Block-Co-polymer-Assisted Synthesis of All Inorganic Highly Porous Heterostructures with Highly Accessible Thermally Stable Functional Centers

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ABSTRACT: Here, we propose a simple approach for the design of highly porous multicomponent heterostructures by infiltration of block-co-polymer templates with inorganic precursors in swelling solvents followed by gas-phase sequential infiltration synthesis and thermal annealing. This approach can prepare conformal coatings, free-standing membranes, and powders consisting of uniformly sized metal or metal oxide nanoparticles (NPs) well dispersed in a porous oxide matrix. We employed this new, versatile synthetic concept to synthesize catalytically active heterostructures of uniformly dispersed ~4.3 nm PdO nanoparticles accessible through three-dimensional pore networks of the alumina support. Importantly, such materials reveal high resistance against sintering at 800 °C, even at relatively high loadings of NPs (~10 wt %). At the same time, such heterostructures enable high mass transport due to highly interconnected nature of the pores. The surface of synthesized nanoporous membranes is highly accessible, which enables their good catalytic performance in methane and carbon monoxide oxidation. In addition, we demonstrate that this approach can be utilized to synthesize heterostructures consisting of different types of NPs on a highly porous support. Our results show that swelling-based infiltration provides a promising route toward the robust and scalable synthesis of multicomponent structures.

KEYWORDS: block co-polymer, infiltration synthesis, catalysis, palladium nanoparticles, nanoporous alumina

1. INTRODUCTION

Sequential infiltration synthesis (SIS) has been developed to pattern metal oxides materials via selective infiltration of the polar domains of the block-co-polymer (BCP) templates with inorganic vapors followed by removal of the polymer using thermal annealing.2,3 SIS has been successfully used to pattern ceramic structures such as alumina, titanium oxide, zinc oxide, and silicon oxide.2,4 However, the thickness of coatings obtained by classical SIS is limited by the depth of diffusion of inorganic vapor-phase precursors into a polymer template. For standard BCP templates, such as poly(methyl methacrylate)/polystyrene (PMMA/PS) and poly(vinyl pyridine)/polystyrene (PVP/PS), this infiltration depth value is ~40 nm.5,6 The swelling of the BCP template in a polar solvent (e.g., ethanol) increases the possible infiltration depth significantly through the introduction of additional porosity channels.7 Quartz crystal microbalance (QCM) studies confirmed high interconnectivity of the resulting pores in inorganic structures prepared via swelling-assisted SIS.7 Swelling-based modification of the SIS approach enabled its use for the design of single-layer and multilayered antireflective alumina coatings on glass with reduced Fresnel reflection down to 0.1% over a broad spectral range.6 Additionally, highly porous alumina coatings obtained by polymer swelling-assisted SIS revealed excellent properties for humidity sensing.8

However, although the synthesis of highly porous single component structures is possible via a number of traditional methods, fabrication of multicomponent heterostructures is challenging. Typically, their synthesis is based on the mechanical mixing of several components or on depositing of the additional constituents inside the porous templates, e.g., zeolites.9–12 Despite progress in the encapsulation of nanoparticles (NPs) in the cages and channels of the zeolites, the efficient synthesis of the NPs uniformly distributed inside the
porous matrix with sizes less than 4.5 nm is still very challenging. For example, aggregation and sintering of metal species under crystallization conditions of zeolites or during utilization of heterostructures at high temperatures present a serious problem.13−16

Meanwhile, highly porous multicomponent heterostructures with easily accessible catalytic centers are of great interest for catalysis.17,18 The development of highly reactive catalysts for the conversion of combustion reaction gasses has remained an active research area over decades.19 Catalytic converters substantially reduce the hazardous gas emission from combustion engines.20,21 Traditional catalytic systems employ precious metals immobilized at the surface of the nonreactive ceramic matrix, typically alumina.22 For this, palladium or platinum NPs are diluted into alumina to minimize sintering of NPs and prevent degradation in the catalytic activity.23 Supported palladium catalysts exhibit great durability and excellent activity related to the presence of a palladium oxide phase.24,25

Atomic layer deposition (ALD) and its modifications are the methods extensively used for improving the performance of catalytic systems.14,26 Mass transport to the catalytic centers can occur via micropores in thick dense alumina coatings formed on the curved surface of the catalysts. However, recently it was shown that even incomplete monolayers of titania and zirconia deposited by solution ALD27 resulted in a remarkable improvement of commercial automotive three-way catalysts.20 Our study was inspired by the significant improvement in the performance of the catalysts covered with protective coatings deposited via ALD and its modifications and by the ability of SIS to generate the highly porous materials with increased mass transport. In contrast to classical ALD and solution ALD enabling deposition of two-dimensional atomic monolayers on inorganic surfaces from gas and solution phase precursors, respectively, SIS creates the possibility to rapidly generate three-dimensional (3D) inorganic structures. We explore the possibility to in situ synthesize functional centers simultaneously with the synthesis of inorganic support by combining the absorption of the corresponding precursors from the solution and gas phases in the same template.

Here, we demonstrate that chemical infiltration of the BCP with metal precursors (metal acetylacetonates) dissolved in a swelling solution followed by SIS can be used to synthesize catalytically active NPs incorporated inside a highly porous alumina matrix. The amount of the infiltrated inorganic precursor, which determines the final NP loading, can be controlled by tuning the precursor concentration in the solvent used for the BCP swelling. We show that thermal annealing removes the polymer template, leaving 4.3 nm PdO NPs uniformly dispersed in the porous alumina matrix. We also demonstrate that NPs can be directly introduced into the BCP. Polymer removal after swelling and alumina infiltration of the NPs-modified BCP template allows the synthesis of highly porous heterostructures with highly accessible surfaces of incorporated NPs. Both approaches allow the synthesis of multicomponent heterostructures with a promising performance in the conversion of methane and carbon monoxide gases. Our results show that swelling-based SIS provides a promising route toward the robust synthesis of multicomponent structures.

2. EXPERIMENTAL PROCEDURE

2.1. Sample Preparation. The samples of palladium oxide nanoparticles incorporated in the amorphous alumina matrix were synthesized using a two-step infiltration process. Polystyrene-block-poly(vinyl pyridine) (PS-b-P4VP) polymer powders with molar weight 75k−25k were purchased from the Polymer Source Inc. The powders were dissolved in toluene at 3 wt % concentration following two steps of filtration through 0.4 and 0.2 μm sized filters to remove any large agglomerates. To prepare larger amounts of the samples, we used a paper filter (Whatman, Grade 1) as a support matrix for the polymer template during the swelling and infiltration steps. Paper filters were immersed in the polymer solution and exposed to 30 min of sonication to absorb the polymer inside the cellulose matrix. The samples were dried afterward using a hot plate at 100 °C for 1 h. For the synthesis of heterostructures using preformed Pd NPs, we mixed colloidal Pd NPs dispersed in toluene with the toluene-based polymer solution. The resulting loading of Pd in such samples after the alumina infiltration and polymer removal was ∼1 wt %.

2.2. Chemical Infiltration from Swelling Solution. Swelling-based infiltration (SBI) of the BCP was used to synthesize NPs in the matrix itself. A solution of the palladium acetylacetonate, Pd(acac)2, in ethanol at different concentrations (from 0.05 wt % up to 1 wt % concentration) was used to initiate swelling-based infiltration of the material inside the polar polymer domains sensitive to swelling in ethanol. For this, the polymer−palladium samples were immersed in the Pd(acac)2 solution heated to 75 °C for 1 h. The temperature of the swelling was selected based on the higher swelling rates of the polymer at such elevated temperature.28 After 1 h, the samples were carefully removed from the solution and dried in the fume hood at room temperature for at least 2−3 h. The low temperature of drying was used to prevent the collapse of the swelling-introduced porosity in the polymers.

2.3. Synthesis of Pd NPs. The 4 nm Pd NPs were synthesized according to the previously reported procedure.29 The preformed NPs were then mixed with the polymer−in-toluene solution.

2.4. Vapor-Phase Infiltration. Next, the infiltration of alumina in the polymer was performed using sequential infiltration synthesis in an atomic layer deposition system (Cambridge ALD system). The polymer-based template was exposed to 5 cycles of trimethylaluminum (TMA) and water exposure, following the previously described procedure. The samples were placed on a stainless steel tray inside the ALD chamber at 90 °C to avoid melting of swelling-formed predefined polymer structures. Nitrogen flow (100 sccm) was introduced to the chamber for 30 min prior to the infiltration. One SIS cycle was performed as: 10 mTorr of the TMA precursor was introduced with 20 sccm nitrogen flow into the reactor for 400 s; after the predetermined time, when the infiltration of the polymer occurs, the excess of the reactant was evacuated and followed by introducing of 10 mTorr of H2O for 120 s; the chamber was then purged with 100 sccm of nitrogen to remove non-infiltrated byproducts.

2.5. Polymer Removal. After the infiltration, the polymer template was removed by burning at 450 °C in oxygen flow (20 sccm) using a ThermoFisher tube furnace. Additional tested polymer removal procedures include UV ozone cleaner and burning at a higher temperature of 600 °C. High-temperature annealing in oxygen also enabled complete removal of the paper filter for the following catalytic activity analysis.

2.6. Characterization. QCM technique was used for the quantitative analysis of the material infiltration process. The PS-b-P4VP polymer (3 wt % solution) in toluene was spin-coated on AT-cut QCM crystals (resonant frequency ~5 MHz) with titanium-coated electrodes to produce a thin uniform film of thickness ~200 nm. The changes in the resonant frequency and mechanical resistance of the QCM film fixed in a specifically designed Teflon holder during different stages of the process were monitored using the SRS QCM200 system. The change in the resonant frequency of the QCM oscillations allows to judge about the changes in the mass of the polymer film and, based on this, estimate the amount of material infiltrated.29−31
AFM measurements were performed to evaluate the changes in the morphology of the PS-b-P4VP polymer during swelling in ethanol and without the Pd(acac)2 precursor added. The samples were dried after the swelling under the fume hood for 2 h prior to the measurements. The images were acquired by an AFM Veeco Microscope at ambient air conditions (relative humidity ~30%) using a silicon tip with k ~ 0.3 N/m (provided by Ted Pella Inc.) in the contact mode. The height profile measurements were performed for the area of 1 μm × 1 μm with the scanning speed of 1 Hz (1 μm/s scanning speed).

Transmission electron microscopy (TEM) analysis was performed using either a JEOL 2100F microscope or an FEI Tecnai operating at 300 kV on the samples crushed and deposited on the carbon mesh TEM grid. Chemical modification of the polymers during swelling and SIS was evaluated using a Nicolet 6700 Fourier transformation infrared spectrometer (FTIR) with 700–4000 cm⁻¹ spectral range. 2.7. Catalytic Activity. The catalyst bed was prepared in a U-shaped quartz microreactor with an internal diameter of 10 mm. The bed was prepared by cutting each membrane approximately into quarters and placed in between 100 mg layers of calcined Al₂O₃, all of which rested in between two layers of calcined and acid-cleaned granular quartz (quartz/Al₂O₃/membrane/Al₂O₃/quartz). In a control experiment to check for hot spots, no differences were observed whether the membrane was sliced into quarters or finely ground into pieces, which were directly mixed with the Al₂O₃ diluent.

The reactor was heated by a square furnace (Micromeritics), and the catalyst temperature was monitored using a K-type thermocouple inserted inside the reactor, touching the catalytic bed. All experiments were conducted at a total pressure of 1 atm.

The reactant mixture composition was controlled by varying the flow rates of CH₄(5%)/Ar, O₂(5%)/Ar, CO(5%)/Ar, and Ar (all purified mixtures with purity >99.999% from Airgas). The following procedure represents standard reaction conditions. The experimental points were taken every 0.5 °C. With no in situ pretreatment, unless stated, reaction gas mixtures were first stabilized, whereas the catalyst was held under a 20 mL/min flow of pure Ar, at which point they were then introduced into the reactor. Ramping from room temperature to 275 °C at 5 °C/min, CO oxidation ignition curves were performed with 0.5% CO, 4.0% O₂, and 95.5% Ar, at a total flow rate of 20 mL/min. Next, at 275 °C, the reactor was switched to Ar flow at 20 mL/min as CH₄ oxidation gases stabilized, with 0.5% CH₄, 4.0% O₂, and 95.5% Ar, at a total flow rate of 20 mL/min. At that point, the reaction gases were introduced to the catalyst bed, and the catalyst was ramped from 275 to 575 °C at 10 °C/min. Finally, the reactor was cooled down from 575 °C to room temperature (rt) at ~50 °C/min under 20 mL/min flowing Ar to preserve the catalyst state and structure under operating conditions. For methane combustion tests (with or without water), the flow rate was estimated to be 23 mL/min or 1380 mL/h; for CO oxidation, the flow rate was 25 mL/min or 1500 mL/h; and for methane partial oxidation, the flow rate was 18 mL/min or 1080 mL/h. Typical catalyst mass introduced to the reactor was ~2–3 mg catalyst. As a result, the gas hourly space velocities were ~460 000 mL/h/gcat for methane combustion, ~500 000 mL/h/gcat for CO oxidation, and ~360 000 mL/h/gcat for methane partial oxidation. For the effects of pretreatment temperature and environment on CO oxidation and CH₄ combustion reactions, experiments were done sequentially with stated in situ pretreatments in between catalytic tests. For all experiments, reactor effluent was measured using an online mass spectrometer (Hiden HPR-20).

3. RESULTS AND DISCUSSION

3.1. Chemical Infiltration of the BCP with an Inorganic Precursor Followed by Synthesis of Highly Porous Alumina Matrix: Swelling-Based Infiltration Method (SBI). Here, we demonstrate the possibility to design multicomponent heterostructures that enable a significant mass transport through the porous network and provide high surface access to functional centers. The proposed synthetic concept includes: (i) deposition of the polymer template in a form of conformal coatings or infiltrated 3D matrices; (ii) two infiltration steps, such as chemical infiltration of the inorganic precursor from the corresponding solution that is also a swelling agent of the BCP template, followed by the infiltration of the alumina precursors from the gas phase during the SIS process; and (iii) oxidative removal of the polymer template (Figure 1). Our study primarily focuses on the synthesis of palladium-based nanoparticles embedded in alumina matrix as a model system. Pd-based nanostructures, in particular PdO NPs deposited on alumina, are very recognized catalytic systems in conversion reactions. The activity of PdO in methane oxidation originates as a result of the activation of the C–H methane bond through sigma-bond metathesis. In turn, the CO oxidation can occur according to Langmuir–Hinshelwood, Eley–Rideal, or Mars and Van Krevelen mechanisms, depending on the reaction conditions. Catalytic tests were used here to estimate the accessibility of the catalytic centers in synthesized heterostructures via two-step infiltration of block co-polymers. We used Pd(acac)₂ as a chemical infiltration precursor for the Pd-based constituent since it is commonly used in the synthesis of Pd-based catalysts. TMA was used as a precursor for alumina SIS.

To tune the loading of palladium in the alumina matrix samples, we used different concentrations of Pd(acac)₂ in ethanol: 0.05, 0.1, 0.5, and 1 wt %. Further increase in the concentration of Pd(acac)₂ is limited by its dissolution in ethanol. The mass increase during the Pd(acac)₂ infiltration and during SIS was analyzed using the QCM technique since this technique captures dynamics of the coating evolution and quantitatively characterizes small changes in the film mass. As it is evidenced from Figure 2a, a higher concentration of Pd(acac)₂ in ethanol results in a larger absorbed amount. Also, QCM data show that subsequent gas-phase SIS-based alumina infiltration capacity is significantly affected by the absorption of the Pd(acac)₂ suggesting that the reactive sites for the TMA absorption and
for the SBI are similar. Changes in the frequency and mechanical resistance of the QCM oscillations (Figure 2b,c, correspondingly) during swelling-induced infiltration indicate that although swollen with ethanol, the BCP exhibits viscous-like behavior leading to higher mechanical resistance of the oscillations; meanwhile, the infiltration of Pd(acac)$_2$ mechanically strengthens the polymer leading to a decrease in delta resistance over time. The monitoring of the evolution of the polymer template in the presence of different concentrations of the Pd(acac)$_2$ revealed that 1 wt % of Pd(acac)$_2$ minimizes the porosity of the swollen BCP template by clogging the pores (Figure 2e–h). Based on the QCM and AFM results (Figure 2), we further selected 0.5 wt % concentration of the Pd(acac)$_2$. This concentration results in ∼10 wt % of palladium loading after conversion of Pd(acac)$_2$ into PdO in the resulting composite. The loadings of commercial catalytic Pd or PdO NPs in alumina typically vary in the range between 1 and 10 wt %. To probe the thermal stability of the prepared materials, we focus our study on heterostructures with high loading that are known to be prone to sintering. Detailed FTIR analysis (Figure 3) of the infiltration stages was performed to identify the reactive sites for the SBI and SIS infiltration stages. The swelling in pure ethanol increases absorption for CH bending of CH$_3$ and CH$_2$ groups at 1580, 1500, 1450, and 1410 cm$^{-1}$ that are the major sites for alumina infiltration.$^5$ However, when Pd(acac)$_2$ is dissolved in ethanol, absorbance peak at ∼3050 cm$^{-1}$ disappears, and the peak intensity at 1610 cm$^{-1}$ reduces. These changes in the FTIR spectrum suggest that Pd(acac)$_2$ suppresses stretching C=N bonds.$^{39}$ Additionally, the intensity increase of the absorbance peaks in the range of 1665–1750 cm$^{-1}$ indicates the presence of ketone functional groups from acetylacetone absorption. The reduction in the intensity of ketone peaks after SIS indicates that Pd(acac)$_2$ undergoes partial hydrolysis upon reacting with water vapors. The formation of PdO is fully completed after removal of the polymer by annealing in an oxygen-rich atmosphere. The FTIR data indicate that palladium precursor and alumina precursor compete for the same infiltration sites of the PS-b-P4VP template. After the infiltration steps, the polymer template and residual organic material were removed using thermally assisted burning in an
oxygen atmosphere and using an UV ozone cleaning procedure. The resulting samples were analyzed with TEM (Figure 4).

Figure 4. TEM images and corresponding electron diffraction patterns of the infiltrated samples after removal of the polymer using: UV ozone cleaning (a, d, g), thermal annealing (450 °C) in oxygen flow (b, e, h), and 600 °C thermal annealing in oxygen flow (c, f, i). The dark spots are the SBI PdO NPs (1.5 ± 0.2 nm PdO in the case of UV ozone cleaning, 4.3 ± 0.2 nm PdO in the case of 450 °C thermal annealing, and 4.3 ± 0.4 nm PdO in the case of 600 °C thermal annealing) inside the lighter amorphous alumina matrix. Different thermal removal process approaches demonstrate changes in the size of the nanoparticles.

It is worth noting that ABC triblock polymer templates have been previously used to synthesize porous networks of metals such as Au, Ni, Cu, etc.8–44 Nanoporous polymer templates with gyroid nanochannels were generated prior to the deposition of the metals by the degradation of the BCP. For example, in the case of polystyrene-b-poly(l-lactide) (PS-PLLA) BCP template, PLLA domains were removed by hydrolysis forming a porous network of nonpolar domains. Nucleation and growth of metals occurred in the nonpolar (e.g., PS) domains in the presence of the reducing agents.40,41 In our approach, the adsorption of the metal precursors from the solution and gas phase takes place at the functional groups belonging to the polymer domains, whereas the template is then removed completely by oxidative annealing.

The removal of the polymer template by UV at room temperature (Figure 4a,d) results in the formation of smaller NPs uniformly distributed in the alumina matrix containing some traces of organic species.8 Thermally assisted removal of the polymer at 450 °C leads to the formation of larger size nanoparticles (4.3 ± 0.2 nm). Importantly, further increase in temperature up to 600 °C does not affect the size distribution of NPs, suggesting that the alumina matrix helps to prevent diffusion of the material (Supporting Information, Figure S1). Electron diffraction analysis of the samples confirms the amorphous nature of the alumina matrix (Supporting Information, Figure S2).7,8,45 and reveals a cubic crystalline structure of synthesized NPs after annealing at 450 and 600 °C.46 XPS analysis of the samples after annealing at 450 °C indicates the full conversion of Pd(acac)2 into PdO NPs as captured from the Pd 3d detailed scan (Figure 5). QCM data indicate that the mass gain during Pd(acac)2 infiltration step and alumina infiltration step are nearly the same (Figure 2). Burning of the polymer film results in substantial lowering of the palladium compound mass due to the removal of the acetylacetonate groups. The presence of both Pd and PdO peaks in XPS Pd 3d detailed scan spectra suggests that the resulting NPs are synthesized in the form of crystalline Pd surrounded by the amorphous PdO shell. The analysis of the peaks indicates that the relative ratio of oxidized to metallic Pd in the samples is ~80:20. This suggestion is also confirmed by the well-defined electron diffraction pattern matching the face-centered cubic lattice of Pd77 (Figure 4).

To estimate the stability of the structures and accessibility of the Pd/PdO NPs in the alumina matrix synthesized via SBI and SIS followed by thermal annealing at 450 °C, we tested their catalytic performance in CO oxidation and methane (CH4) combustion reactions in which Pd is known to demonstrate catalytic activity (Figure 6). To scale up the synthesis for catalytic tests, we infiltrated a paper filter with the solution of the BCP while sonicking. The paper filter with the deposited PS-b-P4VP BCP was then placed into the ethanol solution of 0.5 wt % of Pd(acac)2, which, as estimated from the QCM analysis, should lead to 10 wt % loading of PdO in alumina. The catalytic results, reported in terms of light-off curves (Figure 6), demonstrate that this synthesis method may be used to create porous structures with embedded catalysts for emission control reactions.

In the case of CO oxidation (Figure 6a), the samples without pretreatment (see Experimental Section for details) demonstrate complete CO oxidation by ~180 °C, whereas pretreatments in both oxygen- and hydrogen-containing atmospheres lower the complete oxidation temperature to ~165 °C. These results are in agreement with the data reported for alumina-supported Pd.88 A steep increase in the conversion observed during light-off is consistent with CO coverage of the catalytic surface at low temperature followed by oxygen activation and light-off.

In the case of methane combustion (Figure 6b), the samples were also active and demonstrated 100% methane conversion.
observed changes in the activity of the samples, indicate that our materials have their stability across the treatments. The physisorption data high catalytic activity of synthesized heterostructures (Figures 4e,f and 6d).15 We attribute the high-temperature stability of these materials, as evidenced by overlaying CH$_4$ combustion curves, to the effective sequestration of palladium materials within the alumina matrix while still maintaining the porous network, which allows the reactive gases to access the catalytic surface of the heterostructure. The catalytic tests confirm the accessibility of PdO NPs embedded in alumina matrix to the reactive gases.

The two-step infiltration approach based on SBI followed by SIS is versatile and can be used for the synthesis of other materials such as CoO$_x$ NPs and RuO$_x$ NPs in the alumina matrix (Supporting Information, Figure S4). High stability against sintering of the NPs embedded in alumina enables the catalytic activity of RuO$_x$ NPs in the alumina sample in the methane partial oxidation reaction (Supporting Information, Figure S5).

3.2. Synthesis of Pd-Based Heterostructure Using Preformed NPs Dispersed in the BCP Template. We also studied the applicability of our approach for the synthesis of porous heterostructures using the preformed NPs. The NPs synthesized in a nonpolar organic solvent can be dispersed in the solution of the BCP or triblock polymers allowing the patterning of NPs.44,50 The use of the preformed colloidal NPs allows for additional control of the resulting material systems with NPs of various shapes, sizes, and compositions. The NPs stabilized by hydrophobic coatings are dispersed in the nonpolar domains of the BCP (i.e., polystyrene). After the swelling of the BCP template in ethanol and deposition of alumina using SIS followed by thermal annealing to remove the organic material, heterostructures consisting of NPs interfaced with the porous matrix are generated (Figure 7).

Here, we demonstrate that the heterostructures similar to those obtained by SBI followed by SIS can be obtained using the preformed Pd NPs. However, since Pd NPs stabilized by oleic acid are initially distributed in nonpolar PS domains, which do not react with TMA in the SIS process, the interfacing of NPs and alumina takes place upon removal of the polymer template at elevated temperature (450 °C) leading to a partial agglomeration of NPs (Figure 8b) during the annealing step. XPS data indicating that the presence of Pd (2+) after oxidative annealing of the sample (Figure 8d) suggests the NP oxidation. Despite some sintering during the annealing step, such heterostructures also reveal a good catalytic activity in CH$_4$ and CO oxidation reactions (Figure 9). Importantly, the TEM data for the sample obtained using the preformed Pd NPs after the methane combustion tests up to 550 °C do not reveal noticeable sintering of NPs (Figures 8 and S6).

The catalytic activity data of the samples synthesized with the preformed Pd NPs and SBI followed by SIS is compared in Figure 9. The results suggest that the SBI process allows the higher activity of the samples, which is attributed to better stability of the catalytic NPs enclosed in the alumina matrix.

4. CONCLUSIONS
We proposed a block-co-polymer-assisted approach for scalable synthesis of the porous heterostructures of NPs
can be combined in one heterostructure. Our approach can be used to prepare conformal coatings, free-standing membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix. We believe that the block-co-polymer-assisted approach can be applied for the synthesis of a broad range of highly porous heterostructures with compositions relevant for catalysis, sensing, optics, or design of neural networks.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b09991.

Histograms summarizing the size distribution of the synthesized SBI NPs (Figure S1); TEM image and the corresponding electron diffraction analysis of the alumina films synthesized by SIS (Figure S2); physisorption data on the SBI PdO NPs in porous alumina samples (Figure S3); TEM images of the SBI NPs (cobalt oxide and ruthenium oxide) in alumina (Figure S4); catalytic activity and selectivity of the SBI RuO$_2$ NPs in alumina (Figure S5); TEM image of premixed Pd NPs in alumina after catalysis tests (Figure S6) (PDF)

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Notes
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