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IMMOBILIZED Pd CATALYSIS FOR HYDROGENATION

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Abstract.

This review is dedicated to the memory of scientists Alima Kainekeevna Zharmagambetova and Sabira Gafurovna Mukhamedzhanova, whose pioneering contributions significantly influenced the development of supported catalysts. This manuscript summarizes the fundamental studies on the design of supported palladium–polymer complexes for hydrogenation reactions. Although these studies were conducted between 1975 and 2000, before the emergence of concepts such as enzymatic catalysis and green chemistry, the established approaches to the selection of supports, polymer ligands, and synthesis conditions remain relevant. These principles enable the development of selective and stable catalysts that operate under mild conditions and exhibit long-term activity in hydrogenation processes.

Keywords: Hydrogenation, Palladium-polymer complex, Pd - nanoparticles, Catalyst, Polymer

1. Introduction

The development of immobilized complex catalysts is driven by the need to integrate the excellent catalytic activity and selectivity of homogeneous catalysts with the ease of separation from reaction products, recovery, and reuse that characterize heterogeneous catalytic systems. Two main types of supports are commonly used for complex immobilization: organic polymers and inorganic oxides. Polymer supports offer several advantages in catalysis due to their ability to readily form chemical bonds with metal ions. When the active phase of a catalyst is immobilized on the surface of a polymer support, a polymer–metal complex (PMC) is formed, in which the polymer acts as a macroligand. Interest in PMCs is largely driven by their similarity to natural catalytic systems, particularly enzymes [1–3]. Many enzymes contain strongly bound metal ions, typically transition metals, and function in combination with coenzymes. The polymeric nature of enzyme molecules is essential for maintaining their three-dimensional structure and catalytic activity. In one of the pioneering studies, Yu. I. Ermakov [4] compared homogeneous, heterogeneous, and immobilized metal complexes and demonstrated the advantages of immobilized catalytic systems, which combine the high activity of homogeneous catalysts with the operational benefits of heterogeneous catalysts.

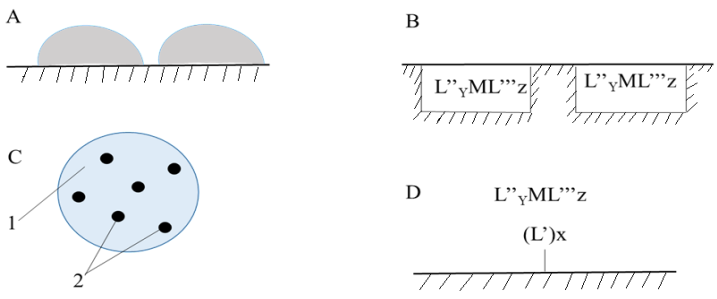

Figure 1 - Different types of catalysts containing immobilized complexes on supports:

A - complexes present as a dispersed phase or adsorbed on the support surface;

B – complexes dissolved in a non-volatile solvent and confined within the pores of the support;

C – complexes immobilized in a polymer gel: (1) an elastomer capable of swelling in the reaction medium; (2) domains containing active centers;

D – complexes immobilized through interaction with a surface ligand (L′) chemically bonded to the support

This manuscript summarizes own fundamental studies on the design of supported palladium–polymer complexes for hydrogenation reactions.

2. Polyvinylpyridine palladium complexes

Polymers containing functional groups are widely used to immobilize metal ions [5-8]. In many cases, even minor variations in the preparation method lead to significant differences in the catalytic activity of the resulting polymer–metal complexes (PMCs). Polyvinylpyridines are promising polymeric materials that can serve as catalytic supports. The polymer complexes P2VP–Pd(II) and P4VP–Pd(II) were synthesized by mixing ethanol solutions of $PdCl_2$ and the corresponding polymer at a 1:1 molar ratio, resulting in catalysts containing 1.2 wt.% Pd. The obtained precipitates were washed with ethanol and air-dried at room temperature. The polymer complexes were subsequently reduced with $NaBH_4$ in aqueous solution, washed with water, and evaluated in the hydrogenation of allyl alcohol. Palladium black was prepared by reducing $PdCl_2$ in aqueous solution using a twofold excess of $NaBH_4$.

Poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) contain nitrogen atoms in different positions within their pendant pyridine groups relative to the polymer backbone. The position of these functional groups influences the polymers' ability to complex and, consequently, may affect their catalytic activity. P2VP can form coordination bonds between neighboring 2-vinylpyridine units, whereas P4VP predominantly forms intermolecular cross-linked structures. Based on the ability of $PdCl_2$ to form binuclear bridged complexes, the following structural models can be proposed for P4VP–Pd (II) (a) and P2VP–Pd (II) (b).

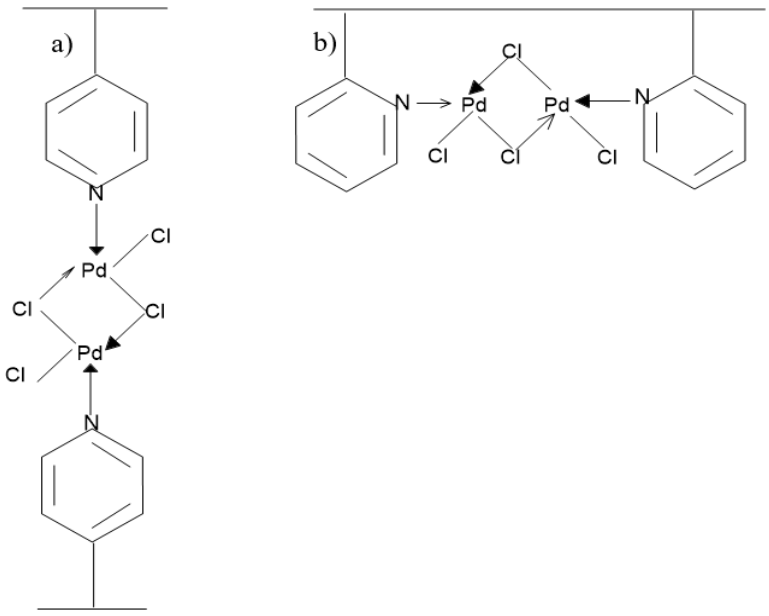

Figure 2 – Pd complexes with: a) P4VP, b) P2VP [6]

Polyvinylpyridine (PVP) is readily soluble in ethanol. Mixing ethanol solutions of PVP and $PdCl_2$ forms yellow precipitates that gradually transform into swollen flakes upon prolonged stirring. The persistent yellow color of the mother liquor indicates incomplete palladium binding. Spectrophotometric analysis confirmed this observation. The N:Pd atomic ratios for P2VP–$PdCl_2$

and P4VP–$PdCl_2$ were 1.6 and 1.8, indicating mixed-composition complexes in which palladium coordinates with one or two pyridine nitrogen atoms. Coordination with more than two polymer chains is sterically hindered. Reduction with $NaBH_4$ changes the complex color from yellow to gray, yielding complexes of the formula L_2 $PdCl_2$. IR spectroscopy confirmed complex formation. Compared with the free ligands, the complexes showed deformation of the C=C and C=N bonds in the pyridine ring. Absorption bands at 1620 cm^{-1} for P2VP–$PdCl_2$ and 1612 cm^{-1} for P4VP–$PdCl_2$ indicate coordination between pyridyl nitrogen atoms and palladium.

Table 1 - Analytical and IR spectroscopic data for PVP–$PdCl_2$ complexes [5]

Catalyst	Contents (%)			Empirical atomic ratios		ν(C=C), ν(C=N) (cm^{-1})
	N	Pd	Cl	N/Pd	Cl/Pd	
Calculated values						
PVP	15.2	—	—	—	—	
PVP–$PdCl_2$	5.2	39.5	19.6	1	2	
$(PVP)_2$ –$PdCl_2$	7.8	29.4	26.4	2	2	
Experimental values						
P2VP	14.0	—	—	—	—	1590
P2VP–$PdCl_2$	5.2	24.6	25.0	1.6	3.0	1620
P2VP–$PdCl_2$ ($NaBH_4$)	6.4	25.9	17.4	1.9	2.0	1600, 1590
P4VP	14.3	—	—	—	—	1596
P4VP–$PdCl_2$	6.5	27.0	24.0	1.8	2.7	1612
P4VP–$PdCl_2$ ($NaBH_4$)	6.6	28.5	18.3	1.9	1.9	1597, 1614

The vibrational bands shifted to higher frequencies, while $NaBH_4$ -treated samples showed bands of both free and coordinated pyridine groups. This indicates partial cleavage of N–Pd bonds and partial reduction of Pd(II) under H_2 or $NaBH_4$ treatment. Reduction of Pd(II) to Pd(0) was achieved using either H_2 or $NaBH_4$, resulting in binding energies of 335.3 and 335.6 eV, respectively. H_2 -reduced samples also showed a Pd $3d_5$ /$_2$ peak at 336.5 eV, attributed to Pd(I). Pd(II) species remained in both samples. After hydrogenation, the catalyst contained Pd(II) and Pd(0), whereas Pd(I) disappeared. Hydrogen treatment reduced 17% of the palladium to Pd(0), while $NaBH_4$ reduced only 4% of the palladium to Pd(0). After hydrogenation of 2-propen-1-ol, the Pd (0) content increased to 30–33%. These values may be uncertain because nanosized palladium particles (10–100 Å) can exhibit binding energies that differ from those of bulk metal.

Investigations of PVP–$PdCl_2$ complexes demonstrate that the active hydrogenation catalyst is not a single species but a composite system comprising the parent PVP–$PdCl_2$ complex and Pd (0) species stabilized within the polymer matrix. The functional groups of PVP ensure the retention and stabilization of Pd (0) particles, minimizing their tendency to aggregate.

The catalytic activity of P2VP–Pd (II) and P4VP–Pd (II) complexes was investigated in the hydrogenation of allyl alcohol.

$$CH_2{=}CH\text{-}CH_2OH + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2OH \quad (1)$$

Polyvinylpyridine palladium complexes promote the selective hydrogenation of allyl alcohol to propanol, providing product yields of 86–89%. Analysis of the specific rate of allyl alcohol hydrogenation revealed the following order of catalytic activity:

P4VP–Pd(0) > P2VP–Pd(0) > P4VP–Pd(II) > P2VP–Pd(II) > Pd black.

The high activity of P4VP–Pd(0) is attributed to the greater steric accessibility of the palladium centers in this complex, which facilitates reduction by hydrogen or $NaBH_4$ and the activation of allyl

alcohol, thereby enabling subsequent catalysis. The catalytic system is believed to consist of palladium species reduced to the zero-valent state and immobilized on the polymer surface, together with unreduced fragments of the poly(2-vinylpyridine) or poly(4-vinylpyridine) complexes.

Both the reaction conditions and the substrate type significantly affect the catalytic behavior of PVP–$PdCl_2$ (Table 3). Compared with palladium black, the PVP–$PdCl_2$ catalyst showed superior activity for the hydrogenation of unsaturated alcohols and aldehydes in both water and ethanol. Aldehydes were hydrogenated only at the double bond, while the carbonyl group remained unaffected. Hydrogenation of 2-propen-1-ol over palladium black produced 48% n-propionaldehyde due to isomerization, whereas PVP–$PdCl_2$ yielded 98–99% n-propanol. No clear correlation was observed between catalytic activity and catalyst pretreatment with reducing agents. The catalytic response to $NaBH_4$ reduction was substrate-dependent. For unsaturated alcohols, treatment in water promoted hydrogenation, whereas reduction in ethanol adversely affected catalytic performance. In contrast, $NaBH_4$ treatment resulted in lower hydrogenation rates of unsaturated aldehydes in both aqueous and ethanolic media.

Table 2 - Effect of catalyst reduction method on the hydrogenation rates [5]

Hydrogenated substrate	Pd black		P2VP–$PdCl_2$			
	Water	Ethanol	Water		Ethanol	
			H_2	$NaBH_4$	H_2	$NaBH_4$
2-propen-1-ol	0.6	0.3	22.0	98.8	190.2	189.2
3-phenylpropen-2-ol-1	0.4	2.3	4.1	17.0	46.3	13.9
butene-2-al	0.7	3.2	5.3	5.0	67.9	14.6
2-phenylpropen-2-al-1	0.9	3.0	5.8	3.5	7.3	1.9

The different behavior of alcohols and aldehydes over $NaBH_4$ -reduced complexes is likely related to their activation mechanisms: alcohols are mainly activated by Pd(0), whereas aldehydes are activated by Pd(II). Hydrogenation over H_2 -treated PVP–$PdCl_2$ proceeds faster in ethanol than in water, which is attributed to enhanced swelling of the polymer–metal complexes and changes in catalyst composition. Elemental analysis indicated a PVP crosslinking degree of 25–29% in the presence of Pd ions. Treatment with H_2 or $NaBH_4$ partially cleaves N–Pd bonds, forming reduced palladium species and increasing catalyst swelling, thereby improving access to active Pd sites and accelerating hydrogenation. This effect is more pronounced for small molecules, while diffusion of phenyl-containing compounds into the swollen matrix is sterically hindered. Swelling of PVP–$PdCl_2$ is significantly greater in ethanol, increasing hydrogenation rates. When $NaBH_4$ is used as the reducing agent in ethanol, catalytic performance deteriorates. A plausible explanation is that the higher Pd(0) content promotes aggregation of reduced palladium species, thereby diminishing their effectiveness in activating unsaturated compounds.

Based on the experimental results, hydrogen activation initially occurs through palladium reduction during treatment with H_2 or $NaBH_4$. Once Pd(0) species are formed, hydrogen activation mainly proceeds on Pd(0) centers, whereas unsaturated compounds can be activated on both Pd(II) and Pd(0) through π-complex formation. In swollen-gel catalytic systems, swelling facilitates access to additional active Pd sites within the polymer matrix. Flexible polymer chains suppress palladium leaching, particle growth, and agglomeration, reducing catalyst deactivation and enabling repeated reuse without significant loss of activity. This behavior is expected to be characteristic of other gel-immobilized polymer–metal catalysts, as their catalytic properties are strongly affected by solvent swelling and the interaction between metal species and the polymer network.

Consequently, the catalytic efficiency of the $PdCl_2$ –PVP system is primarily determined by achieving an optimal equilibrium palladium content within the polymer–metal complex (PMC). This can be accomplished either by prolonged aging of the complex in the mother solution or by heating the initial $PdCl_2$ and PVP solutions to 50–60 °C. An active and stable hydrogenation catalyst was

obtained by reacting ethanol solutions of $PdCl_2$ and PVP at a PVP:Pd ratio of 1:1, followed by aging of the complex in the initial solution for 3 days. The catalytic activity depends on the ratio of reduced to oxidized palladium species. Pretreatment of the complex with $NaBH_4$ increased the hydrogenation rate by 5–5.5 times. The developed catalyst exhibited high activity and stability in the hydrogenation of unsaturated alcohols.

2.1 Anchoring of Polymer–Metal Complexes on Oxide Surfaces

The catalytic efficiency of supported metal systems is strongly influenced by the size and dispersion of the metal particles. However, the immobilization of metal catalysts, particularly coordination complexes, continues to present considerable challenges. Conventional polymer supports are frequently limited by diffusion resistance and insufficient thermal and mechanical stability. These shortcomings can be overcome by modifying inorganic oxide supports with functional polymers. On this basis, a new strategy has been developed in which polymer–metal complexes are formed directly on oxide surfaces, leading to hybrid catalytic materials with improved performance [9–10]. The heterogeneous catalysts with a uniform distribution of metal particles were prepared using a linear polymer (poly(2-methyl-5-vinylpyridine)) and transition-metal ions. A suspension of oxide (0.2 g) in ethanol (5 mL) was mixed with 5 mL of an ethanol solution containing 0.011 g of PMVP (5.55 wt.% relative to the support) and stirred vigorously for 2 h. Then, 5 mL of an ethanol solution of H_2 $PdCl_4$ containing 0.01 g of Pd (5.0 wt.% relative to the support) was added, and the mixture was stirred for at least 3 h until complete palladium binding was achieved. The resulting catalyst was aged in the mother liquor for at least 10 h, separated, washed with 50 mL of ethanol, dried, and stored at room temperature in air. The final catalyst composition (wt.%) was: Pd, 5.0; poly-2-methyl-5-vinylpyridine, 5.55; oxide support, 89.45.

The micrograph of the prepared Pd–P2M5VP/MgO catalyst is shown in Figure 3. A uniform distribution of Pd nanoparticles (6–8 nm in size) is observed on the surface of polymer-coated magnesium oxide.

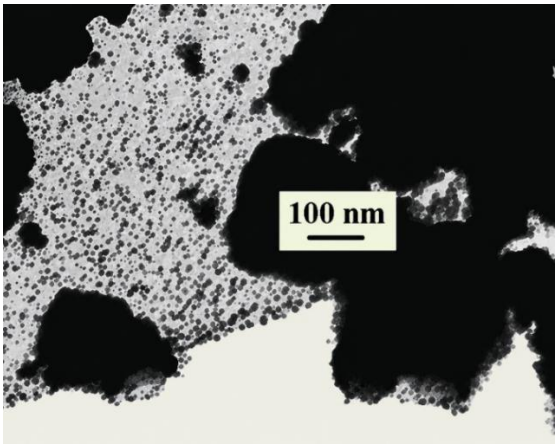

Figure 3 - Micrograph of 5% Pd–P2M5VP/MgO catalysts [10]

The catalytic properties of 5 wt% Pd–P2M5VP supported on ZnO and MgO were examined using the hydrogenation of 3,7,11-trimethyldodecyn-1-ol (TMD) as a model reaction. Hydrogenation experiments were conducted in a thermostatically controlled glass reactor containing 0.025 L of ethanol, stirred continuously at 50 °C and under atmospheric hydrogen pressure. Before each experiment, the catalysts were activated by hydrogen treatment for 30 min. Catalyst durability was evaluated by sequential addition of TMD to the reaction medium, and the conversion of TMD was calculated using the following equations:

$$S_{hydr.} = \frac{[3,7,11\text{-trimethyldodecene-1-ol}]}{[3,7,11\text{-trimethyldodecene-1-ol}] + [3,7,11\text{-trimethyldodecane-1-ol}]} \times 100\%$$

Independent of the catalyst composition, TMD hydrogenation followed a two-step sequence in which 3,7,11-trimethyldodecen-1-ol was formed as an intermediate and subsequently hydrogenated to 3,7,11-trimethyldodecane-1-ol. The hydrogenation results are summarized in Table 1. All catalysts showed nearly identical yields of olefinic alcohol, with process selectivity ranging from 82–85%.

Table 3 - Hydrogenation of TMD on palladium-supported catalysts

Catalysts	Surface area, m^2/g	Isoelectric point of oxides	Particle sizes, nm	$W10^{-5}$ mole/l sec	$S_{c=c}$, %	Stability, TON
Pd/MgO	6.8	12.1-12.7	7-10, 20-25	25.6	82	800
Pd-P2M5VP/MgO			5-7	21.8	85	4800
Pd/ZnO	88	7.0-9.0	30-35	16.5	85	400
Pd-P2M5VP/ZnO			6-8	21.4	85	6700

Only minor differences in catalytic activity and selectivity were observed as a function of the preparation method or the oxide support. By contrast, the P2M5VP modifier played a key role in the catalyst's formation and long-term stability. Analysis of the turnover numbers (TON) demonstrated that incorporating P2M5VP improved catalyst stability by more than an order of magnitude compared with polymer-free systems (Table 3).

Coordination of $PdCl_2$ with poly(vinylpyridines) produces polymer–metal complexes that function as highly active, selective, and stable hydrogenation catalysts. The remarkable stability of these systems is attributed to the stabilizing effect of the polymer network, which limits the aggregation of palladium species. In polymer-modified ZnO and MgO supports, Pd(II) ions are immobilized via coordination to the pyridine nitrogen atoms of P2M5VP, resulting in a more uniform dispersion of palladium across the oxide surface. Evidence for this mechanism is provided by electron microscopy of the Pd/MgO catalyst lacking the polymer coating (Figure 3), which revealed irregularly shaped palladium particles distributed non-uniformly over the support surface.

The available results indicate that soluble functional polymers are promising materials for the fabrication of supported catalysts. Coordination of transition-metal ions with polymer functional groups anchored on oxide supports facilitates uniform metal dispersion, while the polymer framework stabilizes the metal particles by preventing their aggregation and subsequent catalyst deactivation. As a result, these hybrid polymer–metal systems combine high activity with excellent selectivity and operational stability. Nevertheless, optimal catalyst performance requires maximizing the accessibility of the metal surface by minimizing polymer-layer shielding of the active sites.

3. Polymer metal catalysts on oxides as a highly organized system

Active metal ions (e.g., palladium) interact with functional groups of polymers supported on oxides, forming anchored surface polymer–metal complexes. Such systems can be classified as mixed-type systems that simultaneously employ approaches “c” and “d” (Figure 1); that is, complexing polymers are used as ligands (L) immobilized on the solid surface. These polymers impart macromolecular properties to the catalysts, including the flexibility and mobility of polymer chain segments containing embedded metal particles, as well as swelling behavior in various solvents. It is known [11-13] that macromolecules are adsorbed virtually irreversibly on inorganic substrates, particularly oxides, due to cooperative interactions between polymer chain segments and the support. This solves one of the most difficult problems of immobilized complexes—preventing the washout of the active phase.

The factors influencing the properties of the developed catalysts were investigated:

the nature of the carrier – acidic, amphoteric, and basic oxides with different specific surface areas; Polymer–palladium complexes were immobilized on the surfaces of various oxides, including SiO_2 , Al_2O_3 , TiO_2 , CeO_2 , ZnO, and MgO. It was demonstrated that high catalytic activity, selectivity, and stability are maintained when amphoteric ZnO, despite its relatively low specific surface area (2.0 $m^2 g^{-1}$), is used as the support. On oxides with low specific surface areas, PEG is adsorbed predominantly as loops and tails, similar to its adsorption behavior in concentrated polymer solutions [14]. Upon immobilization on such supports, Pd ions become localized near the polymer's functional groups, leading to the formation of nanosized active-phase particles surrounded by polymer chains. As a result, the catalyst retains the advantages of both conventional heterogeneous catalysts and enzyme-like polymer–metal systems, including conformational flexibility, swelling behavior, random-coil characteristics, high activity and selectivity, enhanced productivity, and stability during repeated hydrogenation cycles under mild reaction conditions.

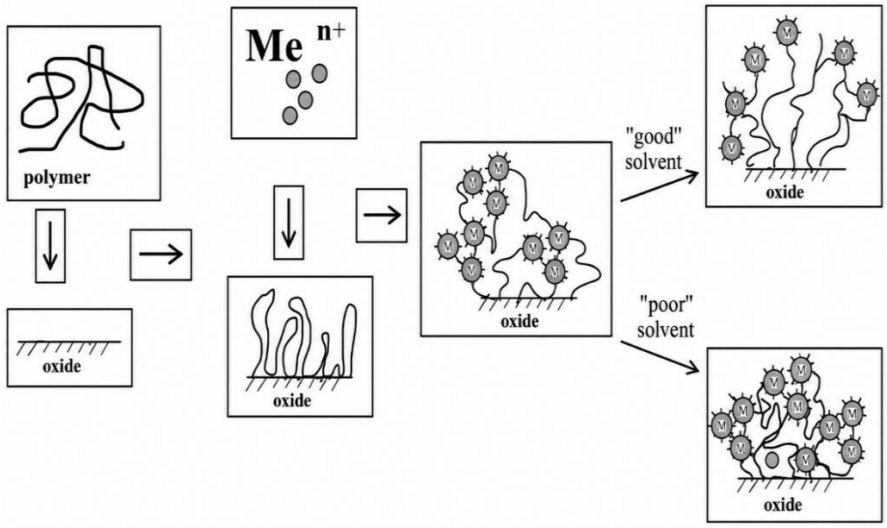

Figure 2 - Scheme for the preparation of PMC-on-oxide surface catalysts

The advantages of oxide-supported PMCs were demonstrated by comparing catalysts prepared with and without polymers. Although the polymer-free catalysts exhibited relatively high initial hydrogenation rates, they rapidly deactivated upon repeated use.

The nature of macromolecules – non-ionic (PEG), polybase (P2M5VP), polyacid (PAA) [15]; Surface modification of magnesium and zinc oxides with polyethylene glycol (PEG, a nonionic polymer), polyacrylic acid (PAA, a polyacid), and poly(2-methyl-5-vinylpyridine) (P2M5VP, a polybase) showed (Table 16) that the nature of both the support and the polymer modifier significantly affects catalytic selectivity. When the more basic support, MgO, was modified with polyacrylic acid, the selectivity toward the formation of C15 olefin alcohol increased. In contrast, treatment of amphoteric ZnO with polyacrylic acid reduced selectivity. Among the modifiers investigated, nonionic PEG proved to be the most effective for ZnO-supported catalysts.

Table 5 - Effect of polymer modification on the properties of Pd catalysts supported on magnesium and zinc oxides.

Catalyst	Polymer characteristics	Selectivity, %	
		(5%Pd)-polymer /MgO	(1%Pd)-polymer/ ZnO
Pd/oxide	-	82	89
Pd-P2M5VP/oxide	Polybase	80	92
Pd-PEG/oxide	Non-ionic	78	98
Pd-PAA/oxide	Polyacid	92	79

The 1% Pd–PEG/ZnO catalyst exhibits a hydrogenation selectivity of up to 98%, with the reaction spontaneously stopping upon consumption of 1 mole of hydrogen. These results demonstrate that the catalytic properties can be effectively tuned by selecting an appropriate polymer modifier. The nature of the polymer primarily influences the selectivity of the hydrogenation process, leading to improved formation of the desired products.

Catalyst preparation conditions: varying the length of the macromolecular chain; varying the contact time between the polymer and palladium in the mother liquor; stabilizing the carrier on the oxide surface by additional calcination [16-18]. Studies have demonstrated that the most effective approach for preparing nanostructured, active, and stable catalysts is the sequential deposition of the polymer, followed by the metal, onto the support. Improved catalytic properties were achieved when the support was contacted with the polymer for 5 h instead of the standard 2 h. Similar results were obtained by extending the catalyst aging time in the mother liquor to at least 10 h. In both cases, catalysts with high activity, selectivity, and stability in the hydrogenation of C15 and C20 acetylenic alcohols were formed. The total preparation time can be reduced to 8 h by drying the polymer-modified oxide at 100 °C after 5 h of polymer adsorption, followed by adsorption of palladium chloride, yielding the most active and selective catalyst studied.

Table 6 summarizes the main characteristics of homogeneous and heterogeneous catalysts, highlights the differences between these catalytic systems, and presents the expected advantages of immobilized catalysts.

Table 6 - Comparison of parameters of different types of catalysts

Properties of catalysts	Catalyst type			
	Homogeneous catalyst	Heterogeneous catalyst	Immobilized complexes	**PMC on oxides**
Activity	-	+	+	+
Typical operating range of catalytic systems	-	+	+ -	+
The possibility of multiple ions participating in the catalytic process	-	+	+ -	+
Stability	-	+	+	+
Ease of separation from the reaction products	-	+	+	+
Variation of ligands coordinated to the transition metal ion at the catalytic active site	+, -	-	+	- +
Identification of active sites	+	-	+	+
Selectivity	+	-	+	+
Asymmetric induction	+	-	+	+

Table 6 summarizes the key properties of homogeneous catalysts, heterogeneous catalysts, immobilized complexes, and oxide-supported polymer–metal complexes. The comparison demonstrates that oxide-supported PMCs combine the high activity and selectivity typical of homogeneous catalysts with the stability, broad operating range, and ease of separation characteristic of heterogeneous catalytic systems.

4. Conclusion

Palladium-based polymer catalysts are widely used in organic synthesis, and their properties depend on the polymer composition, structure, and preparation conditions. The incorporation of polymer ligands into heterogeneous catalysts imparts characteristics typical of linear macromolecules, including swelling and sensitivity to the solvent and environmental conditions.

Therefore, the catalyst preparation and reaction conditions were optimized. Novel nanosized palladium catalysts based on polymer–metal complexes (PMCs) immobilized on various inorganic oxides have been developed for the selective hydrogenation of acetylenic alcohol compounds. The use of oxide supports with low specific surface areas (2–10 $m^2 g^{-1}$) was found to improve both the catalytic activity and long-term stability of the resulting catalysts. The acid–base properties of the oxide support and polymer modifier play a key role in determining the selectivity of hydrogenation of acetylenic alcohols to olefinic products. The optimal performance was achieved with a 1 wt.% Pd catalyst supported on amphoteric ZnO modified with polyethylene glycol (PEG).

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Author Contributions

Conceptualization: Indira Kurmanbayeva, Formal analysis: Bagadat Selenova, Investigation: Sabira Mukhamedzhanova, Bagadat Selenova, Indira Kurmanbayeva, Methodology: Alima Zharmagambetova, Supervision: Alima Zharmagambetova, Visualization: Indira Kurmanbayeva, Writing – original draft: Indira Kurmanbayeva, Writing – review & editing: Bagadat Selenova.

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Data availability statement: The data presented in this study may be obtained on request from the corresponding author.

Disclosure of the use of generative Artificial Intelligence (AI)

The authors used ChatGPT 5.2 to organize the references and Grammarly to improve English grammar.

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