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Ado Ibrahim Yargaya

King Mongkut's University of Technology Thonburi

Shamsudeen Mikail

King Mongkut's University of Technology Thonburi

Suleiman Yusif Sule

King Mongkut's University of Technology Thonburi

Abbas Abdurrahman Yusuf

King Mongkut's University of Technology Thonburi

Manniru Abdullahi Ali

King Mongkut's University of Technology Thonburi

Ahmad Muhammad Sani

King Mongkut's University of Technology Thonburi

Kittichai Chaiseeda

kittichai.cha@kmutt.ac.th

King Mongkut's University of Technology Thonburi

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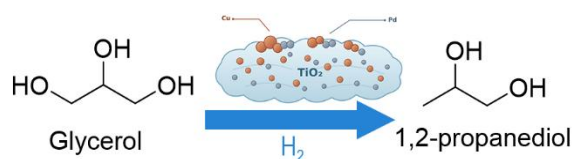
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Ado Ibrahim Yargaya, Shamsudeen Mikail, Suleiman Yusif Sule, Abbas Abdurrahman Yusuf, Manniru Abdullahi Ali, Ahmad Muhammad Sani, and Kittichai Chaiseeda*

Organic Synthesis, Electrochemistry and Natural Product Research Unit (OSEN), Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

* Corresponding author. E-mail: kittichai.cha@kmutt.ac.th



Abstract

A Cu–Pd/TiO₂ catalyst prepared by aqueous NaBH₄ reduction was evaluated for the hydrogenolysis of dilute aqueous glycerol to 1,2-propanediol (1,2-PDO). X-ray diffraction, nitrogen physisorption, electron microscopy, elemental mapping, and infrared spectroscopy were used to characterize the prepared materials. Nominal metal loadings and reaction conditions were varied, and the bimetallic catalyst was compared with Cu/TiO₂ and Pd/TiO₂ under common screening conditions. The bimetallic formulation gave a higher reported 1,2-PDO yield than either monometallic formulation. At nominal loadings of 10 wt% Cu and 0.3 wt% Pd, glycerol conversion reached 63.38% using 1 mmol glycerol, 50 mg catalyst, and 20 mL water after 16 h at 200 °C and an initial H₂ pressure of 20 bar. The measured product distribution changed with hydrogen pressure, reaction time, catalyst amount, and glycerol feed amount. These results characterize the performance of a chemically reduced Cu–Pd/TiO₂ formulation under dilute-feed conditions and identify operating variables relevant to selective 1,2-PDO formation.

Keywords Glycerol hydrogenolysis · 1,2-Propanediol · Cu–Pd/TiO₂ · Sodium borohydride reduction · Heterogeneous catalysis

Highlights

- Cu–Pd/TiO₂ was prepared by aqueous NaBH₄ reduction and tested with dilute glycerol.
- The bimetallic formulation gave a higher reported 1,2-PDO yield than the monometallic controls.
- Nominal Pd loading and reaction conditions altered conversion and liquid-product distribution.

Abbreviations

1,2-PDO, 1,2-propanediol; BET, Brunauer–Emmett–Teller; EDS, energy-dispersive X-ray spectroscopy; FTIR, Fourier-transform infrared spectroscopy; GC–FID, gas chromatography with flame-ionization detection; HR-TEM, high-resolution transmission electron microscopy; SEM, scanning electron microscopy; XRD, X-ray diffraction.

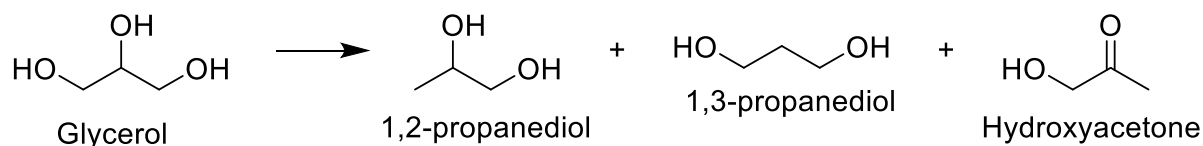
1 Introduction

The rapid growth of biodiesel production has led to a substantial increase in the generation of crude glycerol as a byproduct. During the transesterification of triglycerides, approximately 10 wt% of the biodiesel produced is generated as crude glycerol, resulting in an oversupply of glycerol in the global market [1]. Despite the environmental and economic benefits associated with biodiesel production, the accumulation of surplus glycerol has become a major challenge because of its low commercial value and limited market demand [2, 3]. Consequently, considerable research efforts have focused on developing efficient strategies for glycerol valorization. As an abundant and highly functionalized biomass-derived platform molecule, glycerol can be converted into a wide range of value-added chemicals and fuels through catalytic processes [4, 5]. Among the various catalytic routes for glycerol valorization, including oxidation [6], transesterification [7], etherification [8], esterification [9], dehydration [10], ketalization [11], and hydrogenolysis [12], the latter has attracted considerable attention due to its ability to convert glycerol into high-value chemicals under relatively mild reaction conditions. In particular, glycerol hydrogenolysis enables the production of propanediols, notably 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO), which are widely used in the polymer, pharmaceutical, cosmetic, and food industries [13].

Glycerol hydrogenolysis (Scheme 1) proceeds through the selective cleavage of C–O bonds, and the product distribution depends strongly on the reaction pathway and operating conditions. Selective removal of a terminal hydroxyl group produces 1,2-propanediol (1,2-PDO), whereas cleavage of the secondary hydroxyl group yields 1,3-propanediol (1,3-PDO). Hydroxyacetone could also be a byproduct. Under more severe reaction conditions, further hydrogenolysis may produce propanol isomers, while undesired C–C bond cleavage generates

lighter products such as ethylene glycol, methanol, and methane [14]. Therefore, the development of highly selective catalysts is essential for maximizing glycerol conversion while minimizing side reactions. To achieve this objective, numerous catalytic systems have been investigated. Among them, bimetallic catalysts composed of noble and non-noble metals have attracted significant attention because of their synergistic effects on hydrogen activation and C–O bond cleavage. Transition metals such as Cu, Ni, Pt, Ru, Rh, Re, and Pd have been extensively employed in glycerol hydrogenolysis catalysts [15].

Scheme 1 Glycerol hydrogenolysis



Among the non-noble metal catalysts, copper-based catalysts have attracted considerable attention owing to their high selectivity toward C–O bond cleavage and their low tendency to promote C–C bond scission. Numerous studies have demonstrated that Cu-containing catalysts exhibit excellent performance for the selective conversion of glycerol to 1,2-propanediol (1,2-PDO) [16, 17]. Kang et al. reported that a Cu–Pt/SiO₂ catalyst achieved high glycerol conversion and selectivity toward 1,2-PDO, attributing its superior catalytic performance to Pt-assisted reduction of Cu species, which enhanced the activity of the bimetallic catalyst [1]. Zhang et al. further demonstrated that a Pt–Cu single-atom alloy catalyst exhibited outstanding activity and selectivity for glycerol hydrogenolysis, owing to the synergistic interaction between isolated Pt atoms and neighboring Cu sites, which enhanced hydrogen activation, facilitated glycerol adsorption, and lowered the reaction energy barrier [18]. Ghorbani and Dalai reported that Cu-based bimetallic catalysts supported on various oxides exhibited enhanced hydrogenolysis performance. In particular, TiO₂-supported Ni–Cu catalysts showed improved catalytic activity because of strong metal–support interactions, enhanced metal dispersion, and the moderate Lewis acidity of TiO₂, which collectively promoted efficient hydrogenation and selective formation of 1,2-propanediol [19]. Similarly, NiCu/AlO(OH) catalysts exhibited high selectivity toward 1,2-propanediol owing to the synergistic interaction between Ni and Cu species together with the strong Lewis acid sites of the AlO(OH) support, which facilitated glycerol conversion and improved product selectivity [16]. More recently, Hassenstein et al. reported that a multifunctional Ru–Cu/CNT bimetallic

catalyst achieved nearly complete selectivity toward 1,2-propanediol by promoting selective C–O bond cleavage while suppressing undesired C–C bond cleavage. They further demonstrated that the synergistic interaction between Ru and Cu, together with the sequential dehydration of glycerol to acetol followed by hydrogenation, significantly enhanced catalytic activity and product selectivity [20].

Despite these encouraging advances, several technical challenges remain unresolved. Among them, particle agglomeration is one of the major deactivation pathways, leading to a loss of active surface area and consequently a decline in catalytic performance [15]. Previous studies have demonstrated that incorporating a second metal can effectively suppress particle sintering by improving metal dispersion and stabilizing the active nanoparticles during the reaction, thereby enhancing both catalytic activity and stability [21, 22].

Cu–Pd catalysts have previously been studied for glycerol hydrogenolysis. Both unpromoted and Na-promoted Cu–Pd/TiO₂ catalysts prepared by impregnation and H₂ reduction have been evaluated, and a subsequent study investigated reaction kinetics over the Na-promoted formulation [23]. Consequently, Cu–Pd/TiO₂ itself, the absence of deliberate NaOH promotion, and the proposed acetol pathway cannot be presented as new. The preparation method, metal loading, and dilute glycerol feed distinguish the formulation and operating conditions examined here [16, 24].

In this study, Cu–Pd/TiO₂ catalysts were prepared by aqueous NaBH₄ reduction without deliberate NaOH promotion. Their structure and morphology were examined by XRD, nitrogen physisorption, HR-TEM/EDS, SEM, and FTIR. We compared the bimetallic catalyst with its monometallic counterparts and examined the effects of nominal Pd loading, initial H₂ pressure, temperature, reaction time, catalyst amount, and glycerol amount on conversion and liquid-product distribution. The study reports the performance of this preparation under dilute aqueous-feed conditions without assigning an unverified alloy structure or reaction mechanism.

2 Materials and Methods

2.1 Materials

Cupric nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.5%, Thomas Baker), palladium(II) chloride (PdCl₂, 98.0%, TCI), titanium dioxide (TiO₂, 99.8%, Sigma-Aldrich), citric acid (C₆H₈O₇·H₂O, 99.5–102%, Loba Chemie), and sodium borohydride (NaBH₄, 95.0%, TCI) were used for catalyst synthesis without further purification. Deionized (DI) water was used throughout all experiments. Glycerol (C₃H₈O₃, 99.5%, Carlo Erba), 1,2-propanediol (C₃H₈O₂, 99.5%, Keamus), Hydroxyacetone (C₃H₆O₂, 90.0%, TCI) and methanol (CH₄O, 99.8%, HPLC grade, Thomas Baker) were used as calibration standards for product quantification. Butan-1-

ol ($\text{C}_4\text{H}_{10}\text{O}$, 99.4%, AR grade, APS) was used as the internal standard for gas chromatography (GC) analysis. High-purity hydrogen (H_2 , Linde) was used in the glycerol hydrogenolysis reactions, while high-purity argon (Ar, Linde) was used for catalyst storage.

2.2 Catalyst preparation

Cu/TiO_2 , Pd/TiO_2 , and Cu-Pd/TiO_2 catalysts were synthesized by a NaBH_4 reduction method adapted from the procedure reported by Deng and Cai [25]. Briefly, the required amounts of TiO_2 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and/or PdCl_2 were dispersed in 60 mL of deionized water and stirred for 30 min. Subsequently, 0.2 g of citric acid was added as a complexing agent, and the mixture was stirred at 60 °C for 3 h. After cooling to room temperature, 5 mL of 0.52 M NaBH_4 solution was added dropwise, and the suspension was stirred at 4 °C for 1 h to ensure complete reduction of the metal precursors. Thereafter, 10 mL of acetone was added, and the mixture was aged at room temperature for 24 h. The resulting solid was collected by centrifugation, washed several times with deionized water and ethanol, dried at 80 °C for 5 h, and ground into a fine powder. The catalysts were stored under a high-purity argon atmosphere prior to characterization and catalytic testing. The synthesized catalysts were denoted as Cu/TiO_2 , Pd/TiO_2 , and Cu-Pd/TiO_2 according to their metal compositions.

2.3 Catalyst characterization

The materials used in this study included commercial titanium dioxide (TiO_2) and synthesized Cu/TiO_2 , Pd/TiO_2 and Cu-Pd/TiO_2 catalysts. The support and catalysts were characterized using a range of analytical techniques, including X-ray diffraction (XRD), nitrogen adsorption–desorption analysis (Brunauer–Emmett–Teller, BET), high-resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR).

Crystallographic properties were analyzed by powder X-ray diffraction using a Bruker D8 θ – θ diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) and operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ range of 10–100° with a step size of 0.02° and a counting time of 0.4 s per step. An Eiger2R 250K hybrid pixel detector was used, with fixed divergence and Soller slits and without an incident-beam monochromator.

Textural properties, including specific surface area, pore volume, and pore size distribution, were obtained from nitrogen adsorption–desorption isotherms using a surface area analyzer (Quantachrome Autosorb-iQ3-MP/Kr). Prior to analysis, the samples were degassed at 200 °C for 3 h.

Surface morphology, microstructure, and elemental distribution were examined by high-resolution transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (HR-TEM/EDS, JEOL JEM-ARM200F) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-IT800). Fourier-transform infrared (FTIR) spectra were collected using an ATR accessory (Thermo Scientific Nicolet iS50). Spectra were recorded over the wavenumber range of 400–4000 cm⁻¹ with an acquisition time of 32 s.

2.4 Catalytic activity tests

Glycerol hydrogenolysis was carried out in a TGYF high-pressure reactor equipped with a 100 mL stainless-steel autoclave. Typically, glycerol (92.09 mg, 1 mmol), Cu–Pd/TiO₂ catalyst (50 mg), and deionized water (20 mL) were charged into the reactor. The reactor was purged twice with hydrogen gas at 20 bar and subsequently pressurized with hydrogen to the desired pressure 20 bar. The reaction mixture was heated to 200 °C and stirred at 400 rpm for 16 h. After completion of the reaction, the reactor was allowed to cool naturally to room temperature.

For product analysis, butan-1-ol (15 mg) was added as an internal standard. The reaction mixture was filtered through a microfilter, and a 1.5 mL aliquot of the filtrate was transferred to a GC vial. Liquid products were analyzed using a Shimadzu GC-2030 gas chromatograph equipped with a flame ionization detector (FID) and a VF-WAXms capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The detailed GC operating conditions are provided in Table S1 of the Supporting Information. Glycerol conversion and product selectivity toward 1,2-propanediol were determined using the internal standard method. Glycerol, methanol, and 1,2-propanediol were identified and quantified by comparison with authentic standards analyzed under identical chromatographic conditions.

2.5 Calculation of conversion and selectivity

$$\text{glycerol conversion (\%)} = \frac{(\text{initial glycerol (mmol)} - \text{remaining glycerol (mmol)})}{\text{initial glycerol (mmol)}} \times 100$$

$$\text{1,2-propanediol selectivity (\%)} = \frac{\text{1,2-propanediol yield (\%)}}{\text{glycerol conversion (\%)}} \times 100$$

3 Results and Discussion

3.1 XRD analysis

XRD patterns of the TiO_2 support and prepared catalysts are shown in Fig. 1. The prominent reflections of anatase TiO_2 persist after metal deposition. A Pd-associated reflection is visible for Pd/ TiO_2 , whereas distinct Cu and Pd reflections are not resolved for the bimetallic sample. The absence of resolved reflections is consistent with low metal loading or small crystallites.

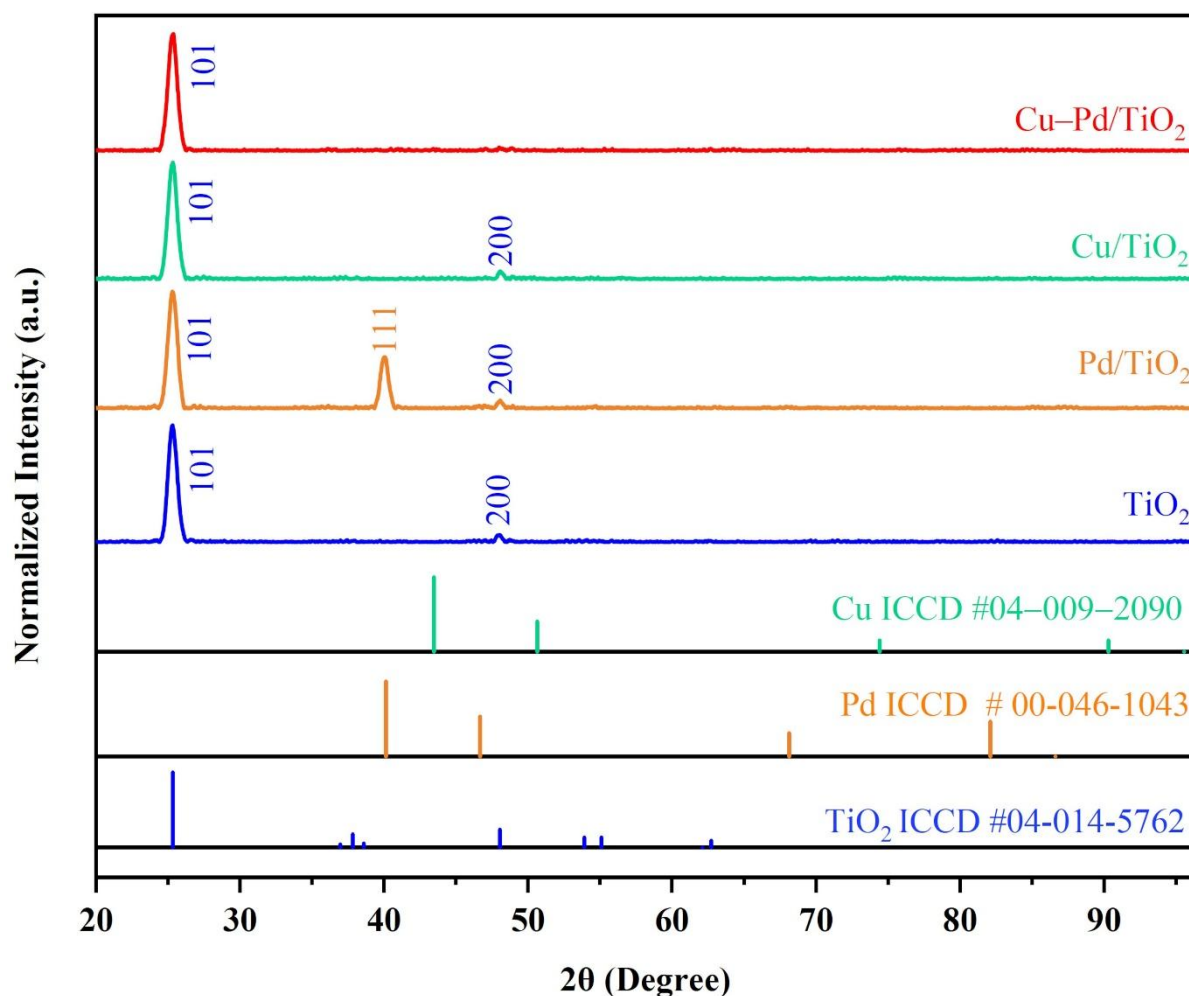


Fig. 1 X-ray diffraction (XRD) patterns of commercial TiO_2 and the prepared Pd/ TiO_2 , Cu/ TiO_2 , and Cu-Pd/ TiO_2 catalysts.

3.2 BET analysis

The nitrogen adsorption-desorption results and textural properties are presented in Table 1 and Fig. 2. The measured surface area decreased from $262 \text{ m}^2 \text{ g}^{-1}$ for TiO_2 to $194 \text{ m}^2 \text{ g}^{-1}$ for Cu-Pd/ TiO_2 , while the reported pore diameter remained near 3.6 nm. These observations show a change in accessible surface and pore volume after preparation; they do not by themselves establish where Cu and Pd are located [26].

The decrease in surface area does not necessarily limit the catalytic performance of Cu–Pd/TiO₂. In glycerol hydrogenolysis, catalytic behavior depends not only on surface area but also on metal dispersion, active-site accessibility, and mass transport [27]. The retention of the 3.62–3.64 nm mesoporous structure can facilitate reactant and intermediate diffusion, while the supported Cu–Pd species provide accessible active sites for the hydrogenolysis reaction. Thus, the textural results indicate that metal incorporation modifies the surface area and pore volume without causing significant structural collapse of the TiO₂ support.

Table 1 Specific surface area, pore volume, and pore diameter of TiO₂, Cu/TiO₂, Pd/TiO₂, and Cu–Pd/TiO₂ determined by the BET method.

Samples	Surface area (m ² g ^{−1})	Pore volume (cm ³ g ^{−1})	Pore diameter (nm)
TiO ₂	262	0.335	3.64
Cu/TiO ₂	205	0.282	3.62
Pd/TiO ₂	205	0.299	3.64
Cu–Pd/TiO ₂	194	0.247	3.62

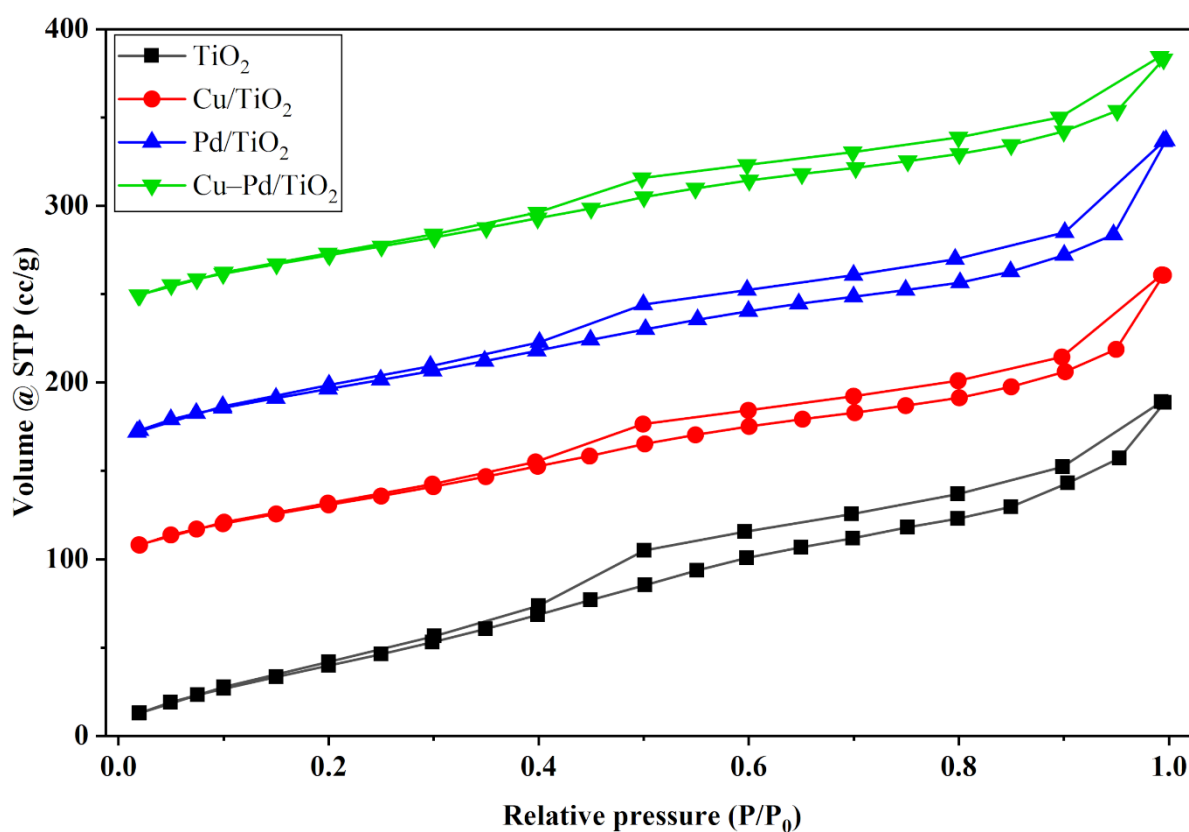


Fig. 2 N₂ adsorption–desorption isotherms of TiO₂, Cu/TiO₂, Pd/TiO₂, and Cu–Pd/TiO₂ catalysts.

3.3 HR-TEM analysis

HR-TEM images (Fig. 3) show lattice fringes assigned to TiO₂ and, in selected regions, to Cu- and Pd-containing phases. These local observations support the presence of crystalline metal-containing domains. Phase assignments based on individual lattice spacings remain tentative where spacings overlap, and the images do not establish a Cu–Pd alloy or quantify overall metal dispersion [28].

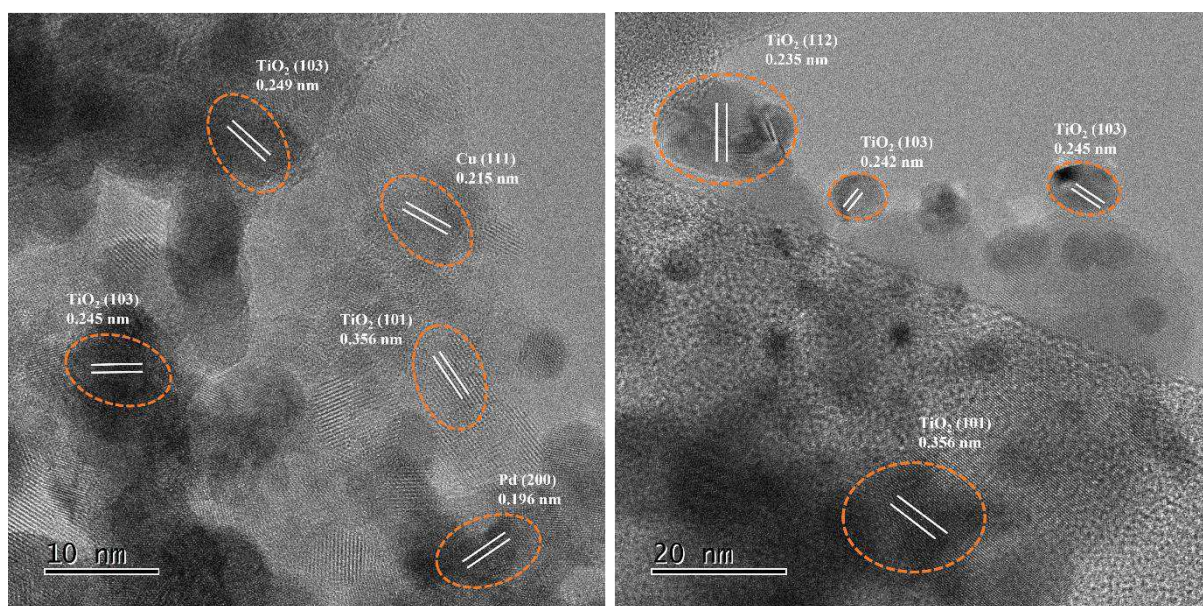


Fig. 3 High-resolution transmission electron microscopy (HR-TEM) images of the Pd–Cu/TiO₂ catalyst at different magnifications (10 and 20 nm), showing the lattice fringes assigned to TiO₂, Cu, and Pd crystalline phases.

3.4 TEM-EDS elemental mapping

Elemental maps (Fig. 4) show Cu and Pd signals in the examined Cu–Pd/TiO₂ region alongside Ti and O. The maps indicate that both elements are present within the imaged area; a broader particle-size distribution and quantitative elemental analysis would be needed to establish sample-wide dispersion and actual loading.

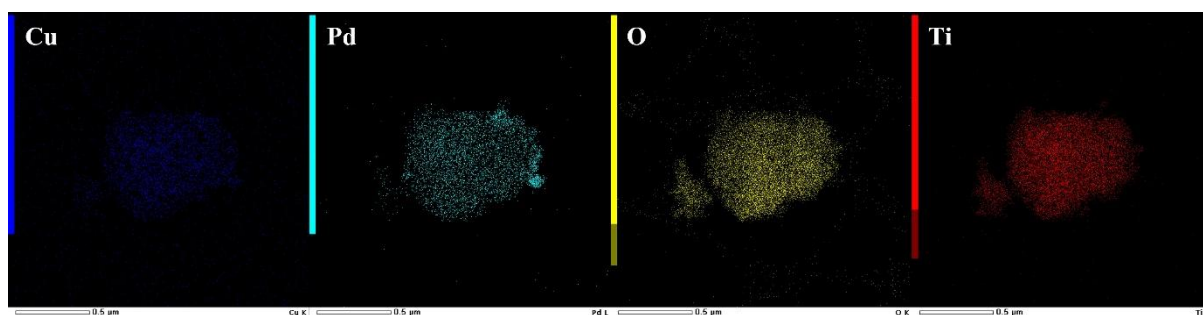


Fig. 4 EDS elemental mapping images showing the spatial distribution of Cu, Pd, Ti, and O within the Cu–Pd/TiO₂ catalyst.

3.5 SEM analysis

Fig. 5 displays the SEM micrographs of pristine (a) TiO₂, (b) Pd/TiO₂, (c) Cu/TiO₂, and (d) Cu–Pd/TiO₂ catalysts. The pristine TiO₂ support (Fig. 5a) consists of Significant particle agglomeration is evident across the support, driven by the high surface energy characteristic of nanoscale TiO₂ powders. Despite this aggregation, visible interparticle voids persist, maintaining an open macro-particulate network.

Following Pd deposition (Fig. 5b), the catalyst preserves the general irregular morphology of the TiO₂ support, demonstrating that the chemical deposition process does not induce structural collapse of the primary oxide particles. The aggregates, however, appear more densely consolidated into secondary clusters. Discrete Pd crystallites or large metal clusters are not distinguishable at this magnification, which indicates that any supported Pd domains remain below the spatial resolution limit of SEM rather than forming micron-scale aggregates.

Similarly, the Cu/TiO₂ catalyst (Fig. 5c) retains the parent TiO₂ framework while presenting closely packed secondary aggregates with relatively smoother exterior boundaries. In line with the Pd-loaded counterpart, distinct Cu-containing phases cannot be resolved by SEM imaging, indicating that Cu does not form large isolated agglomerates on the support exterior.

In comparison, the bimetallic Cu–Pd/TiO₂ sample (Fig. 5d) displays a more textured surface morphology featuring primary TiO₂ aggregates decorated with fine particulate features. Relative to the more compact monometallic analogues, this sample maintains a more porous arrangement of agglomerates with noticeable interparticle spacing. Such aggregate porosity can facilitate the diffusion of liquid-phase reactants toward active interfacial domains.

Overall, the SEM observations confirm that the core particulate morphology of TiO₂ remains intact across all metal-loaded samples. Because conventional SEM imaging cannot directly resolve sub-nanometer clusters, elemental distributions, or oxidation states, these micrographs confirm the absence of large macroscopic metal agglomerates without proving sub-nanometer dispersion. Complementary high-resolution techniques—such as HR-TEM and elemental mapping—are therefore required to verify the local distribution and structural relationship of the Cu and Pd species.

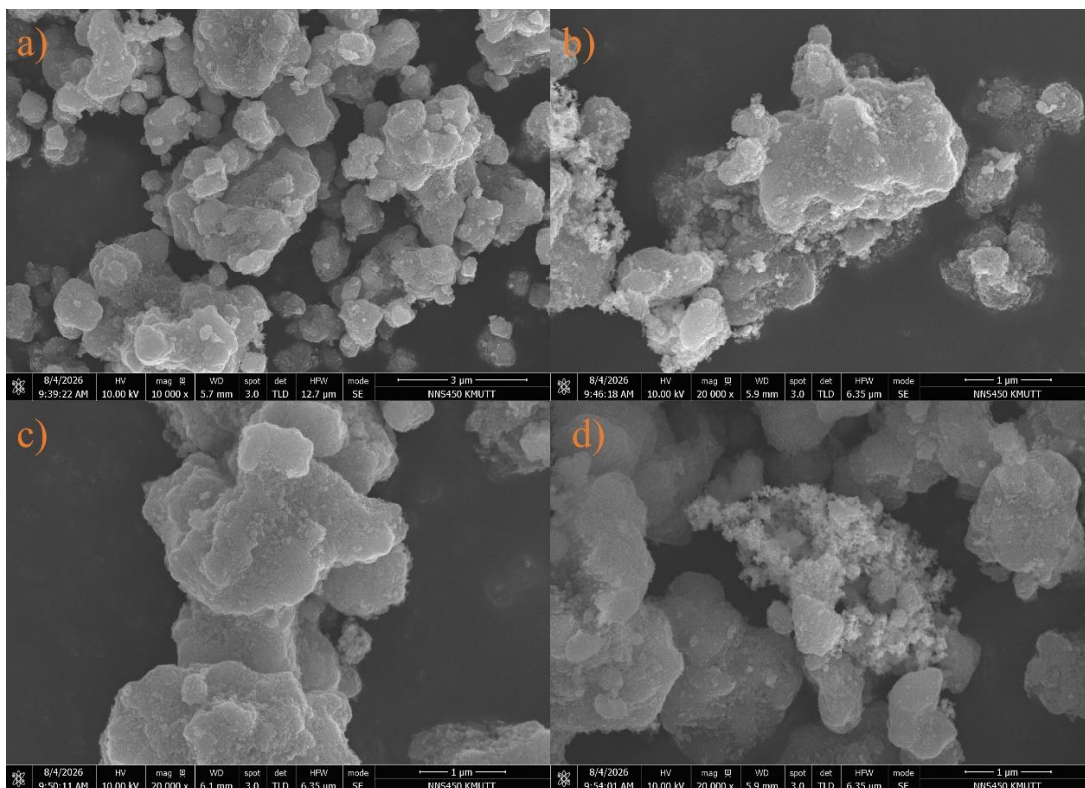


Fig. 5 SEM micrographs of (a) TiO₂, (b) Pd/TiO₂, (c) Cu/TiO₂, and (d) Cu–Pd/TiO₂ catalysts.

3.6 FTIR analysis

Fig. 6 shows the FTIR spectra of the pristine TiO₂, the fresh monometallic and bimetallic catalysts (Cu/TiO₂, Pd/TiO₂, and Cu–Pd/TiO₂), as well as the spent Cu–Pd/TiO₂ catalyst. All samples exhibit similar primary spectral features, indicating that neither the incorporation of Cu and Pd nor the catalytic reaction conditions significantly alter the fundamental structure of the TiO₂ support. A broad absorption band observed in the fresh samples at 3301–3360 cm^{−1} is assigned to the stretching vibration of surface hydroxyl groups and physically adsorbed water [29].

Compared to pristine TiO₂, slight shifts in this band after initial metal deposition suggest that the surface hydroxyl environment is influenced by the interaction between the metal species and the TiO₂ support. In the spent Cu–Pd/TiO₂ catalyst, this band shifts further to 3376 cm^{−1}, suggesting an alteration in surface hydration or a post-reaction rearrangement of the surface hydroxyl coordination. A second band, located at 1617 cm^{−1} for pristine TiO₂, corresponds to the bending vibration of molecularly adsorbed water [30]. This band shifts to lower wavenumbers after initial Cu and Pd incorporation, appearing at 1588, 1595, and 1562 cm^{−1} for fresh Cu/TiO₂, Pd/TiO₂, and Cu–Pd/TiO₂, respectively. The notably larger shift observed for the fresh bimetallic catalyst (1562 cm^{−1}) indicates a substantial perturbation of the surface hydroxyl environment, reflecting strong interactions between the supported bimetallic species

and TiO₂. However, for the spent Cu–Pd/TiO₂ catalyst, this peak relaxes back to 1588 cm⁻¹. This relaxation implies a partial surface restructuring or a slight weakening of the initial metal-support interactions during the catalytic process.

A weak absorption band at approximately 1395–1408 cm⁻¹ is attributed to trace residual organic species or surface functional groups remaining from catalyst preparation [31]. The spent Cu–Pd/TiO₂ catalyst retains a clear peak in this region at 1404 cm⁻¹, indicating either the persistence of these stable functional groups or the minor accumulation of carbonaceous reaction intermediates on the catalyst surface.

Finally, the characteristic Ti–O–Ti lattice vibration of anatase TiO₂ is observed in the 422–436 cm⁻¹ region for all fresh catalysts. In the spent Cu–Pd/TiO₂ sample, this peak appears at 419 cm⁻¹. This confirms that while the local bonding environment experiences minor perturbations—likely due to thermal effects or metal restructuring during the reaction—the bulk TiO₂ framework is excellently preserved following both metal deposition and catalytic testing. Furthermore, no additional absorption bands attributable to bulk CuO or PdO phases are detected in either the fresh or spent samples.

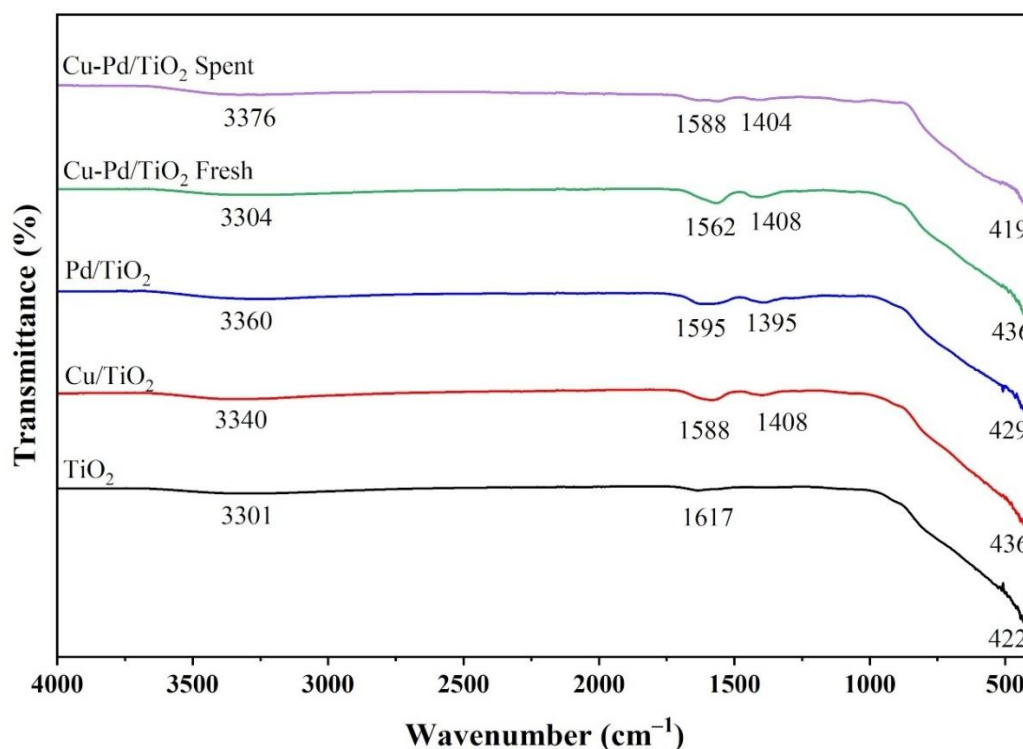


Fig. 6 FTIR spectra of TiO₂, Cu/TiO₂, Pd/TiO₂ and Cu–Pd/TiO₂ catalysts.

3.7 Effect of Nominal Pd Loading

The nominal Pd loading was varied from 0.1 to 0.4 wt% at a nominal Cu loading of 10 wt% (Fig. 7). Glycerol conversion increased from 37.53% at 0.1 wt% Pd to 54.33% at 0.3 wt%

Pd, then decreased to 42.49% at 0.4 wt% Pd. These are nominal mass loadings, not Cu:Pd molar ratios. The 0.3 wt% Pd formulation was selected for subsequent experiments.

A similar trend was observed for 1,2-PDO selectivity, which increased from 53.97% at 10:0.1 to 61.27% at 10:0.2 and reached 91.39% at 10:0.3. Meanwhile, acetol selectivity decreased from 10.13% to 1.83% and 1.05%, respectively. When the Pd content was further increased to 0.4 wt%, 1,2-PDO selectivity decreased to 68.16%, together with the lower glycerol conversion. Thus, the catalyst containing 10 wt% Cu and 0.3 wt% Pd, corresponding to a Cu molar ratio of 10:0.3, was selected for subsequent optimization studies. The observed dependence on Pd content suggests that an appropriate Cu composition is important for achieving favorable glycerol conversion and 1,2-PDO selectivity, although the specific mechanistic origin of this behavior requires further investigation.

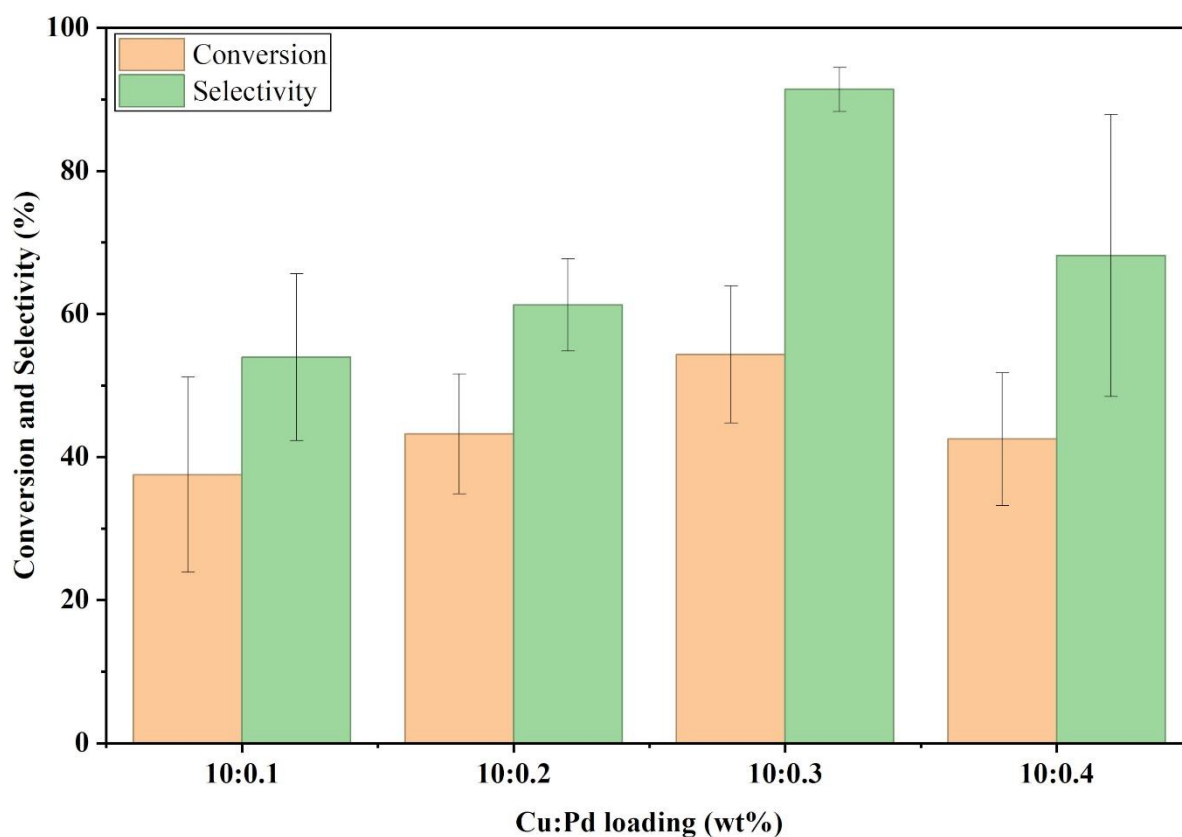


Fig. 7 Effect of molar ratio on glycerol hydrogenolysis. Reaction conditions: glycerol (1 mmol), catalyst (50 mg), H₂ pressure (30 bar), H₂O (20 mL), 200 °C, and 16 h.

Reaction conditions: glycerol (1 mmol), catalyst (50 mg), H₂ (30 bar), temperature (200 °C), reaction time (16 h), water (20 mL), and stirring speed (400 rpm).

3.8 Catalyst screening

The catalytic performance of the different catalyst systems was evaluated under identical reaction conditions, and the results are shown in Fig. 8. Both glycerol conversion and product selectivity were influenced by the catalyst composition, indicating that the choice of active metal and support can affect the catalytic performance of the Cu-based systems.

Under the common screening conditions, Cu–Pd/TiO₂ gave 54.33% glycerol conversion and a reported 49.65% 1,2-PDO yield. The corresponding reported yields were 7.79% for Cu/TiO₂ and 33.29% for Pd/TiO₂. This comparison shows a favorable result for the bimetallic formulation under the tested conditions; it does not independently identify the active-site structure or prove a synergistic mechanism.

In contrast, Cu/TiO₂ afforded a lower glycerol conversion of 19.95%, with a 1,2-PDO selectivity of 39.05%. Although Cu-based catalysts have been widely investigated for the selective hydrogenolysis of glycerol, the lower conversion observed for Cu/TiO₂ under the present reaction conditions indicates that the monometallic catalyst was less effective than the Pd-containing systems. The difference in catalytic performance among the three catalysts suggests that incorporating Pd into Cu/TiO₂ can modify the catalytic behavior and improve the formation of 1,2-PDO under the investigated conditions. Based on its higher glycerol conversion and 1,2-PDO selectivity, Cu–Pd/TiO₂ was selected for subsequent optimization studies.

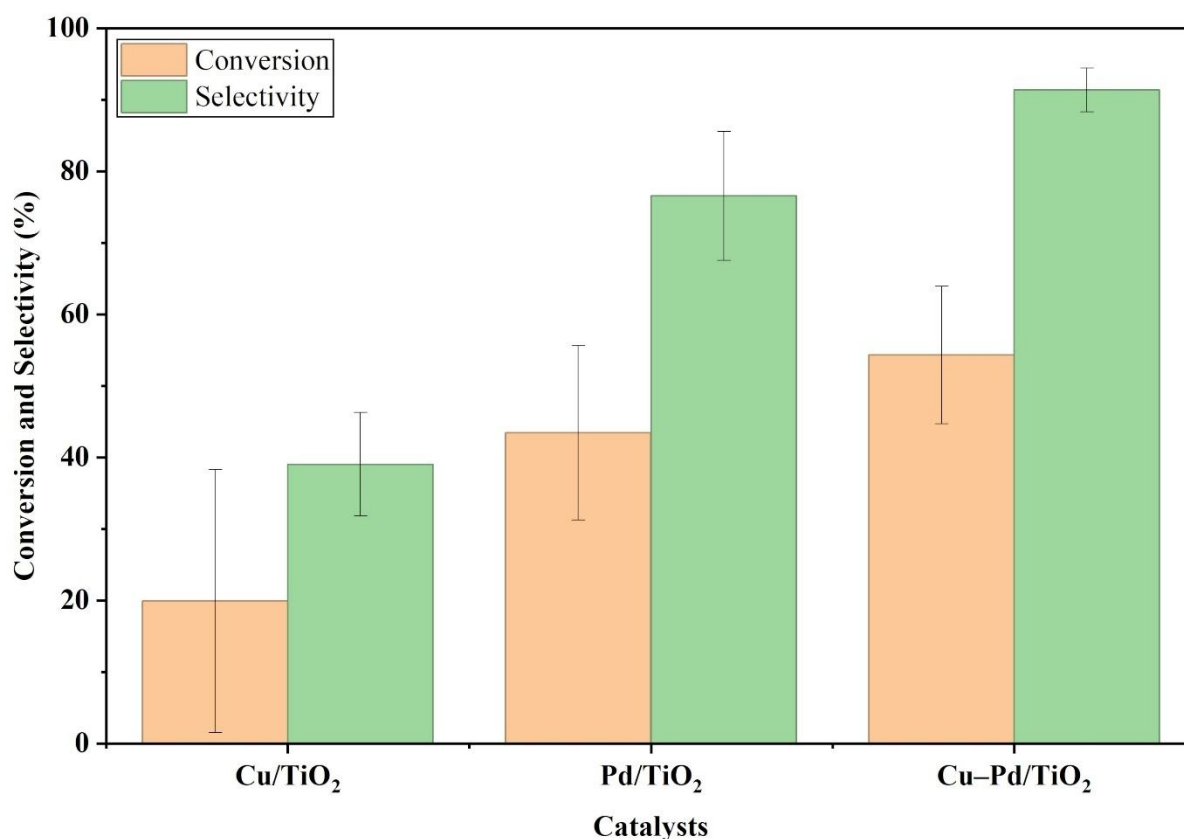


Fig. 8 Catalyst screening for glycerol hydrogenolysis. Reaction conditions: glycerol (1 mmol), catalyst (50 mg), H₂O (20 mL), H₂ pressure (30 bar), 200 °C, and 16 h.

3.9 Effect of hydrogen pressure

The reported 1,2-PDO selectivity was highest at an initial H₂ pressure of 20 bar (Fig. 9). The dependence of product distribution on pressure should be interpreted cautiously until the product balance is reconciled. Changes in H₂ availability are a possible explanation, but adsorption or pathway changes were not measured directly.

The 1,2-propanediol (1,2-PDO) selectivity showed a similar dependence on hydrogen pressure but with a distinct maximum at 20 bar. The selectivity increased from 89.59% at 10 bar to 93.93% at 20 bar, followed by a slight decrease to 91.39% at 30 bar and a substantial decrease to 61.72% at 40 bar. The increased 1,2-PDO selectivity at 20 bar may indicate that this pressure provides suitable hydrogen availability for the conversion of reaction intermediates toward 1,2-PDO. At higher hydrogen pressure, changes in the adsorption behavior of glycerol and reaction intermediates or the promotion of competing reaction pathways may contribute to the decrease in 1,2-PDO selectivity. Similar observations have been reported in recent studies, highlighting the importance of balancing hydrogenation and dehydration reactions in controlling 1,2-PDO selectivity [32].

Overall, 20 bar H₂ provided the highest glycerol conversion (55.20%) and 1,2-PDO selectivity (93.93%) among the investigated pressures. Therefore, 20 bar H₂ was selected for subsequent optimization studies under the present reaction conditions.

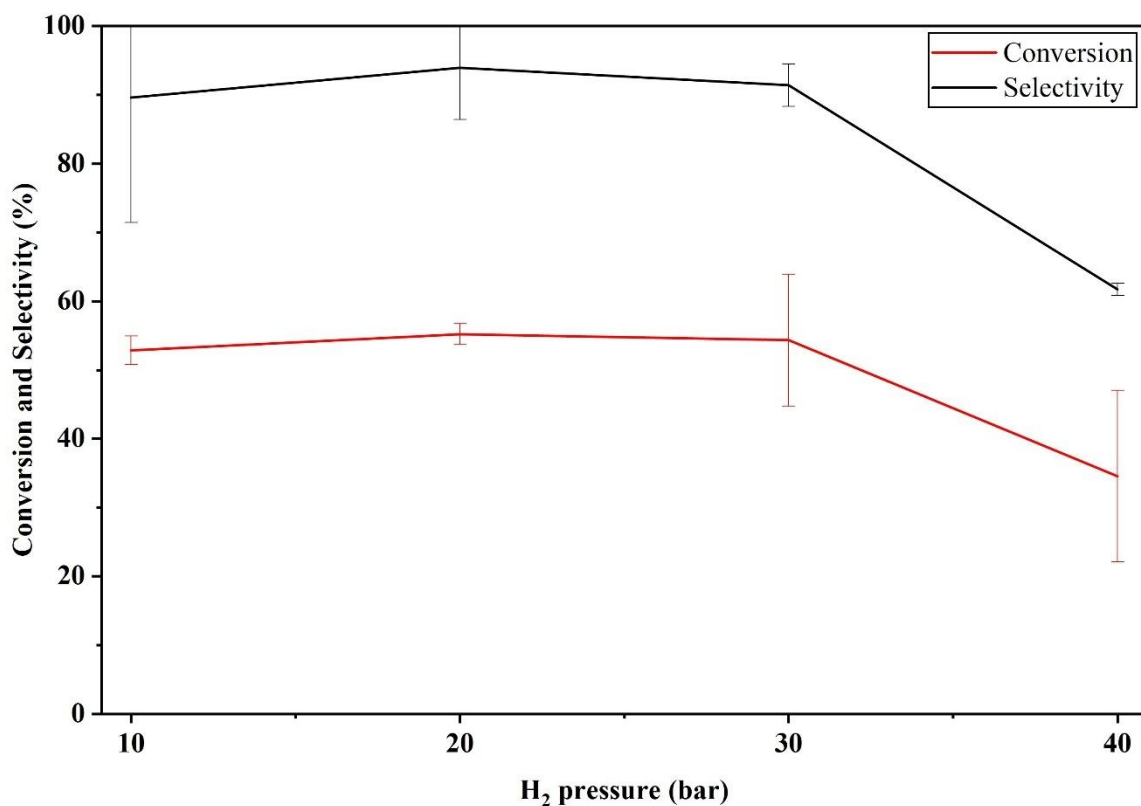


Fig. 9 Effect of hydrogen pressure on glycerol hydrogenolysis. Reaction conditions: glycerol (1 mmol), catalyst (50 mg), H₂O (20 mL), 200 °C, hydrogen pressure (10-40) and 16 h.

3.10 Effect of reaction temperature

At 35 °C, the reported glycerol conversion was 25.44%, while the table reports methanol as a quantified product and no 1,2-PDO. This result is anomalous relative to the measurements at 150 °C and requires verification against the chromatograms and controls before a temperature trend can be assigned.

At 150 °C, the reported conversion was 4.40%, and none of the quantified products were detected. This observation requires a check of calibration, sampling, and carbon recovery.

At 200 °C, the reported conversion was 55.63% and 1,2-PDO was the principal quantified product. Numerical selectivity and carbon balance should be recalculated before drawing a mechanistic conclusion from these data.

When the reaction temperature was increased to 150 °C, glycerol conversion decreased markedly to 4.40%, and no detectable 1,2-PDO, acetol, or methanol was observed. This result indicates that, under the present reaction conditions, the catalyst exhibited very low activity at 150 °C, with negligible formation of the analyzed products.

A significant enhancement in catalytic performance was observed at 200 °C, where glycerol conversion increased sharply to 55.63%, indicating that the higher reaction temperature promoted the hydrogenolysis reaction. The reaction exhibited high selectivity toward the desired product, with 1,2-PDO reaching a selectivity of 98.40%. Only a small amount of acetol was detected, with a selectivity of 3.39%, while methanol was not observed. The high 1,2-PDO selectivity at 200 °C indicates that the elevated temperature favored the reaction pathway toward the desired product. In glycerol hydrogenolysis, acetol is considered an important intermediate that can undergo subsequent hydrogenation to form 1,2-PDO [33].

The improvement in both glycerol conversion and 1,2-PDO selectivity at 200 °C may be associated with enhanced activation of glycerol and more effective hydrogenation of reaction intermediates over the Cu–Pd active sites. Elevated temperature can facilitate the reactions involved in glycerol hydrogenolysis and the subsequent transformation of intermediates toward 1,2-PDO. The absence of detectable methanol at 200 °C further indicates that the formation of this lower-molecular-weight product was not favored under these reaction conditions.

Overall, the results demonstrate that reaction temperature is an important parameter governing glycerol hydrogenolysis over Cu–Pd/TiO₂. Among the temperatures investigated, 200 °C provided the highest glycerol conversion (55.63%) together with the highest 1,2-PDO selectivity (98.40%). Therefore, 200 °C was selected for subsequent optimization studies, providing suitable conditions for the selective production of 1,2-PDO over the Cu–Pd/TiO₂ catalyst.

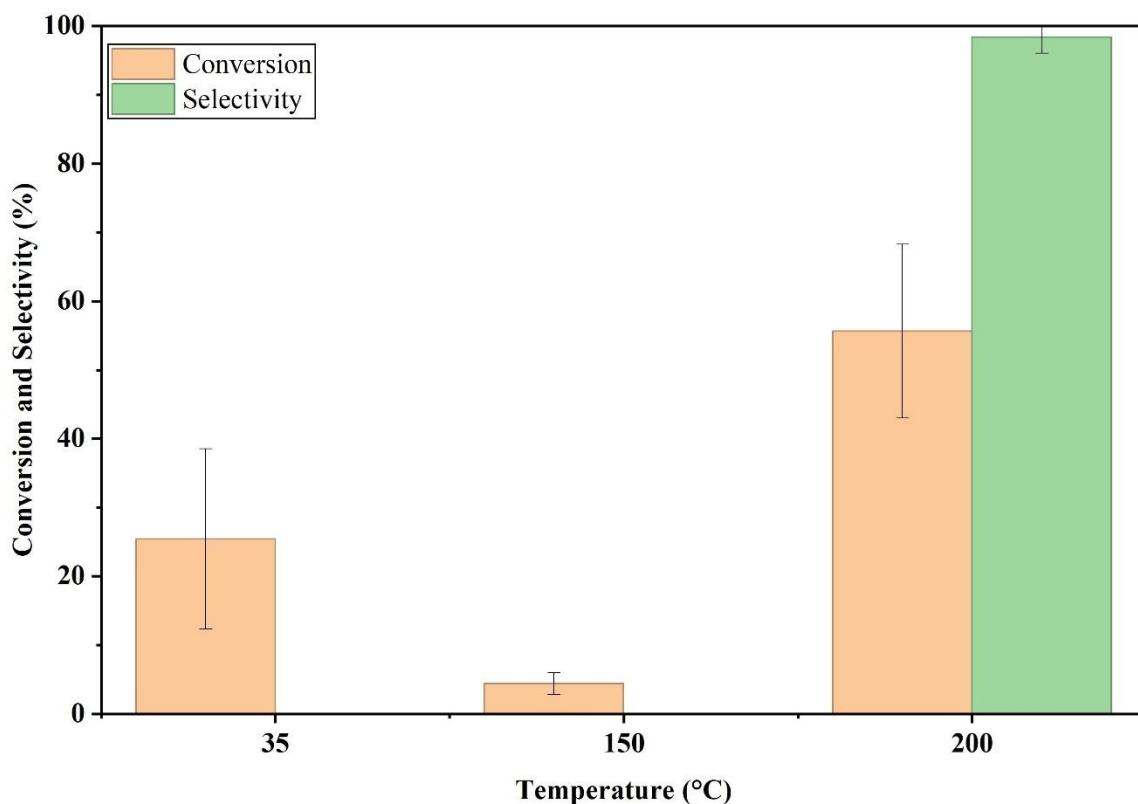


Fig. 10 Effect of reaction temperature on glycerol hydrogenolysis. Reaction conditions: glycerol (1 mmol), catalyst (50 mg), H₂O (20 mL), 35–200 °C, hydrogen pressure (20) and 16 h.

3.11 Effect of reaction time

The influence of reaction time on glycerol hydrogenolysis over the Cu–Pd/TiO₂ catalyst was investigated by varying the reaction duration from 8 to 24 h while maintaining all other reaction parameters constant. As shown in Fig. 11, glycerol conversion and product selectivity varied considerably with reaction time, indicating that the reaction duration influenced both glycerol conversion and product distribution.

At 8 h, the reported conversion was 45.75%, with a low 1,2-PDO yield and a comparatively large methanol signal. At 12 h, the reported conversion was 41.13%, lower than at 8 h. This nonmonotonic conversion trend and the changes in product distribution warrant repeat measurements and consistent product accounting.

The 16 h run gave a reported 55.47% conversion and 54.89% 1,2-PDO yield. At 24 h, the reported conversion increased to 63.17% but the 1,2-PDO yield decreased to 21.94%. Secondary transformations are possible; the present endpoint measurements do not establish their identity or sequence [34, 35].

Overall, reaction time significantly influenced both glycerol conversion and product selectivity. Although the highest glycerol conversion was obtained at 24 h (63.17%), the 1,2-PDO selectivity decreased substantially under these conditions. In contrast, 16 h provided a glycerol conversion of 55.47% together with the highest 1,2-PDO selectivity of 98.95% among the investigated reaction times. Therefore, 16 h was selected as the reaction time for subsequent studies because it provided a favorable balance between glycerol conversion and selective formation of 1,2-PDO.

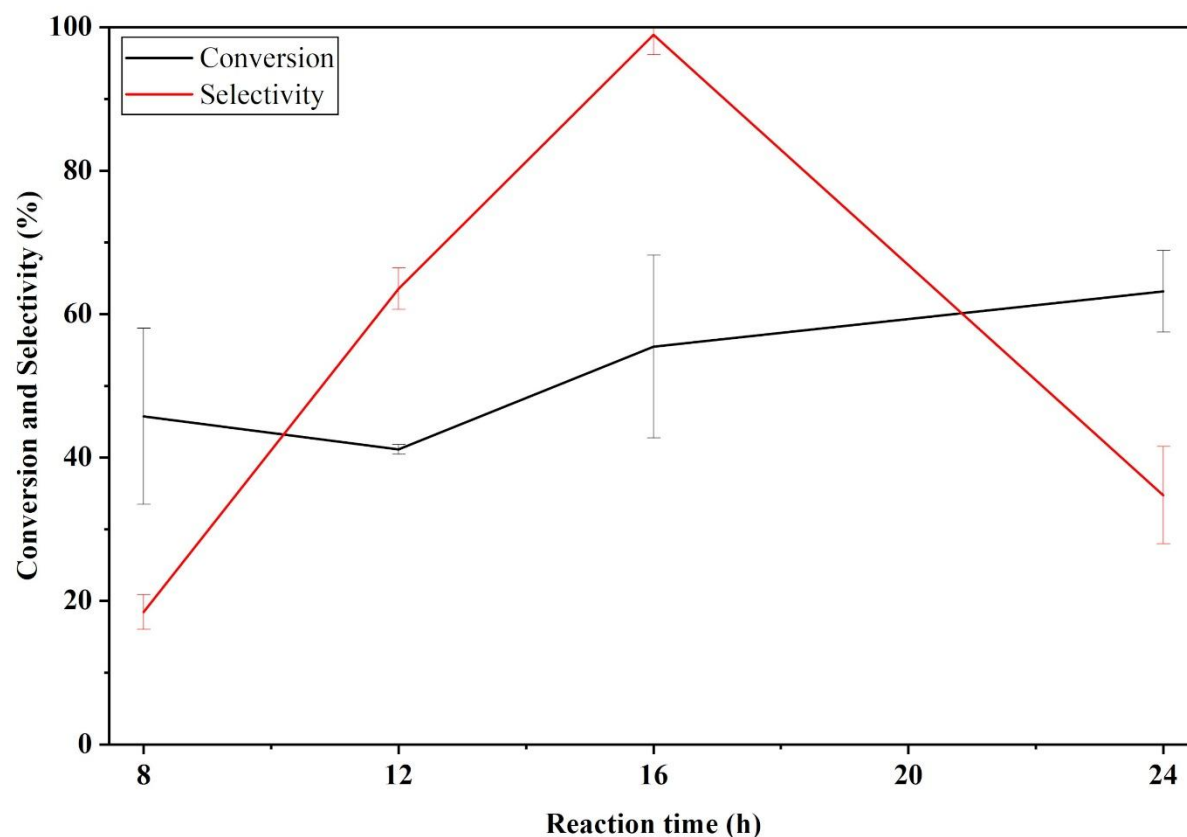


Fig. 11 Effect of reaction time on glycerol hydrogenolysis. Reaction conditions: glycerol (1 mmol), catalyst (50 mg), H₂O (20 mL), 200 °C, hydrogen pressure (20) and (6–16 h).

3.12 Catalyst loading

The effect of catalyst loading on glycerol hydrogenolysis over Cu–Pd/TiO₂ was investigated by varying the catalyst amount from 25 to 100 mg while maintaining the other reaction conditions constant. As shown in Fig. 12, increasing the catalyst loading from 25 to 100 mg increased glycerol conversion from 60.04% to 86.00%, indicating greater availability of active sites.

The 50 mg experiment gave the highest reported 1,2-PDO yield in this catalyst-loading series. Although glycerol conversion increased at 75 and 100 mg, the reported 1,2-PDO yields

were lower. The unexpected lower conversion at 50 mg than at 25 mg, together with variability in the data, requires confirmation before treating these differences as a reproducible loading effect.

These results show that higher catalyst loading enhanced glycerol conversion but reduced selectivity toward 1,2-PDO. Therefore, 50 mg Cu–Pd/TiO₂ was selected as the optimum catalyst loading, providing a favorable balance between glycerol conversion and selective formation of 1,2-PDO.

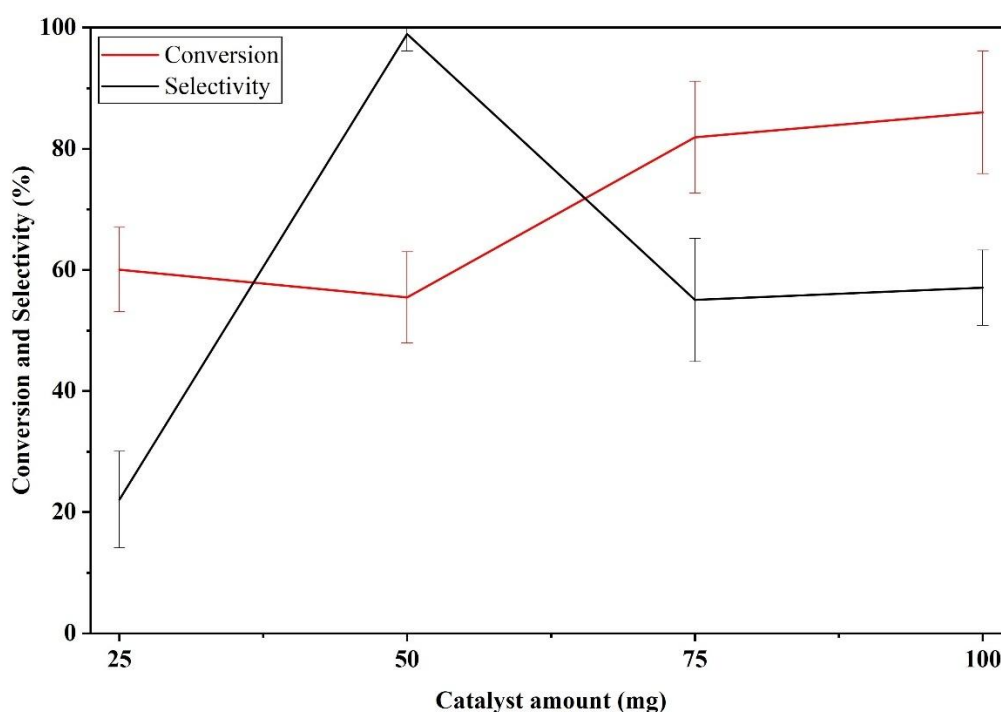


Fig. 12 Effect of catalyst amount on glycerol hydrogenolysis. Reaction conditions: glycerol (1 mmol), catalyst (25–100 mg), H₂O (20 mL), 200 °C, hydrogen pressure (20) and 16 h.

3.13 Effect of glycerol amount

The effect of glycerol amount on hydrogenolysis over Cu–Pd/TiO₂ was investigated by varying the glycerol loading from 0.5 to 4 mmol while keeping the other reaction conditions constant. As shown in Fig. 13, glycerol loading strongly affected both glycerol conversion and product selectivity.

The 1 mmol experiment gave the highest reported 1,2-PDO yield in the glycerol-loading series. The numerical selectivities for this condition must be recalculated because the reported 1,2-PDO and acetol selectivities sum to more than 100%. The higher-feed experiments gave lower reported 1,2-PDO yields under the same catalyst loading and reaction time.

The decrease in conversion at higher glycerol loading indicates that the available catalytic sites became less sufficient relative to the increased amount of glycerol under the fixed reaction conditions. The concurrent decrease in 1,2-PDO selectivity and increase in methanol and acetol selectivities also indicate a shift in product distribution at higher substrate loading. Therefore, among the investigated conditions, 1 mmol glycerol provided the highest glycerol conversion (63.38%) and 1,2-PDO selectivity (99.15%) and was selected as the optimum glycerol amount.

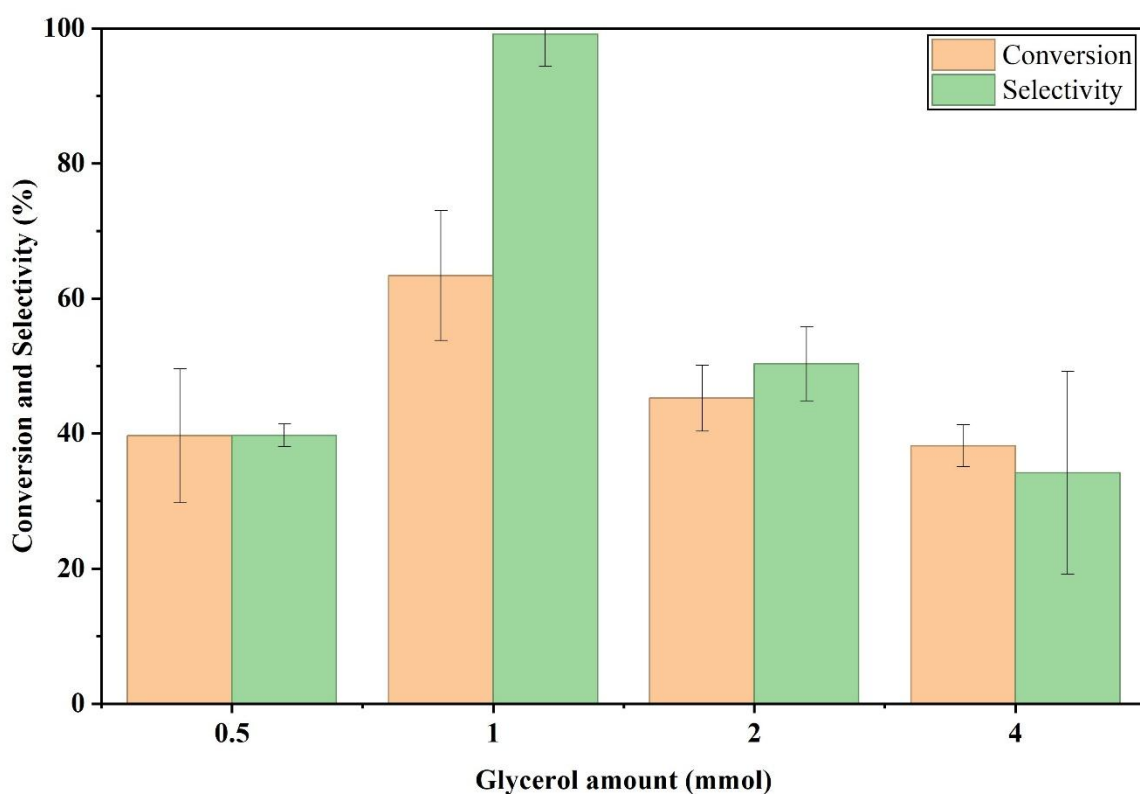


Fig. 13 Effect of glycerol amount on glycerol hydrogenolysis. Reaction conditions: glycerol (0.5–4 mmol), catalyst (50 mg), H₂O (20 mL), 200 °C, hydrogen pressure (20) and 16 h.

3.14 Recyclability

Catalyst recovery and reuse were assessed by centrifuging, washing, drying, and retesting the solid (Fig. 14). Conversion declined across the reported reuse runs, while the reported 1,2-PDO selectivity remained relatively high. The number of total runs, recovered catalyst masses, and uncertainties should be stated consistently before assigning stability or a deactivation mechanism.

The plot shows an initial (fresh) run followed by three labeled reuse runs. The observed decline in conversion may reflect catalyst loss during recovery or changes in the solid; neither explanation has been verified. Report the amount recovered at each stage and assess leaching or changes in catalyst composition before assigning a cause.

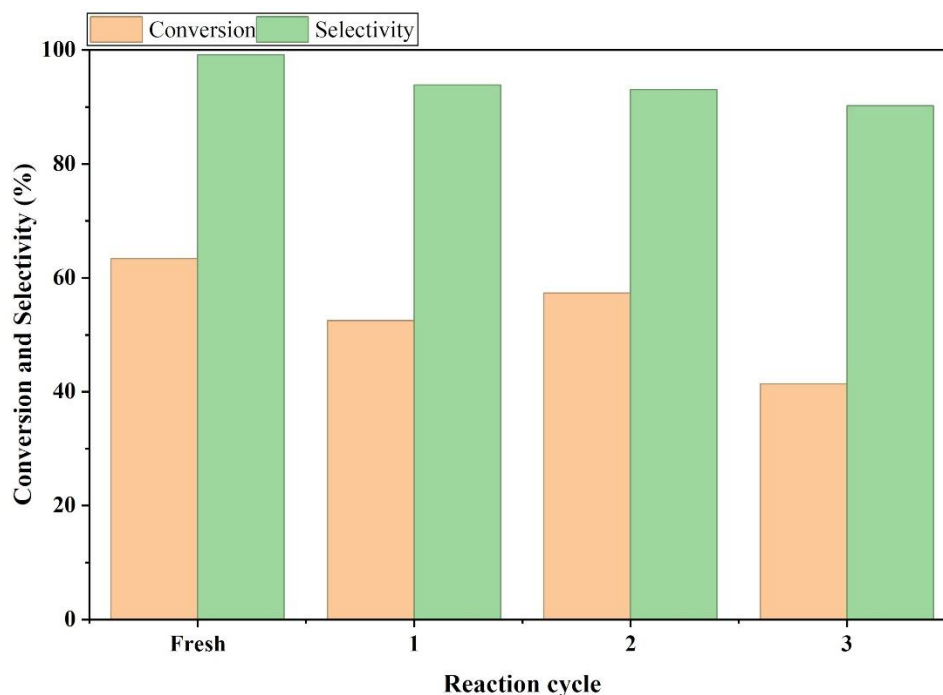


Fig. 14 Reusability of the Cu–Pd/TiO₂ catalyst for glycerol hydrogenolysis under the optimized reaction conditions.

4 Conclusion

Cu–Pd/TiO₂ catalysts were prepared by aqueous NaBH₄ reduction and evaluated for hydrogenolysis of dilute aqueous glycerol to 1,2-propanediol. XRD, nitrogen physisorption, microscopy, elemental mapping, and FTIR characterized the support and deposited metal species.

Under the screening conditions, the bimetallic formulation gave higher glycerol conversion and reported 1,2-propanediol yield than either monometallic formulation. Among the conditions tested, nominal loadings of 10 wt% Cu and 0.3 wt% Pd, 1 mmol glycerol, 50 mg catalyst, 20 mL water, an initial H₂ pressure of 20 bar, 200 °C, and 16 h gave 63.38% glycerol conversion. The product distribution varied with reaction conditions. Numerical selectivity, product balance, and reuse claims require reconciliation with the primary analytical records before submission.

These observations establish the catalytic behavior of a chemically reduced Cu–Pd/TiO₂ preparation under the dilute-feed conditions investigated here. Determining the catalyst

composition, accounting for all carbon-containing products, and measuring the catalyst state before and after reaction would help establish the origins of its activity and selectivity.

Supplementary Information

The online version contains supplementary material available at

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Author Contributions

A.I.Y.: Conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing—original draft. S.M.: Investigation, data analysis. S.Y.S.: Investigation. A.A.Y.: Investigation. M.A.A.: Investigation. A.M.S.: Investigation. K.C.: Conceptualization, methodology, resources, supervision, project administration, funding acquisition, writing—reviewing and editing.

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Data Availability

Data will be made available on request.

Declarations

Competing Interests

The authors declare no competing interests.

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