

Article

Zn Impregnation onto a Zeolite-Supported Metal Catalyst for Improving the Synergy Between Metal and Acid Sites: Facilitating the Production of 3-Acetyl-1-propanol

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Abstract

3-Acetyl-1-propanol (3-AP) is a key intermediate in the pharmaceutical and pesticide industries, which can be synthesized from the biomass derivative 2-methylfuran (2-MF) through a one-step hydrogenation process with significant economic and environmental benefits. Zeolite-supported metal catalysts showed feasible application, but simply regulating the acidic sites was difficult to break the activity–selectivity balance. Traditional single-metal Pd-based catalysts still suffer from low dispersion. This study constructed the PdZn/TS-1 catalyst for the efficient conversion of 2-MF into 3-AP. The low electronegativity of Zn facilitates the electron transfer from Zn to Pd, forming an electron-rich Pd active center. A small amount of Zn embedded in the Pd lattice causes lattice contraction, optimizing the spatial configuration of active sites. The synergy between the electronic and structural effects significantly improves catalytic performance. Under optimized conditions, the conversion rate of 2-MF reached 80.6%, and the yield of 3-AP reached 69.1%, providing a new paradigm for the design of catalysts for the directed hydrogenation of furan derivatives.

Keywords: 2-methylfuran; 3-acetyl-1-propanol; co-doped catalysis; metal effect

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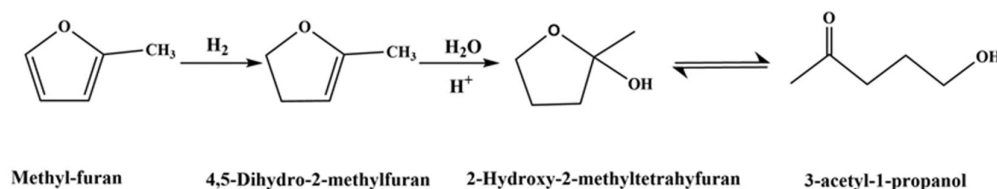
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1. Introduction

3-Acetyl-1-propanol (3-AP) is a key intermediate in organic synthesis and fine chemicals. The coexistence of a ketone carbonyl and a primary hydroxyl group endow it with excellent reactivity. 3-AP could be synthesized through multiple technical routes, including alkene oxidation [1,2], alkyne hydration [3–5], diol oxidation [6–8], hydroformylation [9], thioacetal method [10], and biomass conversion [11,12]. Among the aforementioned synthetic strategies, the catalytic hydrogenation-hydrolysis of 2-methylfuran (2-MF) (Scheme 1) has emerged as a research focus due to its remarkable industrial application potential. However, the current processes still encounter significant bottlenecks. The early Pd/C and 10% hydrochloric acid combined catalytic system was limited by the rapid deactivation of the catalyst. The PdCl₂/acidic aqueous solution system developed by Sun et al. imposed strict requirements on the corrosion resistance of equipment. The Ni/CeO₂ catalytic system with formic acid adopted by Schnipper et al. required neutralization of

the residual inorganic acid in the wastewater, increasing environmental costs and operational complexity. These existing problems provide a clear direction for the development of new green catalytic systems.



Scheme 1. Catalytic conversion of 2-MF into 3-AP.

Zeolite-supported metal catalysts show good bifunctional catalytic performance used in various reactions, such as hydrocracking [13], hydrocarbon isomerization [14] and ammonia synthesis [15]. Zhang Tao's group [16] constructed such a system by confining highly dispersed ultra-small Ru nanoclusters within Y-type zeolite micropores and doping rare earth element La. This design enhances Ru dispersion in zeolite channels and forms a “confined proximity” structure of metal–acid active sites. The short-range synergy between Ru hydrogenation sites and zeolite acid sites significantly promotes ethyl levulinate hydrodeoxygenation activity and valerate yield. In our previous work [17], Pd nanoparticles encapsulated in ZSM-5 molecular sieves exhibited excellent catalytic performance for 2-MF conversion to 3-AP. This advantage stems from the molecular sieve's confinement effect and optimized acid sites, which strengthen metal–acid synergy and thus enhance catalytic performance.

Regulating acidic and metal sites is at the core of optimizing the performance of bifunctional catalysts [18], and this strategy provides an important contribution to addressing the process bottleneck of the conversion of 2-MF to 3-AP. However, existing studies on this reaction mostly focus on the regulation of acidic sites and the constraints on the local microenvironment of the metal–acid, and pay relatively less attention to the state modification of the metal active sites [19].

Research in related fields has confirmed that precise regulation of metal sites can significantly enhance catalytic performance. Qian Ge's team [20] integrated different palladium sites into copper catalysts, optimized the local environment of copper active sites to optimize the hydrogenation path of propyne, and successfully prepared polymer-grade propylene. Lu Jilin's team [21] designed an Au@1ml-Pt bimetallic single-layer core–shell catalyst and achieved efficient conversion of halogenated nitrobenzene to halogenated aniline by regulating the geometry and electronic properties of the active sites, with a selectivity of 99%. These studies provide important references for the design of catalysts for the 2-MF to 3-AP reaction and highlight the feasibility and potential of optimizing catalytic performance through the modification of metal sites [22].

Thus, this study proposes a bifunctional catalytic system of Zn-doped Pd loaded on TS-1 molecular sieve for the catalytic conversion of 2-MF into 3-AP. In this study, PdZn/TS-1 catalysts with varying Pd/Zn molar ratios (12/1, 6/1, 3/1, 2/1) were fabricated via the co-impregnation method, and their physicochemical properties were systematically characterized using advanced techniques including X-ray diffraction (XRD), NH₃ temperature-programmed desorption (NH₃-TPD), transmission electron microscopy (TEM), H₂ temperature-programmed reduction (H₂-TPR), and X-ray photoelectron spectroscopy (XPS). Characterization and catalytic results reveal that doping a small amount of Zn into the Pd-based catalyst system effectively modulates the surface electron-enriched state of Pd. Moreover, Zn doping also caused the lattice contraction of Pd. The regulatory effect exerts a positive promotional impact, not only enhancing the hydrogenation

efficiency of 2-MF but also significantly improving the selectivity toward the target product 3-AP.

2. Results and Discussion

2.1. Experimental Results

The catalytic performance of Pd/Ts-1 catalysts with different Pd loadings (0.1%, 0.3%, 0.6%, and 1.0%) in the catalytic conversion of 2-MF was investigated (Figure 1). For Pd/Ts-1 (0.1%), the conversion was 10% with a 3-AP yield of 5%, attributed to insufficient active Pd sites. With increased loadings of Pd, the conversion and yield of 3-AP were improved, as more Pd sites enhanced the synergy between metal and acidic sites of Ts-1. Pd/Ts-1 (0.6%) exhibited a peak conversion of 70% and 3-AP yield of 40%, benefiting from the optimal synergy between metal and acid sites. When Pd loading further increased to 1.0%, the conversion of 2-MF dropped to 50% and 3-AP yield decreased to 30%. The decreased catalytic efficiency is likely due to insufficient acid sites and aggregation of metal nanoparticles.

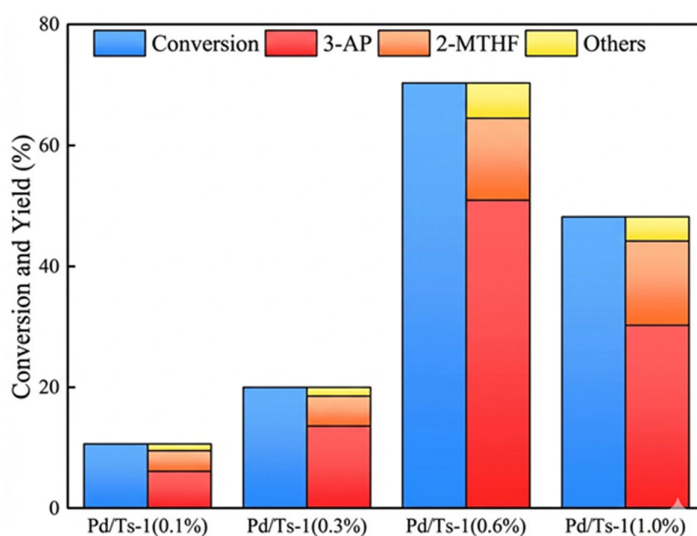


Figure 1. The catalytic performance of catalysts with different Pd loadings. Reaction conditions: 25 mL 10% 2-MF aqueous solution, 0.3 g catalyst, 80 °C, 1 MPa, 6 h.

The catalytic performance of Pd/Ts-1 (0.6%) reduction at different temperatures was evaluated (Figure 2). When the catalysts were reduced at 265 °C, the conversion reached a maximum of 75% and the yield of 3-AP peaked at 60%, indicating that Pd species was sufficiently reduced at this temperature to achieve good catalytic performance with balanced metal–acid synergy. In contrast, the Pd nanoparticles could not be fully reduced at lower reduction temperatures (e.g., 215 °C reduction), leading to poor catalytic performance. When the reduction temperature increased to 315 °C, the catalytic activity and yield of 3-AP was slightly decreased. Further increasing the reduction temperature to 365 °C, the conversion declined further, which might be attributed to the agglomeration of Pd nanoparticles under high temperature.

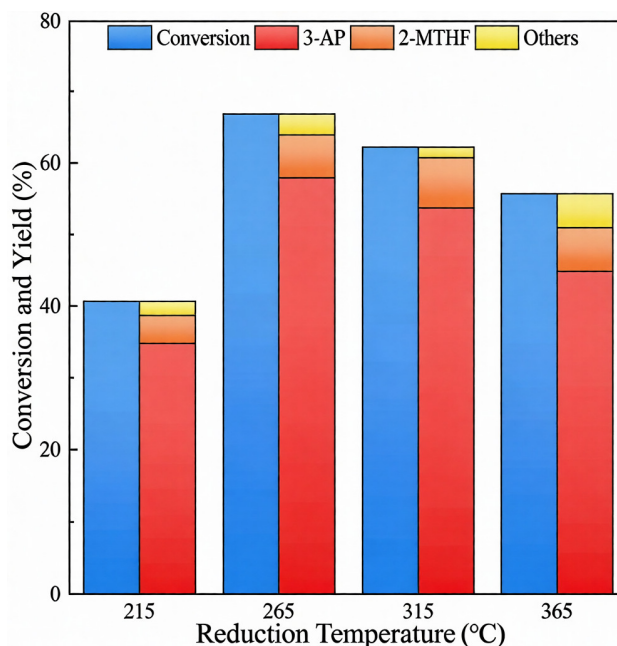


Figure 2. The effect of reduction temperature on the catalytic performance of Pd/TS-1. Reaction conditions: 25 mL 10% 2-MF aqueous solution, 0.3 g catalyst, 80 °C, 1 MPa, 6 h.

To improve the catalytic performance of Pd/TS-1, the second metal was doped into Pd/TS-1 (0.60.%) and a series of bimetallic Pd-based catalysts (PdZn, PdFe, PdPt, PdRu, PdCu, PdNi) supported by TS-1 were prepared (the second metal loadings fixed at 0.1%). The catalytic performance of PdM/TS-1 catalysts were studied under optimal conditions (Figure 3). Among them, PdZn/TS-1 exhibited superior performance with 80% 2-MF conversion and 70% 3-AP yield (3-AP as the dominant product). PdRu/TS-1 and PdCu/TS-1 catalysts show good catalytic activity. However, poor selectivity for 3-AP was obtained due to the increased amount of 2-MTHF. The results indicate that the doping of Ru and Cu diverts the reaction pathway to the byproduct 2-MTHF, sacrificing 3-AP selectivity. The catalytic activity of PdPt/TS-1 was only 70% with a decreased yield of 3-AP; moreover, the activity of PdFe/TS-1 catalysts were obviously reduced, which indicates that doping of Fe is unfavorable for the accessibility of active sites. The activity and selectivity of 3-AP was obviously decreased with PdNi/TS-1 catalysts, resulting from the poor accessibility of active sites after Ni doping. Moreover, the introduction of Ni promotes the full hydrogenation of 2-MF into 2-MTHF, which cannot be further converted into 3-AP.

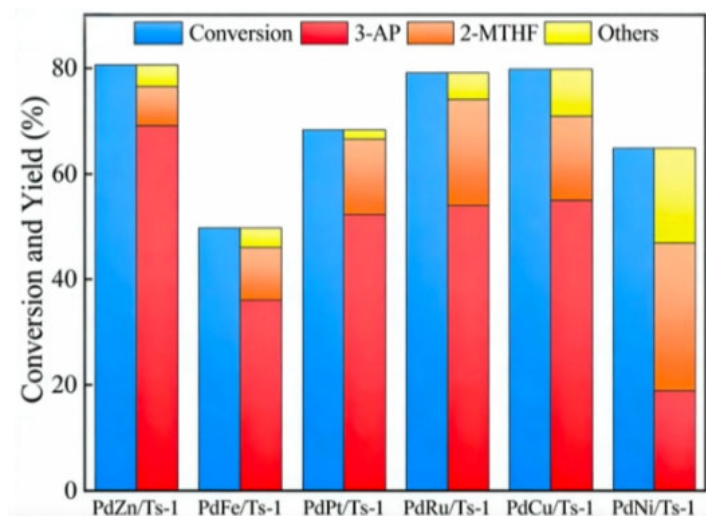


Figure 3. The catalytic performance of PdM/Ts-1 catalysts. Reaction conditions: 25 mL 10% 2-MF aqueous solution, 0.3 g catalyst, 80 °C, 1 MPa, 6 h.

The catalytic performance of PdZn_x/TS-1 (x represents the loading of Zn) catalysts with varying Zn loadings was systematically investigated (Figure 4). For PdZn_{0.05}/TS-1, 70% conversion of 2-MF and a 55% yield of 3-AP were achieved. For the PdZn_{0.1}/TS-1 catalyst, 2-MF conversion reached 80% and 3-AP yield attained 70%. This superior catalytic performance was attributed to the better bifunctional synergy after Zn doping. However, with increased Zn loading higher than 0.1% (e.g., 0.2%, 0.3%, 0.6%), both the conversion of 2-MF and the yield of 3-AP dropped drastically to almost zero. In summary, Zn loading critically regulates the catalytic behavior of Pd and 0.1% loading of Zn is optimal for enhancing the metal–acid synergy, whereas excessive Zn loading results in an almost complete loss of catalytic activity.

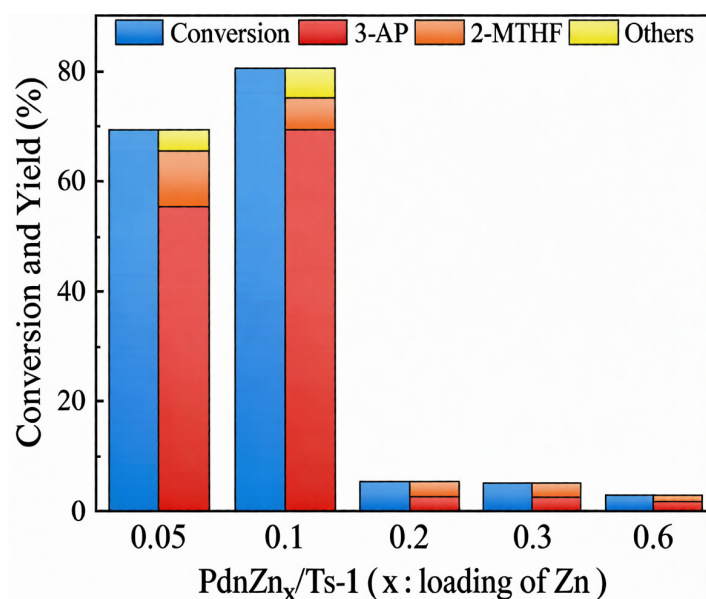


Figure 4. The catalytic performance of PdZn_x/TS-1 catalysts. Reaction conditions: 25 mL 10% 2-MF aqueous solution, 0.3 g catalyst, 80 °C, 1 MPa, 6 h.

2.2. Structural and Morphological Characterization

2.2.1. Structure and Morphology of Catalysts

The XRD patterns of the catalysts are presented in Figure 5a. As observed from Figure 5a, the PdZn_x/TS-1 catalyst shows a diffraction pattern similar to that of zeolite TS-1 (JCPDF: 44-0697) [23]. Furthermore, no distinct Pd diffraction peak is detected at $2\theta = 40^\circ$, which is caused by the low loading or high dispersion of metallic Pd [24]. The N₂ adsorption–desorption isotherm was evaluated to study the structure of PdZn_x/TS-1 catalysts. When the Zn loading is at 0.1%, the specific surface area (S_{BET}) of the catalyst reaches 498 m²/g, which is the highest among all samples. The PdZn_{0.1}/TS-1 catalyst also exhibits the highest adsorption capacity among all samples [25], indicating that the material surface has the largest area available for the adsorption of substrates. The total pore volume corresponding to 0.1% Zn loading is 0.2 cm³/g, which is higher than that of other samples (In Table 1, 0.14 cm³/g for pure Pd/TS-1 and 0.13 cm³/g for the sample with 0.2% Zn loading). The adsorption capacity of PdZn_{0.1}/TS-1 increases more significantly in the medium-to-high pressure region ($p/p_0 \approx 0.5$), suggesting sufficient pore volume [26], which is beneficial for the mass transfer and diffusion of reactants/products.

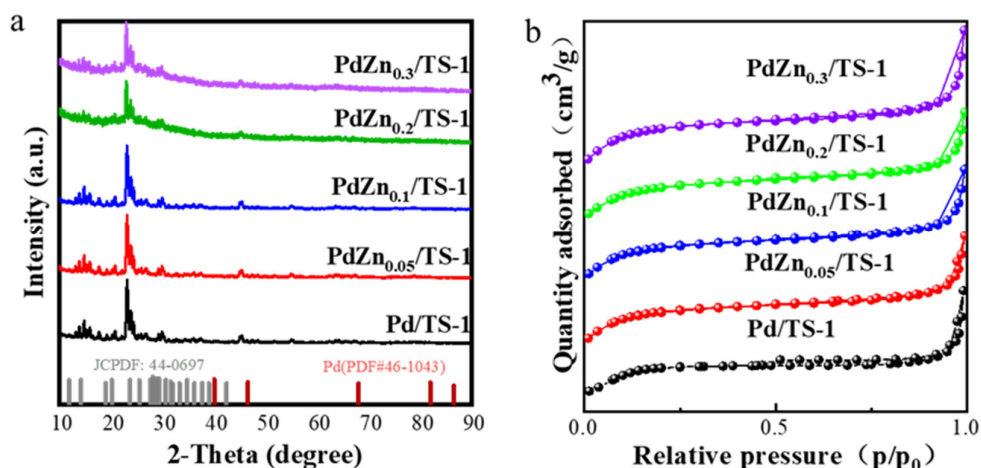


Figure 5. (a) X-ray powder diffraction patterns and (b) N₂ adsorption–desorption isotherms of PdZn_x/TS-1.

Table 1. Physical properties of PdZn_x/TS-1 catalysts with different Pd/Zn molar ratios.

Sample	Pd Loading	Zn Loading	S_{BET}^a (m ² /g)	V_{total}^b (cm ³ /g)	d_p^b (nm)	Average Particle Size (nm)
Pd _{0.6} /TS-1	0.6%	0	450	0.14	5.3	2.95
Pd _{0.6} Zn _{0.05} /TS-1	0.6%	0.05%	475	0.16	5.8	2.92
Pd _{0.6} Zn _{0.1} /TS-1	0.6%	0.1%	498	0.20	6.3	2.89
Pd _{0.6} Zn _{0.2} /TS-1	0.6%	0.2%	430	0.13	4.8	2.94
Pd _{0.6} Zn _{0.3} /TS-1	0.6%	0.3%	428	0.14	4.6	2.98

^a Calculated by N₂ adsorption–desorption isotherm using the Brunauer–Emmett–Teller method (BET) method. ^b Calculated by N₂ adsorption–desorption isotherm using the Barrett–Joyner–Halenda (BJH) method.

Based on the systematic coMParative analysis of electron microscopy characterizations, TEM images show that the PdZn NPs in PdZn_{0.1}/TS-1 are uniformly dispersed with an average particle size centered at 2.89 nm (Figure 6a), which is slightly smaller than the 2.95 nm of Pd NPs in Pd/TS-1 (Figure 6e) [27]. Figure 6b,g confirm the formation of an

ordered PdZn intermetallic phase, where the corresponding lattice fringes match well with the PdZn(111) crystal plane [28]. A direct lattice contraction is observed, with the spacing of PdZn(111) measuring 0.218 nm compared to 0.224 nm for Pd(111). Furthermore, energy-dispersive spectroscopy (EDS) mapping (Figure 6h) clarifies the elemental distribution, confirming the coexistence of both Pd and Zn species. The high degree of spatial overlap between the palladium (yellow) and zinc (blue) signals verifies atomic-level intimate contact within the well-fabricated catalyst [29]. The observed lattice contraction, distinct diffraction patterns, and overlapping elemental signals collectively verify the formation of an atomically ordered PdZn intermetallic phase. This structural transformation provides key evidence for the catalyst's potentially superior activity and selectivity from the perspectives of geometric and electronic effects.

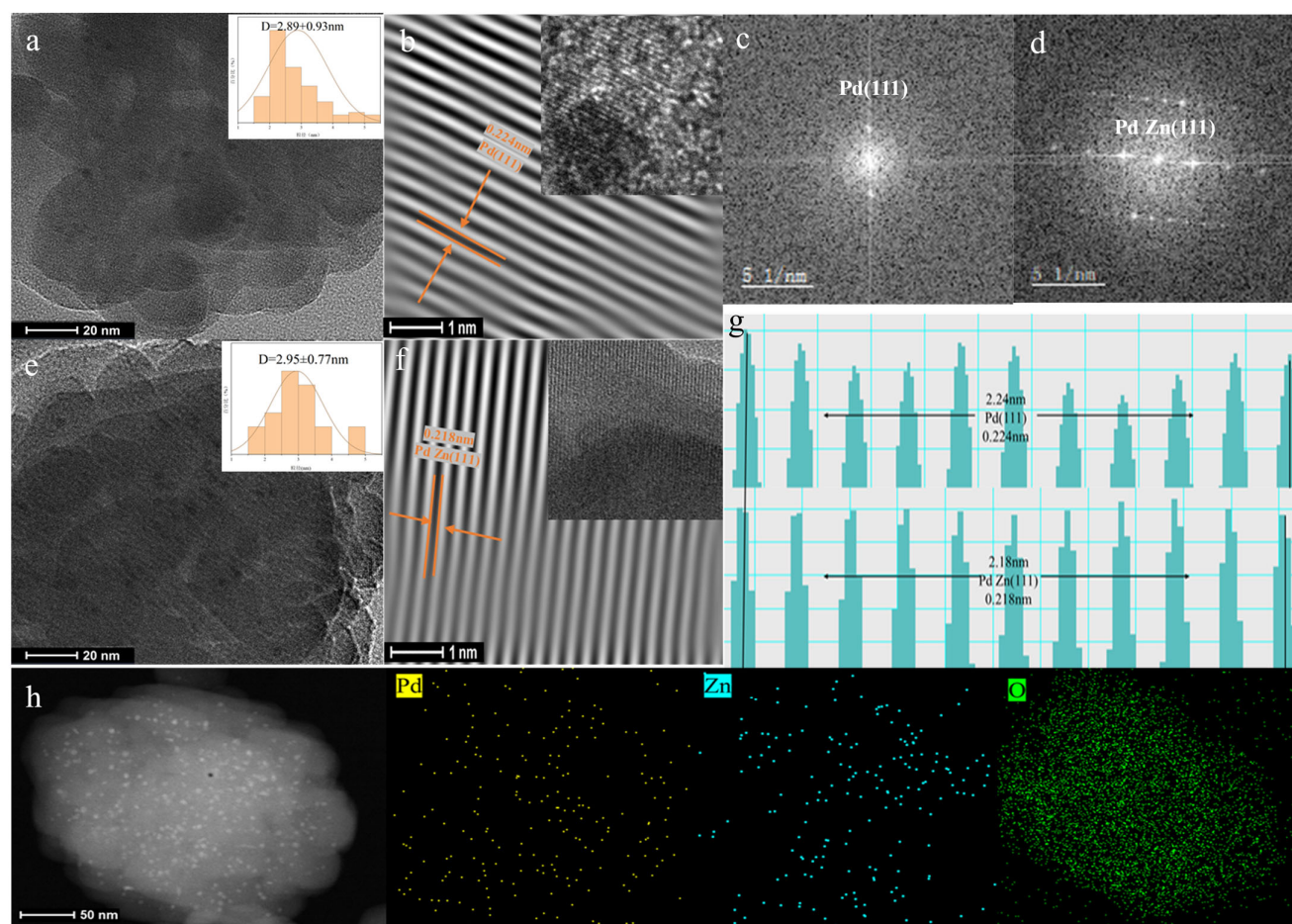


Figure 6. (a,d) TEM image of Pd/TS-1 and PdZn_{0.1}/TS-1. (b,e) HR-TEM image of Pd/TS-1 and PdZn_{0.1}/TS-1. (c,f) Inverse FFT (IFFT) of Pd(111) and PdZn(111). (g) Lattice spacing of Pd(111) and PdZn(111). (h) Corresponding EDS mapping images of the PdZn_{0.1}/TS-1.

2.2.2. Chemical Properties of Catalysts

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical states and electronic structures of elements on the catalyst surface. As shown in Figure 7a, two characteristic peaks at binding energies (BE) of 335.1 eV and 340.4 eV corresponded to the 3d_{5/2} and 3d_{3/2} orbitals of metallic Pd, respectively [30]. Compared with the Zn-free Pd/TS-1 catalyst, the Pd 3d_{5/2} peak of all PdZn_x/TS-1 catalysts shifted to lower binding energies. When Zn loading exceeded 0.1%, the binding energy of Pd no longer shifted

significantly, as the electron enrichment on the Pd surface stabilized with further Zn addition [31,32]. The negative shift in the Pd 3d peak indicates an increased electron cloud density of Pd atoms, which typically arises from electron transfer from Zn (or ZnO) with lower electronegativity to Pd [33] (i.e., the ligand effect). In Figure 7b, the peak at 1021.8 eV corresponds to the $2p_{3/2}$ orbital of Zn^{2+} [34]. For all $PdZn_x/TS-1$ samples, the BE position of the Zn 2p peak remained essentially unchanged, consistent with that of Zn^{2+} in typical zinc oxide (ZnO). The peak intensity increased with increasing Zn loading, indicating that Zn species in the catalyst mainly existed in the oxidized state (Zn^{2+}). Combined with the significant shift in the Pd 3d peak, it can be inferred that there is tight interfacial contact between these surface ZnO species and Pd nanoparticles [35]. Moreover, electron-rich Pd sites are believed to weaken the excessive adsorption of reaction intermediates, thereby suppressing side reactions such as deep hydrogenation and promoting the selective formation of the target product 3-AP. This is fully consistent with the performance results.

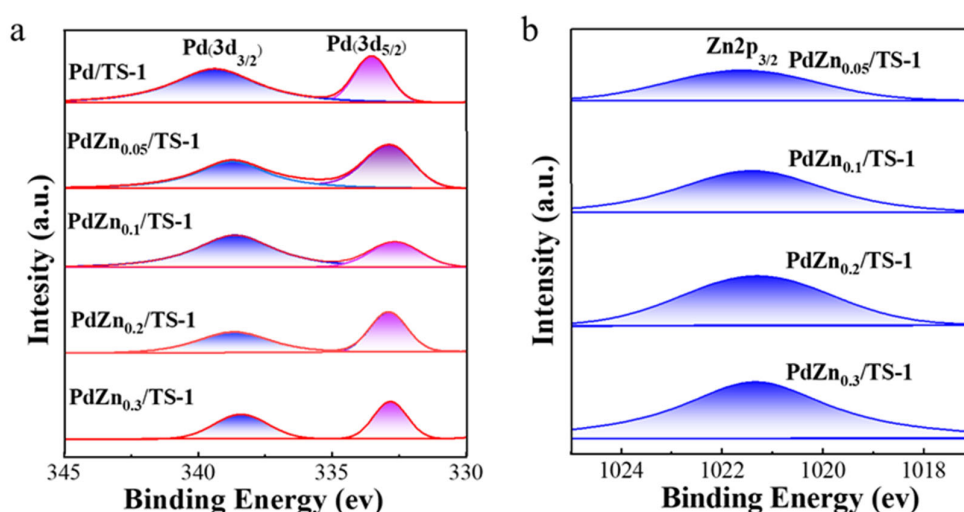


Figure 7. XPS spectra of $PdZn_x/TS-1$ catalysts: (a) Pd 3d and (b) Zn 2p.

As shown in Figure 8a, all samples exhibit a distinct absorption peak at approximately 1455 cm^{-1} , which is attributed to the characteristic vibration of pyridine adsorbed on Lewis' acid sites [36]. The $PdZn/TS-1$ samples with different Zn loadings and the pure $Pd/TS-1$ show highly similar peak shapes at this position, with only minor differences in intensity. The main reason is that titanium silicalite-1 (TS-1) is primarily a weakly Lewis-acidic material, and its acidity mainly originates from the tetrahedrally coordinated titanium centers in the framework [37]. Its Bronsted acid content is extremely low and usually negligible [38]. The NH_3 -TPD curves of all samples showed a gentle and highly overlapping peak, with no obvious peak shift (no difference in acid strength) or sharp change in signal intensity [39] (no difference in acid amount). This confirms that the acid strength distribution and total acid amount of the catalyst remain basically consistent in all samples [40].

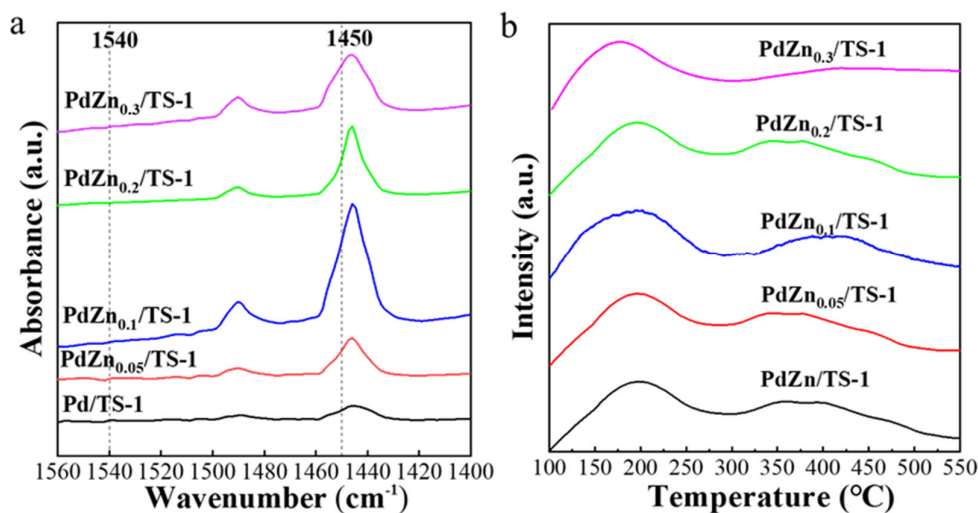


Figure 8. (a) Pyridine IR spectrum and (b) NH₃-TPD spectrum of PdZn_x/TS-1.

The pure Pd/TS-1 sample exhibits a sharp and symmetric reduction peak at approximately 90 °C [41]. This low-temperature reduction peak is attributed to the reduction in PdO species ($\text{Pd}^{2+} \rightarrow \text{Pd}^0$). The sharp peak shape and low reduction temperature indicate that the PdO species are well-dispersed on the support, which is easily reduced by hydrogen [42,43]. PdZn_x/TS-1 samples show a reduction peak shift towards lower temperatures, indicating that the introduction of Zn facilitated the reduction in the Pd species [44]. The consumption of hydrogen in PdZn_{0.1}/TS-1 exceeds that of others, indicating the higher surface hydrogen storage capacity.

In the in situ CO adsorption Fourier transform infrared (FT-IR) spectroscopy (Figure 9b), the absorption peaks at 2110 cm⁻¹ and 1934 cm⁻¹ is assigned to the linear and bridged adsorption of CO on the Pd(111) surface [45], respectively. Compared with the undoped Pd/TS-1 catalyst, the intensity of the Pd⁰-CO peak for all PdZn_x/TS-1 catalysts is significantly weakened and continues to decrease as the Zn loading (x) increases from 0.05% to 0.3%. In contrast, the intensity of the Pd²⁺-CO peak changes relatively slightly [46]. The peak at 2110 cm⁻¹ exhibits varying degrees of red shift with increasing Zn concentration. This is primarily attributed to the strengthening of the Pd–C bond caused by the electron-enriched region on the Pd surface after Zn modification, which enhanced the electron back-donation from the d-orbitals of Pd to the antibonding π^* orbital of CO [47].

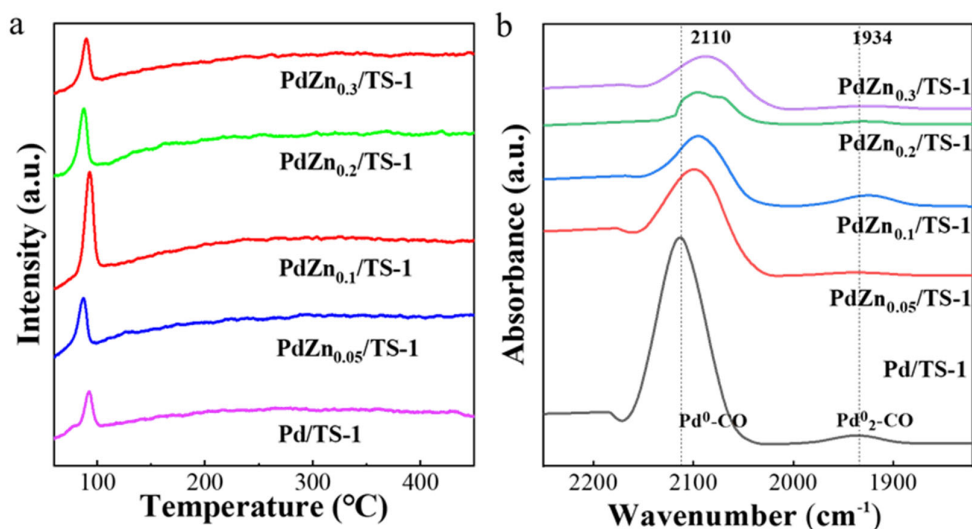


Figure 9. (a) H₂-TPR spectra and (b) CO-FTIR spectra of PdZn_x/TS-1.

2.3. Cycling Performance of PdZn/TS-1 Catalyst

Catalyst stability is a critical parameter for industrial applications, particularly for noble metal-based catalysts. Accordingly, the stability of PdZn_{0.1}/TS-1 was evaluated via reuse tests involving simple centrifugation washing. The catalyst maintained high catalytic conversion (80%) across multiple cycles, indicating no significant activity loss upon repeated use. Target product selectivity remained stable and high in each cycle, while the proportion of the by-product 2-methyltetrahydrofuran (2-MTHF) was consistently low—demonstrating excellent selectivity stability for the target product (Figure 10). In summary, PdZn_{0.1}/TS-1 exhibits good cycle stability, retaining both high conversion and target product selectivity over multiple reaction cycles, thus possessing promising industrial application potential.

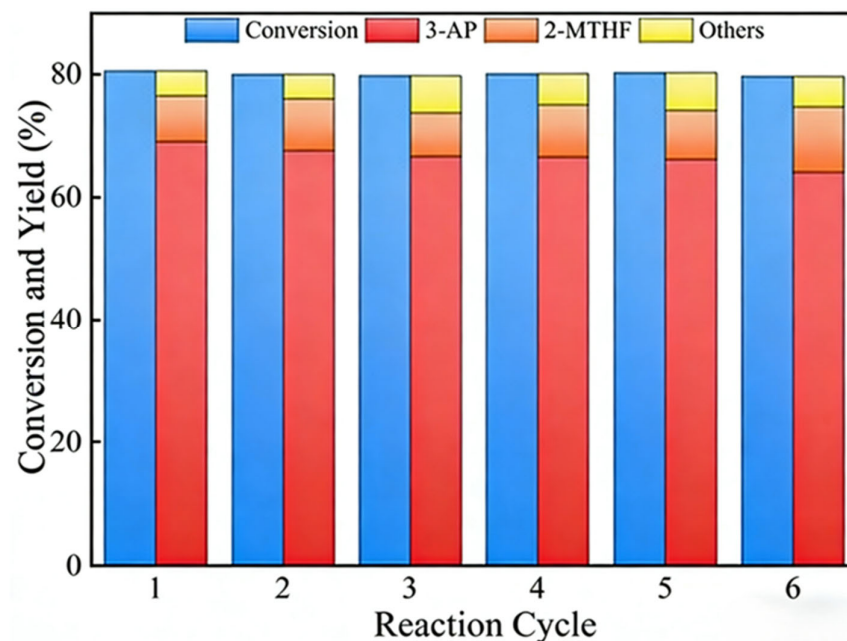


Figure 10. Cycling stability test of PdZn_{0.1}/TS-1 for 2-MF hydrogenation. Reaction conditions: 2.5 mL 2-MF, 25 mL H₂O, 80 °C, 1 MPa H₂, 8 h.

2.4. Reaction Pathway of 2-MF Hydrogenation

As shown in Figure 11, during the reaction, the initial conversion rate of 2-methylfuran during the first hour is very fast, but slows down with greater reaction time. No appreciable conversion of the 2-MF occurs with reaction time longer than 6 h, which might be ascribed to the insufficient substrate concentration. Moreover, the yield of the 4,5-dihydro-2-methylfuran firstly increased and then gradually decreased, indicating that 2-MF was first partially hydrogenated into 4,5-dihydro-2-methylfuran and then converted into 3-AP. Moreover, 2-MTHF increased along with reaction time, consistent with 3-AP, confirming that the production of 2-MTHF competed with the production of 3-AP. Combined with the relevant literature reports, the catalytic conversion of 2-methylfuran to 3-acetyl-1-propanol can be divided into the following steps. First, 2-methylfuran is hydrogenated at metal sites to generate 2-methyltetrahydrofuran and the intermediate 2M45D, and then 2M45D is hydrolyzed at acidic sites to form the product 3-acetyl-1-propanol.

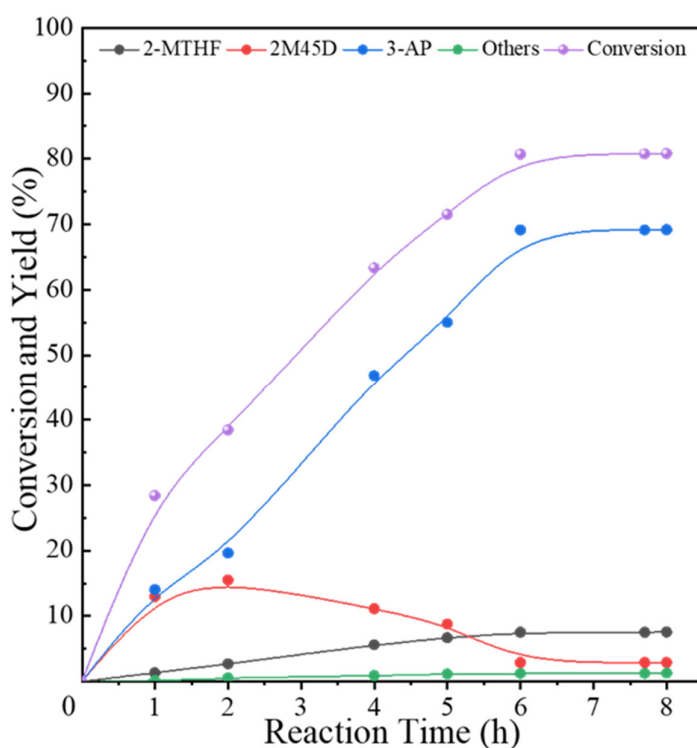


Figure 11. Time curve of product distribution. Reaction conditions: 300 mg catalyst, 2.5 mL 2-MF, 25 mL H₂O, 80 °C, 1 MPa H₂, 8 h.

3. Experimental Section

3.1. Chemical Reagents

2-methylfuran (2-MF, 98%, Aladdin, Shanghai, China), 2methyltetrahydrofuran (2-MTHF, 99%, Aladdin, Shanghai, China), 3-acetyl-1-propanol (3-AP, 95%, Aladdin, Shanghai, China), 4,5-dihydro-2-methylfuran (2M45D, 97%, Aladdin, Shanghai, China), palladium nitrate (Pd metal basis 59%, Aladdin, Shanghai, China).

3.2. Preparation of Catalysts

All supported catalysts in this study were synthesized via an incipient wetness impregnation method. Taking the synthesis of Pd/TS-1 (0.6%) catalyst as an example, 1 g of the required support TS-1 was taken, and its water absorption capacity was tested to be 1 mL. 1 g of TS-1 molecular sieve was weighed into a crucible, and 1 mL of the prepared

$\text{Pd}(\text{NO}_3)_2$ solution was transferred into the crucible using a pipette. The mixture was shaken in an oscillator for 15 min until uniform. It was then placed in a vacuum drying oven and dried at 60 °C for 5 h. After drying, the sample was ground into powder and calcined in a muffle furnace at 350 °C for 3 h. Subsequently, the calcined powder was evenly spread in a porcelain boat and reduced in a tube furnace with 10 vol% H_2/N_2 at 265 °C for 3 h. The resulting gray powder was the Pd/TS-1 catalyst.

3.3. Catalyst Characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a Bruker D8-Advance X-ray diffractometer (Billerica, MA, USA) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The wide-angle 2θ was scanned from 5° to 50° using a secondary monochromator at 40 kV and 40 mA, with a scanning speed of 5°/min.

Under an accelerating voltage of 200 kV, the morphological characteristics of all the tested samples were identified via transmission electron microscopy (JEOL JEM-2011, Akishima, Japan). A JEOL-Grandarm 300f electron microscope was utilized to conduct high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization.

Nitrogen adsorption–desorption tests were performed with a Quantachrome iQ-3 gas adsorption analyzer (Anton Paar GmbH, Graz, Austria). Prior to the test implementation, all samples underwent degassing treatment under vacuum at 300 °C for 10 consecutive hours. The Brunauer–Emmett–Teller (BET) equation ($0.05 < p/p_0 < 0.30$) was applied to calculate the specific surface area of the samples, whereas the t-plot approach was used to determine their micropore area. Additionally, the density functional theory (DFT) approach was adopted to compute the pore size distributions of the prepared samples.

X-ray photoelectron spectroscopy (XPS) spectra of Pd 3d were collected using a Thermo Fisher device equipped with a VG CLAM 4 MCD analyzer (Waltham, MA, USA), with the C 1s peak (binding energy = 284.8 eV) used for calibration.

H_2 temperature-programmed reduction (H_2 -TPR) was performed on an AutoChem II 2920 chemisorption analyzer (Micromeritics, Norcross, GA, USA) equipped with an online thermal conductivity detector (TCD). For H_2 -TPR, approximately 100 mg of the catalyst was loaded into a U-shaped quartz tube and pretreated under Ar flow at 180 °C for 60 min. The H_2 consumption signal was then monitored under a flow of 10 vol% H_2/Ar (50 mL/min) with a heating rate of 10 °C/min from room temperature to 800 °C. Ammonia temperature-programmed desorption (NH_3 -TPD) was employed to characterize the acidic properties of all samples with the aforementioned instrument. Initially, each sample was pretreated with He (50 $\text{cm}^3 \text{ min}^{-1}$) at 315 °C for 1 h, and then the sample was cooled to a temperature of 100 °C. Subsequently, the sample was saturated with a 10 vol% NH_3/He gas mixture at 100 °C for 1 h, and the feed gas was switched to pure He to eliminate physically adsorbed NH_3 for 0.5 h. Ultimately, the NH_3 desorption process was recorded over a temperature range of 100 to 800 °C at a heating rate of 10 °C min^{-1} .

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of CO-adsorbed catalysts were acquired on a Thermo Scientific Nicolet iS50 spectrometer (Waltham, MA, USA) fitted with an MCT detector cooled by liquid nitrogen (N_2). Prior to spectral testing, the catalysts were pretreated with 10% H_2/Ar (100 mL min^{-1}) at 415 °C for 60 min and then cooled to 25 °C under an argon (Ar) atmosphere. Subsequently, a 10% CO/Ar gas mixture was fed into the DRIFTS cell at a flow rate of 100 mL min^{-1} , with this gas flow maintained for 30 min.

3.4. Catalytic Tests

Catalytic conversion of 2-methylfuran (2-MF) was carried out in a 100 mL high-pressure stainless steel autoclave at a stirring speed of 600 rpm. For a typical experimental

procedure, 2.5 mL of 2-MF, 25 mL of H₂O and 0.3 g of the prepared catalyst were blended homogeneously inside the autoclave. Prior to the reaction initiation, the autoclave reactor was purged with high-purity hydrogen at ambient temperature for a minimum of three cycles and thereafter heated to the preset reaction temperature. Subsequently, high-purity hydrogen was charged into the reactor to a pressure of 1.0 MPa, which served to initiate the catalytic reaction. Quantitative analysis of products was performed via gas chromatography (Shimadzu GC-2010, Kyoto, Japan) equipped with an FID detector and HP-INNOWAX column (30 m × 0.32 mm × 0.25 µm).

The conversion, yield, selectivity and carbon balance were defined as the following:

$$\text{2-MF Conversion(\%)} = \frac{2\text{-MF}_{\text{before}} - 2\text{-MF}_{\text{after}}}{2\text{-MF}_{\text{before}}} \times 100\% \quad (1)$$

$$\text{Yield(\%)} = \frac{\text{Product}_{\text{after}}}{2\text{-MF}_{\text{before}}} \times 100\% \quad (2)$$

$$\text{Selectivity(\%)} = \frac{\text{Yield}}{\text{Conversion}} \times 100\% \quad (3)$$

4. Conclusions

This study systematically investigates the effect of Zn doping on the catalytic performance of Pd/TS-1 for the conversion of 2-MF into 3-AP. It is demonstrated that Zn doping effectively induces the formation of ordered intermetallic PdZn compounds, accompanied by a distinct lattice contraction effect. Meanwhile, benefiting from the low electronegativity of Zn, electron transfer from Zn to Pd occurs spontaneously, leading to the formation of electron-enriched Pd active centers. The synergistic effect of electronic modulation and structural optimization collectively enhance the catalytic performance of PdZn/TS-1 compared with Pd/TS-1. The optimal PdZn_x/TS-1 catalysts with an optimal Pd/Zn molar ratio of 6:1 achieve a 2-MF conversion of 85.9% and a 3-AP selectivity of 80.5%, corresponding to a high 3-AP yield. Overall, this work provides a feasible catalyst design paradigm for the efficient and selective hydrogenation of biomass-derived furan compounds, laying a theoretical and technical foundation for the valorization of renewable biomass resources.

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