

Rhodium Complexed C_2 -PAMAM Dendrimers Supported on Large Pore Davisil Silica as Catalysts for the Hydroformylation of Olefins

Jan P. K. Reynhardt, Yong Yang, Abdelhamid Sayari,* Howard Alper*

Centre for Catalysis Research and Innovation (CCRI), Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, Canada K1N 6N5

Fax: (+1)-613-562-5170, e-mail: abdel.sayari@science.uottawa.ca; howard.alper@uottawa.ca

Received: January 30, 2005; Accepted: May 16, 2005

Abstract: Polyamidoamine (PAMAM) dendrimers up to the third generation were grown for the first time on the surface of a large-pore (18 nm) Davisil silica support. The supported dendrimers of generations 0, 1, 2 and 3 were phosphinomethylated and complexed with rhodium. All the generations were found to be very active for the hydroformylation of olefins. The hydroformylation of 1-octene was accomplished with

a turnover frequency of 1700 h^{-1} at 70°C . The G(1) material was found to be the most active when the different generations were compared at 50% conversion at 70°C

Keywords: functionalized dendrimers; hydroformylation; immobilization; mesoporous silica; rhodium; supported catalysts

Introduction

Dendrimers are macromolecules with very distinct structural characteristics.^[1] They are usually synthesized by stepwise polymerization of branched monomers, leading to highly branched macromolecules. The monomers can be diverse, and many different branching molecules have been incorporated into dendrimers.^[2] Dendrimers can be functionalized quite easily, especially on the surface, and this has led to the use of these molecules as “supports” for transition metal catalysts. Authoritative reviews on dendrimer-based catalysts are readily available.^[3] Functionalized dendrimers grown on solid supports such as resins, polymer beads or inorganic oxides, e.g., amorphous silica, have attracted much interest in recent years as recyclable heterogenized homogeneous catalysts.^[4–11] Alper and co-workers^[4–7] have used Rh- and Pd-complexed dendrimers anchored on an amorphous silica, with an average pore size of 6 nm, as catalysts for various reactions including carbonylation and the Heck reaction. These catalysts were highly efficient and unique activity and regioselectivity are observed in many cases. The catalysts can usually be recycled without significant loss in activity. The higher generation catalysts suffered from reduced activity, even though these systems should have higher concentrations of active sites than their lower counterparts. This was attributed to steric crowding,^[4] due to the size of the dendrimers as well as the wide pore size distribution of the amorphous silica support. To investigate the effect of the support porosity we syn-

thesized rhodium-functionalized polyamidoamide (PAMAM) dendrimers on a periodic mesoporous MCM-41 silica with large pore (6.5 nm).^[12] We found that the pore size indeed influences the success of the dendrimer synthesis, and a threshold is reached at G(3), when the dendrimer becomes too large to fit inside the pores of the support. This has the undesirable effect of causing the higher generations to be subject to significant steric crowding, and has a detrimental effect on the activity of the catalysts. In another study,^[13] we used a pore-expanded MCM-41 silica with 10.8 nm pores, and were able to successfully synthesize up to G(4) PAMAM dendrimers within the support channels with an average yield per synthesis step better than 99%. Likewise, Acosta et al.^[14] synthesized up to G(4) triazine-diamine dendrimers inside the channels of 8.3 nm pore SBA-15 silica.

The purpose of the current investigation is to determine if dendrimers synthesized on a silica with an essentially flat external surface would be subject to similar steric interactions, and thereby distinguish between steric effects due to the pore geometry of the support, and those due to the increasing size of the dendrimers themselves. To this end we synthesized PAMAM dendrimers up to the third generation on very large pore (18 nm) amorphous silica available commercially as Davisil grade 643. The relatively large size of the pores when compared to the size of the dendrimers gives a situation where a flat external surface is simulated.

Results and Discussion

Characterization Results

Figure 1 depicts the nitrogen adsorption-desorption isotherms for Davisil silica and the supported dendrimers. All isotherms were IUPAC Type IV with the characteristic nitrogen condensation and evaporation steps. All the structural properties calculated based on nitrogen adsorption data are shown in Table 1. As indicated by the fact that the nitrogen condensation steps are not very sharp, the pore size distributions of all materials are quite broad, and the average sizes given in Table 1 should be used as rough estimates. It is instructive to note that the surface area, the pore volume and pore size decrease significantly, but not linearly, with increasing dendrimer generations. Compared to G(−0.5) material, i.e., pure Davisil silica, the G(0), APTES-grafted Davisil, exhibited a significantly lower BET surface area ($S_{\text{BET}} = 230$ vs. $280 \text{ m}^2 \text{ g}^{-1}$), pore volume ($V = 0.77$ vs. $0.95 \text{ cm}^3 \text{ g}^{-1}$) and pore size ($D_{\text{KJS}} = 16.8$ vs. 18.0 nm). This is consistent with similar observations reported in the literature.^[12–14,15–17] Further decreases of the specific surface area, pore volume and size occurred upon reaction of methyl acrylate with G(0) material to obtain G(0.5). Compared to the starting material, the surface area and pore volume decreased by about 40%, whereas the pore size decreased by *ca.* 14%. However, as shown

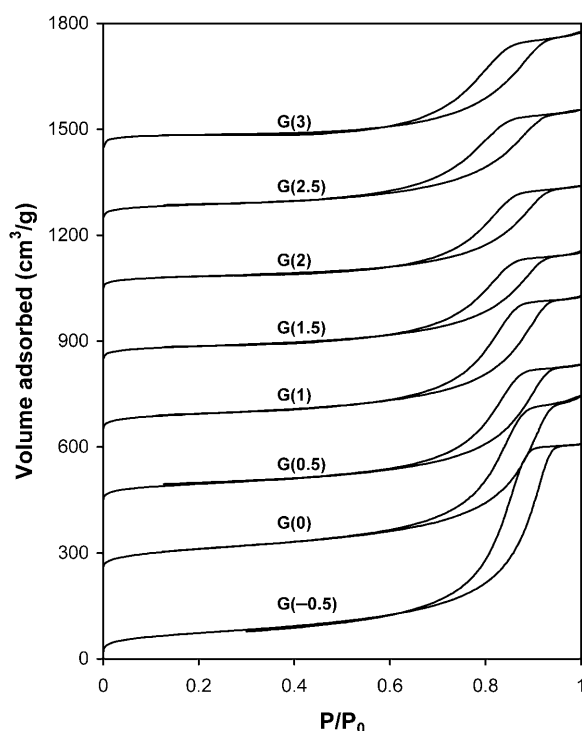


Figure 1. Nitrogen adsorption-desorption isotherms for Davisil supported dendrimers.

in Table 1, upon reaction of methyl propylaminopropionate-functionalized Davisil [G(0.5)] with ethylenediamine to obtain G(1) material, the structural properties hardly changed. This is most likely due to the fact that there is only a small difference in size between the half generations and the next full generations, whereas the radius of the dendrimers changes significantly between full generations and the following half generations.^[12] Thus, a substantial decrease of S_{BET} , V and w takes place only during the branching steps. Consistent with this observation, the surface area, pore volume, and size of G(1.5) were much lower than those of G(1), but almost identical to those of G(2). Similarly, the G(2.5) and G(3) exhibit a drop in the pore size, but for these materials the surface area changed only modestly. This is significantly different from the 6.5 nm pore MCM-41-supported dendrimers prepared previously where pore blocking was observed at G(2.5)–G(3).^[12]

Cross-polarized magic angle spinning (CP/MAS) ^{13}C NMR was used in this study for the identification of functional groups. Figure 2 shows a representative ^{13}C NMR spectrum. This spectrum exhibits the same general features as observed for G(3) dendrimer supported on large-pore (6.5 nm)^[12] or pore-expanded (10.8 nm)^[13] MCM-41 silica, with the signals at 51.56 and 38.04 ppm corresponding to the carbons of the ethylenediamine moiety and the backbone of the methacrylate moiety, respectively. The two remaining carbons from the amino-propylsilane are barely visible at 10.09 and 23.02 ppm. This spectrum serves to show that the amide signal at 173.91 ppm, although clearly visible and large, is subject to considerable line broadening and therefore does not allow for clear distinction between amide and ester groups (172.78 ppm) which occur at a different stage of dendrimer growth. This is a limitation of the ^{13}C NMR technique because the full dendrimer generations were prepared by changing ester groups into amide groups and should therefore only contain amides. It is thus impossible to ascertain from ^{13}C NMR if full conversion between half and full generations was accomplished. As shown below, FTIR spectroscopy was found to be an ideal tool to address this shortcoming.

Table 1. Surface area (S_{BET}), pore size (D_{KJS}) and pore volume (V) for the Davisil series dendrimers.

Generation	S_{BET} [$\text{m}^2 \text{ g}^{-1}$]	D_{KJS} [nm]	V [$\text{cm}^3 \text{ g}^{-1}$]
−0.5 ^[a]	280	18.0	0.95
0	230	17.5	0.77
0.5	169	15.5	0.60
1	163	14.4	0.59
1.5	133	13.4	0.52
2	132	13.2	0.50
2.5	130	11.5	0.48
3	126	11.3	0.50

^[a] Generation (−0.5) refers to the Davisil silica support.

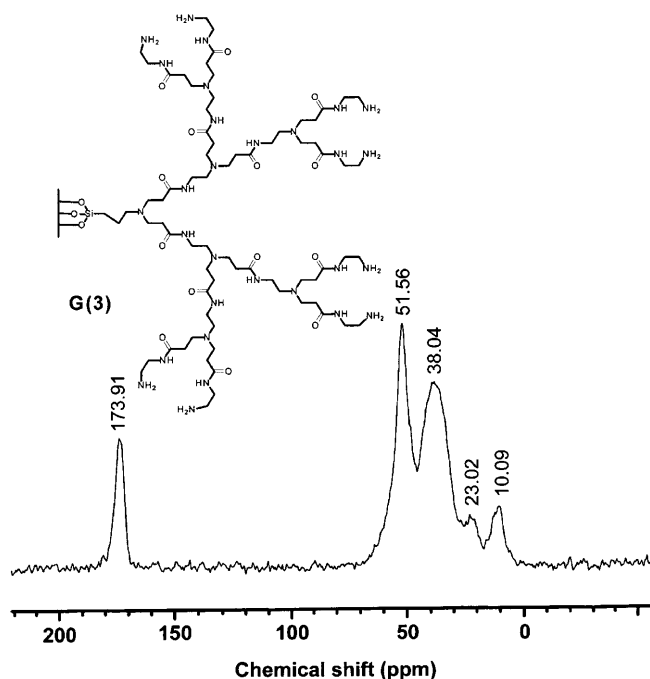


Figure 2. ^{13}C CP/MAS NMR spectrum of the $\text{G}(3)\text{C}_2\text{-PA-MAM}$ dendrimer supported on Davisil silica.

The phosphinomethylated dendrimers were characterized by solid-state ^{31}P and ^{13}C NMR spectroscopy. The ^{13}C NMR spectra showed a new signal at 129 ppm corresponding to the aromatic carbons of the phosphine groups. A signal at -28 ppm in the ^{31}P NMR spectrum compares well with previously reported systems^[5] and the internal standard ($[\text{MeP}^+\text{Ph}_3]\text{Br}^-$) gave a signal at 20.71 ppm. After complexation, the ^{31}P NMR spectrum had 2 signals, one at -28 ppm corresponding to the uncomplexed phosphines, and the other at 24.9 ppm corresponding to the rhodium-complexed phosphines.

Infrared spectroscopy was used to complement the ^{13}C NMR data. The IR spectra for the support [$\text{G}(-0.5)$], the grafted propylamine [$\text{G}(0)$] and the supported dendrimers [$\text{G}(0.5)\text{--G}(3)$] are shown in Figure 3. The absorption band at 1740 cm^{-1} , clearly visible in all the half generations, was attributed to the CO stretching of the ester groups. The signals at 1643 cm^{-1} and 1547 cm^{-1} were due to the CO stretching and the N–H bending/C–N stretching of the secondary amide groups, respectively. It is therefore possible to distinguish between the amide function in the full generation dendrimers and the ester function in the half generations. Thus, FTIR spectroscopy offers a simple tool to determine if the amidation reactions proceed to full conversion. However, FTIR does not provide any evidence as to whether the Michael additions proceed to completion or not. The FTIR spectrum of the $\text{G}(0.5)$ species clearly shows the ester incorporation but at $\text{G}(1)$, some ester functional groups can still be detected even though the amides now represent the largest part of the functional

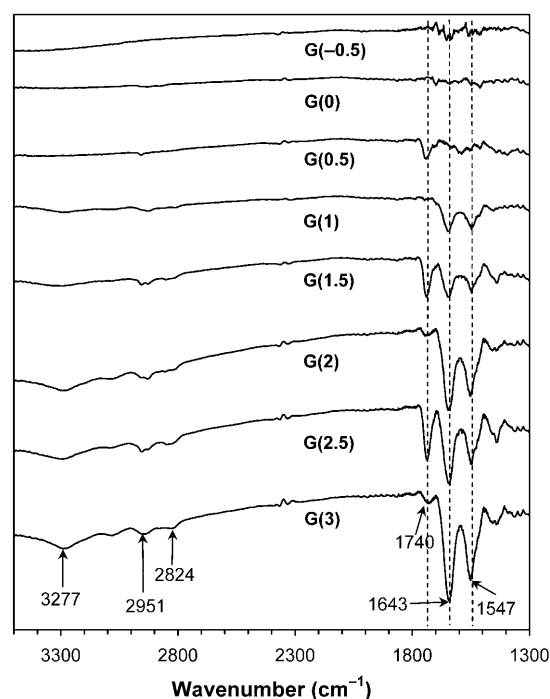


Figure 3. FTIR spectra for the Davisil supported dendrimers.

groups. Then from $\text{G}(1)$ to $\text{G}(1.5)$, the incorporation of the ester groups is again clearly demonstrated. Likewise, at $\text{G}(2)$, FTIR offered evidence of unreacted ester groups and a small amount of ester groups remained even up to $\text{G}(3)$. The spectra were recorded using an ATR system that allows direct comparison between the samples due to the uniform contact of the sample with the ATR crystal. Therefore the increasing intensity of the peaks can be directly related to the amount of amides and esters in the samples. It is, however, difficult to quantify this increase due to the increasing organic mass added to the Davisil silica, and it is impossible to correct these spectra without using other information like silica content from TGA data. The absorption at 3277 cm^{-1} was assigned to the amide N–H stretching, whereas the absorptions at 2951 cm^{-1} and 2824 cm^{-1} were due to C–H stretching in the molecule. However, the bands at 1740 cm^{-1} , 1643 cm^{-1} and 1547 cm^{-1} are the most important indicators as to how successful the dendrimer growth was.

The TGA spectra of all half and full generations are represented together in Figure 4. It is clear that the half generations and their next full generations exhibit similar weight loss indicating that the dendrimers are of similar molecular weights, and by inference similar sizes. This is consistent with the behavior of pore size and volume as determined by nitrogen adsorption (Figure 2, Table 1) and by the theoretical weight losses as shown in Table 2.

To assess the effectiveness of the reactions leading to different dendrimer generations, a method for accurate

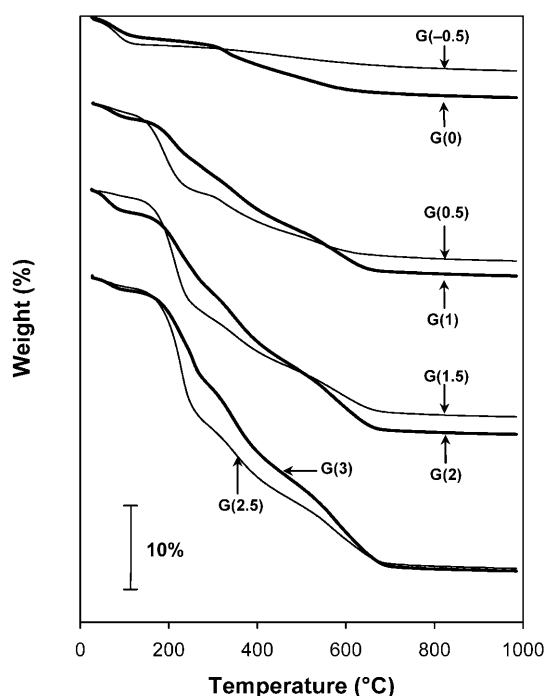


Figure 4. Weight loss as measured by TGA for Davisil supported dendrimers.

determination of the yield of such reactions was developed based on the combined use of TGA data and elemental analysis (EA) data with baseline correction. The EA was used to firstly determine the amount of amines on the surface of the Davisil after grafting of APTES, i.e., G(0). This procedure is, in our view, more accurate and reproducible than previously used acid-base titration.^[18] As shown in Table 2 (column 7), the EA data for the G(0) material allowed us to calculate the weight loss that would correspond to quantitative

formation of dendrimers at every step of the synthesis. The actual weight loss corresponding to the combustion of supported dendrimers was determined by thermogravimetry as the weight loss between 120 and 800 °C, i.e., excluding the weight loss due to the desorption of water (Table 2, column 5). This value was further corrected for the weight loss due to the amount of silica in the sample by using the weight loss of the unmodified Davisil silica support (Table 2, column 6). The weight losses for all materials were also calculated by adding the experimental amounts of C, N and H obtained by EA and the amount of oxygen calculated based on the theoretical oxygen to nitrogen ratio of any given dendrimer (Table 2, column 7). It is interesting to note that the obtained weight losses were consistent within 1–2% with corrected TGA derived weight losses (Table 2, column 6).

Assuming that all synthesis steps proceed with 100% yield, theoretical weight losses (Table 2, column 7) were calculated based on the nitrogen content of material G(0). Comparison between the corrected experimental TGA weight loss and the theoretical weight loss allowed us to calculate the overall yield (OY) for each dendrimer generation (Table 2, column 8). It is seen that as the dendrimer generation increases, the OY decreases to reach 51.30% for the G(3) species. At first glance these results seem disappointing. However, a closer inspection of the statistics of dendrimer growth shows otherwise. At issue is the determination of the average yield (AY) per reaction (i.e., synthesis step) based on the overall yield, which represents the cumulative yield of all the steps involved. To address this question, let us consider the synthesis of the G(3) material. The G(3) dendrimer was obtained from G(0) *via* 28 reaction steps. The following relationship holds: $OY = (AY)^x$, where x is the number of reactions involved.

Table 2. Comparison between experimental (TGA and elemental analysis) and theoretical weight losses for the Davisil series dendrimers.

Generation	Composition ^[a]			Experimental weight loss ^[b] [%] (corrected)	EA weight loss ^[c] [%]	Theoretical weight loss ^[d] [%]	Overall yield [%]
	N [%]	C [%]	H [%]				
0	1.23	3.12	1.09	3.84	5.44	5.10	75.28
0.5	1.16	8.93	1.94	14.48	17.33	17.55	82.51
1	3.22	9.76	2.15	15.83	16.60	20.93	75.64
1.5	2.90	13.51	2.51	23.35	25.55	36.83	63.39
2	4.67	13.74	2.70	23.77	23.57	40.76	58.33
2.5	4.20	17.08	3.03	30.96	32.42	56.98	54.33
3	5.93	17.00	3.23	31.04	29.43	60.51	51.30

^[a] Determined by elemental analysis.

^[b] Determined by TGA as the weight loss between 120 and 800 °C, excluding the loss of water. This loss was corrected by taking into account the weight loss of the unmodified silica support.

^[c] Corresponds to the amount of N, C and H determined by elemental analysis and the amount of oxygen calculated on the basis of the theoretical O/N ratio of any given dendrimer.

^[d] This weight loss, calculated on the basis of amine content of G(0), corresponds to complete formation of dendrimers at every step of the synthesis.

Thus, $AY = (OY)^{1/x}$. In the case of the current G(3) dendrimer, $AY = (0.513)^{1/28} = 0.976$. This shows that although the OY for the dendrimer at G(3) is only 51.3% it is probably as good as is attainable in the divergent dendrimer synthesis approach without purification, and with all the steric interactions involved.^[19]

This finding obviously means that some reactions did not proceed to completion and it is believed that the most hindering factor is the steric interference involved, especially for reactions with the higher dendrimers. Some evidence for this can be seen in the IR study where residual ester functionalities were found in all the full-generation dendrimers. However, compared to smaller pore amorphous silica, the current large pore Davisil silica showed a higher degree of growth and a higher yield of formation of grafted dendrimers.^[7]

Phosphinomethylation and Complexation of the Different Dendrimer Generations

The different dendrimer generations were phosphinomethylated as described earlier.^[12] To carry out further metal complexation, the determination of the amount of phosphine that was incorporated into the material is required. To this end an internal standard method in conjunction with ³¹P NMR measurements was used. This afforded a close approximation of the phosphine content. To determine the phosphine levels more precisely we used ICP MS analysis (Table 3). Although useful, the NMR method was less precise than the ICP MS analysis, but the results nonetheless could be used to determine the amount of rhodium for the complexation. This final synthesis step was achieved by reacting the rhodium-containing metal complex with the phosphinomethylated dendrimer (two equivalents of phosphine for each metal) species under argon in toluene. At this point we were expecting that the higher generations of the dendrimers would suffer from steric encumbrance similar to that observed earlier for the MCM-41 series dendrimers.^[12] Instead, ICP MS analysis and the quantitative ³¹P NMR showed that the higher generations actually contained more phosphorus than the G(0) species

([2.87% for G(3) vs. 1.99% for G(0)]. In our earlier work using a 6.5 nm pore MCM-41 silica we found that the G(3) dendrimer was so sterically hindered due to the size of the dendrimer and the limited space available in the MCM-41 channels that almost no phosphorus was incorporated.^[12] This finding supports the notion that dendrimers supported on external surfaces are less prone to steric factors than ones supported inside the channels of mesoporous materials. It is therefore imperative to investigate the structural characteristics of the support to determine if enough space is available for the desired dendrimer growth before a supported dendrimer synthesis is attempted.

Catalytic Activity for the Hydroformylation of Olefins

The catalytic properties of G(0)–G(3) materials were investigated using the hydroformylation of olefins as a test reaction. Among other substrates, a relatively long-chain linear olefin was used in the hydroformylation test reaction due to the specific separation difficulties facing industrial processes of these olefins. The separation becomes challenging due to the high boiling point of long-chain aldehyde products, and homogeneous catalysts of these olefins should not only be temperature-stable but very robust as distillation is usually used to separate the catalyst and product streams. In the case of a heterogeneous catalyst, a simple separation by filtration would have significant impact on the hydroformylation of these olefins. 1-Octene was selected as the olefin substrate and remarkable activity was achieved with the current catalysts. The G(0) catalyst gave a turnover frequency (TOF) of over 1700 h^{−1} at 70 °C with a total turnover number (TON) of 12000.

Similar to the 6.5 nm pore MCM-41 supported dendrimer series,^[12] the current Davisil silica-supported catalysts were also tested for olefin hydroformylation with 1-octene as the substrate. With the MCM-41-supported dendrimers we observed that the higher generations suffer from lower activity due to the lower levels of phosphorus and rhodium, as well as the considerable steric encumbrance of these systems. For the MCM-41 series dendrimers the G(0) catalyst was the most active, and a negative effect of dendrimer growth was observed with the G(2) dendrimer being essentially inactive. The steric encumbrance was so severe that the G(3) catalyst could not be prepared. However, contrary to the MCM-41 series, the Davisil series showed significant activity even to the third generation (Figure 5).

It is clear from Table 4 that the activity of the catalysts decreases with increasing generation, but the G(3) catalysts still showed activity comparable to previously reported systems.^[12] As the rhodium content of the catalysts differ it is difficult to control the concentration of the active sites, and therefore the activity at 50% conversion was compared. In Figure 6 the activity as a function

Table 3. Rhodium and phosphorus ICP MS analysis of the Davisil series dendrimers.

Generation	P [wt %]	Rh [wt%]
P-G(0)	1.99	
Rh-G(0)	2.43	1.70
P-G(1)	1.86	
Rh-G(1)	1.50	2.87
P-G(2)	1.99	
Rh-G(2)	2.02	3.30
P-G(3)	2.87	
Rh-G(3)	2.10	2.03

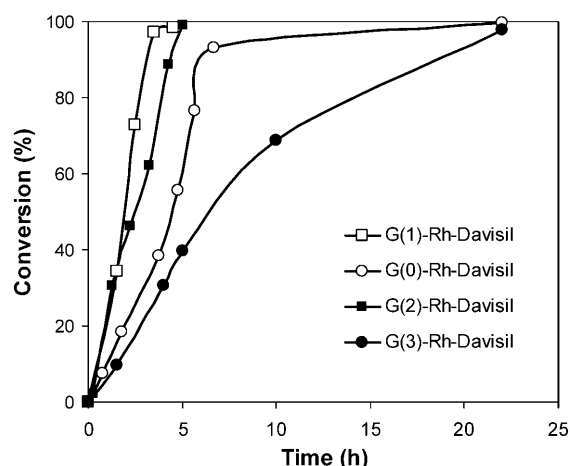


Figure 5. Graphical representation of the conversion vs. time for the G(0)–G(3) Davisil series dendrimer catalysts.

of catalyst mass is compared with the activity as a function of rhodium content. It is interesting to note that the activity of the G(1) catalyst is in both cases the highest and the other generations are normalized using this value. Moreover, it is important to point out that contrary to the MCM-41 series,^[12] the G(1) catalyst has higher activity than the G(0). This shows that the support plays an important role in obtaining high dendrimer generation active catalysts.

The G(1) catalyst was then tested for activity with various other substrates. Vinyl acetate, vinyl benzoate and styrene were selected because these substrates are com-

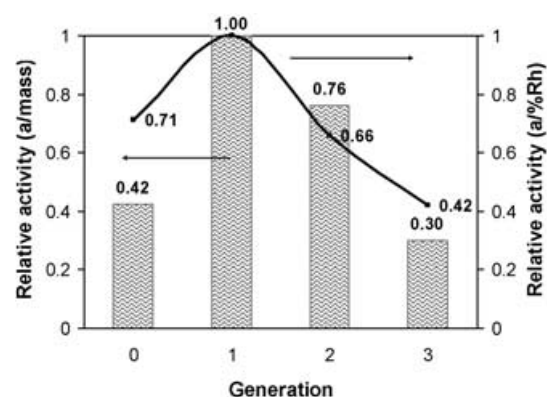


Figure 6. Graphical representation of the relative activity of G(0)–G(3) Davisil series dendrimer catalysts taken at 50% conversion.

monly used in industry. All reactions were affected at 70 °C as the MCM-41 substrates showed the best activity at this temperature (Table 5). The catalysts were tested for recyclability, but none of the generations could be recycled. This is surprising as the MCM-41 catalysts could be recycled without much loss of activity. It therefore appears that the pore structure also has a significant effect on the success of the recyclability. This could be due to the higher local concentration of phosphine in the sterically encumbered environment inside the pores of MCM-41. This would allow leached rhodium to be re-captured before it could diffuse out of the pores, a significant difference between the two supports.

Table 4. Comparison of the activity for the hydroformylation of 1-octene of Rh-complexed Davisil supported dendrimers with different generations.^[a]

Entry	Generation	Time [h]	Conversion [%]	L : B	TOF ^[b] [h ⁻¹]
1	0	6.67	93	1.93	1700
2	1	4.5	99	1.65	1600
3	2	5	99	1.8	1360
4	3	22	98	1.70	300

^[a] Conditions: 50 mg of catalyst, 100 mmol of 1-octene, 70 °C, 1000 psi H₂:CO = 1 : 1 in cyclohexane (90 mL)

^[b] TOF is the number of hydroformylated substrate molecules per hour and per Rh atoms. This is an average turnover frequency over the whole reaction time.

Table 5. Activity in the hydroformylation reaction for the Rh-complexed Davisil supported G(1) dendrimer.^[a]

Entry	Substrate	Amount [mmol]	T [°C]	Conversion ^[c] [%]	B : L ^[d]	TOF [h ⁻¹]
1	styrene	40	70	99	8	325
2	vinyl acetate	40	70	80	14	261
3	vinyl benzoate	40	70	99	26	325
4	1-octene	100 ^[b]	70	99	0.52	1600

^[a] All reaction times: 22 h, 20 mg of catalyst (5.4 μmol Rh) in CH₂Cl₂, 1000 psi H₂:CO = 1 : 1.

^[b] 50 mg of catalyst (14 μmol Rh), 6.67 h.

^[c] Determined by GC.

^[d] Branched to linear aldehyde, determined by ¹H NMR and GC.

Conclusion

Polyamidoamine (PAMAM) dendrimers up to the third generation were grown for the first time on the surface of a large-pore (18 nm) Davisil silica support. Detailed characterization using nitrogen adsorption, solid-state NMR, FTIR, thermogravimetry, and elemental analysis showed that the dendrimers formed inside the channels with an average yield higher than 97%, all synthesis steps being included. Generations 0, 1, 2 and 3 dendrimers supported on Davisil were phosphinomethylated and complexed with rhodium. These catalysts also showed excellent activity for the hydroformylation reaction, with a maximum turnover frequency of 1700 h^{-1} observed for the hydroformylation of 1-octene. The G(1) catalysts was identified as the most active at 50% conversion. The Davisil-supported catalysts could, however, not be recycled.

Experimental Section

Propylamine Grafting

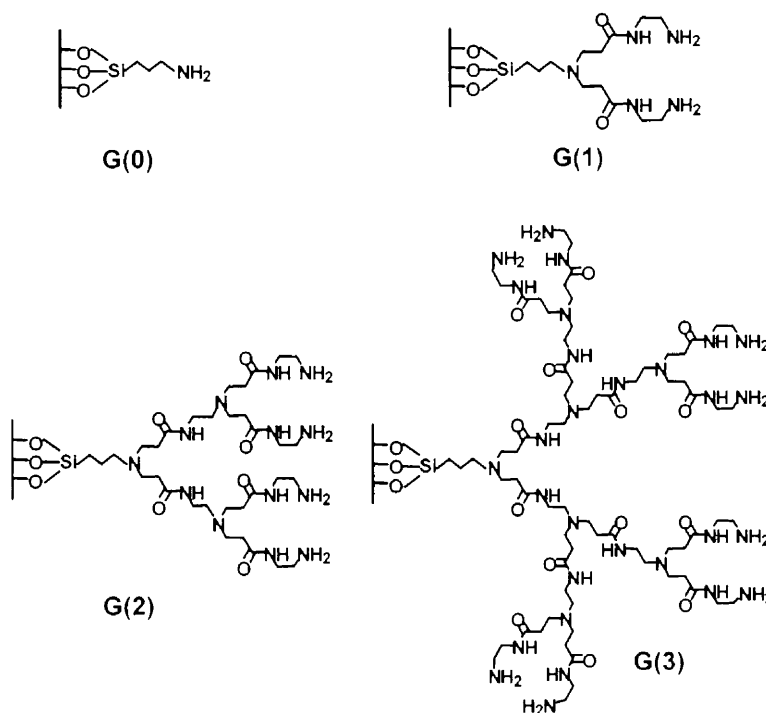
This was performed in a three-necked round flask under nitrogen. 10 g of Davisil (Grade 643, Aldrich) silica gel was first dried at 120 °C for 2 h to remove surface humidity and then added into 200 mL of boiling anhydrous toluene. After 1 h of stirring and refluxing, 4.82 g of 3-aminopropyltriethoxysilane (APTES, Gelest) were added to this mixture, which was then stirred and refluxed at 110 °C for 5 h. The white amine-func-

tionalized Davisil silica was separated by filtration, thoroughly washed with toluene and dried under ambient conditions.

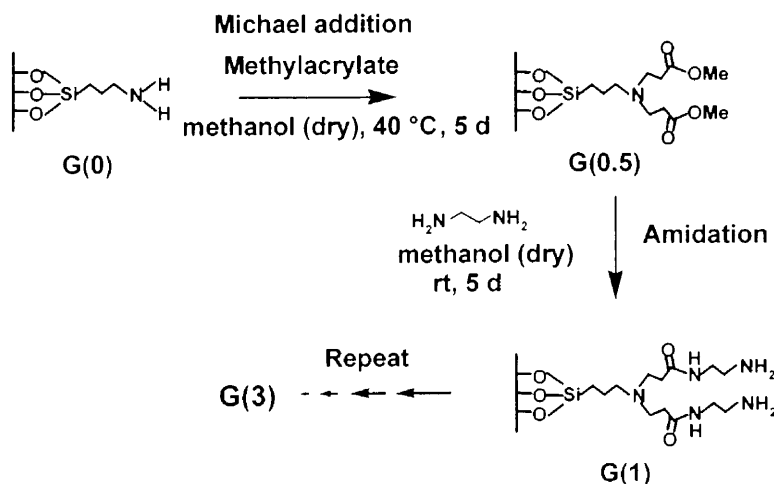
Preparation and Characterization of Dendrimers Supported on Davisil Silica

Polyamidoamine (PAMAM) dendrimers, up to the third generation [G(3)] (Scheme 1) were prepared, on amine-modified large-pore Davisil silica, using a modified multistep procedure based on literature methods^[4] (Scheme 2). Samples will be referred to as G(x), where x is the number of the dendrimer generation. The starting Davisil silica will be designated as G(−0.5), and the propylamine-modified material as G(0). The synthesis of G(0.5) was carried out as follows. Aminopropyl-functionalized Davisil silica (5.2 mmol NH₂, 6 g) and methyl acrylate (0.14 mol, 11.82 g) were stirred at 50 °C in dry methanol (300 mL) under a nitrogen atmosphere for 5 days. The mixture was cooled and filtered through a medium pore frit under nitrogen flow and washed with dry methanol (3 × 50 mL). The residual solvent was removed under vacuum, affording methyl propylaminopropionate-functionalized Davisil in 98% yield.

Supported G(1) dendrimer was prepared as follows. Methyl propylaminopropionate-functionalized Davisil (0.10 mol ester groups, 6 g) was added to ethylenediamine (65 mL) in dry methanol (300 mL) under a nitrogen atmosphere. The reaction mixture was stirred for 5 days and the resulting G(1) dendrimer supported on Davisil was isolated by filtration through a medium pore frit. The solid was washed with dry methanol (3×50 mL), and the residual solvent was removed under vacuum. The higher generations were prepared by repetition of the two steps described above, the amount of reagents being adjusted as required.



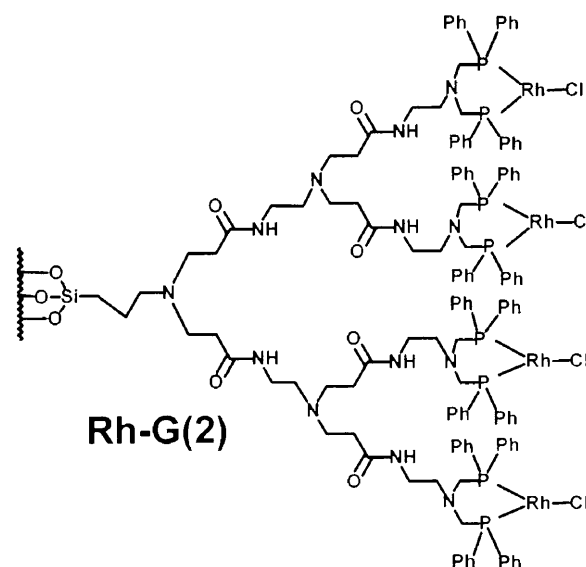
Scheme 1. Structure of generations 0–3 of silica-supported PAMAM dendrimers.



Scheme 2. Preparation of Davisil-supported dendrimers.

Phosphinomethylation of Dendrimers

The dendrimers were phosphinomethylated using diphenylphosphine and paraformaldehyde by modification of the literature method.^[20] The double phosphinomethylation of the terminal amine groups of the dendrimers was achieved by reacting the dendrimers with diphenylphosphinomethanol prepared *in situ* from diphenylphosphine and paraformaldehyde in toluene (110 °C, 48 h). The actual procedure was as follows. To a stirred suspension of paraformaldehyde (0.84 equivs., 1.36 g) in dry toluene (20 mL) under argon was added diphenylphosphine (0.054 mol, 10 g). The resulting mixture was heated to reflux (110 °C) and stirred for 2 h until the mixture became clear. At this stage, aminopropyl-functionalized Davisil (2.25 mmol NH₂, 2.5 g) was added and the resulting suspension was stirred under argon at reflux (110 °C) for 48 h. The phosphinomethylated aminopropyl-functionalized MCM-41 was isolated by filtration through a medium pore frit under a flow of argon and the resulting light yellow solid was washed with toluene (2 × 20 mL). The residual solvent was removed under vacuum. Phosphinomethylated materials will be referred to as P-G(x).



Scheme 3. The Rh-G(2) catalyst.

Complexation of the Phosphinomethylated Dendrimers

The phosphinomethylated dendrimers were readily complexed (Scheme 3) on treatment with the appropriate rhodium complex in toluene (room temperature, 1–2 h under argon). The support turned yellow and decolorization of the supernatant solvent was used as an indication of the extent of complexation. The detailed procedure was as follows. Phosphinomethylated aminopropyl-functionalized Davisil (0.66 mmol PPh₂, 1 g) and [Rh(COD)Cl]₂ (0.165 mmol, 0.0808 g) were stirred under argon for 2 h in dry toluene (20 mL). The mixture was filtered through a medium pore frit under argon flow and washed with toluene (2 × 20 mL). The residual solvent was removed under vacuum to yield the product. The complex was stored under argon. These materials will be designated Rh-G(x).

Characterization

Nitrogen adsorption experiments were performed at 77 K using a Coulter Omnisorp 100 gas analyzer. The specific surface area, S_{BET} , was determined from the linear part of the BET plot ($P/P_0 = 0.05–0.15$). The average pore size (D_{KJS}) for the Davisil-based materials was taken as the maximum of the pore size distribution as calculated from the adsorption branch using the KJS (Kruk, Jaroniec, Sayari) method.^[21] The pore volume, V was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.995.

Quantitative elemental analysis of C, H and N was carried out on a Carlo Erba EA1100 CHNS elemental analyzer. The rhodium and phosphorus contents of the dendrimer species were determined by Galbraith Laboratories, Knoxville, TN, using inductively coupled plasma (ICP MS) atomic emission spectrometry.

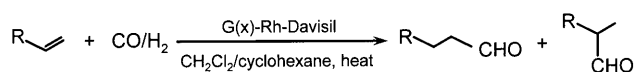
¹³C and ³¹P CP/MAS solid-state NMR spectra were obtained on a Bruker ASX-200 instrument operating at 50.32 and

80.99 MHz, respectively with a spinning rate of 5.0–6.0 kHz and a contact time of 2 ms. $[\text{MeP}^+\text{Ph}_3]\text{Br}^-$ was used as internal standard. ^{29}Si CP/MAS solid-state NMR spectra were also recorded on the same instrument operating at 39.75 MHz with a spinning rate of 5.0–6.0 kHz with a contact time of 2 ms.

Fourier transform infrared spectra were obtained using a Shimadzu FTIR-8400s spectrometer equipped with a Specac Silver Gate (ZnSe crystal) single reflection attenuated total reflectance (ATR) system. Spectra were recorded from 600 cm^{-1} to 4000 cm^{-1} using a resolution of 4 cm^{-1} and 150 scans. Thermogravimetric analysis (TGA) experiments were carried out on a TA Instruments Q500 instrument under air flow (100 mL min^{-1}) at a uniform heating rate of $20^\circ\text{C min}^{-1}$ from 25°C to 1000°C . Approximately 10–20 mg of sample were used for each experiment.

Hydroformylation of 1-Octene (Scheme 4)

To a 300-mL stainless steel, stirred-tank Parr reactor equipped with a pressure transducer and temperature control were added 50 mg of rhodium-containing catalyst (8.3 $\mu\text{mol Rh}$), cyclohexane (90 mL), 1-octene (0.1 mol, 11.2 g) and *m*-xylene (11.2 g) as the internal standard. The reactor was sealed and flushed 3 times with carbon monoxide and then pressurized to 500 psi with carbon monoxide. The reactor was then further pressurized to 1000 psi with hydrogen to give a 1 : 1 ratio of CO/H_2 with a total pressure of 1000 psi. The reactor was stirred at 600 rpm at 70°C . Samples were routinely withdrawn and analyzed by means of GC and NMR.



Scheme 4. The hydroformylation reaction

Acknowledgements

A. S. is a Canada Research Chair in Catalysis Using Nanostructured Materials. We thank the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), and SASOL Technology (R & D) for financial support of this work. We also thank Mike Green at SASOL Technology for support, Tamer El Bokl for recording TGA spectra, and Glenn Facey and Cheryl McDowall for recording NMR spectra.

References

- [1] a) H. Mekelburger, W. Jaworek, F. Vögtle, *Angew. Chem. Int. Ed.* **1992**, 31, 1571; b) G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.* **1985**, 50, 2003; c) G. R. Newkome, G. R. Baker, M. J. Saunders, P. S. Russo, V. K. Gupta, Z. Yao, J. E. Miller, K. Bouillion, *J. Chem. Soc. Chem. Commun.* **1986**, 752; d) G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, P. S. Russo, M. J. Saunders, *J. Am. Chem. Soc.* **1986**, 108, 849.
- [2] a) J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, 266, 1226; b) J. F. G. A. Jansen, E. W. Meijer, E. M. M. de Brabander-van den Berg, *J. Am. Chem. Soc.* **1995**, 117, 4417; c) V. Percec, M. Kawasumi, *Macromolecules* **1992**, 25, 3843; d) V. Percec, P. Chu, M. Kawasumi, *Macromolecules* **1994**, 27, 4441; e) Y. K. Kwon, S. N. Chvalun, J. Blackwell, V. Percec, J. A. Heck, *Macromolecules* **1995**, 28, 1552; f) V. Percec, P. Chu, G. Ungar, J. Zhou, *J. Am. Chem. Soc.* **1995**, 117, 11441; g) U. Stebani, G. Lattermann, M. Wittenberg, H. Wendorff, *Angew. Chem. Int. Ed.* **1996**, 35, 1858; h) S. Watanabe, S. L. Regen, *J. Am. Chem. Soc.* **1994**, 116, 8855; i) G. Bar, R. W. Cutts, T. N. Taylor, T. A. Zawodzinski, *Langmuir* **1996**, 12, 1172; j) S. A. Kuzdzal, C. A. Monnig, G. R. Newkome, C. N. Moorefield, *J. Chem. Soc. Chem. Commun.* **1994**, 2139; k) P. Singh, F. III Moll, S. H. Lin, C. Ferzli, K. S. Yu, R. G. Saul, P. Cronin, *Clin. Chem.* **1994**, 40, 1845; l) R. G. Ispasoiu, L. Balogh, O. P. Varnvski, D. A. Tomalia, T. Goodson III, *J. Am. Chem. Soc.* **2000**, 122, 11005; m) J. C. Roberts, M. K. Bhalgat, R. T. Zera, *J. Biomed. Mater. Res.* **1996**, 30, 53; n) E. C. Weiner, F. P. Auteri, J. W. Chen, M. W. Brechbiel, O. A. Gansow, D. S. Schneider, R. L. Belford, R. B. Clarkson, P. C. Lauterbur, *J. Am. Chem. Soc.* **1996**, 118, 7774; o) M. F. Hawthorne, *Angew. Chem. Int. Ed.* **1993**, 32, 950.
- [3] a) O. A. Matthews, A. N. Shipway, J. E. Stoddard, *Progress in Polymer Sci.* **1998**, 23, 1; b) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* **2001**, 40, 1828; c) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, 101, 2991; d) R. Kreiter, A. W. Kleij, R. J. M. Klein Gebbink, G. van Koten, *Topics in Current Chemistry*, Vol. 217, Springer-Verlag, Berlin, Heidelberg, **2001**, 164; e) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, 102, 3717.
- [4] S. C. Bourque, H. Alper, L. E. Manzer, P. Arya, *J. Am. Chem. Soc.* **2000**, 122, 956.
- [5] S. C. Bourque, F. Maltais, W.-J. Xiao, O. Tardif, H. Alper, P. Arya, L. E. Manzer, *J. Am. Chem. Soc.* **1999**, 121, 3035.
- [6] S. Antebi, P. Arya, L. E. Manzer, H. Alper, *J. Org. Chem.* **2002**, 67, 6623.
- [7] J. P. K. Reynhardt, H. Alper, *J. Org. Chem.* **2003**, 68, 8353.
- [8] P. Arya, G. Panda, N. V. Rao, H. Alper, S. C. Bourque, L. E. Manzer, *J. Am. Chem. Soc.* **2001**, 123, 2889.
- [9] S.-M. Lu, H. Alper, *J. Am. Chem. Soc.* **2003**, 125, 13126.
- [10] a) A. Dahan, M. Portnoy, *Org. Lett.* **2003**, 5, 1197; b) A. Dahan, M. Portnoy, *Chem. Commun.* **2002**, 2700.
- [11] Y. M. Chung, H. K. Rhee, *Chem. Commun.* **2002**, 238.
- [12] J. P. K. Reynhardt, Y. Yang, A. Sayari, H. Alper, *Chem. Mater.* **2004**, 16, 4095.
- [13] J. P. K. Reynhardt, Y. Yang, A. Sayari, H. Alper, *Adv. Funct. Mater.* submitted.
- [14] E. J. Acosta, C. S. Carr, E. E. Simanek, D. F. Shantz, *Adv. Mater.* **2004**, 16, 985.
- [15] C. P. Jaroniec, M. Kruk, M. Jaroniec, A. Sayari, *J. Phys. Chem. B.* **1998**, 102, 5503.
- [16] A. Sayari, S. Hamoudi, *Chem. Mater.* **2001**, 13, 3151.
- [17] H. Y. Huang, R. T. Yang, D. Chinn, C. L. Munson, *Ind. Eng. Chem. Res.* **2003**, 42, 2427.

- [18] N. Tsubokawa, H. Ichioka, T. Satoh, S. Hayashi, K. Fuji-ki, *React. Funct. Polym.* **1998**, 37, 75.
- [19] D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem. Int. Ed.* **1990**, 29, 138.
- [20] M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed.* **1997**, 36, 1526.
- [21] M. Kruk, M. Jaroniec, A. Sayari, *Langmuir* **1997**, 13, 6267.
-