

Tailoring High-Performance Pd Catalysts for Chemoselective Hydrogenation Reactions via Optimizing the Parameters of the **Double-Flame Spray Pyrolysis**

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Supporting Information

ABSTRACT: Tuning the chemical composition during the synthesis is a widely used method to control the activity of catalysts. Here, we reported an alternative synthesis strategy to tune the catalytic properties of nanocatalysts without changing their precursors and compositions. We synthesized a series of Pd catalysts on the most popular SiO2-, Al2O3-, and silica-alumina supports using the double-flame spray pyrolysis (FSP) technique. It was observed that various flow rates used for the synthesis of catalysts with the same composition affected the formation of the catalyst particles and their structures to further tune the surface acidity due to the correlation between acidity and structure, but the flow rates did not influence the electronic properties of Pd particles. It was observed that surface OH groups could associate Pd for the hydrogenation, but Lewis acid sites could not, as Pd/SA-30 and Pd/SiO₂ showed much higher activity than Pd/Al₂O₃ for the same Pd size and surface properties. For Pd catalysts with Brønsted acid sites (silica-alumina) or weak/ nonacidic SiOH groups (SiO₂), their catalytic performance for the chemoselective hydrogenation of acetophenone was obviously enhanced by tuning the surface OH groups via changing the flow rates for the same precursor solution during this ultrafast synthesis.



KEYWORDS: palladium catalysts, silica/alumina supports, double-flame spray pyrolysis, structure-activity correlation, chemoselective hydrogenation

INTRODUCTION

Supported metal catalysts are widely employed in various reactions, including oxidation, catalytic reforming, C-C coupling, and, especially, the chemoselective hydrogenation^{1,2} of aldehyde and ketones to unsaturated alcohols. The chemoselective hydrogenation of organic compounds including carbonyl bonds is a demanding task due to the thermodynamical preference of the C=C hydrogenation compared with C= O bonds.³ However, it is an important reaction both in organic syntheses for industrial chemicals such as fragrances and drugs and in bio-oils upgrading to fuel for the global sustainable development.⁴⁻⁷ For enhancing the catalytic activity and selectivity, the metal particle size and shape, chemical compositions and physical structures, and metal-support interactions are important for the various synthesis methods and preparation procedures.² It was reported recently that the surface properties of supports not only associate the metal sites for the multifunctional catalysts but also optimize the size, shape, dispersity, and electronic properties of the metal particles.^{8–12}

As reviewed earlier,³ as popular supports, various transition, rare earth, and basic and acidic metal oxides with special surface properties have been used as efficient supports for metal nanocatalysts according to the target reactions. For the hydrogenation of alcohols and ketones, the surface acidity of the supports was found to be associated with the metal particles for the higher reactant conversion and the product selectivity during the reactions.^{1,8–10,13} The acid sites on the supports were proposed to withdraw the surface electrons from metal particles and induce an ionic effect from the supports to the metal particles, which change the catalytic properties on the metal surface and influence the reaction process.^{12,14-16}

Zeolites and amorphous silica-alumina based on low-cost and naturally abundant silica and alumina resources are widely used solid acids and acid supports in chemical industry.^{5,17} The surface acidity is generally tuned via changing the Si/Al ratio during the synthesis. Then, the supported metal catalysts will be produced after postloading metal precursors on these acidic

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supports. It is a time-consuming process and takes days to obtain supported catalysts. In addition, the formation of the metal particles could also be influenced by the supports' acidity due to interactions between metal precursors and surface acid sites. Thus, it is hard to produce uniform metal particles on the supports. Recently, an ultrafast synthesis method based on the single-flame spray pyrolysis (FSP) has been used to produce supported metal catalysts in microseconds directly from their mixed metals and support precursors.^{1,9,10,18,19} However, some metal particles may be inserted inside the bulk of the support and may not be available for the surface reactants. In addition, the metal particle size was strongly influenced by the support acidity, making it hard to control their catalytic performance due to the size-induced catalytic effects.

Most recently, we developed supported Pd metal catalysts via decoupling of the support and metal particle formation using the double-flame spray pyrolysis (double FSP, one spray for support' precursors and another spray for the metal precursor). in which the uniform metal particle size and catalytic properties have been obtained with various support acidities. Therefore, these catalysts kept high chemoselectivity during the acetophenone hydrogenation, where the conversion increased 5 times due to the enhanced acidity of the supports.¹³ Similar to most of the current methods, the acidity of the supports was tuned via the Si/Al ratio in the support precursors. It has to be noticed that the FSP is a continuous process to produce catalysts combining ultrafast nucleation, calcination, and aggregation under flame conditions. The operation parameters, such as gas or precursor flow rate, could affect the formation of catalyst particles and their structures to further tune the surface acidity due to the correlation between acidity and structure. It may act as an alternative method to tune support acidity and catalyst properties without changing the precursors.

In the present investigation, we synthesized a series of SiO₂-, Al₂O₃-, and silica-alumina supported Pd catalysts using the double FSP technique with different oxygen and precursor flow rates. It was observed that various flow rates used for the synthesis of catalysts with the same composition influenced the support acidity but did not affect the electronic properties of the Pd particles. The catalysts were analyzed using BET, X-ray diffraction (XRD), HRTEM, XPS, and solid-state NMR spectroscopy for investigating and demonstrating the structure, Pd electron properties, support acidity, and the local framework atom coordination. The hydrogenation of acetophenone was utilized as a reference test reaction for the competitive hydrogenation between carbonyl and aromatic groups. In addition, the selective hydrogenation of acetophenone has practical relevance for the production of phenylethanol, which is used in perfumery products and ethylbenzene for polymer and fuel industry.⁵

EXPERIMENTAL SECTION

Catalyst Preparation by the Double FSP Synthesis Method. Metallorganic-based precursors, such as palladium-(II) acetate trimer (Pd 47.36%, Johnson Matthey Catalysts), aluminum secondary butoxide, tetraethyl orthosilicate (TEOS) (99.9% purity, Sigma-Adrich), were used for the synthesis of the catalysts. For the synthesis of 5%Pd/Al₂O₃ and 5%Pd/SiO₂ nanoparticles, aluminum secondary butoxide and TEOS were dissolved in xylene (0.5 M concentration by metal). In the case of 5%Pd/silica–alumina (Si/Al = 70/30), aluminum and silicon precursor were mixed in the ratio of 3:7 by volume. Then, the support precursor and Pd(OAc)₂ dissolved in xylene were fed into two independent nozzles (placed 11 cm apart) directed at an angle of 20° to the base, where the aerosol streams were homogeneously mixed at a distance of 16 cm perpendicular to the base as described in our earlier works.^{13,20} Two syringe pumps supplied the liquid precursors separately through two independent nozzles for combustion, and each flame had a separate set of fuel and O₂ (1.5 L/min/3.2 L/min) flow combinations. For monitoring the Pd particles on the support surface, different O_2 flow rate (7, 5, 3 mL/min) and precursor flow rate (3, 5, 7 mL/min) were injected into the flame. The nomenclature of the 5% Pd/silica-alumina powders is defined as Pd/X-(m/n), where X is the support composition (Al_2O_3) SiO₂, silica-alumina (SA-30 with Si/Al = 70/30) and (m/n) is the indication of the oxygen flow rate for the Pd flame (m)divided by the precursor flow rate (n) (7/3, 5/5, 3/7). For example, to obtain Pd/SiO₂ (7/3), 50 mL of 2.4 mM Pd²⁺ solution was injected into one nozzle with an oxygen flow rate of 7 mL/min, and a flow rate of 3 mL/min was applied. At the same time, 50 mL of 0.5 M Si⁴⁺ precursor solution was injected into the other one at the same oxygen (7 mL/min) and precursor flow rate (3 mL/min).

Physical Characterization. *BET Measurements*. Nitrogen adsorption–desorption measurements (BET) were performed at 77 K using a 4000e NOVA system to determine the specific surface areas. Before the measurements, the samples were degassed at 200 °C under vacuum. The primary particle size and specific surface areas were determined by BET measurement and summarized in columns 1 and 2 of Table 1. The BET surface area measurement is related to the average equivalent primary particle size by the equation²¹ $d_{\text{BET}} = 6000/(\rho_{\text{p}} \text{-SA})$ (in nm), where d_{BET} is the average diameter of a spherical particle, S_{A} represents the measured surface area of the powder in m²/g, and ρ_{p} is the theoretical density in g/cm³.

X-ray Characterization. Siemens X-ray Diffractometer (XRD-D5000) with Cu K α radiation operated at 40 kV with a current of 30 mA, at a scan range from 1 to 70°, and with continuous scanning mode at a rate of 2° min⁻¹.

TEM Characterization. For preparing the TEM samples, a small amount of the sample material was dispersed in 5 mL of ethanol in an ultrasonic bath and sonicated for 60 min. A drop of the colloidal suspension was placed on a copper grid coated with carbon film. The samples were dried in ambient air. Large regions of the sample were scanned before the investigation of the particle morphology. The low magnification TEM, the corresponding selected area electron diffractions (SAED), and high-resolution transmission electron microscopy (HRTEM) studies were carried out using an FEI Titan 80/300 ST unit. The instrument was equipped with a Cs corrector for spherical aberration of the objective lens. For imaging, a high-angle annular dark field (HAADF) detector and a GATAN postcolumn imaging filter was used. In all investigations, the microscope was operated at an acceleration voltage of 300 kV.

CO Chemisorption. The Pd dispersion was investigated by CO-pulse chemisorption on a Micromeritics Autochem II 2920 unit. The off-gas was analyzed via a mass spectrometer to derive the amount of chemisorbed CO. The number of exposed Pd metal atoms was calculated on the basis of a chemisorption stoichiometry of Pd/CO = 2. Prior to the measurements, all samples were freshly reduced for 30 min at 400 °C under flowing hydrogen (5 mol % in Ar, 20 mL min⁻¹) and then cooled down to 40 °C during flushing with He.

XPS Characterization. The Pd surface analysis was performed by XPS (ESCALAB250Xi spectrometer, Thermo

samples	$A_{\rm BET}$ m ² /g	primary particle size (nm)	amount of SiOH groups (mmol/g)	amount of Brønsted acid sites (mmol/g)	content of Brønsted acid sites ^c (%)	Al ^{IV} (at.%)	Al ^v (at. %)	Al ^{VI} (at.%)
Pd/SA-30 (7/3)	303	5.7	0.86	7.6×10^{-2}	1.4	38.2	29.7	32.1
Pd/SA-30 (5/5)	195	8.8	0.44	4.7×10^{-2}	10.74	38.1	34.7	27.2
Pd/SA-30 (3/7)	145	11.8	0.10	0.3×10^{-2}	8.73	30.5	40.1	29.4
Pd/SiO ₂ (7/3)	118	16.3	1.2	-	-	-	-	-
Pd/SiO ₂ (5/5)	174	11.1	1.5	-	-	-	-	-
Pd/SiO ₂ (3/7)	207	9.3	1.1	-	-	-	-	-
$\begin{array}{c} \text{Pd/Al}_2\text{O}_3\\ (7/3) \end{array}$	227	7.1	-	-	-	-	-	-
$\begin{array}{c} \text{Pd/Al}_2\text{O}_3\\ (5/5) \end{array}$	159	10.1	-	-	-	34.5		66.5
Pd/Al_2O_3 (3/7)	126	12.7	-	-	-	32.2		67.8

Table 1. Properties of the Supported Pd Catalysts Synthesized by the Double FSP Method Using Different Oxygen and Precursor Flow Rates^a

^{*a*}BET surface areas, primary particle size, concentration of OH group and Brønsted acid sites. ${}^{b}A_{BET}$ is specific surface area determined by nitrogen adsorption/desorption isotherms. ^{*c*}Brønsted acidic OH (mol %) = (number of Brønsted acidic OH groups/total number of OH groups on supports) × 100%.

Scientific, U.K.) employing a Al K α (1486.68 eV) X-ray source operated at 15.2 kV and 164 W (10.8 mA). The photoelectron takeoff angle was 90° measured with respect to the surface of the sample. The typical operating pressure in the vacuum chamber was 2 × 10⁻⁹ mbar.

Solid-State NMR Studies. For the ²⁷Al and ²⁹Si MAS NMR investigations, all samples were exposed to the saturated vapor of a $Ca(NO_3)_2$ solution at ambient temperature overnight in a desiccator for full hydration. Before the ¹H MAS NMR experiments, the samples were dehydrated at 723 K in vacuum with a pressure less than 10^{-2} bar for 12 h in glass tubes. The dehydrated samples were sealed or utilized for in situ loading with ammonia on a vacuum line, followed by evacuation at 393 K for 1 h (for ammonia) to remove physisorbed molecules. Subsequently, the samples were transferred into the MAS NMR rotors under dry nitrogen gas inside a glovebox.

¹H, ²⁷Al, and ¹³C MAS NMR investigations were carried out on a Bruker Avance III 400 WB spectrometer at resonance frequencies of 400.1, 104.3, and 100.6 MHz with the sample spinning rate of 8 kHz using 4 mm MAS rotors. Spectra were recorded after single-pulse $\pi/2$ and $\pi/6$ excitation with repetition times of 20 and 0.5 s for studying ¹H and ²⁷Al nuclei, respectively. The 2D ²⁷Al MQMAS NMR spectra were recorded at a Bruker AVANCE III 700 MHz spectrometer at the resonance frequrency of 182.5 MHz using a three-pulse zfilter pulse sequence with pulse lengths of 3.0, 0.8, and 8.0 μ s, the repetition time of 200 ms, 64 to 128 t_1 increments, and the sample spinning rate of 20 kHz. Quantitative ¹H MAS NMR measurements were performed using zeolite H,Na-Y (35% ion-exchanged) as an external intensity standard, which contains 58.5 mg zeolite H,Na-Y with 1.776 mmol OH/g. ¹³C Cross-polarization (CP) MAS NMR spectra were recorded with the contact time of 4 ms and the repetition time of 4 s. ²⁹Si MAS NMR experiments were performed with the same spectrometer at the resonance frequency of 79.5 MHz and the sample spinning rate of 4 kHz using 7 mm MAS rotors. For recording the ²⁹Si MAS NMR spectra, single-pulse $\pi/2$ excitation and high-power proton decoupling with a recycle

delay of 20 s were applied. To separate the different signals and for the quantitative evaluation of spectra, the data were processed using the Bruker software WINNMR and WINFIT.

Catalytic Hydrogenation. Prior to the hydrogenation reactions, the catalyst materials were reduced in a quartz reactor under a hydrogen flow rate of 50 mL/min for 1 h at 573 K. After the materials were cooled to room temperature under a nitrogen flow rate of 50 mL/min, the reduced catalysts were immediately transferred to a 50 mL stainless steel autoclave, which was purged with nitrogen followed by hydrogen for three times. Acetophenone (60 mg) was dissolved in hexane (6 mL) and added to the autoclave. The molar ratio of Pd on the catalyst to reactant was 1:101. The reaction was carried out at a hydrogen pressure of 3 bar at 15 °C under continuous stirring for 3 h. The product mixtures were collected after reaction times of 10, 20, 30, 60, 90, 120, and 180 min. The conversion and composition of the product mixtures were analyzed using a Shimadzu GCMS-QP2010 Ultra with a RTX-5MS capillary column (30 m \times 0.25 mm \times 0.25 μ m) and guantified by a Shimadzu GC-FID equipped with a RTX-5 capillary column $(30 \text{ m} \times 0.32 \text{ mm} \times 3 \mu \text{m})$. Bicyclohexyl (0.1 mmol) was used as an internal standard. The selectivity to a specific product i (S_i) was calculated as S_i (%) = $(C_i)/[(C_{APh})_0 - (C_{APh})]$, where (C_i) is the molar concentration of the products, such as 1phenylehtanol (PhE), and $(C_{APh})0$ and (C_{APh}) correspond to the molar concentration of acetophenone before and after the reaction, respectively.

RESULTS AND DISCUSSION

Catalyst Morphology. The BET surface areas of the prepared catalysts are summarized in Table 1. The BET surface area of silica–alumina or alumina supported catalysts increased from 145 to 303 m²/g or 126 and 227 m²/g with a decreasing precursor flow rate, consistent with flame-made vanadia/titania in a previous study.²² Due to the shorter residence time of precursor in the flame and the rapid atomic nucleation at high-temperatures, the particle coagulation and coalescence are caused at high precursor flow rate, reducing the overall specific surface area and increasing primary particle size in the flame.²³

In the case of silica-supported catalyst, however, the surface area was increased from 118 to 207 m²/g with an increasing precursor flow rate. Accordingly, the average particle size was decreased from 16.3 to 9.3 nm. The possible reason is that the high precursor velocity during the injection into the flame could promote the higher dispersion of Si atoms and hinder the coagulation. Unlike the longer residence time required for the formation of Al_2O_3 clusters (pure Al precursor) or the Si-O-Al network (mixed Si and Al precursors), the short residence time or the high density of Si atoms in the system may be adequate for the formation of small amorphous silica particles. It was partially similar to the previous observation for FSP-made Pd/silica–alumina that the surface areas of Pd/SA materials increased with the silica content.^{10,13}

Similarly, the XRD patterns of all prepared catalysts in Figure 1 show that the change of the oxygen and precursor flow ratios



Figure 1. XRD patterns of different types of supported Pdnanoparticle catalysts synthesized with different flow rates using the double-flame spray pyrolysis method.

had nearly no influence on the bulk structure of Pd/SiO₂, a slight influence on the Pd/SA-30, but strongly changes the structure of Pd/Al_2O_3 . Obviously, the residence time is significant for the formation of alumina and silica-alumina supports rather than for the formation of silica. Silicacontaining catalysts (Pd/SA-30 and Pd/SiO₂) were highly amorphous in nature. A broad peak at $2\theta = 25^{\circ}$ revealed the amorphous nature of silica.²⁴ Only a single reflection peak of 2θ = 35° was detected for Pd/SA-30 (3/7) due to the formation of small alumina clusters. The lower oxygen flow rate and the longer particle residence time influenced the segregation of the alumina clusters during the synthesis. For Pd/Al₂O₃, the diffraction patterns were similar to the catalysts prepared under various flow rates and similar to the previously observed for flame-derived aluminum supported Pd catalysts.¹⁹ However, the reflection intensity decreased with increasing oxygen flow rates. Of course, the smaller alumina particles, which were synthesized under this flow rate made them undetectable by XRD. For all catalysts, the Pd particles were too small to be observed by XRD.

As shown in the TEM and HRTEM images in Figure 2, very fine and uniform Pd particles were homogeneously dispersed on the all supports. The size distribution of Pd particles was similar (2.2-3.0 nm) on all supports, as shown in Figure S2 of Supporting Information. The average size of the Pd catalysts

was in the range of 1.8-3.5 nm. HRTEM images revealed the spherical Pd particle morphology with a similar particle size dispersed on diverse supports. The mean particle size for Pd/SA-30, Pd/Al₂O₃, and Pd/SiO₂ synthesized at the highest oxygen flow (7 mL/min) showed mean particles sizes of 2.2, 1.9, and 1.8 nm, respectively. When decreasing the oxygen flow rate and increasing precursor flow rate, the average Pd particle size was slightly increased up to 2.4–2.6 nm and 3.0–3.5 nm at flow rates of 5/5 and 3/7, respectively. No strongly aggregated Pd particles were observed. The lattice structure of the Pd particles was not affected by the oxygen flow and precursor flow rate.

Local Structure and Surface Properties of Supports. The above-mentioned investigations have shown that the oxygen and precursor flow rates during the double FSP synthesis method obviously influence the particle size of the supports. As the surface properties of the support materials mainly depend on their local structure, the solid-state NMR spectroscopy has been used to clarify the Al and Si coordination and to characterize the properties of the surface active sites. According to the ²⁷Al MAS NMR spectrum in Figure 3d, the Al coordination in alumina has an Al^{IV} to Al^{VI} ratio of about 32 to 68% (similar as the γ -Al₂O₃^{-13,25}).

For pure silica utilized as support material, ²⁹Si MAS NMR spectroscopy was employed to investigate the silicon coordination. The ²⁹Si MAS NMR signals at -110 and -100 ppm in Figure 4 were assigned to dominating Q⁴ species (Si(OSi)₄) and Q³ species (Si(OSi)₃OH), respectively, along with the Q² species (Si(OSi)₂(OH)₂), occurring at -90 ppm.²⁰ Among them, Q³ and Q² species are the origin of the surface SiOH groups on silica materials.^{10,27} For a lower precursor flow rate and a higher oxygen flow rate, the signal of Q³ species was increased in comparison with the signal of Q⁴ species, which indicates that changing the precursor/oxygen flow rates enhances the formation of Q³ species and could change the surface acidity, although the amount of silicon precursor is the same for all the Pd/SiO₂ catalysts under study.

After dehydration of the Pd/SiO₂ catalysts at 400 °C, the ¹H MAS NMR spectra in Figure 5 consisted of a strong signal at ca. 1.8 ppm, which was assigned to silanol groups, and a shoulder at ca. 2.7 ppm resulting from hydrogen-bonded silanol groups, which were also observed in previous studies.^{10,26} The hydrogen bonds between SiOH groups have been observed for all Pd/SiO₂ materials and were found to increase with an increasing fraction of Q³ species (Figure 4 and Figure 5). Considering the effect of the oxygen and precursor flow rates on the formation of Q³ species (vide supra), changing these synthesis parameters can also tune the properties of the surface SiOH groups. Although Pd/SiO₂ (7/3) has the highest fraction of Q³ species contributing to SiOH groups, their total number was limited by its lowest surface area (Table 1). Pd/SiO₂ (5/5) showed the highest amount of SiOH groups.

Interestingly, both the Al and Si coordinations of the silica– alumina supports have been obviously changed with modifying the synthesis parameters, even though the chemical compositions were the same. As shown in the ²⁷Al MAS NMR spectra of Pd/SA-30 in Figure 3a–c, the penta-coordinated (AI^V) aluminum at ca. 28 ppm increased while the tetrahedrally coordinated (AI^{IV}) aluminum and octahedrally coordinated (AI^{VI}) aluminum at ca. 54–55 and 0.6–1.6 ppm were slightly decreased with decreasing the oxygen flow rates. As evidenced by the two-dimensional ²⁷Al MQMAS NMR spectrum of the hydrated samples in Figures 6a–c, up to three peaks occur,



Figure 2. TEM and HRTEM of Pd/SA-30 (7/3) (a,d,g), Pd/SiO₂ (7/3) (b,e,h), and Pd/Al₂O₃ (7/3) (c,f,i).



Figure 3. ²⁷Al MAS NMR spectra of Al containing supported Pd catalysts.

which are caused by three well-separated signals with isotropic chemical shifts of ca. 0, 30, and 55 ppm. The above-mentioned chemical shift values are typical for octahedrally coordinated (AI^{VI}), pentacoordinated (AI^{VI}), and tetrahedrally coordinated aluminum atoms (AI^{IV}), respectively. As previously discussed, AI^{V} species may coordinate to Si–O species and form a



Figure 4. ²⁹Si MAS NMR spectra of dehydrated Pd/SiO₂ with m/n = 3/7 (a), 5/5 (b), and 7/3 (c).



Figure 5. ¹H MAS NMR spectra of dehydrated Pd/SiO₂ with m/n = 3/7 (a), 5/5 (b) and 7/3 (c).

pseudobridging bond with an involved silanol group.^{13,28} It was also confirmed by the ²⁹Si MAS NMR spectra of Pd/SA-30 in Figure 7 that the center of gravity of the ²⁹Si MAS NMR signals was slightly shifted to lower field with increasing oxygen flow rate and decreasing the precursor flow rate, which hints to a slightly enhanced incorporation of aluminum into the silica network.¹⁷ If an increasing number of Al^{IV} and Al^V species are located near surface SiOH groups (Pd/SA-30 catalysts), then probability of pseudobridges between Al^V species and these silanols should also increase. In this case, the electronwithdrawing character of Al^{IV} species would lead to an enhancement of the acid strength of neighboring surface SiOH groups having the potential for acting as Brønsted acid sites.^{10,13,26}



Figure 7. ²⁹Si MAS NMR spectra of Pd/SA-30 with m/n = 3/7 (a) and 7/3 (b).

¹H MAS NMR spectroscopy was carried out to investigate the hydroxyl coverage and the acidity of the Pd/SA-30 catalysts. The ¹H MAS NMR spectra in Figure 8 are dominated by a strong signal at $\delta_{1H} = 1.8$ ppm, which is due to surface silanol groups. A signal of surface AlOH groups at $\delta_{1H} = 0.1$ ppm was only detected in Figure 8a. The formation of AlOH groups at low oxygen and high precursor flow rate could be caused by the formation of a large amount of surface aluminum species. On the other hand, the ²⁷Al MAS NMR spectra showed only the slight change of the fraction of three Al species (Figure 3). Obviously, the change of the flow rates during the double FSP synthesis did not cause a significant change of Al coordination but changed their distribution in the support particles (i.e., caused an enrichment of these species at the outer surface in the vicinity of SiOH groups). By adsorption of ammonia as probe molecules, it was found that only small amount of Brønsted acidic SiOH groups (BAS) exist on Pd/SA-30 (3/7),



Figure 6. 2D ²⁷Al MQMAS NMR spectra of Al containing supported Pd catalysts.



Figure 8. ¹H MAS NMR spectra of Pd/SA-30 with m/n = 3/7 (a), 5/5 (b) and 7/3 (c), recorded before (bottom) and after (top) loading with NH₃ and subsequent evacuation of physisorbed NH₃ at 373 K for 1 h.

which are able to protonate ammonia to ammonium ions causing a ¹H MAS NMR signal at ca. 7 ppm (Figure 8a). For Pd/SA-30 (5/5) and Pd/SA-30 (7/3), however, a significant amount of BAS was observed for both catalysts. Although all Pd/SA-30 catalysts have the same support composition (silica 70: aluminum 30), these materials exhibit different surface properties depending on the conditions of their double FSP synthesis, especially the oxygen and precursor flow rates. By quantitative evaluation of the ¹H MAS NMR signals of the OH groups before (Figure 8, bottom) and after NH₃ adsorption (Figure 8, top), the total number of surface OH groups and the amount of Brønsted acid sites were determined. Both these values increased from the Pd/SA-30 (3/7) to Pd/SA-30 (7/3) with increasing oxygen flow rate and decreasing precursor flow rate (see Table 1, columns 4 and 5, respectively). Similar as in previous studies, 10,13 the Pd/SA-30 (7/3) catalyst had the highest amount of BAS due to the highest amount of total surface SiOH groups (Figure 1 and Table 1).

Surface Electronic Property of Pd Particles. The catalytic property of surface metal particles is based on their surface electronic properties, which are generally determined by XPS.^{29,30} As shown in Figure 9, the binding energies of Pd nanoparticle on silica and alumina supports were similar at 334.8 (Pd $3d_{5/2}$) and 340.2 eV (Pd $\overline{3}d_{3/2}$). It was widely reported that the surface acid sites could withdraw the electrons from the metal surface and change the surface electronic properties of metal particles via ionic effects.^{10,31-34} Pd/SiO₂ has only silanol groups including very weakly acidic SiOH groups from Q3 species. The acidity of SiOH groups is not strong enough to withdraw the electron from the metal surface and its binding energies were identical to those of palladium metal. Interestingly, Pd/Al₂O₃ catalysts (Lewis acid sites on the supports) showed similar binding energies like Pd/SiO₂ catalysts. Therefore, the Lewis acid sites on the supports might not influence the electronic properties of metal nanoparticles. However, the BAS sites on supports obviously



Figure 9. Binding energies of the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ lines of supported Pd catalysts synthesized by the double FSP method.

induced the ionic effects for the metal particles. The Pd binding energies of Pd/SA-30 catalysts were shifted to 334.3 and 339.7 eV, respectively, from 334.8 and 340.2 eV for Pd/SiO₂ and Pd/ Al₂O₃. Pd/SA-30 (3/7) had relatively lower amount of BAS compared with other two Pd/SA-30 catalysts, but showed the similar ionic effects. It was similar as the previous report that the density of BAS on the supports could not change the ionic effects for the supported metal particles.³⁴ The Pd particle size was slightly changed when changing the oxygen and precursor flow ratio from 7/3 to 3/7 (means size from 1.8 to 3.0 nm); however, no change for the electronic properties has been observed on those Pd catalysts.

Chemoselective Hydrogenation of Acetophenone. As discussed above, Pd supported nanocatalysts via the decoupling of the support and metal particle formation using the double FSP synthesis method exhibited the similar particle size of Pd particles on different supports (silica, alumina, or silicaalumina) at the same flow ratio of the precursors (7/3, 5/5, and3/7, respectively). After testing the chemoselective hydrogenation of acetophenone (Aph), all catalysts offered the similar chemoselectivity for the hydrogenation of the C=O group to form phenylethanol (PE) and ethylbenzene (EB) as shown in Table 2. It was also observed previously^{4,13} that the chemoselectivity mainly relies on the Pd surface properties, as the hydrogenation reaction occurs on the metal surface. As shown in Figure 10, the support properties have significant effects for the catalytic reactions. Pd particles on silica-alumina (containing dominant BAS with mediate strength) showed the much higher conversion of Aph compared to Pd particles with the same size distribution on silica (neutral SiOH) and alumina (strong LAS). As summarized in Table 2, the TOFs were $1.1 \times$ $10^{-2} - 5.1 \times 10^{-2}$, $0.9 \times 10^{-2} - 1.6 \times 10^{-2}$, and $0.6 \times 10^{-2} - 1.6 \times 10^{-2}$ $0.7 \times 10^{-2} \text{ s}^{-1}$ for Pd/SA-30, Pd/SiO₂, and Pd/Al₂O₃, respectively. It was reported that the support acidity could withdraw the electrons from the metal surface and enhance the catalytic property of catalysts.^{10,29,32,34} The present study demonstrates that not all acid sites can contribute the ionic effects for the metal surface. Combined with the above XPS investigation, it is concluded that only BAS on support can induce the ionic effect for the metal surface and enhance the catalytic performance of metal in the hydrogenation. The strong LAS of the Al₂O₃ support are not able to withdraw the electrons from the metal surface and result in the ionic effects. It was also confirmed by the above-mentioned XPS study (in the section Surface Electronic Property of Pd Particles) that the



Figure 10. Conversion of acetophenone (Aph) over Pd catalysts as a function of the reaction time at a hydrogen pressure of 3 bar and at 15 $^{\circ}$ C.

electronic property of Pd on Al_2O_3 was the same as it on neutral SiO₂ with SiOH groups only. Interestingly, Pd/SiO₂ obviously showed the higher activity during the hydrogenation and a higher Aph conversion compared to Pd/Al₂O₃ (shown in Figure 10). It indicates that neutral surface hydroxyl groups, such as SiOH groups, performed much better than strong LAS, such as surface Al cations, associated with Pd particles for the Aph hydrogenation. The possible reason is that the flexible surface SiOH groups easily interact with the metal particles on the surface, which are hardly available for LAS.

In addition, supported Pd catalysts with the same composition prepared by the double FSP technique with different oxygen and precursor flow rates showed different support properties (such as support size, variable density, and type of surface OH groups) but the same electronic properties of Pd particles (as shown by the XPS investigation in the section Surface Electronic Property of Pd Particles). The same surface properties of Pd catalysts contributed the similar product chemoselectivity during Aph hydrogenation as shown in Figure S3. As described above, LAS on Al₂O₃ cannot associate Pd for the hydrogenation and promote the reaction performance. Even more LAS are available on the surface when Al₂O₃ support size decreased from 12.7 to 7.1 nm (surface area increased from 126 to 227 m^2/g), both Aph conversion and product selectivity nearly had not changed during the hydrogenation (shown in Figure 11 and Figure S3). For the hydrogenation on Pd/SiO₂, the catalyst containing the highest amount of SiOH groups (Pd/SiO₂ (5/5)) showed the highest activity during the hydrogenation reaction as shown in Figure 11. Because the same surface activity was observed for Pd on SiO_2 , it could be concluded that the flexible surface OH groups can associate the Pd for the catalytic hydrogenation reactions. It was reported that the SiOH groups of Q³ silicon species may contribute to the weak acidity of SiO₂ surfaces.^{10,27} Pd/SiO₂ (7/3) has a similar total number of SiOH groups but more Q³ silicon species than Pd/SiO_2 (3/7). The existence of more acidic SiOH groups on Pd/SiO₂ (7/3) could enhance its catalytic performance as shown in Figure 11, and the TOF was, therefore, increased from 0.7×10^{-2} to 0.9×10^{-2} s⁻¹.



Figure 11. Conversion of acetophenone (Aph) over Pd catalysts as a function of the reaction time at a hydrogen pressure of 3 bar and at 15 $^{\circ}$ C.

The Pd/SA catalysts containing BAS showed a much higher activity in the hydrogenation reactions (apart from Pd/SA-30 (3/7), containing the lower BAS) compared with Pd/SiO₂ and Pd/Al_2O_3 (Figure 11). It is similar to a previous study,³⁴ which showed that increasing the density of uncovered BAS on the support could significantly enhance the conversion of Aph hydrogenation on supported Pt catalysts but keep the same and high chemoselectivity. When most of the Aph converted to PE, some of PE products would be further converted to EB as shown in Figure S3. The selectivity of EB was increased proportionally with the consumption of PE. Because nearly no hydrogenation of the aromatic ring has been observed during the reaction process, it is certificated that the catalysts prepared via the double FSP synthesis method has desired catalytic properties. The selectivity was determined at 30% conversion of Aph to obtain comparable results. As shown in Table 2 and Figure S3a,b,c in Supporting Information, all Pd/SA-30 catalysts revealed a similar chemoselectivity in the Aph hydrogenation, generating only carbonyl hydrogenated products, such as PE (selectivity of 88.2-98%) and EB (selectivity of 2-11.8%). Additionally, there was no selectivity to hydrogenation of the aromatic ring (cyclohexylmethylketone (CMK), ethylcyclohexane (EC), and cyclohexylethonol (CE)). The BAS on the silica-alumina support of the Pd/SA-30 catalysts could have more surface SiOH groups with enhanced acid strength allowing them to react with the C-OH groups of PE after completed reaction of Aph due to the strong electron donor property, which should enhance their interaction with dissociated hydrogen.¹⁰ All Pd/SA-30 catalysts showed similar chemoselectivity in the hydrogenation of Aph and exhibited a preferred hydrogenation activity for carbonyl groups rather than for aromatic groups. This could be explained by the similar surface electronic properties of Pd particles as observed in XPS investigation, which was similar to our earlier work.¹³

Table 2. Conversion, Product Selectivities, and Turnover Frequencies (TOF) for the Chemoselective Hydrogenation of Acetophenone (Aph) over Pd Catalysts Synthesized by the Double FSP Method with Different Oxygen and Precursor Flow Rates

sample	conversion ^a %	$S_{\rm PhE}^{\ b}$ %	$S_{\rm EB}^{b}$ %	$S_{\rm CMK}^{}$ %	$d_{\mathrm{Pd}}{}^{c}$ %	TOFs $(s^{-1})^d$
Pd/SA-30(7/3)	100	88.2	11.8	-	50	5.1×10^{-2}
Pd/SA-30(5/5)	100	91	9	-	47	3.9×10^{-2}
Pd/SA-30(3/7)	61	97.7	2.3	-	42	1.1×10^{-2}
$Pd/SiO_{2}(7/3)$	53	100	0	-	52	0.9×10^{-2}
$Pd/SiO_2(5/5)$	83	98.8	1.2	-	42	1.6×10^{-2}
Pd/SiO ₂ (3/7)	30	100	0	-	39	0.7×10^{-2}
$Pd/Al_2O_3(7/3)$	39	97.6	0	2.4	50	0.7×10^{-2}
Pd/Al_2O_3 (5/5)	31	98.3	0	1.7	44	0.6×10^{-2}
Pd/Al_2O_3 (3/7)	26	98.2	0	1.8	34	0.6×10^{-2}

^{*a*}Conversion is at the reaction time of 3 h. ^{*b*}S_{phE}, S_{EB}, and S_{CMK} are the selectivity to PhE, EB and CMK, respectively, obtained at the Aph conversion of 30% ^{*c*}Pd dispersion is determined by CO chemisorption. ^{*a*}TOFs for Pd/supported catalysts were calculated based on Pd dispersion obtained by CO chemisorption at the Aph conversion of 30%

Combining the results of spectroscopic and catalytic characterization as well as the similar surface electronic properties could indicate a similar hydrogen dissociation energy and adsorption-desorption balance for the hydrogenation of Aph. Therefore, the reaction and chemoselectivities of Aph on all of Pd/SA-30 catalysts under study should be similar.

CONCLUSIONS

The double-flame spray pyrolysis was used to prepare Pd nanocatalysts on three most popular supports (silica-alumina, Al_2O_{3} , and SiO_2) with the same precursor composition but different ratios of the oxygen and precursor flow rates. Changing the flow rates leads to changes of both the Al and Si coordination in spite of the same chemical composition, resulting in different structural and surface properties, such as support size, as well as various densities and types of surface OH group. In the case of silica-alumina-supported Pd nanocatalysts (Pd/SA), the density of BAS was strongly increased from 0.3×10^{-2} mmol/g up to 7.6×10^{-2} mmol/g under the same chemical composition with the change of the specific surface area and the coordination of aluminum species in silica network, when the ratio of the oxygen and precursor flow rates was changed from 3/7 to 7/3. This increased BAS density strongly enhanced the catalytic performance in chemoselective hydrogenation of acetophenone from a conversion of 32% at 120 min on Pd/SA-30 (3/7) up to 100% at same time on Pd/SA-30 (7/3). All samples showed similar selectivity due to the same surface electronic property as confirmed by XPS. A similarly enhanced catalytic performance has also been observed for the Pd/SiO₂ catalysts after tuning the ratio of the oxygen and precursor flow rate for the same quality and quantity of the silicon precursor. Pd/SiO_2 (5/5) has the highest amount of SiOH groups on the support surface and showed the highest activity of all Pd/SiO₂ catalysts under study.

Pd/Al₂O₃ catalysts containing surface Lewis acid sites had a similar Pd surface electronic property as the Pd/SiO₂ catalysts containing exclusively nonacidic SiOH groups. However, the Aph conversion was much lower on Pd/Al₂O₃ than that on Pd/SiO₂ catalysts, and the Pd/SA-30 catalysts containing BAS showed the highest activity. This observation indicates that BAS and SiOH groups could associate and activate the Pd nanoparticles for the hydrogenation reaction, whereas LAS (even strong LAS as γ -Al₂O₃ in this research) could not enhance the conversion of Aph. Therefore, changing the different flow conditions during the double FSP synthesis

leading to a decreased particle size of the alumina support and to an enhancement of the amount of surface LAS could not increase the catalystic performance for hydrogenation of Aph on Pd/Al₂O₃ catalysts. All Pd/Al₂O₃ catalysts in this research showed similar activity.

The present work has demonstrated that after selecting suitable supports, it is possible to produce tunable nanocatalysts with the same chemical composition but very different catalytic performance via the ultrafast double FSP synthesis method, which is promising for the development of custom-made catalysts for high-performance reaction processes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00396.

TEM images, Pd particle size distribution, and chemoselectivity (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Schimmoeller, B.; Hoxha, F.; Mallat, T.; Krumeich, F.; Pratsinis, S. E.; Baiker, A. *Appl. Catal., A* **2010**, 374, 48–57.
- (2) White, R. J.; Luque, R.; Budarin, V. L.; Clark, J. H.; Macquarrie, D. J. Chem. Soc. Rev. **2009**, 38, 481–494.
- (3) Maki-Arvela, P.; Hajek, J.; Salmi, T.; Murzin, D. Y. Appl. Catal, A 2005, 292, 1–49.
- (4) Chen, M. M.; Maeda, N.; Baiker, A.; Huang, J. ACS Catal. 2012, 2, 2007–2013.
- (5) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044–4098.
- (6) Minnermann, M.; Grossmann, H. K.; Pokhrel, S.; Thiel, K.; Hagelin-Weaver, H.; Baumer, M.; Mädler, L. *Catal. Today* **2013**, *214*, 90–99.
- (7) Minnermann, M.; Pokhrel, S.; Thiel, K.; Henkel, R.; Birkenstock, J.; Laurus, T.; Zargham, A.; Flege, J. I.; Zielasek, V.; Piskorska-Hommel, E.; Falta, J.; Mädler, L.; Baumer, M. *J. Phys. Chem. C* **2011**, *115*, 1302–1310.
- (8) Handjani, S.; Marceau, E.; Blanchard, J.; Krafft, J. M.; Che, M.; Maki-Arvela, P.; Kumar, N.; Warna, J.; Murzin, D. Y. *J. Catal.* **2011**, 282, 228–236.
- (9) Hoxha, F.; Schimmoeller, B.; Cakl, Z.; Urakawa, A.; Mallat, T.; Pratsinis, S. E.; Baiker, A. J. Catal. 2010, 271, 115–124.
- (10) Huang, J.; Jiang, Y. J.; van Vegten, N.; Hunger, M.; Baiker, A. J. Catal. 2011, 281, 352–360.
- (11) Li, J. J.; Xu, X. Y.; Jiang, Z.; Hao, Z. P.; Hu, C. Environ. Sci. Technol. 2005, 39, 1319–1323.
- (12) Ramaker, D. E.; Oudenhuijzen, M. K.; Koningsberger, D. C. J. Phys. Chem. B 2005, 109, 5608-5617.
- (13) Wang, Z. C.; Pokhrel, S.; Chen, M. M.; Hunger, M.; Mädler, L.; Huang, J. J. Catal. 2013, 302, 10–19.
- (14) Ji, Y. Y.; van der Eerden, A. M. J.; Koot, V.; Kooyman, P. J.; Meeldijk, J. D.; Weckhuysen, B. M.; Koningsberger, D. C. *J. Catal.* **2005**, 234, 376–384.
- (15) Oudenhuijzen, M. K.; van Bokhoven, J. A.; Miller, J. T.; Ramaker, D. E.; Koningsberger, D. C. J. Am. Chem. Soc. 2005, 127, 1530–1540.
- (16) Stakheev, A. Y.; Zhang, Y.; Ivanov, A. V.; Baeva, G. N.; Ramaker, D. E.; Koningsberger, D. C. J. Phys. Chem. C 2007, 111, 3938–3948.
- (17) Sun, B.; Pokhrel, S.; Dunphy, D. R.; Zhang, H.; Ji, Z.; Wang, X.; Wang, M.; Liao, Y. P.; Chang, C. H.; Dong, J.; Li, R.; Mädler, L.;
- Brinker, C. J.; Nel, A. E.; Xia, T. ACS Nano 2015, 9, 9357–9372. (18) Pratsinis, S. E. Prog. Energy Combust. Sci. 1998, 24, 197–219.
- (19) Strobel, R.; Stark, W. J.; Mädler, L.; Pratsinis, S. E.; Baiker, A. J. Catal. 2003, 213, 296–304.
- (20) Pokhrel, S.; Nel, A. E.; Mädler, L. Acc. Chem. Res. 2013, 46, 632-641.
- (21) Pokhrel, S.; Birkenstock, J.; Schowalter, M.; Rosenauer, A.; Mädler, L. *Cryst. Growth Des.* **2010**, *10*, 632–639.
- (22) Schimmoeller, B.; Schulz, H.; Ritter, A.; Reitzmann, A.; Kraushaar-Czametzki, B.; Baiker, A.; Pratsinis, S. E. *J. Catal.* **2008**, 256, 74–83.
- (23) Strobel, R.; Pratsinis, S. E. J. Mater. Chem. 2007, 17, 4743–4756.
 (24) Gerardin, C.; Sundaresan, S.; Benziger, J.; Navrotsky, A. Chem. Mater. 1994, 6, 160–170.
- (25) Feng, R.; Liu, S. T.; Bai, P.; Qiao, K.; Wang, Y. H.; Al-Megren,
- H. A.; Rood, M. J.; Yan, Z. F. J. Phys. Chem. C 2014, 118, 6226–6234.
 (26) Huang, J.; van Vegten, N.; Jiang, Y. J.; Hunger, M.; Baiker, A.
- Angew. Chem., Int. Ed. 2010, 49, 7776-7781.
- (27) Rosenholm, J. M.; Czuryszkiewicz, T.; Kleitz, F.; Rosenholm, J. B.; Linden, M. *Langmuir* **2007**, *23*, 4315–4323.
- (28) Chizallet, C.; Raybaud, P. Angew. Chem., Int. Ed. 2009, 48, 2891–2893.
- (29) Mojet, B. L.; Miller, J. T.; Ramaker, D. E.; Koningsberger, D. C. J. Catal. **1999**, *186*, 373–386.
- (30) Zhang, H.; Pokhrel, S.; Ji, Z.; Meng, H.; Wang, X.; Lin, S.; Chang, C. H.; Li, L.; Li, R.; Sun, B.; Wang, M.; Liao, Y. P.; Liu, R.; Xia, T.; Mädler, L.; Nel, A. E. J. Am. Chem. Soc. **2014**, *136*, 6406–6420.

(31) Koningsberger, D. C.; de Graaf, J.; Mojet, B. L.; Ramaker, D. E.; Miller, J. T. *Appl. Catal., A* **2000**, *191*, 205–220.

(32) Lepage, M.; Visser, T.; Soulimani, F.; Beale, A. M.; Iglesias-Juez, A.; van der Eerden, A. M. J.; Weckhuysen, B. M. J. Phys. Chem. C 2008, 112, 9394–9404.

- (33) Lepage, M.; Visser, T.; van der Eerden, A. M. J.; Soulimani, F.; Weckhuysen, B. M. *Vib. Spectrosc.* **2008**, *48*, 92–100.
- (34) Wang, Z. C.; Kim, K. D.; Zhou, C. F.; Chen, M. M.; Maeda, N.; Liu, Z. W.; Shi, J.; Baiker, A.; Hunger, M.; Huang, J. *Catal. Sci. Technol.* **2015**, *5*, 2788–2797.