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# Aqueous-phase hydrodechlorination of trichloroethylene on Ir catalysts supported on SBA-3 materials

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**Abstract:** This work investigates the catalytic properties of silica and aluminosilicate SBA-3 supported iridium catalysts in aqueous phase hydrodechlorination of trichloroethylene. SBA-3, AISBA-3, Ir/SBA-3 and Ir/AISBA-3 were thoroughly characterized by XRD, BET, TPR-H<sub>2</sub>, H<sub>2</sub> chemisorption, TPD-NH<sub>3</sub> and investigated in catalytic removal of trichloroethylene from water in batch reactor under mild operation conditions. Uniformly dispersed small iridium nanoparticles (~3 nm) was found to be active in catalytic purification of water from chloroorganic compound. The studies showed that the differences in catalytic behavior of Ir/SBA-3 and Ir/AISBA-3 depended on the properties of the support. The best catalytic properties in purification of water from trichloroethylene was obtained for Ir supported on more hydrophilic and ordered AISBA-3 with acid sites.

#### Introduction

Ordered mesoporous materials have attracted considerable attention during last decades due to their unique textural properties such as high surface area and large pore volume with a narrow pore size distribution.<sup>[1]</sup> Investigations on synthesis and properties of the mesoporous molecular sieves develop enormously due to the potential application of such materials as catalysts, catalyst supports, absorbents and host materials.<sup>[2]</sup> Many efforts have been made to design mesoporous materials for use in heterogeneous catalyst systems. Their mesoporosity has many advantages in catalysis, e.g. may reduce the extent of deactivation due to coke formation and plugging that are frequently observed in the microporous catalyst systems (zeolites).<sup>[3]</sup> The possibility of controlling the pore size by adjusting the preparation conditions make ordered mesoporous materials well suited as catalysts or catalyst supports. Moreover, high surface area of ordered mesoporous materials used as supports can be exploited to create highly dispersed active species on their surface. All of these properties make them an excellent materials in an aqueous - phase hydrodechlorination of chloroorganic compounds.<sup>[4]</sup>

Besides of the support, selection of the appropriate active phase plays the crucial role in catalytic properties of metal/support systems. In the case of hydrodechlorination processes, noble metals such as Pd, Pt and Rh are the most

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Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa (Poland) often used catalysts.<sup>[5]</sup> However, due to its hydrogenolytic properties Pd is one of the most used catalyst in aqueous phase hydrodechlorination of trichloroethylene.<sup>[6]</sup> Nevertheless, in search of efficiency and stability in TCE hydrodechlorination, both noble and non-noble metals in form of monometallic and bimetallic catalysts are used in aqueous phase hydrodechlorination of TCE, e.g. Rh,<sup>[7]</sup> Ni-Fe,<sup>[8]</sup> Ni.<sup>[9]</sup>

From the platinum metal group, iridium catalysts have been used in selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes,<sup>[10]</sup> toluene hydrogenation,<sup>[11]</sup> naphthenic ring opening reactions,<sup>[12]</sup> and selective reduction of nitrogen oxide (NO).<sup>[13]</sup> It has been also employed in the commercial process of acetic acid (the process)<sup>[14]</sup> manufacture Cativa™ and in hydrodesulphurization processes.<sup>[15]</sup> There are some information in the US patents issued in the end of twentieth century on activity of supported iridium catalysts in the removal of chlorine from organic compounds. It was shown that iridium was active in catalytic oxidation of different aqueous organic contaminants with low molecular weight including trichloroethylene.[16] It also showed activity in bimetallic catalysts (e.g iridium-copper) in gas phase hydrogenation of 1,2-dichloropropane with high selectivity propene.<sup>[17]</sup> Monometallic iridium to applications in hydrodechlorination reactions are rare, although its high resistance to HCI attack and stability under severe reaction conditions makes iridium attractive alternative for another metals. Some discussion on its use can be found in the publications concerning the gas phase hydrodechlorination of CCl<sub>3</sub>F,<sup>[18]</sup> CCl<sub>2</sub>F<sub>2</sub><sup>[19]</sup> and CCl<sub>4</sub>.<sup>[20]</sup> Until now, not a lot of attention has been paid on the application of iridium in the aqueous-phase hydrodechlorination process. The application of clay-supported CeO<sub>2</sub> and Ir in the aqueous phase hydrodechlorination of 4chlorophenol (4-CP) and 4-chloroaniline (4-CA) showed its activity. However, the partial coverage of Ir crystallites by cerium oxide, significantly decreased the activity of this material.<sup>[21]</sup> This phenomenon clearly indicates, that the activity of supported catalysts depends on the composition of the catalyst, which may modify the properties of the active phase. Physical as well chemical properties of the support, its acidity or reducibility and the extent of interaction with the active metal, play important roles in the complex chemistry of supported metal catalysts.<sup>[22]</sup>

Therefore, in the present work, we describe the preparation of new mesoporous catalytic materials containing highly dispersed reduced particles of Ir<sup>0</sup> on silica and aluminosilicate SBA-3 supports. Their catalytic activity was investigated in the aqueous-phase hydrodechlorination of trichloroethylene as a model reaction. To the best of our knowledge, no data are available on the use of iridium catalysts in the aqueous-phase hydrodechlorination of trichloroethylene. The information on mesoporous ordered SBA-3 usina as support of hydrodechlorination catalyst is also nonexistent, therefore our investigations seem to be fully justifiable.

#### **Results and Discussion**

The pore ordering of the samples was confirmed by low angle XRD analysis (Fig.1A). Both supports (SBA-3 and AISBA-3) and iridium catalysts showed the typical characteristic patterns of the hexagonal phase of SBA-3 structure, matching well those reported in the literature.<sup>[23]</sup> The XRD patterns of AISBA-3 support showed well-resolved sharp reflections of higher intensity in comparison to intensity of reflections of siliceous counterpart. It indicated better ordering of AISBA-3 sample than that of pure silica SBA-3. XRD patterns of iridium

catalysts indicate that the hexagonally ordered structure of SBA-3 was maintained after the impregnation and reduction procedures. Incorporation of Ir into the AISBA-3 matrix did not change the ordering of the support (similar intensity of the reflections), whereas some decrease in intensity and broadening after Ir deposition on SBA-3 was observed. It suggested some loss of the ordering of the pore structure. The reflections position slightly shifts to lower angles and the unit cell parameter ( $a_o$ ) decreases for iridium catalysts in comparison to the pristine supports (Table 1).

| Table 1. Characterization of | supports (ca | alcined at 550 °C | ) and iridium catal | vsts reduced at 400 °C. |
|------------------------------|--------------|-------------------|---------------------|-------------------------|
|                              |              |                   |                     |                         |

| Sample     | Physical characterization of<br>iridium catalysts   |  |                                    |                              | Total                    | Hydrogen chemisorption data for<br>Ir/support catalysts <sup>c)</sup> |  |      | Average Ir particle size,<br>nm |      |                   |        |       |
|------------|---|--|------------------------------------|------------------------------|--------------------------|---|--|------|---------------------------------|------|-------------------|--------|-------|
|            | Surface<br>area,<br>m <sup>2</sup> ·g <sup>-1</sup> | Total<br>pore<br>volume,<br>cm <sup>3</sup> .g <sup>-1</sup> | Average<br>pore<br>diameter,<br>nm | d <sub>[100]</sub> a),<br>nm | a <sub>0</sub> a),<br>nm | of acid<br>sites <sup>b)</sup> ,<br>µmol⋅g <sup>-1</sup>              | Volume adsorbed,<br>cm <sup>3</sup> ·g <sup>-1</sup> |      | Dispersion,<br>%                |      | TEM <sup>e)</sup> |        |       |
|            |   |  |                                    |                              |                          |   | Ht   | Hirr | Hr                              | Dirr | OTIEM             | before | after |
| SBA-3      | 1292  | 0.72   | 2.2                                | 3.29                         | 3.80                     | 0   | -  | -    | -                               | -    | -                 | -      | -     |
| Ir/SBA-3   | 1293  | 0.71   | 2.2                                | 3.16                         | 3.65                     | 0   | 0.49   | 0.27 | 0.22                            | 46   | 2.4               | 3.1    | 3.6   |
| AISBA-3    | 1316  | 0.83   | 2.5                                | 3.24                         | 3.74                     | 25  | - 24   | e -  | -                               | -    | -                 | -      | -     |
| Ir/AISBA-3 | 1271  | 0.80   | 2.5                                | 3.14                         | 3.63                     | 26  | 0.53   | 0.24 | 0.29                            | 42   | 2.7               | 2.8    | 3.4   |

<sup>a)</sup> d<sub>[100]</sub> interplanar spacing obtained from XRD;  $a_0$  – lattice parameter ( $a_0 = 2d_{[100]}/\sqrt{3}$ )

<sup>b)</sup> Number of acid sites determined by TPD-NH<sub>3</sub> method.

<sup>a)</sup> H<sub>i</sub> – total adsorbed hydrogen, H<sub>r</sub> – reversibly adsorbed hydrogen, H<sub>irr</sub> – hydrogen adsorbed irreversibly, D<sub>irr</sub> – dispersion calculated from irreversibly adsorbed hydrogen. The conditions of H<sub>2</sub> chemisorption measurements are specified in Experimental Section.

d) Mean size of metal particles calculated from the amount of irreversibly chemisorbed hydrogen (Hirr).

<sup>e)</sup> Mean size of metal particles calculated from TEM – before and after hydrodechlorination of trichloroethylene.



Figure 1. Low- (A) and wide- (B) angle XRD patterns of supports and catalysts.

XRD patterns in the wide angle range (Fig. 1B) were recorded in order to determine the crystallite size of iridium. However, one should remember that XRD technique is not sensitive if the amount of phase is too low (less than 5 wt.%) as was in the case of investigated catalysts. Moreover, if the

particle size of iridium is very small (below 3 nm), XRD analysis cannot detect them. XRD patterns of the iridium catalysts in the wide angle range (Fig. 1B) show only a very broad reflection in the 2O range of 15-30°, which is always attributed to the amorphous silica. No metallic iridium (Ir<sup>o</sup>) 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). Similarly, Silvennoinen at al.<sup>[24]</sup> showed lack of reflections from metallic iridium in the case of very small metal crystallites (~2 nm), whereas Haneda et al.<sup>[25]</sup> did not record Ir<sup>o</sup> reflection for 1 wt.% Ir/SiO<sub>2</sub> catalysts if the iridium dispersion was above 40%.

The iridium catalyst supported on AISBA-3 (Fig. 1B) showed extra reflections at 2O of 48.3 and 50.8° which can originate from some extra-framework aluminium species. In our previous work we showed that aluminosilicate SBA-3 synthesized with high aluminum content (Si/AI=10) indicated some amount of extra-framework alumina that probably are sintered during impregnation and reduction procedures and became visible in XRD pattern.<sup>[26]</sup>

The Ir contents in fresh Ir/SBA-3 and Ir/AISBA-3 catalysts are the same as the intended ones (ICP-OES analysis). Such a good agreement between the actual and target contents results from the fact that the catalysts were obtained by the impregnation method with cyclohexane solution of tetrairidium dodecacarbonyl followed by solvent evaporation to dryness.

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The TEM analysis confirmed the well-ordered hexagonal pore system of catalysts (Fig. 2A,C), which is in accordance with the results of low angle XRD. The ordering of the catalysts is

also preserved after hydrodechlorination of trichloroethylene process (Fig. 2B,D).



Figure 2. TEM images and histograms (insets) of iridium particle size distribution of catalysts before (A and C) and after (B and D) hydrodechlorination of trichloroethylene.

The pure silica and aluminosilicate SBA-3 supports show almost similar nitrogen adsorption-desorption isotherms of type IV(b) characteristic for mesoporous materials (Fig. 3A).<sup>[27]</sup> As the relative pressure increases isotherms of the supports show a sharp step, in the range of  $p/p_0 = 0.15-0.3$ , characteristic of

capillary condensation of nitrogen within uniform mesopores. This step for SBA-3 is less prominent and shifted to lower  $p/p_0$ . It indicates that silica SBA-3 possesses smaller mesopores.<sup>[28]</sup> The nitrogen adsorption-desorption isotherms and pore size distributions of the catalysts are similar to those of supports.

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This indicates that the texture of the supports is not altered by the impregnation and heat treatment. The nitrogen adsorptiondesorption isotherms of presented supports and catalysts are similar to those presented in literature for SBA-3 materials. These isotherms show no hysteresis loop between adsorption and desorption branches, similar to that reported in the literature.<sup>[29]</sup> Steep slope in the initial part of the isotherms implies the presence of micropores in investigated materials.<sup>[29a,30]</sup>



Figure 3.  $N_{\rm 2}$  adsorption–desorption isotherms (A) and pore size distributions (B) of supports and catalysts.

Textural properties calculated by the N<sub>2</sub> adsorptiondesorption isotherms are listed in Table 1. The impregnation with iridium precursor of siliceous support does not change its textural properties. The iridium catalyst on SBA-3 and pristine SBA-3 support have similar surface areas and pore size and only the pore volume is slightly lower in the case of the Ir catalyst. The introduction of iridium on the surface of AISBA-3 leads to slight decrease of surface area (~3.4%) and pore volume of the catalyst but maintains the pore diameter. Probably in the case of both supports, use the inert tetrairidium dodecacarbonyl that decomposes directly into metallic iridium and carbon monoxide allows to introduce iridium phase on the supports in mild conditions without changing the textural properties. Another explanation of unchanged textural properties can be the introduction of relatively small amount of metallic phase on the supports with high surface areas. The unchanged textural properties of the catalyst with small amount of the active phase in comparison to these properties of the support were presented in literature.<sup>[31]</sup> Usually the decrease of surface area or pore diameter was observed in the case of high metal loading on the supports (>5 wt. %)[32] or use the acidic metal precursor (e.g. chlorides or chlorometallic acids).[33] For these reasons the textural properties of the presented catalysts are similar to the properties of the supports. The unchanged surface area and pore diameter as well the decrease of pore volume for catalysts suggests the deposition of iridium particles inside the pores.

Incorporation of aluminum into the amorphous walls of mesoporous SBA-3 generate some acidity of the sample (TPD-NH<sub>3</sub> analysis, Table 1). The TPD-NH<sub>3</sub> profile (Fig. S1, Supporting Information) showed one broad peak in the temperature range of 200-500 °C with maximum at 300 °C. It corresponds to the desorption of NH<sub>3</sub> from the weak, medium and strong acid sites of the material with great majority of medium acid sites.<sup>[34]</sup> Our previous studies (FT-IR studies of adsorbed pyridine) have shown that the acidity originates mostly from Lewis acid sites.<sup>[26]</sup> The TPD-NH<sub>3</sub> analysis indicated that the introduction of Ir particles on the surface of silica and aluminosilicate SBA-3 did not influence their total acidity (Table 1). It can be explained by relatively low Ir content and using of inert tetrairidium dodecacarbonyl as iridium precursor.[35] The increase of total acidity of the supported noble metal catalysts in comparison to the acidity of the supports have been reported in the literature only in the case of using metal chlorides or chlorometallic acids as a metal precursor. It was shown that introduction of chlorides produced new acid sites by the replacement of OH groups by CI and the displacement of water coordinated to surface atoms.[36]



Figure 4. TPR-H\_2 profiles of dried iridium samples and iridium precursor -  $\mbox{Ir}_4(CO)_{12}.$ 

Temperature programmed reduction with hydrogen was used to determine temperature needed to remove ligands of iridium precursor from the catalyst surface. Studies of TPR-H<sub>2</sub> were carried out on the iridium precursor-impregnated samples dried at 100 °C. No reduction signals were seen in TPR-H<sub>2</sub> profiles of the supports (data not shown), which proved that the

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supports were irreducible. Figure 4 presents the reduction profiles of the Ir/support-D samples and TPR-H<sub>2</sub> profile of the active phase precursor -  $Ir_4(CO)_{12}$  supported on a quartz sand. The reduction profile of tetrairidium dodecacarbonyl showed the signals testifying to the occurrence of decarbonylation process with the maxima at 130 and 270 °C, and to the reaction of hydrogen with carbonyl ligands in methanation of CO with the maximum at 397 °C.[11d] The TPR-H2 profiles of Ir/SBA-3-D and Ir/AISBA-3-D samples exhibit weak first two signals originating as in the case of precursor from decarbonylation process and a more pronounced peak above 400 °C. The high temperature signals (270 and 397 °C - for precursor) are shifted to higher temperatures for iridium precursor supported on mesoporous materials. The fact that the reduction of catalysts takes place mainly at higher temperatures indicates that iridium species strongly interact with the supports making their reduction process more difficult.<sup>[37]</sup> The TPR-H<sub>2</sub> profile of Ir/AISBA-3-D showed mainly high temperature signal at 413 °C with negligible shoulder in temperature range of 330-350 °C and very low signal at 130 °C. It indicated stronger metal-support interactions on AISBA-3 in comparison to interactions of Ir precursor with SBA-3 support. The TPR-H<sub>2</sub> profiles of catalysts after activation (H<sub>2</sub> 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. X-ray photoelectron spectra (Ir 4f core levels) for Ir/SBA-3 (A) and Ir/AISBA-3 (B) samples.

XPS analyses were performed for reduced Ir/SBA-3 and Ir/AISBA-3 samples (Fig. 5). The peak corresponding to Ir 4f<sub>7/2</sub> has been analyzed. Two types of binding energies are found for both catalysts. The core electrons of iridium (4f<sub>7/2</sub> signal) at ~61.8 eV is assigned to Ir-O (Ir<sup>δ+</sup>) and BE of 60.7 eV corresponds to metallic iridium.<sup>[38]</sup> The presence of Ir<sup>δ+</sup> is caused by oxidation of Ir<sup>0</sup> as a result of contact with air during transferring the samples to XPS cell. The contribution of iridium oxide for iridium catalyst on AISBA-3 support is lower (21%) than for Ir/SBA-3 (33%). It indicates less susceptibility to oxidation of Ir<sup>0</sup> on AISBA-3 due to its stronger interaction with support. The position of the peaks of both iridium forms is slightly shifted to

higher binding energies for Ir/AISBA-3 catalyst. It also confirms stronger interaction of iridium species with AISBA-3 support.<sup>[39]</sup>

An important parameter characterizing metallic catalysts is the dispersion of the metal. The dispersion and size of iridium particles were determined by chemisorption of H<sub>2</sub> on the reduced catalysts. The iridium catalysts prepared from both supports showed high dispersion of metal calculated from irreversibly adsorbed hydrogen (Table 1). The analysis indicated particle size smaller than 3 nm in the case of both catalysts. These results are in good agreement with XRD data. The high dispersion and small particle size explain the lack of reflections from metallic iridium in XRD patterns. The Ir/SBA-3 exhibit slightly higher dispersion (46%) and lower particle size (2.4 nm) when compared to iridium catalyst on AISBA-3 (42%, 2.7 nm). Higher dispersion of iridium particles on SBA-3 could be due to easier reduction of iridium species on this support what was confirmed by H<sub>2</sub>-TPR analysis.<sup>[40]</sup> Lower dispersion of iridium on Ir/AISBA-3 catalyst results from specific adsorption of Ir<sub>4</sub>(CO)<sub>12</sub> on AISBA-3 surface. Probably, iridium carbonyl is adsorbed on the AISBA-3 surface with the involvement of the acidic centres leading to the stronger interaction of iridium with the support. Strong interaction of iridium carbonyl with the AISBA-3 support was confirmed by TPR-H<sub>2</sub> studies.

The TEM micrographs of the catalysts indicated a homogeneous dispersion of the nanoparticles on the surface of supports for fresh as well for used catalysts (Fig. 2). The mean particle size estimated from TEM images is in good agreement with particle size calculated by hydrogen chemisorption technique for iridium catalyst supported on AISBA-3 and slightly differs for Ir/SBA-3. The lower mean particle size obtained by H<sub>2</sub> chemisorption studies for the latter sample results from the fact that this technique allows to detect even single metal atoms present on the surface of the support, whereas in TEM photographs it is difficult to notice very small particles and the mean size is calculated only from visible, larger particles. The size distribution diagram for Ir/AISBA-3 (inset in Figure 2C) exhibit a narrow size distribution with majority of particle with diameter of 3 nm. The iridium particle size distribution for Ir/SBA-3 is broader with predominance of particle with diameter of 2-3 nm and some contribution of bigger ones (inset in Figure 2A). The TEM analysis indicated an increase of around 20% in metal particle size after reaction caused by some metal aggregation.

Catalytic properties of Ir/SBA-3 and Ir/AISBA-3 materials have been investigated in aqueous phase hydrodechlorination of trichloroethylene. Based on the literature data concerning the beneficial role of water on Pd/C activity in hydrodechlorination of aromatic halides,<sup>[41]</sup> the catalytic phase aqueous hydrodechlorination of trichloroethylene was performed without additional organic chemicals. Therefore the effect of organic solvent on HDC rate and products distribution was eliminated. Due to the fact that the particle size and mixing rate are two major factors that can control mass transfer rates during catalytic process,<sup>[42]</sup> using Ir catalysts with small particles sizes and high mixing rates (1000 rpm) allowed to lower the likelihood of mass transfer limitation.[42c]

Control test confirmed that the chloroorganic compound removal did not proceed in the absence of the SBA-3, AISBA-3,

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Ir/SBA-3 and Ir/AISBA-3 (Fig. 6). Chromatographic analysis of the reaction mixture formed during TCE removal in the presence of supports (SBA-3 and AISBA-3) showed only the decrease of TCE concentration without formation of any products. The unchanged pH value during catalytic test (Fig. 7) confirmed that hydrodechlorination on pure supports did not occur. It indicates that the decrease of TCE concentration is caused by its adsorption on supports. Although both of the supports have shown similar efficiency of trichloroethylene sorption from water, slightly better results were obtained for AISBA-3 material with better ordered structure (Fig. 6).

The sorption phenomenon could be also related with surface hydrophobicity of the supports. Hydrophobicity index calculated on the basis of the amount of water desorbed at 150 °C and 400 °C for both iridium catalysts indicate that both catalysts are characterized by hydrophobic nature of their surface.<sup>[43]</sup> Received results indicate, however slightly higher hydrophilicity of Ir/AISBA-3 catalyst (0.79) than Ir/SBA-3 catalyst (0.87). It is caused by higher hydrophilicity of Al containing SBA-3 support in comparison to pure siliceous SBA-3. It is in agreement with literature data and could be explained by the presence of a strong electrostatic field created on framework anion sites of AISBA-3 support.<sup>[44]</sup>

A comparative study between iridium catalysts have shown activity for both samples in aqueous phase hydrodechlorination of trichloroethylene indicating catalytic activity of iridium in hydrodechlorination of TCE. It means that very small iridium nanoparticles (Table 1) are active in water purification. Our results are in line with earlier studies concerning the relationship between size of metals (e.g. Pd, Pt, Au nanoparticles) and their activity in the aqueous phase hydrodechlorination of TCE confirming activity of metal in nanoparticle forms.<sup>[45]</sup> Although iridium dispersion is similar in both samples, Ir/AISBA-3 has shown higher activity than Ir/SBA-3 (Fig. 6, Table 2). After 60 minutes of reaction almost 80 % of TCE is removed from water for Ir/AISBA-3, in contrast to Ir/SBA-3 where ~ 50 % of TCE conversion is observed (Fig. 6A). Moreover, the carrying out the reaction on Ir/AISBA-3 and Ir/SBA-3 for a further 30 minutes led to 93 and 66 % of trichloroethylene conversion, respectively. The selectivity of the products depends on the used catalyst. However, in both cases the formation of mono- and dichlorinated compounds (if any) was under the limit of ECD detection (Fig. S2, S3, Supporting Information). The iridium catalyst on SBA-3 support show selectivity to ethene (53 %) and ethane with some contribution of methane (6 %). The Ir/AISBA-3 catalyst show higher selectivity to ethene (74 %) without formation of methane. The differences between the catalysts behaviour concerning selectivity towards products could be related with the presence of mainly Lewis acid active sites which influent the mechanism of aqueous could phase hydrodechlorination of trichloroethylene on Ir/AISBA-3 catalyst.



Figure 6. TCE removal (A) and kinetics (B) of aqueous phase TCE hydrodechlorination.

Due to the lack of the significant differences in the dispersion of the active phase (Table 1), the acidity, hydrophobicity and especially the ordering of the structure are believed to play the crucial role in catalytic behaviour of Ir/SBA-3 and Ir/AISBA-3. Based on the XRD results (Fig. 1A) AISBA-3 support possesses better ordered structure than SBA-3. In accordance with the

literature data, this specific surface feature could improve activity of this catalyst in aqueous phase hydrodechlorination of the chloroorganic compounds.<sup>[4,5b,9a]</sup> It was shown that the application of ordered materials as the supports for active phase leads to formation of uniformly dispersed, resistant for agglomeration and leaching, rather small metal nanoparticles.

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Figure 7. pH of the reaction mixture during catalytic tests.

Only slight changes in average iridium particles size for spent catalysts in comparison with fresh samples indicate that ordering structure of SBA-3 and AISBA-3 can affect the properties of iridium catalysts. On the other hand, our results are opposite to studies of Munoz et al.[46] showing that the catalysts with higher surface areas and lower ordered structures showed higher HDC rates than the materials with higher ordered structure in hydrodechlorination of 4-chlorophenol. This may suggest that the phenomenon of the relationship between the ordering of the material and the activity is not trivial problem and could depend on many factors such as the kind of the support and metal particles size, and kind of the substrate. The activity can be also influenced by hydrophobicity of the catalysts. Based on the literature data<sup>[47]</sup> hydrophobicity plays beneficial role in protection of active phase from poisoning and leaching and helps the kinetics. Hence, the properties of Ir/SBA-3 and Ir/AISBA-3 in removal of TCE from water could be strongly related with the hydrophobicity of these materials. Additionally, the hydrophobic nature of Ir/AISBA-3 and Ir/SBA-3 acts as a benign protection layer to restrict both the agglomeration or redispersion or leaching effect, as it was confirmed by TEM analysis for spent catalysts (Fig. 2).[47]

**Table 2.** The reaction rate constant k, initial reaction rate, TOF values and selectivity towards products for aqueous phase hydrodechlorination of trichloroethylene on iridium catalysts.

| Catalyst   | Initial<br>reaction<br>rate, | TOF <sup>a)</sup>     | Reaction rate<br>constant       | Selectivity, % |          |          |  |
|------------|------------------------------|-----------------------|---------------------------------|----------------|----------|----------|--|
| ·          | mmol⋅min⁻<br>¹⋅gır⁻¹         | 5                     | 0 – 90 min,<br>s <sup>-1</sup>  | CH₄            | $C_2H_6$ | $C_2H_4$ |  |
| Ir/SBA-3   | 0.36                         | 2.48·10 <sup>-3</sup> | 1.79·10 <sup>-2</sup><br>± 0.02 | 6              | 41       | 53       |  |
| Ir/AISBA-3 | 0.84                         | 5.86·10 <sup>-3</sup> | 3.77·10 <sup>-2</sup><br>± 0.06 | -              | 26       | 74       |  |

<sup>a)</sup> TOF calculated according to Molina et. al.<sup>[48]</sup>

Due to the predominant amount of hydrogen in reaction mixture, aqueous phase hydrodechlorination of TCE over Ir/SBA-3 and Ir/AISBA-3 is assumed to be pseudo-first-order. Figure 8 shows the kinetic data according the linearized pseudofirst-order rate equation. So the reaction kinetic can be ascribed as  $ln(C/C_0) = -kt$ , where k is the apparent first-order rate constant (s<sup>-1</sup>), and t is the reaction time (s). The initial reaction rates r<sub>0</sub>, TOF and reaction rate constants k values, are presented in Table 2. To the best of our knowledge there are no available literature data concerning the application of iridium catalysts in aqueous phase hydrodechlorination of trichloroethylene. It makes impossible the direct comparison our studies with results obtained by other groups. However, it should be stressed here that activity of Ir/SBA-3 and Ir/AISBA-3 in TCE hydrodechlorination looks promising. It is comparable or better than the activity of other catalysts supported on mesoporous material in similar conditions.<sup>[4]</sup> The k value obtained for Ir/AISBA-3 is approximately two times higher than that obtained for Ir/SBA-3. Due to the fact that the amounts of iridium active sites are similar in both catalysts, the differences in catalytic behaviour of iridium samples are probably related with the properties of the surface. The higher TOF value obtained for Ir/AISBA-3 than for Ir/SBA-3, both with similar iridium dispersion, confirm our supposition that catalytic properties of these materials depends on the acidity, hydrophobicity and ordering of the supports.



Figure 8. Plot of  $ln(C/C_0)$  versus reaction time for hydrodechlorination of TCE on Ir/SBA-3 and Ir/AISBA-3.

The XRF analysis of water portions after reaction did not show any amounts of iridium within the limits of the detection. Therefore, the effect of active phase leaching from the catalysts to reaction mixture in the case of Ir/SBA-3 and Ir/AISBA-3 is believed to be negligible. To confirm this conjecture, the additionally experiments were done. The fresh catalysts were stirred separately in water for 15 min at reaction temperature and then the TCE hydrodechlorination tests were performed over water separated from the catalysts.

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Figure 9. Three cycles of TCE hydrodechlorination in aqueous phase on Ir/SBA-3 (A) and Ir/AISBA-3 (B).

However, no reaction progress was observed and obtained results were similar to control curve. It confirms no leaching of iridium from catalysts. To check the stability of the iridium catalysts, the same portions of Ir/SBA-3 and Ir/AISBA-3 were used three times in the hydrodechlorination of TCE. As it was shown in Fig. 9, differences in TCE conversion obtained after 150 min of subsequent reactions could be related to catalysts mass loss during filtration and drying between the cycles than to the deactivation by the formation of deposits. It indicates high stability of investigated iridium catalysts.

#### Conclusions

Using of mesoporous SBA-3 materials of different composition as supports for iridium catalyst allowed to obtain catalyst with very small, well dispersed metal crystallites (~3 nm). The unchanged surface area and pore diameter as well the decrease of pore volume for catalyst in comparison to supports indicated the deposition of iridium particles inside the pores. The reducibility of iridium precursor depended on the chemical composition of the support and was more difficult on acidic aluminosilicate SBA-3. The differences in the reducibility did not have a significant impact on the dispersion and particle size of the iridium active phase.

Catalytic properties of Ir/SBA-3 and Ir/AISBA-3 have been evaluated in aqueous phase hydrodechlorination of trichloroethylene. Our results clearly show that iridium supported catalysts are active in hydrodechlorination of TCE. The catalytic performance of iridium catalysts depends on their acidic, hydrophobic and textural properties. More hydrophilic AISBA-3 supported iridium catalyst containing acidic sites was found to be more active than Ir/SBA-3.

### **Experimental Section**

#### Supports and catalysts preparation

Pure silica (symbol SBA-3) and aluminosilicate (symbol AISBA-3) supports were prepared by hydrothermal synthesis performed under acidic conditions according to our own procedure. Tetraethyl orthosilicate (TEOS - Aldrich, 98%) was used as a silica source and cetyltrimethylammonium bromide (CTMABr - Aldrich, 95%) as a surfactant. The silica SBA-3 sample was synthesized according to following procedure. First, CTMABr (8.3 g) was dissolved in 165 cm<sup>3</sup> of deionized water followed by an addition of TEOS dropwise (23 cm<sup>3</sup>). After stirring for 15 minutes, 38% HCl was added (34 cm<sup>3</sup>, POCh - Polish Chemicals Reagents, Poland) with continuous stirring for next 30 min. After this, the additional 36 cm<sup>3</sup> of hydrochloric acid were added, which resulted in precipitation of white gel. The mixture was stirred for next 1.5 h at room temperature. Then, aging of the gel was carried out at room temperature for 8 days in static conditions. The resulting solid was filtered, washed, dried and calcined at 550 °C for 8 h in air.

The synthesis of aluminosilicate SBA-3 (AISBA-3) was done according to the above procedure with minor modification. The source of aluminum (3.86 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (POCh) dissolved in 5 cm<sup>3</sup> H<sub>2</sub>O) was admitted dropwise to the CTABr solution before introducing the TEOS to the mixture. The Si/Al molar ratio was 10. After introducing two parts of HCl, the pH of the suspension was increased up to 2.2 with aqueous ammonia (25%, POCh) in order to introduce aluminium atoms to the framework.

After calcination, SBA-3 and AISBA-3 supports were modified with iridium by means of impregnation, using the cyclohexane solution of tetrairidium dodecacarbonyl (Ir<sub>4</sub>(CO)<sub>12</sub>, 98%, Aldrich). The required quantity of tetrairidium dodecacarbonyl was dissolved in cyclohexane and this solution was added to the evacuated support (the amount of precursor was calculated to achieve iridium loading of 1 wt%). Cyclohexane was removed on a rotary evaporator. The impregnated samples were dried at 100 °C for 24 h and labeled as Ir/SBA-3-D and Ir/AISBA-3-D (D stands for dried catalyst).

Prior to the characterization each precursor-impregnated support was placed in a porcelain boat and reduced with H<sub>2</sub> (50 cm<sup>3</sup>·min<sup>-1</sup>, 99.99%, Linde). At the beginning, the system was purged at room temperature with argon (150 cm<sup>3</sup>·min<sup>-1</sup>, 99.99%, Linde) which was later replaced with hydrogen (150 cm<sup>3</sup>·min<sup>-1</sup>). After 30 minutes, the hydrogen flow was decreased to 50 cm<sup>3</sup>·min<sup>-1</sup> and the temperature ramp (10 °C·min<sup>-1</sup>) started. After reaching the setpoint (400 °C), the reduction of catalyst precursor was carried out for 2 h. Then the catalyst was cooled to room temperature in hydrogen flow. The last step consisted in flushing with argon for 15 min and passivation with 5 vol.% O<sub>2</sub>/He mixture. The reduced catalysts were labelled as Ir/SBA-3 and Ir/AISBA-3.

#### Supports and catalysts characterization

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

Textural characterization of supports calcined at 550 °C and catalysts reduced at 400 °C was obtained by low-temperature (-196 °C) nitrogen adsorption using a sorptometer ASAP 2010 manufactured by Micromeritics. Prior to the measurements of adsorption-desorption isotherms, the samples were outgassed at 300 °C for 4 h. The surface area was determined by Brunauer-Emmett-Teller (BET) method, whereas total pore volume and average pore diameter were calculated using Barrett-Joyner-Halenda (BJH) method.

Transmission electron microscope (TEM) images were recorded on a JEOL 2000 microscope operating at accelerating voltage of 80 kV or on a Hitachi HT7700 operating at 100 kV (sample Ir/AISBA-3 after reaction). The results were used to estimate ordering of the samples and to estimate the Ir particle size. The materials studied were deposited on nickel grids coated with a carbon film. The average particle size was calculated from 100 particles using following formula:<sup>[48]</sup>

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where: d stands for particle size and n is the number of particles.

Dispersion and mean size of Ir particles were determined by static  $H_2$  chemisorption method using a Micromeritics ASAP2010C sorptometer. Prior to hydrogen chemisorption measurements, fresh dried catalysts were reduced with  $H_2$  at 400 °C for 2 h and then the catalyst samples were pretreated in situ to purify their surfaces from adsorbed gases. The pretreatment consisted in the evacuation at room temperature for 15 min and then at 350 °C for 60 min, followed by reduction in hydrogen flow (40 cm<sup>3</sup>·min<sup>-1</sup>, 99.999%, Linde) at 350 °C for 60 min and evacuation at 350 °C for 120 min. 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<sub>t</sub> - total adsorbed hydrogen). Then the catalyst was evacuated at 35 °C for 30 min to remove reversibly adsorbed hydrogen (H<sub>r</sub>) 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<sub>irr</sub>).

The metallic surface area (S), expressed in  $m^2 \cdot g_{lr}{}^1$ , was calculated from the following equation:  $^{[49]}$ 

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

where  $v_m$  - volume of adsorbed hydrogen expressed in cm<sup>3</sup>,  $N_A$  - Avogadro's number (6.022·10<sup>23</sup> mol<sup>-1</sup>), n - chemisorption stoichiometry (n=2),  $a_m$  - surface area (m<sup>2</sup>) 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. The average size of Ir particles (P, expressed in nm) were calculated from the formula: <sup>[49]</sup>

$$P = \frac{6000}{\mathrm{S} \cdot \rho}$$

where S – the metallic surface area (S), expressed in m<sup>2</sup>·g<sub>Ir</sub><sup>-1</sup>;  $\rho$  – metal density expressed in g·cm<sup>-3</sup>.

Iridium content in fresh 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.

Energy dispersive X-ray fluorescence analysis (EDXRF) was carried out using MiniPal 4 equipment from PANalytical Co., with an Rh-tube and silicon drift detector (resolution 145 eV). EDXRF method was used to gain information on the elemental composition of liquid samples after catalytic experiments.

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 $\alpha$  radiation (1486.6 eV). The operating pressure in the chamber was close to 2 × 10<sup>-9</sup> mbar. Binding energies were referenced to the C1s peak from the carbon surface deposit at 284.6 eV.

The temperature-programmed desorption of ammonia measurements (TPD-NH<sub>3</sub>) were carried out on Pulse ChemiSorb 2705 (Micromeritics) instrument. In the typical experiment a sample (~100 mg) was heated in He (99.999%, Linde) at the rate of 10 °C·min<sup>-1</sup> up to 400 °C and then maintained at this temperature for 1 h. Afterwards it was cooled down to 110 °C and saturated with ammonia for 1 h. The physically adsorbed NH<sub>3</sub> was removed by purging with helium flow at 110 °C for 1 h. The TPD-NH<sub>3</sub> analysis was carried in the range of 110 – 600 °C with a heating rate of 10 °C·min<sup>-1</sup>.

Measurements of temperature-programmed reduction with hydrogen (TPR-H<sub>2</sub>) 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<sub>2</sub> – Ar (99.999%, Linde) at the flow rate of 30 cm<sup>3</sup>·min<sup>-1</sup>. In the TPR-H<sub>2</sub> studies, a quartz sand (Aldrich) impregnated with metal precursors (Ir<sub>4</sub>(CO)<sub>12</sub>) 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<sup>-1</sup>. The TPR-H<sub>2</sub> analysis were also performed for catalysts after activation (H<sub>2</sub>, 400 °C, 2 h). All TPR-H<sub>2</sub> profiles, presented in this work, have been normalized to the same sample weight.

Surface hydrophilicity of the catalysts was measured by water adsorption. For this purpose, the samples were moisturized in a desiccator containing demineralized water at room temperature for 24h. The amount of water adsorbed in the catalysts were determined by using thermogravimetric analysis (Mettler). The value of *HI* (hydrophobicity index) was calculated based on the loss of water at 150 °C over weight loss at 400 °C determined by thermogravimetric analysis:<sup>[41]</sup>

$$HI = \frac{\text{Weight loss up to 150 °C}}{\text{Weight loss up to 400 °C}}$$

where HI = 1 is representative for a very hydrophobic sample and HI = 0 is characteristic for a very hydrophilic sample.

#### Catalytic test

The aqueous – phase hydrodechlorination tests in batch mode were performed under atmospheric pressure at room temperature (25 °C) in a glass reactor equipped with a magnetic stirring bar, pH-meter and a temperature controller. Every time, 350 cm<sup>3</sup> of Milipore water was saturated with hydrogen for 30 minutes before adding 20  $\mu$ l of TCE (about 8000 times higher concentration than accepted in drinking water). Prior to catalyst addition (0.1 g), the reaction mixture was stirred (1000 rpm) for 30 minutes to provide homogeneity. To check activity of used sample in the repeat experiments, iridium catalyst was recovered by filtration and then washed with distilled water and dried in the oven at temperature 393 K for the subsequent catalytic run. The catalytic procedure was repeated three times. The reaction products were analyzed after 0, 2, 5, 10, 15, 20, 60, 90, 120 and 150 min of the reaction. The concentration of trichloroethylene and products of TCE

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hydrodechlorination were monitored using gas chromatography system

(Bruker 456-GC with ECD and FID, Headspace SHS-40).

**Keywords:** SBA-3 • Ir • iridium catalyst • trichloroethylene (TCE) • aqueous phase hydrodechlorination (HDC)

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Efficient preparation of new mesoporous catalysts containing highly dispersed nanoparticles of Ir<sup>0</sup> on silica and aluminosilicate SBA-3 supports. The catalyst are active in aqueous phase hydrodechlorination of trichloroethylene. The results show that Ir/AISBA-3 catalyst containing acidic sites was found to be more active than Ir/SBA-3.



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Aqueous-phase hydrodechlorination of trichloroethylene on Ir catalysts supported on SBA-3 materials