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Importance of Zeolite Wettability for Selective Hydrogenation of Furfural over Pd@Zeolite Catalysts

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ABSTRACT: The metal-catalyzed selective hydrogenation of biomass-derived molecules is great demand but challengeable due to the complex reaction pathways. Herein, we report a persuasive example for achieving selective hydrogenation of furfural over Pd catalysts by controllable sorption of molecules in zeolite micropores. The key to this success is fixation of Pd nanoparticles inside of Silicalite-1 zeolite with controllable wettability (Pd@S-1-OH) by functionalizing silanol groups into the zeolite framework. In the hydrogenation of furfural as model reaction, the Pd@S-1-OH catalyst with appropriate hydrophilicity exhibits extraordinary selectivity for the formation of furan, giving furan selectivity as high as >99.9% with a complete conversion of furfural, outperforming the conventional Pd nanoparticles supported on zeolite crystals (Pd/S-1) and S-1 zeolite fixed Pd catalysts without artificially functionalized silanol group (Pd@S-1). The extraordinary performance of Pd@S-1-OH is reasonably attributed to the controllable diffusion of molecules within the hydrophilic zeolite micropores, which favors the adsorption furfural and a series of by-products but promotes the desorption of furan. Very importantly, the Pd@S-1-OH is stable and gives the furan productivity at ~583.3 g·gpd⁻¹·d⁻¹ in a continuous test. KEYWORDS: Biomass conversion; Zeolite; Wettability; Selective hydrogenation; Pd catalyst

1. INTRODUCTION

Metal nanoparticle catalyzed hydrogenation has been regarded as a crucial story in the field of heterogeneous catalysis.¹⁻¹⁰ Generally, the reactions occur on the surface of metal nanoparticles, where it is difficult to control the selectivity when more than one reducible groups is present in the substrates.9-16 Many strategies have been developed for improving the hydrogenated selectivity over the metal catalysts, such as adjusting the metal nanoparticles sizes,¹⁷⁻¹⁹ alloying with additional metals,^{20,21} enhancing the interaction with oxide support,^{22,23} and selectively poisoning the active centers.²⁴⁻²⁶ On the basis of these strategies, an ocean of catalysts have been synthesized and displayed improved selectivities in the hydrogenation of chemicals.^{19,20,23,26,27} For example, the Pd nanoparticle catalysts modified with long-tail organic groups or metal oxides exhibit significantly enhanced selec-tivities in the catalytic decarbonylation.^{26,28,29} However, it is still challengeable to control the selectivity for the reactions with complex pathways. For example, in the hydrogenation of biomass-derived molecules, which is a key process for upgrading biomass feedstock to valuable fuels and/or chemicals, the yield of target product is usually low due to the formation of various by-products.³⁰⁻³⁸

The catalyst wettability has emerged to be sensitive to the performances of heterogeneous catalysts by constructing hydrophobic or hydrophilic surface to influence the diffusion

of substrate and product molecules.³⁹⁻⁵⁰ One of the examples is the enhanced catalytic activity of titanosilicate (*e.g.* TS-1, Ti-Beta) zeolite for the catalytic oxidation of organic molecules by adjusting the wettability.⁴⁵⁻⁵⁵ Recent results show that the acid or base centers in hydrophobic/hydrophilic environment significantly enhance the activity and selectivity in heterogeneous catalysis.^{42,47,56,57} However, the potentiality of wettability control for the supported metal nanoparticle catalysts is rarely studied, which might be due to the limitation of synthesis methodology for rationally localizing metal nanoparticles in environments with controllable wettability.^{40,43,58}

Herein, we report a strategy for achieving wettabilitydriven Pd-catalyzed hydrogenation of biomass-derived furfural as a model reaction (Scheme 1). The key to this success is fixation of Pd nanoparticles within zeolite crystals to form Pd@zeolite core-shell catalysts, where the wettability of zeolite sheath is controllable by functionalizing silanol groups into the framework. In the hydrogenation of furfural, the Pd nanoparticles fixed inside of Silicalite-1 zeolite with appropriate hydrophilicity (Pd@S-1-OH) exhibit simultaneously high activities and superior selectivities for the production of biofuran, giving furan selectivity as high as >99.9% with complete conversion of furfural. In contrast, the conventional zeolite supported Pd catalyst is non-selective. The extraordinary performances of Pd@S-1-OH are attributed to the fixed structure with hydrophilic zeolite sheath, which facilitates

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the adsorption and enrichment of furfural in the hydrophilic zeolite micropores, as well as promotes the desorption of furan rather than other by-products. Very importantly, the Pd@S-1-OH is stable and gives the furan productivity at \sim 583.3 g·g_{Pd}⁻¹·d⁻¹ in a continuous test.



Scheme 1. The catalytic strategy for producing bio-furan via selective hydrogenation of furfural.

2. EXPERIMENTAL SECTION

2.1 Materials. Tetraethylorthosilicate (TEOS, >99%), diethoxydimethylsilane (DEMS, 97%), sodium borohydride (97%), ammonium hydroxide (AR, 25%~28%), Al₂O₃ (AR), furfural (AR, 99%), furan (GC, 99.5%), furfuryl alcohol (97%), tetrahydrofuran (98%), 2,3-Dihydrofuran (99%), tetrahydrofurfuryl alcohol (AR, >98%(GC)), methylfuran (98%), *n*-butyl alcohol (99.5%), and octane (GC, 99.5%) were obtained from Aladdin Chemical Reagent Company. Ethanol (AR, 99.7%) was obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd, tetrapropylammonium hydroxide (TPAOH, 40 *wt%*) was supplied by Shanghai Cairui Chemical Technology Co. Ltd. NaCl (AR, 99.5%), urea (99.5%) was obtained from J&K China Chemical Ltd, and PdCl₂ (59~60%) was obtained from Zhejiang Metallurgical Research Institute.

2.2 Synthesis of zeolite S-1-OH. The hydroxyl groups modified S-1 zeolite was synthesized using DEMS and TEOS as precursors, and the final products was denoted as S-1-OH-*x*, where *x* is the molar percentage of DEMS in the total amount of silica in the starting solution.

As a typical run for the synthesis of S-1-OH-10, 80 mL of ethanol was added into 100 mL of water solution containing 6 mL of aqueous ammonia under stirring. After addition of 3.75 g of TEOS and 0.30 g of DEMS, the solution was stirred at room temperature for another 8 h, followed by distilling under vacuum to remove the water and ethanol and drying at 100 °C overnight. Then, the solid powder of amorphous silica modified with methyl group (SiO₂-Me) was obtained. The S-1-OH-10 zeolite was synthesized by solvent-free crystallization with SiO₂-Me in the presence of TPAOH. After grinding the mixture of 0.5 g of TPAOH and 0.6 g of SiO2-Me at room temperature for 10 min, the mixture was transferred into an autoclave for crystallization at 180 °C for 3 days to obtain the methyl group modified S-1 zeolite. After calcination at 550 °C for 4 h, the organic template was removed, and the methyl groups are transformed into hydroxyl groups,48 which was denoted as S-1-OH-10. S-1-OH-20 was synthesized in the same procedures except using 3.33 g of TEOS and 0.60 g of DEMS as the silica precursors.

2.3 Synthesis of Pd/S-1-OH and Pd/S-1 seeds. As a typical run for the synthesis of Pd/S-1-OH, 1 g of S-1-OH-10 zeolites were added into 1.1 mL of water and 0.93 mL of aqueous Na_2PdCl_4 solution (Pd concentration at 8.6 mg/mL), followed by ultrasonic treatment for 1 h and static treatment for 20 h. Then, the solution was transferred into a 250 mL bowl to remove the water under continuously stirring at 50-60 °C. After drying at 80 °C for 4 h, calcining at 400 °C for 4 h in air, and reducing at 300 °C in 10% H₂/Ar for 2 h, the Pd/S-1-OH-10 seeds were obtained. The Pd/S-1 seeds were synthesized *via* the same procedures except for using S-1 zeolite instead of S-1-OH-10 zeolite as the support.

2.4 Synthesis of Pd@S-1-OH and Pd@S-1. Direct addition of Pd salt (e.g. Na₂PdCl₄) into the zeolite crystallization system caused the formation of bulky Pd particles and failed to be fixed in the zeolite crystals because of the Pd aggregation under the zeolite crystallization condition with high temperature and strong basicity. In order to overcome this issue, the seeds of Pd/S-1-OH (or Pd/S-1) were used to introduce Pd species into the zeolite crystallization system. As a typical run for the synthesis of Pd@S-1-OH-10, 0.3 g of Pd/S-1-OH-10 seeds, 0.3 g of SiO₂-Me and 0.5 g of TPAOH were mixed and grinded at room temperature for 15 min, then the mixture was transferred into an autoclave and thermally treated at 180 °C for 3 days.⁵⁹ After removal of the organic template and transforming methyl groups to silanol by calcination at 550 °C for 4 h, the Pd@S-1-OH-10 was finally obtained. These procedures are shown in Scheme 2. The Pd@S-1 was synthesized following the same procedures except using Pd/S-1 and pure fumed silica instead of Pd/S-1-OH-10 and SiO₂-Me-10 as seeds and silica sources, respectively.

2.5 Synthesis of Pd/Al₂O₃. 1 g solid support Al₂O₃ was added into 50 mL of aqueous solution of urea (45 mg) and Na₂PdCl₄ (molar ratio of urea/Pd at 20). After stirring at 80 °C for 4 h, the liquor was cooled to room temperature, followed by the quick addition of 10 mL of newly made NaBH₄ aqueous solution (0.1 M). After stirring for another 1 h, the Pd/Al₂O₃ sample was obtained by filtering, washing with distilled water, and drying at 100 °C for 12 h.

2.6 Synthesis of Pd@S-1-OH-10-HF. 1 g of Pd@S-1-OH-10 sample was added to 10 mL of hydrofluoric acid solution (0.5 *wt%*), followed by stirring at room temperature for 20 min. Then, the mixture was centrifuged, washed with a large amount of water, and dried at 100 °C for 12 h to obtain the Pd@S-1-OH-10-HF sample.



Scheme 2. Synthesis of Pd@S-1-OH.

2.7 Characterization. X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX 2550 diffract meter with CuK α radiation (λ =1.5418Å). Pd loadings were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Nitrogen sorption isotherms were measured using

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a Micromeritics ASAP 2020 system. Transmission electron microscopy (TEM) images were performed on a JEM-2100F electron microscopy (JEOL, Japan) with an acceleration voltage of 200 kV. Thermogravimetric curves (TG) were performed on a SDT Q600 Simultaneous DSC-TGA in flowing air with heating rate of 10 °C/min. The IR spectra of molecules adsorbed on solid samples were performed on a Bruker Vertex 70 (diffuse reflection mode) under in-situ condition. As a typical run, 50 mg of Pd@S-1-OH sample was put into the crucible and reduced under 10% H₂/Ar at 300 °C for 2 h prior to the experiment. A three-way valve was used to switch gases through the crucible. Firstly, a certain amount of furan (or other molecules such as tetrahydrofuran, methylfuran, furfural, furfuryl alcohol, and tetrahydrofurfuryl alcohol) was introduced to the crucible by Ar flow at room temperature until adsorption saturation. Then the gas flow was switched to pure Ar to remove the furan from the crucible. The spectra were recorded under pure Ar flow at room temperature each 4 min.

2.8 Catalytic tests. The furfural hydrogenation was carried out in a continuous fixed-bed glass vertical reactor (length at 400 mm and diameter at 6 mm) with two inlets. For each reaction run, quartz sands were placed into both ends of the catalyst to maintain the bed height. o.1 g of catalyst (20-40 mesh) was diluted with 0.2 g of guartz sands (20-40 mesh) in the catalyst bed. Prior to reaction test, the catalyst was reduced in 10% H₂/Ar at 300 °C for 2 h. 5 wt% furfural (mass ratio of furfural to *n*-butyl alcohol at 1:19) was introduced to one inlet of the reactor by a pump (rate at 0.5 mL/h). Hydrogen (10% H₂/Ar) was introduced to another inlet of the reactor with a rate of 10 mL/min. The reaction temperature was programmed by a temperature-controlled instrument. During the reaction process, the reaction temperature was increased from 150 °C with heating rate of 5 °C/min. At 175, 200, 225, 250, and 275 °C, the temperature was constant for 20 min to collect the products with a cold trap. Then the products were analyzed by a Shimadzu GC-2014 chromatograph equipped with flame ionization detector (FID). The gas phase products (the main products were formaldehvde with slight amount of CO, which are from the cleavage of C-C bond in furfural) were analyzed by a Fu Li-9790 chromatograph equipped with Thermal Conductivity Detector (TCD) and a PPM-400 ST formaldehyde detector.

3. RESULTS and DISCUSSION

3.1 Characterization. Figure 1A shows XRD patterns of S-1, Pd@S-1-OH-10, and Pd@S-1-OH-20 samples, giving typical peaks associated with MFI structure. Notably, the peaks related to Pd nanoparticles are undetectable in the XRD patterns, suggesting the high dispersion. Figure 1B shows the N2 sorption isotherms of S-1, Pd@S-1-OH-10, and Pd@S-1-OH-20 samples, giving typical steps in the very low relative pressure $(<0.01 \text{ P/P}_{0})$. These samples have high surface area and large pore volume (Supporting Information, Table S1). In addition, the Pd@S-1 and Pd@S-1-OH-10 samples give very similar micropore sizes (Supporting Information, Figure S1), confirming that pore size is almost not changed by inner surface modification. By ICP analysis, the Pd loading amount on Pd@S-1-OH-x was 0.34-0.35 wt% (Supporting Information, Table S1), which is almost the same as that (0.32-0.33 wt%) of Pd/S-1 and Pd/Al₂O₃.

When a water droplet is brought into contact with the surface of the S-1 zeolite, the contact angle is measured at 38° (Figure 2A). In contrast, the contact angles of water droplet on the Pd@S-1-OH samples are much smaller than that on S-1. For example, Pd@S-1-OH-10 and Pd@S-1-OH-20 exhibit the contact angles at 23° and 15°, respectively (Figure 2B and 2C), respectively. The lower contact angles indicate more hydrophilic surfaces of the Pd@S-1-OH-10 and Pd@S-1-OH-20.^{60,61} To compare their difference in the structure, we acquired the ²⁹Si MAS NMR spectra of Pd@S-1-OH-10 and Pd@S-1, as shown in Figure 2E. Obviously, the Pd@S-1-OH-10 display an additional signal at -104 ppm, assigned to the Si species related to hydroxyl groups. These results support the successful hydrophilization of Pd@S-1-OH samples by functionalization of hydroxyl group on the zeolite frameworks.⁶²



Figure 1. (A) XRD patterns and (B) N_2 sorption isotherms of (a) S-1, (b) Pd@S-1-OH-10, and (c) Pd@S-1-OH-20.



Figure 2. Contact angles of water-droplet on the surface of (A) S-1, (B) Pd@S-1-OH-10, (C) Pd@S-1-OH-20, and (D) used Pd@S-1-OH-10 in a long-term catalytic test; (E) ²⁹Si NMR spectra of (a) Pd@S-1-OH-10 and (b) Pd@S-1.

Figure 3 shows tomogram-section transmission electron microscopy (TEM) images of the Pd@S-1-OH-10, Pd@S-1 and Pd/S-1, which provided sectioned view of the samples and avoid the influence of Pd nanoparticles on the external surface of zeolite crystals. In the TEM images of Pd@S-1-OH-10 (Figures 3A and 3B) and Pd@S-1 (Figures 3C and 3D), the Pd

nanoparticles are directly observed, confirming that these particles are indeed fixed within the S-1 crystals. Additional TEM images show that the size distribution of the Pd nanoparticles in the Pd@S-1-OH-10 and Pd@S-1 mainly falls in the range 3-11 (Supporting Information, Figure S2A) and 5-11 nm (Supporting Information, Figure S2B) with a mean size at 6 and 7 nm, respectively. On the contrary, the sectioned view of the Pd/S-1 only gives the Pd nanoparticles on the side of S-1 crystals, confirming that the Pd nanoparticles are localized on the external surfaced of S-1 zeolite on Pd/S-1. Additionally, the Pd/S-1 gives the Pd nanoparticle size distribution at 4-10 nm (Supporting Information, Figure S2C) with a mean size at 6.4 nm, which is similar to those on Pd@S-1 and Pd@S-1-OH-10.

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Figure 3. Tomogram-section TEM images of (A and B) Pd@S-1-OH-10, (C and D) Pd@S-1, (E and F) Pd/S-1.

3.2 Hydrogenation of furfural. Table 1 presents catalytic data in the hydrogenation of furfural in continuous flow fixed-bed reactor over various catalysts. The reaction involves different pathways (Supporting Information, Scheme S1), giving furfuryl alcohol, furan, dihydrofuran, tetrahydrofuran, tetrahydrofurfuryl alcohol, and bulky ether molecules as detectable products. The Pd@S-1-OH-10 exhibits the furfural conversion and furan selectivityd at 56.7 and 82.5% at 150 °C. By increasing the reaction temperature from 150 to 275 °C, both the furfural conversions and furan selectivities are significantly enhanced (Supporting Information, Figures S₃). Very interestingly, the furan selectivities higher than 99.9% with full conversion of furfural are achieved at 250 and 275 °C. In contrast, the Pd@S-1 catalyst always gives lower furfural conversions than Pd@S-1-OH-10 under the same reaction conditions. The best performance over the Pd@S-1 is obtained at 250 °C, giving the furfural conversion at 92.9%

and furan selectivity at 97.1%. Additionally, the Pd/S-1 displays poor furan selectivities at 6.3-12.6% during the tests. All these results demonstrate excellent catalytic performances of Pd@S-1-OH-10 in the selective hydrogenation of furfural to furan, which is even much better than that of industrial catalyst, Pd/Al₂O₃ (Supporting Information, Table S2) reported previously.²⁶

In the catalytic tests over Pd@S-1-OH-10 catalyst, rich formaldehyde and slight amount of CO are also detected in the gaseous products, which are resulted from the cleavage of C-C bond in furfural. The formation of formaldehyde also indicate that the reaction proceeds through a hydrogenationdecarbonylation route ($C_5H_4O_2 + H_2 \rightarrow C_4H_4O + CH_2O$), different from the general decarbonylation route without hydrogen giving CO as major product.^{63,64,65} In addition, the bulky molecules from the condensation of the furfural on the Pd sites are formed as major products over the Pd/S-1 and Pd/Al₂O₃ catalysts, but undetectable over Pd@S-1-OH-10 and Pd@S-1 catalysts. This phenomenon might be assigned to that the Pd sites of Pd@S-1-OH-10 and Pd@S-1 are fixed in zeolite crystals, where the bulky molecules are difficult to form in the zeolite micropores with diameter at only 0.55 nm.

Considering the Pd@S-1 and Pd@S-1-OH-10 catalysts have similar Pd nanoparticle size distribution and loadings as well as the same S-1 zeolite support, better catalytic properties of Pd@S-1-OH-10 than those of Pd@S-1 are reasonably attributed to more hydrophilic zeolite sheath of Pd@S-1-OH-10 rather than other factors. Furthermore, Pd@S-1-OH-20 with more hydrophilic zeolite sheath has been employed, but it is shown lower furan selectivities (Supporting Information, Table S₃) than that of Pd@S-1-OH-10, which might be related to low zeolite crystallinity of Pd@S-1-OH-20 (Supporting Information, Figure S₄). Lower zeolite crystallinity leads to reduced surface area and micropore volume (Supporting Information, Table S1), which might fail to control the mass transfer of the reactants and products in the reaction. To understand the importance of hydrophilic zeolite sheath, we performed the treatment of Pd@S-1-OH-10 with hydrofluoric acid to partly destroy the zeolite sheath (Supporting Information, Figure S5), the HF-treated sample (Pd@S-1-OH-10-HF) exhibits a significant reduction of both furfural conversion (80.1%) and furan selectivity (57.7%, entry 19), confirming the crucial role of S-1-OH zeolite sheath for contribution of the conversion and selectivity in furfural hydrogenation over Pd catalysts.

3.3 Kinetic study. Figure 4 shows kinetic studies in furfural hydrogenation over the Pd@S-1-OH-10 and Pd@S-1 catalysts. The reactions were performed at low temperature at 60-80 °C for achieving low conversion of furfural, which benefit the calculation of the turnover frequencies (TOFs) and reaction rates. It is worth noting that the Pd@S-1-OH-10 always gives faster reaction rate than Pd@S-1. On the basis of the initial reaction rate at different temperatures, the apparent activation energies (E_a) of Pd@S-1-OH-10 and Pd@S-1 are calculated to be 21 and 36 KJ/mol (Figure 4B), respectively. These results confirm that the conversion of furfural over the Pd@S-1-OH-10 is much easier than that over the Pd@S-1.66 Considering that the two catalysts have very similar Pd nanoparticle size and loading, the distinguishable E_a values should be reasonably assigned to the different mass transfer efficiency in the catalysts.

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Table 1. Catalytic data in furfural hydrogenation over various catalysts.^a

Entry	Catalyst	Temp. (°C)	Conv. (%)	Selectivity (%)						_
				€	$\left \right\rangle$	\bigcirc	ſ∕→		∕ ^{OH} Others ^b	Balance ^c
1	Pd@S-1-OH-10	150	56.7	82.5	9.0	8.5	0.0	0.0	0.0	1.09
2	Pd@S-1-OH-10	175	89.5	89.7	4.7	5.6	0.0	0.0	0.0	0.95
3	Pd@S-1-OH-10	200	>99.9	95.9	1.3	2.8	0.0	0.0	0.0	0.92
4	Pd@S-1-OH-10	225	>99.9	98.4	0.7	0.9	0.0	0.0	0.0	0.97
5	Pd@S-1-OH-10	250	>99.9	>99.9	0.0	0.0	0.0	0.0	0.0	0.94
6	Pd@S-1-OH-10	275	>99.9	>99.9	0.0	0.0	0.0	0.0	0.0	1.09
7	Pd@S-1	150	48.9	85.0	7.9	7.1	0.0	0.0	0.0	1.03
8	Pd@S-1	175	62.8	91.4	3.0	5.6	0.0	0.0	0.0	1.08
9	Pd@S-1	200	86.6	92.8	3.0	4.2	0.0	0.0	0.0	0.99
10	Pd@S-1	225	91.3	93.2	3.2	3.6	0.0	0.0	0.0	0.90
11	Pd@S-1	250	92.9	97.1	1.0	1.9	0.0	0.0	0.0	o.88
12	Pd@S-1	275	86.6	82.6	0.4	0.5	0.0	0.0	16.4	0.92
13	Pd/S-1	150	41.3	7.3	26.5	21.5	9.0	0.0	35.7	1.04
14	Pd/S-1	175	42.2	12 .6	10.5	29.4	11.2	0.0	36.3	0.89
15	Pd/S-1	200	62.8	10.4	4.2	19.2	11.6	0.0	54.6	0.93
16	Pd/S-1	225	87.5	9.3	2.7	12.3	12.1	0.0	63.6	0.90
17	Pd/S-1	250	89.1	6.3	1.8	12.1	11.7	0.0	68.1	0.91
18	Pd/S-1	275	93.6	6.8	0.6	12.5	7.9	0.0	72.2	1.03
19	Pd@S-1-OH-10- HF ^d	200	80.1	57.7	1.0	11.4	18.0	1.9	10.0	1.06

^{*a*} Reaction condition: 5 wt% furfural (mass ratio of furfural/*n*-butyl alcohol at 1:19), feed rate at 0.5 mL/h, 10% H_2/Ar at 10 mL/min, 0.1 g of catalyst, atmospheric pressure; ^{*b*} Bulky molecules from the condensation of furfural and some others; ^{*c*} Molecular balance during the reaction, calculated from the amount of furan and tetrahydrofuran rings in feeds and products. The coke formed in the reactions was not included in calculating the balance values; ^{*d*} The HF-treated catalyst was used.



Figure 4. Kinetic studies in furfural hydrogenation over Pd@S-1-OH-10 and Pd@S-1 catalysts. (A) Reaction rates of Pd@S-1-OH-10 and Pd@S-1 in hydrogenation of furfural at different temperatures. (B) Experimental points correlating the inverse of the absolute temperature (1/T) with the initial reaction rates ($ln r_o$) over the Pd@S-1-OH-10 and Pd@S-1 catalysts.

3.4 IR spectra of molecular sorption. To understand the effect of zeolite wettability to the molecular sorption, we performed the IR spectra for desorption tests of various molecules on the Pd@S-1 and Pd@S-1-OH-10 catalysts. At first, the molecules of furfural, furan, tetrahydrofuran, methylfuran, furfuryl alcohol, and tetrahydrofurfuryl alcohol were adsorbed on Pd@S-1 and Pd@S-1-OH-10 catalysts. After desorption under the same conditions, the intensity of the IR band assigned to the C-O bond in the furan or tetrahydrofuran rings of these molecules, is decreased on these catalysts. The percentages of molecular desorption were calculated on the basis of the decreased intensity of IR bands. Figure 5 shows in-situ FTIR spectra for desorption of furfural and furan on the Pd@S-1 and Pd@S-1-OH-10 catalysts. The IR

spectra for the desorption of other molecules are given in Supporting Information, Figure S6. Notably, the furan desorbs more significantly than other molecules on both samples under the same conditions, as evidenced by fast decrease of the C-O bond (1190-1203 cm⁻¹). These results also suggest that furan diffuses much faster than other molecules in the zeolite micropores. For example, the removal percentage of furan is 67% over Pd@S-1 at desorption time of 12 min, while the value reaches 90% over Pd@S-1-OH-10, demonstrating that the relative hydrophilic zeolite channels benefit the diffusion of furan. In contrast, the diffusion of furfural molecule in the hydrophilic zeolite channels is strongly hindered, as given by the decreased removal percentage from 8.9% over Pd@S-1 to 5.0% over Pd@S-1-OH-10 (Supporting Information, Table S4 and Figure S7). The dependences of removal percentage of various molecules on time over Pd@S-1 and Pd@S-1-OH-10 catalysts are summarized in Figures 5E and 5F.

On the basis of these data, it is concluded that the superior selectivity of Pd@S-1-OH-10 catalysts is from the combined contribution of zeolite-fixed structure and hydrophilic zeolite channels. In this case, the zeolite-fixed structure can significantly improve the furan selectivity in Pd-catalyzed furfural hydrogenation by controlling the diffusion of various molecules, and the hydrophilic zeolite micropores could maximize the effect in adsorbing the reactant of furfural, but quickly desorb the product of furan.

3.5 Theoretical simulation. To further understand the diffusion behavior of various reactant molecules in the S-1 zeolite with or without hydrophilic OH groups, adsorption energies for each reactant have been theoretically calculated. Figure 6A shows the average adsorption energy (including adsorbate-zeolite and adsorbate-adsorbate potential experi-

enced per molecule) inside S-1-OH (see the models in Supporting Information, Figure S8) under saturation adsorption at 303 K and 101 kPa.



Figure 5. *In-situ* FTIR spectra of (A and B) furfural, (C and D) furan on the Pd@S-1 and Pd@S-1-OH-10 catalyst during the desorption test. Remove percentage of various molecules over (E) Pd@S-1 and (F) Pd@S-1-OH-10 during the molecule desorption IR test.

Clearly, the adsorption of furan molecule in zeolite (-14.7 kcal/mol) is much weaker than all of the other organic molecules involved in the catalytic reaction (tetrahydrofuran,-16.8 kcal/mol; methylfuran,-17.5 kcal/mol; furfural, -20.6 kcal/mol; furfuryl alcohol, -20.4 kcal/mol; tetrahydrofurfuryl alcohol, -20.2 kcal/mol). According to experimental results (Figure 5F), about 90% furan molecule has been removed from S-1-H-10 catalyst at desorption time of 12 min, while the desorption of the other molecules is less than 20%, which are well consistent with those of theoretical simulation. Apparently, it's indicated that these molecules can't easily be removed and diffused out of the S-1-H-10 zeolite micropores.

Furthermore, to gain insight the influence of hydroxyl group concentration on the diffusion, we also investigated the adsorption of furan in zeolite S-1-OH-x (x = 0, 9, 17 and 27) with the varied hydroxyl concentration. As shown in Figure 6B, the corresponding distribution curve of average adsorption energies of furan are gradually decreased to -14.8, -14.7, -14.5 and -14.1 kcal/mol upon the increasing of hydroxyl groups in zeolite S-1-OH-x (x = 0, 9, 17 and 27). It is demon-

strated that the hydrophilic property strongly promotes the diffusion of furan in the zeolite micropores.



Figure 6. (A) Probability distribution of adsorption energy for various molecules in zeolite S-1-OH-9; and (B) Probability distribution of adsorption energy of furan in zeolites with the varied hydroxyl concentration S-1-OH-x (x = 0, 9, 17, 27).

3.6 Catalyst stability. The Pd leaching in the catalytic process is a general challenge for the supported Pd catalysts, and their stabilities and regeneration properties are crucial for the practical applications. Figure 7 shows the dependences of furfural conversion and furan selectivity on reaction time over Pd@S-1-OH-10 catalyst at 200 °C. For the selectivity, it is very stable at higher than 95%. For the reduced conversion, it come back again to higher than 99% after calcination at 550 °C for 4h in oxygen. The catalyst deactivation is owing to the coke formation, which is supported by the change in catalyst color and TG analysis (Supporting Information, Figure S9). TEM images of the used Pd@S-1-OH-10 catalyst after the 90 h reaction still exhibit the Pd nanoparticle diameter distribution at 3-11 nm with a mean size at 6.5 nm (Supporting Information, Figure S10), which is very similar to that of the fresh catalyst. ICP-OES analysis demonstrates that the Pd leaching is negligible during this longterm test. These phenomena should be assiged to that the zeolite sheath is stable and prevent the sintering/leaching of Pd nanoparticles.^{67,68}

More importantly, the hydrophilicity of Pd@S-1-OH-10 is also well maintained during the catalytic test, which is confirmed by the water droplet on the surface of used Pd@S-1-OH-10 displaying the contact angle at 22° (Figure 2D). It is worth mentioning that, during the long-term test, the productivity of furan can reach as high as ~583.3 g·g_{Pd}⁻¹·d⁻¹, which is potentially important for practical applications in the future.

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Figure 7. Dependence of conversion of furfural and selectivity of furan over the Pd@S-1-OH-10 in hydrogenation of furfural to furan. Reaction conditions are: 5 wt% furfural (mass ratio of furfural/*n*-butyl alcohol at 1:19), feed rate at 0.5 mL/h, 10% H₂/Ar at 10 mL/min, 0.1 g of Pd@S-1-OH-10, 200°C, and atmospheric pressure.

4. CONCLUSIONS

In summary, we report a novel strategy to achieve selective hydrogenation over a core-shell Pd@S-1 zeolite catalyst with controllable wettability of the zeolite sheath. Because the zeolite micropores with appropriate hydrophilicity change the diffusion of various molecules, the Pd@S-1-OH catalysts obtained from functionalizing the silanol groups on the zeolite framework exhibit extraordinary activity, selectivity and stability in the hydrogenation of furfural to furan. This work delineates a persuasive example on wettability-driven selective hydrogenation over Pd nanoparticles, which might open an avenue for developing a class of high selective metal catalysts by rationally controlling the catalyst wettability.

ASSOCIATED CONTENT

Supporting Information. Computational methods; TEM, FTIR, addition experiment results in catalytic tests and computational simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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