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SBA materials as support of iridium catalyst

for hydrogenation reactions

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Graphical abstract



Research Highlights

- New heterogeneous catalytic systems for hydrogenation reactions were developed
- SBA materials were employed as a catalyst support and Ir as active phase
- Hydrogenation of toluene and o-chloronitrobenzene (o-CNB) to ortho-chloroaniline (o-CAN) were performed
- Hydrogenation of o-CNB to o-CAN using in-situ generated hydrogen from the aqueousphase reforming (APR) of methanol
- Activities of Ir/SBA-3 was higher than iridium supported on SBA-15, SiO₂ or Al₂O₃ supports

Abstract

This paper investigates the catalytic properties of SBA-3 and SBA-15 supported iridium catalysts. The produced catalysts (1 wt.% Ir) were tested for their performance in hydrogenation of toluene and the selective nitro group hydrogenation of ortho-chloronitrobenzene (o-CNB) to ortho-chloronaniline (o-CAN) using in-situ generated hydrogen from the aqueous-phase reforming (APR) of methanol. The obtained results were compared with the hydrogenation performance of iridium catalysts supported on the most widely used supports such as alumina and silica. The catalysts were characterized by XRD, BET, TPR-H₂, H₂ chemisorption, XPS and TEM techniques. The highest activities were observed in the case of the iridium catalysts supported on ordered mesoporous silica, both in hydrogenation of toluene and o-chloronitrobenzene. The catalytic activity of iridium supported on SBA-3 was much higher than that of Ir supported on the commonly used supports such as Al₂O₃ or SiO₂.

Keywords: iridium catalyst, SBA-3, SBA-15, toluene hydrogenation, selective hydrogenation of chloronitrobenzene, aqueous-phase reforming (APR) of methanol

1. Introduction

The processes of hydrogenation of aromatic compounds and aromatic nitro compounds play important role in the chemical industry. The products of selective hydrogenation of chloronitrobenzene to corresponding chloroanilines have found many applications as an intermediate in the manufacture of drugs, pesticides, pigments, and dyes [1]. The hydrogenation of aromatic compounds is also important reaction from the industrially and environmentally point of view. The large amount of aromatic-free fuels and solvents are produced using processes of hydrogenation of aromatic hydrocarbons. These reactions have also the significant factor in synthesis of many organic compounds. The product of benzene hydrogenation, cyclohexane, is a raw material for the production of caprolactam (a substrate for obtaining nylon) and adipic acid (a substrate for the manufacture of saturated polyesters and plasticizers) [2].

The performance of catalytic activity in the processes of hydrogenation mainly depends on the type of the metallic active phase and type of the support. Recently, more attention has been paid to synthesis and modification of the commonly known supports (Al₂O₃, SiO₂, mesoporous materials) used in these processes [3-5]. The most promising supports are mesoporous silica materials, particularly SBA types, which represent a unique class of silica-based materials, because of their outstanding properties like high specific surface area, large pore volume and a uniform pore size distribution [6]. In the last decade these materials have found a number of nanotechnological applications, for example, as catalysts, supports, adsorbents, photochemicals, optical and drug delivery agents [7-11]. From the among of SBA types materials, several catalytic reactions using SBA-15 as a support for metal active phases were examined and showed promising results [12,13]. In the literature the applications of SBA-3 as catalyst supports for iridium active phase in the process of hydrogenation of toluene to methylocyclohexane and selective hydrogenation of o-chloronitrobenzene to o-chloroaniline. The textural properties of the supports and chemical characters of their surface are affecting the dispersion and reducibility of the active phase [14-17].

The commonly used active phases in the processes of hydrogenation are platinum group metals, particularly Pt, Pd, Rh [18-20]. Noble metal-based catalysts are an interesting choice, since they have high activity for hydrogenation processes, and the reaction can then perform at low temperatures and pressures. Among the metallic phases the most active and often used in

hydrogenation reaction is platinum. The interesting metal from this group is iridium that is characterized by greater resistance to deactivation caused by impurities than other noble metals, but studies devoted to monometallic Ir catalysts in relation to hydrogenation processes are very rare [21-24]. For example, iridium catalysts have been employed for selective hydrogenation of unsaturated aldehydes to corresponding unsaturated alcohols [25] and in the selective hydrogenation of furfural to 2-methylfuran [26]. On industrial scale it is used for production of acetic acid (Cativa[™] process) [27], and in the processes of hydrodesulphurization [28].

The present work compares the activity of iridium particles as the active metal species supported on the ordered mesoporous silica (SBA-3, SBA-15) and commercial (Al₂O₃, SiO₂) supports. The aim of this work was to determine the influence of texture of support in the processes of hydrogenation. The catalysts were tested in hydrogenation of toluene and in the selective nitro group hydrogenation of ortho-chloronitrobenzene (o-CNB) to ortho-chloronailine (o-CAN). The latter reaction was carried out by flow method using in-situ generated hydrogen from the aqueous-phase reforming (APR) of methanol. To the best of our knowledge, no data are available on the use of ordered mesoporous silica as supports of iridium catalysts in the process of hydrogenation of toluene and o-chloronitrobenzene.

2. Experimental

2.1. Preparation of supports and catalysts

The SBA-15 material was synthesized by hydrothermal synthesis performed under acidic conditions according to the procedures described elsewhere [29]. The support was prepared by the following procedure: 4.0 g of Pluronic P123 (Aldrich) was dissolved in 30 cm³ of deionized water and 116 cm³ of 2M HCI (Polish Chemicals Reagents, Inc., Poland). Reactants were stirred at 35 °C until obtained homogeneous solution, then 9.1 cm³ of tetraethyl orthosilicate (TEOS - Aldrich) was added directly into the solution with stirring for 20 h at 35 °C. Then the mixture was aged at 90 °C for 24 h. The white powder was separated by filtration, washed with distilled water, and dried in the air at room temperature (RT). Template was removed by calcination at 550 °C for 8 h in air.

The SBA-3 support was prepared by hydrothermal synthesis performed under acidic conditions according to our own procedure [14]. First, 8.3 g of cetyltrimethylammonium bromide (CTAB - Aldrich) was dissolved in 165 cm³ of deionized water followed by an addition of TEOS

dropwise (23 cm³). After stirring for 15 minutes, 34 cm³, 38 vol.% HCl was added with continuous stirring for next 30 min. After this, the additional portion of hydrochloric acid was added, which resulted in precipitation of white gel. The mixture was stirred for next 2 h at RT. Then, aging of the gel was carried out at room temperature for 8 days in static conditions. The resulting material was filtered, washed, dried in air at RT and then calcined at 550 °C for 8 h in air.

Aluminium oxide was prepared by the reaction of aluminium isopropoxide (98+%, Aldrich) with the excess of water according to the procedure described elsewhere [30]. The resulting aluminum hydroxide was washed with isopropyl alcohol (Polish Chemicals Reagents, Inc.) followed by drying at 110 °C for 24 h and calcination at 550 °C for 4 h.

Silica was an amorphous SiO₂ (silica gel, Polish Chemicals Reagents Inc.) that was activated by thermal treatment in air at 550 °C for 4 h.

The Ir/support (support = SBA-3, SBA-15, SiO₂ or Al₂O₃) catalysts were prepared by the conventional impregnation method using hexachloroiridium(IV) acid hydrate (H₂IrCl₆·xH₂O, 99.995%, Aldrich) as a metal precursor. The required quantity of H₂IrCl₆ xH₂O was dissolved in water and this solution was added to the evacuated support (the amount of precursor was calculated to achieve iridium loading of 1 wt.%). Water was removed on a rotary evaporator. Then the impregnated samples were dried at 100 °C for 24 h and labelled as Ir/SBA-3-D, Ir/SBA-15-D, Ir/SiO₂-D and Ir/Al₂O₃-D.

2.2. Activation of catalysts

Prior to the measurements of hydrogen chemisorption, as well as before the measurements by transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS) and low-temperature nitrogen adsorption-desorption (BET), each precursor-impregnated support was placed in a fixed-bed flow reactor and reduced in hydrogen flow (99.99%, Linde, 50 cm³·min⁻¹). At the beginning, the system was flushed at RT with argon (150 cm³·min⁻¹, 99.99%, Linde) which was then replaced with hydrogen (150 cm³·min⁻¹). After 15 min, the hydrogen flow was reduced to 50 cm³·min⁻¹ and the temperature ramp (10 °C·min⁻¹) started. After reaching the setpoint (400 °C), the catalyst precursor reduction was continued for 2 h. Then the catalyst was cooled down to the room temperature in hydrogen flow. The last step consisted in flushing of the sample with argon for 15 min. The reduced catalysts were labelled as Ir/SBA-3, Ir/SBA-15, Ir-Al₂O₃ and Ir/SiO₂.

2.3. Catalysts characterization

2.3.1. Determination of surface area, pore volume and pore diameter

The Brunauer-Emmet-Teller (BET) surface areas were determined by N₂ adsorption at -196 °C using a Micromeritics ASAP 2010 sorptometer. Total pore volume and average pore radius were determined by applying the Barrett-Joyner-Halenda (BJH) method to the desorption branch of the isotherm. Prior to the measurements of adsorption-desorption isotherms, the samples were outgassed at 300 °C for 4 h.

2.3.2. Determination of metal content

Iridium content in catalysts reduced at 400°C for 2 h was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Varian Vista-MPX spectrometer.

The elemental analysis of all the iridium catalysts has indicated practically the same Ir content in the catalysts (0.99; 1.01; 1.02 and 0.95 wt.% for SBA-3, SBA-15, SiO₂ and Al₂O₃, respectively). The ICP measurements were carried out for the catalysts reduced for 2 h at 400 $^{\circ}$ C.

2.3.3. Temperature-programmed reduction with hydrogen – TPR-H₂

Measurements of temperature-programmed reduction with hydrogen were carried out on Pulse ChemiSorb 2705 (Micromeritics) instrument. Dried metal precursor-impregnated supports (~50 mg) were reduced in the flow of 10 vol.%. $H_2 - Ar$ (99.999%, Linde) at the flow rate of 30 cm³·min⁻¹. In the TPR-H₂ studies, a quartz sand (Aldrich) impregnated with metal precursors (H₂IrCl₆ xH₂O) was used as a reference material. The measurements were conducted in the temperature range from 50 to 900 °C at a linear temperature ramp of 10 °C·min⁻¹. The TPR-H₂ analyses were also performed for catalysts after activation in H₂ at 400 °C for 2 h. All TPR-H₂ profiles, presented in this work, have been normalized to the same sample weight – 100 mg.

2.3.4. Determination of metal dispersion by hydrogen chemisorption

The measurements of hydrogen chemisorption on supported metal catalysts were conducted by the static method at 35°C on an ASAP 2010C sorptometer.

Prior to hydrogen chemisorption, fresh dried catalysts were reduced with H₂ at 400 °C for 2 h (see "Activation of catalysts") and then the catalyst samples were pretreated in situ to purify their

surfaces from adsorbed gases. The pretreatment consisted in evacuation at room temperature for 15 min. and then at 350 °C for 60 min., followed by reduction in hydrogen flow (40 cm³·min⁻¹, 99.999%, Linde) at 350 °C for 60 min. and evacuation at 350 °C for 120 min.

The metallic surface area (S), expressed in $m^2 \cdot g_{lr}^{-1}$, was calculated from the following equation [31]:

$$S = \frac{v_m \cdot N_A \cdot n \cdot a_m \cdot 100}{22414 \cdot m \cdot wt}$$

where v_m -volume of adsorbed hydrogen expressed in cm³, N_A - Avogadro's number (6.022·10²³ mol⁻¹), n - chemisorption stoichiometry (n=2), a_m - surface area (m²) occupied by one iridium atom, m- sample weight (g), wt (%) - metal loading.

The dispersion (D) of iridium was calculated from the formula:

$$D = \frac{S \cdot M}{a_m \cdot N_A}$$

where *S* is metallic surface area, *M* is iridium atomic weight, N_A is Avogadro's number and a_m is the surface covered by one iridium atom.

2.3.5. Transmission electron microscopy (TEM)

Transmission electron microscope (TEM) images were recorded on a JEOL 2000 microscope operating at accelerating voltage of 80 kV. The results were used to estimate ordering of the samples and to estimate the Ir particle size.

2.3.6. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra (XPS) were recorded on an Ultra High Vacuum (UHV) System (Specs, Germany). The examined materials were irradiated with a monochromatic Al K α radiation (1486.6 eV). The operating pressure in the chamber was close to 2 × 10⁻⁹ mbar. Binding energies were referenced to the C1s peak from the carbon surface deposit at 284.6 eV.

2.3.7. X-ray diffraction analysis (XRD)

The X-ray powder diffraction was performed on a Bruker AXS D8 Advance diffractometer with Ni-filtered CuK α radiation (λ =1.54056 Å) over the 2 Θ ranges of 2-8° and 10-60°.

2.4. Catalytic tests

2.4.1. Hydrogenation of toluene to methylcyclohexane

Toluene hydrogenation was performed at atmospheric pressure using a fixed-bed flow reactor and H₂ as a carrier gas. Fresh dried catalyst (25 mg) was placed into the reactor and reduced in situ with hydrogen (100 cm³·min⁻¹, 99.99 %, Linde) at 400 °C for 2 h. After that time, the reactor temperature was lowered to a desired level and hydrogen flow (50 cm³·min⁻¹), that passed through a saturator filled with toluene and equilibrated at 10 °C (99.8 %, Aldrich), was directed to the reactor. Inner diameter of the reactor was 8.0 mm, and the volume of catalyst bed was from 0.15 to 0.25 cm³ depending on the density of tested catalyst. The concentration of toluene in the hydrogen feed was stable and equal to 0.75 µmol·cm⁻³. The catalysts were heated at the rate of 10 °C·min⁻¹ until reaching the temperature of the catalytic test (75-250 °C). The reaction products were analyzed on a gas chromatograph equipped with a capillary column RESTEK-MXT-1. The catalytic activity was presented as apparent rate calculated by following equation:

$$r_t = \frac{FYC}{N} \left[\frac{mol_{Tl}}{mol_{Ir} \min} \right]$$

where F - total flow rate of feed ($cm^3 \cdot min^{-1}$); Y - fractional conversion; C - concentration of toluene in the feed ($mol_{TI} \cdot cm^3$) and N - iridium content (mol_{Ir}) in the sample. Turnover frequency (TOF, min^{-1}) was calculated by dividing the number of molecules converted per second by the number of active iridium atoms measured by H₂ chemisorption.

2.4.2. Hydrogenation of ortho-chloronitrobenzene to ortho-chloroaniline with hydrogen generated in situ in APR of methanol

Hydrogenation of o-CNB to o-CAN with in situ generated hydrogen from aqueous-reforming of methanol was conducted in an X-Cube[®] reactor (ThalesNano, Inc.). The reaction was carried out in continuous-flow mode in an isothermal fixed-bed reactor at 225 and 275 °C. Both reactions, i.e. aqueous-phase reforming of methanol (that is the source of hydrogen) and hydrogenation of chloronitrobenzene proceed at the same time in the same reactor and in the presence of the same catalyst. Flow rate of the reaction mixture (0.05 M o-CNB in the mixture of methanol : water = 2:1 by volume) was 0.2 cm³ min⁻¹, catalyst weight 50 mg, and liquid pressure 5 MPa. Inner diameter of the reactor was 3.8 mm and the volume of catalyst bed was 0.08 cm³. At the above parameters, liquid

hourly space velocity (LHSV) was 150 h⁻¹ and space time (ST = volume of catalyst bed/volume flow rate) was ~24 s. The reaction products were collected in a receiver and analyzed in 30-minute intervals on a gas chromatograph equipped with a capillary column DB-1 and FID detector. A blind test carried out in the absence of catalyst proved that no conversion of o-CNB occurred under used conditions. Turnover frequency (TOF, min⁻¹) was calculated by dividing the number of molecules converted per second by the number of active iridium atoms measured by H₂ chemisorption.

Since the subject of this study was hydrogenation of o-CNB using APR of methanol as a source of hydrogen, a quantitative analysis of gaseous products was not carried out. Qualitative analysis has shown the presence of H₂, CO₂, CH₄ and trace amounts of CO originating from the reaction of methanol reforming.

3. Results and discussion

Very important parameters characterizing supports and catalysts are their surface area and porosity. The textures of supports after calcination at 550 °C (Table 1, Figure 1) and iridium catalysts after reduction at 400 °C (Table 2) were characterized by the low-temperature nitrogen adsorption-desorption measurements. All isotherms of the supports (Figure 1a) are typical for SBA-3, SBA-15, SiO₂ and Al₂O₃ materials presented in the literature [14,32,33].

The SBA-3 support shows nitrogen adsorption/desorption isotherms of type IV(b) characteristic for mesoporous materials (Fig. 1a) [34]. As the relative pressure increases isotherms of the support show a sharp step, in the range of $p/p_0 = 0.15-0.30$, characteristic of capillary condensation of nitrogen within uniform mesopores. This step for SBA-3 is less prominent and shifted to lower p/p_0 in comparison to the other supports. It indicates that silica SBA-3 possesses smaller mesopores [35]. Other supports (SBA-15, SiO₂ and Al₂O₃) were characterized by type IV(a) isotherms (according to the IUPAC classification) with a clearly marked hysteresis loop (H1 for SBA-15, H2(b) for SiO₂, and H4 for Al₂O₃), that testifies to their mesoporosity [34]. The loop of type H1 is found in materials which exhibit a narrow range of uniform mesopores, as for instance in templated silicas (e.g., MCM-41, MCM-48, SBA-15). Usually, network effects are minimal and the steep, narrow loop is a clear sign of delayed condensation on the adsorption branch. The shape of the hysteresis loop (type H2(b)) indicates that the SiO₂ has mainly cylindrical pores as results from the parallel course of the isotherm adsorption and desorption branches in the range of $p/p_0=0.7$ - 0.9. The fact that the hysteresis loop closes at p/p₀=0.4 indicates that small cone-shaped pores are present as well. The average pore size of SiO₂ support, calculated by the BJH method on the basis of the isotherm desorption branch, is 7.1 nm. The hysteresis loop recorded for Al₂O₃ can be classified as H4, that is often found for materials with aggregated crystals [34]. The pore size distribution covers the range from 2 to 10 nm, with two maxima at 4 and 8 nm (Figure 1b). The average pore size calculated by the BJH method is 7.5 nm (Table 1).

The low-temperature nitrogen adsorption/desorption isotherms were used to calculate surface area, average pore diameter and average pore volume of iridium catalysts - Table 2. The impregnation with iridium precursor does not change the texture of the supports. The BET surface area, pore volume and average pore size (Table 2) remain close to the values obtained for the supports before impregnation (Table 1). Only in the case of Ir/Al₂O₃, introduction of iridium leads to decrease of surface

area (~20%), pore volume of the catalyst (from 0.34 to 0.22 cm³·g⁻¹) and average pore diameter from 7.5 to 5.9. These diminishments are related to incorporation of iridium active phase into the porous structure and blocking its surface [21].

An important parameter characterizing metallic catalysts is the dispersion of the metal. The Ir/SBA-3 and Ir/SBA-15 catalysts prepared from hexachloroiridium(IV) acid as a metal precursor show very high dispersion (Table 2). From among the reduced catalysts the highest dispersion calculated from irreversibly adsorbed hydrogen was observed for Ir/SBA-15 catalyst. This catalyst exhibits slightly higher dispersion (~80%) and lower particle size (1.4 nm) when compared to iridium catalyst supported on SBA-3 (D~75%). Using the SBA supports with unique mesoporous structure provides higher dispersion and lower particles size compared to iridium catalysts supported on commercial Al_2O_3 and SiO_2 supports, where dispersion was ~38 and ~57%, respectively. It indicates that the pore structure and large surface area of the supports can affect the metal dispersion. The H₂ chemisorption analysis showed particles size of iridium smaller than 3 nm for all catalysts. These results were confirmed by TEM analysis - Figure 2. As results from Fig. 2, the TEM micrographs of the catalysts indicate the particles size below 3 nm and a homogeneous dispersion of the nanoparticles on the surface of supports. The TEM analysis confirmed also the well-ordered hexagonal pore system of SBA catalysts. The pore ordering of the samples was also confirmed by low angle XRD analysis (Fig.3A, 3B). Both ordered mesoporous supports and iridium catalysts (Ir/SBA-3 and Ir/SBA-15) showed the typical characteristic patterns of the SBA structures, matching well those reported in the literature [6]. In the case of Ir/ SBA-15 some decrease in intensity and broadening after Ir deposition on SBA-15 was observed. It suggested some loss of the ordering of the pore structure, especially for used catalyst. It may be related to the lower hydrothermal stability of SBA-15 material in comparison to stability of SBA-3 due to its lower contribution of micropores [36]. XRD patterns in the wide angle range show only reflection attributed to the amorphous silica and Al₂O₃ (Figure 3). No metallic iridium (Ir⁰) was observed by XRD (absence of reflections at 40.6° and 47.3°), suggesting the presence of very small, well dispersed metal crystallites (under 3 nm) [14,37]. These results are consistent with TEM as well as with hydrogen chemisorption data.

The SBA materials reveals stronger interactions of the adsorbed iridium species with the support surface compared to the other presented supports, which favours high dispersion of the active phase. The interactions of iridium particles with the support were confirmed by TPR-H₂ studies, Figure

4. Measurements of temperature-programmed reduction with hydrogen (TPR-H₂) provide information about reducibility of chemical compounds present in a sample and about their interactions with support. TPR studies were carried out on dried samples. No reduction signals were seen in TPR-H₂ profiles of the supports (data not shown), which proves that the supports were irreducible. For the fresh catalysts (Figure 4) two maxima were observed at 130-190 °C and 350-530 °C ranges, and the peak intensities depended on the type of used support. The peak at ~200 °C assigned to the reduction of highly dispersed iridium species originate from the precursor or to the reduction of IrOx to metallic iridium [38-40]. Only this peak is observed in H₂IrCl₆ sample, which means that the iridium precursor is fully-reduced at this temperature [38]. The signals at 350-530 °C range are assigned to iridium stronger bonded to the support surface [21]. This peak is more intensive and slightly shifted to the higher temperature for iridium catalysts based on SBA type supports than those for Ir/SiO₂-D and Ir/Al₂O₃-D samples. The fact that the reduction of catalysts takes place mainly at higher temperatures for Ir/SBA materials indicates that interaction between iridium species and these supports is stronger making their reduction process more difficult. These results are confirmed by chemisorption study, the Ir/SBA-3 and Ir/SBA-15 samples are characterized by higher dispersion and smaller size of iridium particles compared to those for Ir/SiO₂ and Ir/Al₂O₃. The total degree of reduction of the supported iridium precursor calculated on the basis of hydrogen consumption at the temperature range RT-600 °C was over 90% for Ir/SiO₂ (93.9%), Ir/SBA-15 (94.6%) and Ir/SBA-3 (99.2%) catalysts, which indicates an almost complete reduction of the active phase and presence of iridium in the catalyst at zero oxidation state. The lower intensity of the TPR-H₂ profile for Ir/Al₂O₃ is a result of lower reduction degree (85.9%) in comparison to the reduction of iridium phase on silica supports. It may also result from the smaller amount of iridium introduced during the impregnation of the Al₂O₃ support, as was indicated by ICP analysis. The TPR-H₂ profiles of catalysts after activation (H₂ reduction, 400 °C, 2 h) showed no reduction signals (data not shown) that proved the metallic state of iridium in the investigated catalysts.

Figure 5 displays the XPS Ir 4f spectra for the reduced Ir/SBA-3 and Ir/SBA-15 catalysts. The peak corresponding to Ir $4f_{7/2}$ has been analyzed. Its deconvolution indicates the presence of two iridium species with binding energies at 60.7 eV related to metallic iridium and at ca. 62 eV assigned to Ir-O (Ir⁵⁺) [41-43]. The latter is a result of interaction of Ir atoms with the oxide support, giving rise to an oxidic state denoted as Ir⁵⁺. The presence of Ir⁵⁺ can be also caused by oxidation of Ir⁰ as a result

of contact with air during transferring the samples to XPS cell. The contribution of partially oxidized iridium (Ir^{5+}) is higher for Ir/SBA-15 catalyst due to larger influence of the support on Ir^{0} that is usually observed for smaller Ir nanoparticles [42]. The results of XPS are in agreement with TPR-H₂ data confirming the interaction of iridium species with oxide supports.

Catalytic activity of the investigated materials has been studied in hydrogenation of toluene and in the reaction of selective hydrogenation of o-chloronitrobenzene (o-CNB) to o-chloroaniline (o-CAN). The last reaction was carried out using flow method in conditions of *in-situ* hydrogen generation from alcohol (methanol) and water by aqueous phase reforming without using compressed hydrogen.

The results of the hydrogenation of toluene performed at several temperatures are presented in Fig. 6. The catalytic measurements carried out on the supports alone, i.e. SBA-3, SBA-15, SiO₂ and Al₂O₃, proved their inactivity in the hydrogenation of toluene, while the reduced Ir-catalysts showed a considerable activity in this reaction. Methylcyclohexane was the only reaction product obtained over the catalysts tested. The activity of the iridium catalysts supported on SBA-3 material for toluene hydrogenation, expressed as the apparent rate (rt) of reaction (Fig. 6) as well as the turnover frequency (TOF, min-1 - Table 2) was higher than that obtained over the catalyst supported on commonly used SiO₂ or Al₂O₃. The activity increased with the rise in the reaction temperature reaching a maximum at 125-150 °C for catalyst supported on SBA-3. In the case of Ir/SBA-15 the maximum of activity was recorded at 150 °C while for Ir/SiO2 it was 125 °C. Only for Ir/Al2O3 catalyst the hydrogenation activity increase with temperature of reaction reached the maximum at 175 °C. For all catalysts, a further increase in temperature caused a decrease in the activity. The decline in the catalytic activity at higher temperatures is explained in the literature by the occurrence of dehydrogenation [44], cracking of methylcyclohexane formed in the reaction studied [45]. The drop of catalytic activity could also results from a loss of catalytically active sites caused by poisoning of the catalyst surface by carbon produced in cracking of reactants [46]. However, we did not observe any cracking products and, as was already mentioned, the only detected product was methylcyclohexane. This permits to conclude that the only possible reason for the decrease in the catalytic activity at higher temperatures was the reaction proceeding in the opposite direction, i.e. dehydrogenation of methylcyclohexane. Calculations of TOF (min⁻¹) - Table 2, performed using the values of metal dispersion, have shown that the most active catalyst was Ir/SBA-3, whose activity was almost 25% higher than that of Ir/SBA-15 or Ir/SiO2. The activity of Ir/Al2O3 was comparable with the activity of

Ir/SBA-15 and Ir/SiO₂ due to its twice lower iridium dispersion. The lower dispersion of Ir/Al₂O₃ is probably related to its twice lower BET surface area in comparison to SiO₂ and four times lower than for SBA-15 support. To check the stability, the most active catalysts Ir/SBA-3 and Ir/SBA-15 were tested at 150°C for 25 hours and the results are presented in Figure 7. In the evaluated period of time all catalysts showed a stable work. The activity of Ir/SBA-3 catalyst increased for the first 40 minutes of the reaction to the level of $\sim 27 \text{ mol}_{\text{T}} \cdot \text{mol}_{\text{T}}^{-1} \cdot \text{min}^{-1}$, then it gradually decreased and stabilized after few hours. Similarly, the activity of Ir/SBA-15 catalyst diminished during the first 6-7h and then stabilized. The activity of Ir/SBA-3 in 25 h test decreased by less than 24%, while the activity of Ir/SBA-15 fell down by 30%. The characterisation of the used catalysts by means of XRD indicates the decrease of ordering of the Ir/SBA-15 catalyst (Fig. 3) whereas the ordering of Ir catalyst supported on SBA-3 is unchanged as was mentioned above. The textural properties of the catalysts after reaction are almost unchanged. For both catalysts, the decrease of surface area about 14% (Ir/SBA-3 - 1108 m²/g, Ir/SBA-15 - 582 m²/g) and slightly decrease of pore volume are observed. The average pore size of the fresh and used Ir/SBA-3 catalysts are similar whereas it is higher for the used Ir/SBA-15 catalyst in comparison to the fresh Ir/SBA-15 catalyst. The H₂ chemisorption analysis showed decrease of hydrogen volume adsorbed about 10% for both catalysts.

A comparison of the apparent rate and TOF values obtained for the best Ir/SBA-3 catalyst ($r_t=28.7 \text{ mol}_{T1}\cdot\text{mol}_{1r}^{-1}\cdot\text{min}^{-1}$; TOF=38.1 min⁻¹ at 150 °C) with the results reported in the literature for iridium supported on modified acidic silica [33], magnesium fluoride and alumina [21], as well as magnesium oxo-fluoride [24], shows that the iridium catalyst supported on SBA-3 is more promising catalyst. Hydrogenation activities of Ir/MgF₂-MgO catalysts at 125 °C, after reduction at 500 °C, were $r_t=8.5 \text{ mol}_{T1}\cdot\text{mol}_{1r}^{-1}\cdot\text{min}^{-1}$ and TOF=~12 min⁻¹ [24] whereas the apparent rate on Ir supported on SiO₂ modified with NH₄Cl reduced at 400 °C was below 23 mol}_{T1}\cdot\text{mol}_{1r}^{-1}\cdot\text{min}^{-1} at 150 °C [33]. Based on the paper [47], presenting the influence of different active phase (Pt, Ir, Ru) on catalytic activity for toluene hydrogenation, it can be concluded that iridium may have a great potential for hydrogenation of aromatic compounds.

The second reaction, in which the catalysts were tested, was selective nitro group hydrogenation of ortho-chloronitrobenzene (o-CNB) to ortho-chloroaniline (o-CAN) in a flow reactor in aqueous phase reforming (APR) conditions in the absence of external hydrogen. In the APR, reaction proceeds between an organic compound (methanol) and water, which yield mainly hydrogen of high

purity [48,49]. According to literature reports [49], this hydrogen can be utilized in a simultaneous reaction of hydrogenation, if a reducible compound (for example ortho-chloronitrobenzene) is present in the reaction medium.

The reaction was carried out in an X-Cube[®] flow, pressurized reactor at 225 and 275 °C (such a high temperature is necessary to start the APR reaction) under pressure of 5 MPa, using o-CNB dissolved in the mixture of methanol : water (2:1 by vol.) as reactants. Results of catalytic activity measurements, expressed as TOF min⁻¹, are presented in Table 2. The most active catalyst at both tested temperatures was Ir/SBA-3. The high activity, but almost ~40% lower than for Ir/SBA-3 catalyst, was also shown for Ir/SBA-15, whereas other catalysts were poorly active. It is worth notice that during hydrogenation of o-CNB in APR conditions the selectivity to o-CAN was always 100%, irrespective of catalyst employed and conversion obtained. The research has shown that the method based on hydrogen obtained in-situ from aqueous phase reforming of methanol, is promising method from the viewpoint of utilization of reactants. The above method admittedly requires a higher temperature, however, the advantage of the method is its 100% selectivity.

The highest activity in both investigated reactions showed iridium catalyst supported on SBA-3 material. This material has already been presented as the best support in comparison to the other mesoporous ordered silica supports [50]. The authors considered the advantage of this support as a result of its structure feature such as small pore diameter. Appropriate pore diameter generates the required intimate contact between potentially active sites and reactant molecules allowing their reaction. Such observation was done also by Pérez-Ramírez et al. [51]. Perhaps in the case of our catalysts on supports with larger pores (SBA-15, SiO₂, Al₂O₃) their lower activity compared to the narrower SBA-3 also results from insufficient opportunity for contact of reagents with iridium active sites resulting in lower activity of these catalysts.

Conclusion

The use of iridium active phase and SBA materials as supports has allowed to obtain new catalysts with high activities in the hydrogenation of toluene and the selective hydrogenation of orthochloronitrobenzene to ortho-chloroaniline, greater than that of the iridium system supported on Al₂O₃ or SiO₂. The Ir/support catalysts prepared from H₂IrCl₆ xH₂O precursor are characterised by different dispersion of metallic phase. The dispersion has particularly significant effect on the activity of

catalysts. The catalysts with the greatest dispersion showed the highest activities in hydrogenation reactions. Exceptionally high activity of the iridium phase supported on SBA-3 proves that this support allows to obtain an active and selective catalysts of hydrogenation of aromatic hydrocarbons and nitro group present in o-CNB. High activity of the latter can also be a result of its textural parameters such as appropriate pore size allowing for sufficient contact time between reagents and the active sites.

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Sample code ^{a)}	Physical characterization of supports								
	Method of activation	Surface area ^{b)} m ² ·g ⁻¹	Total pore volume, cm ^{3.} g ⁻¹	Average pore diameter, nm					
SBA-3		1292	0.72	2.2					
SBA-15	calcination	641	0.72	4.5					
SiO ₂	(air, 8 h, 550 °C)	381	0.68	7.1					
AI_2O_3		184	0.34	7.5					

Table 1. Characterization of supports calcined at 550 °C.

^{a)} For code explanation, see Experimental section.
^{b)} The Brunauer-Emmet-Teller surface areas were determined by N₂ adsorption at -196 °C using a Micromeritics ASAP2010 sorptometer. Total pore volume and average pore size were determined by the Barrett-Joyner-Halenda (BJH) method.

Table 2. Characterization of iridium catalysts reduced at 400 °C.

Sample codel ^{a)}	Physical characterization of iridium catalysts				Hydrogen chemisorption data for Ir/support catalysts ^{c)}				,c)	Toluene hydrogenation ^{e)}	Hydrogenation of ortho-chloronitrobenzene ^{e)}		
	Method of activation	Surface area ^{b)} , m ² ·g ⁻¹	Total pore A volume, p cm ³ ·g ⁻¹ n	Average pore diameter, nm	$\begin{array}{ccc} Volume & adsorbed, \ Dispersion, \\ cm^3 \cdot g^1 & \% \end{array}$		Ir Me surface siz	Mean size of	150 °C	225 °C	275 °C		
					Ht	H _{irr}	H _r	D _{irr}	area ^{d)} m² g _{lr} -1	Ir ^{d)} , nm	TOF, min ⁻¹	TOF, min ⁻¹	TOF, min ⁻¹
Ir/SBA-3	reduction (H ₂ , 2h, 400°C)	1290	0.68	2.1	0.71	0.44	0.27	75.4	181.7	1.5	38.1	0.79	0.91
Ir/SBA-15		675	0.70	4.2	0.94	0.46	0.48	79.8	190.0	1.4	25.3	0.48	0.59
Ir/SiO ₂		379	0.66	7.0	0.66	0.33	0.33	56.9	136.3	2.0	29.4	0.13	0.26
Ir/Al ₂ O ₃		150	0.22	5.9	0.39	0.22	0.17	37.4	90.9	2.9	28.3	0	0.15

^{a)} For code explanation, see Experimental section.

^{b)} The Brunauer-Emmet-Teller surface areas were determined by N₂ adsorption at -196 °C using a Micromeritics ASAP2010 sorptometer. Total pore volume and average pore size were determined by the Barrett-Joyner-Halenda (BJH) method.

^{c)} Dispersion and mean size of Ir particles (in nm) were determined by H₂ chemisorption using a Micromeritics ASAP2010C sorptometer. Prior to hydrogen chemisorption, fresh samples were reduced with H₂ at 400 °C for 2 h. Chemisorption of hydrogen was carried out at 35 °C, and the isotherms were determined using five different pressures in the range of 12-40 kPa (H_t - total adsorbed hydrogen). Then the catalyst was evacuated at 35 °C for 30 min. to remove reversibly adsorbed hydrogen (H_t) and the same procedure was repeated. The difference between adsorbed hydrogen extrapolated to zero pressure value for two isotherms equals to the amount of hydrogen irreversibly bound (H_{irr}). D_{irr} – dispersion calculated from irreversibly adsorbed hydrogen.

^{d)} Ir surface area and mean size of metal particles calculated from the amount of irreversibly chemisorbed hydrogen.

^{e)} Catalytic activity was expressed as turnover number (TOF, *min⁻¹*) in moles of toluene or ortho-chloronitrobenzene reacted per surface metal atoms (determined by hydrogen chemisorption).



Figure 1. Nitrogen physisorption isotherms (the curves shifted along Y axis for clarity) and pore size distribution for samples calcined in air at 550 °C.

Ir/SBA-3

Ir/SBA-15



Figure 2. TEM images of iridium catalysts after reduction at 400 °C.



Figure 3. Low- (A and B) and wide- (C) angle XRD patterns of supports and catalysts.



Figure 4. TPR-H₂ profiles of the dried Ir catalysts and iridium precursor - H₂IrCl₆ (signal intensity for catalysts has been normalized to 100 mg).



Figure 5. X-ray photoelectron spectra (Ir 4f core levels) for Ir/SBA-3 (A) and Ir/SBA-15 (B) samples.



Figure 6. The effect of support on the apparent rate (calculated on total iridium) of hydrogenation of toluene as a function of temperature.

Activation of catalyst: 400 °C, H₂=100 cm³·min⁻¹, 2 h;

Reaction: $c_T = 0.75 \mu mol \cdot cm^{-3}$, $H_2 = 50 cm^3 \cdot min^{-1}$, activity after 20 min.





Reaction: $c_{TI}=0.75 \ \mu mol \cdot cm^{-3}$, $H_2=50 \ cm^3 \cdot min^{-1}$.