>100	60	1.67×10^{-8}	6.41×10^{-10}	$<2.08 \times 10^{-8}$

^a Initial rate—Calculated from reactant consumption at the end of the induction period. ^b Mass normalized rate—Calculated as highest conversion % with catalyst mass of 26 mg, iodobenzene 0.5 mmols. ^c Avg rate—Calculated at highest conversion reached/time to completion (Fe and Sn do not reach completion) with catalyst mass of 26 mg, iodobenzene 0.5 mmols. ^d >100—Rates calculated at 100 min although reactions do not reach completion.

Despite being the weakest Lewis acid, ZnCl_2 shows a high initial reaction rate of $3.83 \times 10^{-7} \text{ mol.s}^{-1}$ after a short 10 min induction period. However, this high initial rate is not sustained, resulting in an average rate of $9.26 \times 10^{-8} \text{ mol.s}^{-1}$ and requiring 90 min to reach completion. In comparison, the additive-free catalyst TEA shows a higher initial rate and higher average rate ($3.92 \times 10^{-7} \text{ mol.s}^{-1}$ and $1.19 \times 10^{-7} \text{ mol.s}^{-1}$), albeit after a 30 min induction period. This discrepancy between initial and average rates suggests that while Zn^{2+} may facilitate early catalytic steps, such as oxidative addition, possibly by weakly polarizing the aryl halide or mildly modifying the electronic properties of surface Pd sites without strong coordination. However, this initial advantage is not sustained because the average rate of $9.26 \times 10^{-8} \text{ mol.s}^{-1}$ remains lower than that of the promoter-free system, and completion time extends to 90 min, albeit after a longer 30 min induction period. This indicates that while Zn^{2+} aids initiation, it also introduces limitations, likely such as reversible site blocking or equilibrium constraints that retard the overall catalytic cycle.

SnCl_4 with moderate to high Lewis acidity shows a high initial rate of $2.08 \times 10^{-7} \text{ mol.s}^{-1}$, but with a 10 min improvement in the induction period. However, the initial and average rates are not improved at $2.08 \times 10^{-7} \text{ mol.s}^{-1}$ and an average rate of less than $<7.25 \times 10^{-8} \text{ mol.s}^{-1}$, and the reaction does not reach completion (87 mol%) in the observed time of 100 min. This result is lower than that of both ZnCl_2 (9.26×10^{-8}) and TEA (1.19×10^{-7}). This suggests that Sn^{4+} interacts strongly with surface Pd sites, initially promoting reactivity but eventually leading to inhibition. This is possibly through site blocking, catalyst degradation, or the formation of stable Sn–O–Pd/Co bridges that hinder catalyst turnover.

FeCl_3 shows the poorest reactivity, with no improvement to the induction period (60 min induction period) and has the lowest initial rate of $1.67 \times 10^{-8} \text{ mol.s}^{-1}$ and an average rate of $<2.08 \times 10^{-8} \text{ mol.s}^{-1}$ without reaching completion. The severe inhibition observed with Fe^{3+} cannot be explained by Lewis acidity alone, as the stronger acid AlCl_3 performs better. Instead, it likely reflects oxidation of surface Pd^0 to Pd^{2+} by Fe^{3+} or the formation of stable Fe–O–Pd/Co bridges that permanently deactivate catalytic sites. Additionally, FeCl_3 hydrolysis may result in further degradation of the catalyst or react with TEA, limiting oxidative addition under the reaction conditions.

Despite AlCl_3 being the strongest acid in the series, early activation with a 20 min induction period is observed. Nevertheless, a lower initial rate of $5.00 \times 10^{-8} \text{ mol.s}^{-1}$ and a lower average rate of $8.33 \times 10^{-8} \text{ mol.s}^{-1}$ compared to TEA are observed, resulting in a completion time of 100 min. The finite induction time suggests that Al^{3+} does not immediately activate the catalyst but may initially interact with inhibitory TEA species or gradually modify the catalyst surface before promoting turnover. Although Al^{3+} hydrolyses readily, it likely forms a precipitated $\text{Al}(\text{OH})_3$ layer or a passivating Al–silicate complex that limits further corrosion, allowing reactivity to be maintained to completion despite slower kinetics.

The stratified architecture of the $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ with surface-accessible Pd^{2+} species incorporated into the silicate lattice presents ideal coordination sites for Lewis acids, while the silicate framework offers oxygen atoms for interaction. Weak acids like Zn^{2+} likely engage in reversible, surface-limited coordination that mildly modifies catalytic properties without complete site blocking, hence decreasing the induction period but reducing average rates. However, as Lewis acidity increases, catalyst surface disruption becomes more pronounced, reducing overall efficiency. Interestingly, the promoter-free TEA system ultimately surpasses all Lewis acid-modified systems in both initial and average rates, achieving the fastest overall conversion. This establishes an inverse relationship between Lewis acid strength and sustained reaction rates in our heterogeneous system, which is contrary to trends often observed in homogeneous catalysis [13]. The conversion over

time profiles for each Lewis acid, presented in Figure 7, provide further insight into reaction pathways.

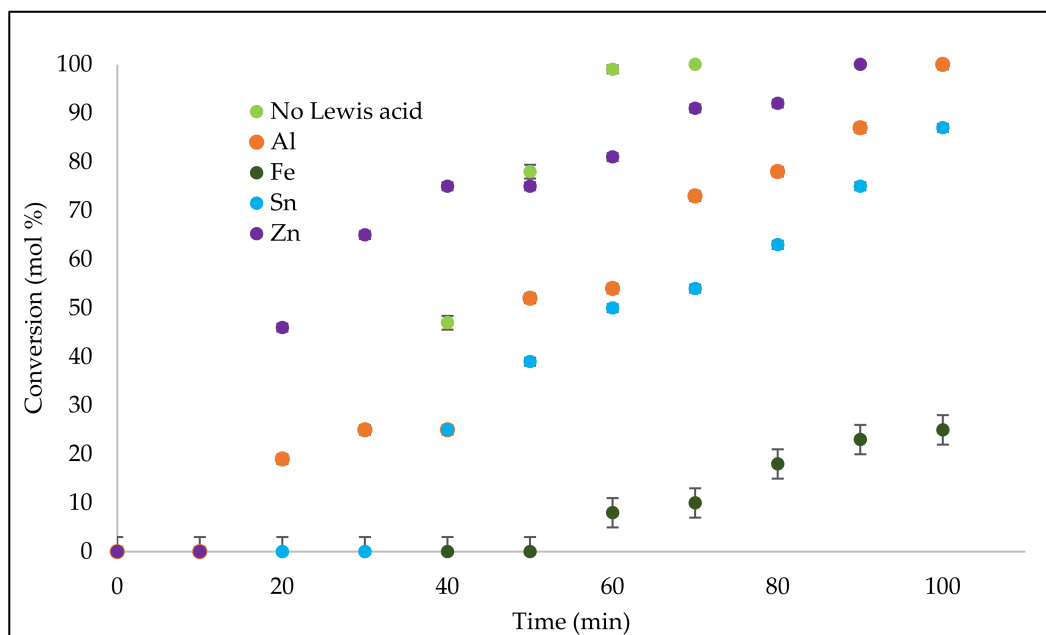


Figure 7. The conversion over time reaction profile of iodobenzene over (93:7) $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ using FeCl_3 , SnCl_4 , AlCl_3 , and ZnCl_2 as Lewis acids.

The promoter-free TEA system exhibits a classic delayed-onset profile, with a 30 min induction period followed by rapid acceleration reaching ~47 mol% conversion. Within 10 min after a 30 min induction period, complete conversion of >99 mol% is reached by 60 min. This sharp, sigmoidal shape suggests a cooperative activation mechanism, where accumulated active Pd sites trigger the catalytic cycle or the initial material is transformed into the active catalyst. In contrast, ZnCl_2 displays a rapid initiation but stepwise progression profile, with a short 10 min induction period followed by an initial high conversion to 46 mol% in the first 10 min of activity. However, distinct plateaus, most notably at ~75 mol% conversion between 40 and 50 min, indicate periodic saturation or equilibrium limitations. This likely arises from Zn^{2+} coordination creating transient active complexes or intermediates that dissociate before further conversion. The reaction eventually reaches completion at 90 min, but the overall rate remains lower than that of the promoter-free system. AlCl_3 shows a 20 min induction period and a lower initial conversion rate, reaching ~19 mol% in the first 10 min after induction. Conversion then accelerates steadily, progressing from ~40 mol% at 40 min and then 100 mol% at 100 min. This near-linear profile suggests that Al^{3+} modifies the catalyst surface sufficiently to affect the catalytic pathway but not enough to cause deactivation. Despite being the strongest Lewis acid in the series, AlCl_3 only improves the induction period by 10 min rather than the overall rate. This indicates that AlCl_3 primarily modifies the catalyst surface rather than improving the overall rate.

SnCl_4 shows a 30 min induction period and thereafter progresses steadily from ~25 mol% at 40 min to ~87 mol% at 100 min. Although SnCl_4 has moderate to high acidity, unlike ZnCl_2 , this profile shows no improvement in the induction period, suggesting that SnCl_4 does not participate in the activation of the aryl halide as in the case with ZnCl_2 . The moderate yet incomplete conversion implies that Sn^{4+} coordinates reversibly with surface sites, allowing for catalyst turnover but eventually limiting access or resulting in gradual site blocking. Furthermore, the catalyst profile shows a steady rate and less

complex reaction pathways without any intermediary phases where periodic site saturation or equilibrium limitations.

FeCl_3 shows a severely inhibited, delayed activation profile that remained near-zero through 50 min before a slow, almost linear increase was observed. This profile suggests initial catalyst poisoning followed by gradual reactivation, where Fe^{3+} initially coordinates strongly to surface sites, blocking catalysis until either the Fe-Pd complexes slowly decompose or alternative pathways emerge. The lack of any acceleration phase indicates that even after initial inhibition is overcome, FeCl_3 continues to hinder efficient catalysis throughout the reaction.

Therefore, Lewis acids in this system function primarily as catalyst surface modifiers rather than as substrate activators, except for ZnCl_2 . The promoter-free curve shows efficient, cooperative catalysis once induction is overcome, while Lewis acid additives show distinct kinetic variability where Zn^{2+} enables fast initiation but with stepwise saturation, Al^{3+} also decreases the induction period like ZnCl_2 but shows slower reaction progression, Sn^{4+} allows moderate yet incomplete conversion and no early activation, and Fe^{3+} shows severe inhibition through likely redox-mediated deactivation which increases the induction period and retards conversion. An inverse correlation is observed between Lewis acid strength and overall catalytic effectiveness, with stronger acids extending the induction and reducing average rates, and weaker Lewis acids like ZnCl_2 showing earlier activation. The influence of Lewis acids on the selectivity is shown in Figure 8.

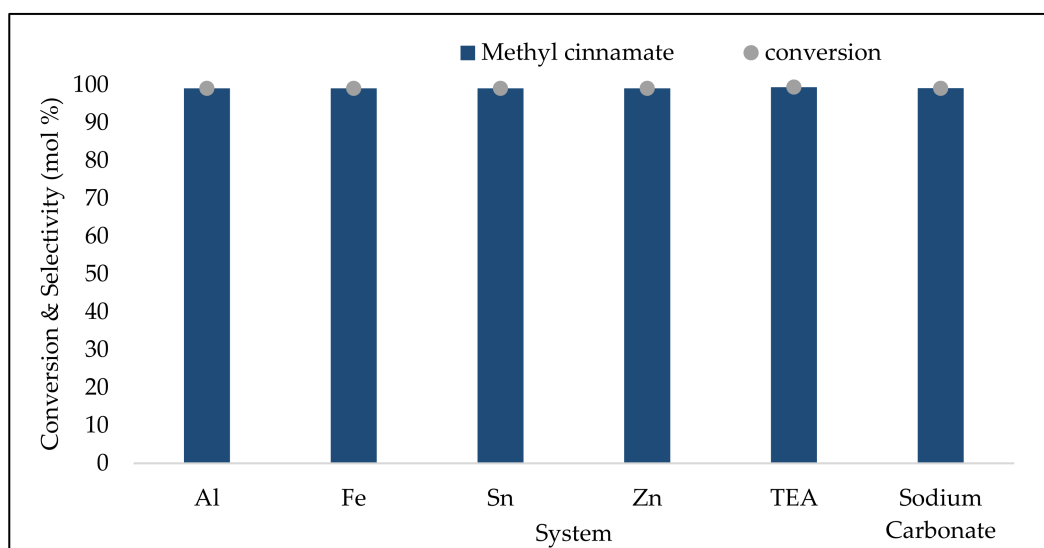


Figure 8. Selectivity and product scope when each Lewis acid was used as a promoter.

Figure 8 shows uniform selectivity of >99 mol% towards methyl cinnamate formation across all Lewis acid systems despite the differences observed in kinetic rates and pathways.

Although FeCl_3 and SnCl_4 showed kinetic inhibition, selectivity was maintained, as with the highly active ZnCl_2 and promoter-free systems, which indicates that Lewis acids do not alter the reaction mechanism that leads to methyl cinnamate. This then suggests that the influence of Lewis acids is not primarily activating the aryl halide through polarization of the C-I bond as proposed in homogeneous literature, since there was no correlation between acid strength and performance. Moreover, substrate activation based on Lewis acid strength would result in changes in selectivity with different acids, as modified substrate reactivity results in alternative pathways.

Instead, Lewis acids are likely surface modifiers or poisons that influence accessibility, activation energy, or the number of active sites and do not redirect the fundamental coupling mechanism toward side reactions. Additionally, the same selectivity between TEA (organic

base) and Na_2CO_3 (inorganic base) confirms that the base itself does not alter product distribution under these conditions. Therefore, the active site geometry or electronic environment required for selectivity of this catalyst is preserved under these conditions, albeit overall activity is reduced. Thus, the decoupling of rate and induction effects from selectivity suggests that in this Pd/Co-silicate system, selectivity is dictated by the intrinsic properties of the bimetallic silicate framework and the Heck coupling mechanism, which are not easily overridden by Lewis-acid additives or base used. Quantification of metals leached as influenced by the Lewis acids was performed by ICP-OES, and the results are summarized in Table 4.

Table 4. Quantification of metal leaching by ICP-OES as a function of base and Lewis acid used at >99 mol% conversion.

System	Pd Leaching (ppb)	Co Leaching (ppb)
TEA	68 ± 2	6 ± 0.2
Na_2CO_3	62 ± 2	12 ± 0.3
ZnCl_2	58 ± 2	3 ± 0.04
FeCl_3	59 ± 2	21 ± 0.7
AlCl_3	588 ± 14	279 ± 9
SnCl_4	701 ± 17	766 ± 19

Table 4 shows the robust nature of the heterogeneous catalyst with metal loss lower than thresholds limits as stipulated by the European Medicines Agency/Committee for Medicinal Products for Human Use/International Council for Harmonisation (EMA/CHMP/ICH) Q3D where daily dose does not exceed 10 mg per day in drug products of 10,000 ppb Pd oral, 1000 ppb for parenteral and 100 ppb inhalation drugs and medicines [23,55,56]. In the case of Co, threshold limits are 5000 ppb in oral drugs and medicines, 500 ppb for parenteral, and 300 ppb for inhalations. These low concentrations confirm the public health viability of this catalytic system. These low metal leaching concentrations observed in our system are comparable to other well-designed heterogeneous catalysts that maintain structural integrity and minimize active species loss [12,24]. However, the only exceptions are the leaching of Pd in the presence of the AlCl_3 and SnCl_4 Lewis acids and the leaching of Co in the presence of SnCl_4 that exceed inhalation concentration thresholds. Nevertheless, the relative leaching patterns of Pd and Co as a function of Lewis acid provide more insight into the catalyst–Lewis acid interactions. TEA shows slightly higher Pd leaching of 68 ppb than Na_2CO_3 at 62 ppb but lower Co leaching of 6 ppb compared to 12 ppb of Na_2CO_3 . TEA with stronger coordinating ability likely extracts surface Pd through soluble amine complexes, while carbonate ions may promote mild dissolution of the cobalt silicate matrix through pH effects or carbonate complexation. Characterization information confirmed that Pd exists as both surface-accessible species and nanoparticles, while Co is more firmly incorporated into the olivine lattice.

Catalyst interactions with ZnCl_2 show the lowest overall metal loss of 58 ppb Pd and 3 ppb Co. This indicates that ZnCl_2 shows highly selectively and exclusively interacts with surface Pd atoms through weak, reversible coordination that minimally perturbs the silicate framework, likely preserving the structure. Additionally, early activation of substrates was seen, characterized by a shorter induction period, suggesting that ZnCl_2 does provide substrate activation, allowing for low Pd leaching but high conversion and early conversion. Additionally, the near-zero Co leaching confirms that Zn^{2+} functions as a surface modifier rather than a structural modulator, resulting in preserved catalytic activity without significant catalyst leaching.

FeCl_3 also shows low leaching of 59 ppb Pd but higher Co leaching of 21 ppb Co than ZnCl_2 . This suggests stronger surface and structural interactions with the catalyst.

Rather than hydrolyzing to attack the silicate network, Fe^{3+} probably coordinates at Pd-Co interface sites, potentially participating in electron transfer processes that modify local oxidation states without structural damage, electronically disrupting active sites rather than physically destroying them, resulting in the poor catalytic performance observed for FeCl_3 despite higher leaching. AlCl_3 showed the highest leaching of 588 ppb for Pd and 279 ppb for Co. These high metal dissolution values suggest structural attack on the silicate framework, likely through hydrolysis mechanisms to produce HCl. The generated hydrochloric acid likely attacks Si-O-Co and Si-O-Pd bonds, solubilizing both metals from the olivine lattice to varying degrees based on their Lewis acidity. However, a preference for Pd is observed, likely resulting in less destruction of the olivine frame and likely leaching mostly surface Pd with lower affinity for bulk Pd, which allows for conversion to completion. In contrast, SnCl_4 , being a moderate to high Lewis acid, showed the highest leaching of 701 ppb and 766 ppb for Pd and Co. This likely results in displacement mechanisms of Co and Pd from the olivine framework, resulting in non-selective high leaching of both metals, resulting in the reaction being hindered from reaching completion, and conversion likely occurs from leached Pd species instead of the catalyst solid.

4. Conclusions

This study demonstrates that the stratified $(\text{Co}^{2+}, \text{Pd}^{2+})_2\text{SiO}_4$ with Pd^0 olivine catalyst exhibits excellent intrinsic activity for the Heck–Mizoroki coupling of iodobenzene and methyl acrylate, achieving >99 mol% conversion and >99 mol% selectivity toward methyl cinnamate without requiring Lewis acid promoters. Contrary to literature reports in homogeneous systems, where Lewis acids like FeCl_3 significantly enhance rates through substrate activation, our heterogeneous catalyst shows that these additives generally impair rather than improve performance. The promoter-free system with triethylamine base, despite a 30 min induction period, achieved the highest initial rate of $3.92 \times 10^{-7} \text{ mol.s}^{-1}$ and an average of $1.19 \times 10^{-8} \text{ mol.s}^{-1}$, outperforming all Lewis acid-modified systems. Lewis–catalyst interactions in this catalyst system show three key factors. Firstly, Lewis acids function primarily through direct catalyst interaction rather than substrate activation; however, the catalyst can recover from such interactions through alternative reaction pathways that maintain selectivity. However, ZnCl_2 and AlCl_3 showed strong substrate activation, resulting in decreased induction periods. Secondly, the nature of interaction and mechanism vary with acid strength from surface modification to structural destruction, where surface interactions improve initial reaction rates, while stronger interactions also target the olivine framework, resulting in a slower homogeneous component driving the reaction. Thirdly, the catalyst was shown to have robust and intrinsic control over catalyst selectivity regardless of the Lewis acid used or base choice.

The catalyst demonstrates a predominantly heterogeneous character with a leachable homogeneous character; with minimal metal leaching of <62 ppb Pd for most systems, excellent recyclability with maintained >99 mol% conversion over three cycles, and Hg^0 -resistant leached species that maintain high selectivity, confirming mechanistic continuity between heterogeneous and solution-phase catalysis. This is consistent with a release-and-catch reservoir mechanism. While selectivity toward methyl cinnamate remains consistently high >99 mol% across all conditions, catalyst recycling gradually promotes dibenzosuberone formation up to ~5.39 mol%, indicating surface evolution toward sites favoring aldol condensation. This study has set the premise for a comprehensive substrate scope investigation to further investigate the robustness of the catalyst as future work [12]. Additionally, future work could also employ advanced mechanistic experiments, such as radical trapping experiments and EPR spectroscopy [53], to further elucidate the nature of Lewis acid–catalyst interactions and the role of $\text{Pd}^0/\text{Pd}^{2+}$ redox cycling in the catalytic mechanism [24].

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Conflicts of Interest: The authors confirm that there no conflicts of interest.

Appendix A

Table A1. GC-MS oven temperature program.

Entry	Rate in °C.m ⁻¹	Final Temp. in °C	Hold Time in mins
1	10	80	1
2	20	180	1
3	30	240	20

Table A2. GC-MS instrument settings.

Entry	Rate in °C.m ⁻¹
Mode	split
Split ratio	10
Injection temp.	260 °C
Gas type	He
Total flow Rate	9.9 mL.min ⁻¹
Column	ZB-5MS plus (30 m × 0.25 mm × 0.25 µm)
	MS-QP Detector
Ion source temp.	230 °C
Interface temp.	280 °C
Gas type	He

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