Article

Sol-Gel Synthesis of Organically Modified Silica Particles as Efficient Palladium Catalyst Supports to Perform Hydrogenation Process

Adele R. Latypova 1,2,*, Maxim D. Lebedev 1, Ilya A. Tarasyuk 1,*, Alexander I. Sidorov 3, Evgeniy V. Rumyantsev 1,4, Artur S. Vashurin 1 and Yuriy S. Marfin 1

1 Department of Inorganic Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetevsky Ave. 7, 153000 Ivanovo, Russia; maximlebedev37@gmail.com (M.D.L.); evr@isuct.ru (E.V.R.); asvashurin@mail.ru (A.S.V.); ymarfin@gmail.com (Y.S.M.)
2 N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russia
3 Department of Biotechnology, Chemistry and Standardization, Tver State Technical University, Nab. A. Nikitina 22, 170026 Tver, Russia; sidorov_science@mail.ru
4 Federal State Budget Educational Institution of Higher Education, Ivanovo State Polytechnic University, Sheremetevsky Ave. 21, 153000 Ivanovo, Russia
* Correspondence: LatAdel@yandex.ru (A.R.L.); TarasyukIA@inbox.ru (I.A.T.)

Abstract: Modern approaches to the production of new materials require the improvement of synthesis techniques towards simplifying the processes of their preparation and reducing the number of stages. Thus, in this study, one-stage synthesis of organomodified silica materials is developed using a special surfactant—dodecyl(dimethylamino)dimethylaminonitrosoimidazolium (DDAO). The peculiarity of this approach is that there is no need for heat treatment of the material, since DDAO is removed by washing in alcohol. Amino-, mercapto-, methyl-, and phenyl-modified silicas were synthesized using this method. The SEM images showed the morphology of all the obtained materials is close, all particles are spherical, and the diameter of individual particles is about 500 nm. Palladium particles were precipitated on these supports, then the experiments were carried out to study the catalytic activity of these materials in a model reaction of nitroaniline reduction. The phenyl modified matrix-based materials showed very low activity. This is due to the fact that the support and the substrate contain aromatic fragments, thus, hydrophobic interactions arise between them, which complicates the diffusion of the products. The leader is a matrix with an amino fragment, which is associated with its electron-donor effect. The XPS method revealed the amount of fixed palladium, as well as the binding energy shifts, which are 0.68 eV for 5% Pd/SiO2–C6H5; 0.56 eV for 5% Pd/SiO2–C6H5–NH2; 0.26 eV for 5% Pd/SiO2–C6H5; and 0.13 eV for 5% Pd/SiO2.

Keywords: sol-gel; organomodified silica; palladium catalysts

1. Introduction

One of the most important synthetic approaches of new materials is a functional nanoparticles synthesis with given structure and morphological parameters. Development actuality of such materials is conditioned by utilization increase through the functionalization and special composition of the surface. Silica nanoparticles are the perspective materials that are used as sorbents, drug delivery, and catalyst supports.

Scientists’ interest in silica particles is caused by the vast number of valuable properties that they have: high specific surface area, low toxicity, biocompatibility, chemical inertness, and thermal stability [1–3]. Possible fields of silica application were significantly expanded with the beginning of the production of hybrid materials based on it due to
surface modification [1,4,5] and the development of the core-shell type materials [2,3,6]. Hybrid silica particles are used as drug delivery systems [7–10] and biosensors [10–13].

The effect of modifying functional groups on the adsorption properties of silicas and the catalytic activity of deposited metal phases on such supports is of particular interest [14–25]. Various combinations in the modification of supports open up wide possibilities for the obtainment of new and more efficient catalysts. The authors of [16] used modified silicas with different organic groups R, phenyl, propyl, hexyl, hexadecyl, as adsorbents of 2-chloro-4-methoxyphenol. According to the results obtained, modified silica adsorbed 2-chloro-4-methoxyphenol in larger amounts than unmodified silica. Modified silicas can also have a good ability to adsorb Group VIII metals, such as palladium [23]. This fact leads to the expectation that metals, such as palladium, will be more efficiently immobilized on organomodified silicas due to additional coordination interactions with the functional groups of the support matrix.

Significant influence is given to materials functionalized with amino groups due to their ability to stabilize metal nanoparticles and cause a positive effect on the catalytic activity of a metal in various chemical processes [14,18,24,26–35]. Palladium nanoparticles on a silicon-containing mesoporous foam functionalized with aminopropyl are very effective in cross-coupling Suzuki reactions, hydrogenation of alkenes [30], oxidation of alcohols [31], carboxylation of Suzuki–Miyaura [33–35], and in the hydrogenation of nitro aromatic compounds [30]. Other modifying groups are also capable of a similar effect. In [19], the authors studied the effect of PEG chains covalently attached to silica on the efficiency of palladium in the processes of selective oxidation of alcohols to aldehydes and ketones. In the work of [25], an efficient palladium catalyst on silica-earth obtained by co-condensation of tetraethylorthosilane (TEOS) and bis-silylated ionic liquid monomer is reported. The catalyst showed high activity in three different processes: carboxylation of iodarenes, and Heck and Suzuki combination reactions. Silica modified with silicon hydride groups can be used for the synthesis of palladium nanoparticles on the surface and in the pores of the silica matrix [21]. Palladium catalysts on a silica matrix functionalized with mercapto or diphenylphosphine can be successfully used for the synthesis of biaryls in the Suzuki–Miyaura reaction [22].

One can conclude that the topic of catalysts supported on organomodified silica is gaining instant growth and palladium is one of the most popular catalysts due to the combination of high activity, selectivity, and long utilization life. Methods for the deposition of palladium have been widely studied [36–44], whereas, at present, methods for obtaining hybrid materials with a given structure and morphological characteristics need to be developed and simplified in their implementation. In the field of obtaining silica by the sol-gel method, work is divided into two directions: postmodification and copolycondensation [14,22,45–48].

The first method is the most attractive because it provides the possibility of synthesis of particles with more predictable results in terms of structural and morphological characteristics. It has one significant disadvantage—multistage synthesis, it is one of the key factors of application complexity in industrial scale [49–51].

Copolycondensation, as the second method, is the simplest in technical implementation of the process. Modifiers are injected directly with SiO2 precursor and the process finishes in one stage. The drawback is the dependence of hydrolysis and polycondensation on the nature of organosilanes that are used in synthesis. Matrix formation can be difficult when bulky organic substituents are used. This creates some difficulties in obtaining the required morphology and surface structure of materials. An additional negative factor may be the localization of organic groups in closed pores, which neutralizes their effect and reduces the efficiency of the material [52–56].

In this work, the silica particles were synthesized by the sol-gel method. The advantages of this method are the simplicity of the synthesis, which does not require complex technological equipment, “harsh” reaction conditions, the use of additional reagents, or time-consuming procedures, which significantly reduces the cost of particles.
The novelty of the discussed process of obtaining silica particles consists in carrying out all stages in one reaction medium (one-pot) and using a surfactant—dodecyldimethylamine N-oxide [57–59].

Unique properties of this compound allow to reduce ethanol consumption as a solvent due to increased solubility of alkoxysilanes in water. It is also important that this surfactant is removed from the final materials by washing in ethanol, unlike most commonly used surfactants, which are removed by heat treatment. This aspect makes it possible to classify the method used as energy-saving. Moreover, conducting no thermal treatment allows to save the organic functional groups.

Thus, the purpose of this work were to develop methods for the synthesis of organo-modified silicas, such as aminopropyl, phenyl, methyl, and mercapto silica, and their further practical application as palladium supports.

In addition, an assessment was carried out on the possibility of using the obtained palladium catalysts in the hydrogenation process of p-nitroaniline and sodium maleate (SM). The influence of functional group nature on catalysts activity in a process of liquid-phase hydrogenation of 4-nitroaniline (NA) and sodium maleate was investigated. Both processes were chosen due to its valuable products—1,4-phenylenediamine and sodium succinate [60–67]. Moreover, these processes are well-studied and a good model, as well as structure-sensitive [68–73].

2. Results and discussion

2.1. SEM

In the first step, attention was drawn to the influence of the organosilane amount on the structure and morphology on the formed silica particles. It was noted that with an increase in concentration of organosilane, its influence on the formed particles morphology also increases [74]. It is important to note that this effect can be very diverse: from the formation of layered structures to an increase in particle aggregation, all these side processes prevent the formation of spherical particles.

Microscopic analysis of the obtained silica particles showed that DDAO, in addition to increasing the solubility of alkoxysilanes in water and facilitating hydrolysis due to the formation of hydroxide ions on account of interacting with water molecules, also has a great effect on the morphology of materials. Its use significantly reduced the aggregation of the resulting particles—Figure 1.

![Figure 1](image1.png)

Figure 1. Scanning electron microscopy of SiO$_2$–C$_3$H$_6$–NH$_2$: (a) using a surfactant; (b) without the use of surfactants.

2.1.1. Amino-Modified Silica

The effect of the APTMOS amount on the morphology of the resulting particles is shown. The synthesis conditions are summarized in Table 3. With an increase in the APTMOS volume fraction, the degree of particle aggregation increased. In this case, the size of the particles increased, and the shape of the particles was not spherical—Figure 2.
Sample NH$_2$–0.4-0.1 had a spherical particle shape. Almost non-aggregated spherical particles with an average size of individual particles around 500 nm were clearly visible on the picture—Figure 2a.

The sizes of individual particles in samples NH$_2$–0.3-0.2 and NH$_2$–0.25-0.25 were the same. The degree of aggregation increased slightly—Figure 2b,c.

Particles of sample NH$_2$–0.2-0.3 practically did not have a spherical shape due to strong aggregation—Figure 2d. This can be explained by the fact that an increase in the APTMOS concentration led to an increase in the pH of the medium due to the protonation of the amino group. In this case, the stages of hydrolysis and polycondensation, aggregation and particle size rises for both precursors were significantly accelerated with an increase in the pH of the reaction mixture.

In this regard, another task of the study was to evaluate the maximum possible concentration of silanes at which the spherical shape of the particles and their size were remaining. Analysis of microscopic data showed that with an increase in the concentration of silanes, the average particle size decreased—Figure 3.

This is due to a combination of two factors. An increase in the concentration of silanes led to an increase in the number of nucleation centers. However, if one of the silanes was APTMOS, then the pH of the reaction mixture was higher, and with a larger quantity of nucleation centers, the stage of hydrolysis prevailed in comparison with the stage of polycondensation. As a result, a larger quantity of smaller particles was formed.
2.1.2. Silica Modified with Methyl, Phenyl, and Mercapto Groups

To achieve similar results to aminopropyl-modified silica, TEOS was replaced by TMOS due to its higher reactivity and, as a consequence, a large quantity of nucleation centers of particles with increasing silane concentration—Table 4.

Based on the SEM data, an assessment was carried out of the effect of the organosilane nature on the resulting particle’s morphology. The highest aggregation was observed in the case of phenyltrimethoxysilane—Figure 4c. This is probably due to the lower solubility of this organosilane, higher hydrophobicity, and the ability of phenyl rings for $\pi-\pi$ stacking.

In the case of methyltrimethoxysilane, spherical particles were formed, but with a wide particle size distribution (400–1300 nm). The reason is probably the fact that intermediate products of the hydrolysis stage are involved in polycondensation. However, the process of polycondensation of completely hydrolyzed silane molecules, forming larger particles, proceeds more slowly [75].

The best result was obtained for mercaptopropyltrimethoxysilane. This result can be associated with the slower kinetics of polycondensation of mercaptopropyltrimethoxysilane in alkaline media [76].

A decrease in the concentration of organosilanes (methyl-, mercapto-) (Figure 5) led to a decrease of particle aggregation. However, in the course of hydrolysis and polycondensation of phenyltrimethoxysilane, the formation of significantly aggregated particles continued. Element distribution maps showed that functional groups were evenly distributed over the silica surface. The absence of traces of nitrogen in all cases also indicates that DDAO was completely washed out from the obtained materials.
Figure 5. SEM data and surface mapping: (a) SH-0.33-0.13; (b) Me-0.33-0.09; (c) Ph-0.33-0.13.
2.2. *Infrared Spectroscopy*

The determination of the chemical composition of the synthesized organomodified silicas surface was carried out using FTIR spectroscopy in order to confirm the modification fact (Figure 6). The interpretation and analysis of the IR spectra were performed on the basis of the available literature data [77,78]. A characteristic broad absorption band of 3700–3000 cm\(^{-1}\) was observed for materials, which included the vibrations of adsorbed water molecules and vibrations of the surface hydroxyl groups of the silica surface.

![IR spectroscopy of SiO\(_2\)-Ph, SiO\(_2\)-SH, SiO\(_2\)-CH\(_3\), and SiO\(_2\)-NH\(_2\).](image)

Phenyl-modified silica: a number of bands from 3100 to 3000 cm\(^{-1}\) characterize stretching vibrations of aromatic C–H bonds. The peaks at 2925 cm\(^{-1}\) and 2850 cm\(^{-1}\) refer to asymmetric and symmetric stretching vibrations of C–H bonds. The range of bands from 2000 cm\(^{-1}\) to 1750 cm\(^{-1}\) are overtones of the aromatic ring. The band on 1594 cm\(^{-1}\)—in-plane stretching vibrations of the C=C bond of the phenyl fragment. The 1431 cm\(^{-1}\) band includes stretching vibrations C=C and bending C–H vibrations of the aromatic ring. The weak peak at 950 cm\(^{-1}\) characterizes the symmetric stretching vibrations of the C–C bond.

Mercaptopropyl-modified silica: 2926 cm\(^{-1}\)—stretching vibrations of aliphatic C–H bonds. The peak at 2558 cm\(^{-1}\)—S–H stretching vibration band. The band on 1627 cm\(^{-1}\)—deformation vibrations of adsorbed water. The peaks at 1446 cm\(^{-1}\) and 1408 cm\(^{-1}\) characterize asymmetric and symmetric bending vibrations of C–H bonds, respectively. The peak at 966 cm\(^{-1}\)—in-plane stretching vibrations of silanol groups Si–OH. The band at 804 cm\(^{-1}\)—symmetric stretching vibrations of Si–O bond.

Methyl-modified silica: the weak peak at 2980 cm\(^{-1}\) refers to the symmetric stretching vibrations of the C–H bond in the –CH\(_3\) group. The peak at 1632 cm\(^{-1}\) shows deformation vibrations of the H–O–H bond of adsorbed water. The broad peak at 1340 cm\(^{-1}\) refers to bending symmetric and asymmetric vibrations of the C–H bond. The broad peak from 1200 cm\(^{-1}\) to 1060 cm\(^{-1}\) characterizes the asymmetric stretching vibrations of the Si–O bond; the band at 950 cm\(^{-1}\)—in-plane stretching vibrations of silanol groups Si–OH; the band at 804 cm\(^{-1}\)—symmetric stretching vibrations of the Si–O bond, and 450 cm\(^{-1}\)—deformation vibrations of the Si–O bond.

Aminomodified silica: peaks at 3360 and 3290 cm\(^{-1}\) correspond to the stretching symmetric and asymmetric vibrations of the amino group. The bands at 2935 cm\(^{-1}\) and 2885 cm\(^{-1}\) correspond to the stretching vibrations of CH\(_2\) groups. The band at 1638 cm\(^{-1}\) is defined as the cumulative bending vibrations of adsorbed water molecules. The band at ≈1470 cm\(^{-1}\) is the bending vibrations of methylene groups. The region at 1300–850 cm\(^{-1}\)—
a series of silica vibrations: asymmetric vibrations of bridging silanol bonds Si-O-Si, deformation vibrations of a tetrahedron (1200–850 cm\(^{-1}\)), stretching and deformation vibrations of Si–O (1180–1000 cm\(^{-1}\)), and also Si–OC and CO (1260–1000 cm\(^{-1}\)) vibrations.

The 960 cm\(^{-1}\) band is responsible for the stretching vibrations of the Si-O-H silanol groups. That of 800 cm\(^{-1}\)—symmetric Si–O–Si vibrations. The peak at 1544 cm\(^{-1}\) is clearly discernible, which is defined as the bending vibration of the primary amino group. Vibrations of C–N were overlapped by vibrations of the matrix of the bulk phase of silica. In the region of 700 cm\(^{-1}\), a peak of Si-C vibrations appeared.

2.3. Analysis of the Catalytic Activity of the Developed Catalysts

The preparation of palladium catalysts on the synthesized matrices was carried out by the method of hydrolytic deposition of palladium hydroxide from an aqueous solution of H\(_2\)PdCl\(_4\) and its subsequent thermal decomposition to bivalent oxide and reduction in a hydrogen stream. The following matrices were used: NH\(_2\)-0.5-0.2, Me-0.33-0.09, and Ph-0.33-0.13. This choice was caused by the closer sizes of individual particles of the obtained materials.

Hydrogenation of 4-nitroaniline was carried out on the developed catalysts in solution of 2-propanol-water (0.68 mol fraction of 2-propanol) at 298K. As a comparison, the 10% Pd/C\(_{AR-D}\) (plant named after Ya.M. Sverdlov, Dzerzhinsk), as an industrial sample and a synthesized sample of 5% Pd/SiO\(_2\) were taken. The reaction kinetics was measured using hydrogen uptake (Figure 7).

![Figure 7](image_url)

**Figure 7.** Kinetic curves of hydrogen uptake in the hydrogenation of p-nitroaniline in an aqueous solution of 2-propanol-water. T = 298K, m (cat) = 0.3 ± 0.05 g, m (NA) = 0.5 ± 0.05 g.

Despite the twofold difference in the amount of supported metal, the activity of the 5% Pd SiO\(_2\)-NH\(_2\) catalyst was almost two times higher than that for 10% Pd/C. The effect of aminomodification of silica on the activity of palladium catalysts in the hydrogenation of 4-nitroaniline is discussed in more detail in [79]. The activity of 5% Pd/SiO\(_2\)-CH\(_3\) was the same as that of 10% Pd/C\(_{AR-D}\).

The least active catalyst was found to be 5% Pd/SiO\(_2\)-Ph. Mercaptopropyl-modified silica was not used for the preparation of catalysts, since it is known that sulfur is a catalytic poison and can lead to a complete loss of catalytic activity.
The stability of the catalysts was also established under the conditions of hydrogenation of 4-nitroaniline. Five portions of 4-nitroaniline were successively restored on the same portion of catalyst. The reaction rate per gram of catalyst is shown in Table 1.

For all catalysts, within five runs a decrease in activity was observed in different degrees: 17.6% for 5% Pd/SiO₂; 20.8% for 5% Pd/SiO₂–NH₂; 46.9% for 5% Pd/SiO₂–CH₃; and 59.8% for 5% Pd/SiO₂–Ph. The most stable catalyst was the 5% Pd/SiO₂ and the least stable the 5% Pd/SiO₂–Ph.

Table 1. Indicators of the reaction rate for various catalysts.

| Sample                          | 1 run | 2 run | 3 run | 4 run | 5 run |
|---------------------------------|-------|-------|-------|-------|-------|
| 10% Pd/C₃R₃-D                   | 4.88  | 4.20  | 3.90  | 3.60  | 3.30  |
| 5% Pd/SiO₂                      | 1.70  | 1.50  | 1.40  | 1.40  | 1.40  |
| 5% Pd/SiO₂–CH₃                  | 4.65  | 3.50  | 2.70  | 2.53  | 2.47  |
| 5% Pd/SiO₂–C₆H₅–NH₂ [79]        | 10.1  | 9.50  | 8.80  | 8.30  | 8.00  |
| 5% Pd/SiO₂–C₆H₅                 | 0.82  | 0.76  | 0.50  | 0.39  | 0.33  |

The low activity of phenyl-modified silica may be explained by the fact that the substrate and organomodified silica include aromatic rings in their structure. In this case, π–π stacking can occur between the substrate molecules and the matrix of the support. As a result, the hydrogenation process limits the stage of adsorption of 4-nitroaniline on palladium active sites. This hypothesis has not been directly supported, but is consistent with the results of studies published by other authors [16,20,22].

To test this hypothesis, propyl-urea-pyridine modified silica was synthesized, which also contains an aromatic ring, but is less hydrophobic than phenyl-modified silica. The kinetic experiment on the hydrogenation of 4-nitroaniline showed that the catalyst on pyridine-modified silica has a lower activity than that on phenyl-modified silica (Figure 7). Moreover, in contrast to all other samples, the conversion and product yield in the presence of this catalyst did not reach 100% and amounted to about ~70%.

Considering the data of obtained catalyst activity on pyridine-modified support, it can be concluded that not only the hydrophobicity of the support determines the catalytic activity of the metal precipitated from the aqueous solution. Pyridine-modified material has a sufficiently hydrophilic surface and is easily dispersed in water. However, the activity of palladium catalyst on this support in liquid phase hydrogenation of 4-nitroaniline was low. Accordingly, one of the possible explanations for the low activity of these catalysts was the π–π stacking effect (Figure 8), which is possible between the aromatic fragments of the functional group of the support and the starting substance and/or the reaction product.

![Figure 8. Schematic representation of π–π stacking.](image-url)
In this case, the main reason for the low activity was the non-covalent interaction of the initial reagents with aromatic rings or hydrogenation products with phenyl groups on the silica surface. This hindered access to the active sites of the catalyst or the diffusion of products from the near-surface layer of the catalyst. In this regard, it became necessary to evaluate the catalytic activity in the other catalyzed model process that proceeds without the participation of aromatic compounds. Hydrogenation of sodium maleate was chosen as a model, well-studied, and structure-sensitive process (Figure 9). The following catalytic systems were tested in the reaction: Pd/SiO$_2$; Pd/SiO$_2$–C$_3$H$_6$–NH$_2$; Pd/SiO$_2$–CH$_3$; Pd/SiO$_2$–C$_6$H$_5$; and Pd/SiO$_2$–NH–Pyr.

![Figure 9. Sodium maleate reduction reaction scheme.](image)

According to the results of the kinetic experiment of sodium maleate hydrogenation, palladium on supports modified with phenyl and pyridine showed much higher activity than in the hydrogenation of p-nitroaniline (Figure 10). Moreover, the catalyst based on SiO$_2$–NH–Pyr, which also includes N–H bonds, turned out to be better than the catalyst based on SiO$_2$–C$_6$H$_5$. The least active catalyst in this line was found to be palladium on unmodified silica. It is important to note that the catalysts 5% Pd/SiO$_2$–C$_3$H$_6$–NH$_2$ and 5% Pd/SiO$_2$–NH–Pyr are also not inferior in activity to 10% Pd/C$_{AR-D}$ in the hydrogenation of sodium maleate.

Thus, we can conclude that the hypothesis of the negative role of π–π stacking is confirmed and is of certain interest for the development of the theoretical foundations for the selection of catalysts based on the structure of the reagents in the chemical process.

![Figure 10. Kinetic curves of hydrogen uptake in liquid-phase hydrogenation of sodium maleate in water.](image)

**2.4. Analysis of Specific Surface Area and Porosity**

The specific surface area of the synthesized silicas were determined using the Langmuir and Brunauer–Emmett–Teller adsorption models, and using the t-plot method (Table 2). The best convergence of the specific surface area values was obtained for 5%
Pd/SiO$_2$–CH$_3$. For all other samples, the most accurate results were obtained using the t-plot method.

The pyridine-modified support SiO$_2$–NH–Pyr had the highest specific surface area, probably due to a most voluminous functional substituent (Figure 8), whereas in the case of amino groups, the smallest specific surface area corresponded to the SiO$_2$–C$_6$H$_5$–NH$_2$ sample.

Table 2. Specific surface area values of supports with correlation coefficients and porosity values.

| Sample            | Specific Surface Area, m$^2$/g | Vpore, mL/g |
|-------------------|-------------------------------|-------------|
|                   | Langmuir  | BET        | t-plot  |
| SiO$_2$–C$_6$H$_5$–NH$_2$ | 8.07    | 14.01      | 28.51   | 0.05   |
|                   | (0.99219)| (0.99409)  | (0.99660) |
| SiO$_2$–C$_3$H$_6$ | 55.19   | 70.23      | 99.00   | 0.32   |
|                   | (0.99370)| (0.99971)  | (0.99994) |
| SiO$_2$–NH–Pyr    | 68.08   | 81.37      | 114.95  | 0.13   |
|                   | (0.99655)| (0.99954)  | (0.99989) |
| SiO$_2$–CH$_3$    | 81.89   | 84.40      | 84.03   | 0.09   |
|                   | (0.99890)| (0.99998)  | (0.99995) |

Due to the fact that the most reliable results were obtained by the t-plot method, they were used to further search for the relationship between the activity of deposited palladium, the specific surface area of their supports and nature of functional groups—Figure 11.

Figure 11. The relationship between the activity of deposited palladium in hydrogenation of p-nitroaniline and (a) the specific surface area of their supports, (b) the nature of the functional groups.

Figure 11a,b shows that the larger the functional substituent, the higher the specific surface area and pore volume of the material. In this case, an inverse dependence of the values of the activity of the supported palladium in the hydrogenation of 4-nitroaniline was observed. Most likely, this is due to the distribution of the metal predominantly on the surface of the supports. Thus, as the porosity of the supports decreased, the contribution of the kinetic region of the process increased, whereas the contribution of diffusion processes decreased.

However, a comparison of the values of the activity of palladium catalysts in the hydrogenation of sodium maleate showed an inverse relation—Figure 12. With a decrease in the specific surface area and pore volume, a decrease in the reaction rate was also observed. It is likely that the landing areas for the adsorption of 4-nitroaniline and sodium maleate are different. In addition, the carboxyl groups of sodium maleate are capable of creating a steric effect for each other during adsorption on active sites, which increased with a decrease in specific surface area and porosity.
Figure 12. The relationship between the activity of deposited palladium in hydrogenation of sodium maleate and (a) the specific surface area of their supports, (b) the nature of functional groups.

2.5. X-ray Photoelectron Spectroscopy

According to XPS, the catalysts can be arranged in the following order based on the total palladium content on the surface of the support matrices: Pd/SiO₂ (1.6 At.%) < Pd/SiO₂–CH₃ (1.9 At.%) < Pd/SiO₂–C₆H₅ (2.1 At.%) < Pd/SiO₂–C₃H₆–NH₂ (2.3 At.%).

The interpretation of the high-resolution spectra of Pd 3d sublevel showed that palladium on unmodified silica was present in the form of Pd⁰ metal and PdO bivalent oxide, while on all organomodified supports in the form of Pd⁰ metal and metal coated with a PdO/Pd⁰ bivalent oxide film—Figures 13. The obtained data were in good agreement with the values of the activity of catalysts, where Pd/SiO₂ was the least active. Decomposition of the peaks into individual components made it possible to establish the atomic concentrations of metallic palladium and to plot the dependences of the content of metallic palladium on the support’s surface and the catalyst’s activity in both catalyzed processes on the nature of silica surface groups—Figure 13.

There is the correlation between the dependences of the catalysts’ activity in the hydrogenation of 4-nitroaniline, sodium maleate, and the surface content of metallic palladium on the nature of functional groups on the supports’ surface. The only exception is the value of the activity of Pd/SiO₂–C₆H₅ in the process of liquid-phase hydrogenation of 4-nitroaniline—Figure 14a.

Figure 13. XPS of Pd 3d for Pd/SiO₂, Pd/SiO₂–NH₂, Pd/SiO₂–CH₃, and Pd/SiO₂–C₆H₅ catalysts.

This was previously attributed to the influence of π–π stacking. When passing to the process of hydrogenation of sodium maleate, the activity of Pd/SiO₂–C₆H₅ turned out to
be higher in value and the dependence of the catalyst activity on the functional groups’ nature on the supports’ surface became more linear—Figure 14b.

Figure 14. Dependences of the catalysts activity in the hydrogenation of 4-nitroaniline (a), sodium maleate (b), and the surface content of metallic palladium on nature of functional groups on the support surface.

Moreover, certain interest was induced by the different values of the bond energy shifts for metallic palladium, depending on the nature of surface functional groups of supports—Figure 15.

It is known that the standard value of the binding energy of metallic palladium is 335 eV. However, different values of the binding energy shifts were established for metallic palladium on different supports: 0.68 eV for Pd/SiO2-C6H5; 0.56 eV for Pd/SiO2-C3H6-NH2; 0.26 eV for Pd/SiO2-CH3; and 0.13 eV for Pd/SiO3.

Dependences comparison of the catalysts activity in the hydrogenation of 4-nitroaniline (a), sodium maleate (b), and the shift of the bond energy Pd4+ on the functional groups nature of the supports’ surface showed that next correlation exist. The higher the shift value, the higher the activity of the supported palladium can be. The reason for the observed binding energy shifts may be caused by the electron-donor properties of functional groups [18].

Figure 15. Dependences of the catalysts activity in the hydrogenation of 4-nitroaniline (a), sodium maleate (b), and the value of the binding energy shift Pd4+ on the functional groups nature on the support surface.

Data comparison for two catalytic systems (Figure 15) also showed that for processes proceeding without consumption or formation of aromatic compounds, the activity of Pd/SiO2-C6H5 should be higher. Therefore, π-π stacking can prevent the adsorption of the substrate and/or the desorption of the product having benzene rings.
3. Materials and Methods

3.1. Reagents

Tetraethoxysilane (TEOS, 99.9%, Vekton, Russia), tetramethoxysilane (TMOS, SigmaAldrich, USA), aminopropyltrimethoxysilane (APTMOS, Sigma Aldrich, Darmstadt, Germany), mercaptopropyltrimethoxysilane (MPTMOS, Sigma Aldrich, St. Louis, MO, USA), methyltrimethoxysilane (MTMOS, SigmaAldrich, USA), phenyltrimethoxysilane (PhTMOS, SigmaAldrich, USA) dodecyldimethylamine N-oxide, 30% solution in water (DDAO, SigmaAldrich, Saint-Quentin-Fallavier, France), ethanol (96%, ChimMed, Moscow, Russia), Commercial palladium chloride (PdCl$_2$·2H$_2$O) (JSC “Aurat”, Moscow, Russia), sodium carbonate (Vecton, Novosibirsk, Russia), 2-propanol (99% Vecton, Russia), and 4-nitroaniline (NA, Vecton, Russia) were used. Gases (Ar 99.998%; H$_2$ 99.999%) of high purity were purchased from a local supplier and used for the experiments.

3.2. Synthesis Methodology

In this study, one-pot methods were developed for the preparation of functionalized silica particles. The main goal of the work was to develop new methods for one-stage synthesis of hybrid materials based on silicon oxide particles by copolycondensation of alkoxysilanes with the corresponding organosilanes.

The main work was focused on the synthesis of four types of silica particles with different functional groups: aminopropyl, mercaptopropyl, methyl, and phenyl. The synthesis conditions were selected for each organoalkoxysilane. In particular, the synthesis with aminopropyltrimethoxysilane is the most complex. At neutral pH, the amino group is protonated to form a positive charge on the nitrogen atom. The solution also contains DDAO, which is an ionic surfactant and negatively charged oxygen is also protonated at neutral pH values. Both of these processes proceed with the generation of a hydroxyl ion, which is a catalyst for hydrolysis and polycondensation reactions. Due to this total effect, the synthesis can be carried out without the additional alkaline agents, and APTMOS and DDAO are the initiators of the sol-gel process.

However, other organosilanes do not exhibit such properties, which makes the synthesis process more complicated. In this regard, TEOS was replaced by TMOS, since methoxygroups hydrolyze more easily than ethoxy groups [80].

3.2.1. Aminomodified Silica Synthesis

The initial solution contained 26 mL of water (45 M) and 4 mL of ethanol (2.06 M). Then, to form an emulsion, 1.2 mL (0.05 M) DDAO was injected with stirring at 1500 rpm. Thereafter, 0.5 mL of TEOS (0.07 M) and 0.2 mL of APTMOS (0.034 M) were added. In the experiments, TEOS:APTMOS ratio was varied (Table 3). Furthermore, different total volumes of added alkoxysilanes were used in the synthesis. The resulting solution was stirred for 2 h at room temperature. The final solution was a viscous, stable, opaque colloidal solution of white color, which did not transform into a gel even with prolonged settling.

| Sample     | TEOS, mL | TEOS, M | APTMOS, mL | APTMOS, M | W, % (APTMOS) |
|------------|----------|---------|------------|-----------|---------------|
| NH$_2$:0.5-0.2 | 0.50     | 0.070   | 0.20       | 0.032     | 29            |
| NH$_2$:0.75-0.3 | 0.75     | 0.100   | 0.30       | 0.052     | 29            |
| NH$_2$:1-0.4  | 1.00     | 0.140   | 0.40       | 0.069     | 29            |
| NH$_2$:0.4-0.1 | 0.40     | 0.056   | 0.10       | 0.017     | 20            |
| NH$_2$:0.3-0.2 | 0.30     | 0.042   | 0.20       | 0.034     | 40            |
| NH$_2$:0.25-0.25 | 0.25    | 0.035   | 0.25       | 0.043     | 50            |
| NH$_2$:0.2-0.3  | 0.20     | 0.028   | 0.30       | 0.052     | 60            |
To separate the dispersed phase from the dispersion medium, we used the method of vacuum filtration on a Bunsen flask with a Schott filter (pore size 16 nm). In the process of filtration, the surfactant was removed from the material by repeated flushing with ethanol until foaming ceased in the wash water. The materials were dried in a vacuum drying oven at a pressure of 0.4 bar and a temperature of 100 °C.

The method of vacuum filtration on a Bunsen flask with a Schott filter (pore size 16 nm) was used for separate the dispersed phase from the dispersion medium. The materials were dried in a vacuum oven at a pressure of 0.4 bar and 100 °C.

3.2.2. Synthesis of Phenyl-, Methyl-, and Mercapto-Modified Silica Particles

The original solution contained: 2.6 mL of water (45 M) and 4 mL of ethanol (2.06 M). Then, to form an emulsion, 1.2 mL (0.05 M) DDAO was injected with stirring at 1500 rpm.

For the synthesis of particles, 0.3 mL of TMOS (0.07 M) and the corresponding amount of organosilane were added to the initial solution (Table 4). The resulting solution was stirred for 2 h at room temperature. The final solution was a viscous, stable, opaque colloidal solution of white color, which did not transform into a gel even with prolonged settling.

To separate the dispersed phase from the dispersion medium, we used the method of vacuum filtration on a Bunsen flask with a Schott filter (pore size 16 nm). In the process of filtration, the surfactant was removed from the material by repeated flushing with ethanol until foaming ceased in the wash water.

The materials were dried in a vacuum drying oven at a pressure of 0.4 bar and a temperature of 100 °C. The table with all syntheses is presented below. Sample designation as an example SH-0.33-0.2:1; SH—functional group, 0.33—amount of TMOS in mL, 0.2—amount of R-TMOS in mL, and W, %—mass fraction of functional groups in the final material.

| Sample  | TMOS, mL | TMOS, M | R-TMOS, mL | R-TMOS, M | W, % (R-TMOS) |
|---------|----------|---------|------------|-----------|---------------|
| SH-0.33-0.2 | 0.33 | 0.07 | 0.20 | 0.032 | 41 |
| SH-0.33-0.13 | 0.33 | 0.07 | 0.13 | 0.021 | 31 |
| Ph-0.33-0.2 | 0.33 | 0.07 | 0.20 | 0.032 | 42 |
| Ph-0.33-0.13 | 0.33 | 0.07 | 0.13 | 0.021 | 32 |
| Me-0.33-0.14 | 0.33 | 0.07 | 0.14 | 0.032 | 29 |
| Me-0.33-0.09 | 0.33 | 0.07 | 0.09 | 0.021 | 21 |

3.2.3. Catalyst Synthesis Method

Palladium nanoparticles were synthesized on the supports' surface by hydroxide precipitation due to aqueous alkaline hydrolysis of a hydrochloric solution of palladium chloride [81]. The solution was prepared as follows: 0.7 g of PdCl₂·2H₂O was dissolved in 30 mL of 0.5 M HCl by heating to 70 °C. Then, the volume of the solution was brought to 40 mL by adding 10 mL of distilled water. For the synthesis of 1 g of 5% palladium catalyst, 5 mL of the resulting solution was used.

The synthesis of the catalysts was carried out as follows. The support (1 g) was suspended in 40 mL of 0.08 M sodium carbonate solution. An aliquot of 5 mL of the obtained H₂PdCl₂ solution was slowly added dropwise to a suspension of the support in a sodium carbonate solution. The resulting suspension was stirred for three hours at 40 °C. Further, the powdered material was filtered, washed with water until neutral pH, and dried in a vacuum oven at a pressure of 0.4 bar and a temperature of 100 °C.

The catalyst activation procedure was carried out in a quartz glass flow reactor placed in a tubular furnace. The sample was pre-degassed in a flow of argon for 20 min. Then, hydrogen was supplied from a cylinder and linear heating of the furnace began at
a speed of 10 degrees per minute up to 250 °C. The holding time of the sample at 250 °C was 60 min. After the temperature was maintained, the sample cooled naturally to room temperature. Before the immediate withdrawal of the finished catalyst, an argon flow was supplied to the activation reactor to remove residual hydrogen and prevent the catalyst from igniting in air.

3.3. Research Methods

3.3.1. Scanning Electron Microscopy (SEM)

A scanning electron microscope VEGA 3 (TESKAN, Brno, Czech Republic) was used to determine the morphology and elemental composition of the material’s surface. The samples were sprayed onto carbon tape. Accelerating voltage was 5 kV.

3.3.2. Infrared Fourier Spectroscopy

To determine the qualitative composition of the material surface, IR spectra were obtained on an IR Fourier spectrometer IRPrestige-21 (Shimadzu, Kyoto, Japan) equipped with a DRS-8000 diffuse reflection attachment (Simadzu, Kyoto, Japan). As a background sample, a mirror of the optical system DRS-8000 attachment was used. All spectra were recorded in the range of wave numbers 450–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3.3.3. Kinetics Investigation of Catalytic Process

The study of the activity and stability of the synthesized catalysts was carried out in a model reaction of hydrogenation of 4-nitroaniline in the aqueous azeotropic solution of 2-propanol (0.68 molar fractions of 2-propanol) in a thermostatic semibatch reactor with overhead stirring of the reaction mixture. A weighted portion of the catalyst (~0.30 ± 0.01 g) and an aliquot of the solvent (~100 ± 0.01 mL) were placed into the reactor. After that, the reactor was thermostated to 25 °C and purged with hydrogen for 15 min. Then, the catalyst was pretreated with hydrogen under stirring conditions (3000 rpm). The hydrogen was continuously fed into the reactor for 15 min. Then the hydrogen supply was stopped.

The reactor was opened due to the loading of a weighed portion of 4-nitroaniline (~0.5 ± 0.01 g) in the form of a powder. Further the reactor was closed and air was purged with hydrogen purge for 15 min. In the case of sodium maleate, the substrate was introduced as a solution through a special injector without the need to open the reactor. The experiment was started from the moment the stirring was switched on. The completion of the reaction corresponded to the ending of hydrogen uptake.

To determine the stability of the operation of the synthesized catalysts during the hydrogenation of 4-nitroaniline, 5 portions of 4-nitroaniline were successively reduced on each catalyst. The reactor was opened, a new weighed portion of 4-nitroaniline (~0.5 ± 0.01 g) was loaded into the reaction mixture, and the experiment was repeated.

The process of sodium maleate hydrogenation was also carried out in a thermostated semibatch reactor with overhead stirring of the reaction mixture. The reactor contained solvent, catalyst, pretreated with hydrogen, and 20 mL of 0.18 M sodium maleate solution (SM) was injected.

The rate of hydrogen uptake was used as the kinetic characteristic of the catalysts activity. The hydrogen consumption was measured by volumetric method. Additionally, the qualitative and quantitative control of the completeness of the process was carried out by gas chromatography.

3.3.4. Nitrogen Physisorption

Nitrogen physisorption was studied under the temperature of liquid nitrogen boiling point using a Beckman Coulter SA 3100 apparatus (Coulter Corporation, Brea, CA, USA). Samples were previously dried in a Beckman Coulter SA-PREP apparatus for sample preparation (Coulter Corporation, USA) at 150 °C in flow of inert gas before the analysis.
3.3.5. X-ray Photoelectron Spectroscopy

The spectra were obtained using Mg Kα radiation (hv = 1253.6 eV) on an ES-2403 spectrometer (manufacturer: Institute for Analytical Instrumentation, Russian Academy of Sciences, St. Petersburg, Russia) equipped with a PHOIBOS 100-MCD5 energy analyzer (SPECS, Germany) and an X-ray source -50 (SPECS, Germany). The survey spectra were recorded with an energy step of 0.5 eV, and high-resolution spectra were recorded with an energy step of 0.05 eV. Decoding was performed based on literature and the NIST X-ray Photoelectron Spectroscopy Standard Reference Database.

4. Conclusions

The advantages of the described sol-gel synthesis of silica are the possibility of obtaining a material with certain morphological and dimensional characteristics. A distinctive feature of the used silica particles formation process is that the whole process is carried out in one pot. At the same time, the co-condensation method allows avoiding the gelation phase, which often requires significant time and energy resources for further separation of the product. It was shown in the work that dodecyl(dimethyl)amine N-oxide is highly effective as a surfactant. Dodecyl(dimethyl)amine N-oxide promotes the growth of the silica matrix by increasing the pH of the reaction mixture, and the agent is easily removed from the material upon subsequent washing with alcohol.

The obtained materials were used as supports for palladium catalysts as a possible practical application. The study of the hydrogenation kinetics of 4-nitroaniline and sodium maleate showed that the final product yield in all cases was ~100%, except for palladium on pyridine-modified silica. It was found that the amino modification of silica significantly increases the activity of the metallic palladium supported on its surface. Both hydrogenation processes were catalyzed with maximum efficiency on the Pd/SiO2–C6H5–NH2 catalyst.

It was shown that the larger the functional substituent, the higher the specific surface area and pore volume of the material. In this case, an inverse dependence of the values of the activity of the supported palladium in the hydrogenation of 4-nitroaniline was observed.

As the porosity of the supports decreased, the contribution of the kinetic region of the hydrogenation of p-nitroaniline process increased, whereas the contribution of the diffusion processes decreased. With a decrease in the specific surface area and pore volume, a decrease in the rate of the sodium maleate hydrogenation reaction was observed due to the steric action of the carboxyl groups of sodium maleate during adsorption on active sites.

Analysis of XPS made it possible to reveal a direct relationship between the value of the binding energy shift of metallic palladium and the functional groups nature of the support matrix. This fact proves that the presence of functional groups in the composition of the support matrix affects the electronic state of the metal and can be considered a tool for controlling the catalyst activity.

Author Contributions: Conceptualization, A.R.L.; methodology, A.R.L. and M.D.L.; software, A.R.L., M.D.L., and I.A.T.; validation, A.R.L. and M.D.L.; formal analysis, A.R.L., M.D.L., I.A.T., and A.I.S.; investigation, A.R.L., M.D.L., I.A.T., and A.I.S.; data curation, Y.S.M.; writing—original draft preparation, A.R.L., M.D.L., and I.A.T.; writing—review and editing, Y.S.M.; visualization, A.R.L., M.D.L., and I.A.T.; supervision, Y.S.M., A.S.V., and E.V.R.; project administration, Y.S.M.; funding acquisition, I.A.T. and Y.S.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Russian Foundation of Basic Research, grant number 19-33-90190.

Acknowledgments: The authors thank the Center for Shared Use of Tver State Technical University for assistance in obtaining XPS data. The study was carried out using the resources of the Center for
Shared Use of Scientific Equipment of the ISUCT (with the support of the Ministry of Science and Higher Education of Russia, grant No. 075-15-2021-671).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Liberman, A.; Mendez, N.; Trogler, W.C.; Kummel, A.C. Synthesis and surface functionalization of silica nanoparticles for nanomedicine. Surf. Sci. Rep. 2014, 69, 132–158, doi:10.1016/j.surfrep.2014.07.001.

2. Wang, J.; Shah, Z.H.; Zhang, S.; Lu, R. Silica-based nanocomposites via reverse microemulsions: Classifications, preparations, and applications. Nanoscale 2016, 4, 4418–4437, doi:10.1039/C3NR06025J.

3. Guerrero-Martínez, A.; Pérez-Juste, J.; Liz-Marzán, L.M. Recent Progress on Silica Coating of Nanoparticles and Related Nano-materials. Adv. Mater. 2010, 22, 1182–1195, doi:10.1002/adma.200901263.

4. Mugica, L.C.; Rodriguez-Molina, B.; Ramos, S.; Kozina, A. Surface functionalization of silica particles for their efficient fluorescence and stereo selective modification. Colloids Surf. A Physicochem. Eng. Asp. 2016, 500, 79–87, doi:10.1016/j.colsurfa.2014.04.002.

5. Bagwe, R.P.; Hilliard, L.R.; Tan, W. Surface Modification of Silica Nanoparticles to Reduce Aggregation and Nonspecific Binding. Langmuir 2006, 22, 4357–4362, doi:10.1021/la052797j.

6. Nasir Baig, R.B.; Varma, R.S. Magnetic Silica-Supported Palladium Catalyst: Synthesis of Allyl Aryl Ethers in Water. Ind. Eng. Chem. Res. 2014, 53, 18625–18629, doi:10.1021/ie501081q.

7. Geszke-Moritz, M.; Moritz, M. APTES-modified mesoporous silicas as the carriers for poorly water-soluble drug. Modeling of diffusional adsorption and release. Appl. Surf. Sci. 2016, 368, 348–359, doi:10.1016/j.apsusc.2016.02.004.

8. Wang, A.; Yang, Y.; Qi, Y.; Qi, W.; Fei, J.; Ma, H.; Zhao, J.; Cui, W.; Li, J. Fabrication of Mesoporous Silica Nanoparticle with Well-Defined Multicompartment Structure as Efficient Drug Carrier for Cancer Therapy in Vitro and in Vivo. ACS Appl. Mater. Interfaces 2016, 8, 8900–8907, doi:10.1021/acsami.5b12031.

9. Rajanna, S.K.; Kumar, D.; Vinjamur, M.; Mukhopadhyay, M. Silica Aerogel Microparticles from Rice Husk Ash for Drug Delivery. Ind. Eng. Chem. Res. 2015, 54, 949–956, doi:10.1021/ie503867p.

10. Roy, I. Synthesis, Surface Modification, Characterization, and Biomedical In Vitro Applications of Organically Modified Silica (ORMOSIL) Nanoparticles. In Nanoparticles in Biology and Medicine: Methods and Protocols; Soloviev, M., Ed.; Humana Press: Totowa, NJ, USA, 2012; pp. 365–379.

11. Wang, Y.; Zhang, M.; Song, H.; Yu, C. Silica-Based Nanoparticles for Biomedical Applications: From Nanocarriers to Biomodulators. Acc. Chem. Res. 2020, 53, 1545–1556, doi:10.1021/acs.accounts.0c00280.

12. Wang, K.; Liu, P.; Ye, Y.; Li, J.; Zhao, W.; Huang, X. Fabrication of a novel laccase biosensor based on silica nanoparticles modified with phytic acid for sensitive detection of dopamine. Sens. Actuators B Chem. 2014, 197, 292–299, doi:10.1016/j.snb.2013.04.002.

13. Zhao, W.; Fang, Y.; Zhu, Q.; Wang, K.; Liu, M.; Huang, X.; Shen, J. A novel glucose biosensor based on phosphonic acid-functionalized silica nanoparticles for sensitive detection of glucose in real samples. Electrochim. Acta 2013, 89, 278–283, doi:10.1016/j.electacta.2012.11.031.

14. Putz, A.-M.; Mihaela, C.; Adina, N.; Grad, O.; Ianasi, C.; Ivankov, O.; Milanović, M.; Stijepović, I.; Almásy, L. Comparison of Structure and Adsorption Properties of Mesoporous Silica Functionalized with Aminopropyl Groups by the Co-Condensation and the Post Grafting Methods. Materials 2021, 14, 628, doi:10.3390/ma14030628.

15. Lesniewska, B.; Arciszewska, Z.; Wawrzyńczak, A.; Jarmoliksińska, S.; Nowak, I.; Godlewksa-Żylkiewicz, B. Method development for determination of trace amounts of palladium in environmental water samples by ICP-MS/MS after pre-concentration on thiol-functionalized MCM-41 materials. Talanta 2020, 217, 121004, doi:10.1016/j.talanta.2020.121004.

16. Baccile, N.; Babonneau, F. Organosol-modified mesoporous silicas for organic pollutant removal in water: Solid-state NMR study of the organic/silica interactions. Microporous Mesoporous Mater. 2008, 110, 534–5422, doi:10.1016/j.micromeso.2007.06.056.

17. Celik, G.; Ailawar, S.A.; Sohn, H.; Tang, Y.; Tao, F.F.; Miller, J.T.; Edmiston, P.L.; Ozkan, U.S. Swellable Organically Modified Silica (SOMS) as a Catalyst Scaffold for Catalytic Treatment of Water Contaminated with Trichloroethylene. ACS Catal. 2018, 8, 6796–6809, doi:10.1021/acscatal.8b01700.

18. Saptal, V.B.; Saptal, M.V.; Mane, R.S.; Sasaki, T.; Bhanage, B.M. Amine-Functionalized Graphene Oxide-Stabilized Pd Nanoparticles (Pd@APGO): A Novel and Efficient Catalyst for the Suzuki and Carboxylative Suzuki–Miyaura Coupling Reactions. ACS Omega 2019, 4, 643–649, doi:10.1021/acsomega.8b03023.

19. Hou, Z.; Theyssen, N.; Leitner, W. Palladium nanoparticles stabilised on PEG-modified silica as catalysts for the aerobic alcohol oxidation in supercritical carbon dioxide. Green Chem. 2007, 9, 127–132, doi:10.1039/B606740A.

20. Corral, J.A.; López, M.I.; Esquivel, D.; Mora, M.; Jiménez-Sanchidrián, C.; Romero-Salguero, F.J. Preparation of Palladium-Supported Periodic Mesoporous Organosilicas and their Use as Catalysts in the Suzuki Cross-Coupling Reaction. Materials 2013, 6, 1554–1565, doi:10.3390/ma6041554.

21. Ivashchenko, N.; Tertykh, V.; Yanishpolskii, V.; Khainakov, S.; Dikhitarenko, A. Controlled reduction of palladium nanoparticles on surface of chemically modified silicas. Materialwissenschaft Werkstofftechnik 2011, 42, 64–69, doi:10.1002/maw.201100733.
22. Lemay, M.; Pandarus, V.; Simard, M.; Marion, O.; Tremblay, L.; Béland, F. SiliaCat® S-Pd and SiliaCat DPP-Pd: Highly Reactive and Reusable Heterogeneous Silica-Based Palladium Catalysts. *Top. Catal.* 2010, 53, 1059–1062, doi:10.1007/s11244-010-9532-6.

23. Carreño, G.A.; Schott, E.; Zarate, X.; Arratia-Perez, R.K.J.; Mardones, M.; Manriquez, J.M.I. Adsorption essays of palladium in modified silica gel with thiouronium groups: Experimental and theoritical studies. *J. Chil. Chem. Soc.* 2010, 56, 692–696, doi:10.4067/S0717-9707201000200015.

24. Veisi, H.; Abassi, P.; Mohammadi, P.; Tamoradi, I.; Karmakar, B. Gold nanoparticles decorated biguanidine modified mesoporous silica KIT-5 as recoverable heterogeneous catalyst for the reductive degradation of environmental contaminants. *Sci. Rep.* 2021, 11, 2734, doi:10.1038/s41598-021-82242-z.

25. Omar, S.; Abu-Reziq, R. Palladium Nanoparticles Supported on Magnetic Organic-Silica Hybrid Nanoparticles. *J. Phys. Chem. C* 2014, 118, 30045–30056, doi:10.1021/jp510472t.

26. Guin, D.; Baruwati, B.; Manorama, S.V. Pd on Amine-Terminated Ferrite Nanoparticles: A Complete Magnetically Recoverable Facile Catalyst for Hydrogenation Reactions. *Org. Lett.* 2007, 9, 1419–1421, doi:10.1021/ol070290p.

27. Lewis, L.N. Chemical catalysis by colloids and clusters. *Chem. Rev.* 1993, 93, 2693–2730, doi:10.1021/cr00024a006.

28. Crooks, R.M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L.K. Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Applications to Catalysis. *Acc. Chem. Res.* 2001, 34, 181–190, doi:10.1021/ar000110a.

29. Shakeri, M.; Tai, C.-w.; Gothelid, E.; Oscarsson, S.; Bäckvall, J.-E. Small Pd Nanoparticles Supported in Large Pores of Mesocellular Foam: An Excellent Catalyst for Racemization of Amines. *Chem A Eur. J.* 2011, 17, 13269–13273, doi:10.1002/chem.201101265.

30. Verho, O.; Nagendiran, A.; Johnston, E.V.; Tai, C.-W.; Bäckvall, J.-E. Nanopalladium on Amino-Functionalized Mesocellular Foam: An Efficient Catalyst for Transfer Hydrogenations. *ChemCatChem* 2013, 5, 612–618, doi:10.1002/cctc.201202427.

31. Johnston, E.V.; Verho, O.; Kärkäsi, M.D.; Shakeri, M.; Tai, C.-W.; Palmgren, P.; Eriksson, K.; Oscarsson, S.; Bäckvall, J.-E. Highly Dispersed Palladium Nanoparticles on Mesocellular Foam: An Efficient and Recyclable Heterogeneous Catalyst for Alcohol Oxidation. *Chem. A Eur. J.* 2012, 18, 12202–12206, doi:10.1002/chem.201201257.

32. Verho, O.; Nagendiran, A.; Tai, C.-W.; Johnston, E.V.; Bäckvall, J.-E. Nanopalladium on Amino-Functionalized Mesocellular Foam as an Efficient and Recyclable Catalyst for the Selective Transfer Hydrogenation of Nitroarenes to Anilines. *ChemCatChem* 2014, 6, 205–211, doi:10.1002/cctc.201300769.

33. Rana, S.; Maddila, S.; Yalagala, K.; Jonnalagadda, S.B. Organo functionalized graphene with Pd nanoparticles and its excellent catalytic activity for Suzuki coupling reaction. *Appl. Catal. A Gen.* 2015, 505, 539–547, doi:10.1016/j.apcata.2015.07.018.

34. Rana, S.; Maddila, S.; Jonnalagadda, S.B. Synthesis and characterization of Pd(ii) dispersed over diame functionalized graphene oxide and its scope as a catalyst for selective oxidation. *Catal. Sci. Technol.* 2015, 5, 3235–3241, doi:10.1039/C5CY00192G.

35. Varadwaj, G.B.B.; Rana, S.; Parida, K. Pd(0)/Nanoparticles Supported Organofunctionalized Clay Driving C–C Coupling Reactions under Benign Conditions through a Pd(0)/Pd(II) Redox Interplay. *J. Phys. Chem. C* 2014, 118, 1640–1651, doi:10.1021/jp410709n.

36. Hussain, Z.; Schwalin, C.; Rambo, R.; Dias, R.; Steiler, R.; Monteiro, A. Synthesis of Mono- and Bis-Pyrazoles Bearing Flexible p-Tolyli Ether and Rigid Xanthene Backbones, and Their Potential as Ligands in the Pd-Catalysed Suzuki–Miyaura Cross-Coupling Reaction. *Catalysts* 2019, 9, 718, doi:10.3390/catal9090718.

37. Karanjit, S.; Tamura, A.; Kashihara, M.; Ushiyama, K.; Shrestha, L.K.; Ariga, K.; Nakayama, A.; Namba, K. Hydrotalcite-Supported Ag/Pd Bimetallic Nanoclusters Catalyzed Oxidation and One-Pot Aldol Reaction in Water. *Catalysts* 2020, 10, 1120, doi:10.3390/catal1011120.

38. Keller, K.; Lott, P.; Stotz, H.; Maier, L.; Deutschmann, O. Microkinetic Modeling of the Oxidation of Methane Over PdO Catalysts—Towards a Better Understanding of the Water Inhibition Effect. *Catalysts* 2020, 10, 922, doi:10.3390/catal10080922.

39. Ramírez Côté, C.; Ciriminna, R.; Pandarus, V.; Béland, F.; Pagliaro, M. Comparing the Pyrophoricity of Palladium Catalysts for Heterogeneous Hydrogenation. *Org. Process. Res. Dev.* 2018, 22, 1852–1855, doi:10.1021/acs.oprd.8b00242.

40. Sauvage, J.-F.; Baker, R.H.; Hussey, A.S. The Hydrogenation of Cycloalkenes over Supported Palladium Catalysts. *J. Am. Chem. Soc.* 1961, 83, 3874–3877, doi:10.1021/ja01479a032.

41. Suh, D.J.; Park, T.J.; Ihm, S.K. Characteristics of carbon-supported palladium catalysts for liquid-phase hydrogenation of nitroaromatics. *Ind. Eng. Chem. Res.* 1992, 31, 1849–1856, doi:10.1021/ie90008a003.

42. Wei, Z.; Xie, Z.; Gao, L.; Wang, Y.; Sun, H.; Jian, Y.; Zhang, G.; Xu, L.; Yang, J.; Zhang, W.; et al. Highly Crystallized Pd/Cu Nanoparticles on Activated Carbon: An Efficient Heterogeneous Catalyst for Sonogashira Cross-Coupling Reaction. *Catalysts* 2020, 10, 192, doi:10.3390/catal10020192.

43. Wood, J.; Bodenes, L.; Bennett, J.; Deplanche, K.; Macaskie, L.E. Hydrogenation of 2-Butyne-1,4-diol Using Novel Bio-Palladium Catalysts. *Ind. Eng. Chem. Res.* 2010, 49, 980–988, doi:10.1021/ie900663k.

44. Zhu, Y.; Bai, Z. Pd–Ce/ZIF-8 Nanocomposite for Catalytic Extraction of Sinomenine from Sinomenium acutum. *Catalysts* 2020, 10, 174, doi:10.3390/catal10020174.

45. Putz, A.-M.; Almasy, L.; Len, A.; Janasi, C. Functionalized silica materials synthesized via co-condensation and post-grafting methods. *Fuller. Nanotub. Carbon Nanostruct.* 2019, 27, 323–332, doi:10.1016/j.fuson.2019.1593154.

46. Ab Rahman, I; Jafarzadeh, M.; Sipaut, C. Physical and optical properties of organo-modified silica nanoparticles prepared by sol–gel. *J. Sol–Gel Sci. Technol.* 2011, 59, 63–72 doi:10.1007/s10971-011-2464-1.
71. Udayakumar, V.; Alexander, S.; Gayathri, V.; Shivakumaraiah; Viswanathan, B. Study on the influence of substituents upon the hydrogenation of nitrobenzene using a polymer-supported palladium-imidazole complex catalyst. React. Kinet. Mech. Catal. 2011, 103, 341–352, doi:10.1007/s11144-011-0308-1.

72. Tallon, M.A. Reactions Involving Maleic Anhydride. In Handbook of Maleic Anhydride Based Materials: Syntheses, Properties and Applications; Musa, O.M., Ed.; Springer International Publishing: Cham, Switzerland, 2016; pp. 59–149.

73. Korosteleva, P.O.; Ulitin, M.V.; Lukin, M.V.; Filippov, D.V. The kinetics of liquid-phase hydrogenation of sodium maleate by hydrogen adsorbed on the surface of Raney nickel. Russ. J. Phys. Chem. A 2009, 83, 1715–1719, doi:10.1134/S003602440910015X.

74. Hoffmann, F.; Fröba, M. Vitalising porous inorganic silica networks with organic functions—PMOs and related hybrid materials. Chem. Soc. Rev. 2011, 40, 608–620, doi:10.1039/C0CS00076K.

75. Smith, K.A. Polycondensation of methyltrimethoxysilane. Macromolecules 1987, 20, 2514–2520, doi:10.1021/ma00176a033.

76. Brochier Salon, M.-C.; Bayle, P.-A.; Abdelmouleh, M.; Boufi, S.; Belgacem, M.N. Kinetics of hydrolysis and self condensation reactions of silanes by NMR spectroscopy. Colloids Surf. A Physicochem. Eng. Asp. 2008, 312, 83–91, doi:10.1016/j.colsurfa.2007.06.028.

77. Silverstein, R.M.; Bassler, G.C. Spectrometric identification of organic compounds. J. Chem. Educ. 1962, 39, 546, doi:10.1021/ed039p546.

78. Al-Oweini, R.; El-Rassy, H. Synthesis and characterization by FTIR spectroscopy of silica aerogels prepared using several Si(OR)4 and R'Si(OR)3 precursors. J. Mol. Struct. 2009, 919, 140–145, doi:10.1016/j.molstruc.2008.08.025.

79. Latypova, A.R.; Lebedev, M.D.; Rumyantsev, E.V.; Filippov, D.V.; Lefedova, O.V.; Bykov, A.V.; Doluda, V.Y. Amino-Modified Silica as Effective Support of the Palladium Catalyst for 4-Nitroaniline Hydrogenation. Catalysts 2020, 10, 375, doi:10.3390/catal10040375.

80. Osterholtz, F.D.; Pohl, E.R. Kinetics of the hydrolysis and condensation of organofunctional alkoxysilanes: A review. J. Adhes. Sci. Technol. 1992, 6, 127–149, doi:10.1163/156856192X00106.

81. Belskaya, O.; Roman, M.; Gulyaeva, T.; Trenikhin, M.; Likholobov, V. Effect of the reduction conditions of the supported palladium precursor on the activity of Pd/C catalysts in hydrogenation of sodium 2,4,6-trinitrobenzoate. Russ. Chem. Bull. 2018, 67, 71–78, doi:10.1007/s11172-018-2039-1.