Improved Stability of Pd/Al₂O₃ Prepared from Palladium Nanoparticles Protected with Carbosilane Dendrons in the Dimethyl Ether Steam Reforming Reaction

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The dimethyl ether steam reforming reaction to generate hydrogen was tested over 1 wt% Pd/Al₂O₃ catalysts prepared from different precursors. The conventional catalyst prepared by incipient wetness impregnation from palladium nitrate underwent strong deactivation under reforming conditions at 823 K because of metal sintering and carbon deposition. The same occurred over the catalyst prepared from preformed Pd

nanoparticles protected with dodecanethiol. In contrast, catalysts prepared from Pd nanoparticles protected with carbosilane dendrons showed enhanced stability and good performance for the production of hydrogen. This was because of the formation of SiO₂ at the Pd–Al₂O₃ interface that acted as a pinning center and prevented Pd migration under the reaction conditions as well as the accumulation of carbon.

Introduction

Dimethyl ether (DME) is a promising source of hydrogen because it has several advantages such as a high hydrogen-to-carbon ratio and because it can be handled, stored, and transported easily as it can be liquefied at low pressure.^[1,2] In addition, the synthesis gas-to-DME process has been developed recently for the direct synthesis of DME from the product of the gasification of biomass (CO and H₂) in a single step,^[3–5] which thus provides the possibility to obtain hydrogen from a renewable source. One of the most attractive methods to produce hydrogen from renewable bio-derived liquids such as DME and bioalcohols is steam reforming because of its simplicity and high H₂ yield.^[6–9] The steam reforming of DME [Eq. (1)] involves two consecutive reactions. Ideally, the first step is the hydration of DME to form methanol [Eq. (2)] followed by the steam reforming of methanol [Eq. (3)] with the participation of the water gas shift (WGS) reaction [Eq. (4)]. However, other reactions are usually involved, such as DME decomposition [Eq. (5)] and CO_x methanation [Eqs. (6) and (7)] that decrease the hydrogen yield.

A solid acid catalyst (e.g., Al₂O₃, ZrO₂, zeolites, and WO₃) is needed to convert DME into methanol, whereas the steam reforming of methanol usually employs either a Cu-^[10–41] or Pd-based^[42] catalytic system. In recent years, several studies have been reported with regard to the architecture of the support^[43–54] and the use of Mo₂C.^[55] One of the major drawbacks of the catalysts used for DME steam reforming is the sintering of the metal phase under the operation conditions required for the reaction with the concomitant loss of activity. This is particularly relevant if real operation conditions are selected, in which high temperatures are required for an effective operation because of the endothermic character of the process and no diluents are allowed. In the case of Cu-based catalysts, the beneficial effect of ZnO it is well known to avoid Cu sintering

under steam reforming at high temperature as well as the presence of other metals able to form Cu-M alloys.^[18, 21] Another strategy is to employ Cu spinels,^[8, 11, 19, 20, 25, 26, 30, 32, 33, 37, 47] although the segregation of Cu usually takes place at the surface as the reaction proceeds and sintering finally occurs. Pd-based catalysts also suffer from sintering, although they are considerably more resistant.^[8]

In this work we report new Pd/Al₂O₃ catalysts for DME steam reforming prepared from preformed Pd nanoparticles protected with carbosilane dendrons (Pd-G0, Pd-G1, and Pd-G2), which are stable under practical operational conditions. Usually, the use of organic shells prevents the aggregation of the nanoparticles and allows shape- and size-controlled metal

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nanoparticles to be obtained. If carbosilane dendrons are used, the result is the formation of SiO₂ patches in contact with the metal nanoparticles and the support upon calcination, which thus prevents the agglomeration of the metal nanoparticles under reaction conditions.^[56] These new catalysts perform much better than conventional Pd/Al₂O₃ prepared by impregnation (Pd-IW) and catalysts prepared from preformed nanoparticles protected with dodecanethiol (Pd-D).

Results and Discussion

Characterization before reaction

The preformed Pd nanoparticles were first characterized by TEM to determine their morphology and size distribution. Representative images recorded for the different preformed Pd nanoparticles prepared are shown in Figure 1, and their mean particle sizes (the deviation reported corresponds to $\pm 95\%$ of the particles measured) are compiled in Table 1. Pd nanoparticles protected with a dodecanethiol shell form aggregates of

Catalyst	Pd _{nanoparticles}	Pd/Al ₂ O ₃ before reaction	Pd/Al ₂ O ₃ after reaction
Pd-IW	–	7 $\pm$ 2	12 $\pm$ 5
Pd-D	3.5 $\pm$ 0.5	6 $\pm$ 2	11 $\pm$ 4
Pd-G0	4.0 $\pm$ 0.5	5 $\pm$ 1	6 $\pm$ 2
Pd-G1	4.3 $\pm$ 0.6	5 $\pm$ 1	6 $\pm$ 2
Pd-G2	4.1 $\pm$ 0.5	5 $\pm$ 1	6 $\pm$ 1

individual Pd crystallites that measure (3.5 $\pm$ 0.5) nm (Figure 1 a). The inset in Figure 1b corresponds to the Fourier-transformed (FT) image of the aggregate shown in high-resolution transmission electron microscopy (HRTEM) mode in Figure 1b. Rings at 2.2 and 1.9 Å correspond to the (111) and (200) crystallographic planes of metallic Pd, according to the crystalline nature of the nanoparticles. The Pd nanoparticles are not faceted as is usually observed in metal nanoparticles capped by organic shells. The mean particle size of the Pd nanoparticles protected with carbosilane dendrons is slightly larger (4–4.3 nm), which probably results from a different architecture of the metal–shell interaction during particle growth. There is no difference in the particle size of Pd protected with the different carbosilane dendrons G0 (Figure 1 c), G1 (Figure 1 e), and G2 (Figure 1 g). Interestingly, Pd nanoparticles protected with carbosilane dendrons do not form aggregates, and individual Pd crystallites are well dispersed, which means that the carbosilane shells provide full protection. The distance between individual Pd nanoparticles increases as the molecular volume of the carbosilane dendron increases according to the existence of a full carbosilane shell around each Pd nanoparticle. In all cases, HRTEM images show crystalline nanoparticles with lattice fringes that correspond to metallic Pd. The insets shown in Figure 1d (Pd protected with carbosilane dendron

Figure 1. Bright-field TEM and HRTEM images of the preformed Pd nanoparticles used to prepare catalysts a, b) Pd-D, c, d) Pd-G0, e, f) Pd-G1, and g, h) Pd-G2. The inset in b) corresponds to the FT image of the aggregated Pd nanoparticles. The insets in d), f), and h) correspond to individual Pd nanoparticles.

G0) show high-magnification and FT images of an individual Pd nanoparticle oriented along the [100] crystallographic direction that exhibit {200} planes at 1.9 Å. In the case of the Pd nanoparticles protected with the larger carbosilane dendron G2, the HRTEM image (Figure 1 h) shows individual Pd nanoparticles (see, for instance, the insets that show a Pd nanoparticle oriented along the [110] crystallographic direction and show {111} planes at 2.2 Å) as well as an amorphous structure around them, which is ascribed to the carbosilane dendron.

These preformed Pd nanoparticles were used to prepare Pd/Al₂O₃ catalysts by impregnation from toluene solutions to promote the DME steam reforming reaction and to compare their

catalytic performance with that shown by a conventional Pd/Al₂O₃ catalyst prepared by incipient wetness impregnation from palladium nitrate. All these samples were calcined at 773 K to remove the protecting shells (in the case of pre-formed nanoparticles with dodecanethiol and carbosilane dendrons) and to anchor the nanoparticles onto the alumina support. The resulting as-prepared catalysts were examined by TEM and X-ray photoelectron spectroscopy (XPS). As expected, the thermal treatment resulted in the growth of the Pd nanoparticles and to a higher dispersion of their mean particle size (Table 1). The Pd particle size distribution was rather similar in all cases, between 5 and 7 nm, and the largest particles were present in the conventional catalyst (Pd-IW) and in the sample prepared from preformed Pd nanoparticles protected with dodecanethiol (Pd-D). In all cases, the Pd nanoparticles were well dispersed over the alumina support and no metal aggregates were found, as deduced from the TEM images depicted in Figure 2a, c, and e. The inset in Figure 2e (catalyst Pd-G0) shows an individual Pd nanoparticle with lattice fringes at 2.2 Å that corresponds to the {111} planes of metallic Pd. The Pd nanoparticles did not restructure upon calcination and remained poorly faceted.

Figure 2. TEM images of catalysts a, b) Pd-IW, c, d) Pd-D, and e, f) Pd-G0 as prepared (a, c, e) and after DME steam reforming at 673–823 K (b, d, f). S/C = 3, W/F = 0.2 g_{catalyst} s N mL_{gas}⁻¹.

Table 2. Surface atomic composition obtained by XPS over the Pd/Al₂O₃ catalysts as prepared (after calcination at 773 K) and after DME steam reforming at 673–823 K (S/C = 3, W/F = 0.2 g_{catalyst} s N mL_{gas}⁻¹). The last column corresponds to the amount of carbon deposited after the reaction as inferred from TPO.

Catalyst	Pd/Al ₂ O ₃ before reaction			Pd/Al ₂ O ₃ after reaction			
	Pd/Al	Si/Al	C/Al	Pd/Al	Si/Al	C/Al	-1 -1
Pd-IW	0.014	–	0.02	0.008	–	0.24	0.057
Pd-D	0.016	–	0.03	0.010	–	0.20	0.038
Pd-G0	0.021	0.012	0.04	0.019	0.014	0.06	<10 ⁻⁴
Pd-G1	0.020	0.021	0.05	0.019	0.022	0.06	<10 ⁻⁴
Pd-G2	0.021	0.030	0.02	0.020	0.029	0.04	<10 ⁻⁴

The surface atomic composition of the different as-prepared catalysts was recorded by XPS (Table 2). In all cases, the only species present at the surface were Al (Al 2p at a binding energy (BE) δ 74.3 eV), O (O 1s at BE δ 531.4 eV), Pd (Pd 3d_{5/2} at BE δ 337.5 eV), and C (C 1s at BE δ 284.8 eV). In addition, the catalysts prepared from preformed Pd nanoparticles protected with carbosilane dendrons also exhibited Si photoelectrons, which indicates that the Si atoms from the carbosilane shells remained at the surface of the catalysts after calcination. The BE of the Si 2p signal at 103.5 eV indicated that Si was present as SiO₂.^[56] The dispersion of Pd (measured as the Pd/Al atomic ratio) follows the trend Pd-G0 ~ Pd-G1 ~ Pd-G2 > Pd-D > Pd-IW, which is in accordance with the size of the Pd nanoparticles measured by TEM. However, the amount of SiO₂ (measured as the Si/Al atomic ratio) follows the trend Pd-G2 > Pd-G1 > Pd-G0 according to the content of Si in the carbosilane dendrons used.

DME steam reforming

The catalytic performance at steady state in terms of product yield of the different Pd/Al₂O₃ catalysts and the bare Al₂O₃ support attained at each temperature tested is shown in Figure 3. In these plots, the conversion of DME is related directly to the height of the columns, whereas the distribution of products is given within each column. According to the endothermic character of the reforming process, the higher the temperature the higher the conversion of DME. However, significant differences in product distribution exist between the various samples tested. At low temperature (673–723 K), the alumina support exclusively catalyzes the hydration of DME into methanol, and only at high temperature (823 K) is the hydration of DME accompanied to some extent by the decomposition of methanol into hydrogen and carbon monoxide: CH₃OH $\rightarrow$ 2H₂ + CO. Minor amounts of methane are also produced, which can be explained in terms of CO methanation: CO + 3H₂ $\rightarrow$ CH₄ + H₂O or by direct DME decomposition: CH₃OCH₃ $\rightarrow$ 2H₂ + CO + CH₄. In contrast, the Pd/Al₂O₃ catalyst prepared by the conventional route, Pd-IW, is much more active, and the yield of hydrogen is much higher. This is because of the presence of the metal that strongly promotes methanol transformation reactions.^[42] Methanol is only detected at the lowest temperature tested, 673 K. At this temperature, the only products of the reaction besides

Figure 3. Yield of the products obtained by the steam reforming of DME over different samples at 673–823 K ($S/C=3$, $W/F=0.2 \text{ g}_{\text{catalyst}} \text{ s N mL}_{\text{gas}}^{-1}$).

methanol are H_2 , CO , and CH_4 , which are likely produced by the decomposition of methanol and DME and/or CO methanation. At a higher temperature, 723–823 K, methanol is no longer detected and CO_2 is present in the reaction products, which implies that the reforming of methanol takes place: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$. The CO_2/CO molar ratio shows a maximum at 773 K. This is explained in terms of the WGS reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. At 673–773 K, the WGS reaction is kinetically controlled and the CO_2/CO ratio increases progressively to $\text{CO}_2/\text{CO} \sim 2$, but at 823 K, the ratio decreases because the reverse WGS reaction is favored because of thermodynamic limitations. The yield of methane increases following the trend of DME conversion up to 773 K, but at 823 K the amount of methane decreases significantly, probably because of the steam reforming of methane: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$ (the reverse of the CO methanation reaction), which requires a high temperature to operate. The catalytic behavior of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst prepared from preformed Pd nanoparticles protected with dodecanethiol, Pd-D, is very similar to that of the Pd-IW

sample, both in terms of DME conversion and product distribution.

The $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst prepared from preformed Pd nanoparticles protected with the carbosilane dendron G0, Pd-G0, exhibits the highest DME conversion values at all the temperatures tested. Moreover, the yield of hydrogen is higher over Pd-G0 because less methane is produced and because the CO_2/CO molar ratio is higher with respect to the other catalysts (especially at 773 K). This means that the reforming of methanol is favored over decomposition reactions and/or that the methanation of CO is inhibited over Pd-G0. At 823 K, the conversion of DME is 91% and the distribution of products is 72% H_2 , 20% CO_2 , 7% CO , and 1% CH_4 . At this temperature, the conversion of DME obtained in a separate test performed in the absence of steam was only 7.4%, which thus indicates that the decomposition of DME [Eq. (5)] was not significant under the DME steam reforming conditions. A completely new scenario appears over the $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts prepared from preformed Pd nanoparticles protected with the larger carbosilane dendrons, Pd-G1 and Pd-G2. Over these catalysts, the DME conversion decreased significantly and the methanol yield was the highest of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts tested. A plausible explanation is that less metal active sites are available in these catalysts to transform the methanol molecules synthesized over the alumina support. This can be explained if we take into account the XPS data presented in Table 2. The larger the carbosilane dendron the higher the surface Si/Pd atomic ratio and, consequently, the lower the catalyst activity in the transformation of methanol because less metallic function is available.

Characterization after reaction

To gain insight into the different catalytic behavior of the $\text{Pd}/\text{Al}_2\text{O}_3$ samples prepared from different precursors, the catalysts were studied after reaction by TEM, XPS, and temperature-programmed oxidation (TPO). Mean particle sizes of Pd nanoparticles after the DME steam reforming test at 673–823 K are shown in Table 1, and representative TEM images of the catalysts Pd-IW, Pd-D, and Pd-G0 after reaction are shown in Figure 2. Interestingly, both the conventional catalyst (Pd-IW) and that prepared from preformed Pd nanoparticles protected with dodecanethiol (Pd-D) experienced strong sintering, and the size of Pd nanoparticles almost doubled (from 6–7 nm before reaction to 11–12 nm after reaction), whereas Pd nanoparticles in catalysts prepared from preformed Pd nanoparticles protected with carbosilane dendrons (Pd-G0, Pd-G1, and Pd-G2) did not undergo sintering (5 nm before reaction to 6 nm after reaction). This is an outstanding result that demonstrates that the presence of SiO_2 at the surface of the catalysts prepared from preformed Pd nanoparticles protected with carbosilane dendrons prevents Pd sintering under reforming conditions. The ability of SiO_2 to act as a pinning center for Au nanoparticles supported on TiO_2 prepared from preformed Au nanoparticles protected with similar carbosilane dendrons to avoid sintering at temperatures up to 973 K has been demonstrated.^[56] Therefore, the use of carbosilane dendrons as protecting shells in the preparation of preformed Pd nanoparticles

that decompose and originate SiO_2 upon calcination at the Pd- Al_2O_3 interface allows Pd/ Al_2O_3 catalysts to be used for DME steam reforming at high temperature without sintering. However, the performance of the catalysts depends strongly on the amount of SiO_2 , which in turn depends on the size of the carbosilane dendron employed, as large amounts of silica are detrimental because it would lower the overall acidity of the catalyst (less DME is transformed to methanol) and block the metal active sites for methanol transformation.

The surface atomic ratios recorded by XPS in the catalysts after reaction and the amount of carbon deposited determined by TPO are summarized in Table 2. According to the TEM results, samples Pd-IW and Pd-D exhibited much lower Pd/Al ratios after reaction (0.008–0.010) with respect to the as-prepared catalysts (0.014–0.016) because of Pd sintering, whereas the Pd/Al ratio was nearly identical for the Pd-G0, Pd-G1, and Pd-G2 catalysts in both the as-prepared and used states (0.019–0.021). However, the surface C/Al atomic ratio increases in those samples that experience Pd sintering after DME steam reforming (from ~ 0.02 –0.03 to 0.20–0.24), whereas the catalysts prepared from preformed Pd nanoparticles protected with carbosilane dendrons maintain a similar C/Al ratio (0.02–0.06), which indicates that the accumulation of carbon is not important. This is corroborated by the quantitative analysis of deposited carbon by TPO (Table 2), which indicates that the rate of carbon deposited over samples Pd-IW and Pd-D (0.038 – $0.057 \text{ g}_{\text{C}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$) is much higher than that over samples prepared from preformed Pd nanoparticles protected with carbosilane dendrons ($< 10^{-4} \text{ g}_{\text{C}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$). Therefore, it appears that different reaction pathways occur over both types of catalysts. The yield of methane is considerably higher over Pd-IW and Pd-D (Figure 3) at all the temperatures tested compared to that produced over Pd-G0. This could be a direct consequence of the Pd nanoparticle size, as larger Pd nanoparticles are known to be effective in methanation reactions, which, in turn, favor carbon deposition,^[57] or derived from a surface modification of the metallic function because of the presence of silica. The participation of the Boudouard reaction, $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$, as a source of carbon is ruled out as the ratio $[\text{H}_2]/[\text{CO}_2]$ obtained in the catalytic runs is incompatible with its stoichiometry.

Stability test

To further explore the effect of the use of preformed Pd nanoparticles protected with carbosilane dendrons to prepare Pd/ Al_2O_3 catalysts for DME steam reforming with respect to conventional Pd/ Al_2O_3 catalysts, a stability test was performed over Pd-IW and Pd-G0 at 823 K under the same operational conditions ($\text{S/C}=3$, $\text{W/F}=0.2 \text{ g}_{\text{catalyst}} \text{ s N mL}_{\text{gas}}^{-1}$). The conversion of DME and the selectivity on a dry basis of the products obtained over time on stream are shown in Figure 4.

Clearly, the Pd-G0 catalyst was stable under these DME steam reforming conditions, whereas the conventional Pd-IW catalyst was not. After 48 h on stream, the conversion of DME only decreased slightly from ~ 90 to 89.5% over Pd-G0 and the distribution of all reaction products was approximately

Figure 4. DME conversion and product selectivity obtained over Pd-IW and Pd-G0 at 823 K ($\text{S/C}=3$, $\text{W/F}=0.2 \text{ g}_{\text{catalyst}} \text{ s N mL}_{\text{gas}}^{-1}$).

constant. At the end of the stability test over Pd-G0, the selectivity values were: 69% H_2 , 18% CO_2 , 9% CO , and 4% CH_4 . In contrast, a significant deactivation occurred over the Pd-IW sample, with which the conversion of DME decreased from ~ 86 to 69% at the end of the stability test. In addition, after approximately 15 h on stream a significant change in the product distribution was observed, as the selectivity to the reforming products, H_2 and CO_2 , decreased considerably and, at the same time, the selectivity to CO and CH_4 increased, and methanol appeared among the reaction products. At the end of the stability test over Pd-IW the selectivity values were: 32% H_2 , 31% CO , 27% CH_4 , and 10% CH_3OH . The appearance of methanol in the reaction products is a clear indication that the metallic function of the catalyst transforms under the reaction conditions, which results in the suppression of the reforming activity of the catalyst. However, the fact that $[\text{H}_2] \sim [\text{CO}] \sim [\text{CH}_4]$ at the end of the stability test indicates that the main reaction that occurs over Pd-IW is the decomposition of DME [Eq. (5)].

Both catalysts were studied by HRTEM and TPO at the end of the stability tests. A representative image of a single Pd crystallite of Pd-IW is shown in Figure 5a. Clearly, the Pd nanoparticles initially present in the catalyst, which measured 5–9 nm, sintered to large Pd crystallites of ~ 20 –30 nm at the end of the stability test. The Pd particles were well anchored to the Al_2O_3 support. The lattice fringe analysis of the particles reveals interplanar distances that correspond to metallic Pd in all cases. In addition, a poorly crystalline carbon layer ~ 2 –3 nm thick developed over the catalyst with a characteristic interplanar spacing of $3.5 \text{ \AA}$, which is ascribed to the (002) basal plane of graphite. The rate of carbon deposition measured by TPO over Pd-IW after the stability test was

Figure 5. HRTEM images of a) Pd-IW and b–f) Pd-G0 after DME steam reforming stability tests at 823 K for 48 h ($S/C=3$, $W/F=0.2 \text{ g}_{\text{catalyst}} \text{ s mL}_{\text{gas}}^{-1}$). The FT images shown in e) and f) correspond to the individual Pd nanoparticles depicted in c) and d), respectively.

$0.063 \text{ g}_{\text{C}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$). Therefore, the deactivation of the Pd-IW catalyst in the stability test and the change of selectivity of the reaction products observed can be explained in terms of the sintering of the Pd phase with the concomitant loss of the metal surface area, which is likely responsible for the appearance of methanol among the reaction products, as well as by the formation of carbonaceous deposits. Clearly, this catalyst prepared by conventional means is not adequate for practical DME steam reforming. In contrast, the architecture of the Pd-G0 catalyst after the stability test is virtually identical to that of the as-prepared sample. A representative HRTEM image of the catalyst after the stability test is shown in Figure 5b. Well-dispersed and isolated Pd nanoparticles of $\delta 4\text{--}5 \text{ nm}$ in diameter are identified over the alumina support. All the nanoparticles show lattice fringes that correspond to metallic Pd (i.e., $\{111\}$ and $\{200\}$ crystallographic planes at 2.2 and 1.9 Å, respectively). Detailed HRTEM images of two of these Pd nanoparticles oriented along the $[110]$ crystallographic direction are depicted in Figure 5c and d, and the corresponding Fourier-transformed images are shown in Figure 5e and f. Interestingly, the interface between the Pd nanoparticles and the Al_2O_3 support is poorly defined, which is in accordance with the existence of amorphous SiO_2 in contact with both the metal nanoparticles and the support, as discussed above. The existence of SiO_2 at the anchoring points between the Pd nanoparticles and the support is likely responsible for the lack of sintering of the Pd nanoparticles under the reaction conditions, which results in a stable and robust catalyst for the steam reforming of DME. The TPO analysis of Pd-G0 after the stability test confirmed the absence of deposited carbon ($<10^{-4} \text{ g}_{\text{C}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$).

In situ XPS

To corroborate our interpretations, in situ XPS experiments were performed on Pd-IW and Pd-G0 following the sequence: (i) as prepared, (ii) after treatment under H_2 at 573 K, (iii) after methanol steam reforming ($\text{MeOH}/\text{H}_2\text{O}=1:6$) at 823 K, and (iv) after H_2 treatment at 823 K. The steam reforming of methanol was selected for the experiments as it is the second step of the steam reforming of DME [Eq. (3)] that occurs over the Pd phase. In addition, XPS spectra were recorded over Pd-G0 following the impregnation of the preformed Pd nanoparticles

protected with the carbosilane dendron G0 and after calcination at 473, 573, 673, and 773 K. The results are summarized in Table 3.

The spectrum recorded after the impregnation of the alumina support with preformed Pd nanoparticles protected with the carbosilane dendron G0 indicates the presence of large quantities of carbon in addition to Pd, Si, O, and Al. The analysis of the Pd3d photoelectrons indi-

Table 3. Surface atomic composition of Pd-G0 and Pd-IW recorded by in situ XPS at different stages.

Treatment	Pd/Al	Pd _{red} /Pd _{ox}	Si/Al	C/Al	Pd/Al	Pd _{red} /Pd _{ox}	C/Al
Impregnation	0.027	4.4	0.015	0.27	–	–	–
O ₂ 473 K	0.026	2.9	0.016	0.26	–	–	–
O ₂ 573 K	0.025	0.5	0.013	0.18	–	–	–
O ₂ 673 K	0.023	0.6	0.012	0.06	–	–	–
O ₂ 773 K	0.021	0.6	0.014	0	0.014	0.5	0
H ₂ 573 K	0.021	1.5	0.013	0	0.013	2.1	0
MSR 823 K	0.021	4.1	0.014	0	0.010	4.5	0.06
H ₂ 823 K	0.020	3.9	0.014	0	–	–	–

cated that Pd was largely reduced, as expected from the starting Pd nanoparticles. Upon progressive calcination at 473–773 K, the amount of carbon diminished progressively, whereas the Si/Al atomic ratio was approximately constant at 0.012–0.014, in accordance with the formation of SiO_2 following the decomposition of the carbosilane dendrons. Pd was partially oxidized upon calcination, as expected,^[58] and sintered slightly, as the Pd/Al atomic ratio decreased from 0.027 to 0.021. For Pd-IW, the surface Pd/Al atomic ratio was lower, 0.014, because of the presence of larger Pd nanoparticles, as discussed previously. After oxidation at 773 K, no carbon remained at the surface of either sample. The activation of the catalysts under H_2 at 573 K maintained their surface atomic ratios, and the only significant change recorded was the reduction of Pd. This reduction was more severe in Pd-IW than Pd-G0, which is explained in terms of Pd particle size; the smaller the Pd nanoparticles the stronger the interaction with the support and the more difficult the reduction of Pd. Under methanol steam reforming (MSR) conditions, important changes in the surface of the catalysts were observed. First, the Pd nanoparticles sintered in Pd-IW (the Pd/Al atomic ratio decreased from 0.013 to 0.010), whereas the Pd dispersion remained unchanged in Pd-G0 (Pd/Al=0.021). Second, an accumulation of carbon was observed on the surface of the Pd-IW catalyst, whereas no carbon build-up was detected over Pd-G0. Finally, Pd was reduced strongly because of the formation of hydrogen through the steam reforming of methanol and temperature. This was corroborated in Pd-G0 by H_2 treatment at the same temperature (823 K), which did not change the Pd_{red}/Pd_{ox} ratio significantly.

Conclusions

A new strategy to design robust catalysts for the steam reforming of dimethyl ether (DME) has been accomplished over Pd/Al₂O₃ catalysts prepared from preformed Pd nanoparticles protected with carbosilane dendrons. Upon calcination, the protecting shell decomposes and leaves the Pd nanoparticles anchored to the support in contact with SiO₂, which prevents metal sintering under the reaction conditions. However, a large amount of SiO₂ is detrimental for the reaction as some of the active sites are blocked; therefore, an optimum length of the carbosilane dendron should be selected. High-resolution TEM studies reveal that Pd nanoparticles prepared from preformed Pd protected with carbosilane dendrons are much smaller, well dispersed, and catalytically active for DME steam reforming than Pd prepared from preformed Pd nanoparticles protected with dodecanethiol or Pd/Al₂O₃ prepared by conventional impregnation. Under DME steam reforming conditions, Pd nanoparticles sinter in the conventional Pd/Al₂O₃ catalyst and in the catalyst prepared from preformed Pd nanoparticles protected with dodecanethiol and, at the same time, carbon deposition occurs, with the concomitant deactivation of catalysts. No carbon accumulation was observed over the catalysts prepared from preformed Pd nanoparticles protected with carbosilane dendrons, which show an outstanding stability under real catalytic operation conditions (823 K, S/C=3, W/F=0.2 g_{catalyst} s mL_{gas}⁻¹).

in toluene. This toluene solution was used to impregnate the Al₂O₃ support, which was subsequently dried at 353 K for 2 h and calcined at 773 K for 3 h (2 K min⁻¹). This catalyst is denoted as Pd-D (D stands for dodecanethiol).

Three different Pd/Al₂O₃ catalysts were prepared with carbosilane dendrons that belong to different generations of the same family (G0, G1, and G2). The Pd nanoparticles protected with dodecanethiol and the three different carbosilane dendrons are shown in Figure 6. The carbosilane dendrons were first synthesized following the procedure described in Ref. [60]. Pd nanoparticles protected with the carbosilane dendrons were prepared by adding a solution

Figure 6. Scheme of the preformed Pd nanoparticles prepared protected with a) dodecanethiol and the carbosilane dendrons b) G0, c) G1, and d) G2.

Experimental Section

Catalyst preparation

Several Al₂O₃-supported Pd catalysts (Pd loading of 1 wt%) were prepared by incipient wetness impregnation from different precursors. The precursors were PdCl₂ and preformed Pd nanoparticles protected with dodecanethiol or carbosilane dendrons. The Al₂O₃ support was prepared by the calcination of boehmite (g-AlO(OH), Sasol) at 773 K for 4 h (47 m² g⁻¹, 27.8 mmol_{NH₃} g⁻¹). The conventional Pd/Al₂O₃ catalyst was prepared by impregnation from an ethanolic solution of Pd(NO₃)₂ followed by calcination at 773 K for 3 h (2 K min⁻¹). This sample is denoted as Pd-IW. Pd nanoparticles protected with dodecanethiol were prepared following the procedure described in Ref. [59]. The resulting nanoparticles were solved

of 1 mmol of dendron G0 (0.148 g) or G1 (0.449 g) in THF to a solution of [Pd(OAc)₂]₃ (0.225 g, 0.33 mmol) in THF (10 mL). After stirring for 30 min, a 1.0 M THF solution of LiBH(C₂H₅)₃ (10 mL; 84 mmol) was added dropwise. The resulting solution was stirred for 3 h, and the nanoparticles were precipitated upon the addition of ethanol. The suspension was centrifuged, and the resulting nanoparticles were washed four times with ethanol and dried under vacuum. Finally, the nanoparticles were solved in toluene. An analogous procedure was followed to obtain Pd nanoparticles stabilized with G2 but using 0.21 mmol of G2 (0.288 g) and 0.046 mmol of [Pd(OAc)₂]₃ (0.031 g). The resulting nanoparticles were characterized by IR spectroscopy, NMR spectroscopy, and thermogravimetric analysis (TGA).

Pd NPs protected with G0: ^1H NMR (400.1 MHz, CDCl_3 , 298 K), δ = 1.03–0.45 (br, CH_2), 0.26–0.29 ppm (br, SiMe_3); IR (KBr): $\tilde{\nu}$ = 2962 (n(C-H)), 1413, 1261, 1095, 1020, 860, 801 (n(Si-C)), 688 cm^{-1} ; TGA: weight loss 26.9%.

Pd NPs protected with G1: ^1H NMR (400.1 MHz, CDCl_3 , 298 K), δ = 1.70–1.20 (br, CH_2), 0.85–0.46 (br, SiCH_2), 0.11–0.20 ppm (br, SiMe_3); IR: $\tilde{\nu}$ = 3427, 2943 (n(C-H)), 1622, 1420, 1261, 1095, 1022, 863, 801 (n(Si-C)), 683 cm^{-1} ; TGA: weight loss 48.4%.

Pd NPs protected with G2: ^1H NMR (400.1 MHz, CDCl_3 , 298 K): δ = 1.63–1.22 (br, CH_2), 0.69–0.46 (br, CH_2), 0.15–0.10 ppm (br, SiMe_3); IR (KBr): $\tilde{\nu}$ = 2954, 2912 (n(C-H)), 1634, 1415, 1248, 1079, 1023, 863, 835 (n(Si-C)), 693 cm^{-1} ; TGA: weight loss 69.1%.

The Pd/ Al_2O_3 catalysts were prepared by impregnation from toluene solutions that contained Pd nanoparticles protected with the different carborane dendrons followed by calcination at 773 K for 3 h (2 K min^{-1}). These catalysts are denoted as Pd-G0, Pd-G1, and Pd-G2, in which G0, G1, and G2 correspond to the zero generation (G0), the first generation (G1), and the second generation (G2) of dendrimers.

Catalyst characterization

HRTEM was performed by using a JEOL JEM 2010F electron microscope equipped with a field-emission source at an accelerating voltage of 200 kV. For the thiol- and dendrimer-protected nanoparticles, the sols were dropped directly onto carbon-coated grids. For the Pd/ Al_2O_3 catalysts, powders were suspended in methanol under ultrasonic treatment before they were deposited on holey carbon-coated grids. The point-to-point resolution achieved was 0.19 nm, and the resolution between lines was 0.14 nm. A minimum of 200 particles were measured in each sample for particle size determination. The size limit for the detection of nanoparticles on the support was $\delta 1$ nm. The average particle diameter was calculated from the mean diameter frequency distribution with the formula: $d = \sum n_i d_i / \sum n_i$, in which n_i is the number of particles with particle diameter d_i in a certain range. XPS was performed by using a SPECS system equipped with an Al anode XR50 source that operated at 150 mW and a Phoibos 150 MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. The BE values were referenced to the C 1s peak at 284.8 eV. In situ experiments were performed under dynamic conditions in an adjacent chamber at atmospheric pressure equipped with a mass spectrometer to monitor the reaction and an IR lamp to heat the sample. The sample was transferred under ultra-high vacuum between the in situ chamber and the analysis chamber. Gases were accurately dosed into the in situ chamber by using mass flow controllers, and the temperature was measured by using a K-type thermocouple in contact with the sample holder. TPO (10 vol% O_2 in Ar, 30 mL min^{-1}) was performed by using a Catalyst Analyzer BELCAT-M (BEL Japan, Inc.) equipped with a thermal conductivity detector (TCD). The evolution of gases was monitored by MS by using a Cirrus spectrometer from MKS spectra products equipped with a multiplier detector.

Catalytic tests

The DME steam reforming reaction evaluation was accomplished at 673–823 K and atmospheric pressure by using a lab-scale set up. Before reaction, samples were activated at 573 K for 1 h in 10% H_2/N_2 . The temperature of the reactor was increased up to 673 K under N_2 and, at this temperature, the inert gas was replaced by

a gaseous mixture of DME and H_2O in a 1:6 molar ratio ($\text{S/C}=3$), and the catalysts were tested at 673, 721, 773, and 823 K for 2 h at each temperature. Stability tests were performed with the same reaction mixture at 823 K for 48 h. The feed load was $\text{W/F} = 0.2\text{ g}_{\text{catalyst}}\text{ s mL}_{\text{gas}}^{-1}$, which accounted for a gas hourly space velocity (GHSV) of $4.2 \times 10^4\text{ h}^{-1}$. The composition of the gaseous effluent stream was evaluated quantitatively on-line by using a micro GC (Agilent 3000A) equipped with MS 5A, Plot U, and Stabilwax capillary columns and TCD detectors. The products of the reaction were exclusively H_2 , CO_2 , CO, CH_4 , and CH_3OH . Outlet molar flow rates were calculated from the measured composition by GC and using N_2 as an internal standard. DME conversion (C_{DME}) was calculated as $\text{C}_{\text{DME}} = 100 n_{\text{DME,conv}} / 2 n_{\text{DME,in}}$, in which $n_{\text{DME,conv}}$ represents the number of moles of DME converted measured as the sum of moles of CO_2 , CO, CH_4 , and CH_3OH at the reactor outlet and $n_{\text{DME,in}}$ is the initial number of moles of DME. Product selectivity (S_i) was calculated on a dry basis as $\text{S}_i = 100 (n_i / \sum n_i)$, in which n_i is the number of moles of product i . The yield of each product (Y_i) was obtained as $\text{Y}_i = \text{C}_{\text{DME}} \text{S}_i / 100$.

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