Synthesis of Pd/SiO₂ Catalysts in Various HCl Concentrations for Selective NBR Hydrogenation: Effects of H⁺ and Cl⁻ Concentrations and Electrostatic Interactions

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ABSTRACT: A series of silica supported Pd (Pd/SiO₂) catalysts were prepared in various HCl concentrations (C_HCl) of the impregnation solution with different electrostatic interactions between Pd precursor and support, and their catalytic properties were evaluated by the selective hydrogenation of nitrile butadiene rubber (NBR). The results show that with the C_HCl increasing from 0.1 to 5 M, the particle size of Pd nanoparticles dramatically decreases from 24.2 to 5.1 nm and stabilizes at ∼5 nm when C_HCl is higher than 2 M. Using the catalysts prepared with a high C_HCl (>2 M), an excellent hydrogenation degree (HD) of ∼94% with 100% selectivity to C==C can be acquired under mild conditions. Interestingly, the HD could be remarkably increased from 65 to 92% by increasing only C_Cl⁻ from 0.1 to 2 M with the addition of NaCl while keeping C_H⁺ at 0.1 M. This is because PdCl₄⁻ is the predominant existing form of precursor at high C_Cl⁻, which has a strong electrostatic attraction with the positively charged support favorable for the formation of small-sized Pd nanoparticles over silica. Notably, Pd leaching behavior during the hydrogenation reaction is closely related to C_H⁺, and the higher the C_H⁺, the less Pd residues are detected in the hydrogenated NBR. Our contribution is to provide a facile strategy to synthesize effective and stable Pd/SiO₂ catalysts via adjusting the electrostatic interaction, which exhibits a high activity and selectivity for NBR hydrogenation.

1. INTRODUCTION

Nitrile butadiene rubber (NBR) has been widely applied as an oil-resistant rubber, adhesives, coatings, plastics modifiers, and so forth because of its high strength and excellent oil resistance and elastic properties. However, due to the presence of C==C double bonds, NBR suffers from low weather resistance and poor aging properties, which limits its applications in harsh conditions. Therefore, the selective reduction of C==C groups while retaining the nitrile groups (–CN) in the rubber to produce high value-added hydrogenated NBR (HNBR) is of great importance and necessity to improve the properties and extend its applications, which has been increasingly attracting the attention of academic and industry researchers.

Nowadays, the main process for the production of HNBR in industry is solution hydrogenation, including homogeneous and heterogeneous hydrogenation. In a homogeneous system, the reaction occurs at milder operation conditions and without any diffusion problems however, the removal of noble catalysts from HNBR is quite difficult and the residual catalysts in HNBR can accelerate its aging and degradation. Compared with the homogeneous method, the heterogeneous system has received high attention as an alternative in the past few decades due to its facile catalyst recovery and recyclability, and the heterogeneous hydrogenation of NBR to HNBR has a great value both in research and in reality. According to the literature, the silica supported Pd catalyst is regarded as one of the most widely explored heterogeneous catalysts for the hydrogenation of NBR. Among all kinds of preparation methods for the supported catalysts, the impregnation method is considered to be the most simple and universal method and quite suitable for a large-scale production, which has been widely used in commercial applications. But unfortunately, poor catalyst dispersion is often found with the traditional incipient wetness impregnation method due to the weak binding force between the metal and the support, which will lead to low catalytic activity and leaching of active components from the support during reactions. Therefore, how to improve the interaction between the Pd precursor and the silica support is significantly
important for the preparation of stable and highly dispersed supported Pd catalysts.

de Jong and co-workers\textsuperscript{22} have reviewed the synthesis of supported Pd catalysts with different kinds of supports and indicated that the charges of Pd precursors and supports were important properties during synthesis, affecting both dispersion and distribution of Pd over the support. Li et al.\textsuperscript{23} demonstrated that PdCl\textsubscript{2} as the precursor was better than Pd(NO\textsubscript{3})\textsubscript{2} and Pd(OAc)\textsubscript{2} and the Cl addition had a remarkable influence on the particle size, reduction behavior, and catalytic performance of the Pd–Re catalyst in glycerol hydrogenolysis. Recently, Wong and co-workers\textsuperscript{24} proposed a simple and generalizable method to produce highly dispersed and ultrasmall (\textasciitilde1 nm) bimetallic nanoparticles based on strong electrostatic adsorption. It is well accepted that the size and dispersion of the deposited active metal particles are strongly dependent on the metal–support interaction, which is closely related to the existing forms of metal precursors and support surface properties.\textsuperscript{25,26} Therefore, how to adjust the electrostatic interaction is significant but the effect of impregnation solution properties (e.g., the concentrations of H\textsuperscript{+} (C\textsubscript{HCl}) and Cl\textsuperscript{−} (C\textsubscript{Cl\textsuperscript{−}})) on the particle size, dispersion, and stability of the Pd/SiO\textsubscript{2} catalyst are rarely reported and their effect on NBR hydrogenation is still unknown to the best of our knowledge.

Herein, a series of silica supported Pd (Pd/SiO\textsubscript{2}) catalysts have been prepared in various HCl concentrations (C\textsubscript{HCl}) via the incipient wetting impregnation method and the individual and combined effects of C\textsubscript{HCl} and C\textsubscript{Cl\textsuperscript{−}} on catalyst properties and catalytic performance in NBR hydrogenation are systematically investigated. As illustrated in Scheme 1, C\textsubscript{Cl\textsuperscript{−}} mainly affects the existing forms of Pd(II) ion coordination, and PdCl\textsubscript{4}\textsuperscript{2−} exists primarily in solution when C\textsubscript{Cl\textsuperscript{−}} is higher than 2 M, which is the most utilized negatively charged palladium complex ion and is stable in acid solutions. C\textsubscript{HCl} has an effect on the surface charge density of silica and subsequently affects the interaction between the Pd precursor and the support. The high concentrations of H\textsuperscript{+} and Cl\textsuperscript{−} could significantly improve the dispersion and distribution of Pd nanoparticles over silica and enhance the catalytic activity and also effectively decrease Pd leaching during the NBR hydrogenation reaction.

2. RESULTS AND DISCUSSION

2.1. Effect of C\textsubscript{HCl} on the Particle Size and Distribution of Catalysts. Figure 1 shows X-ray diffraction (XRD) patterns of catalysts prepared with various C\textsubscript{HCl} at different states: before calcination (Figure 1A), PdO/SiO\textsubscript{2} samples after calcination (B), and Pd/SiO\textsubscript{2} samples after reduction (C), where x represents various C\textsubscript{HCl} in the preparation process: (a) 0.1 M; (b) 0.3 M; (c) 1 M; (d) 2 M; (e) 4 M; and (f) 5 M.
the severe aggregation of active components during the subsequent calcination and reduction process.

The XRD patterns of PdO/SiO$_2$-x catalysts (Figure 1B) exhibit five diffraction peaks, representing (101), (110), (112), (103), and (211) planes of PdO nanoparticles. The full width at half maximum of the strongest characteristic reflection (101) is used to estimate the average crystallite size of PdO nanoparticles according to the Scherrer equation and the results are listed in Table 1. The particle size of PdO gradually decreases from 13.3 to 6.2 nm with the increase in C$_{\text{HCl}}$ from 0.1 to 5 M. After reduction, Pd/SiO$_2$-x catalysts show different diffraction peaks at 2$\theta$ = 40, 46, 68, and 82° assigned to (111), (200), (220), and (311) planes of Pd nanoparticles, respectively (Figure 1C). The average Pd particle sizes are calculated from the Pd(111) peak by the Scherrer equation and are also shown in Table 1. It is noteworthy that with the increase in C$_{\text{HCl}}$ from 0.1 to 2 M, the Pd particle size dramatically decreases from 24.2 to 5.6 nm, but further increase in C$_{\text{HCl}}$ to 5 M leads to almost no change in the particle size. In combination with the results obtained for PdO/SiO$_2$-x, it is interesting to find that the particle size changes differently before and after reduction. When C$_{\text{HCl}}$ is lower than 1 M, the particle size in the reduced state is larger than that in the oxidized state and the lower C$_{\text{HCl}}$, the larger particle size can be acquired after reduction (Pd particle size is nearly twice larger than that before reduction when C$_{\text{HCl}}$ is 0.1 M). Whereas the opposite phenomenon is observed when C$_{\text{HCl}}$ is higher than 2 M and the Pd particle size is stabilized at $\sim$5 nm with further increase in C$_{\text{HCl}}$. This might be related to the different binding force between the Pd precursor and the support. If the interaction of the Pd precursor and the support is weak, the calcination and reduction processes will induce reaggregation of active components, nevertheless, the reduction process will help in the redispersion of Pd particles over silica, if strong interactions exist between the metal and the support.

The morphology and dispersion of Pd/SiO$_2$-x prepared in various C$_{\text{HCl}}$ of impregnation solution were characterized by transmission electron microscopy (TEM) (Figure 2) and the particle size distributions were obtained by counting more than 100 particles from TEM images (insets of Figure 2). When C$_{\text{HCl}}$ is very low (0.1 M), large Pd particles with severe aggregation in some areas can be observed in Pd/SiO$_2$-0.1, inducing a wide particle size distribution as shown in the inset of Figure 2a. With the increase of C$_{\text{HCl}}$ to 0.3–1 M, the particle dispersion is improved but the average particle size is still large, ca. 10 nm (Figure 2b,c). When C$_{\text{HCl}}$ is further increased to 2–5

### Table 1. Particle Size of Catalysts Prepared with Various C$_{\text{HCl}}$ in Oxidized and Reduced States

| C$_{\text{HCl}}$ (mol L$^{-1}$) | Pd$^{2+}$ | PdO | Pd |
|-----------------------------|----------|-----|----|
| 0.1                         | 13.3     | 24.2|    |
| 0.3                         | 10.3     | 12.1|    |
| 1                           | 9.0      | 10.0|    |
| 2                           | 7.7      | 5.6 |    |
| 4                           | 6.3      | 4.9 |    |
| 5                           | 6.2      | 5.1 |    |

"Calculated from the Scherrer equation $D = \lambda(B \cos \theta)^{-1}$, where $\lambda$ is the X-ray wavelength of Cu K$_\alpha$, $B$ is full width at half maximum of the (101) peak for PdO and the (111) peak for Pd, and $\theta$ is the Bragg angle."
M, Pd particles are uniform and dispersed well with the narrow particle size distribution centered at 5–6 nm (Figure 2d–f).

To investigate the interaction between the metal and the support, X-ray photoelectron spectroscopy (XPS) was carried out for PdO and Pd/SiO2-x (x = 0.1, 1, 2, and 5 M) catalysts as shown in Figure 3. Pd 3d spectra present two sets of doublet peaks corresponding to Pd 3d3/2 and Pd 3d5/2, respectively, and the binding energies (BEs) of PdII 3d3/2 and PdII 3d5/2, or Pd 3d3/2 and Pd 3d5/2 for the tested PdO or Pd/SiO2-x catalysts (x = 0.1, 1, 2, and 5 M) are shown in Table 2. The BE of PdII 3d5/2 for free PdO is measured to be 337.1 eV as reported in the literature.29 It is clear from Table 2 that the BEs of Pd 3d3/2 and Pd 3d5/2 also have a slightly negative shift with an increase in CCl from 0.1 to 5 M, indicating more electron donation from the support to Pd and the stronger metal–support interaction. The transfer of electrons from the support to the Pd metal is beneficial for Pd to provide sufficient feedback electrons to the C=C antibonding orbital, thus enhancing the activation of the C=C double bonds of NBR.

It can be clearly seen that CCl could significantly affect the particle size and dispersion of Pd nanoparticle over silica and with the increase of CCl, the Pd particle sizes become smaller and the dispersion is better obviously. XPS result also confirms that the electrostatic interaction between the metal and the support is enhanced as CCl is increased. The characterization of XRD and TEM gives a consistent result that when CCl is higher than 2 M, the particle size can be stabilized at 5–6 nm for Pd/SiO2-x (x = 2, 4, 5), but actually, the binding force of Pd with the support is different from each other as revealed by XPS. Pd/SiO2-5 has a larger negative shift of BEs than Pd/SiO2-2, indicating that the electrostatic interaction between Pd and the support is continuously strengthened as CCl increases from 2 to 5 M, although the Pd particle size has almost no change.

Table 2. XPS Data for PdO/SiO2-x and Pd/SiO2-x Catalysts

| sample     | binding energy (eV) |
|------------|---------------------|
|            | PdII 3d3/2 | PdII 3d5/2 | Pd 3d3/2 | Pd 3d5/2 |
| PdO or Pd/SiO2-0.1 | 337.02 | 342.37 | 335.48 | 340.71 |
| PdO or Pd/SiO2-1 | 337.01 | 342.36 | 335.36 | 340.55 |
| PdO or Pd/SiO2-2 | 336.98 | 342.33 | 335.33 | 340.51 |
| PdO or Pd/SiO2-5 | 336.67 | 342.02 | 335.23 | 340.47 |

of PdII 3d5/2 for free PdO is measured to be 337.1 eV as reported in the literature.29 It is clear from Table 2 that the BEs of PdII 3d5/2 for PdO/SiO2-x (x = 0.1, 1, 2, and 5 M) are 337.02, 337.01, 336.98, and 336.67 eV, respectively, which shift to lower BEs by 0.08, 0.09, 0.12, and 0.43 eV, respectively, in comparison with 337.1 eV (the BE of PdII 3d5/2 in free PdO as a standard). The negative shift is caused by the electron donation from the support to PdII and the shift is greater as CCl is higher, implying the existence of strong coordination between PdII and the support at high CCl. To further verify the metal–support interaction and detect the surface electronic properties of the final catalysts, XPS results for Pd/SiO2-x (x = 0.1, 1, 2, and 5 M) catalysts are also provided in Table 2. It is shown that the BEs of Pd 3d3/2 and Pd 3d5/2 also have a slightly negative shift with an increase in CCl from 0.1 to 5 M, indicating more electron donation from the support to Pd and the stronger metal–support interaction. The transfer of electrons from the support to the Pd metal is beneficial for Pd to provide sufficient feedback electrons to the C=C antibonding orbital, thus enhancing the activation of the C=C double bonds of NBR.

2.2. Effect of CCl on the Adsorption and Catalytic Performance of Pd/SiO2 Catalysts in NBR Hydrogenation. Figure 4 displays Fourier transform infrared (FT-IR) spectra of SiO2, Pd/SiO2-0.1, and Pd/SiO2-2 after dipping in NBR solution for 2 h. It is clear that Pd/SiO2-0.1 and Pd/SiO2-2 exhibit a new adsorption peak at 2236 cm⁻¹ assigned to the stretching vibration of −CN, indicating that Pd catalysts can effectively adsorb NBR macromolecules but the support
smaller Pd particle size compared with Pd/SiO$_2$-0.1, and thus on Pd/SiO$_2$-2. This is probably because Pd/SiO$_2$-2 has a suggesting that there are more NBR macromolecules adsorbed catalyst. resulting in more NBR macromolecules adsorbed on the has more exposed active sites under the identical Pd loadings ascribed to the symmetric and asymmetric stretching vibration peaks of the CN stretching vibration for Pd/SiO$_2$-2 is relatively stronger than that for Pd/SiO$_2$-0.1, and thus has more exposed active sites under the identical Pd loadings adsorbed on the catalyst. Figure 5 shows the FT-IR spectra of NBR and HNBR (Figure 5a–f) obtained by the selective hydrogenation of NBR and from Figure 5d–f, it can be seen that the peak at 920 cm$^{-1}$ almost disappeared, implying the complete hydrogenation of $\text{C} \equiv \text{C}$ and also indicating the easier hydrogenation of $\text{C} \equiv \text{CH}_2$ than $\text{C} \equiv \text{CH}_2$.. It is worth noting that there is a new peak at 723 cm$^{-1}$ appearing after hydrogenation, assigned to $\text{C} \equiv \text{CH}_2$ vibration in the saturated $\text{C} \equiv \text{CH}_2$ group $(n > 4)$, which is induced by the hydrogenation of C$ \equiv $C. On the basis of the strength of three characteristic peaks at 2236, 970, and 723 cm$^{-1}$ the HD can be calculated by following eqs 1–4

$$\text{HD (mol %)} = 100 - \frac{\text{C(NBR)}}{\text{C(NBR) + C(HNBR)}} \times 100$$  

(1) 

$$\text{C(NBR)} = \frac{\bar{A}(970)}{(970)}/(970)$$  

(2) 

$$\text{C(HNBR)} = \frac{\bar{A}(723)}{(723)}/(723)$$  

(3) 

$$F = 1 + \frac{\bar{A}(723) - \bar{A}(970)}{(723) - (970)}$$  

(4) 

where, $\bar{A}$ is the peak intensity ratio of $A$ (970 or 723) to $A$ (2236) and $k$ is the absorption constant specific to the HNBR polymer $(k(723) = 0.255, k(970) = 2.3)$. The peak of $\text{C} \equiv \text{CH}_2$ (2236 cm$^{-1}$) is used as the internal standard for the HD calculation. The HD can be calculated to be 65, 83, 89, 93, and 94%, respectively, for the six HNBR obtained by different Pd/SiO$_2$-x $(x = 0.1, 0.3, 1, 2, 4, 5)$.

NMR is a precise and convenient technique for characterization to resolve the composition of polymers, which is pervasively employed to analyze the microstructure and determine the HD in hydrogenated elastomers. Therefore, to confirm the HD values obtained from the IR method, NMR was further carried out for two HNBR samples obtained by Pd/SiO$_2$-0.1 and Pd/SiO$_2$-2 as shown in Figure 6. The polymerization of butadiene usually gives rise to a mixture of 1,4 and 1,2 C$ \equiv $C units, and the 1,4-addition products have cis- and trans-isomers, whereas 1,2-addition may result in isomers with isotactic, syndiotactic, and atactic structural units. The main peaks are assigned as follows: 5.3–5.6 ppm (−$\text{CH} \equiv \text{CH}$ of 1,4-cis and trans units), 4.9–5.1 ppm (−$\text{CH} \equiv \text{CH} \equiv \text{CH}$ of 1,2-unit), 2.6 ppm (−$\text{CH} \equiv \text{CN}$, acrylonitrile units), 2.0–2.4 ppm (−$\text{CH}_2$ of 1,4 unit), 1.7 ppm (−$\text{CH}_2$ of 1,2-unit), 1.2–1.4 ppm (−$\text{CH}_2$), and 0.8–0.9 ppm (−$\text{CH}_3$). It can be clearly seen that after hydrogenation,
the intensity of signals for the olefinic protons (5–5.6 nm) has obviously decreased (Figure 6b) or even disappeared (Figure 6c), but the signal for −CH(CN)− is well maintained and no characteristic peaks for −NH2 or −NH− are observed in the 1H NMR spectra of the two HNBR with different extents of hydrogenation, further confirming that the selectivity to C==C is 100%. Additionally, the peaks from about 2.0–2.4 ppm for the aliphatic protons are shifted to the region of 0.8–1.0 ppm due to the reduction of C==C. The HD can be calculated using the following equation:

$$\text{HD} (\%) = \left(1 - \frac{[8 - 3C(\text{AN})]/[2 + 4(A/B)]}{1 - C(\text{AN})}\right) \times 100\%$$

(5)

where, C(AN) is the mole fraction of acrylonitrile in HNBR, $A$ is the integral of peaks representing protons of the residual C==C units in HNBR, and $B$ is the integral of peaks of protons in methylene chains in NBR. The proton peak for −CH(CN)− is used as the internal standard, and the integral of which is set to be 1. Thus, the HD values for HNBR produced by Pd/SiO2-0.1 and Pd/SiO2-2 are calculated to be 63 and 95%, respectively, which is similar to FT-IR results, verifying the reliability of the IR method.

### 2.3. Effect of $C_{\text{Cl}}^-$ on the Catalyst Properties and Catalytic Performance

The above results reveal that $C_{\text{Cl}}^-$ has a great influence on the size and dispersion of catalysts and their catalytic performance. To explore the individual role of $H^+$ and $Cl^-$, we designed a comparative experiment, in which $C_{\text{Cl}}^-$ was kept at 0.1 M but $C_{\text{Cl}}^-$ was increased to 2 M by the addition of NaCl as the Cl− supplement. With such impregnation solution, the Pd/SiO2-0.1 + 2 catalyst was prepared. XRD patterns of this catalyst in different states are shown in Figure 7. Seven diffraction peaks, representing (111), (200), (220), (222), (400), (420) and (422) planes of NaCl crystallites are observed due to the over-high concentration of NaCl in the impregnation solution. The peak at 2θ of 40° which can be observed in Pd$^{++}$/SiO2-0.1 is not detected in Pd$^{++}$/SiO2-0.1 + 2. After calcination, two peaks at 2θ = 34, 42, and 55° can be found, corresponding to the (101), (110), and (112) planes of PdO crystalline, and after H2 reduction, the diffraction peaks of Pd(111) and Pd(200) are seen. On the basis of the Scherrer equation, the average sizes of PdO and Pd particles are calculated to be 10.2 and 8.7 nm, respectively. Compared with the catalyst prepared in $C_{\text{Cl}}^-$ of 0.1 M, the Pd particle sizes of Pd/SiO2-0.1 + 2 are much smaller than those of Pd/SiO2-0.1. It is very interesting to find that the particle size becomes smaller after reduction, which is opposite to the catalysts prepared at $C_{\text{Cl}}^-$ < 1 M but consistent with catalysts acquired at $C_{\text{Cl}}^-$ > 2 M (Table 1). Pd/SiO2-0.1 + 2 was further applied to hydrogenate NBR into HNBR under the same conditions. As can be seen from FT-IR spectrum in Figure 8, HNBR produced by Pd/SiO2-0.1 + 2 has a much weaker peak at 970 cm$^{-1}$ compared with NBR and HNBR obtained by Pd/SiO2-0.1, indicating less residual C==C units in HNBR. According to the peak intensity of 723, 970, and 2236 cm$^{-1}$, the HD is calculated to be 92%, which is 27% higher than that produced by Pd/SiO2-0.1 and comparable with that acquired by Pd/SiO2-x ($x = 2, 4, 5$). It is shown that by increasing only $C_{\text{Cl}}^-$ from 0.1 to 2 M but keeping $C_{\text{H}}^+$ the same, as low as 0.1 M, the Pd particle size can be dramatically decreased from 24.2 to 8.7 nm and the catalytic activity is greatly enhanced from 65 to 92%, revealing that $C_{\text{Cl}}^-$ plays an important role in catalyst preparation to control the particle size and dispersity of Pd and has a significant effect on its properties and catalytic performance.

The residual Pd in HNBR will affect its life and performance, and therefore the residue of the catalyst should be avoided as much as possible. Pd residues in different HNBR samples are detected by inductively coupled plasma (ICP) characterization and the results are shown in Figure 9. The Pd leaching from the catalyst during the hydrogenation reaction is due to the instability of Pd nanoparticles over the support, which can indirectly reflect the strength of the interaction between Pd and the support. When Pd/SiO2-0.1 was used as the catalyst, the residual amount of Pd in the HNBR is as high as 463.6 ppm. By increasing only $C_{\text{Cl}}^-$ from 0.1 to 2 M, the Pd residues in HNBR can be drastically reduced to 282.6 ppm for Pd/SiO2-0.1 + 2, whereas the simultaneous increase of $C_{\text{H}}^+$ to 2 M leads to the leaching of a much less amount of Pd (only 105.9 ppm) from Pd/SiO2-2. It is indicated that both $C_{\text{Cl}}^-$ and $C_{\text{H}}^+$ can improve the Pd leaching behavior but the role of $C_{\text{Cl}}^-$ is more important, which can be further verified by the result for Pd/SiO2-5 that only 49.5 ppm of Pd residues is detected in the product. Therefore, although Pd/SiO2-x ($x = 2, 4, 5$) catalysts have similar particle size distribution and similar catalytic performance, the reliability of the IR method.
activities, their Pd leaching behavior is quite different from each other. Obviously, the increase of $C_{H^+}$ can greatly reduce the amount of Pd residues in HNBR and significantly enhance the interaction between the metal and the support, which agrees well with the XPS results.

The nature and quantity of the surface charge on the support in combination with the charge of metal precursors are important properties to be considered during synthesis, which will remarkably affect both distribution and dispersion of the metal over the support.$^{22}$ The catalytic dispersion is optimal when there is an electrostatic attraction between the positively charged surface and the precursor anions or vice versa. It has been reported that Pd(II) species have different existing forms in various $C_{HCl}$ due to the hydration of Pd(II) chloride complexes, and the types of Pd(II) ion coordination are dependent on $C_{H^+}$, as follows: $[\text{Pd} (\text{H}_2\text{O})_2\text{Cl}_4-n\text{H}_2\text{O}]^{n-2}$ ($0 \leq n \leq 4$). When $C_{HCl}$ is less than 0.1 M, a majority of $[\text{Pd} (\text{H}_2\text{O})_2\text{Cl}_4]$ and $[\text{Pd} (\text{H}_2\text{O})_2\text{Cl}_3]^-$ exist in solution and when $C_{HCl}$ is in the range of 0.1–2 M, $[\text{Pd} (\text{H}_2\text{O})_2\text{Cl}_4]^-$ and $\text{PdCl}_4^{2-}$ are present primarily in solution, whereas $\text{PdCl}_4^{2-}$ exclusively exists with $C_{HCl}$ higher than 2 M, which is the most utilized negatively charged palladium complex ion and very stable in acid solutions. On the other hand, the isoelectric point of silica is 1.0–2.0,$^{22}$ thus the higher the $C_{HCl}$ the more positive charges on the silica surface. Therefore, as shown in Scheme 1, there is a very weak interaction between Pd(II) species ($[\text{Pd} (\text{H}_2\text{O})_2\text{Cl}_4]$ and $[\text{Pd} (\text{H}_2\text{O})_2\text{Cl}_3]^-$) and silica (with a low amount of positive charges) in the impregnation solution of $C_{HCl}$ = 0.1 M, inducing a severe aggregation of Pd particles with a low catalytic performance. With the increasing $C_{H^+}$, Pd(II) ions predominately exist in the form of $\text{PdCl}_4^{2-}$ which can increase the electrostatic attraction to the positively charged support, thus the Pd particle size is decreased effectively and the catalytic activity is enhanced remarkably. Whereas the simultaneous increase of $C_{H^+}$ can increase the quantity of positive charges on silica which may strengthen the electrostatic interactions between Pd and the support, resulting in a dramatic decrease of the Pd leaching amount during the hydrogenation reaction. Therefore, the strong electrostatic interaction is favorable to stabilize Pd particles over silica to reduce the particle size and avoid Pd leaching.

3. CONCLUSIONS

The effect of $C_{H^+}$ and $C_{H^+}$ in the impregnation solution on both distribution and dispersion of Pd/SiO$_2$-$x$ catalysts was investigated and their catalytic activity for NBR hydrogenation was evaluated. It is shown that with the increase in $C_{HCl}$ from 0.1 to 2 M, the Pd particle size is dramatically decreased from 24.2 to 5.6 nm, but further increase in $C_{HCl}$ to 5 M, leads to almost no change in the particle size. The catalytic activity exhibits a similar tendency, and the degree of hydrogenation in HNBR is significantly enhanced from 65 to 94% and then kept stable at ~94% as $C_{HCl}$ increases from 2 to 5 M. But the ICP results indicate that with the similar hydrogenation degree, the higher the $C_{H^+}$, the less Pd residues can be detected in HNBR. It is indicated that $C_{HCl}$ could decide the existing forms of Pd(II) chloride complexes and $C_{H^+}$ could alter the quantity of positive charges on the surface of silica, which will synergistically affect the electrostatic interaction between Pd and the support as a result. Therefore, with the high $C_{HCl}$, small particle-sized and well-dispersed supported Pd catalyst could be acquired, which exhibits a high catalytic performance and less Pd leaching. Our work sheds light on the preparation of stable supported Pd catalyst with a controllable particle size via adjusting the interaction between the Pd precursor and the silica support, and provides an effective catalyst for high-value-added HNBR production.

4. EXPERIMENTAL SECTION

4.1. Materials. All chemicals used were commercially available without further purification. Sodium polystyrene ($M_w$ = 30 000) was purchased from Sigma-Aldrich Co., Ltd. Span 80 and Tween 80 were purchased from Aladdin Co., Ltd. Sodium silicate (Na$_2$SiO$_3$, 26 wt %) and ammonium bicarbonate (99.0%) were purchased from Beijing Chemical Co., Ltd. Hydrochloric acid (36–38%), n-hexane (97%), acetone (99.5%), and ethanol (95%) were obtained from Beijing Modern Eastern Fine Chemical Co., Ltd. Palladium chloride (palladium content: 59.5 wt %) was purchased from Shanghai Civi Chemical Technology Co., Ltd. NBR ($M_w$ = 360 000, ACN: 36.5 wt %) was provided by the Lanzhou Petrochemical Co., Ltd. High purity hydrogen and nitrogen were supplied by Beijing AP BAIF Gases Industry Co., Ltd. Water used in the experiments was deionized, doubly distilled, and deoxygenated prior to use.

4.2. Synthesis of Silica Support. The preparation method for the silica support was through the ternary water/oil/water (W/O/W) emulsion system as described in our previous work.$^{33}$ First, an oil phase (a 72 mL solution of Tween 80 (1.5 g) and Span 80 (1.5 g) in n-hexane) and water phase (14.0 g of sodium silicate solution, 22.0 g of deionized water and 1.6 g of sodium polystyrene) were emulsified using a homogenizer (JB-12KD) with 10 000 rpm for 1 min to form a stable W/O emulsion. Then, this mixture was added into the outer water phase (250 mL of 2 M NH$_4$HCO$_3$ solution) to form a W/O/W emulsion system. After emulsifying for several minutes, the mixture was further magnetically stirred for another 2 h at room temperature. Finally, the resulting white precipitates were filtered, washed with deionized water and methanol several times, and dried at 100°C for 6 h.

4.3. Preparation of Pd/SiO$_2$ Catalysts. Pd/SiO$_2$ catalysts with 5 wt % Pd loading were prepared by using prepared silica as the support and palladium(II) chloride solution as the precursor via the incipient wetness impregnation method. In a typical preparation, $\text{PdCl}_2$ (0.56 mmol) was dissolved in a certain amount of HCl solution with stirring for 2 h, then the impregnation solution was added dropwise to the support (1 g), and was dried at room temperature for 24 h. The resulting solids were dried at 100°C for 24 h and calcined at 480°C in air for 4 h. The $C_{HCl}$ of impregnation solution was set to be 0.1,
To investigate the individual effect of $C_{\text{NBR}}$ on the catalyst properties and catalytic performance, NaCl (2 M) was used as the Cl supplement and introduced into the 0.1 M HCl impregnation solution and the preparation process was the same as described above. The obtained catalyst was named as Pd/SiO$_2$-0.1 + 2.

4.4. NBR Hydrogenation. The hydrogenation reaction was carried out in a 0.5 L high pressure agitated autoclave reactor. NBR (1 g) was dissolved in acetone (80 g) to obtain a NBR solution (1.2 wt %). The NBR solution and catalyst (1 g) were placed into the autoclave. Then the autoclave reactor was sealed and flushed with N$_2$ and H$_2$ three times to remove air. Afterwards, the reactor was pressurized with H$_2$ to 2.0 MPa. The magnetic agitation rate was adjusted to 800 rpm and the reaction temperature was set to be 60 °C. After the reaction for 2 h, the autoclave reactor was allowed to reach room temperature before the reaction mixture was removed. The hydrogenated NBR solution was centrifuged to separate the catalyst from the system. Finally, the product HNBR was precipitated and washed with ethanol and then dried in a vacuum oven at 60 °C for 8 h. The hydrogenation degree (HD) of the NBR sample was analyzed by FT-IR$^{30}$ and confirmed by $^1$H NMR spectroscopy.$^{32}$

4.5. Characterization. The physical and chemical properties of the prepared samples were measured by several characterization methods. The crystal phases were determined by X-ray diffraction (XRD, Bruker AXS D8 Advance, Germany) using Cu K$_\alpha$ radiation. The operation voltage and current were 40 kV and 30 mA, respectively. The scanning speed was set as 2° min$^{-1}$ in the 2θ range of 10–90°. The observed reflections were subjected to Rietveld refinement using the Jade software. X-ray photoelectron spectroscopy (XPS) was performed using an ESCA Lab 250 system with monochromatized Al K$_\alpha$ radiation at 15 kV. The binding energies were calibrated using a C 1s binding energy of 284.8 eV. The peaks were fitted by a nonlinear least squares fitting program using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction, according to Shirley and Sherwood. Transmission electron microscopy (TEM) was performed using a Philips Tecnai G2 F20 operating at 200 kV. The samples were prepared by dropping the ethanol dispersed sample onto 300 mesh carbon-coated copper grids and immediately evaporating the solvent. The Pd residues in HNBR were determined by inductively coupled plasma (ICP, OPTIMA 7300V). For ICP analyses, the HNBR was first calcined in air at 600 °C for 8 h, and then the sample was digested in nitrohydrochloric acid and finally diluted in 50 mL volumetric flasks.

Fourier transform infrared (FT-IR) spectra were obtained by Nexus 470 (Nicolet) in a wave-number range of 400–4000 cm$^{-1}$. The NBR and HNBR samples were prepared by casting a rubber film on KBr plates. The NBR and HNBR samples were characterized by $^1$H NMR spectra recorded on a JNM-LA300FT-NMR (Japan). Deuterated chloroform was used as the solvent in all cases.
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