Highly selective etherification of fructose and 5-hydroxymethylfurfural over a novel Pd-Ru/MXene catalyst for sustainable liquid fuel production

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Summary
Sustainable liquid fuel production from bio-oil compounds has attracted considerable attention in recent years. The catalytic etherification of 5-hydroxymethylfurfural (HMF) to ethoxymethylfurfural (EMF) is an effective approach for the production of liquid fuels. However, the development of high-performance and chemically stable catalysts has remained challenging. In this work, ultra-small Pd-Ru NPs were successfully immobilized on the surfaces of 2D MXene nanosheets (Pd-Ru/MXene) via fish sperm DNA-assisted microwave process. HR-TEM imaging results with SAED analysis showed that the hexagonal closed-pack (hcp) Pd-Ru NPs were grown on the surfaces of sheet-like MXene, thus enhancing the specific surface area of 117 m^2 g^{-1} and providing a higher density of the acid-base sites. Furthermore, Pd-Ru/MXene was employed for the etherification of HMF into EMF. The results showed that the Pd-Ru/MXene catalyst exhibited 98% EMF yield and 100% HMF conversion with the prolonged usage of catalyst for five consecutive reuse cycles. Additionally, fructose was directly converted into EMF with a higher yield of 82% over the Pd-Ru/MXene catalyst at lower reaction conditions. The recyclability test of the used Pd-Ru/MXene catalyst demonstrated its chemical stability under prolonged usage for several hours and is therefore suitable for commercial renewable liquid fuel production.

Novelty Statement
- The catalytic transformation of biomass into diesel-miscible biofuel is a sustainable route for liquid fuel production and has recently attracted massive attention.
- The chemically stable and high-performance Pd-Ru/MXene catalyst was successfully prepared and characterized.
The study demonstrated that the Pd-Ru/MXene catalyst exhibits superior catalytic activity toward the direct conversion of fructose and 5-hydroxymethylfurfural (5-HMF) into 5-ethoxymethylfurfural (5-EMF), which is a promising conversion method for the production of biofuels from biomass.

**KEYWORDS**

5-ethoxyethyl-2-furfural, etherification, functional catalyst, MXene, sustainable liquid fuel

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### 1 | INTRODUCTION

Energy production from renewable resources of lignocellulosic biomass has attracted much attention in recent years as a possible solution of the energy- and environment-related problems arising from fossil fuel consumption.¹,² The catalytic transformation of lignocellulosic biomass into diesel-miscible biofuel is considered to be a sustainable route for energy production and has recently attracted immense attention.³⁻⁸ Especially, bio-oil-based oxygen-containing organic compounds are successfully upgraded over different catalysts.¹,⁹⁻¹¹ Starch-rich biomass conversion can lead to the production of 5-hydroxymethyl-2-furfuraldehyde (HMF) that can then be catalytically converted into the 5-ethoxymethyl-2-furfural (EMF), levulinic acid (LA), 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-carboxylic acid (FFCA), and maleic anhydride (MA) diesel-miscible biofuels.¹²⁻¹⁵ Specifically, EMF is considered for use as a diesel additive that can be efficiently synthesized over various homogeneous and heterogeneous catalysts.¹⁶⁻¹⁹ In recent years, a very large number of catalytic systems have been developed for the conversion of HMF into EMF. However, these catalytic systems show very low HMF conversion efficiencies and low EMF yields with longer reaction times. In particular, beta Zeolite (BEA300), TaTPA/SnO₂, H₄SiW₁₂O₄₀/MCM-41 nanospheres, Cs₂STA, Fe₃O₄@C-SO₃H, Al-MCM-41, H₁₁.₅Nb₁₅.₅Mo₆.₅O₆₆, MCM-41-supported phosphotungstic acid, and MCM-41-supported phosphotungstic acid are the commercially applied catalysts for the conversion of HMF into EMF.¹²⁻¹₄,¹₆⁻²⁵ However, these catalysts suffer from chemical instability in prolonged usage, poor catalytic activity, toxicity, and high costs that hinder the commercial production of EMF from HMF. Recently, many research efforts both in industry and academia have focused on the development of novel catalysts from various waste streams, as equivalent to these commercial catalysts with an ability to overcome these shortcomings.²⁶ To ensure the chemical stability and high activity in prolonged usage, researchers have focused on the synthesis of novel catalytically active sites on chemically stable platforms; however, this effort has met only limited success to date.

Over the course of the last decade, graphene, transition metal dichalcogenides (TMDCs), hexagonal boron nitride (h-BN), and phosphorene have been some of the promising members of the family of 2D materials used for the conversion of HMF into EMF.²⁷⁻²⁹ Motivated by the synergistic features of 2D materials, an ongoing research effort has been pursued to develop a novel and abundant catalytic material for both of the above-described catalytic applications. For instance, in 2011, MXenes have been introduced as emerging and robust 2D catalytic materials that can be used either as supports for accommodating the active sites or as precious-metal-free catalysts for the conversion of HMF into EMF.

MXenes are generally represented as $\text{M}_n + 1 \text{AX}_n$ ($n = 1, 2, 3$), where ‘$\text{M}$’ denotes a transition metal, ‘$\text{A}$’ is usually any element from groups 12 to 16 of the periodic table (such as Cd, Al, Si, P, S, Ga, Ge, As, In, Sn, Ti, Pb), while ‘$\text{X}$’ represents C and/or N.²⁰⁻³¹ To date, 30 different compositions of MXenes have been reported and successfully used for various applications such as environmental remediation and renewable energy generation.³² Due to their high density of acid-base sites, tunable surface structure, and a wide variety of possible chemical compositions, MXenes can be easily exfoliated and coupled with other preferred materials to achieve the anticipated morphologies and to enhance the catalytic performances.³³ Importantly, Ti₃C₂ and M₃C₂ have exhibited intriguing catalytic applications, and hence, are considered to be the promising MXene candidates for the successful conversion of etherification.³²

The main goal of this work was to develop a novel MXene-based hybrid catalyst by incorporating alloyed Pd-Ru onto the surface of MXene nanosheets (NSs). The as-prepared catalyst was thoroughly characterized using modern analytical tools and tested as a common catalyst for the conversion of fructose and HMF into EMF. Furthermore, recyclability and a possible catalytic mechanism are also presented.
2 EXPERIMENTAL SECTION

2.1 Materials

The multilayer MXene was purchased from the Jiangsu XFNANO Materials Tech Co., Ltd., China. Fish sperm DNA, 5-(hydroxymethyl)furfural (≥99%, FG), sodium borohydride (NaBH₄, 98%), ruthenium(III) chloride hydrate (RuCl₃·xH₂O, 99.98%), formic acid (98%), acetone (CH₃COCH₃, 99.8%), 5-ethoxymethylfurfural (97%), methanol (99%), ethanol (CH₃CH₂OH, 99.8%), palladium(II) chloride (PdCl₂, 99.99%), ethylene glycol solution (50 mL), and the complete f-DNA/MXene solution was stirred for 30 minutes. Then, the supernatant was collected and dried in an oven at 120°C for 10 hours to obtain single-layer MXene NSs. To prepare the Pd-Ru/MXene nanocatalysts, a conventional microwave oven was used. Typically, 200 mM HMF, catalysts (50 mg), and anhydrous ethanol (EtOH, 20 mL) were added into the above-described 100 mL lab-made stainless-steel autoclave. The mixture was magnetically stirred, and the reactor was heated to a fixed optimized temperature of 120°C for 90 minutes of desirable reaction time at an N₂ pressure of 10 bar. The various catalytic systems of control-a (without catalyst and ethanol), control-b (without catalyst and in the presence of ethanol), Pd-Ru, MXene, and Pd-Ru/MXene were used in this study. Furthermore, investigations of the effect of the reaction time duration (30-150 minutes) on the performance of the etherification of HMF to EMF of the post-treated Pd-Ru/MXene catalyst were conducted. The reaction mixture was removed from the catalytic reactor at a given reaction time and diluted with a suitable solvent for the HPLC (Agilent 1200 equipped with a column of Bio-Rad Aminex HPX87H) and GC-MS (Agilent Technologies 7890A GC and GC-FID) analyses. For the recyclability test, used Pd-Ru/MXene catalyst (50 mg) was thermally reduced at 300°C for 2 hours under an H₂ atmosphere of 10 bar. Then, the etherification performances of HMF to EMF of the post-treated Pd-Ru/MXene catalyst were tested using the same experimental procedure. After first recycling, the used catalyst was separated by centrifugation and washed a few times with acetone and ethanol, and dried at 120°C for 2 hours in a vacuum oven prior to thermal reduction. Furthermore, the thermally reduced postreacted Pd-Ru/MXene catalyst was reused for up to five cycles using the same etherification procedure. The catalytic performance characteristics of HMF conversion (X, %), EMF selectivity (S, %), and EMF yield (Y, %) were determined according to Equations (1) to (3), respectively:

\[
\text{HMF conversion (\%)} = \frac{I_{\text{HMF}} - F_{\text{HMF}}}{I_{\text{HMF}}} \times 100, \tag{1}
\]

\[
\text{EMF selectivity (\%)} = \frac{m_{\text{EMF}}}{I_{\text{HMF}} - F_{\text{HMF}}} \times 100, \tag{2}
\]

2.2 Synthesis of Pd-Ru/MXene nanocatalysts via microwave irradiation

Initially, multilayer MXene sheets (1 g) were dispersed in N-Methyl 2-pyrrolidone (50 mL) by ultrasonication (VWR sonicator operate at 132 kHz frequency) for 10 minutes. Then, the supernatant was collected and dried in an oven at 120°C for 10 hours to obtain single-layer MXene NSs. To prepare the Pd-Ru/MXene nanocatalysts, a conventional microwave oven was used. Typically, 200 mM HMF, catalysts (50 mg), and anhydrous ethanol (EtOH, 20 mL) were added into the above-described 100 mL lab-made stainless-steel autoclave. The mixture was magnetically stirred, and the reactor was heated to a fixed optimized temperature of 120°C for 90 minutes of desirable reaction time at an N₂ pressure of 10 bar. The various catalytic systems of control-a (without catalyst and ethanol), control-b (without catalyst and in the presence of ethanol), Pd-Ru, MXene, and Pd-Ru/MXene were used in this study. Furthermore, investigations of the effect of the reaction time duration (30-150 minutes) on the performance of the etherification of HMF to EMF of the post-treated Pd-Ru/MXene catalyst were conducted. The reaction mixture was removed from the catalytic reactor at a given reaction time and diluted with a suitable solvent for the HPLC (Agilent 1200 equipped with a column of Bio-Rad Aminex HPX87H) and GC-MS (Agilent Technologies 7890A GC and GC-FID) analyses. For the recyclability test, used Pd-Ru/MXene catalyst (50 mg) was thermally reduced at 300°C for 2 hours under an H₂ atmosphere of 10 bar. Then, the etherification performances of HMF to EMF of the post-treated Pd-Ru/MXene catalyst were tested using the same experimental procedure. After first recycling, the used catalyst was separated by centrifugation and washed a few times with acetone and ethanol, and dried at 120°C for 2 hours in a vacuum oven prior to thermal reduction. Furthermore, the thermally reduced postreacted Pd-Ru/MXene catalyst was reused for up to five cycles using the same etherification procedure. The catalytic performance characteristics of HMF conversion (X, %), EMF selectivity (S, %), and EMF yield (Y, %) were determined according to Equations (1) to (3), respectively:

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\[
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\]
Yield (\%) = \frac{m_{\text{EMF}}}{I_{\text{HMF}}} \times 100, \quad (3)

where \( I_{\text{HMF}} \) is the initial HMF concentration in M, \( F_{\text{HMF}} \) is the final HMF concentration in M, and \( m_{\text{EMF}} \) is the final number of moles of EMF in the obtained products. Additionally, the optimal experimental conditions are used for the direct conversion of fructose into EMF over Pd-Ru/MXene (Reaction conditions: reaction temperature of 120°C, 20 mL of ethanol, 200 mmol of fructose, and catalyst dosage of 50 mg).

3 | RESULTS AND DISCUSSION

3.1 | Formation mechanism of the Pd-Ru/MXene catalyst

The multilayered MXene was subjected to ultrasonication and filtration, and the dried exfoliated MXene powder was used as the basis for the preparation of the Pd-Ru/MXene catalyst. Figure 1 presents a schematic illustration of the preparation of the Pd-Ru/MXene catalyst in the presence of fish sperm DNA (f-DNA). Initially, f-DNA interacts with the MXene NSs via the π-π stacking between the graphite structure of MXene NSs and the aromatic nucleobases of DNA to prevent the agglomeration of the MXene NSs, enhancing the surface area and increasing the number of the anchoring sites for the adsorption of the Pd(II)/Ru(III) ions.35 Furthermore, the Pd(II)/Ru(III) were converted to the metallic Pd0/Ru0 using NaBH4 as the reducing agent. Thus, the initially formed Pd3+/Ru3+ cluster undergoes microwave irradiation for 30 seconds, resulting in the formation of sphere-like Pd-Ru NPs that can then be electrostatically assembled on the surfaces of the MXene NSs. The individual Pd-Ru NPs on the MXene NSs can amplify the catalytic activity toward the etherification reaction of HMF to EMF compared to the Ru-Pd-based nanomaterials and bulk materials. The microstructure of the received MXene displayed a multilayer stack of the MXene layers separated by gaps, as shown in Figure 2A,B. The TEM image of Pd-Ru in Figure 2C shows sphere-like Pd-Ru nanoparticles with average sizes of 5 nm were uniformly observed throughout the micrograph.

The morphology of the Pd-Ru/MXene catalyst observed by SEM (Figure 2D) showed MXene layers that were completely covered with the ultra-small Pd-Ru NPs. Figure 2E shows the results of the EDS analysis of the Pd-Ru/MXene catalyst that consists of Ti, C, O, Ru, and Pd, while no other elements are observed in the depicted EDS spectrum. The TEM images in Figure 2F,G clearly show that the sphere-like Pd-Ru NPs with a size of 8 nm were grown on the surfaces of MXene NSs under microwave irradiation. The HR-TEM image in Figure 2H shows a crystalline structure with the lattice lines of the Pd-Ru/MXene catalyst. The results of this investigation reveal that the Pd-Ru hcp crystalline phase grown on the surfaces of MXene sheets had the lattice constants of the Pd-Ru(111) plane that was determined as \( a = 0.22 \) nm and \( c = 0.31 \) nm.35,36 The SAED pattern of the Pd-Ru/MXene catalyst showed a polycrystalline structure with small grains, as shown in Figure 2I. The (111), (200), and (220) diffraction peaks associated with the hcp crystalline phase of Pd-Ru and the diffraction peak of (002) corresponding to the crystalline phase of the MXene are observed in the SAED pattern.37,38 Figure 3A depicts the XRD patterns of the multilayered MXene, Pd-Ru, and Pd-Ru/MXene catalysts. The diffraction peaks at 8.2°, 18.7°, 34.5°, 42.6°, and 60.5 are assigned to the (002), (004), (008), (101), and (110) planes of pure MXene, respectively. The Pd-Ru NPs showed major diffraction peaks at 40.7°, 46.3°, and 68.3° that correspond to the (111), (200), and (220) Miller indices, respectively, and are attributed to hcp Pd3+/Ru3+, according to the JCPDS no. 01-089-4903.37,39,40 The lattice constants of the major diffraction peak corresponding to the (111) lattice plane were estimated by Rietveld refinement as \( a = 0.2117 \) nm and \( c = 0.3651 \) nm for the hcp Pd-Ru lattice.

The XRD pattern of the Pd-Ru/MXene catalyst displayed the existence of two crystalline phases, namely MXene and hcp Pd-Ru, as depicted in Figure 3A. The diffraction angles at 40.6°, 46.1°, and 68.2° corresponding to the (111), (200), and (220) Miller indices, respectively, are attributed to hcp Pd3+/Ru3+, while the diffraction peaks at 5.2°, 15.7°, 32.5°, 41.6°, and 61.5° are assigned to the (002), (004), (008), (101), and (110) planes of pure MXene,
respectively.38 Using Rietveld refinement, the lattice constants of the (111) Miller index for the hcp Ru-Pd were determined as \( a = 0.2027 \text{ nm} \) and \( c = 0.3025 \text{ nm} \).41,42 This result revealed that the lattice cell parameters of the Pd-Ru/MXene are estimated to be lower than those of the pure Pd-Ru NPs due to the smaller particle sizes of the Pd-Ru NPs that are completely immobilized on the surfaces of the MXene NSs with no agglomeration. Specifically, the agglomeration-free individual NPs provide a larger number of catalytic sites, promoting faster and more selective catalytic reactions. Furthermore, the SSA and pore size distribution of the Pd-Ru/MXene catalyst was estimated from \( \text{N}_2 \) physisorption isotherms and pore size distribution analysis as depicted in Figure 3B,C. As shown in Figure 3B, the Brunauer-Emmett-Teller (BET) SSA of the Pd-Ru/MXene catalyst was estimated as 117 m\(^2\) g\(^{-1}\). From the isotherms. Importantly, the as-prepared Pd-Ru/MXene catalyst possessed higher SSA than the recently reported MXene-based composites due to the presence of the ultra-small Pd-Ru NPs on the surfaces of 2D MXene NSs that can adsorb more \( \text{N}_2 \) gas. As shown in Figure 3C, the Barrett-Joyner-Halenda (BJH) pore size of the Pd-Ru/MXene catalyst was estimated to be 10 to 20 nm from the desorption isotherm curve. A large SSA and pore sizes of the catalyst typically lead to high catalytic activity, particularly for MXene-based materials.43 The XPS analysis was used to determine the chemical states and chemical composition of the Pd-Ru/MXene catalyst. The survey XPS spectra in Figure 3D showed clear signals of C 1s + Ru 3d, Pd 3d, Ti 2p, and O 1s peaks are observed at the binding energies of 283.2, 338.3, 461.4, and 526.9 eV, respectively.34 Figure 3E shows the deconvoluted Ru 3d spectra in the Pd-Ru/MXene catalyst display Ru\(^0\) 3d\(_{5/2}\) and Ru\(^{0+}\) 3d\(_{3/2}\) attributed at 278.6 and 283.3 eV, while the RuO\(_2\) 3d\(_{5/2}\) peak is noticed at 281.5 eV, suggesting the mild surface oxidation.

FIGURE 2 A,B, FE-SEM images of multilayered MXene sheets at different magnifications, C, TEM image of Pd-Ru nanoparticles, D, FE-SEM image of the Pd-Ru/MXene catalyst, E, EDS spectra of the Pd-Ru/MXene catalyst, F,G, TEM images of the Pd-Ru/MXene catalyst at different magnifications, H, HR-TEM image of individual Pd-Ru NPs on MXene nanosheets, and I, SAED pattern of the Pd-Ru/MXene catalyst [Colour figure can be viewed at wileyonlinelibrary.com]
Additionally, a broad deconvoluted peak was attributed at 284.2 eV correspond to the C–C (sp²) structure. The deconvoluted C 1s second in Figure 3F displayed three main peaks at 278.5, 282.7, and 284.2 eV that are associated with C=Ti=Tx, C=C, and C=C, respectively. Figure 3G shows the deconvoluted Pd 3d, which exhibits two spin-orbit split peaks of Pd 3d⁵/₂ and Pd 3d⁷/₂ with an energy gap of 4.5 eV. The high intense metallic deconvoluted peaks of Pd⁰ 3d⁵/₂ and Pd⁰ 3d⁷/₂ are attributed at the binding energies of 336.49 and 341.91 eV, while the less intense oxidized deconvoluted peaks of Pd²⁺ 3d⁵/₂ and Pd²⁺ 3d⁷/₂ are attributed at 331.01 and 342.68 eV, respectively. The deconvoluted Ti 2p spectra in Figure 3H exhibited two main spin-orbit split peaks of Ti p₃/₂ and Ti p₁/₂ at the binding energies of 457.3 and 462.5 eV, respectively. The deconvoluted peaks of Ti–C (sp³), Ti²⁺, and Ti–O are attributed to the binding energies of 458.13, 460.85, and 463.27 eV, respectively, that are correlated with the chemical state of the MXene. The O 1s peak is deconvoluted into two peaks at 529.73 and 532.94 eV corresponding to Ti–O (TiO₂), and Ti₃C₂(OH)ₓ·H₂O_ads, respectively, as shown in Figure 3I. The O and OH signals especially suggest the addition of the H₂O and surface termination of the MXene NSs due to the exposure of the catalyst to the atmosphere. H₂-TPD was used to examine the correlation between the active catalytic sites on the surfaces of the catalysts and the hydrogenation performances of the catalysts. H₂-
TPD profile of Pd-Ru in Figure 4A exhibits a major desorption peak at 210°C, which can be associated with the chemisorbed hydrogen. Although the H₂-TPD profile of Pd-Ru/MXene catalysts in Figure 4A displayed two distinguished desorption peaks at 200°C can be related to the chemisorbed hydrogen for Pd-Ru, and 370°C can be related to the chemisorbed hydrogen for MXene, respectively. The high amount of hydrogen was significantly desorbed at higher temperatures due to strongly-chemisorbed hydrogen and subsurface hydrogen on the MXene nanosheets. These studies indicate that the Pd-Ru/MXene catalysts show stronger hydrogen desorption behaviors at a higher temperature, which can be correlated to the intense metal-MXene interactions. On the other hand, NH₃-TPD profiles of Pd-Ru and Pd-Ru/MXene nanocatalysts were used to observe the acidic sites of the catalysts. Figure 4B shows the NH₃-TPD profiles of Pd-Ru and Pd-Ru/MXene nanocatalysts at a temperature range of 50 to 600°C. The desorption peak intensity of Pd-Ru/MXene nanocatalysts is obviously stronger than that of Pd-Ru nanocatalysts. Notably, Pd-Ru showed weak acidic sites, while Pd-Ru/MXene nanocatalysts provided a high amount of weak acidic sites and the highest total acidity (6.01 μmol g⁻¹) than Pd-Ru catalyst (1.07 μmol g⁻¹).

3.2 Etherification reaction of HMF to EMF

To evaluate the high-performance catalyst system, the Pd-Ru, MXene, and Pd-Ru/MXene catalysts were used for the catalytic etherification of HMF to EMF under the optimal reaction conditions, with the complete conversion results shown in Figure 5A. Prior to the catalytic test, the control-a (without catalyst and solvents) and control-b (without catalyst and in the presence of solvents) runs were carried out at the optimal experimental conditions of 120°C, 90 minutes, 200 mM HMF, ethanol as the solvent, and an N₂ pressure of 10 bar. The catalytic results of the control-a run showed negligible HMF conversion and EMF selectivity, while the control-b run showed a noticeable catalytic activity with 8% EMF selectivity at 10% HMF conversion due to the solvent effect as depicted in Figure 5A. However, noticeable amounts of by-products such as DEF and EL were also observed during the catalytic reaction. Furthermore, the as-prepared Pd-Ru, MXene, and Pd-Ru/MXene catalysts were employed for the catalytic etherification of HMF under optimal experimental conditions. Initially, the Pd-Ru catalyst was employed for the etherification of HMF using ethanol as the solvent with a catalyst dosage (50 mg) at 120°C for 90 minutes in 200 mM HMF with 10 bar N₂ pressure. The Pd-Ru catalyst showed significant EMF selectivity (%), EMF yield (%), and HMF conversion (%) of 85%, 36%, and 42%, respectively. Meanwhile, the exfoliated MXene NSs catalyst was found to possess a higher catalytic activity as observed from the HMF conversion efficiency (54%), EMF selectivity (98%), and EMF yield (53.4%) values and also generated the DEF and EL by-products due to the higher number of acid-base sites present on the individual MXene NSs. It is clear that the MXene NSs based catalyst has a higher acid site density (4.37 μmol g⁻¹) than the base site density (3.01 μmol g⁻¹), enhancing the production of EMF. Furthermore, the Pd-Ru/MXene catalyst showed higher catalytic activity with the EMF yield of 67%, EMF selectivity of 98%, and HMF conversion of 68%, as displayed in Figure 5A. This higher catalytic activity indicates that the Pd-Ru/MXene catalyst has a higher acid site density (6.01 μmol g⁻¹) and lower base site density (2.81 μmol g⁻¹) and these acid and base

![Figure 4](wileyonlinelibrary.com)
sites are the active catalytic centers that carry the catalytic etherification process of HMF. The more acidic nature of the Pd-Ru/MXene catalyst provided a favorable catalytic platform for the catalytic etherification of HMF to EMF. These preliminary results proved the higher catalytic performance of the Pd-Ru/MXene catalyst compared to that of Pd-Ru and that of the MXene catalyst and motivated the detailed testing of the use of the Pd-Ru/MXene catalyst for HMF etherification described below.

As shown in Figure 5B, the time of the reaction influenced the HMF conversion and the yields of EMF and other byproducts over the Pd-Ru/MXene catalyst at the optimal reaction conditions. The use of different time periods for the reaction (30-150 minutes) had a remarkable effect on the yields of EMF, DEF, and EL at various HMF conversion ratios. The EMF yield increased from 32% at the HMF conversion of 36% for 30 minutes, and then rapidly increased to 98% EMF yield at 100% conversion of HMF for 90 minutes. Furthermore, the EMF yield declined slightly to 78% at 100% conversion of HMF for 150 minutes, while the DEF and EL yields increased to 9% and 13%, respectively, due to the decomposition of EMF over the Pd-Ru/MXene catalyst. The results show a complete etherification reaction of HMF to EMF with trace levels of DEF and EL at the end of 90 minutes, confirming that 90 minutes is the optimal reaction time for the etherification reaction. Figure 5C shows the
selectivity of Pd-Ru/MXene catalyst for EMF and other side products along with HMF conversion at 120°C in 200 mM and 10 mL of ethanol with 10 bar N₂ plotted vs reaction time. Over the Pd-Ru/MXene catalyst, EMF selectivity increased from 83% at 36% HMF conversion for the first 30 minutes to 99% at 100% HMF conversion for 90 minutes. The maximum EMF selectivity observed at the reaction time of 90 minutes was attributed to the higher acid site density (6.01 μmol g⁻¹) on the surfaces of the catalyst that affected the spontaneous etherification reaction. The synergistic catalytic activity of the ultrasmall Pd-Ru NPs that were well-dispersed on the MXene substrate ultimately resulted in the spontaneous etherification reaction of HMF to EMF with a negligible generation of other byproducts. Meanwhile, higher selectivity for DEF (8%) and EL (12%) was obtained at the end of the reaction (150 minutes), indicating the decomposition of EMF over the catalyst in the reaction medium.

Recycling experiments were carried out to evaluate the practical applicability and chemical stability of the Pd-Ru/MXene catalyst, with the results shown in Figure 5D. Recycling experiments for the Pd-Ru/MXene catalyst were conducted at the optimal reaction conditions. After each etherification reaction, the spent catalyst was separated by centrifugation, washed several times with acetone and ethanol, and dried in a vacuum oven at 120°C for 3 hours. Prior to each catalytic test, the spent catalyst was thermally reduced at 300°C for 2 hours under a 10 bar N₂ atmosphere to remove the surface oxidation of the catalyst. As shown in Figure 5D, 98% EMF yield at 100% of HMF conversion was obtained for the first run, and then the EMF yield decreased slightly to 97% at 98% of HMF conversion for the fifth run. Overall, a decrease in the EMF yield and HMF conversion of only 2% was observed for the fifth run using the same experimental procedure, indicating that the as-prepared Pd-Ru/MXene catalyst was chemically stable and effectively promoted the etherification of HMF into EMF. A plausible reaction pathway for the etherification of HMF to EMF over the Pd-Ru/MXene catalyst was proposed based on the earlier reported studies and the present experimental results, as depicted in Figure 6.1,12,13,20-25 In particular, the proposed reaction pathway was suggested based on the results for the time dependence of the HMF etherification to the targeted EMF product and the byproducts 5-(diethoxymethyl)-2-furanmethanol (DEF) and ethyl levulinate (EL) at the optimal reaction conditions. Three parallel products of EMF, DEF, and EL were observed during the HMF etherification reaction over the Pd-Ru/MXene catalyst. Initially, the HMF conversion and EMF yield increased with increasing reaction time up to 90 minutes due to the direct etherification reaction between the HMF molecules and ethanol over the acid sites of the Pd-Ru/MXene catalyst. In this direct etherification reaction, water molecules were released and then reacted with the excess of HMF in the reactor, producing the noticeable formation of DEF over the catalyst. On the other hand, the EL yield increased as the reaction time was increased to 150 minutes. It is clear that the two main reactions that gave rise to the EL yield increase were the decomposition of EMF at a longer reaction time and the direct reaction of HMF with ethanol to produce EL through a hydration/ring-opening mechanism.1 In particular, longer reaction time leads to the decomposition of EFM over the Pd-Ru/MXene catalyst, enhancing EL formation. These results indicate that the developed Pd-Ru/MXene catalyst showed better etherification performance of HMF into EMF at a shorter reaction time which is beneficial for the industrial application of these catalysts. Furthermore, the catalytic performances of the Pd-Ru/MXene catalyst and several recently reported catalysts such as H₁.₁₅Nb₁.₁₅Mo₀.₃₅O₆,β zeolite (BEA300),12 35% TaTPA/SnO₂,13 H₆SiW₁₂O₄₀/MCM-41 nanospheres,20 Cs₂STA,21 Fe₂O₆@C-SO₂H,22 Al-MCM-41,23 MCM-41-supported phosphotungstic acid,24 and mesoporous niobiumoxophosphinate (NbP) were compared.25

In particular, the MXene-based catalyst is a promising and suitable candidate for use in the acid-catalyzed system for the conversion of agricultural biomass into value-added chemicals and sustainable liquid fuel production. On the basis of the superior catalytic property of Pd-Ru/MXene catalyst, fructose was used for the direct conversion of EMF at optimal reaction conditions (reaction temperature, 120°C; ethanol, 20 mL; fructose, 200 mmol; catalyst dosage, 50 mg). Figure 7A depicted the general fructose dehydration reaction mechanism over Pd-Ru/MXene catalyst. Initially, fructose was dehydrated to produce 5-HMF over Pd-Ru/MXene catalyst by Lewis and Bronsted acid sites present in the MXene nanosheets while the obtained 5-HMF would be further etherified to formed EMF using ethanol as a reaction medium. Notably, Pd-Ru/MXene catalyst showed a higher acid-base density that arises from the MXene nanosheets could...
effectively involve the dehydration process, resulting in the formation of EMF through the etherification process. Studies confirmed that the Pd-Ru/MXene catalyst exhibited a higher amount of acid sites of 6.01 μmol g⁻¹, thus enhancing the yield of EMF. This synergistic catalytic effect was further confirmed with the experimental results, as shown in Figure 7B. Prolonging reaction time, the conversion of the fructose (Frct) and yield of the products increases with increasing the reaction time from 30 to 240 minutes at a fixed reaction temperature of 120°C in ethanol. The direct fructose etherification reaction is examined at 30 minutes, 25% of fructose conversion with 15% EMF yield, 8% of HMF, and 2% other by-products are achieved. Further, the reaction time is increased from 30 to 150 minutes, and the fructose conversion efficiency increases to 86% along with increasing the yield of EMF (82%) and EL (2%), while the yield of HMF decreased to 0.5% at 150 minutes. Notably, HMF has been completely converted into EMF within 150 minutes reaction time, indicating that the Pd-Ru/MXene catalyst afforded enough acid sites for the complete dehydration and etherification of fructose. Figure 7C shows the effect of reaction time vs selectivity of the products over Pd-Ru/MXene catalyst. As estimated, the selectivity of the EMF is largely promoted at 120°C, which increased 89% at 30 minutes to 94% at 150 minutes, while the selectivity of the HMF decreased from 18% at 30 minutes to 1% at 150 minutes. However, a further increase in the reaction time beyond 150 minutes, the EL selectivity increased to 6% at 150 minutes, which suggesting that the longer reaction time is promoted to the formation of EL via alcoholysis of HMF. Significance of this study demonstrated that the Pd-Ru/MXene catalyst exhibits the superior catalytic activity toward the direct conversion of fructose into 5-EMF which is promising conversion method for the production of biofuels from biomass.

4 | CONCLUSION

In summary, microwave irradiation was used to synthesis the Pd-Ru and Pd-Ru/MXene nanocatalysts. TEM and SEM micrographs showed that the sphere-like Pd-Ru NPs with a size of 8 nm are uniformly decorated on the 2D MXene NSs. The XRD and XPS analysis clearly demonstrated that the successful formation of the hcp Pd-Ru/MXene nanocatalysts showed a higher SSA of 117 m² g⁻¹ with a pore size distribution of 10 to 20 nm, and the systematic formation mechanism was proposed to explain the effectiveness of the synthesis process. Furthermore, Pd-Ru/
MXene catalyst was used as the high-performance catalyst for the selective etherification of HMF to EMF toward sustainable liquid fuel production. The Pd-Ru/MXene catalyst exhibits a higher EMF yield of 98% at 100% HMF conversion was attained at the optimal reaction conditions. This catalyst showed a higher acid site density (6.01 μmol g⁻¹) that influenced the spontaneous etherification of HMF to EMF with a negligible content of the by-products. A recyclability study showed that the Pd-Ru/MXene was chemically stable over several consecutive cycles and participated effectively in the etherification reactions. More importantly, the fructose was directly converted into EMF over Pd-Ru/MXene catalyst at 120°C for 150 minutes. A high EMF yield of 82% and selectivity of 94% was obtained from fructose over Pd-Ru/MXene catalyst. Hence, the Pd-Ru/MXene catalyst is a suitable catalyst for the etherification of biomass-derived bio-oil compounds for industrial application.

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DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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