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Oxidative Cleavage of 9,10-Dihydroxystearic Acid on Supported Au, Pd and PdAu Nanoparticle-Based Catalysts

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Abstract: The oxidative C-C cleavage of a C_{18} substrate is an important transformation in synthetic organic chemistry, facilitating the synthesis of valuable C_8-C_9 acids widely used in many industries. Through a comparative analysis of the catalytic and physicochemical properties of catalysts, comprising mono- (Pd or Au) and bimetallic (PdAu) nanoparticles deposited on oxides, oxyhydroxides and graphite-like carbon material Sibunit (Cp), it was shown that the efficiency of the catalyst in the oxidative cleavage of 9,10-dihydroxystearic acid relies on the nature of the active component, the support and the average size of metal nanoparticles (NPs). The dependency of 9,10-DSA conversion on the average size of metal NPs shows the structural sensitivity of the oxidative cleavage reaction. Notably, catalysts with an average size of gold particles less than 3 nm exhibit the highest activity. The nature of the active component and the support material are crucial factors determining the process selectivity. Among the catalysts studied, the most effective for the oxidative cleavage of 9,10-DSA is a material based on Au NPs deposited on Cp.

Keywords: oxidative C-C cleavage; 9,10-dihydroxystearic acid; supported metal NPs; structural sensitivity

1. Introduction

Nowadays, the importance of developing new sources of energy and chemicals cannot be overestimated. According to British Petroleum (BP) [1], Earth's oil reserves amount to ~1.7 trillion barrels. At the current consumption rate, this supply should only last for 47 years, i.e., until 2070. Additionally, according to a previous BP report [2], natural gas reserves are expected to last until 2069. Thus, the search for new renewable resources is extremely relevant, as confirmed by numerous studies in this direction [3–9].

Biomass emerges as a sustainable alternative, capable of replacing conventional raw materials in an environmentally friendly manner. Statistics show that in 2015, the world produced 11.9 billion tons of biomass, with 61% originating from agriculture and 39% from forestry [10]. Various methods can be employed to extract fatty acids from agricultural raw materials [11–13]. Subsequently, these fatty acids find applications in diverse fields, such as oilfields, organic synthesis, medicine and polymer production [14–17]. Nevertheless, an

alternative and promising approach involves the catalytic cleavage oxidation of biomass-derived fatty acids to produce valuable organic compounds, such as azelaic, pelargonic, suberic and caprylic acids.

Azelaic acid (AA) has applications in several industries. In cosmetics, it is used to treat acne, reduce inflammation and improve skin texture. In pharmaceuticals, AA is a component of medications used in the treatment of various skin diseases. In addition, the potential for using AA as a monomer to create biodegradable plastics is substantial, suggesting its role in the development of environmentally friendly materials [11], suggesting its role in the development of environmentally friendly materials [18].

Pelargonic acid (PA) is applied in agriculture for the production of weed and pest control agents. In addition, PA can be used in the manufacture of paints and coatings with enhanced properties [19,20].

Both suberic acid (SA) and caprylic acid (CA) have a wide range of medical applications. SA can be used as an inhibitor of angiogenesis (formation of new blood vessels), a crucial aspect in the treatment of some diseases. CA has potential applications as an antimicrobial agent or fat burner, which makes it valuable in the therapy of various ailments [21,22].

In industry, the above-mentioned acids are typically obtained through methods characterized by a range of significant disadvantages, including the use of explosion and fire hazardous reagents, the generation of toxic waste and the implementation of complex technological schemes [23,24]. For example, the production of AA and PA involves the ozonolysis of oleic acid or linoleic acid, introducing potential hazards due to the use of flammable and toxic ozone [23]. In the case of SA and CA, the production process uses nitric acid as an oxidizing agent, which contributes to the formation of poisonous NO and NO_2 [24]. An alternative approach to produce these acids is the oxidation of biomass-derived substrates using various catalytic systems (Table 1).

Table 1. Production of azelaic and pelargonic acids from various substrates.

№	Substrate *	Catalyst	Conditions	Conversion (%)	Yield or Selectivity (%)				Ref.
					AA	PA	SA	CA	
1	MDS	Au/Al_2O_3	1 mmol of substrate, 0.2 mol % Au, 5 mmol NaOH, 20 mL H_2O, 80 °C, 5 bar O_2	100	86	99	~7	~7	[25]
2	9,10-DHSA	$CoAc_2/$ $H_2WO_4/$ CH_3COONa	360 min, 15 bar O_2, 70 °C	100	15	56	-	-	[26]
3	HOSO	$CeO_2/$ $Nb_2O_5/$ TiO_2 + MeOH	12 bar O_2 (180 °C), 6 bar N_2 (160 °C), 5 h	-	34				[27]
4	OA	Silica-supported W-oxide	20 g of substrate, 60 mL H_2O_2 (30%), 150 mL tert-butanol, 1.5 g of catalyst, 130 °C, 1 h	79	32	36	-	-	[28]
5	OA	H_2WO_4	5 g of substrate, 7.5 g H_2O_2 (60%), ratio cat/sub = 1/400, 100 °C, 24 h	94	60	16	-		[29]
6	OA	[Fe(OTf)$_2$ (6-Me-PyTACN)]	Solvent – MeCN, 4.5 eq. $NaIO_4$, 100 eq. H_2O, 24 h, then H_2SO_4 (0.5 eq.) in H_2O (50 eq.), 12 h, and $NaHCO_3$ (1 eq.) and catalyst (1 mol %)	100	85	-	-	-	[30]
7	OA	Cr/MCM-41	1 g of substrate, 40 mg of catalyst, 180 °C, 8 h, pO_2 = 1 Mpa and pCO_2 = 10 MPa	>95	32	32	10	10	[31]

Table 1. *Cont.*

№	Substrate *	Catalyst	Conditions	Conversion (%)	Yield or Selectivity (%)				Ref.
					AA	PA	SA	CA	
8	9,10-DSTG	$CuFe_2O_4$	1 wt% catalyst, 80 °C, stirring 500 rpm, pO_2 = 25 bar, 5 h	96	70	52	-	-	[18]
9	OA	-	2 g of substrate, flow rate for OA 1 mL/min, flow rate for O_3/O_2 500 mL/min, 0 °C, solvent—50 mL of acetone:H_2O (95:5)	-	84	-	-	-	[32]
10	SO	V_2O_5/TiO_2	1 g of substrate, 30 wt. % of catalyst, TBHP (20 volume), 80 °C, 12 h	-	66	-	-	-	[33]
11	VDFE	$Ru(OH)_x/\gamma$-Al_2O_3	4 g of substrate, 12 mL dodecane, 60 mL H_2O, 6 mol % of catalyst, pO_2 = 5 bar	99	83	86	6	4	[34]
12	OA	$KMnO_4/NaOH/$ TEBAC	2 g of substrate, 2 g of $KMnO_4$, 0.2 g TEBAC, 50 mL H_2O, 50 °C, 8 h	100	96	81	-	-	[35]
13	OA	$WO_3 \cdot H_2O$	1 g of substrate, 7.5 mL of tert-butanol, 4 mL of H_2O_2, 0.45 g of catalyst, stirring 400 rpm, 120 °C, 5 h	100	77	69	-	-	[36]
14	OA	Surfactant-capped NPs WO_3	2 g of substrate, 15 mL of tert-butanol, 6 mL of H_2O_2, 0.9 g of catalyst, 120 °C, 5 h	95	58	24	-	-	[37]
15	OA	ACO-Ru (2%)	0.5 mmol of substrate, solvent—H_2O/MeCN/AcOEt (4/2/1), 8 equivalents of $NaIO_4$, 100 mg of catalyst, stirring 1500 rpm, r.t., 24 h	53	16	16	-	-	[38]
16	OA	CBO-Ru (2%)	0.5 mmol of substrate, solvent—H_2O/MeCN/AcOEt (4/2/1), 8 equivalents of $NaIO_4$, 100 mg of catalyst, stirring 1500 rpm, r.t., 24 h	100	75	75	-	-	[38]

* MDS—methyl-9,10-dihydroxystearate; 9,10-DHSA—9,10-dihydroxystearilic alcohol; HOSO—High oleic sunflowers oil; OA—Oleic acid; 9,10–DSTG—9,10-Dihydroxystearic triglyceride; SO—Triadica sebifera seed oil; VDFE—Vicinal diol fatty esters.

In the considered studies, various catalytic systems and substrates were used for the synthesis of C_8-C_9 acids. The best result was obtained using the Au/Al_2O_3 catalyst [25], with a yield of 86% for AA and 99% for PA, with minimal formation of SA and CA. The high activity of the catalyst in this study is attributed to the small size of gold nanoparticles and their interaction with the support surface. However, other physicochemical properties of the catalyst and their influence on the oxidative C-C cleavage activity of the C_{18} substrate were not explored. Additionally, when using Al_2O_3 as a support, its instability in an alkaline medium should be taken into account [39].

Table 1 also presents the results of other studies [30,34,35,38], where relatively high yields of AA (75–96%) and PA (69–86%) were obtained. Nevertheless, these described catalysts either involve complex multicomponent systems or operate under specific process conditions, which imposes certain difficulties in their practical implementation.

Thus, it is obvious that in order to establish scientifically grounded approaches to select the most effective, economical, environmentally feasible and technically viable methods to intensify biomass processing into valuable chemical products, it is necessary to conduct systematic studies. This is particularly relevant to the choice of catalyst, also taking into account issues related to its deactivation [40–47] and, accordingly, the choice of its operating

conditions. Therefore, the aim of this work is to elucidate the catalyst characteristics that determine its efficiency in the oxidative cleavage process of 9,10-dihydroxystearic acid. This investigation focuses on mono- (Pd or Au) and bimetallic (Pd-Au) nanoparticles deposited on oxides, oxyhydroxides and graphite-like carbon material Sibunit (Cp) through a comparative analysis of their catalytic and physicochemical properties.

2. Materials and Methods

As catalytic systems for the comparative study, Au/AlOOH_S5, Au/AlOOH_C, Au/La$_2$O$_3$/TiO$_2$, Au/CeO$_2$/TiO$_2$, Pd/Cp-NH$_4$OH, Au/Cp-NH$_4$OH and PdAu/Cp-NH$_4$OH materials were chosen. These materials previously demonstrated efficiency as catalysts in processes such as low-temperature CO oxidation and liquid-phase oxidation of n-octanol, glycerol, 5-HMF and betulin [39,48–52]. Other than Au/Cp-NH$_4$OH material, it is used for the first time. They exhibit significant variations in their physicochemical properties.

2.1. Preparation of Supports and Synthesis of Catalysts

2.1.1. Modification of Titanium Oxide

Titania Degussa P25 (45 m^2/g, nonporous, 70% anatase and 30% rutile, purity > 99.5%, Merck, Darmstadt, Germany) was used as starting support. MeTiO$_2$ supports with a molar ratio Ti/Me = 40 (where Me represents La or Ce) were synthesized by impregnation of the initial titanium oxide with aqueous solutions of La(NO$_3$)$_3$·6H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O nitrates (Merck, Darmstadt, Germany). Subsequently, the samples were dried at room temperature for 48 h and at 110 °C for 4 h, followed by calcination at 550 °C for 4 h.

2.1.2. Modification of Sibunit

Sibunit (CNCT BIC, Omsk, Russia) was modified with NH$_4$OH as follows: boiling in 20 wt. % nitric acid solution for 1 h, then washed with distilled water and dried at 80 °C for 2 h.

2.1.3. Synthesis of Catalysts

Gold (4% by weight) was deposited on metal oxides using a deposition precipitation method with urea at 80 °C for 16 h, in the absence of light [53–56], using HAuCl$_4$·3H$_2$O (Merck, Darmstadt, Germany) as the gold precursor. In order to decompose the hydrolysis products of the gold (III) complex with urea on the support surface, the synthesized catalysts were pretreated in a hydrogen atmosphere at 300 °C for 1 h (15% of H$_2$ in Ar, flow rate 300 mL/min).

Monometallic catalysts containing 1 wt. % Au or Pd were synthesized using the sol immobilization method [57]. In this process, 1 mL of Na$_2$PdCl$_4$ (Merck, Darmstadt, Germany) or HAuCl$_4$·3H$_2$O (Merck, Darmstadt, Germany) solution containing 10 mg of Pd or Au in the count of pure metal and 0.5 mL of a solution containing 1 wt. % PVA (Merck, Darmstadt, Germany) was introduced into a certain volume of water. After 5 min, 0.1 M NaBH$_4$ solution (Merck, Darmstadt, Germany) was rapidly injected under vigorous stirring, with the metal:NaBH$_4$ ratio at 1:4 mol/mol. After 30 min, a sample of support required for obtaining a catalyst with 1 wt. % metal content and a few drops of H$_2$SO$_4$ (Panreac AplliChem, Barcelona, Spain) was added to the obtained sol. Deposition of nanoparticles was carried out for 1 h, and then the catalyst powder was thoroughly washed with deionized water and dried at 80 °C for 2 h in air atmosphere.

The bimetallic PdAu catalysts were prepared similarly to the monometallic synthesis method previously described. To a defined amount of water, 684 µL of Na$_2$PdCl$_4$ solution (10 mg Pd/1 mL H$_2$O), 316 µL of HAuCl$_4$·3H$_2$O solution (10 mg Au/1 mL H$_2$O) and 0.5 mL of a solution containing 1 wt. % PVA were added. After 5 min, under vigorous stirring, 0.1 M NaBH$_4$ solution was rapidly injected into the solution, with the metal:NaBH$_4$ ratio at 1:4 mol/mol. After 30 min, a weight of support required to prepare a catalyst containing 1 wt. % metal and a few drops of H$_2$SO$_4$ was added to the obtained sol. Deposition of

nanoparticles was carried out for 1 h, then the catalyst powder was thoroughly washed with deionized water and dried at 80 °C for 2 h in an air atmosphere.

2.2. Synthesis of 9,10-Dihydroxystearic Acid

For the dihydroxylation of oleic acid, an oxidizing mixture was prepared as follows: 250 mL of tert-butanol (Merck, Darmstadt, Germany) and 105 mL of 30% H_2O_2 solution (Merck, Darmstadt, Germany) were added to a three-neck flask equipped with a reflux condenser, overhead stirrer and thermometer. In addition, 69.9 g of anhydrous $MgSO_4$ (Merck, Darmstadt, Germany) was gradually added in portions. The reaction mixture was stirred for 4 h at 30 °C. The temperature of reaction was controlled using an ice bath. The obtained solution was then filtered on a vacuum station.

Subsequently, 0.71 g of methyltrioxorhenium (Merck, Darmstadt, Germany) and 99 g of oleic acid were dissolved in 210 mL of the resulting oxidizing solution. The dihydroxylation process was performed for 48 h at 40 °C.

At the end of the process, to neutralize the residual H_2O_2, a suspension of $NaHSO_3$ (Merck, Darmstadt, Germany) was added to the reaction mixture, and a special indicator paper was used to check for remaining H_2O_2. After neutralization, tert-butanol was removed using a rotary evaporator, and the precipitate was dissolved in 500 mL of heptane (Merck, Darmstadt, Germany). The resulting solution was left in the refrigerator for 24 h at −5 °C. Then, the precipitate was filtered off, washed with petroleum ether (40–60 °C fraction) and dried under vacuum.

2.3. Catalytic Experiments

The autoclave reactor was charged with 0.317 g of 9,10-dihydroxystearic acid, a catalyst loading (metal/substrate ratio is 1:500 mol/mol) and 20 mL of 0.25 M NaOH solution (Merck, Darmstadt, Germany). Subsequently, the reactor was purged with argon several times and heated to the desired temperature at 2 atm of Ar while stirring at 200 rpm. Once the temperature reached 80 °C, 5 atm of O_2 were pressurized into the reactor, stirring was adjusted to 1500 rpm and the reaction was carried out for 260 min. Scheme of reaction is shown in Figure 1.
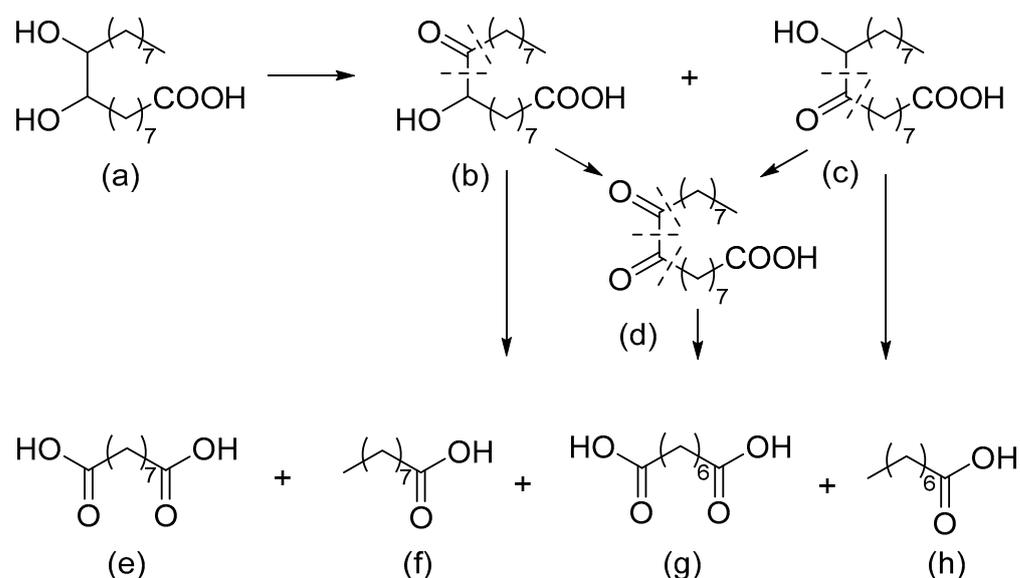

Figure 1. Oxidative cleavage of 9,10-dihydroxystearic acid: (**a**)—9,10-dihydroxystearic acid; (**b**)—9-hydroxy-10-oxostearic acid; (**c**)—10-hydroxy-9-oxostearic acid; (**d**)—9,10-dioxostearic acid; (**e**)—azelaic acid; (**f**)—pelargonic acid; (**g**)—suberic acid; (**h**)—caprylic acid. Reproduced from [58] with permission from the Royal Society of Chemistry.

After the designated time elapsed, the reaction mixture was cooled to room temperature and then filtered from the catalyst using a vacuum station. The filter was washed with 25 mL of 0.1 M NaOH solution and 50 mL of distilled water to extract any remaining reaction products. To precipitate the obtained acids, an aqueous HCl solution was added to the filtered mixture until reaching pH values of 2–3. To transfer the reaction products and unreacted substrate to the organic solvent, the resulting solution was placed in a separating funnel, and 15 mL of methyl tert-butyl ether (Acros Organics, Verona, Italy) was added. The solution was shaken, left to stand for a few minutes and drained. This procedure was repeated 5 times. In the solution, 10 g of anhydrous $MgSO_4$ (Merck, Darmstadt, Germany) was added to remove the residual water and left for 2 h at room temperature. When the time elapsed, the mixture was filtered and transferred to a measuring flask, and the volume of the solution was adjusted to 100 mL with methyl tert-butyl ether.

From the final mixture, 1 mL was taken, and the methyl tert-butyl ether was removed using a rotary evaporator. Then, 250 μL of silylating agent was added, and the silylation process was carried out for 1 h at 80 °C. The solution with silylated products was transferred to a 2 mL volumetric flask. The required amount of the standard—diethylene glycol dibutyl ether (Merck, Darmstadt, Germany)—was added and brought to the mark with methyl tert-butyl ether. The reaction products were analyzed by a GC-MC Shimadzu GCMS-QP2010S (Shimadzu Corp., Kyoto, Japan) chromatograph on a Rtx-5MS column (30 m × 0.25 mm × 0.25 μm) manufactured by BGB Analytik (Boeckten, Switzerland).

To check the material balance, the recovery rate was calculated, indicating how much of the substrate (i.e., 9,10-dihydroxystearic acid) was converted into the target products or remained unreacted. The recovery rate is estimated as the sum of moles of all products and unreacted substrate divided by the original number of substrate moles and multiplied by 100%:

$$\text{Recovery rate} = \frac{\sum \eta \text{ products} \cdot 0.5 + \eta \text{ substrate}}{\eta_0 \text{ substrate}} \times 100\%, \tag{1}$$

where "$\sum \eta$ products" is the total number of moles of products formed, "η substrate" is the number of moles of unreacted substrate, "η_0 substrate" is the number of moles of substrate before the reaction.

To evaluate the activity of the synthesized catalysts, the conversion and product yields were calculated using the following equations:

$$\text{Conversion} = \frac{\eta_0 \text{ substrate} - \eta \text{ substrate}}{\eta_0 \text{ substrate}} \times 100\%, \tag{2}$$

where "η substrate" is the number of moles of unreacted substrate, and "η_0 substrate" is the number of moles of substrate before the reaction.

$$\text{Yield} = \frac{\eta \text{ product}}{\eta_0 \text{ substrate}} \times 100\%, \tag{3}$$

where "η product" is the number of moles of product formed, and "η_0 substrate" is the number of moles of substrate before the reaction.

Turnover frequency was calculated with regard to the number of moles of metal as follows:

$$\text{TOF} = \frac{\text{conversion} \times \eta_0 \text{ substrate}}{\eta \text{ metal} \times 100 \times 4.33 \text{ h}}, \tag{4}$$

where "η_0 substrate" is the number of moles of substrate before the reaction, and η metal represents metal content in the catalyst weight.

2.4. Characterization of Catalysts and Supports

The mass fractions of gold and palladium were determined by atomic emission spectroscopy with inductively coupled plasma (AES ICP) using a Thermo Scientific iCAP 6300 Duo spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) and X-ray energy dispersive spectroscopy (XEDS) in a JEOL JEM-2100F (JEOL Ltd., Tokyo, Japan)

electronic microscope. The specific surface area, pore size and pore volume of the catalysts and corresponding supports were investigated using the low-temperature nitrogen adsorption–desorption method on a Micromeritics 23x-Tristar 3000 Apparatus (Micromeritics Instrument Corporation, Norcross, GA, USA). The phase composition of the supports and catalysts was analyzed by X-ray phase analysis on Philips XPert PRO (Philips, Amsterdam, The Netherlands) and Bruker D8 (Bruker Corp., Billerica, MA, USA). The electronic state of gold and palladium on the surface of catalysts was studied by X-ray photoelectron spectroscopy on ESCALAB 200A (Thermo Fisher Scientific, Waltham, MA, USA) and SPECS GmbH custom-made system using a PHOIBOS 150 WAL (SPECS Surface Nano Analysis GmbH, Berlin, Germany). The size and distribution of gold and palladium nanoparticles were analyzed by transmission electron microscopy on a JEOL JEM-2100F instrument (JEOL Ltd., Tokyo, Japan). More details of the methods used for the study of supports and catalysts are described in the Supplementary Material.

3. Results

The physicochemical properties of the samples used in this work are detailed in our previous publications [39,48–52] and summarized in Table 2, with graphical representations presented in Figures S1–S4 in Supplementary Information. With the exception of the data for Au/Cp-NH$_4$OH material, they are presented for the first time.

Table 2. Physicochemical characteristics of supports and corresponding catalysts [39,48–52].

Sample	Indicated Phase [a]	$w_i/\Sigma w$ (%) [a]	S_{BET} (m²/g) [b]	Pore Size (nm) [b]	Pore Volume (cm³/g) [b]	Metal Content (wt. %) [c]		d_{NPs} (nm) [d]	Relative Content (%) [e]					
						Pd	Au		Pd			Au		
									Pd^0	Pd^{2+}	Pd^{4+}	Au^0	Au$^+$	Au^{3+}
AlOOH_S5	AlO(OH) (orthorhombic)	100	385	5.7	0.67	-	-	-	-	-	-	-	-	-
AlOOH_C	AlO(OH) (orthorhombic)	100	321	5.8	0.41	-	-	-	-	-	-	-	-	-
Au/ AlOOH_S5	AlO(OH) (orthorhombic) Au	96 4	293	6.0	0.55	-	3.94	4.2	-	-	-	100	0	0
Au/ AlOOH_C	AlO(OH) (orthorhombic) Au	96 4	254	5.6	0.52	-	3.95	2.9	-	-	-	81	19	0
La$_2$O$_3$/TiO$_2$	TiO$_2$ (tetragonal)	-	45.3	356.3	0.38	-	-	-	-	-	-	-	-	-
CeO$_2$/TiO$_2$	TiO$_2$ (tetragonal) CeO$_2$ (cubic)	- -	43.4	292.4	0.35	-	-	-	-	-	-	-	-	-
Au/La$_2$O$_3$/ TiO$_2$	TiO$_2$ (tetragonal)	-	45.2	211.5	0.24	-	3.3	2.6	-	-	-	83	17	0
Au/CeO$_2$/ TiO$_2$	TiO$_2$ (tetragonal)	-	46.6	211.1	0.26	-	4.1	2.8	-	-	-	68	20	12
Cp-NH$_4$OH	C (hexagonal)	-	318	6.4	0.58	-	-	-	-	-	-	-	-	-
Pd/Cp-NH$_4$OH	C (hexagonal) Pd (cubic)	- -	320	6.8	0.62	1.2	-	4.3	59	31	10	-	-	-
Au/Cp-NH$_4$OH	C (hexagonal)	-	322	5.0	0.55	-	0.9	2.9	-	-	-	100	0	0
PdAu/Cp-NH$_4$OH	C (hexagonal)	-	331	6.5	0.62	0.56	0.20 *	4.0	91	7	2	92	8	0

$w_i/\Sigma w$—mass fraction of the phase according to XRD; S_{BET}—specific surface area calculated by BET method; d_{NPs}—average diameter of nanoparticles; [a] XRD; [b] N$_2$ adsorption–desorption; [c] AES ICP; [d] HRTEM; [e] XPS; *—determined by XEDS.

3.1. X-ray Diffraction

The structural characteristics of the supports and the corresponding catalysts were determined by XRD (Figure S3, Table 2).

The $2\theta = 14.1°$, $28.2°$, $38.4°$, $49.3°$, $65.0°$ and $72.2°$ reflections observed in the X-ray diffraction patterns of aluminum supports (AlOOH_S5 and AlOOH_C) belong to aluminum oxyhydroxide (boehmite) with an orthorhombic crystal lattice [59]. It should be noted that according to the manufacturer's data, AlOOH_S5 material is a mixture of 5% SiO_2 and 95% boehmite, but no reflexes related to SiO_2 were detected, possibly due to the amorphous structure of the silicon oxide included in the material. Gold deposition did not lead to any structural changes in these supports. A gold phase was identified for both catalysts at $2\theta = 44.3°$ and $77.7°$ [60]. The gold content determined using the Rietveld method agreed well with the AES ICP data (Table 2).

The X-ray diffraction patterns of La_2O_3/TiO_2 and CeO_2/TiO_2 supports show reflections corresponding to the phases of rutile ($2\theta = 27.6°$ and $41.5°$) and anatase ($2\theta = 25.5°$, $38.0°$, $48.2°$, $62.9°$ and $75.2°$) [61]. Additionally, diffraction peaks at $2\theta \sim 28.6°$ and $33.1°$ belonging to the CeO_2 phase were observed [62]. The analysis of the phase composition of the related catalysts revealed no changes in the structure of the supports after gold deposition. In addition, no reflexes belonging to the gold phase were detected, possibly attributable to the small size of gold NPs (below the sensitivity level of the method) and their uniform distribution on the support surface or to their X-ray amorphous structure.

The XRD spectra of carbon samples showed diffraction maxima at $2\theta = 25.5°$ and $43.2°$, which is consistent with literature data corresponding to the carbon material "Sibunite" [63]. The deposition of gold and/or palladium did not change the structure of the support. Notably, no reflexes belonging to the deposited metals were found on the diffractograms measured for $Au/Cp-NH_4OH$ and $PdAu/Cp-NH_4OH$ catalysts. The exception is $Pd/Cp-NH_4OH$, where maxima were observed at $2\theta = 40.0°$ and $68.5°$, corresponding to the palladium phase [64].

3.2. AES ICP and XEDS

According to AES ICP data, gold was deposited on the surface of boehmite, and titanium oxide was modified with cerium oxide in an amount close to nominal (Table 2). However, in the case of TiO_2-modified La_2O_3 and Sibunit, the completeness of gold deposition is below nominal, specifically 67% for $Au/La_2O_3/TiO_2$, 90% for $Au/Cp-NH_4OH$ and 83% for $PdAu/Cp-NH_4OH$. It is worth noting that the completeness of metal deposition is influenced by many factors, such as the nature of the metal precursor, method of preparation and nature of the support (hydride, hydroxyl, carbonyl, carboxyl and other groups, i.e., functional surface coverage, point of zero surface charge). In addition, the functional coating of the support may change due to reagents used in catalyst synthesis, affecting the amount of metal deposition. A specific cause cannot be established based on the available experimental data.

For $Pd/Cp-NH_4OH$ and $PdAu/Cp-NH_4OH$, the completeness of palladium deposition was 100 and 80%, respectively. In the case of the bimetallic catalyst, competitive adsorption of metal precursors during synthesis might occur.

3.3. N$_2$ Adsorption–Desorption

According to the data presented in Table 2, the initial boehmite and Sibunit, along with their corresponding catalysts, are mesoporous materials with extended specific surface area. However, for AlOOH_S5 and AlOOH_C materials, gold deposition on their surface results in a significant decrease in the specific surface area of the synthesized catalysts. This reduction may be a consequence of an increase in the average size of support crystals due to agglomeration during catalyst synthesis and a decrease in the available pores.

CeO_2- and La_2O_3-modified TiO_2 and their corresponding catalysts exhibit a macroporous structure with considerably lower specific surface area values compared to boehmite and Sibunit materials.

3.4. Transmission Electron Microscopy

The size distribution of the metal particles and TEM images are shown in Figure S4, and the values of the average sizes of metal NPs are summarized in Table 2.

For gold catalysts deposited on AlOOH_S5 and AlOOH_C, the average nanoparticle sizes were 4.2 nm and 2.9 nm, respectively. The significantly larger size of gold nanoparticles on the boehmite Siral 5 is probably due to the presence of SiO_2 in its composition. The existence of SiO_2 potentially alters the point of zero charge on the surface compared to AlOOH_C, leading to a modification in the interaction nature of the gold precursor with the surface of the support [39,65].

For $Au/La_2O_3/TiO_2$ and $Au/CeO_2/TiO_2$, the average size of Au nanoparticles (2.6 nm and 2.8 nm) and their distribution range (1–7 nm) are similar.

An analysis of TEM images of carbon samples reveals that the average size of nanoparticles on the surface of $Au/Cp-NH_4OH$, $Pd/Cp-NH_4OH$ and $PdAu/Cp-NH_4OH$ are 2.9 nm, 4.3 nm and 4.0 nm, respectively. As demonstrated in [66], the reduction rate of the metal precursor plays a crucial role in the nucleation and growth processes, serving as one of the main factors influencing the final size and shape of the NPs. The rate of metal atom generation is influenced by the nature of the precursor and reducing agent. In this case, $HAuCl_4 \cdot 3H_2O$ and Na_2PdCl_4 were used as gold and palladium precursors, with $NaBH_4$ acting as the reducing agent. The oxidizing potential of $NaBH_4$ strongly depends on the solution pH, rising with increasing pH. The elevated oxidizing potential of $NaBH_4$ is associated with an increase in its reduction capacity. Consequently, the differing reduction rates of gold and palladium precursors likely contribute to the observed variations in the average size of gold and palladium NPs, as well as their mixture.

3.5. X-ray Photoelectron Spectroscopy

The results detailing the electronic state of gold and palladium on the surface of the investigated catalysts are presented in Table 2 and Figures S1 and S2.

On the surfaces of $Au/AlOOH\_S5$ and $Au/Cp-NH_4OH$ materials, gold is only present in the metallic state. However, for all other samples, along with the metallic state, an additional gold state, Au^+, was detected. The contribution of Au^+ increases in the following sequence: $PdAu/Cp-NH_4OH$ (8%), $Au/La_2O_3/TiO_2$ (17%), $Au/AlOOH\_C$ (19%) and $Au/CeO_2/TiO_2$ (20%). Moreover, in addition to Au^0 and Au^+, Au^{3+} (12%) was also found on the surface of $Au/CeO_2/TiO_2$ material.

The deconvolution of Pd 3d XRD spectra revealed that palladium on the surface of $Pd/Cp-NH_4OH$ and $PdAu/Cp-NH_4OH$ catalysts is present in three states: Pd^0, Pd^{2+} and Pd^{4+}. A significant portion is in the metallic state, namely 59% for monometallic and 91% for bimetallic catalysts. In the case of $Pd/Cp-NH_4OH$, the involvement of Pd^{2+} and Pd^{4+} states accounts for 31% and 10%, respectively, while for $PdAu/Cp-NH_4OH$, the corresponding amounts are 7% and 2%.

3.6. Catalysis

The activity of the investigated catalysts in the process of oxidative C-C cleavage was evaluated under the following conditions: 0.317 g (1 mmol) of the substrate, Me/substrate ratio = 1:500, 20 mL of 0.25 M NaOH solution, T = 80 °C, p = 5 bar O_2, t = 260 min, stirring 1500 rpm. The catalytic data are presented in Table 3.

For gold deposited on aluminum oxyhydroxides (Table 3, entries 1 and 2), the catalyst with boehmite Catapal B as the support for gold NPs exhibited the highest activity. This catalyst achieved 100% conversion of 9,10-DSA with a recovery rate of 69%. In contrast, the $Au/AlOOH\_S5$ material showed nearly three times lower conversion (35%) but a higher recovery rate (83%). Similarly, the yield of products was also higher for $Au/AlOOH\_C$, with 51% for azelaic acid and 66% for pelargonic acid, along with small amounts of caprylic and suberic acids (11% and 9%, respectively). These observed variations in catalytic behavior can be attributed to the structural sensitivity of the oxidative C-C cleavage reaction, considering the significantly smaller size of Au NPs on the $Au/AlOOH\_C$ surface compared to

Au/AlOOH_S5 (2.9 nm and 4.2 nm, respectively) (Table 2, Figure S4). The influence of the average size of gold NPs on the catalytic properties of Au NP catalysts in oxidative C-C cleavage was also observed in previous studies [25].

Table 3. Results of catalytic experiments.

Entry	Catalyst	Conv., (%)	Y AA, (%)	Y PA, (%)	Y CA, (%)	Y SA, (%)	Recovery Rate
1	Au/AlOOH_S5	35	11	19	4	3	83
2	Au/AlOOH_C	100	51	66	11	9	69
3	Au/La$_2$O$_3$/TiO$_2$	99	51	56	7	7	62
4	Au/CeO$_2$/TiO$_2$	100	29	37	6	7	40
5	Pd/Cp-NH$_4$OH	46	0	0	0	0	54
6	Au/Cp-NH$_4$OH	88	48	61	21	14	84
7	PdAu/Cp-NH$_4$OH	77	0	0	0	0	23

Reaction conditions: 0.317 g (1 mmol) of substrate, ratio Me/substrate = 1:500, 20 mL of 0.25 M NaOH solution, T = 80 °C, p = 5 bar O$_2$, t = 260 min, stirring 1500 rpm. Conv.—conversion; Y AA—yield of azelaic acid; Y PA—yield of pelargonic acid; Y CA—yield of caprylic acid; Y SA—yield of suberic acid.

Additionally, it is essential to consider the different chemical compositions of the supports and, consequently, their different functional coatings, which play a crucial role in this kind of reaction. This might explain the observed values of the recovery rate. With a substrate conversion of 100% and a recovery rate of 69%, it is evident that a portion of 9,10-DSA converts not only to the target products. Thus, side reactions catalyzed by the acid-base sites of the support also likely take place on the catalyst surface. An example of a side reaction catalyzed by functional groups of the support, particularly its strong acid-base sites, is the oxidation of betulin on Au/alumina supports. The products of this reaction were oligomers/polymers that remained on the catalyst surface and, thus, were not detected by chromatography [39].

Similar to the case of Au/AlOOH _C material with an average gold particle size of 2.9 nm, Au/La$_2$O$_3$/TiO$_2$ and Au/CeO$_2$/TiO$_2$ catalysts with an average gold particle size of 2.6 and 2.8 nm, respectively, showed high activity in the oxidative C-C cleavage process, achieving 99% and 100% conversion of 9,10-DSA, respectively (Table 3, entries 3 and 4). However, the yields of AA and PA (with a similar ratio between them for each of the catalysts), as well as the recovery rate, were different among these catalysts. Specifically, for the Ce-modified sample, these values are, on average, 20 points lower than for the La-modified sample. One possible explanation for the observed differences in Au/La$_2$O$_3$/TiO$_2$ and Au/CeO$_2$/TiO$_2$ could be attributed to the electronic state of gold on the surface of these supports. For La$_2$O$_3$-modified TiO$_2$, more than 80% of gold exists in the metallic state, whereas for CeO$_2$-modified TiO$_2$, it is 68% (Table 2). Additionally, on the surface of CeO$_2$-modified TiO$_2$, in addition to Au+, which exhibits similar content for both supports, there is also Au^{3+}. Another potential factor contributing to the variations is the different functional coatings of La$_2$O$_3$- and CeO$_2$-modified TiO$_2$ supports, which determines the acid-base properties of the materials. This, in turn, may be responsible for selectivity; in this case, the recovery rate, as noted above, serves as an indicator.

Among carbon catalysts (Table 3, entries 5–7), the generation of target products from the oxidative cleavage reaction of 9,10-DSA was exclusively observed for Au/Cp-NH$_4$OH. It is noteworthy that despite incomplete substrate conversion (88% conversion), this sample exhibits the highest recovery rate (84%) among all the catalysts studied. As it is known, graphite (Sibunit—mesoporous graphite-like carbon material) is a chemically inert substance. Its functionalization with strong acids or bases, leading to the formation of defects, serves mainly to stabilize the NPs immobilized on its surface. At the same time, during functionalization on the surface of carbon, carboxyl, carbonyl and other groups are formed, but these groups are usually much weaker than the acid-base sites found on the surface of oxide materials. Thus, it can be assumed that the high recovery rate values observed for Au/Cp-NH$_4$OH are likely due to the unique features of the ammonia-modified Sibunit

functional coating, and gold NPs with an average size $\geq$ 3 nm are responsible for the activity, as in the cases of Au/AlOOH_C, Au/La$_2$O$_3$/TiO$_2$ and Au/CeO$_2$/TiO$_2$ materials.

It should be noted that Pd/Cp-NH$_4$OH and PdAu/Cp-NH$_4$OH materials are active in the oxidative C-C cleavage process, with the conversion of 9,10-DSA reaching 46% and 77%, respectively. However, no formation of target products was observed for them (Table 3, entries 5 and 7). A possible explanation could be attributed to the unique properties of palladium, which is capable of absorbing hydrogen generated during intermediate steps or from substrate/intermediates. During the operation of Pd-containing catalysts, released hydrogen might return to the reaction atmosphere, potentially initiating non-target processes. In addition, Pd is a "classical" catalyst for C-C bond formation processes, contributing to the production of off-target products [67–69].

For a more demonstrative confirmation of the hypothesis regarding the structural sensitivity of the oxidative cleavage reaction of 9,10-dihydroxystearic acid, Table 4 includes TOF values compared with the average size of metal NPs. The presented data clearly show that the TOF values for catalysts with particles with an average size of around 3 nm are several times higher than the corresponding values for catalysts characterized by an average particle size of 4 nm or more.

Table 4. TOF dependence on average nanoparticle size.

Entry	Catalyst	Particle Size, nm	TOF, h^{-1}
1	Au/AlOOH_S5	4.2	40
2	Au/AlOOH_C	2.9	115
3	Au/La$_2$O$_3$/TiO$_2$	2.6	114
4	Au/CeO$_2$/TiO$_2$	2.8	115
5	Pd/Cp-NH$_4$OH	4.3	53
6	Au/Cp-NH$_4$OH	2.9	101
7	PdAu/Cp-NH$_4$OH	4.0	89

4. Conclusions

This study focused on comparatively evaluating the catalytic properties of materials with significantly different physicochemical characteristics in the oxidative C-C cleavage of the C$_{18}$ substrate.

Regardless of the nature of the support, the most active catalysts were those with an average size of gold NPs below 3 nm (Table 3, Entry 2-4, 6), demonstrating the structural sensitivity of the oxidative cleavage reaction of 9,10-DSA. Simultaneously, the functional coating of the support, depending on its nature, considerably influenced the selectivity of the oxidative C-C cleavage process (yield of target products), including the recovery rate, reflecting the occurrence of nontarget processes. Metal oxyhydroxides (AlOOH_S5 and AlOOH_C) and oxides (La$_2$O$_3$/TiO$_2$ and CeO$_2$/TiO$_2$) were found to be inefficient supports for Au-containing catalysts in the oxidative cleavage of 9,10-DSA due to low recovery rate values, consequently promoting nonselective processes. On the other hand, graphite-like carbon material Sibunit, owing to its unique functional cover, allowed us to obtain an Au NPs catalyst exhibiting the highest recovery rate (84%) among all investigated catalysts, achieving a conversion level of 88% for 9,10-DSA. The proximity of substrate conversion and recovery rate values indicates a minimal possibility of non-target processes on Au/Cp-NH$_4$OH.

Notably, palladium, including in bimetallic system, proved to be an inefficient active component for catalysts in the oxidative cleavage of 9,10-DSA. Similar to Au/AlOOH_S5, Au/AlOOH_S5, Au/La$_2$O$_3$/TiO$_2$ and Au/CeO$_2$/TiO$_2$ materials, the use of Pd-based catalysts (Pd/Cp-NH$_4$OH and PdAu/Cp-NH$_4$OH) led to non-target processes, with this inefficiency being most pronounced in this case.

In summary, the main factors determining the efficiency of the catalyst in the oxidative cleavage of 9,10-DSA include the nature of the active component, the support and the average size of metal NPs.

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