Article

Sol–Gel Approach for Design of Pt/Al₂O₃-TiO₂ System—Synthesis and Catalytic Tests

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Abstract: Al₂O₃-TiO₂ systems with Ti:Al 0.1, 0.5 and 1.0 molar ratio obtained by the sol–gel method have been used as a platinum support. As a precursor of alumina gel, aluminum isopropoxide has been chosen. Titanium *tert*-butoxylate was applied to obtain titania gel and hexachloroplatinic acid was applied as a source of platinum. The systems have been characterized by the following methods: thermogravimetric analysis (TGA), Fourier transformation infrared spectroscopy (FTIR), X-ray powder diffraction (XRPD), low-temperature nitrogen adsorption–desorption isotherms (BET, BJH), temperature-programmed reduction with hydrogen (TPR-H₂) and hydrogen chemisorption. Reactions of toluene to methylcyclohexane and selective *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) hydrogenation were used as the tests of systems' catalytic activity. The application of Al₂O₃-TiO₂ as a support has enabled the obtaining of platinum catalysts showing high activities for hydrogenation of toluene and selective hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline in the liquid phase. The highest activity in both reactions has been found for Pt/Al₂O₃-0.5TiO₂ catalyst and the highest selectivity for Pt/Al₂O₃-. The activity of Pt/Al₂O₃-TiO₂ catalysts was higher than that of alumina-supported ones.

Keywords: sol–gel; TiO₂; Al₂O₃; catalytic; hydrogenation; platinum; hydrogen; chemisorption; catalyst

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1. Introduction

Metal oxides (i.a. Al₂O₃, SiO₂, MgO, TiO₂, ZrO₂), aluminosilicates and zeolites are most frequently used supports for metallic catalysts. Multi-component oxide carriers are also employed, e.g., Al₂O₃-SiO₂, Al₂O₃-La₂O₃, Al₂O₃-La₂O₂CO₃ [1], Al₂O₃-CaO, Al₂O₃-CaO-CaCO₃ [2], leading to improvement of the catalytic system's textural properties, better thermal stability and higher mechanical strength. Above that, surface acid–base property modifications and higher dispersion of the active phase can be expected in these systems. To enhance these properties, alumina modification with rare-earth elements oxides (La₂O₃, CeO₂) are effective [3]. Introduction of TiO₂ to Al₂O₃ matrix increases the resistance of platinum catalyst against chlorine poisoning in chlorobenzene dehydrochlorination reaction [4].

Hydrogenation reactions are usually performed using metallic catalysts, and Fe, Ni, Co, Pd, Pt, but also Ag and Cu are the active phase. Pd–Pt bimetallic catalysts allow for elimination of catalyst poisoning with sulfur compounds present in the feed stream during the reduction process. Oxide and sulfide catalysts can be also used; however, due their lower activity, higher process temperature is required. To enhance catalyst's activity, materials with increased acidic surface properties are often used as metal support [5]. In

that case, not only metallic centers but also support's acidic ones are active in hydrogenation reaction. This type of support is beneficent for the process cost lessening.

In hydrogenation reactions, platinum can be used either after deposition on a support for example C [6] or usually of oxide type [7], for example Al_2O_3 [8,9], or as a bare metal [10], or platinum (IV) oxide PtO_2 [11], or as another metallic catalyst's modifier [12]. As mentioned above, platinum is also used in bimetallic systems, such as Pt-Ni, Pt-Co and Au-Pt [13,14]. Single component metal-only catalyst, e.g., wire net degrades and is being spent much faster than supported one, and metal loss after its recovery from the reaction product can be higher. Platinum (or, generally, any metal) deposition on a non-metallic support can be of many benefits, which include greater poisoning resistance, higher activity thanks to larger contact area surface. All commercially available carriers, i.e., aluminum oxide, silica, zeolites, aluminosilicates, activated carbon can be regarded as potentially useful platinum supports [15]. TiO_2 - or Al_2O_3 -supported Pt is often used in toluene to methylcyclohexane and benzene to cyclohexane hydrogenation reactions [16,17].

This work is aimed at determining the influence of the Al_2O_3 to TiO_2 ratio in the Al_2O_3 - TiO_2 support on the efficiency of the resulting platinum catalysts for toluene and *o*-chloronitrobenzene hydrogenation reactions. Platinum catalysts supported on unmodified and titania-modified Al_2O_3 have been compared. Our choice to use titania-modified alumina has been motivated by various reasons, such as long-term experience with sol-gel alumina systems modification and numerous advantages of this material. To name a few, it is relatively high surface area up to 600 °C, amorphous structure and very mild acid-base surface properties. At low Ti:Al molar ratios, Al_2O_3 also shows TiO_2 stabilizing properties of amorphous anatase to crystalline rutile transformation. The titania-alumina combination in oxide support is expected to have less drawbacks than any of these two alone [18].

2. Materials and Methods

2.1. Materials

Titanium(IV) *t*-butoxylate, aluminum isopropoxide, acetic acid, toluene, *o*-chloronitrobenzene and chloroplatinic acid hexahydrate were purchased from Sigma-Aldrich (Saint Louis, MO, USA) and used as received. Gases—hydrogen, helium, 10 vol.%. H_2 in Ar mixture, air and oxygen were purchased from Linde (Pullach im Isartal, Germany).

2.2. Preparation

Alumina gel (sample designation: Al) was prepared according to the procedure described in our previous papers [19,20], and the Al_2O_3 - TiO_2 binary oxide systems of different molar ratios of Ti to Al: 0.1; 0.5 and 1.0 were synthesized by aqueous sol-gel chemistry. As a precursor of the starting alumina gel, aluminum isopropoxide was used, while acetic acid was applied as a moderator of hydrolysis and condensation rates (regulation of pH). The reaction took place in a two-liter glass reactor upon stirring under reflux. The precursor of alumina (100 g of fine powder) was slowly added and hydrolyzed in 880 mL of water at 75 °C and after 2 h of stirring the resulting slurry was peptized with 35 g (33.5 mL) of 100% acetic acid. In all preparations, the molar ratio of $\text{Al}(i\text{-C}_3\text{H}_7\text{O})_3$, water and acetic acid was constant and equal to 1:100:1.2. The sol was refluxed for more than 24 h at 75 °C. After that time, $\text{Ti}(\text{O-}t\text{-Bu})_4$ was added in small portions as the second oxide component precursor.

Next, the systems were stirred for 72 h with a magnetic stirrer and under reflux at room temperature. A portion of the resulting gel was transferred to the Petri dishes to produce air-dried thin films, and most part of the gel was dried in a vacuum rotary evaporator prior to calcination in a tube furnace at 500 °C (initial temperature ramp: 10 °C·min⁻¹) in air flow (4 h, 110 dm³·h⁻¹) and in oxygen flow (2 h, 110 dm³·h⁻¹).

For the catalyst preparation and porous structure determination, the fraction of the grain size between 0.1 and 0.2 mm in diameter was used, which was obtained by grinding the annealed gel in a mortar and subsequently sieving to collect two required grain fractions, 0.1–0.2 mm and <0.1 mm. For the XRD analysis the latter fraction was used. Table 1 shows the samples labeling, composition, and the amount of titanium additive for each oxide

system (per 100 g of aluminum isopropoxide). The binary supports were labeled as Al-*x*Ti, where *x* denotes the molar content of TiO₂ (Al-0.1Ti; Al-0.5Ti; Al-1.0Ti)—Table 1.

Table 1. Composition and labeling of the studied systems and the amount of added titanium *t*-butoxylate.

Sample Name	Al	Al-0.1Ti	Al-0.5Ti	Al-1.0Ti
Relative molar amount of Al	1	1	1	1
Relative molar amount of Ti	0	0.1	0.5	1
Mass of added Ti(O- <i>t</i> -Bu) ₄ [g]	0	2.66	13.32	26.64

The Pt/support catalysts were prepared by the conventional impregnation method. To prepare the platinum catalysts, 2.08 mg_{Pt}/mL hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) solution was added in an amount corresponding to 1% Pt by weight to the given amount of the produced oxide support. The impregnated supports were dried in a cabinet dryer for 24 h at 70 °C. Raw catalyst were calcined in the tube furnace under air atmosphere for 4 h and for 2 h under oxygen at 500 °C. The catalysts were labeled as Pt-S, where S denotes a support (Al—alumina, Al-0.1Ti; Al-0.5Ti; Al-1.0Ti—binary oxide systems). Precursor-impregnated supports were reduced in hydrogen flow (99.99%, 50 cm³·min^{−1}) with a temperature ramp of 10 °C·min^{−1}. After reaching the setpoint (400 °C), the catalysts reduction was continued for 2 h.

2.3. Characterization

2.3.1. Thermal Analysis

Thermal transformation of unprocessed gel samples was carried out on a NETZSCH TG 209 F1 Libra thermogravimetric apparatus. A 5.0 ± 0.2 mg sample was placed in an Al₂O₃ pan (85 µL volume) and heated at a rate of 20 °C·min^{−1} to 1000 °C. For all experiments the fraction of the grain size below 0.1 mm was used. The TG traces were recorded in air atmosphere (20 cm³·min^{−1} flow) with a resolution of 0.1 µg. No drying under vacuum or at elevated temperature was applied.

2.3.2. Porous Structure

The textural characterization of supports calcined at 500 °C and reduced catalysts was obtained by the low-temperature nitrogen adsorption using a sorptometer ASAP 2010 (Micromeritics, Norcross, GA, USA). Prior to the measurements of the adsorption–desorption isotherms, the samples were outgassed at 300 °C for 4 h. The surface area was determined by the Brunauer–Emmett–Teller (BET) method, while the total pore volume and average pore diameter were calculated using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of isotherms.

2.3.3. X-ray Powder Diffraction Analysis

The X-ray powder diffraction (XRPD) measurements were carried out using a Philips PW1050 diffractometer working in the θ – 2θ geometry with Ni-filtered CuK α radiation. The following measurement conditions were applied: 2θ 5–100°, voltage 35 kV, current 20 mA, scan step 0.040° at 1° per minute. The positions of reflections were calculated by the Philips APD program.

2.3.4. Temperature-Programmed Reduction with Hydrogen—TPR-H₂

Measurements of temperature-programmed reduction with hydrogen (TPR-H₂) were carried out on a PulseChemiSorb 2705 (Micromeritics, Norcross, GA, USA) instrument. Dried metal-precursor-impregnated supports were reduced in the flow of 10 vol.% H₂–Ar mixture at the flow rate of 30 cm³·min^{−1}. The measurements were conducted in the temperature range 40–850 °C at a linear temperature ramp of 10 °C·min^{−1}. The hydrogen consumption was monitored with a thermal conductivity detector (TCD) and the signal has

been normalized to the same sample weight. The products of the reduction were retained by an isopropanol/liquid nitrogen cold trap held at about $-70\text{ }^{\circ}\text{C}$.

2.3.5. Determination of Metal Dispersion by Hydrogen Chemisorption

Prior to hydrogen chemisorption, the dried catalysts were reduced with H_2 at $400\text{ }^{\circ}\text{C}$ for 2 h. The reduced samples were placed in an ASAP 2010C sorptometer (Micromeritics, Norcross, GA, USA) and evacuated for 15 min. at room temperature and then at $350\text{ }^{\circ}\text{C}$ for 60 min, followed by additional reduction in hydrogen flow ($40\text{ mL}\cdot\text{min}^{-1}$) at $350\text{ }^{\circ}\text{C}$, and evacuation for 2 h at $350\text{ }^{\circ}\text{C}$.

Hydrogen chemisorption measurements were carried out at $35\text{ }^{\circ}\text{C}$. Platinum dispersion was calculated from total amount of chemisorbed hydrogen.

Metal surface area S was calculated using the following equation [21]:

$$S = \frac{v_m \cdot N_A \cdot n \cdot a_m \cdot 100}{22414 \cdot m \cdot wt} \left(\text{m}^2 \text{g}_{\text{Pt}}^{-1} \right) \quad (1)$$

where v_m is volume of adsorbed hydrogen, expressed in cm^3 , N_A is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), $n = 1$ is the chemisorption stoichiometry, a_m is the surface area (m^2) occupied by a metal atom, m is the sample mass (g), wt (%) is the metal loading.

The dispersion of active phase was calculated from the formula:

$$D = \frac{S \cdot M}{a_m \cdot N_A} \quad (2)$$

where S is the metal surface area, M is platinum atomic weight, N_A is Avogadro's number and a_m is the surface occupied by one platinum atom.

2.3.6. FTIR Measurements

FTIR measurements were carried out using a Thermo Scientific Nicolet iS50 FTIR spectrometer. A total of 4 mg samples were mixed with 200 mg of KBr and pressed at 10 tons press into the form of discs.

2.3.7. Catalytic Tests

Hydrogenation of Toluene

Toluene hydrogenation was performed at atmospheric pressure using a fixed-bed flow reactor and H_2 as a carrier gas. Freshly dried metal-precursor-impregnated support ($20.0 \pm 0.2\text{ mg}$) was loaded into the reactor and reduced in situ with hydrogen (at $100\text{ mL}\cdot\text{min}^{-1}$ flow) at $400\text{ }^{\circ}\text{C}$ for 2 h. Next, the reactor temperature was lowered to a desired value and an adjusted hydrogen flow ($50\text{ mL}\cdot\text{min}$) was directed to a saturator filled with toluene and passed to the reactor. The steady concentration of toluene in the feed was $0.7\text{ }\mu\text{mol}\cdot\text{mL}^{-1}$. The catalysts were heated at the rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ until the catalytic test temperature (75 to $225\text{ }^{\circ}\text{C}$) was reached. The post-reaction mixture was analyzed on a gas chromatograph equipped with a Restek MXT-1 capillary column and a TCD detector.

The catalytic activity, expressed as *apparent rate*, was calculated using the following equation [22]:

$$r_t = \frac{FYC}{N} \left[\frac{\text{mol}_{\text{Tl}}}{\text{mol}_{\text{Pt}}\text{min}} \right] \quad (3)$$

where F is the total flow rate of feed ($\text{cm}^3\cdot\text{min}^{-1}$); Y —the fractional conversion; C —the concentration of toluene in the feed ($\text{mol}_{\text{Tl}}\cdot\text{mL}^{-1}$) and N —the platinum content (mol_{Pt}) in the sample. *Turnover frequency* (TOF, min^{-1}) was calculated by dividing the number of molecules converted per second by the number of active platinum atoms measured by H_2 adsorption [22]. The toluene hydrogenation reaction shown below (Figure 1):

Figure 1. Reaction scheme for the hydrogenation of toluene.

Hydrogenation of *o*-Chloronitrobenzene

Hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) on Pt catalysts was carried out in the liquid phase at 30 °C for 2 h under hydrogen pressure of 4.0 MPa in a 200 mL stainless steel autoclave with an internal glass tube and equipped with a magnetic stirrer. The autoclave was loaded with 25.0 ± 0.2 mg of reduced (H_2 , 400 °C, 2 h) catalyst and 50 mL of 0.1 M solution of *o*-CNB in methanol/water mixture (2:1 vol.). Then the autoclave was purged several times with helium followed by purging with hydrogen to remove air. In each case, the reaction time was two ours and stirring rate was 1000 rpm. Results of the experiments show that the reaction was conducted in the absence of external mass transport limitations (the stirring rates from 800 to 1000 rpm did not affect the reaction rate). The reaction products were analyzed on a gas chromatograph equipped with a DB-1 capillary column and an FID detector. The *o*-CNB hydrogenation reaction shown (Figure 2):

Figure 2. Reaction scheme for the *o*-CNB hydrogenation.

3. Results

3.1. TG and DTG Measurements

Air-dried alumina gel losses 5%, 14%, 30% and 45% of its initial mass at ~80, 200, 300 and 370 °C, respectively (Figure 3a,b). The processes of mass loss are completed before reaching 500 °C and therefore temperature 600 °C was chosen for the final thermal processing of the obtained supports. First thermal effect (DTG—Figure 1b) at 77–92 °C is related to desorption of a physisorbed water and is observed for each studied composition. The following thermal effects correspond to decomposition of $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2$ to $\text{Al}_2\text{O}(\text{CH}_3\text{COO})_4$ (~200 °C), $\text{Al}_2\text{O}(\text{CH}_3\text{COO})_4$ to $\text{AlO}(\text{CH}_3\text{COO})$ (~300 °C) and $\text{AlO}(\text{CH}_3\text{COO})$ to Al_2O_3 (~380 °C) [23]. Total mass loss of the binary systems ranges from approximately 30% for Al-1.0Ti to more than 50% for Al-0.1Ti. Decreasing in content Al_2O_3 correlates with lower total mass losses of the system. Above 600 °C the mass loss is almost non-existent in each of the compositions (Figure 3a) and constant mass is reached (completion of gel transformation processes, oxidation and volatiles removal). Derivatographic curves (Figure 3b) of the two-component systems show a multi-stage character of the decomposition processes and their complexity and intensity decreases in line with the titania modifier content in the alumina matrix. Some of the effects diminish and finally disappear. The decomposition peaks of $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2$ to $\text{Al}_2\text{O}(\text{CH}_3\text{COO})_4$ and $\text{Al}_2\text{O}(\text{CH}_3\text{COO})_4$ to $\text{AlO}(\text{CH}_3\text{COO})$ are not observed in the Al-1.0Ti system. Two maxima located between 200 and 400 °C indicate alumina precursor decomposition and oxidation of $\text{Ti}(\text{O}-t\text{-Bu})_4$ alkoxylate groups. As the $\text{Ti}(\text{O}-t\text{-Bu})_4$ content in the systems increases, their position shifts to lower temperatures. Additional thermal effect occurring at 538 °C in the Al-1.0Ti and Al-0.5Ti systems is a result of titania precursor decomposition and formation of $\text{Al}_2\text{O}_3\text{-TiO}_2$ stable structure. Further small thermal decomposition effects observed above 550 °C can be linked to surface dehydroxylation of the binary systems [24].

Figure 3. Thermogravimetric (a) and derivatographic (b) curves of the oxide systems under air atmosphere.

3.2. Surface Area and Porosity of the Supports and Catalysts

Introduction of TiO_2 to Al_2O_3 structure results in shifting of an adsorption–desorption hysteresis loop onset to lower p/p_0 relative pressure values (Figure 4a) and change of the loop shape as the content of the modifier increases. According to the IUPAC classification, all isotherms are of IV(a) type, which is characteristic to mesoporous materials. Additionally, all the catalysts are characterized by this isotherm type and compared to the parent supports, their shapes are not very different for the samples after impregnation with hexachloroplatinic acid and after consecutive thermal processing. Pore distribution curves are based on the desorptive branch of BJH isotherm. Average pore diameter decreases from 5.9 nm for the unmodified Al_2O_3 to 3.1 nm for the Al-1.0Ti system (Figure 4b, Table 2). Specific surface area of the binary systems is higher than alumina one, but this value is unrelated to the TiO_2 content. However, for binary systems, after slight initial increase, pore volume decreases with titania loading with respect to an alumina (a reference) and in series. In the catalytic systems, presence of the dispersed platinum at the surface leads to decrease in textural parameters (surface area, pore volume—Table 2) and increase in the average pore diameter (but not for the $\text{Pt}/\text{Al}_2\text{O}_3$ system) as a consequence of small pores blockage by Pt clusters.

Figure 4. Low-temperature nitrogen adsorption–desorption isotherms (a) and pore volume distribution (b) of the Al_2O_3 and binary Al-Ti oxide supports calcinated at 500 °C.

3.3. X-ray Powder Diffraction Analysis

The XRPD results (Figure 5) indicate high homogeneity and amorphicity of the Al/Ti binary oxide systems. No signals corresponding to crystalline phases were recorded. With the TiO_2 content, the initially increased signals intensities (at the 2θ angles of 36–37°, 46° and 67°) of amorphous $\gamma\text{-Al}_2\text{O}_3$ in the two-component Al-0.1Ti system decrease (compared

to the pure alumina matrix), but large part of this observation is due to lower molar content of the alumina in the subsequent compositions. For the Al-1.0Ti, two broad bands of crystalline TiO_2 rutile phase at 54.7° and 63.3° were identified [25] but no presence of any new phases was found.

Table 2. BET surface area, pore volume and average pore diameter of oxide supports and platinum catalysts.

Sample Name	Al:Ti Molar Ratio	BET Surface Area [m^2/g]		Pore Volume [cm^3/g]		Average Pore Diameter [nm]	
		Support	Catalyst	Support	Catalyst	Support	Catalyst
Al_2O_3	-	301.1	233.7	0.61	0.39	5.9	4.7
$\text{Al}_2\text{O}_3\text{-TiO}_2$	1:0.1	373.0	301.9	0.65	0.62	5.2	6.4
	1:0.5	377.2	310.2	0.50	0.44	3.8	4.3
	1:1.0	376.0	283.4	0.40	0.33	3.2	3.7

Figure 5. XRPD of the oxide supports.

3.4. FTIR Spectra of the Al-Ti Binary Oxide Systems

In the $3600\text{--}3100\text{ cm}^{-1}$ range a broad absorption band of the surface hydroxyl groups bonded to the aluminum and titanium cations and interlinked with hydrogen bonds is characteristic and a 3400 cm^{-1} -OH stretching oscillations band is also present (Figure 6). Lower intensity vibrational oscillations band of surface-bonded -OH groups at 1635 cm^{-1} increases with the modifier content. An 801 cm^{-1} band of Al-O and 1091 cm^{-1} Al-O-H band (Al system only) related to transformation of amorphous alumina to $\gamma\text{-Al}_2\text{O}_3$ [26–28]

are visible in the Al and Al-0.1Ti systems. Strong 568 cm^{-1} structural band of Ti-O that is characteristic to titania [29] coincides with the Al-O oscillations range.

Figure 6. FTIR spectra of the Al-Ti binary oxide systems.

3.5. Temperature-Programmed Reduction with Hydrogen—TPR- H_2

To obtain information on the reducibility of active phase precursors introduced into the studied supports, temperature-programmed reduction with hydrogen (TPR- H_2) was performed. TPR- H_2 profiles of catalysts calcined at $500\text{ }^\circ\text{C}$ are presented in Figure 5. Reduction profiles of platinum catalysts show pronounced hydrogen consumption in two temperature regions, i.e., between 150 to $300\text{ }^\circ\text{C}$ and from 350 to $450\text{ }^\circ\text{C}$ (Figure 7). System denoted as Pt-Al exhibits only one broad reduction band spanning from 200 to $300\text{ }^\circ\text{C}$ with a maximum at $241\text{ }^\circ\text{C}$. It is also present with decreasing intensity in the Pt-Al-0.1Ti and Pt-Al-0.5Ti reduction profile in favor of the lower temperature $185\text{ }^\circ\text{C}$ peak that dominates in the subsequent systems. High temperature (350 to $450\text{ }^\circ\text{C}$) reduction band is more prominent in the titania-doped systems. The hydrogen consumption scheme in these catalysts is typical for the reduction of various PtO_x species. This reduction pattern has been frequently observed [30] and it seems to be generally accepted that the first peak is due to the reduction of the bulk of PtO_x weakly interacting with alumina. At higher content of TiO_2 the first reduction peak increases and shifts to lower temperature with a maximum at $185\text{ }^\circ\text{C}$. It indicates weakening of interactions between the support surface and the PtO_x phase. Intensity of reduction in the above-mentioned high temperature range also follows in this manner. Several authors have attributed this signal to the reduction of oxy- or more probably hydroxychlorided $\text{Pt}(\text{Pt}(\text{OH})_4\text{Cl}_2)$ species formed by the oxidation

of a platinum precursor during calcination, strongly interacting with the support [29,31]. At the same time, this may be an effect of the modifier component reduction [32], since its intensity is related to the TiO₂ content.

Figure 7. Temperature-programmed reduction (TPR-H₂) profiles of Pt catalysts.

3.6. Determination of Metal Dispersion by Hydrogen Chemisorption

An important parameter characterizing metallic catalysts is the dispersion of metallic phase. The techniques most frequently used for the determination of metal dispersion are transmission electron microscopy, X-ray powder diffraction and chemisorption. The latter was employed in the present study (Table 3), because the amount of chemisorbed hydrogen permits the determination of not only the average size of metallic particles, but also the number of metal surface atoms that is required for the calculation of turnover frequency (TOF, min^{−1}) of toluene and o-chloronitrobenzene hydrogenation.

Table 3. Hydrogen chemisorption on platinum catalysts reduced at 400 °C.

Sample Name	Volume of Adsorbed Hydrogen [cm ³ /g]			Pt Dispersion [%]	Average Size of Pt Particles [nm]
	H _t	H _{irr}	H _r	D _{irr}	
Pt-Al	0.81	0.30	0.51	51.6	1.8
Pt-Al-0.1Ti	0.54	0.17	0.37	29.9	3.2
Pt-Al-0.5Ti	0.50	0.14	0.36	23.7	3.9
Pt-Al-1.0Ti	0.29	0.13	0.16	22.6	4.2

H_t—total amount of adsorbed hydrogen, H_{irr}—total amount of irreversibly adsorbed hydrogen, H_r—total amount of reversibly adsorbed hydrogen; D_{irr}—metal dispersion calculated from the amount of irreversibly adsorbed hydrogen.

Among the studied catalysts, highest dispersion, estimated on a base of irreversibly adsorbed hydrogen, was measured for the unmodified aluminum oxide Pt-Al system (Table 3). Average Pt crystallite size of that system is 1.8 nm, which is lowest value in the series of the prepared catalysts. Incorporation of titania modifier to the alumina systems results in a significant decrease of platinum dispersion, especially compared to Pt-Al system. Consequently, Pt dispersion changes from ~30% for the Pt-Al-0.1Ti to less than 23% for the Pt-Al-1.0Ti system.

3.7. Catalytic Activity

The series of 1% Pt on $\text{Al}_2\text{O}_3\text{-TiO}_2$ catalysts have been tested in the reaction of hydrogenation of toluene to methylcyclohexane. Results of the catalytic activity tests performed at several temperatures are presented in Figure 8a,b.

Figure 8. The effect of metallic phase support on TOF (calculated by dividing the number of molecules converted per minute by the number of active (surface) metal atoms measured from irreversibly adsorbed H_2) of hydrogenation of toluene as a function of temperature (a) and at 200 °C as a function of TiO_2 content (b). Catalyst activation conditions: temperature: 400 °C, hydrogen flow: $100 \text{ cm}^3 \cdot \text{min}^{-1}$, activation time: 2 h. Reaction conditions: toluene concentration $c_{\text{Ti}} = 0.75 \text{ } \mu\text{mol} \cdot \text{cm}^{-3}$, hydrogen flow: $50 \text{ cm}^3 \cdot \text{min}^{-1}$, activity after 20 min.

As follows from the presented data (Figure 6a), the catalysts' activity increased with the reaction temperature and reaching a maximum at 200 °C for each of them. Further increase in temperature resulted in an activity diminishing. This is because kinetic/equilibrium of aromatic hydrocarbons hydrogenation that proceeds at higher temperatures favors the opposite reaction of dehydrogenation [33]. Some authors suggested that the drop of catalytic activity may result from the loss of catalytically active sites caused by poisoning with surface carbon produced by cracking of the reactants [34].

Calculations of TOF (min^{-1}) performed using the values of dispersion, have shown that the most active catalyst at 200 °C is Pt-Al-0.5Ti, the activity of which surpassed by almost 10% that of Pt-Al-0.1Ti and is two times higher than the activity of Pt-Al-1.0Ti catalyst (Figure 6a,b).

It clearly shows that Al₂O₃-supported catalysts are characterized by higher dispersions (Table 3), i.e., smaller particle sizes; however, higher number of accessible active centers is not reflected by catalytic activity because hydrogenation of toluene is a facile reaction, i.e., structure insensitive, according to Boudart classification [34].

The most active in toluene hydrogenation reaction Pt-Al-0.5Ti catalyst has also been tested in another reaction, namely hydrogenation of *o*-CNB to *o*-CAN. Results of the catalytic tests performed on Pt-Al-0.5Ti and Pt-Al catalysts are presented in Table 4. Catalytic tests of *o*-CNB hydrogenation were performed in a batch reactor at 30 °C under pressure of 4 MPa for 2 h. The reaction was carried out using 0.1M *o*-CNB solution in ethanol/water mixture with volume ratio of 2:1. Optimum reaction conditions were identified based on results reported in Refs. [35,36].

Table 4. Conversion and selectivity of *o*-CNB hydrogenation reaction, percentage of components in the post-reaction mixture.

Sample Name	Conversion [%]	Selectivity [%]	An [%]	Nb [%]	<i>o</i> -CAN [%]	<i>o</i> -CNB [%]
Pt/Al	58.0	72.9	2.8	13.0	42.2	42.0
Pt/Al-0.1Ti	88.2	74.5	4.06	18.42	65.75	11.78
Pt/Al-0.5Ti	79.0	68.5	2.7	22.2	54.1	21.0

An—aniline, Nb—nitrobenzene, *o*-CAN—*o*-chloroaniline, *o*-CNB—*o*-chloronitrobenzene.

From the three catalysts studied, the Pt-Al-0.1Ti system shows higher hydrogenation activity than other studied ones and its selectivity to *o*-CAN have appeared to be the highest one (slightly more than 74%). Both the selectivity and conversion decrease as the content of TiO₂ in the systems increases. This confirms the information known from the literature that platinum catalysts employed in hydrogenation reaction of halogenated nitroaromatic compounds to halogenated anilines are characterized by high activity and poor selectivity [37]. A small (0.1) Ti content significantly improves the Pt/Al selectivity toward the main product, but a larger amount (0.5 Ti) has an adverse effect.

4. Conclusions

The aim of the research on alumina-titania Pt-supported systems was to determine their usability in the reaction of toluene hydrogenation and *o*-chloronitrobenzene reduction. Introduction of the metallic phase precursor and its further reduction with hydrogen on support's surface resulted in decrease of initially relatively high specific surface area of the binary supports. Temperature-programmed reduction of the platinum precursor with hydrogen to the metallic phase shows that this process occurred at 100–200 °C. From hydrogen chemisorption experiments it was stated that still the highest Pt dispersion is achieved on non-modified γ -Al₂O₃ and introduction of titania to the alumina matrix has an adverse effect on the metal dispersion. One of the reasons for that (observed as increasing mean Pt crystallites size) is decrease in specific surface area of the binary oxide systems.

Depending on the amount of introduced titania to the two-component oxide system, the Pt catalyst exhibited different activity in the two aforementioned test reactions. For the 1% Pt-Al-Ti-0.5 system, the rate of the toluene hydrogenation was highest at 175–200 °C. Therefore, it was also tested in the reaction of selective hydrogenation of *o*-chloronitrobenzene. In that case, the conversion was higher than for the Pt-Al system, but selectivity was slightly lower, which is in accordance with literature data.

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