Hydrogenation of Toluene to Methyl Cyclohexane over PtRh Bimetallic Nanoparticle-Encaged Hollow Mesoporous Silica Catalytic Nanoreactors

Kaijie Li, † Heliang An, † Peijian Yan, Caoping Yang, Tao Xiao, Junyou Wang, and Shenghu Zhou *

ABSTRACT: PtRh bimetallic nanoparticle (NP)-encaged hollow mesoporous silica nanoreactors (PtRh@HMSNs) are prepared by employing metal-ion-containing charge-driven polymer micelles as templates. These nanoreactors feature ∼1−2 nm PtRh NPs in ∼11 nm hollow cavities of HMSNs. Among various PtRh@HMSNs, Pt0.77Rh1@HMSNs show the best catalytic performance for toluene hydrogenation. Under 30 °C, atmospheric H2 pressure, and a toluene/(Pt+Rh) molar ratio of 200/1, Pt0.77Rh1@HMSNs reach 100.0% of methyl cyclohexane yield and demonstrate a much better catalytic performance than monometallic Pt@HMSNs and Rh@HMSNs and their physical mixtures. Moreover, Pt0.77Rh1@HMSNs exhibit a good catalytic stability during recycling experiments. The enhanced performance of Pt0.77Rh1@HMSNs is ascribed to the interaction between Pt and Rh, the beneficial effect of the relatively large mesoporous channels for mass transfer, as well as the confinement effect of functional NPs inside hollow cavities.

1. INTRODUCTION

Hydrogen is well recognized as a clean and environmentally friendly energy source. However, due to its characteristics of large diffusion coefficient, wide explosion limit, and low ignition temperature, H2 energy has not been used on a large scale. To safely use H2 energy, storage and transport of hydrogen securely and expeditiously are prerequisites. Instead of H2 gas, liquid organic hydrogen carriers, such as benzene/cyclohexane and toluene/methyl cyclohexane, which can safely store and release H2 and are considered as alternative H2 energy sources. Among these mentioned chemicals, liquid organic hydrogen carriers are composed of unsaturated aromatics and their corresponding liquid organic hydrogen carriers, such as benzene/cyclohexane and toluene/methyl cyclohexane, which can be hydrogenated and dehydrogenated reversibly without destroying the main structure of the carbon ring. Due to their easy transportation and low toxicity, toluene/methyl cyclohexane is a good candidate for H2 storage and utilization.

Transition metals including Ni, Pt, Ru, and Rh have been studied in hydrogenation of toluene to methyl cyclohexane. To achieve high yields of methyl cyclohexane, non-noble metals such as Ni catalysts usually require relatively high reaction temperatures, while noble metals such as Rh can perform hydrogenation under room temperature and atmospheric H2 pressure. In addition, PtRh bimetallic catalysts are selected for toluene hydrogenation because they could have a better performance due to the synergistic effect. For instance, Miyamura and co-workers reported a polysilane-immobilized PtRh catalyst for hydrogenation of toluene to methyl cyclohexane with a high yield (>99%) under the reaction conditions of 50 °C, 0.1 MPa of H2, and 20 h. Al2O3-supported PtRh catalysts achieve a yield of 90% at 22 °C, 0.1 MPa H2, and 7 h. The underlying principle is to utilize the metal-metal interaction to adjust the electronic state of the active metals resulting in the enhanced catalytic performance of bimetallic systems.

In the last decades, hollow nanoreactors have been considered as good supports due to the confinement effect related to their small size and encapsulation of metal nanoparticles (NPs) into mesoporous silica, which have attracted more attention. Due to the protection effect of mesoporous silica shells, the synthesized materials such as Pt@mSiO2 show a significantly enhanced catalytic stability for high temperature reactions. Moreover, mesoporous silica shells can facilitate the mass transportation for reactions relative to the microporous materials. Recently, our group reported the synthesis of hollow mesoporous nanoreactors with encaged functional NPs using charge-driven micelles as templates.
protection of mesoporous silica shells, the relatively large mesoporous channels (≈8−10 nm), and the confinement effect of functional NPs inside hollow cavities, the catalytic efficiency and stability have been greatly improved.29−31

In this work, we extended the charge-driven template method to synthesize hollow mesoporous nanoreactors with encaged PtRh bimetallic NPs (PtRh@HMSNs) for hydrogenation of toluene to methyl cyclohexane. Scheme 1 presents the synthetic procedures for PtRh@HMSNs, which feature tiny PtRh NPs (≈1−2 nm) in the ≈11 nm hollow cavities of ≈24 nm of mesoporous silica nanospheres. Pt0.77Rh1@HMSNs exhibit a high yield of >99% of methyl cyclohexane for toluene hydrogenation under the reaction conditions of 30 °C and 0.1 MPa of H2, showing a much better performance than monometallic Pt@HMSNs and Rh@HMSNs and their physical mixtures. The catalytic enhancement of Pt0.77Rh1@HMSNs is ascribed to the Pt−Rh interaction and the confinement effect of functional PtRh bimetallic NPs inside hollow cavities.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. In the synthesis, negatively charged coordination complex networks were formed by the coordination of L3 and metal ions (Pt2+ and Rh3+), which further combine with the positively charged diblock copolymer P2MVP128-b-PEO477 to give metal-ion-containing core−shell-like micelles by electrostatic attraction. Hydrolysis of tetraethyl orthosilicate (TEOS) will deposit silica onto micelles to give silicified micelles. After calcination and reduction of silicified micelles, hollow mesoporous Pt\textsubscript{x}Rh\textsubscript{y}@HMSNs are obtained. During the synthesis, pH values of the solution are the key parameters for the synthesis of such hollow mesoporous nanoreactors. Generally, lower pH values will protonate L3 ligands (decreasing the coordination of metal ions and L3 ligands), while higher pH values will favor deprotonation of L3 ligands but will cause the formation of metal hydroxides. Therefore, a pH value of 4.15 is selected in this work.

Figure 1 presents transmission electron microscopy (TEM) images of various HMSNs. The silicified micelles in Figure 1a...
exhibit the structures of connected solid nanospheres, which consist of silica shells and metal-ion-containing micelles. As shown in Figure 1b−f, distinct hollow nanoreactors with small NPs inside their hollow cavities are observed due to the removal of organic components by calcination and reduction. Apparently, monometallic HMSNs exhibit relatively large hollow cavities and whole nanoreactors (Figure 1b,c). Moreover, the average size of inner NPs of Pt@HMSNs is larger than those of Rh@HMSNs and Pt$_{0.77}$Rh$_1$@HMSNs. Figure S1 shows size analyses of various HMSNs. Pt@HMSNs and Rh@HMSNs (Figure S1b,c) demonstrate ∼17−22 nm hollow cavities and ∼31−37 nm whole nanoreactors, while bimetallic Pt$_{x}$Rh$_y$@HMSNs (Figure S1d−f) present smaller hollow cavities/whole nanoreactors (∼11−12/∼24−25 nm), possibly due to the formation of smaller metal-ion-containing micelles by use of two metal ions. Figure S2 presents the size analyses of inner NPs of various HMSNs. The inner Pt particle sizes shown in Figure S2a are ∼3.7 nm, while the particle sizes of Rh and Pt$_{x}$Rh$_y$ NPs are ∼1−2 nm (Figure S2b−e), suggesting that the incorporation of Rh into Pt will decrease the particle size.

Figure 2a shows X-ray diffraction (XRD) patterns of Pt@HMSNs, Rh@HMSNs, and Pt$_{0.77}$Rh$_1$@HMSNs. The diffraction at ∼22 2θ degree is ascribed to SiO$_2$. As shown in Figure 2a, Pt@HMSNs show distinct fcc Pt diffractions, while those of Rh@HMSNs and Pt$_{0.77}$Rh$_1$@HMSNs present weak or even no obvious metal diffractions. These weak diffractions of Rh@HMSNs and Pt$_{0.77}$Rh$_1$@HMSNs are consistent with their extremely small sizes (∼1 nm, Figure S2b,c). Figure 2b presents the energy-dispersive spectroscopy (EDS) measurement of Pt$_{0.77}$Rh$_1$@HMSNs. The copresence of Rh and Pt in Pt$_{0.77}$Rh$_1$@HMSNs is confirmed. Moreover, inductively coupled plasma-atomic emission spectroscopy (ICP-OES) measurements of various HMSNs further confirm the copresence of Pt and Rh in Pt$_{0.77}$Rh$_1$@HMSNs (will discuss later).

H$_2$-temperature-programmed reduction (TPR) studies of Pt$_{0.77}$Rh$_1$@HMSNs calcined at 500 °C are shown in Figure S3a. Two distinct peaks centered at 85 and 356 °C are observed, where the former is assigned to the reduction of Rh$_x$O$_y$ to metallic Rh and the latter can be ascribed to the reducibility of supports by H$_2$ spillover in the presence of Rh or the Rh$_x$O$_y$ species having strong interaction with supports.32−34 It is well known that metallic Pt is formed by calcination at high temperatures. Therefore, no reduction peak for Pt oxides is reasonable, which is also consistent with previous reports.35,36 A previous study reported that PtRh alloys show (111) diffraction at ∼39.9 2θ degree,37 which is very close to 39.7 2θ degree of Pt (111) diffraction. Because the inner NPs of Pt$_{0.77}$Rh$_1$@HMSNs are extremely small (∼1 nm), the PtRh alloy formation cannot be confirmed by XRD studies. Moreover, the Pt$_{0.77}$Rh$_1$ NPs are encaged inside hollow cavities; so, X-ray photoelectron spectroscopy (XPS) studies are also not applicable (shown in Figure S3b,c, high noise/signal ratios for Pt and Rh). The formation of bimetallic PtRh NPs can only be inferred from indirect evidence. As shown in Figure 2b, EDS measurements show the copresence of Pt and Rh in Pt$_{0.77}$Rh$_1$@HMSNs, confirming the incorporation of Pt and Rh into the HMSNs. Moreover, the size of inner NPs of Pt$_{0.77}$Rh$_1$@HMSNs is significantly smaller than those of Pt@HMSNs, suggesting the effect of Rh incorporation on particle sizes. Furthermore, Pt$_{0.77}$Rh$_1$@HMSNs show greatly enhanced catalytic performance relative to Rh@HMSNs, Pt@HMSNs, and their physical mixtures (will discuss later), suggesting the promoting effect of Pt on Rh (Pt@HMSNs show no observable activity). Therefore, it is speculated that the
encaged NPs of Pt₀.₇₇Rh₁@HMSNs are most likely bimetallic PtRh NPs.

Figure 3a shows thermogravimetry/differential thermal analysis (TG/DTA) curves of the precursors of Pt₀.₇₇Rh₁@HMSNs (before calcination). The DTA curve has a sharp peak near 410 °C, indicating that the organic components are dramatically oxidized around this temperature. This sharp peak in the DTA curve is consistent with the obvious mass loss in the same temperature range in the TG curve. Figure 3b presents the Fourier transform infrared (FT-IR) spectra of Pt₀.₇₇Rh₁@HMSNs calcined at different temperatures. As shown in the black spectrum, the peaks from 1360 to 1470 cm⁻¹ are clearly visible and can be assigned to the in-plane bending vibration of the C–H bond, while the peaks at 1596 and 2910 cm⁻¹ are attributed to the asymmetric stretching vibration of carboxylic groups of L₃ ligands and methylene of polymer, respectively. After calcination at 300 °C, the sample shows trace signals of the above-mentioned peaks (orange spectra), indicating incomplete removal of organic components at 300 °C. Although the sharp peak of the DTA curve is at 410 °C, it can be seen from the blue spectrum in Figure 3b that the organic components are completely removed after calcination at 400 °C for 3 h. Moreover, the spectrum calcined at 500 °C is the same as that at 400 °C, further confirming the complete removal of organic components by calcination at 400 °C for 3 h. Furthermore, the weight of Pt₀.₇₇Rh₁@HMSNs calcined at 700 °C for 3 h is only 0.4% lower than that of Pt₀.₇₇Rh₁@HMSNs calcined at 400 °C for 3 h, once again indicating a complete removal of organic components by calcination at 400 °C for 3 h.

Figure 4 shows the N₂ adsorption–desorption isotherms and pore size distributions of Pt₀.₇₇Rh₁@HMSNs calcined at different temperatures and subsequently reduced at 200 °C by H₂. As shown in Figure 4a, type IV isotherms with characteristic hysteresis loops are obvious for all tested HAMSNs, confirming the formation of mesopores. The formation of aggregation voids between connected nanoreactors is proved by the sharp absorption at ~P/P₀ of 0.9, and the enforced closures at ~P/P₀ of 0.45 indicate the presence of hollow cavities. Although the hysteresis loops become smaller with the increase of calcination temperature from 400 to 700 °C, the hysteresis loop is still visible at calcination of 700 °C. As shown in Figure S4, distinct hollow nanoreactors with extremely small NPs inside cavities are still observed even at the calcination temperature of 700 °C, which is consistent with its N₂ adsorption–desorption isotherms. Figure 4b shows the corresponding pore size distributions of Pt₀.₇₇Rh₁@HMSNs, where mesoporous pores between 8 and 10 nm are observed. It is worth mentioning here that these relatively large mesoporous channels could facilitate the mass transfer for catalytic reactions.

Table 1 summarizes the textural properties of Pt₀.₇₇Rh₁@HMSNs calcined at different temperatures and subsequently reduced at 200 °C by H₂. As the calcination temperature increases from 400 to 700 °C, the Brunauer–Emmett–Teller (BET) specific surface areas of Pt₀.₇₇Rh₁@HMSNs decrease from 490.4 to 198.9 m²/g, while pore volumes decrease from 0.65 to 0.41 cm³/g in the same calcination temperature range, certainly due to the pore collapse at higher temperatures. The average pore sizes show a slight increase in the same calcination temperature range, due to the decrease of the number of micropores by sintering.

### Table 1. Textural Properties of Pt₀.₇₇Rh₁@HMSNs Prepared by Calcination at Various Temperatures and Subsequent H₂ Reduction at 200 °C

| samples                | S BET (m²/g) | pore volume (cm³/g)¹ | average pore size (nm)² |
|------------------------|--------------|----------------------|-------------------------|
| Pt₀.₇₇Rh₁@HMSNs-400 °C | 490.4        | 0.65                 | 16.3                    |
| Pt₀.₇₇Rh₁@HMSNs-500 °C | 409.4        | 0.59                 | 16.0                    |
| Pt₀.₇₇Rh₁@HMSNs-600 °C | 285.7        | 0.48                 | 17.9                    |
| Pt₀.₇₇Rh₁@HMSNs-700 °C | 198.9        | 0.41                 | 18.8                    |

¹Pore volume is the single point adsorption total pore volume of pores. ²Average pore size is the BHJ adsorption average pore diameter.

The toluene hydrogenation reactions were carried out under the reaction conditions of 30 °C, 0.1 MPa of H₂, and organic solvents. Moreover, catalytic reactions were performed at a molar ratio of toluene/(Pt+Rh) of 200/1. Table 2 summarizes the actual Pt and Rh loadings of various PtₓRhᵧ@HMSNs determined by ICP-OES. To keep the same molar ratio of toluene/(total metal) of 200/1, different weights of catalysts were used since their Pt and Rh loadings are different.

### Table 2. Metal Loadings of Various PtₓRhᵧ@HMSNs Determined by ICP-OES

| samples                | Pt loading (moll%) | Rh loading (moll%) |
|------------------------|--------------------|--------------------|
| Pt₀.₇₇Rh₁@HMSNs-400 °C | 49.6               | 0.4                |
| Pt₀.₇₇Rh₁@HMSNs-500 °C | 40.9               | 0.4                |
| Pt₀.₇₇Rh₁@HMSNs-600 °C | 28.6               | 0.4                |
| Pt₀.₇₇Rh₁@HMSNs-700 °C | 19.9               | 0.4                |

The influences of Pt/Rh ratios of PtₓRhᵧ@HMSNs on their catalytic performance were investigated to correlate the relationship between Pt/Rh ratios and their catalytic activities. In this reaction, the selectivity for methyl cyclohexane is 100.0%. Therefore, the yield of methyl cyclohexane is used, which is the same as the toluene conversion. As shown in Figure 5a, monometallic Pt@HMSNs exhibit no obvious

References:
[1] 64,–65
[2] 65
[3] 66
[4] 67

ACS Omega 2021, 6, 5846–5855
5849
activity (1.2% of methyl cyclohexane yield) for toluene hydrogenation at the selected reaction conditions, which is consistent with a previous work. In contrast, Rh@HMSNs achieve a yield of 66.2% at 2.0 h. With the constant total metal atoms, Pt11.1Rh1@HMSNs and Pt2.5Rh1@HMSNs achieve yields of 17.6 and 61.7% at 2.0 h, respectively, which are lower than that of Rh@HMSNs. However, Pt0.77Rh1@HMSNs attain 100.0% of yield at 2.0 h, showing a much better catalytic performance than that of Rh@HMSNs.

Under the selected reaction conditions, monometallic Pt@HMSNs show no obvious activity, while monometallic Rh@HMSNs demonstrate a good activity, confirming that Rh is a better catalyst than Pt for hydrogenation of toluene. With the same total (Pt+Rh) atoms, the physical mixture of Pt@HMSNs and Rh@HMSNs (the molar ratio of Pt/Rh of 0.77/1) approaches only 18.0% of yield at 2.0 h (Figure S5a), while proper incorporation of Pt atoms into Rh atoms at the Pt/Rh ratio of 0.77/1 results in even better catalytic performance than monometallic Rh@HMSNs, indicating the promoting effect of Pt on Rh. The interaction between Pt and Rh could adjust the electronic state of Rh and thereby improve the catalytic activity. Moreover, the addition of too much Pt into Rh (Pt11.1Rh1@HMSNs) results in the decrease of the activity, possibly due to the excessive dilution of the Rh surface with Pt atoms. Furthermore, the commercial silica-supported Pt0.83Rh1/SiO2 catalysts (nominal Pt/Rh ratio of 0.77/1), prepared by a typical impregnation method and same treatments, show a yield of 8.7% at 2.0 h (Figure S5a), which is much lower than that of Pt0.77Rh1@HMSNs. Figure S5b shows TEM images of Pt0.83Rh1/SiO2, where ∼3.0 nm particles are observed and are larger than those inner NPs of Pt0.77Rh1@HMSNs. It is concluded that Pt0.77Rh1@HMSNs

Table 2. The Actual Metal Loadings of Pt and Rh of PtRxRh1@HMSNs by ICP-OES

| samples \(^{a}\) | nominal Pt/Rh | Pt/Rh by ICP-OES | metal loadings (wt %) |
|-----------------|---------------|-------------------|----------------------|
| Pt@HMSNs       | N/A           | N/A               | Pt 3.8 Rh N/A        |
| Pt11.1Rh1@HMSNs| 3/1           | 11.1/1            | Pt 5.9 Rh 0.28       |
| Pt1.1Rh1@HMSNs | 1/1           | 2.5/1             | Pt 1.7 Rh 0.35       |
| Pt0.77Rh1@HMSNs| 1/3           | 0.77/1            | Pt 1.2 Rh 0.82       |
| Rh@HMSNs       | N/A           | N/A               | Pt N/A Rh 1.6        |

\(^{a}\) All materials were calcined at 500 °C and subsequently reduced at 200 °C.

Figure 5. (a) Effects of the Pt/Rh molar ratios on methyl cyclohexane yields over PtRxRh1@HMSNs; (b) effects of solvents on the catalytic performance over Pt0.77Rh1@HMSNs. All catalysts were calcined at 500 °C and reduced by H2 at 200 °C. Reaction conditions: toluene, 32.9 μL; toluene/(Pt+Rh) molar ratio, 200/1; solvents 10.0 mL; 2-propanol for (a); H2, 0.1 MPa; reaction temperature, 30 °C; and speed of agitation, 500 rpm.

Figure 6. Effects of (a) calcination temperatures and (b) reduction temperatures of Pt0.77Rh1@HMSNs on methyl cyclohexane yields over Pt0.77Rh1@HMSNs. Reduction at 200 °C for (a) and calcination at 500 °C for (b). Reaction conditions: toluene, 32.9 μL; toluene/(Pt+Rh) molar ratio, 200/1; 2-propanol, 10.0 mL; H2, 0.1 MPa; reaction temperature, 30 °C; and speed of agitation, 500 rpm.
possess smaller active NPs due to the coordination method employed and show much better performance than their conventional silica-supported counterparts. In this work, Pt0.77Rh1@HMSNs were selected for further studies since they exhibit the best toluene hydrogenation activity.

It is well known that solvents can provide a unique reaction environment for catalytic reactions to happen. Previous studies have reported that a solvent could influence the dispersion of solid catalysts and also the H₂ solubility. It is mentioned that no obvious reactions occurred with the selected solvents in the blank experiments (only solvents, H₂, and catalysts). As indicated in Figure 5b, the solvents indeed dramatically influence the hydrogenation activity of Pt0.77Rh1@HMSNs. Using acetone, ethanol, and methanol as solvents resulted in only 2.0, 14.8, and 55.3% of yields, respectively, while 2-propanol showed 100.0% of yield for toluene hydrogenation. The detailed explanation for solvent effects is unclear and may be related to the H₂ solubility and/or the dispersion of the catalysts. A previous study has reported that a solvent could influence their catalytic performance. Among various calcination temperatures, calcination at 500 °C can achieve the best catalytic performance for toluene hydrogenation.

Figure 6b shows the effects of reduction temperatures of Pt0.77Rh1@HMSNs on their catalytic performance. All Pt0.77Rh1@HMSNs with different reduction temperatures are previously calcined at 500 °C. As shown in Figure 6b, reduction at 200 °C gives the best performance for toluene hydrogenation. Figure S6 shows TEM images of Pt0.77Rh1@HMSNs with different reduction temperatures. No significant change in particle size is observed, suggesting that the particle size change induced by reductions at different temperatures is not the main reason for the performance difference. Therefore, we speculate that the lower reduction temperature at 100 °C may not form PtRh bimetallic alloy structures. Currently, the reason for the worse performance at higher reduction temperatures ≥250 °C is unclear, possibly due to an unsuitable metal–support interaction at higher reduction temperatures. Moreover, the influence of the weights of Pt0.77Rh1@HMSNs on their catalytic performance was studied. As shown in Figure S7, the yields of methyl cyclohexane at 2.0 h of reaction time first increased with the increase of catalyst weights and attained 100.0% at a reaction time of 1.5 h when the catalyst weight was 14.2 mg (toluene/(Rh + Pt)-154/1). The increase of yields with the increase of catalyst weights is apparently due to the larger amount of catalyst used in the reaction.

The catalytic stability of Pt0.77Rh1@HMSNs with 500 °C calcination and reduction at 200 °C was investigated, and the results are shown in Figure 7. To reduce the loss of the catalyst during the recovery process, the stability experiments were performed under a high toluene/(Pt+Rh) molar ratio of 1000/1 that is 5 times higher than that of the normal tests. After the experiment with a toluene/(Pt+Rh) ratio of 1000/1, the catalysts were collected by centrifugation, washing, and drying for a subsequent normal test at a toluene/(Pt+Rh) ratio of 200/1. Based on the amount of reactants treated, the overall experiments are equal to six cycles of normal experiments, and the reaction time is equal to total reaction time in six typical cycle experiments. As shown in Figure 7a, the hydrogenation reaction at a toluene/(Pt+Rh) ratio of 1000/1 achieves 99.3% of yield at 10.0 h. The turnover frequency (moles of products
per total molar (Pt+Rh) atoms per hour, TOF, h⁻¹) is 99.3 h⁻¹ at a yield of 99.3% (achieved at 10.0 h), which is very close to the TOF of 100 h⁻¹ of the fresh catalyst at 100.0% of yield (achieved at 2.0 h, Figure 5a, blue curve). As shown in Figure 7b, after having treated five times with reactants, the recovered Pt0.77Rh1@HMSNs exhibit a nearly same performance with a 97.9% of yield at 2.0 h as that of the fresh catalysts, showing a superior catalytic stability. This excellent catalytic stability could have originated from their unique structures.

Previous studies have reported the application of hollow mesoporous nanoreactors in various reactions, and a significantly enhanced catalytic performance has been achieved due to the protection and confinement effects of hollow mesoporous nanoreactors. By encaging PtRh NPs into the hollow cavities of mesoporous silica nanoreactors, we can expect increased catalytic stability due to the protection of silica shells. Indeed, no detectable metal in the reaction solution is observed by ICP-OES, confirming the protection of silica shells for inner NPs. Moreover, PtRh@HMSNs have relatively large mesoporous channels with mesopore sizes around 8–10 nm and thereby facilitate the mass transportation during reactions. Furthermore, we speculate that the residence of PtRh NPs inside hollow cavities could increase the collision times between reactants and PtRh NPs, thus enhancing their catalytic efficiency.

3. CONCLUSIONS

In this study, using metal-ion-containing polymer micelles as templates, bimetallic PtRh NP-engaged hollow mesoporous silica nanoreactors are prepared, which feature ~1–2 nm tiny PtRh NPs in ~11 nm hollow cavities of nanoreactors. The synthesized Pt0.77Rh1@HMSNs show a much better toluene hydrogenation activity than monometallic Pt@HMSNs and Rh@HMSNs and their physical mixtures. Under reaction conditions of 30 °C, 0.1 MPa, and a toluene/(Pt+Rh) ratio of 200/1, 100.0% of methyl cyclohexane yield is achieved for toluene hydrogenation at a reaction time of 2.0 h. The enhanced catalytic performance of Pt0.77Rh1@HMSNs is ascribed to the protection effect of silica shells and the confinement effect of functional NPs inside hollow cavities. We believe that such bimetallic NP-engaged hollow mesoporous nanoreactors may find more applications in heterogeneous catalytic reactions, and the synthetic method could be extended to other systems.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Nitric acid (HNO₃, 65–68%) and sodium hydroxide (NaOH, ≥96.0%) were purchased from Shanghai Chemical Reagent Company. Toluen (C₆H₆, ≥99.5%) and acetone (CH₃COCH₃, ≥99.5%) were purchased from General Reagents. Ethanol (AR), methyl cyclohexane (C₈H₁₄, 99.0%), and tetrahydrofuran (C₄H₈O, ≥99.0%) were purchased from Aladdin. Potassium hexachlororhodate (K₂RhCl₆, Rh ≥23.3%) was purchased from Macklin. Methanol (CH₃OH, ≥99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd., while potassium tetrachloroplatinate (K₂PtCl₆, Pt ≥246.4%) and 2-propanol (C₃H₇OH, ≥99.5%) were purchased from Al LAN (Shanghai) Chemical Technology Ltd. and Sun Chemical Technology (Shanghai) Co., Ltd., respectively. P2MVP₁₂₈-b-PEO₄₇₇ (Mₐ/Mₕ = 1.1, Mₕ = 34.5k) was synthesized according to a previously reported work. The positively charged diblock copolymer was obtained by quaternization of P2MVP₁₂₈-b-PEO₄₇₇ by methyl iodide, and the quaternization level is ~90%. 1,3,5-Tris(2,6-dicarboxypyridin-4-yl)methyl) benzene (L₃) was synthesized in based on a previous study. All reagents were used as received.

4.2. Syntheses of Bimetallic Pt₉₇Rh₁@HMSNs and Monometallic Pt@HMSNs and Rh@HMSNs. In the syntheses of Pt₉₇Rh₁@HMSNs, the nomenclature of Pt₉₇Rh₁@HMSNs is based on the real molar ratios of Pt/Rh determined by ICP-OES. The nominal molar ratios of Pt/Rh are significantly larger than the real ratios of Pt/Rh determined by ICP-OES due to the weak coordination between Rh ions and L₃ ligands. Only a small percentage of Rh ions are incorporated into HMSNs, and the uncoordinated Rh ions are left in the solution and will be separated from HMSNs by centrifugation. According to our previous work, the synthesis of Rh@HMSNs will result in low Rh loading with extremely small Rh nanoclusters inside hollow cavities.

4.2.1. Pt₀.₇₇Rh₁@HMSNs. The synthetic procedures for Pt₀.₇₇Rh₁@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 360 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 1320 μL of 5.0 mM L₃ aqueous solution, and 35.26 mL of deionized water were mixed in a 50 mL beaker with magnetic stirring at 200 rpm. The pH value of the solution was adjusted to about 4.15 by diluted NaOH or HNO₃ aqueous solution. Subsequently, 290 μL of TEOS was added into the above solution. The obtained mixture was stirred for 48 h to allow the deposition of silica onto the micelles (white precipitates will appear during 24–48 h). The system was left untouched for 1 more day. Afterward, the white precipitates were collected by centrifugation and washing several times with water and ethanol successively. The collected white precipitates were dried in an oven at 55 °C for 12 h, then calcined at 400–700 °C in a muffle furnace for 3 h, and subsequently reduced in a tube furnace with H₂ at 200 °C for 3 h to obtain Pt₀.₇₇Rh₁@HMSNs. The synthetic procedures for Pt₁₁.₃Rh₁@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 360 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 1080 μL of 5.0 mM K⁺PtCl₆ aqueous solution (nominal molar ratio of Pt/Rh of 1/3), 1980 μL of 0.087 mM quaternized P2MVP₁₂₈-b-PEO₄₇₇ aqueous solution, 1320 μL of 5.0 mM L₃ aqueous solution, and 35.26 mL of deionized water were mixed in a 50 mL beaker with magnetic stirring at 200 rpm. The pH value of the solution was adjusted to about 4.15 by diluted NaOH or HNO₃ aqueous solution. Subsequently, 290 μL of TEOS was added into the above solution. The obtained mixture was stirred for 48 h to allow the deposition of silica onto the micelles (white precipitates will appear during 24–48 h). The system was left untouched for 1 more day. Afterward, the white precipitates were collected by centrifugation and washing several times with water and ethanol successively. The collected white precipitates were dried in an oven at 55 °C for 12 h, then calcined at 400–700 °C in a muffle furnace for 3 h, and subsequently reduced in a tube furnace with H₂ at 200 °C for 3 h to obtain Pt₁₁.₃Rh₁@HMSNs. The synthetic procedures for Pt₁₁.₃Rh₁@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 360 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 1080 μL of 5.0 mM K⁺PtCl₆ aqueous solution (nominal molar ratio of Pt/Rh of 1/3), 1980 μL of 0.087 mM quaternized P2MVP₁₂₈-b-PEO₄₇₇ aqueous solution, 1320 μL of 5.0 mM L₃ aqueous solution, and 35.26 mL of deionized water were used.

4.2.2. Pt₁₁.₃Rh₁@HMSNs. The synthetic procedures for Pt₁₁.₃Rh₁@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 360 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 1080 μL of 5.0 mM K⁺PtCl₆ aqueous solution (nominal molar ratio of Pt/Rh of 1/3), 1980 μL of 0.087 mM quaternized P2MVP₁₂₈-b-PEO₄₇₇ aqueous solution, 1320 μL of 5.0 mM L₃ aqueous solution, and 35.26 mL of deionized water were used.

4.2.3. Pt₂₅Rh₁@HMSNs. The synthetic procedures for Pt₂₅Rh₁@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 720 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 1200 μL of 5.0 mM K⁺PtCl₆ aqueous solution (nominal molar ratio of Pt/Rh of 1/1), 1440 μL of 0.087 mM quaternized P2MVP₁₂₈-b-PEO₄₇₇ aqueous solution, 1200 μL of 5.0 mM L₃ aqueous solution, and 35.26 mL of deionized water were used.

4.2.4. Pt₁₆Rh₁@HMSNs. The synthetic procedures for Pt₁₆Rh₁@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 360 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 1080 μL of 5.0 mM K⁺PtCl₆ aqueous solution (nominal molar ratio of Pt/Rh of 1/1), 1440 μL of 0.087 mM quaternized P2MVP₁₂₈-b-PEO₄₇₇ aqueous solution, 1200 μL of 5.0 mM L₃ aqueous solution, and 35.26 mL of deionized water were used.

4.2.5. Rh@HMSNs. The synthetic procedures for Rh@HMSNs were the same as that of Pt₀.₇₇Rh₁@HMSNs except that 1440 μL of 5.0 mM K⁺RhCl₆ aqueous solution, 2160 μL of
0.087 mM quaternized P2MVP$_{128}$-b-PEO$_{477}$ aqueous solution, 1440 μL of 5.0 mM L$_{1}$ aqueous solution, and 34.96 mL of deionized water were used.

### 4.3. Catalyst Characterization

A Bruker D8 advanced diffractometer with Cu Kα radiation was used to obtain X-ray diffraction (XRD) patterns of various materials in the 2θ range from 10 to 80°. Images of transmission electron microscopy (TEM) were obtained using a JEM-2100 transmission electron microscope operated at 200 kV. A PE Optima 2100DV inductively coupled plasma emission spectrometer (ICP-OES) was used to analyze the actual Pt and Rh loadings in different HMSNs. A Micromeritics ASAP-2020 automatic specific surface area and porous physical adsorption analyzer was used to obtain the Brunauer–Emmett–Teller (BET) specific surface area, pore size distribution, and adsorption/desorption isotherms of various materials by N$_{2}$ adsorption at 77 K. A Nicolet Nexus 670 spectrophotometer was used to obtain Fourier transform infrared (FT-IR) spectra of HMSNs before and after calcination. A PerkinElmer Pyris Diamond thermogravimetric analyzer (TG/DTA) was used to investigate the thermal property of the samples in the temperature range from 40 to 1200 °C at a heating rate of 10 °C/min with a gas flow rate of 100 mL/min in an air atmosphere.

### 4.4. Catalytic Activity Measurement

All catalytic reactions were carried out in a 25 mL three-neck round-bottomed flask under atmospheric H$_2$ pressure. As an example, 10.9 mg of Pt$_{0.77}$Rh$_{0.23}$@HMSNs (Pt-6.70 × 10$^{-4}$ mmol; Rh-8.69 × 10$^{-4}$ mmol) and 10.0 mL of 2-propanol solution containing 32.9 μL of toluene (0.31 mmol, the molar ratio of toluene/(Pt + Rh) was 200/1) were charged into a 25 mL three-neck round-bottomed flask under magnetic stirring at 500 rpm. Catalytic reactions were carried out under H$_2$ bubbling at 30 °C and 0.1 MPa of H$_2$. The catalytic products were analyzed by gas chromatography (GC) with a flame ionization detector (FID). The quantification of components is based on relative response factors of components and their surface areas in GC. After hydrogenation, the product samples were first analyzed by GC to obtain relative surface areas of components, and then known amount of toluene or methyl cyclohexane was added to the samples as the external standards to obtain the corresponding GC chromatograms. Based on the relative response factors of components, and GC chromatograms of samples and samples with a known amount of reactants or main products, reactant conversions and main product selectivity can be accurately calculated.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06268.

Further materials characterizations, size analysis and catalytic reactions (PDF)

**AUTHOR INFORMATION**

Corresponding Author

Shenghu Zhou — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China; orcid.org/0000-0002-8203-6546; Email: zhoushenghu@ecust.edu.cn; Fax: (+86) 21-64253159

**Authors**

Kaijie Li — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

Heliang An — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

Peijian Yan — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

Caoping Yang — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

Tao Xiao — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

Junyou Wang — Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China; orcid.org/0000-0002-4693-850X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c06268

**Author Contributions**

K.L. and H.A. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

S.Z. thanks the National Natural Science Foundation of China for financial support (Grant Nos. 22078099 and 21776090), and this work is also partially supported by the Natural Science Foundation of Shanghai (Grant No. 17ZR1440500)

**REFERENCES**

(1) Hosseini, S. E.; Wahid, M. A. Hydrogen from solar energy, a clean energy carrier from a sustainable source of energy. Int. J. Energy Res. 2020, 44, 4110–4131.

(2) Abdin, Z.; Zafaranloo, A.; Rafiee, A.; Mérida, W.; Lipiński, W.; Khalipour, K. R. Hydrogen as an energy vector. Renewable Sustainable Energy Rev. 2020, 120, No. 109620.

(3) Alhumaidan, F.; Cresswell, D.; Garforth, A. Hydrogen Storage in Liquid Organic Hydride: Producing Hydrogen Catalytically from Methylcyclohexane. Energy Fuels 2011, 25, 4217–4234.

(4) Hu, P.; Ben-David, Y.; Milette, D. Rechargeable Hydrogen Storage System Based on the Dehydrogenative Coupling of Ethylenediamine with Ethanol. Angew. Chem., Int. Ed. 2016, 55, 1061–1064.

(5) Latroche, M.; Surlée, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J.; Chang, J.; Jiang, S. H.; Féréy, G. Hydrogen Storage in the Giant-Pore Metal-Organic Frameworks MIL-100 and MIL-101. Angew. Chem., Int. Ed. 2006, 45, 8227–8231.

(6) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. Hydrogen Storage in Microporous Metal-Organic Frameworks. Science 2003, 300, 1127–1129.

(7) Bakhshi, F.; Farhadian, N. Co-doped graphene sheets as a novel adsorbent for hydrogen storage: DFT and DFT-D3 correction dispersion study. Int. J. Hydrogen Energy 2018, 43, 8355–8364.
(8) Schneemann, A.; White, J. L.; Kang, S.; Jeong, S.; Wan, L. F.; Cho, E. S.; Heo, T. W.; Prendergast, D.; Urban, J. J.; Wood, B. C.; Allendorf, M. D.; Stavila, V. Nanostructured Metal Hydrides for Hydrogen Storage. Chem. Rev. 2018, 118, 10775–10839.

(9) Belkova, N. V.; Epstein, L. M.; Filippov, O. A.; Shubina, E. S. Hydrogen and Dihydride Bonds in the Reactions of Metal Hydrides. Chem. Rev. 2016, 116, 8545–8587.

(10) Rossin, A.; Peruzzini, M. Ammonia-Boron and Amine-Boron Dehydrogenation Mediated by Complex Metal Hydrides. Chem. Rev. 2016, 116, 8848–8872.

(11) Patil, S. P.; Bindwal, A. B.; Pakade, Y. B.; Biniwale, R. B. On H2 supply through liquid organic hydrides-Effect of functional groups. Int. J. Hydrogen Energy 2017, 42, 16214–16224.

(12) Mu, X.; Meng, J.; Li, Z.; Kou, Y. Rhodium Nanoparticles Stabilized by Ionic Copolymers in Ionic Liquids: Long Lifetime Nanooclcuster Catalysts for Benzene Hydrogenation. J. Am. Chem. Soc. 2005, 127, 9694–9695.

(13) Pelisson, C.-H.; Denicourt-Nowicki, A.; Roucoux, A. Magnetically Retrievable Rh(0) Nanocomposite as Relevant Catalyst for Mild Hydrogenation of Functionalized Arenes in Water. ACS Sustainable Chem. Eng. 2016, 4, 1834–1839.

(14) Nasiruzzaman Shaikh, M.; Aziz, M. A.; Kalanthoden, A. N.; Helal, A.; Hakeem, A. S.; Bououdina, M. Facile hydrogenation of N-heteroarenes by magnetic nanoparticle-supported sub-nanometric Rh catalysts in aqueous medium. Catal. Sci. Technol. 2018, 8, 4709–4717.

(15) Sugiyama, Y.; Nagatsuka, T.; Kubo, K.; Hirano, Y.; Sekine, Y.; et al. Dehydrogenation of Methylcyclohexane over Pt/TiO2-Al2O3 Catalysts. Chem. Lett. 2017, 46, 1601–1604.

(16) Atsumi, R.; Kobayashi, K.; Xieli, C.; Nanba, T.; Matsumoto, H.; Matsuda, K.; Tsujimura, T. Effects of steam on toluene hydrogenation over Pt/TiO2-Al2O3 catalysts. React. Kinet. Mech. Catal. 2011, 107, 729–743.

(17) Zahnakran, M.; Tonbul, Y.; Özkar, S. Ruthenium(0) Nanoclusters Stabilized by a Nanospace Framework: Isolable, Reusable, and Green Catalyst for the Hydrogenation of Neurosteroids under Mild Conditions with the Unprecedented Catalytic Activity and Lifetime. J. Am. Chem. Soc. 2010, 132, 6541–6549.

(18) Snelders, D. J. M.; Yan, N.; Gan, W.; Laurentczy, G.; Dyson, P. J. Tuning the Chemoselectivity of Rh Nanoparticle Catalysts by Site-Selective Poisoning with Phosphine Ligands: The Hydrogenation of Functionalized Aromatic Compounds. ACS Catal. 2012, 2, 201–207.

(19) Giannoccaro, P.; Gargano, M.; Fanizzi, A.; Ferragina, C.; Aresta, M. Rh-ions and Rh-complexes intercalated in γ-alumina and γ-zirconium hydrogen phosphate as highly efficient catalysts for arene hydrogenation. Appl. Catal., A 2005, 284, 77–83.

(20) Miyamura, H.; Suzuki, A.; Yashikawa, T.; Kobayashi, S. Polysilane-Immobilized Rh-Pt Bimetallic Nanoparticles as Powerful Arene Hydrogenation Catalysts: Synthesis, Reactions under Batch and Flow Conditions and Reaction Mechanism. J. Am. Chem. Soc. 2018, 140, 11325–11334.

(21) Lin, R.; Ma, X.; Cheong, W.; Zhang, C.; Zhu, W.; Pei, J.; Zhang, K.; Wang, B.; Liang, S.; Liu, Y.; et al. PdAg bimetallic electrocatalyst for highly selective reduction of CO2 with low COOH formation energy and facile CO desorption. Nano Res. 2019, 12, 2866–2871.

(22) Wen, J.; Chen, Y.; Ji, S.; Zhang, J.; Wang, D.; Li, Y. Metal-organic frameworks-derived nitrogen-doped carbon supported nanostructured PtNi catalyst for enhanced hydroisolation of 1-octene. Nano Res. 2019, 12, 2584–2588.

(23) Liu, J.; Yang, Q.; Zhang, L.; Yang, H.; Gao, J.; Li, C. Organic-Inorganic Hybrid Hollow Nanospheres with Microwindows on the Shell. Chem. Mater. 2008, 20, 4268–4275.

(24) Ren, X.; Guo, M.; Li, H.; Li, C.; Yu, L.; Liu, J.; Yang, Q. Microenvironment Engineering of Ruthenium Nanoparticles Incorporated into Silica Nanoreactors for Enhanced Hydrogenations. Angew. Chem., Int. Ed. 2018, 58, 14483–14488.

(25) Liu, S.; Zhao, J.; Wang, X.; Wang, L.; Liu, H.; Wang, G.; Huang, J.; Liu, J.; Liu, G. Q. Construction of hollow mesoporous silica nanoreactors for enhanced photo-oxidations over Au-Pt catalysts. Natl. Sci. Rev. 2020, 7, 1621–1624.

(26) Joo, S. H.; Park, J. Y.; Tsung, C.; Yamada, Y.; Yang, P.; Somorjai, G. A. Thermally stable Pt/mesoporous silica core-shell nanocatalysts for high-temperature reactions. Nat. Mater. 2009, 8, 126–131.

(27) Ding, S.; Chen, J. S.; Qi, G.; Duan, X.; Wang, Z.; Giannelis, E. P.; Archer, L. A.; Lou, X. W. Formation of SnO2 Hollow Nanospheres inside Mesoporous Silica Nanoreactors. J. Am. Chem. Soc. 2011, 133, 21–23.

(28) Fang, X.; Liu, Z.; Hsieh, M.; Chen, M.; Liu, P.; Chen, C.; Zheng, N. Hollow Mesoporous AluminoSilaSpheres with Perpendicular Pore Channels as Catalytic Nanoreactors. ACS Nano 2012, 6, 4434–4444.

(29) Allendorf, M. D.; Stavila, V. Nanostructured Metal Hydrides for Hydrogen Supply through Liquid Organic Hydrides-Effect of functional groups. ACS Omega 2020, 6, 16214–16224.

(30) Matsuda, K.; Tsujimura, T. Effects of steam on toluene hydrogenation over Pt/TiO2-Al2O3 catalysts. React. Kinet. Mech. Catal. 2011, 107, 729–743.

(31) Atsumi, R.; Kobayashi, K.; Xieli, C.; Nanba, T.; Matsumoto, H.; Matsuda, K.; Tsujimura, T. Effects of steam on toluene hydrogenation over a Ni catalyst. Appl. Catal., A 2020, 590, No. 113734.

(32) Dehn, N. A.; Zhang, X.; Buriak, J. M. Screening of Bimetallic Heterogeneous Nanoparticle Catalysts for Arene Hydrogenation Activity under Ambient Conditions. Inorg. Chem. 2010, 49, 2706–2714.

(33) Maximov, A.; Zolotukhina, A.; Kulikov, L.; Kardasheva, Y.; Karakhanov, E. Ruthenium catalysts based on mesoporous aromatic frameworks for the hydrogenation of areses. React. Kinet. Mech. Catal. 2016, 117, 729–743.

(34) Zahnakran, M.; Tonbul, Y.; Özkar, S. Ruthenium(0) Nanoclusters Stabilized by a Nanospace Framework: Isolable, Reusable, and Green Catalyst for the Hydrogenation of Neurosteroids under Mild Conditions with the Unprecedented Catalytic Activity and Lifetime. J. Am. Chem. Soc. 2010, 132, 6541–6549.

(35) Snelders, D. J. M.; Yan, N.; Gan, W.; Laurentczy, G.; Dyson, P. J. Tuning the Chemoselectivity of Rh Nanoparticle Catalysts by Site-Selective Poisoning with Phosphine Ligands: The Hydrogenation of Functionalized Aromatic Compounds. ACS Catal. 2012, 2, 201–207.

(36) Giannoccaro, P.; Gargano, M.; Fanizzi, A.; Ferragina, C.; Aresta, M. Rh-ions and Rh-complexes intercalated in γ-alumina and γ-zirconium hydrogen phosphate as highly efficient catalysts for arene hydrogenation. Appl. Catal., A 2005, 284, 77–83.

(37) Miyamura, H.; Suzuki, A.; Yashikawa, T.; Kobayashi, S. Polysilane-Immobilized Rh-Pt Bimetallic Nanoparticles as Powerful Arene Hydrogenation Catalysts: Synthesis, Reactions under Batch and Flow Conditions and Reaction Mechanism. J. Am. Chem. Soc. 2018, 140, 11325–11334.

(38) Lin, R.; Ma, X.; Cheong, W.; Zhang, C.; Zhu, W.; Pei, J.; Zhang, K.; Wang, B.; Liang, S.; Liu, Y.; et al. PdAg bimetallic electrocatalyst for highly selective reduction of CO2 with low COOH formation energy and facile CO desorption. Nano Res. 2019, 12, 2866–2871.

(39) Wen, J.; Chen, Y.; Ji, S.; Zhang, J.; Wang, D.; Li, Y. Metal-organic frameworks-derived nitrogen-doped carbon supported nanostructured PtNi catalyst for enhanced hydroisolation of 1-octene. Nano Res. 2019, 12, 2584–2588.

(40) Liu, J.; Yang, Q.; Zhang, L.; Yang, H.; Gao, J.; Li, C. Organic-Inorganic Hybrid Hollow Nanospheres with Microwindows on the Shell. Chem. Mater. 2008, 20, 4268–4275.
and the superiority of water as a functional solvent.

(44) Aliaga, C.; Park, J. Y.; Yamada, Y.; Lee, H. S.; Tsung, C.; Yang, P.; Somorjai, G. A. Sum Frequency Generation and Catalytic Reaction Studies of the Removal of Organic Capping Agents from Pt Nanoparticles by UV-Ozone Treatment. J. Phys. Chem. C 2009, 113, 6130−6135.

(45) Tan, B.; Lehmler, H. J.; Vyas, S. M.; Knutson, B. L.; Rankin, S. E. Fluorinated-Surfactant-Templated Synthesis of Hollow Silica Particles with a Single Layer of Mesopores in Their Shells. Adv. Mater. 2005, 17, 2368−2377.

(46) Wu, S.; Hung, Y.; Mou, C. Compartmentalized Hollow Silica Nanospheres Templated from Nanoemulsions. Chem. Mater. 2013, 25, 352−364.

(47) Han, Y.; Guo, Z.; Teng, S.; Xia, H.; Wang, D.; Han, M.; Yang, W. Rationalized Fabrication of Structure-Tailored Multishelled Hollow Silica Spheres. Chem. Mater. 2019, 31, 7470−7477.

(48) Yoshida, H.; Onodera, Y.; Fujita, S. I.; Kawamori, H.; Arai, M. Solvent effects in heterogeneous selective hydrogenation of acetophenone: differences between Rh/C and Rh/Al2O3 catalysts and the superiority of water as a functional solvent. Green Chem. 2015, 17, 1877−1883.

(49) Bertero, N. M.; Trasarti, A. F.; Apesteguía, C. R.; Marchi, A. J. Solvent effect in the liquid-phase hydrogenation of acetophenone over Ni/SiO2: A comprehensive study of the phenomenon. Appl. Catal., A 2011, 394, 228−238.

(50) Trasarti, A. F.; Bertero, N. M.; Apesteguía, C. R.; Marchi, A. J. Liquid-phase hydrogenation of acetophenone over silica-supported Ni, Co and Cu catalysts: Influence of metal and solvent. Appl. Catal., A 2014, 475, 282−291.

(51) Shi, W.; Thompson, R. L.; Macala, M. K.; Resnik, K.; Steckel, J. A.; Siefert, N. S.; Hopkinson, D. P. Molecular Simulations of CO2 and H2 Solubility, CO2 Diffusivity, and Solvent Viscosity at 298 K for 27 Commercially Available Physical Solvents. J. Chem. Eng. Data 2019, 64, 3682−3692.

(52) Shaw, J. M. A correlation for hydrogen solubility in alicyclic and aromatic solvents. Can. J. Chem. Eng. 1987, 65, 293−298.

(53) Valderrama, J. O.; Cortés, F. H.; Ibrahim, A. A.; Celiker, H. Literature Survey on Solubility Data of Hydrogen in Liquid Solvents. Chem. Ing. Tech. 1992, 64, 750−751.

(54) Trinh, T. K. H.; De Hemptinne, J. C.; Lugo, R.; Ferrando, N.; Passarello, J. P. Hydrogen Solubility in Hydrocarbon and Oxygenated Organic Compounds. J. Chem. Eng. Data 2016, 61, 19−34.

(55) Gao, X.; Tian, S.; Jin, Y.; Wen, X.; Zhou, C.; Chen, R.; Dai, Y.; Yang, Y. Bimetallic PtFe-Catalyzed Selective Hydrogenation of Furfural to Furfuryl Alcohol: Solvent Effect of Isopropanol and Hydrogen Activation. ACS Sustainable Chem. Eng. 2020, 8, 12728−12730.

(56) Dong, C.; Yu, Q.; Ye, R. P.; Su, P.; Liu, J.; Wang, G. H. Hollow Carbon Sphere Nanoreactors Loaded with PdCu Nanoparticles: Void-Confinement Effects in Liquid-Phase Hydrogenations. Angew. Chem., Int. Ed. 2020, 59, 18374−18379.

(57) Yang, T.; Wei, L.; Jing, L.; Liang, J.; Zhang, X.; Tang, M.; Monteiro, M. J.; Chen, Y. I.; Wang, Y.; Gu, S.; et al. Dumbbell-shaped bi-component mesoporous Janus solid nanoparticles for biphasic interface catalysis. Angew. Chem., Int. Ed. 2017, 56, 8459−8463.

(58) Jiang, P.; Chen, S.; Wang, C.; Wang, D.; Diao, J.; Cao, Z.; Lin, Z.; Luo, Q.; Lu, J.; Huang, H.; et al. Atomically dispersed Fe-N-S-C anchored on pomegranate-shaped carbon spheres for oxygen reduction reaction and all-solid-state zinc-air battery. Mater. Today Sustainability 2020, 9, No. 100039.

(59) Fung, C.; Tang, J.; Tan, L.; Mohamed, A. R.; Chai, S. Recent progress in two-dimensional nanomaterials for photocatalytic carbon dioxide transformation into solar fuels. Mater. Today Sustainability 2020, 9, No. 100037.

(60) Biesalski, M.; Johannsmann, D.; Rühe, J. Electrolyte-induced collapse of a polyelectrolyte brush. J. Chem. Phys. 2004, 120, 8807−8814.

(61) Wang, J.; Wang, J.; Ding, P.; Zhou, W.; Li, Y.; Drechsler, M.; Guo, X.; Cohen Stuart, M. A. A Supramolecular Crosslinker to Give Salt-Resistant Polyion Complex Micelles and Improved MRI Contrast Agents. Angew. Chem., Int. Ed. 2018, 57, 12680−12684.

(62) Yan, P.; Tian, P.; Li, K.; Cohen Stuart, M. A.; Wang, J.; Yu, X.; Zhou, S. Rh nanoclusters engendered in hollow mesoporous silica nanoreactors with enhanced catalytic performance for phenol selective hydrogenation. Chem. Eng. J. 2020, 397, No. 125464.