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Original Research Article

Partial Hydrogenation of Sunflower and Soybean Oil Over Zirconia Supported Platinum Catalyst

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Abstract

1.0% Pt/ZrO_2 catalyst was synthesized and thoroughly characterized to evaluate its structural, morphological, and surface properties, as well as its catalytic performance in the selective hydrogenation of sunflower and soybean oils. XRD analysis confirmed the formation of mixed monoclinic and tetragonal zirconia phases, with platinum highly dispersed on the support. Nitrogen adsorption–desorption studies revealed a surface area of 25.0 m^2/g and an average pore diameter of 19.0 nm. SEM and TEM analyses showed nanosized particles (55–100 nm) with uniformly distributed Pt nanoparticles (2–8 nm). XPS spectra identified Pt^0, Pt^{2+}, and Pt^{4+} oxidation states, while TPR-H_2 and TPD-H_2 profiles demonstrated strong metal–support interaction and the predominance of weakly bound hydrogen species conducive to selective hydrogenation. Catalytic tests showed that the 1.0% Pt/ZrO_2 catalyst enabled partial hydrogenation of sunflower and soybean oils at 90 °C and 0.5 MPa, achieving high activity and low trans-isomer contents (6.0% and 5.6%, respectively). Compared with conventional Ni catalysts, which require higher temperatures (130–150 °C) and generate over 25% trans-isomers, the Pt-based system exhibited superior selectivity and energy efficiency. The catalyst retained its activity and selectivity over eight reuse cycles, maintaining stable structure and low trans-isomer formation. The resulting hydrogenated products met international regulations (<2.0% trans-isomers in final fat blends) and displayed favorable solid fat contents for food applications. These results demonstrate that the 1.0% Pt/ZrO_2 catalyst is an efficient, selective, and reusable system for producing high-quality, trans-fat–compliant hydrogenated oils under mild operating conditions.

Keywords: sunflower oil; soybean oil; hydrogenation; trans isomer; platinum catalyst

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1. Introduction

Hydrogenation of vegetable oils is a catalytic process in which hydrogen atoms are added to unsaturated fatty acids to convert them to saturated or partially saturated forms. This reaction takes place at controlled temperatures and pressures in the presence of a catalyst [1]. A schematic representation of this process is shown in Figure 1. The primary objective of hydrogenation is to increase the shelf life and stability of the oil by reducing the number of double bonds in the fatty acid chains, thus making the oil more solid at room temperature. This transformation is commonly used in the production of margarine and shortening [2]. However, partial hydrogenation may lead to trans fat formation, which has been associated with adverse health effects, including increased risk of cardiovascular disease [3,4].

Currently, nickel catalysts are widely used in the hydrogenation of vegetable oils. This process, which employs nickel catalysts, is conducted at high temperatures (180–200 °C), promoting the

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thermal decomposition of fatty acids. As a result, toxic nickel salts with carcinogenic properties may be present in the final products [5]. However, the primary concern is the formation of significant quantities of undesirable trans isomers [6]. Modern medical research strongly indicates that high levels of trans fatty acids in food are linked to severe health issues, including ischemic heart disease, myocardial infarction, coronary artery disease, vascular disorders, certain cancers, metabolic dysfunction, and weakened immune response [7-9].

The regulation of trans fatty acids in fats and oils varies globally, with many countries setting standards or limits to reduce their intake due to the associated health risks [10-12]. These regulations are typically set by food safety authorities and health organizations. Since 2006, the U.S. Food and Drug Administration (FDA) has required that all food products containing 0.5 g or more of trans fat per serving must list the amount on the nutrition label [13]. It has been recommended that trans fat intake no exceed 1% of total daily energy consumption by the WHO because of the harmful effects it has on public health. Therefore, it has called on governments to implement stringent policies and regulations aimed at eliminating industrially produced trans fats from the global food supply by 2023 [14].

The Eurasian Economic Union EAEU Technical Regulations on Food Safety (TR TS 021/2011) stipulate the need for reducing trans fats in foods across member states, including Kazakhstan. This regulation ensures that food products do not exceed a certain level of trans isomer (2%), especially in oils and fats [15]. Currently, hydrogenation of vegetable oils is the primary method of their modification in Kazakhstan, which can result in the content of trans isomers in some products (margarine and spread) reaching 20-40% [16,17].

As a result, reducing trans isomer content in hydrogenated oils has become a significant research focus. Recent advancements in catalytic technologies aim to improve the selectivity of hydrogenation processes, minimizing the production of trans fats. Researchers have developed catalysts, such as modified nickel-based catalysts [18], noble metals catalysts [19,20], bimetallic catalysts [21], and enzyme-based systems [22], to achieve more efficient hydrogenation with reduced trans isomer formation.

This study synthesizes platinum (Pt) catalysts supported on ZrO_2 for hydrogenation of sunflower and soybean oils. The performance of these catalysts is evaluated based on their activity, changes in fatty acid composition, formation of trans isomers, and solid fat content, thereby providing insight into their effectiveness at altering the physicochemical properties of oils.

2. Materials and Method

2.1 Materials

In this study, used sunflower and soybean oils were sourced from the local market in Almaty, Kazakhstan. The chemicals employed included zirconia powder (ZrO_2, 99.9% purity) from Zhengzhou Xinli Wear-resistant Materials Co., Ltd., China; polyvinylpyrrolidone (*M*M: 360 000, Sigma-Aldrich, USA); sodium borohydride (purity ⩾99.8%, Sigma- Aldrich, USA), hexahydrate chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, with ≥37.5% Pt content) from Sigma-Aldrich, USA; and hydrogen gas supplied by LLP "Kaztechgas," Kazakhstan, Ni catalyst (Pricat 9920, Johnson Matthey Catalysts, with 23% Ni).

2.2 Catalyst Preparation and Characterizations Methods

The 1.0 wt% Pt/ZrO_2 catalyst was synthesized via a colloidal deposition method. Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was dissolved in 50 mL of distilled water, followed by the addition of a 1 wt% polyvinylpyrrolidone (PVP) solution as a stabilizer. The mixture was stirred for 30 minutes at room temperature. A 0.1 M sodium borate solution was then added dropwise, forming a stable platinum colloid. This

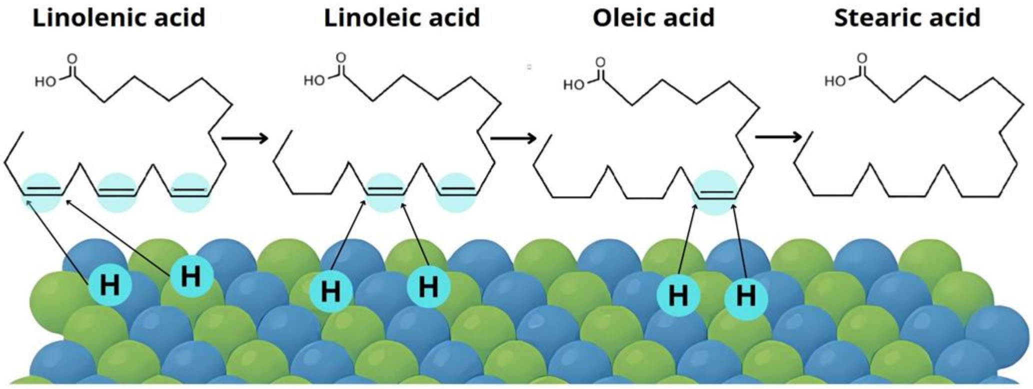

Figure 1. Reaction scheme: hydrogenation of fatty acids.

colloidal solution was mixed with zirconia (ZrO_2) powder and stirred for 1 hour to enable adsorption of the Pt nanoparticles onto the support. The resulting solid was filtered, washed thoroughly with distilled water, and dried at 110 °C. Finally, the catalyst was calcined in air at 300 °C for 3 hours. X-ray phase analysis (XRD) was performed using a D8 Advance powder X-ray diffractometer (Bruker) with Cu-Kα radiation (λ = 0.15406 nm) and a position-sensitive linear detector Lynxeye. The textural characteristics of the catalyst was analyzed using a Micromeritics ASAP 2020 gas adsorption analyzer. Prior to measurements, the samples were degassed at 300 °C for 4 hours under a vacuum to remove any adsorbed moisture or impurities. The surface area, pore volume, and pore size distribution of the catalysts were analyzed using nitrogen adsorption at 77 K. The specific surface area was calculated using the BET (Brunauer-Emmett-Teller) method, while the BJH (Barrett-Joyner-Halenda) method was employed to determine the pore size distribution. The surface morphology of the catalyst was meticulously examined using a field-emission scanning electron microscope (FE-SEM), specifically a Hitachi SU-8000 model, operated at an acceleration voltage of 20 kV. The microstructure of the catalyst was investigated using high resolution transmission electronic microscopy (HR TEM) on a JEM-2010 apparatus (JEOL, Japan) with an accelerating voltage of 200 kV and a spatial resolution of 0.14 nm. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a XSAM-800 spectrometer (KRATOS Co.). An Al-Kα radiation source was used, and the binding energy values were calibrated using the C1s peak at 284.8 eV. The instrumental error was ±0.2 eV. Hydrogen temperature-programmed reduction (TPR-H_2) and hydrogen temperature-programmed desorption (TPD-H_2) experiments were performed using a Micromeritics AutoChem 2920 instrument equipped with a thermal conductivity detector (TCD). TPR-H_2 experiment was conducted using 0.1 g of the catalyst sample. The sample was initially heated to 500 °C under a nitrogen flow (40 cm^3/min) and maintained at that temperature for 60 minutes. After cooling to room temperature, the gas was switched to a 95% N_2–5% H_2 mixture (20 cm^3/min). The temperature was then ramped from room temperature to 600 °C at a rate of 8 °C/min, and hydrogen consumption was monitored using a TCD. For the TPD -H_2 analysis, 50 mg of the catalyst was first reduced under a 10% H_2/Ar flow at 400 °C for 1 hour. After the reduction step, the sample was cooled to room temperature. Subsequently, it was heated to 800 °C at a rate of 10 °C/min under a continuous flow of helium.

2.3 Hydrogenation of Soybean and Sunflower Oil

Hydrogenation reactions were carried out in a 100 mL batch reactor (Parr 4848 autoclave, Parr Instruments, USA) equipped with a high-pressure kinetic unit measurement system. The experimental setup is detailed in previous research [23]. In each experiment, 60 mL of sunflower or soybean oil and 0.06 g of catalyst were added to the reactor. The progress of the reaction was monitored by measuring hydrogen consumption, which corresponded to a final product with an iodine value ranging from 73 to 76. Details on the reaction rate calculations can be found in previous studies [24].

2.4 Analysis of Fatty Acid Composition

The fatty acid composition of the initial oil and hydrogenated products was determined by gas chromatography following GOST 31754-2012 [25]. Triglycerides were transesterified into methyl esters (FAMEs) according to GOST 31665-2012 [26]. FAMEs were analyzed using a Chromos GC-1000 gas chromatograph (Chromos, Russia) with a flame ionization detector and a CP-Sil 88 capillary column (100 m × 0.25 mm × 0.20 µm, Agilent Technologies). Helium served as the carrier gas, and the injection volume was 0.5 µL. FAME identification was based on peak retention times compared to a standard FAME mix (Supelco #. 19945, C4-C24).

2.5 Iodine Value

The iodine value (IV) of the initial and hydrogenated oils was determined ISO 3961:2013 Method [27].

2.6 Melting Point

An open capillary tube (1 mm inner diameter) was filled with molten hydrogenated fat and cooled in a refrigerator at 5 °C/h to solidify. It was then heated in a water bath at 3 °C/min, and the melting point was recorded as the temperature at which the fat column began to move [28].

2.7 Solid Fat Content

The solid fat content (SFC) in the hydrogenated products was measured using pulsed Nuclear Magnetic Resonance (NMR) with a Bruker Minispec PC 120 analyzer. The analysis was performed at temperatures of 10, 20, 30, and 40°C, in accordance with GOST R 31757-2012 [29].

3. Results and Discussion

3.1. Characterizations of Catalyst

The diffraction patterns of the 1.0% Pt/ZrO_2 catalyst are shown in Figure 2. XRD analysis of the 1.0% Pt/ZrO_2 catalyst confirms the successful synthesis of a mixed-phase zirconia support, predominantly comprising monoclinic ZrO_2 (m-ZrO_2), with reflections at 28.2° (−111), 31.5° (111), and 34.2° (002), alongside a minor tetragonal ZrO_2 (t-ZrO_2) component, indicated by peaks at 30.2° (101) and 50.3° (112). The coexistence of these phases suggests partial stabilization of the tetragonal structure, likely facilitated by the nanoscale nature of the support and the interaction with platinum species. The coexistence of these phases indicates a partially stabilized zirconia structure, likely influenced by small crystallite sizes and the presence of platinum. The absence of distinct Pt reflections in the diffraction pattern suggests that platinum is highly dispersed onto the zirconia.

The nitrogen adsorption–desorption isotherms at 77 K for the 1.0% Pt/ZrO_2 catalyst, together with the corresponding differential pore size distribution curves, are presented in Figures 3a and 3b, respectively. The isotherm exhibits a typical type IV profile with an H1-type hysteresis loop, which is characteristic of mesoporous materials according to the IUPAC classification. This behavior indicates the presence of a well-defined mesoporous structure with uniform pore channels and good textural stability. The specific surface area of the 1.0% Pt/ZrO_2 catalyst, as determined by the BET method, was 25.0 m²/g, suggesting a moderate surface area suitable for catalytic applications. The pore size distribution, derived from the desorption branch using the BJH method, revealed that the pores are predominantly distributed in the mesoporous range between 15.0 and 21.0 nm. The average pore diameter was calculated to be 19.0 nm, consistent with the observed hysteresis pattern. Such textural properties imply that the incorporation of platinum nanoparticles does not significantly alter the intrinsic porosity of the zirconia support. The relatively uniform mesopore distribution facilitates effective diffusion of reactant molecules and enhances the accessibility of active Pt sites, which are crucial factors for catalytic performance in reactions involving bulky intermediates or products.

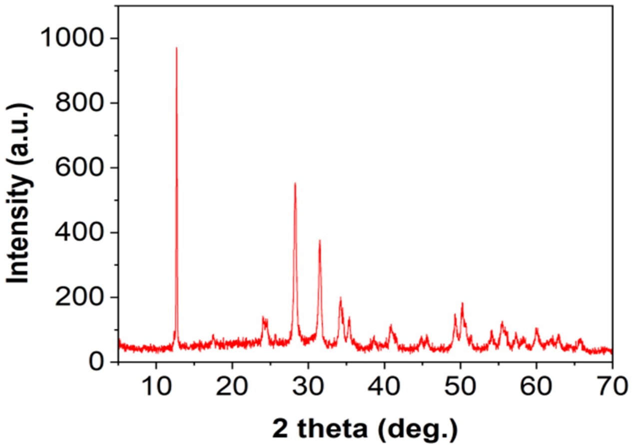

Figure 2. XRD pattern of 1.0% Pt/ZrO_2 catalyst.

The morphology of the 1.0% Pt/ZrO_2 catalyst was examined by scanning electron microscopy (SEM), and the results are presented in Figure 4a. The micrograph reveals that the catalyst particles exhibit irregular, flaky-shaped morphologies, typical of zirconia-based materials synthesized under similar conditions. The observed particle size for the 1.0% Pt/ZrO_2 catalyst ranges from approximately 55 to 100 nm, indicating a nanoscale dispersion of particles. Depending on the particle size and aggregation state, the SEM image displays areas with either relatively smooth surfaces or granular textures. Such variations are likely associated with the degree of agglomeration of the Pt-loaded zirconia particles. The catalyst appears to consist of fine, nearly uniform grains that tend to cluster into larger secondary aggregates, which is commonly observed in metal-supported oxide catalysts. The corresponding elemental mapping of the 1.0%

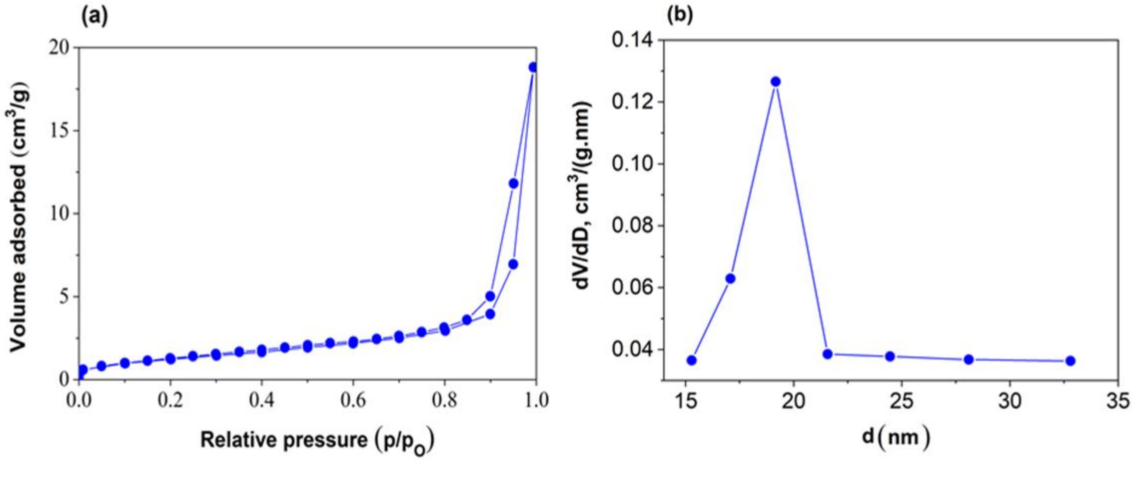

Figure 3. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of 1.0%Pt/ZrO_2 catalyst.

Pt/ZrO_2 catalyst, obtained via SEM–EDS (Figure 4b), confirms the presence and spatial distribution of platinum (Pt) and zirconium (Zr) within the sample. The homogeneous dispersion of Pt throughout the ZrO_2 matrix suggests an effective incorporation of the metal nanoparticles onto the support surface. This uniform distribution is essential for ensuring good catalytic performance, as it enhances the availability of active sites and promotes efficient interaction between reactant molecules and the catalyst surface.

Figure 5 presents the TEM images of the platinum catalyst supported on ZrO_2. The TEM micrographs reveal a uniform dispersion of platinum nanoparticles across the zirconia surface, indicating successful metal deposition and strong metal–support interaction. Statistical analysis of the particle size distribution shows that the platinum nanoparticles in the 1.0% Pt/ZrO_2 catalyst range from 2 to 8 nm, with an average diameter of approximately 4 nm. The majority of Pt particles exhibit a nearly spherical morphology, which is typical for metallic nanoparticles formed under controlled synthesis conditions. The small particle size and uniform dispersion of Pt nanoparticles are indicative of efficient reduction and anchoring of the metal species onto the zirconia support. Such nanoscale features are particularly advantageous for catalytic applications, as they increase the number of accessible active sites and improve the overall surface reactivity of the catalyst.

The XPS spectra of the Pt/ZrO_2 catalyst is shown in Figure 6. XPS analysis of the 1%Pt/ZrO_2 catalyst provides valuable insight into the chemical states of platinum present on the surface of the zirconia support. The high-resolution spectrum of the Pt $4f_{7/2}$ region was deconvoluted into three distinct peaks centered at approximately 71.2, 72.4, and 73.6 eV, which correspond to Pt^0, Pt^{2+}, and Pt^{4+} oxidation states, respectively. The dominant peak at ~71.2 eV is

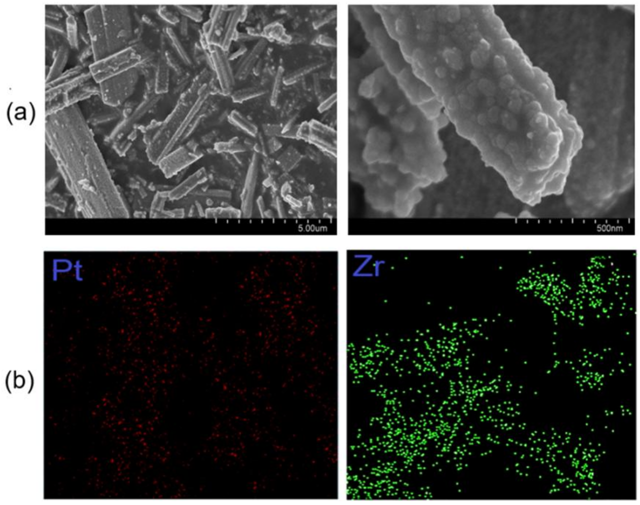

Figure 4. SEM images (a) and elemental mapping (b) of 1.0%Pt/ZrO_2 catalyst.

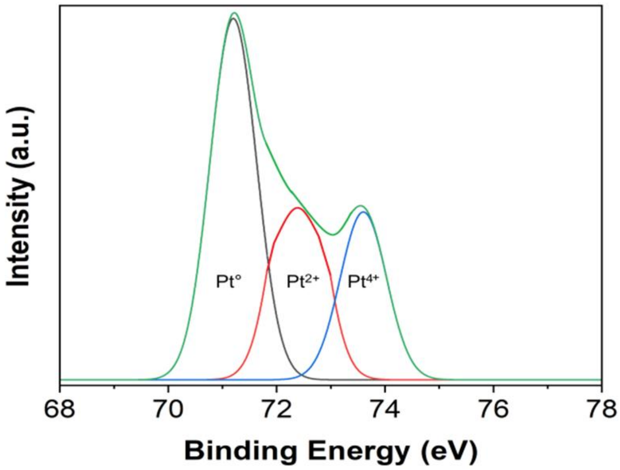

Figure 6. XPS (Pt 4f7/2) spectra of 1% Pt/ZrO_2 catalyst.

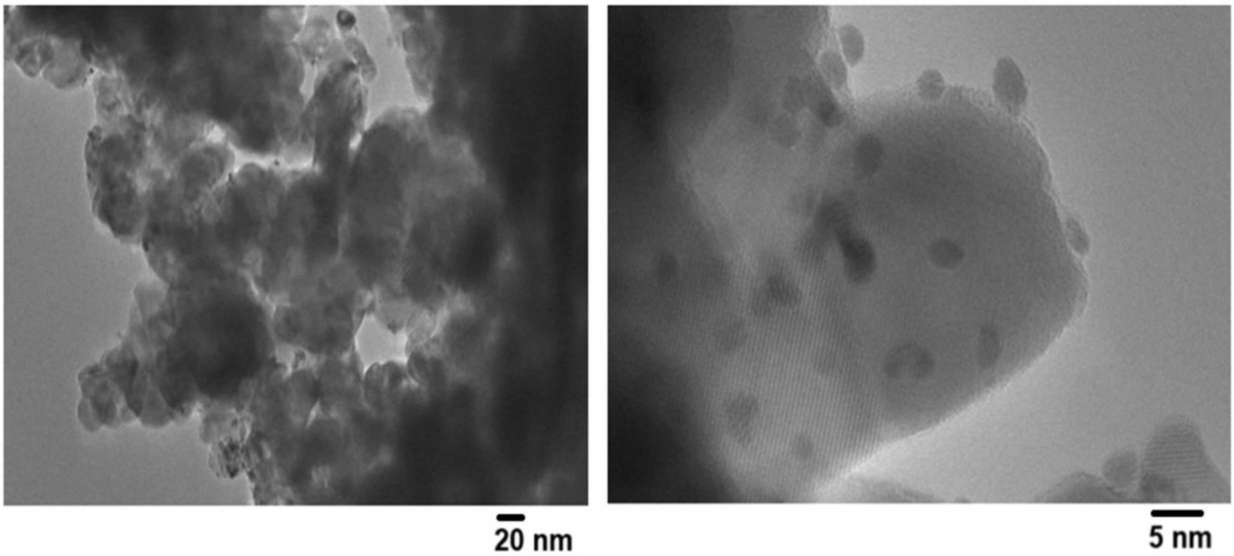

Figure 5. TEM images of 1.0%Pt/ZrO_2 catalyst.

attributed to metallic platinum (Pt^0), indicating the presence of Pt nanoparticles in their elemental state. This metallic component is essential for catalytic activity in hydrogenation reactions, where electron-rich platinum surfaces promote efficient bond breaking and formation. The second peak, located at ~72.4 eV, corresponds to Pt^{2+}, typically assigned to PtO or partially oxidized platinum species. This state often forms due to surface exposure to ambient conditions or partial interaction with oxygen-containing functional groups. The third component at ~73.6 eV is assigned to Pt^{4+}, a more oxidized state commonly associated with PtO_2 species or strong metal–support interactions that stabilize higher oxidation states.

The TPR-H_2 profile of the 1% Pt/ZrO_2 catalyst reveals three distinct hydrogen consumption peaks, indicating the presence of multiple reduction processes (Figure 7). The first peak, observed at approximately 150 °C, is attributed to the reduction of Pt^{4+} to Pt^{2+}, suggesting the presence of highly oxidized platinum species that are relatively easy to reduce. The second peak, appearing around 220 °C, corresponds to the further reduction of Pt^{2+} to metallic Pt^0, reflecting the formation of catalytically active metallic platinum sites. A broad third peak centered near 450 °C is likely associated with the reduction of surface oxygen species or lattice oxygen in the ZrO_2 support. This high-temperature feature suggests a notable interaction between platinum and the support, potentially indicative of strong metal–support interaction.

The TPD-H_2 profile of the 1.0%Pt/ZrO_2 catalyst demonstrates (Figure 8) a dominant desorption peak at ~120 °C, indicating that approximately 80% of hydrogen is weakly bonded form. This feature highlights the catalyst's potential for low-temperature hydrogenation applications, such as vegetable oil processing, where facile hydrogen desorption is essential for enhancing catalytic activity, selectivity and energy-efficient performance.

3.2. Hydrogenation of Sunflower and Soybean Oil

The hydrogenation of sunflower and soybean oils was conducted using a 1.0% Pt/ZrO_2 catalyst at 90 °C and a hydrogen pressure of 0.5 MPa. The dependence of the reaction rate on hydrogen uptake and the reaction kinetics for the hydrogenation of sunflower and soybean oils using a 1.0% Pt/ZrO_2 catalyst are illustrated in Figure 9a and 9b, respectively.

As demonstrated in Figure 9a, the reaction rate remains constant for both oil types under a hydrogen pressure of 0.5 MPa. The kinetic profiles (Figure 9b) reveal that the hydrogenation of sunflower oil using a platinum catalyst at 90 °C is completed within 60 minutes, whereas the hydrogenation of soybean oil requires 70 minutes. The disparity in reaction time can be attributed to the higher iodine value of soybean oil, which reflects a greater number of unsaturated bonds that must undergo hydrogenation. Furthermore, the extent of partial hydrogenation can vary among different vegetable oils, leading to differences in both the amount of hydrogen required and the duration of the hydrogenation process, depending on the specific characteristics of each oil type [24,30].

The chromatograms of the original sunflower and soybean oils, as well as those of the products obtained after hydrogenation using platinum catalysts, are presented in Figure 10. The fatty acid compositions of both the original and hydrogenated oil samples are summarized in Table 1. As presented in Table 1, it has been determined that the utilization of a platinum catalyst significantly reduces the content of trans isomers in the resulting product. Specifically, the product derived from the hydrogenation of sunflower oil using the platinum catalyst contains

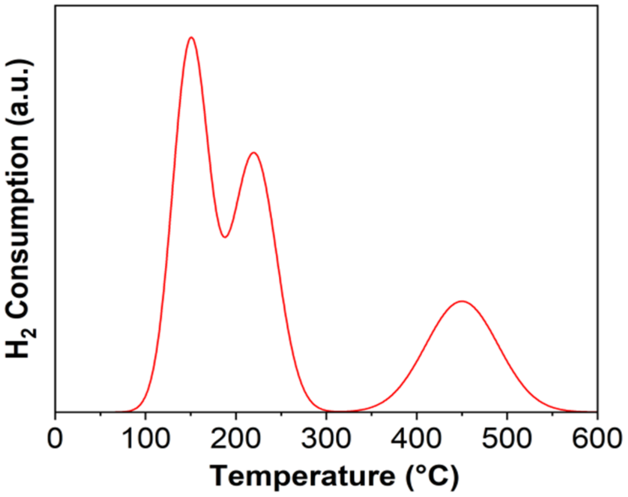

Figure 7. TPR-H_2 profile of 1.0%Pt/ZrO_2 catalyst.

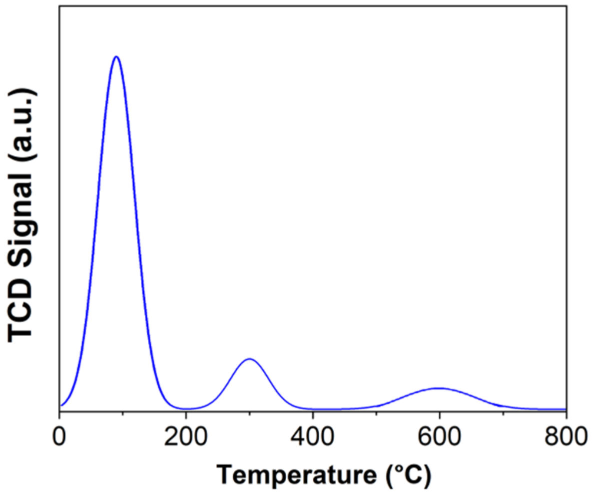

Figure 8. TPD-H_2 profile of 1.0%Pt/ZrO_2 catalyst.

6.0% trans isomers, while the product from the hydrogenation of soybean oil contains 5.6% trans isomers.

Figures 11(a–d) illustrate the hydrogenation of sunflower and soybean oils using a nickel (Ni) catalyst at two different temperatures, 130 °C and 150 °C, while keeping other parameters constant (0.5 MPa H_2, 800 rpm, 60 mg catalyst, 60 mL oil). At both temperatures, the reaction rate initially increases rapidly and then stabilizes as hydrogen uptake proceeds. However, increasing the temperature from 130 °C to 150 °C significantly accelerates the reaction. At 130 °C, the hydrogenation of sunflower oil is completed in about 70 minutes and soybean oil in about 80 minutes, whereas at 150 °C, the reaction times decrease to 50 and 55 minutes, respectively. This clearly demonstrates the strong temperature dependence of Ni-catalyzed hydrogenation reactions. Nickel catalysts are practically inactive at low temperatures and do not promote the hydrogenation reaction under these conditions.

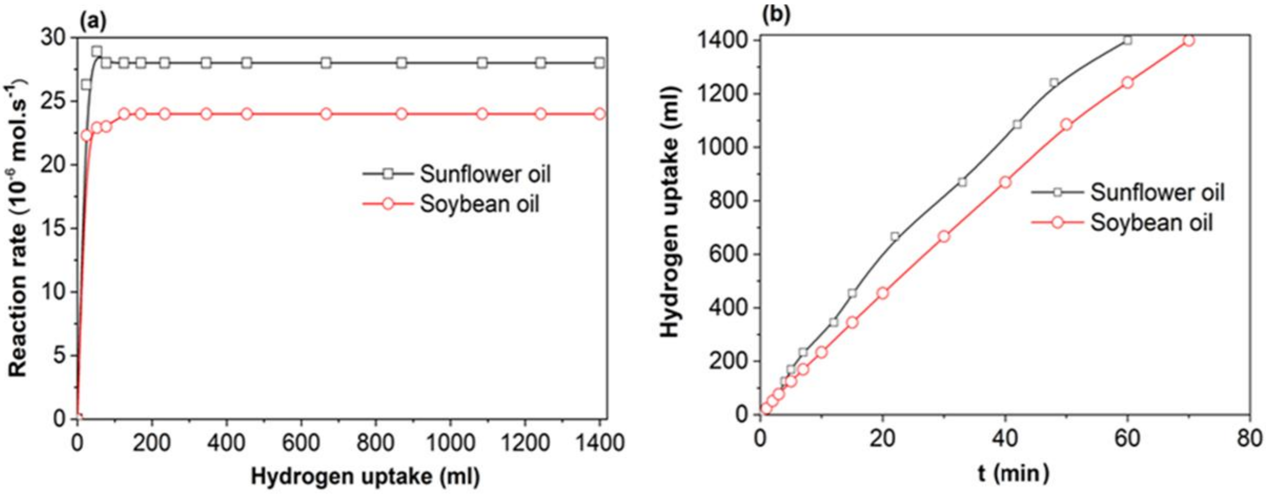

Figure 9. (a) The dependence of the reaction rate on hydrogen uptake and (b) the reaction kinetics for the hydrogenation of sunflower and soybean oils using a 1.0% Pt/ZrO_2 catalyst. (90 °C, 0.5 MPa H_2, 800 rpm, 60 mg catalyst, 60 mL oil).

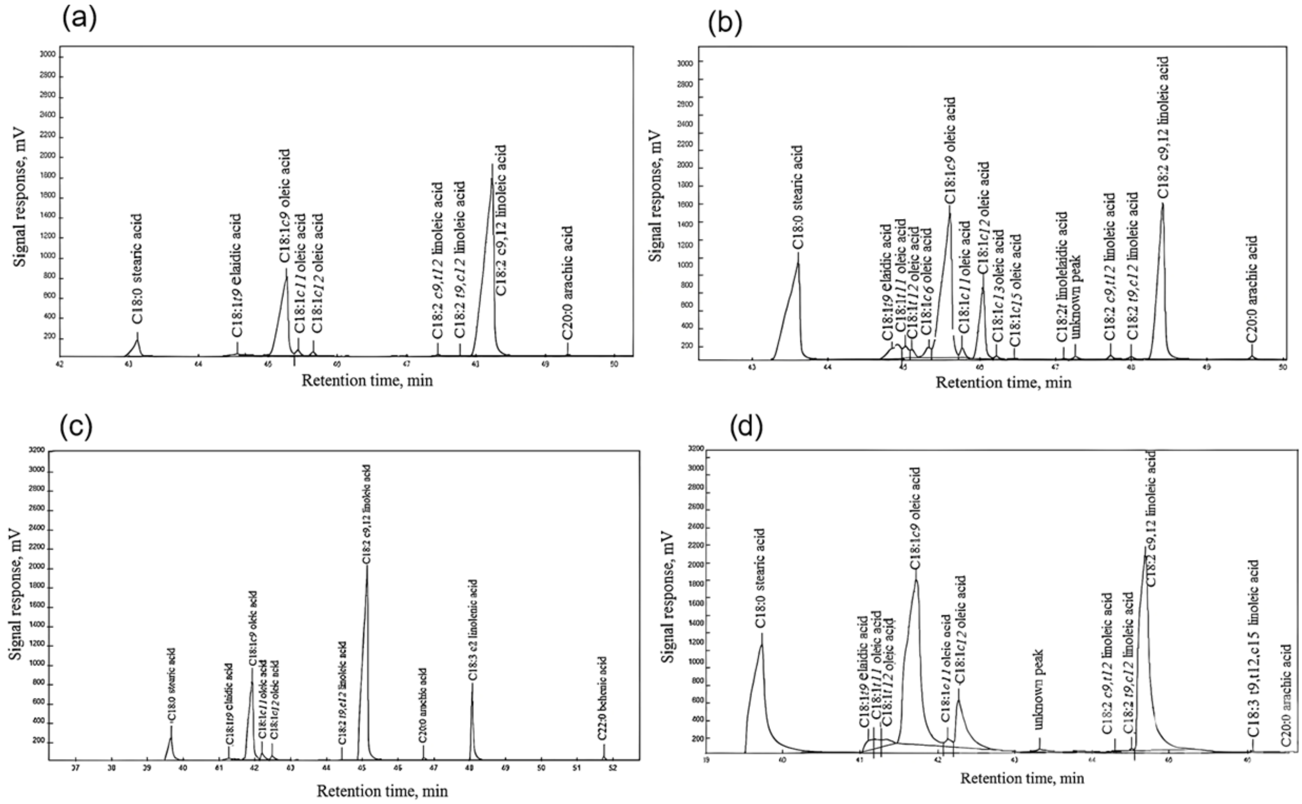

Figure 10. The chromatograms of sunflower oil (a), soybean oil (c) and products obtained from sunflower oil (b), soybean oil (d) hydrogenation over 1.0%Pt/ZrO_2 catalyst.

The formation of trans isomers was also strongly temperature-dependent, with total trans isomers rising from around 1–2% to over 20% in both oils after hydrogenation. At 150 °C, total trans isomer content reached 25.7% in sunflower oil and 26.9% in soybean oil (Table 2), indicating that high temperatures promote trans-fat formation. The platinum catalyst can achieve the desired degree of hydrogenation under milder reaction conditions, such as lower temperatures and pressures, which can reduce energy consumption and high selectivity in hydrogenation reactions. These findings indicate a significant reduction (by 5-6 times) in the trans isomer content in the hydrogenation products, as compared to those obtained with nickel-based catalysts [7,18,31].

Table 1. Fatty acid composition of original and hydrogenated oils over 1.0% Pt/ZrO_2 catalyst.

Fatty acid composition, (%)	Sunflower oil	Hydrogenated sunflower oil	Soybean oil	Hydrogenated soybean oil
C14:0 –myrictic acid	0.1	0.1	0.1	0.1
C16:0 –palmitic acid	6.4	6.5	9.6	9.5
C18:0 –stearic acid	4.0	24.4	5.5	20.9
C18:1c –cis-isomer of oleic acids	24.8	39.1	22.0	34.7
C18:1t – trans- isomer of oleic acids	1.3	5.3	1.0	4.4
C18:2c –cis -isomer of linoleic acid	61.7	22.5	50.7	25.7
C18:2t –trans-isomer of linoleic acid	0.4	0.7	0.1	1.2
C18:3 –linolenic acid	0.1	0.0	9.1	1.8
C20:0 –arachic acid	0.3	0.3	0.4	0.3
C22:0 –behenic acid	0.7	0.7	0.3	0.3
Total trans isomers	1.7	6.0	1.1	5.6
IV, gJ_2/100g	127.0	79.6	134.0	80.0
MP, (°C)	-	38.4	-	36.5

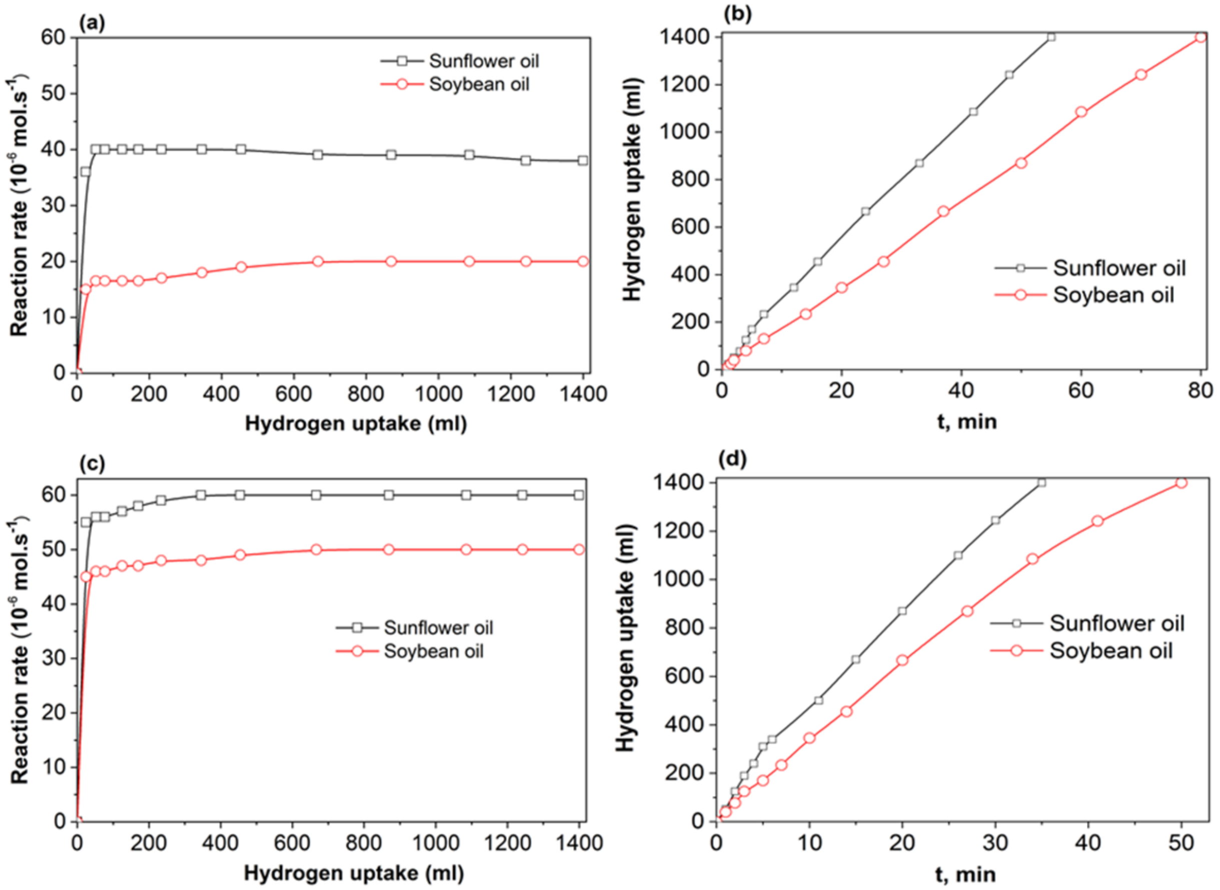

Figure 11. The dependence of the reaction rate on hydrogen uptake and the reaction kinetics for the hydrogenation of sunflower and soybean oils using a Ni catalyst. (130 °C (a) and (b), 150 °C (c) and (d), 0.5 MPa H_2, 800 rpm, 60 mg catalyst, 60 mL oil).

In numerous studies [19,32-35], it has been reported that, in the hydrogenation of vegetable oils, the formation of trans-isomers is strongly influenced not only by the intrinsic nature of the catalyst but also by various process parameters, including temperature, hydrogen pressure, catalyst loading, and agitation intensity. Among these factors, temperature is regarded as the most decisive variable, as its increase predominantly accelerates the generation of trans-isomers content.

The extent of cis–trans isomerization is strongly influenced by temperature, with higher temperatures markedly promoting this transformation. This behavior is consistent with the classical hydrogenation mechanism proposed by Horiuti and Polanyi, in which molecular hydrogen undergoes dissociative adsorption on the catalyst surface, followed by the formation of a transient half-hydrogenated intermediate with the adsorbed fatty acid. At lower temperatures, this intermediate is more likely to undergo configurational isomerization prior to complete saturation of the double bond. These observations highlight that the isomerization step is more temperature-sensitive than the hydrogenation reaction itself [36].

The distinction between Pt and Ni catalysts is closely related to the nature and binding strength of hydrogen species adsorbed on their surfaces. Metal surfaces can stabilize at least four different forms of hydrogen (Figure 12), each characterized by specific binding energy and reactivity in liquid-phase hydrogenation: weakly bound molecular hydrogen ($H_2^{\delta+}$) and strongly bound atomic species, including ionized $H^{\delta+}$, $H^{\delta-}$, and non-ionized H. These species are interdependent through adsorption equilibria, which play a crucial role in determining catalytic activity and selectivity [37,38].

The results reveal that the active hydrogen species on Pt catalysts are weakly bound and easily desorb at temperatures above 60 °C. This is consistent with the TPD-H_2 profile (Figure 8), which shows a maximum desorption temperature of approximately 100 °C. The presence of weakly bound hydrogen accounts for the high selectivity of Pt catalysts, as desorption at relatively low temperatures limits trans-isomer formation. Optimization of hydrogenation conditions, particularly by lowering the reaction temperature, can therefore substantially reduce trans-isomer content. As explained in a previous article [6], the high activity but low selectivity of Ni catalysts originates from the predominance of strongly bound hydrogen species, which desorb at elevated temperatures (>150 °C).

A low trans isomer content in hydrogenated products is required to ensure that in the final fat

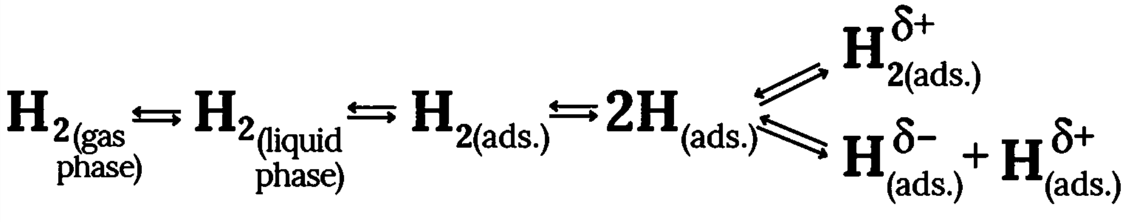

Figure 12. Hydrogen adsorption equilibria in liquid-phase hydrogenation reactions.

Table 2. Fatty acid composition of original and hydrogenated oils over Ni catalyst.

Fatty acid composition, (%)	Sunflower oil	Hydrogenated sunflower oil		Soybean oil	Hydrogenated soybean oil	
		130 °C	150 °C		130 °C	150 °C
C14:0	0.1	0.1	0.1	0.1	0.1	0.1
C16:0	6.4	6.5	6.6	9.6	9.7	9.6
C18:0	4.0	16.4	20.0	5.5	15.9	16
C18:1c	24.8	41.1	32.9	22.0	30.8	29
C18:1t	1.3	16.7	23.7	1.0	17.6	23
C18:2c	61.7	14.5	12.5	50.7	20	16.4
C18:2t	0.4	3.7	2.0	0.1	3.5	3.9
C18:3	0.1	0.0	0.0	9.1	0.4	0.3
C20:0	0.3	0.3	0.3	0.4	0.4	0.4
C22:0	0.7	0.7	0.7	0.3	0.3	0.3
Total trans isomers	1.7	20.4	25.7	1.1	21.1	26.9
IV, gJ_2/100g	127.0	79.0	79.6	134.0	81.5	77.5
MP, (°C)	-	38.4	39.6	-	37.5	38.6

products (such as margarines and cooking fats), the trans isomer content does not exceed 2.0%, in accordance with international standards [39]. The platinum catalysts allow for the hydrogenation products with trans isomer contents ranging from 6.0% to 5.6%. It is important to note that the initial oil for hydrogenation already contains, on average, 1.7% (sunflower oil) and 1.1 % (soybean oil) trans isomers. Considering that the hydrogenated products content in the final product is 25-30%, the overall trans isomer content in the final fat products will not exceed 2.0%.

When comparing Figures 9 and 11, it becomes evident that the Pt/ZrO_2 catalyst enables efficient hydrogenation at a much lower temperature (90 °C) with shorter reaction times and reduced trans-isomer formation compared to the Ni catalyst. Nickel catalysts currently employed in edible oil processing (22–23% Ni) exhibit several drawbacks. The hydrogenation process typically requires elevated temperatures (150–170 °C, nickel catalysts are essentially inactive at temperatures below 130 °C), which substantially increases energy consumption. Furthermore, residual nickel in the hydrogenated product (Figure 13a) cannot be completely removed by conventional filtration, necessitating an additional bleaching step using sorbents. More importantly, nickel catalyst promotes the formation of a high proportion of trans-isomers, which significantly exceeds nutritional and regulatory limits. In contrast, hydrogenation with platinum catalysts yields products that retain a light color (Figure 13b), and since the catalyst can be effectively removed by simple filtration, further bleaching with adsorbents is unnecessary.

The 1.0% Pt/ZrO_2 catalyst was recovered after each hydrogenation cycle of vegetable oil by filtration, followed by washing with a hexane solution and drying under vacuum at 90 °C for 2 hours. The stability and reusability of the 1.0% Pt/ZrO_2 catalyst during the hydrogenation of sunflower and soybean oils (110 °C, 0.5 MPa, 800 rpm) were evaluated, and the results are presented in Figure 14. As shown in Figure 14, the reaction rate for both sunflower and soybean oils remained nearly constant over eight consecutive reuse cycles, indicating high catalyst stability and reusability. The reaction rate of sunflower oil (approximately 27×10^{-6} mol.s^{-1}) was slightly higher than that of soybean oil (approximately 24×10^{-6} mol.s^{-1}), which may be attributed to differences in fatty acid composition.

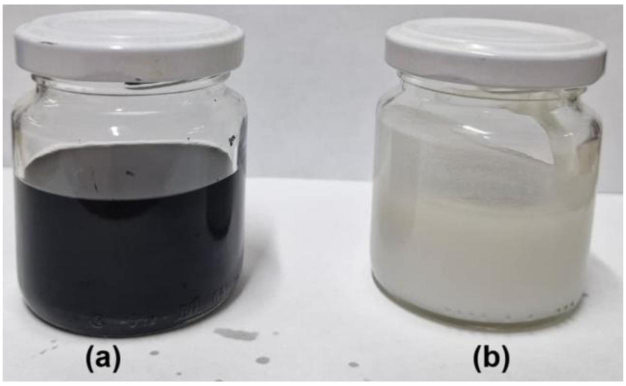

Figure 13. Products obtained from the hydrogenation of sunflower oil using nickel (a) and platinum (b) catalysts.

The reuse of the 1.0% Pt/ZrO_2 catalyst in the hydrogenation of sunflower and soybean oils resulted in stable trans-isomer formation over eight consecutive cycles (Figure 15). For all reuse experiments, the iodine value (IV) of the hydrogenated sunflower oil was 79.6, while that of the soybean oil was 80, indicating a comparable degree of hydrogenation. The content of trans-

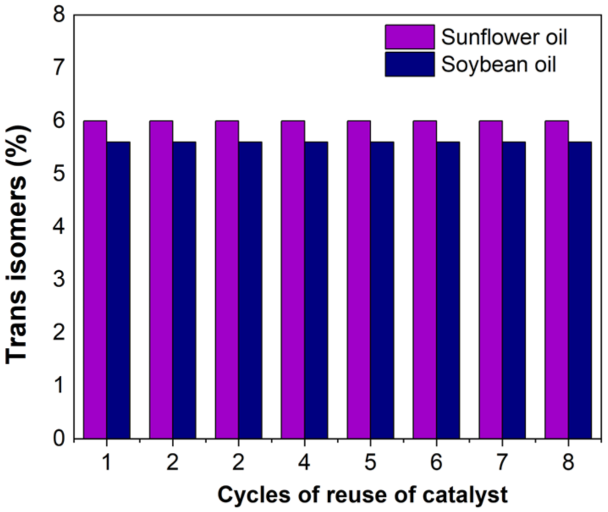

Figure 15. Effect of catalyst reuse on the trans-isomer content in hydrogenated sunflower and soybean oils.

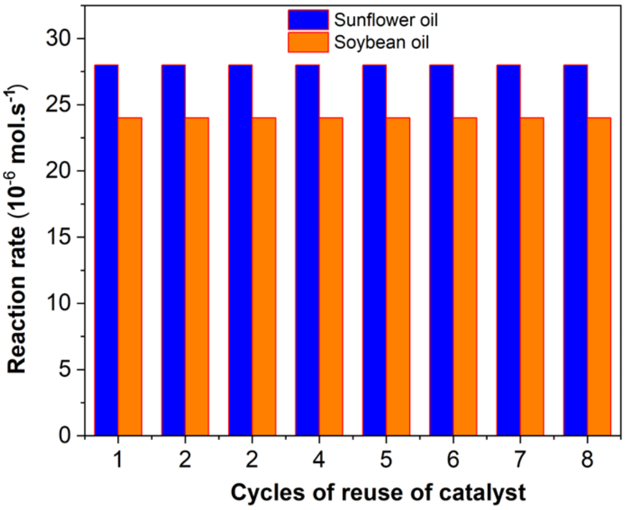

Figure 14. Reusability of 1.0% Pt/ZrO_2 catalyst in hydrogenation of sunflower and soybean oil (90 ^{o}C, 0.5 MPa, 800 rpm, 60 mg catalyst, 60 mL oil).

isomers remained nearly constant at 5–6% for both oils, with slightly higher values observed in sunflower oil compared to soybean oil. These results demonstrate that the catalyst maintained its hydrogenation activity and selectivity throughout repeated uses without a noticeable increase in trans-isomer formation.

Figure 16 shows the TEM images of the 1.0% Pt/ZrO_2 catalyst after reuse in the hydrogenation of vegetable oils. The images reveal that the catalyst retained its overall structural integrity after 8 hydrogenation cycles. Platinum nanoparticles are well dispersed on the zirconia support, with particle sizes generally below 8 nm, as seen in the higher-magnification image. Only slight aggregation of Pt nanoparticles is observed (10 nm), indicating minimal sintering during repeated use. These results confirm the good structural stability and strong metal–support interaction of the 1.0% Pt/ZrO_2 catalyst, which contribute to its stable catalytic activity and selectivity during multiple reuse cycles.

Solid fat content (SFC) is important because it influences the texture, stability, and functionality of fat-containing food products. It affects attributes like spreadability, firmness, and melting behavior, which are critical for products such as margarine, spreads, and confectionery [40]. Figure 17 shows the SFC of products obtained by hydrogenating sunflower and soybean oils with a platinum catalyst.

As shown in Figure 17, even a slight change in the iodine value of the hydrogenated products has a pronounced effect on the solid triglyceride content. For the hydrogenated soybean oil obtained at 90 °C, with an iodine value of 79.6, the solid fraction at 20 °C is 27%. In comparison, the hydrogenated sunflower oil product, with an iodine value of 80.0, exhibits a solid fraction of 24.0%. Although the iodine values of the hydrogenated soybean and sunflower oils are nearly identical, the inherent differences in their fatty acid compositions and trans isomer contents result in distinct solid fat contents. These variations strongly influence the crystallization behavior and melting characteristics of the hydrogenated fats [41].

4. Conclusion

In conclusion, the 1.0% Pt/ZrO_2 catalyst demonstrates effective performance in the hydrogenation of sunflower and soybean oils, achieving significant reduction in trans isomers compared to nickel-based catalysts. Structural analyses confirmed the formation of a mixed-phase zirconia support with finely dispersed Pt nanoparticles, which promote the generation of weakly bound hydrogen species responsible for selective hydrogenation and low trans-isomer formation. The platinum catalyst allows for the hydrogenation process to be completed under milder conditions, reducing energy consumption and enhancing selectivity. Despite similar iodine values, the fatty acid composition and trans

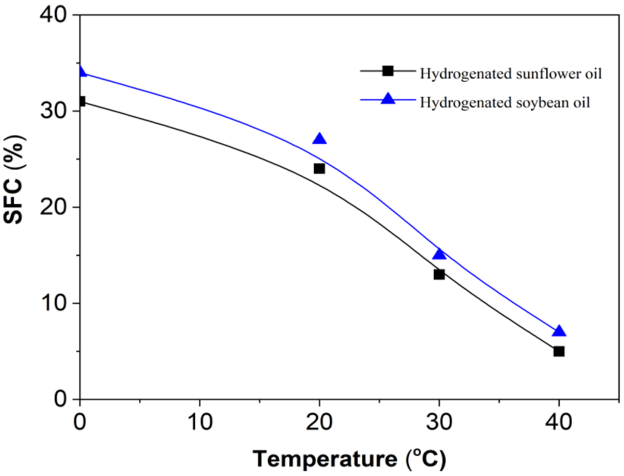

Figure 17. Solid fat content of hydrogenated products over using 1.0%Pt/ZrO_2 catalyst.

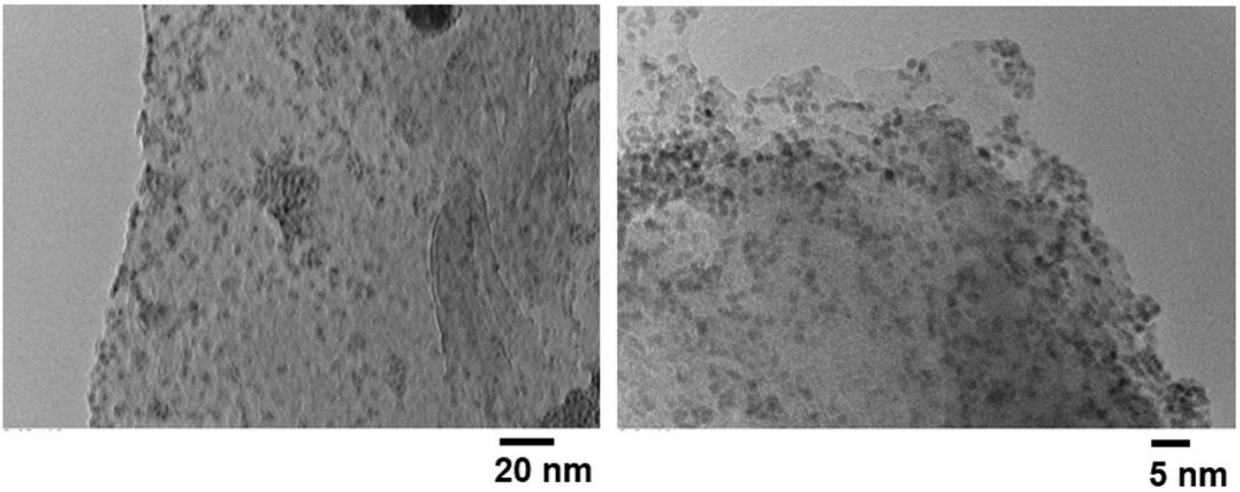

Figure 16. TEM image of the reused 1.0% Pt/ZrO_2 catalyst.

isomer content of the oils result in differences in solid fat content, with soybean oil exhibiting a higher solid fraction at 20 °C. The hydrogenation products meet the required standards for trans isomer content in final fat products, making this platinum catalyst a promising alternative for efficient and high-quality oil hydrogenation.

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CRedit Author Statement

Author Contributions: Kainaubek Toshtay- Writing – original draft, Methodology, Investigation, Data curation, Conceptualization, Writing – review & editing, Supervision. The author has read and agreed to the published version of the manuscript.

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