Growth of Aluminum Nitride on Porous Alumina and Silica through Separate Saturated Gas−Solid Reactions of Trimethylaluminum and Ammonia

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Received July 17, 2001

Aluminum nitride-type species were prepared on porous alumina and silica by repeated separate, saturated reactions of gaseous trimethylaluminum (TMA) and ammonia with solid substrates. Reaction cycles of TMA at 423 K and ammonia at 823 K were performed up to six times. Growth per cycle was on average 2.4 AlN units/nm^2, but it increased slightly with the number of reaction cycles. The amount of hydrogen present in NH_x groups increased with the increasing number of reaction cycles. AlN_4 units were observed by ^{27}Al NMR on alumina, but the AlN remained amorphous to X-ray diffraction. Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy revealed that the AlN-type species were spread out evenly on the surface of the particles. TMA reacted with equal probability with the still-exposed silica and the AlN-type species present on the surface, as shown by low-energy ion scattering. ^{29}Si and ^{27}Al NMR suggested that transition from the oxide substrates to aluminum nitride occurred through silicon oxynitride for the silica substrate and through aluminum oxynitride for both substrates.

Introduction

A new type of metal−support interaction is expected through the use of nitrides instead of oxides as catalyst supports. Experiments have been made with aluminum nitride,[1] silicon nitride,[2] and aluminophosphate oxynitride[3] as support for metal catalysts. As an example, silicon nitride support retains a higher dispersion of palladium in methane oxidation at about 1100 K than do conventional oxide supports.[2] The physical properties of nitrides, such as high thermal stability and mechanical strength, are favorable for many catalyst applications. However, nitrides are usually obtained in low-surface-area forms not well suited as a catalyst support. The present work is a continuation of earlier studies,[4−6] whose general aim has been to prepare high-surface-area AlN and to test its suitability as a catalyst support.

Our approach to obtaining AlN in a high-surface-area form was to coat a porous substrate with a layer of AlN-type species. Atomic layer deposition (ALD) was chosen as the coating technique. In ALD, gaseous precursors are reacted with a solid surface up to saturation separately, one at a time.[7] The reaction temperature of the precursors is chosen so that chemisorption, not physisorption or decomposition, takes place. The surface of porous materials can be modified with other materials by ALD without pore blocking taking place.[7] For the growth of AlN, we chose trimethylaluminum (TMA) and ammonia as the precursors, because these are the simplest forms of aluminum alkyl and nitrogen hydride available and their suitability for the production of bulk AlN is known.[8−11]

Separate, saturating reactions of TMA and ammonia have been used to grow AlN on nonporous[12−18] and

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10.1021/cm011176i CCC: $22.00 © 2002 American Chemical Society
Published on Web 01/30/2002

porous[4–6] high-surface-area alumina and silica. Bartram et al.[13] demonstrated the growth of AlN on silica in five reaction cycles of TMA and ammonia at 600 K, Bertolet et al.[15] on alumina in three reaction cycles at 600 K, Soto et al.[18] on alumina in four reaction cycles at 573 K, and Puurunen et al.[5] on porous silica in three reaction cycles of TMA and ammonia at 423 and 673 K, respectively. Quantitative results have shown that, depending on the growth temperatures, steady growth of 3.5 (ref 18) or 2.2 (ref 5) Al and N atoms per square nanometer takes place per reaction cycle of TMA and ammonia. (The 3.5 Al and N atoms per nm^2 was estimated from the 0.073 nm per cycle given in ref 18, assuming a density of 3.26 g cm^{-3} for AlN.[19])

The growth proceeds through two steps. In the first step, TMA reacts with OH groups and oxygen bridges on alumina[6] and silica,[4,20,21] and $AlMe_y$ species with $y = 0$, 1, or 2 are attached to the surface.[4,6,20,21] Aluminum does not remain three-coordinated on the surface but almost always coordinates additionally to a surface oxygen atom.[22] On silica, $O_{4-n}SiMe_n$ species with $n = 1$, 2, or 3 are also formed.[4,20] Independent of the types of reactive sites on the substrates, the number of methyl groups remaining on the surface settles to a value of 5–6 Me nm^{-2} in the reaction.[4–6] The number of attached aluminum atoms is a function of the surface hydrogen content, however.[6] In the second step, that is, the ammonia reaction, the aluminum-bonded methyl groups are replaced with primary amino groups (NH_2) and methane is released. The NH_2 groups may condense to secondary and tertiary amino groups, or they may react further with methyl groups to release methane and form secondary and tertiary amino groups. Few of the silicon-bonded methyl groups react with ammonia at 600 K,[4,13] but at 823 K ammonia removes most of them, replacing them with silicon-bonded amino groups.[4] The amount of nitrogen attached to the TMA-modified surface is a function of the type of the substrate and the reaction temperature.[4,6] For the growth of AlN the two steps are repeated; hydrogen atoms in amino groups serve as reactive sites for TMA during the repeated cycles.

The goal of this work was to prepare AlN-type species in several cycles of TMA and ammonia on porous alumina and silica and to characterize the structure of the formed Al- and N-containing layer. Six reaction cycles of TMA at 423 K and ammonia at 823 K were performed on both substrates. The reaction temperatures were chosen previously.[4,6] The samples were characterized by chemical analysis, nitrogen physisorption, IR and NMR spectroscopy, X-ray diffraction (XRD), scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM–EDS), and low-energy ion scattering (LEIS). The results enabled us to construct a general picture of the growth and to evaluate the suitability of the obtained surface as a catalyst support.

Experimental Section

Materials. AKZO 001–1.5E, crushed and sieved to a particle size of 250–500 μm, was used as the alumina substrate. The alumina was heated for 16 h at 1073 K in ambient air in a muffle furnace to stabilize the number and type of bonding sites at the applied reaction temperatures and, in addition, it was heated in the ALD reactor under vacuum for 6 h at 833 K to remove water physisorbed on it during transfer to the reactor. Grace 432 with particle size 315–500 μm was used as the silica substrate. It was heated for 16 h at 1023 K in ambient air and for 3 h at 823 K under vacuum.

Nitrogen (Aga, H_2O < 3 ppm, O_2 < 3 ppm) was used as an inert carrier gas. TMA (Witco, 97.5 wt %, Cl < 0.01 wt %) and ammonia (Aga, 99.998%, H_2O < 5 ppm) were used as received.

Reaction Procedure. The experimental setup was as described previously.[4–6] Ten grams of the substrate was typically loaded into the reactor. TMA was reacted with the substrate at 423 K and ammonia at 823 K, unless otherwise stated. A nitrogen purge separated the reactions. The ammonia feed was started at the reaction temperature of TMA, and the temperature was elevated, under a flow of ammonia, to the target reaction temperature. This was done to avoid the decomposition of chemisorbed TMA. The samples, cooled to room temperature in a nitrogen flow, were treated inertly to avoid oxidation of the AlN-type surface by ambient air.

The samples are referred to below as "z·AlN/Al_2O_3" and "z·AlN/SiO_2", where z denotes the number of reaction cycles of TMA and ammonia. For $z = 1$, 2, 4, and 6, the reaction cycles were completed, that is, they terminated with the ammonia reaction, whereas for $z = 0.5$, 1.5, and 6.5, the reaction cycles were incomplete and terminated with the TMA reaction.

Characterization. The aluminum contents of the samples were measured with a Siemens X-ray fluorescence spectrometer. The nitrogen and carbon contents were measured with a LECO CHN analyzer by burning at 1223 K in air. Samples were analyzed from the top and bottom parts of the substrate bed and were compared to ensure sample homogeneity. It is possible that the nitrogen analysis cannot detect all the nitrogen present in aluminum nitride, because AlN that is protected by a layer of Al_2O_3 resists oxidation at least up to 1073 K.[23] The measured nitrogen contents should thus be treated not as the true values but as lower-limit estimates of the true values. Nevertheless, the analysis did give valuable information on the trend in the nitrogen content with respect to the number of reaction cycles performed.

Surface areas were measured to evaluate possible pore blocking in the samples and to calculate the element contents per nm^2 of substrate. The specific surface areas were measured with a Micromeritics Asap 2400 instrument by nitrogen adsorption according to the Brunauer–Emmett–Teller method.

The element contents were calculated as atoms per square nanometer of the original substrate surface, denoted as at_i $nm^{-2}_{substrate}$ (substrate = alumina or silica). The measured masses of aluminum, nitrogen, carbon, and hydrogen were subtracted from the mass of the sample. For alumina, where the amount of aluminum attached to the surface in the TMA reaction could not be measured, an Al/N atomic ratio of one was assumed. For the experiments that ended in TMA reaction, the hydrogen content was estimated by assuming methyl groups (with H/C of 3) and tertiary amino groups without hydrogen. If secondary amino groups had been assumed, the calculated element contents would have been at most 0.002 at_i nm^{-2} higher. Note that the unit used for the

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amount of adsorbed atoms, "$at_i\ nm^{-2}_{substrate}$", is a measure of the bulk atomic content only and does not reveal whether the atoms are on the outermost surface. In contrast, the true surface concentration was measured by LEIS.

The surface species were qualitatively characterized by diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy. The spectra were measured inertly as described previously.[4−6]

For the NMR measurements, all samples were transferred under dry nitrogen. The hydrogen-containing species present in the samples were quantified by ^{1}H magic-angle spinning (MAS) NMR, and the silicon-bonded methyl groups were investigated by ^{29}Si cross-polarization (CP) MAS NMR, as described previously.[4−6]

The state of the aluminum atoms in the samples was characterized by ^{27}Al MAS NMR. Spectra were recorded with a Bruker AMX500 spectrometer by using a self-built 3.5-mm probe. Quantitative NMR spectra were taken with a single nonselective pulse of 10° and with a repetition time of 0.2 s. A repetition time of 10 s did not give any additional signal intensity. Samples were loaded into airtight NMR rotors under dry N_2 atmosphere (1 ppm O_2; 2 ppm H_2O), delivered to the NMR probe, and spun in dry nitrogen gas at a speed of 13−14 kHz. For silica samples the number of scans was 50 000−100 000, and for alumina samples the number of scans was 2000. In 6·AlN/Al_2O_3 and 6·AlN/SiO_2, additional long-pulse experiments were made to obtain an estimate for the quadrupolar coupling (QC) and to invert selectively the signal from the Al sites with strong QC. Al sites with very strong QC have three times the nutation frequency as sites with weak QC.[24] The radio frequency field strength was 65 kHz. The external chemical shift reference (0 ppm), and also the intensity reference, was $KAl(SO_4)_2 \cdot 12H_2O$.

The samples were analyzed by wide-angle X-ray diffraction to identify AlN. The instrument was a Siemens D500 diffractometer equipped with a Cu-anode and a curved graphite monochromator in the reflected beam. Crystalline phases were identified automatically through reference to the library of the International Center for Diffraction Data.

SEM−EDS was used to evaluate possible elemental gradients inside the particles. For the examination, the sample particles were embedded in epoxy resin. The cured block was cut with a microtome until a sufficient number of cross-sectioned particles were exposed in the face of the block. The sample was coated with carbon to prevent charging under the electron beam. Examination was made with a JEOL JSM 840A scanning electron microscope fitted with a PGT IMIX III energy-dispersive X-ray analyzer. An accelerating voltage of 15 keV was used in the SEM examination. Al Kα radiation was used, resulting in a resolution of about 1 μm.

LEIS measurements were performed to investigate the coverage of silica by AlN-type species as a function of reaction cycles. In LEIS, the sample surface is bombarded in ultrahigh vacuum with noble gas ions. Part of the ions scatter because of collision with surface atoms; most are neutralized because of multiple collisions. The energy loss of the scattered ions is measured, giving a "mass spectrum" of the outermost atomic layer of the surface. The LEIS experiments were performed in the Calipso LEIS setup, where ions are directed perpendicular to the target, and ions scattered over 145° are analyzed with an energy-resolved ion-scattering spectrometer. An overview of the LEIS technique and the apparatus used can be found in ref 25. Charging of the insulating samples was compensated with low-energy electrons. The total exposures of the samples were about 15×10^{15} ions cm^{-2}.

For the LEIS measurements, the AlN/SiO_2 samples and reference silica and alumina were pressed to tablets under nitrogen and transferred inertly to the vacuum chamber. The Al/Si ratio was calculated as a means of determining the coverage of silica by AlN-type species. In principle, the N/O ratio should have given the same information, but even though care was taken to avoid contamination of the samples by air, the signal of nitrogen was too unreliable for quantitative investigation. Before the measurements the sample surfaces were pretreated with atomic oxygen at room temperature to obtain a clean and well-defined sample surface consisting of silicon and aluminum oxides. The experimental conditions were optimized for the best separation of the overlapping peaks of aluminum and silicon by using 5 keV $^4He^+$ ions as the probe.

The LEIS peaks of Al and Si were fitted by assuming Gaussian peaks for the signals and descending cumulative Gaussian functions with their centers at the corresponding peak centers for the backgrounds of the peaks. An additional linear background was needed to fit the high-energy edge of the spectrum. The widths and energies of the peaks were adopted from the silica and alumina references. Despite charging compensation, minor charging of the sample was unavoidable, which resulted in a slight shift in the energy scale of the spectra. This was corrected by using the oxygen peak position as a reference.

Results

Six reaction cycles of TMA at 423 K and ammonia at 823 K were performed on alumina and silica. The samples prepared on alumina became pale yellow and the samples prepared on silica became light gray when the number of reaction cycles was increased up to six. Pale yellow is the color of AlN;[26] the gray color on silica was probably caused by residual carbon.

Elemental Analysis. The results of the elemental analysis are summarized in Table 1. Because the top and bottom element contents in all cases agreed within analytical accuracy, the samples were concluded to be homogeneous. Previously,[4] we showed that the reactant doses were sufficient for saturation of the substrate surface with the chemisorbed species. The amounts of aluminum and nitrogen per surface area of alumina and silica are shown in Figure 1. Steady increase of the Al and N contents with number of reaction cycles was observed for both substrates, in accordance with previous observations.[6,18] Furthermore, the contents measured for the two substrates were similar. The N/Al ratio in the silica samples was less than one when the number of reaction cycles was four or six. This may have been caused by the difficulty of detecting all the nitrogen that was present in the nitridic species by the analytical method used.

The average amounts of carbon in the 0.5·AlN/Al_2O_3, 1.5·AlN/Al_2O_3, 0.5·AlN/SiO_2, and 1.5·AlN/SiO_2 samples were 5.0, 4.2, 5.4, and 4.8 at_C nm^{-2}. These amounts are close to the saturation level of carbon in methyl groups determined for TMA-modified surfaces, 5−6 Me nm^{-2}.[4,6]

To examine the sensitivity of the samples to air, we left the samples in ambient air for about 2 months. The nitrogen content decreased in both series. On alumina, the amount of nitrogen left in the air-exposed samples was about 20% of the original amount, irrespective of the number of reaction cycles performed. On silica, the fraction of nitrogen that was left seemed to increase with the number of reaction cycles so that about 30% of the original nitrogen remained in the 4·AlN/SiO_2 and 6·AlN/SiO_2 samples.

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Table 1. Results of Chemical Analysis, ^{1}H MAS NMR, and Nitrogen Physisorption Measurements

sample	Al (wt %) top	Al (wt %) bottom	C (wt %) top	C (wt %) bottom	N (wt %) top	N (wt %) bottom	H (wt %)	surface area ($m^2\ g^{-1}$)	pore volume ($cm^3\ g^{-1}$)
Al_2O_3	n.a.[a]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	196[6]	0.65
0.5·AlN/Al_2O_3	n.a.	n.a.	1.8[6]	1.8[6]	n.a.	n.a.	n.a.	n.a.	n.a.
0.5·AlN/Al_2O_3	n.a.	n.a.	1.9[6]	1.9[6]	n.a.	n.a.	n.a.	n.a.	n.a.
1·AlN/Al_2O_3	n.a.	n.a.	<0.1	<0.1	0.9	0.9	0.082	192	0.63
1.5·AlN/Al_2O_3	n.a.	n.a.	1.6	1.6	0.9	0.9	n.a.	n.a.	n.a.
2·AlN/Al_2O_3	n.a.	n.a.	<0.1	<0.1	1.7	1.6	0.12	193	0.62
4·AlN/Al_2O_3	n.a.	n.a.	<0.1	<0.1	3.7	3.5	0.18	172	0.53
6·AlN/Al_2O_3	n.a.	n.a.	<0.1	<0.1	5.7	5.6	0.20	167	0.47
SiO_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	288[4]	1.0[4]
0.5·AlN/SiO_2	2.9[b,4]		2.9[b,4]		n.a.	n.a.	n.a.	n.a.	n.a.
1·AlN/SiO_2	2.8[4]	2.9[4]	0.1[4]	<0.1[4]	1.4[4]	1.5[4]	0.13[4]	273[4]	0.89
1.5·AlN/SiO_2	5.2	5.2	2.5	2.5	1.1	1.2	n.a.	n.a.	n.a.
2·AlN/SiO_2	5.4[b]		<0.1	0.1	2.5	2.5	0.18	275	0.88
4·AlN/SiO_2	10.3	10.3	<0.1	<0.1	4.0	4.1	0.20	240	0.71
6·AlN/SiO_2	15.9	15.4	<0.1	<0.1	6.2	6.0	0.22	223	0.65

[a] n.a., not analyzed. [b] Average content in the sample.

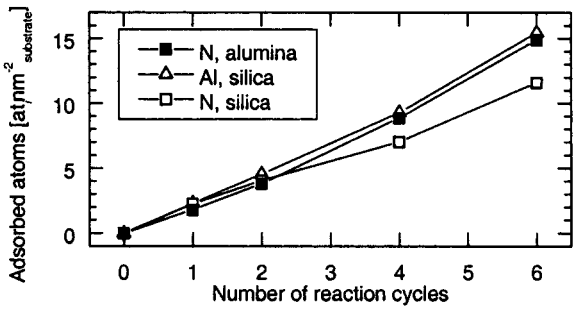

Figure 1. The Al and N contents on alumina and silica as a function of the number of reaction cycles.

Nitrogen Physisorption. The surface areas and pore volumes of the AlN/Al_2O_3 and AlN/SiO_2 series are presented in Table 1. After six reaction cycles, decreases of about 15% and 23% were observed for the surface area of the alumina and silica, respectively. This is of the same magnitude as the weight percentage of the adsorbed layer, indicating that pore blocking did not occur.

DRIFT Spectroscopy. The methyl and amino groups in the samples were investigated by DRIFT spectroscopy. The spectral features of the alumina (Figure 2A, curve a) and the 0.5·AlN/Al_2O_3 sample (Figure 2C, curve a) have been discussed in detail.[6] When the TMA-modified alumina was reacted with ammonia (see Figure 2A, curve b), changes were similar as reported previously:[6] the peaks due to methyl groups (2937, 2897, 2830, 1428, and 1214 cm^{-1}) disappeared, and peaks due to the NH_2 groups appeared in the N–H stretching region (3395 and 3335 cm^{-1}) and in the N–H bending region (1553 and 1512 cm^{-1}). An intense and wide band appeared at 2123 cm^{-1}, and it had a small, sharp shoulder at 2018 cm^{-1}. The origin of these two peaks is unknown.

When TMA was reacted in the second reaction cycle, the peaks due to methyl groups reappeared (Figure 2C, curve b). Compared with the spectrum of the 0.5·AlN/Al_2O_3 sample (curve a), the C–H vibration maxima had shifted to 2933, 2893, 2825, and 1211 cm^{-1}. Absorption bands due to amino groups were seen at 3383, 3325, 3271, and 1510 cm^{-1}, indicating that not all the hydrogen atoms in amino groups had reacted with TMA.

When alumina was modified in two to six complete reaction cycles of TMA and ammonia, the absorbance increased in the N–H stretching region and the peaks became wider (see Figure 2A, curves c–e). A broad feature appeared at about 3221 cm^{-1}, and a smaller absorbance maximum was seen at 3258 cm^{-1}. This indicates that more hydrogen and perhaps a wider variety of NH_x groups were present in these samples. The peak at about 2120 cm^{-1} remained intense in all the spectra, and it shifted from 2123 to 2101 cm^{-1} when the number of reaction cycles increased from one to six.

The spectral features of the silica (Figure 2B, curve a), the 0.5·AlN/SiO_2 sample (Figure 2D, curve a), and the 1·AlN/SiO_2 sample (Figure 2B, curve b) have been discussed in detail.[4] When TMA reacted at 423 K in the second reaction cycle, peaks caused by aluminum-bonded methyl groups[4] reappeared at 2958 (shoulder, sh), 2939, 2897, and 2830 cm^{-1} (Figure 2D, curve c). The peak of the Al–Me groups (2939 cm^{-1}) was more intense than the peak of the Si–Me groups (2958 cm^{-1}, sh), in contrast to what was observed in the first reaction cycle.[4] Absorption bands were left in the N–H stretching region centered at 3381, 3331, and 3273 cm^{-1}, indicating that not all the hydrogen atoms in the amino groups had reacted. Also, a peak was seen at 1511 cm^{-1} in the N–H bending region. To study the effect of the TMA reaction temperature in the second reaction cycle, samples were prepared where TMA was reacted at 523 or 353 K. In the spectrum of the 523 K sample (Figure 2D, curve d), the Si–Me peak was more intense than the Al–Me peak and there was less absorption by NH_x groups. The spectrum of the 353 K sample (Figure 2D, curve b) resembled the spectrum for TMA reacted at 423 K, although there was more absorption by NH_x groups. Evidently, fewer NH_x groups remain and more Si–Me groups are formed as the reaction temperature increases.

When the number of completed reaction cycles was increased from two to six (Figure 2B, curves c–e), absorbance increased especially at the low-wavenumber side of the N–H stretching region, centered at 3260 cm^{-1}, and the N–H stretching peaks lost their sharpness. These trends were like those observed on alumina, although less pronounced. In the N–H bending region, the peak of bridging NH_2 groups (~1504 cm^{-1}) became more intense relative to the peak of terminal NH_2 groups (~1548 cm^{-1}). In accordance with earlier observations,[13] the spectral windows of silica at 950–850

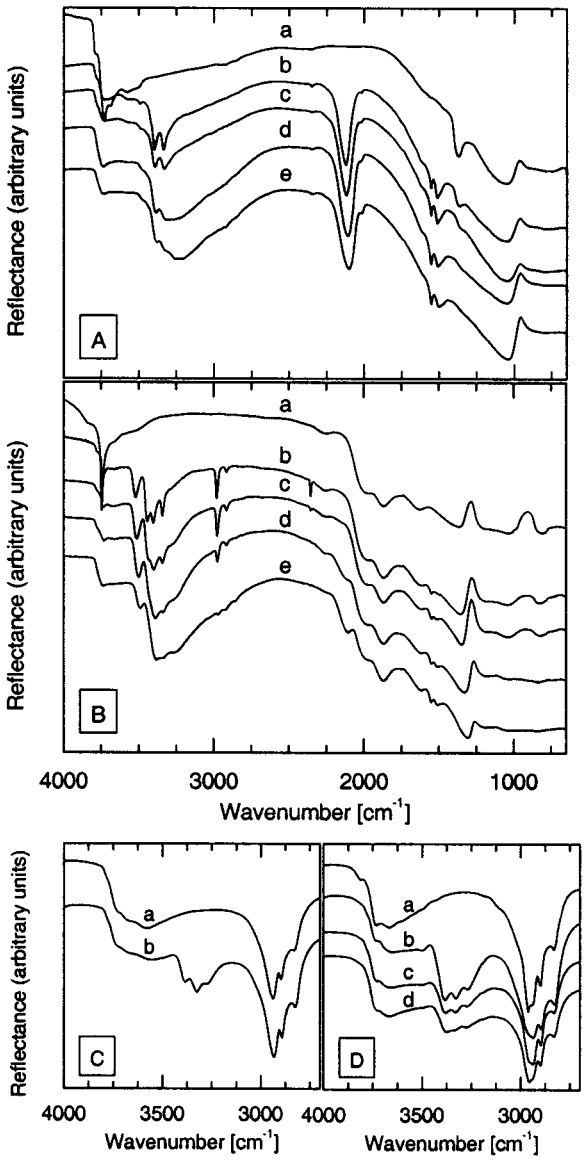

Figure 2. DRIFT spectra of substrates and samples. (A) Spectra of the alumina substrate (a) and of samples 1·AlN/Al_2O_3 (b), 2·AlN/Al_2O_3 (c), 4·AlN/Al_2O_3 (d), and 6·AlN/Al_2O_3 (e). (B) Spectra of the silica substrate (a) and of samples 1·AlN/SiO_2 (b), 2·AlN/SiO_2 (c), 4·AlN/SiO_2 (d), and 6·AlN/SiO_2 (e). (C) Spectra of samples 0.5·AlN/Al_2O_3 (a) and 1.5·AlN/Al_2O_3 (b). (D) Spectra of the 0.5·AlN/SiO_2 sample (a) and of the 1.5·AlN/SiO_2 sample with TMA reacted at 353 K (b), at 423 K (c), and at 523 K (d).

cm^{-1} and 750−650 cm^{-1} gradually filled with the increasing number of reaction cycles. This was caused by the formation of AlN-type species; crystalline AlN has an absorption band centered at ~720 cm^{-1} with a full-width-at-half-maximum of ~300 cm^{-1}.[27] The absorbances of silicon-bonded methyl groups at 2980−2971 and 2917−2914 cm^{-1} decreased with the increasing number of reaction cycles, and almost no peaks were left after six reaction cycles. The absorbance of presumably residual OH groups in the O−H stretching region decreased with the increasing number of cycles. No peak

(27) *Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts: Infrared Spectra*; Nyquist, R. A., Putzig, C. L., Leugers, M. A., Eds.; Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts, Vol. 3; Academic Press: San Diego, 1997; p 66.

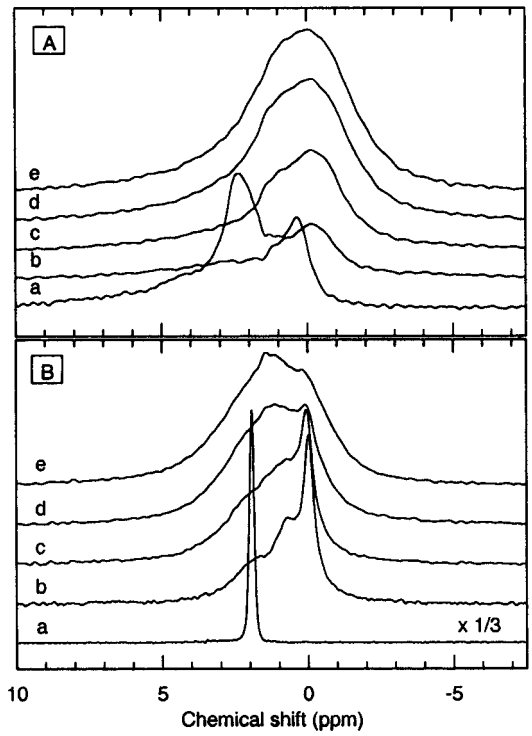

Figure 3. ^1H MAS NMR spectra of substrates and samples. (A). Spectra of the alumina substrate (a) and of samples 1·AlN/Al_2O_3 (b), 2·AlN/Al_2O_3 (c), 4·AlN/Al_2O_3 (d), and 6·AlN/Al_2O_3 (e). (B) Spectra of the silica substrate (a) and of samples 1·AlN/SiO_2 (b), 2·AlN/SiO_2 (c), 4·AlN/SiO_2 (d), and 6·AlN/SiO_2 (e). The intensity of spectrum a in panel B has been reduced by a factor of 3.

was observed at 2355 cm^{-1} in the samples modified with more than two AlN cycles. However, in the spectrum of sample 4·AlN/SiO_2 brought to air (not shown), a wide peak appeared immediately after exposure to air at 2257 cm^{-1}. The peak disappeared after the sample was kept in air for a few days.

^1H MAS NMR. The amount of hydrogen in the samples modified with completed reaction cycles was measured by ^1H MAS NMR. The quantitative results are collected in Table 1.

The spectra of the AlN/Al_2O_3 series are shown in Figure 3A. The total amount of hydrogen in amino groups increased with the number of reaction cycles. The peak maximum shifted slightly from −0.2 to 0 ppm, but the general shape of the peak remained unaltered. Many different types of amino groups possibly were present on the surface. The number of hydrogen atoms in the 1·, 2·, 4·, and 6·AlN/Al_2O_3 samples was 2.6, 3.8, 6.2, and 7.2 $at_H\ nm^{-2}_{alumina}$, respectively.

The spectra of the AlN/SiO_2 series are shown in Figure 3B. Absorption of hydrogen in amino groups increased with the number of reaction cycles, whereas absorption of hydrogen atoms in methyl groups at 0 ppm decreased. The total number of hydrogen atoms in the 1·, 2·, 4·, and 6·AlN/SiO_2 samples was 2.8, 4.0, 4.7, and 5.9 $at_H\ nm^{-2}_{silica}$, respectively. Simulation of the spectra showed the amount of hydrogen in NH_x groups to be 1.5, 3.3, 4.4, and 5.6 $at_H\ nm^{-2}_{silica}$ in the same samples; the rest of the hydrogen was in methyl groups. An example of the simulation can be found in ref 4.

^{29}Si CPMAS NMR. The types of silicon-bonded methyl groups and the number of nitrogen bonded to

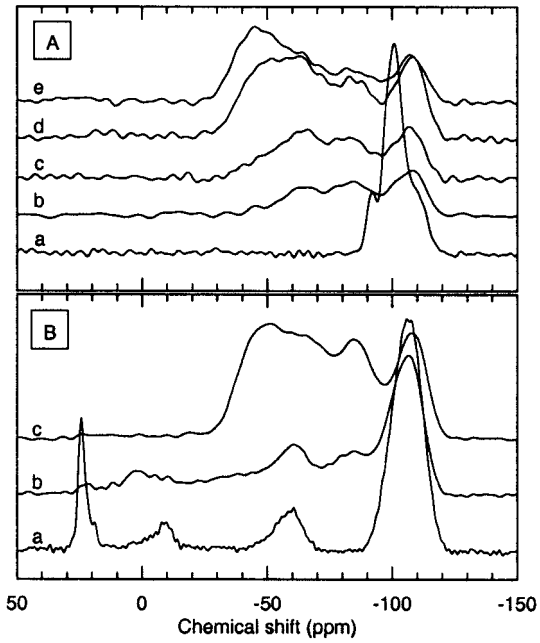

Figure 4. (A) ^{29}Si CPMAS NMR spectra of the silica substrate (a), the 1·AlN/SiO_2 (b), the 2·AlN/SiO_2 (c), the 4·AlN/SiO_2 (d), and the 6·AlN/SiO_2 sample (e). (B) Spectra of the 0.5·AlN/SiO_2 (a), the 1.5·AlN/SiO_2 (b), and the 6.5·AlN/SiO_2 sample (c).

silicon atoms on silica were investigated by ^{29}Si CPMAS NMR. The spectral features of silica and the 0.5·AlN/SiO_2 and 1·AlN/SiO_2 samples have been discussed in detail.[4] In the spectrum of the 1.5·AlN/SiO_2 sample (curve b in Figure 4B), the presence of some $OSiMe_3$ was indicated by a peak at 24 ppm. In addition, $OSiMe_2N$, O_2SiMe_2, and O_3SiMe species were present, with resonance at 1, −9, and −59 ppm, respectively. The peaks centered at −85 and −112 ppm were caused by O_3SiNH_x and O_4Si species, respectively.[4] When ammonia was reacted in the second reaction cycle (Figure 4A, curve c), the peaks of species with multiple methyl groups were lost, and the spectrum was similar to that after one reaction cycle, with peaks at −65 and −85 ppm (Figure 4A, curve b). When the number of completed reaction cycles was increased to six, the peak at −45 ppm increased relative to the other peaks. The peak at −85 ppm is due to the O_3SiNH_x species,[4] and we tentatively assigned the peaks at −65 and −45 ppm to $O_2Si(NH_x)_2$ and $OSi(NH_x)_3$, respectively. The peak centered at −65 ppm may contain a contribution of unreacted O_3SiMe species, which resonate at −59 ppm.[4] The increase of the peak at −45 ppm indicates that the amount of $OSi(NH_x)_3$ units increased with the number of reaction cycles. Furthermore, the presence of SiN_4 species, which appear at −49 ppm,[28] cannot be excluded.

To get an idea of the coverage of silica by AlN after six reaction cycles, the 6·AlN/SiO_2 sample was reacted with TMA. The spectrum of this 6.5·AlN/SiO_2 sample (Figure 4B, curve c) closely resembles the spectrum of the 6·AlN/SiO_2 sample (Figure 4A, curve e), indicating that $YSiMe_3$ or Y_2SiMe_2 units (Y = O or N) had no longer formed. The intensity of the peaks centered at −65 and −85 ppm had increased, however. The increase at −65 ppm could be due to the formation of some

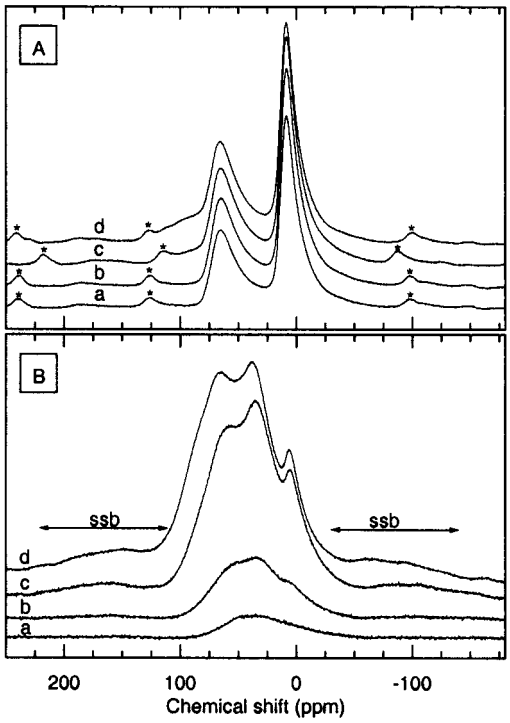

Figure 5. (A) ^{27}Al MAS NMR spectra of samples 1·AlN/Al_2O_3 (a), 2·AlN/Al_2O_3 (b), 4·AlN/Al_2O_3 (c), and 6·AlN/Al_2O_3 (d). (B) Spectra of samples 1·AlN/SiO_2 (a), 2·AlN/SiO_2 (b), 4·AlN/SiO_2 (c), and 6·AlN/SiO_2 (d).

additional Y_3SiMe species, whereas the increase of the O_3SiN peak at −85 ppm could be caused by an increased hydrogen density around the silicon atoms, giving rise to a more efficient cross-polarization process. Comparison of curves a–c in Figure 4B also indicates that fewer silicon-bonded methyl groups were formed per reaction cycle as the number of cycles increased.

^{27}Al MAS NMR. ^{27}Al MAS NMR spectra were recorded to investigate the coordination state of aluminum atoms in the samples. The spectra of the AlN/Al_2O_3 series are shown in Figure 5A. Two intense peaks were present in all spectra, centered at 65 and 8.5 ppm. These were caused by the four- and six-coordinate aluminum atoms in O_4Al and O_6Al units, respectively.[29,30] The spectrum of the 6·AlN/Al_2O_3 sample showed a peak at 115 ppm, indicating the formation of AlN_4 units.[31] Simulation of the spectrum (Figure 6) revealed that this peak contained 0.5 $at_{Al}\ nm^{-2}_{alumina}$. A further peak was seen at about 90 ppm in the spectra of the 4· and 6·AlN/Al_2O_3 samples. Varied pulse-length experiments and line-width analysis provided an estimate of 4–6 MHz for the QC. This gives an isotropic chemical shift of 102 ± 2 ppm, which falls into the region of tetrahydroaluminates.[32] The sites responsible for the peak at 90 ppm were sensitive to moisture. This indicates that they probably contained NH_2 groups (and perhaps NH

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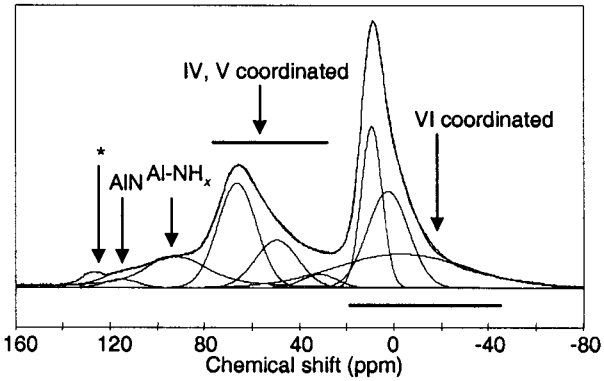

Figure 6. Simulation of curve d in Figure 5A.

groups), because these are easily replaced by OH groups. We assigned the peak at 90 ppm to Al−NH$_x$ groups, where the nitrogen may be either three- or four-coordinated.

The spectra of the AlN/SiO$_2$ samples are shown in Figure 5B. With the increasing number of reaction cycles, peaks evolved with maxima at 59, 38, and 6 ppm (peak maxima given for the 6·AlN/SiO$_2$ sample). The peaks at 59 and 6 ppm were close to the respective peaks of the O$_4$Al and O$_6$Al sites on alumina. The origin of the peak at 38 ppm is not clear, but most likely it is caused by a five-coordinate species containing some nitrogen in addition to oxygen. Although AlN sites with a chemical shift at about 115 ppm were not identified in any of the spectra, their presence in minor amount in the 6·AlN/SiO$_2$ sample could not be excluded because the spinning sidebands were overlapping the 115-ppm region. Deconvolution revealed the presence of Al−NH$_x$ sites in the 4· and 6·AlN/SiO$_2$ samples. The relatively strong spinning sidebands probably resulted from dipolar coupling with ^{1}H atoms. Because a long-pulse experiment showed that most of the Al sites had relatively weak QC (except the Al−NH$_x$ sites), the spinning sidebands could not have resulted from the QC. Unfortunately, we were unable to make any ^{27}Al MAS NMR experiments with decoupling from ^{1}H. The H atoms usually are not directly attached to Al atoms and 13−14 kHz spinning is sufficient to average out the dipolar interaction. The amount of aluminum detected by ^{27}Al MAS NMR in the 1·, 2·, 4·, and 6·AlN/SiO$_2$ samples was 0.5, 1.4, 4.6, and 6.6 wt %. Comparison with the values presented in Table 1 shows that NMR-invisible aluminum sites were present in the samples. This indicates the presence of sites with poorly defined crystallinity.

XRD Measurements. X-ray diffractograms were measured for the 4·AlN/Al$_2$O$_3$, 6·AlN/Al$_2$O$_3$, 4·AlN/SiO$_2$, and 6·AlN/SiO$_2$ samples to determine whether crystalline AlN had been formed. No peaks in addition to the broad features of microcrystalline alumina or amorphous silica were seen in these spectra. However, the peaks of crystalline Al$_2$O$_3$ and AlN are too close to each other to totally exclude the presence of a small amount of aluminum nitride in the 4·AlN/Al$_2$O$_3$ and 6·AlN/Al$_2$O$_3$ samples. Heating the 6·AlN/SiO$_2$ sample in air at 1273 K for 4.5 h did not generate XRD peaks, but the sample turned from gray to white.

SEM−EDS Measurements. A SEM−EDS linegraph of sample 6·AlN/SiO$_2$ is shown in Figure 7. The signals

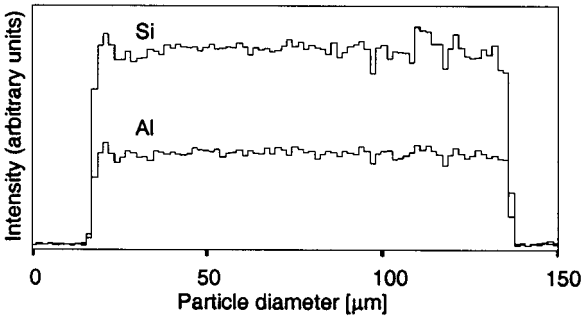

Figure 7. SEM−EDS linescan of the 6·AlN/SiO$_2$ sample.

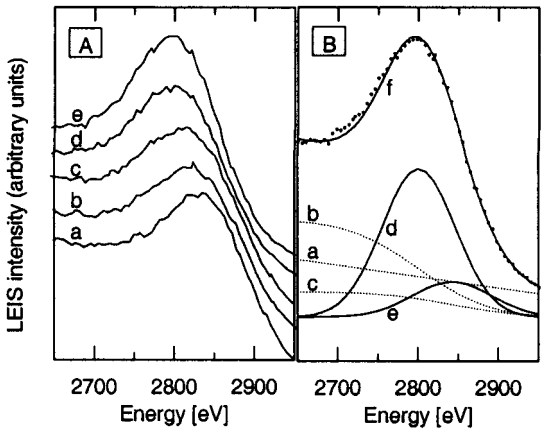

Figure 8. (A) The Al/Si peak of the LEIS spectra of the silica substrate (a) and of samples 1·AlN/SiO$_2$ (b), 2·AlN/SiO$_2$ (c), 4·AlN/SiO$_2$ (d), and 6·AlN/SiO$_2$ (e). (B) An example of the LEIS fitting procedure for the 6·AlN/SiO$_2$ sample: the linear background (a), the background of Al (b), the background of Si (c), the peak of Al (d), the peak of Si (e), and the sum of all peaks (solid line) superimposed on the original spectrum (dots) (f).

of aluminum and silicon were constant within the particle, indicating that elemental gradients were not present.

LEIS Measurements. LEIS spectra were measured for the AlN/SiO$_2$ series to study the coverage of silica by AlN-type species as a function of the aluminum content of the samples. ^{3}He$^+$ was used for measuring a complete mass spectrum of the surface atoms. In the spectrum of the silica reference, peaks of oxygen and silicon and a small peak of a heavier element (possibly Ni, Co, Fe, Mn, Cr, or V) were seen. These peaks were also seen in the spectra of the AlN-modified samples. Additionally, the combined peak of Si and Al shifted to lower energy because of the increasing amount of aluminum.

To obtain maximum separation for the Al and Si peaks, we used 5 keV ^{4}He$^+$ as the probe. The Al/Si regions of the spectra of the oxidized AlN/SiO$_2$ samples are shown in Figure 8A. The Al/Si peak maxima were located between the maxima measured for the silica and alumina references; the peak maximum approached the peak on alumina as the amount of oxidized AlN in the samples increased.

Gaussian peaks were fitted for Al and Si in all the spectra to investigate the fraction of the sample surface that was covered by oxidized AlN. An example of the fitting is shown in Figure 8B. The Al and Si peak maxima fitted for the alumina and silica references were at 2801.0 and 2842.7 eV, respectively. The fitted area of the Al peak was a linear (R^2 = 0.9744) function of

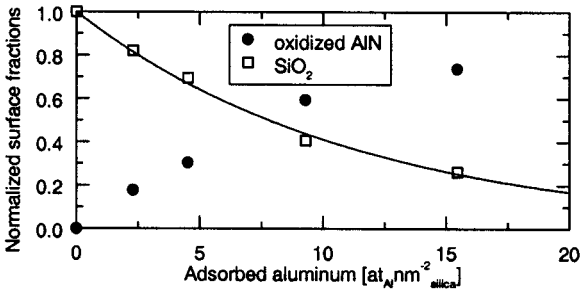

Figure 9. The normalized surface fractions of oxidized AlN and SiO_2 in the AlN/SiO_2 series as a function of the aluminum content.

the fitted area of the Si peak. Because a linear relationship existed between the Al and Si peak areas, the signal intensity of the pure oxidized AlN could be obtained by extrapolating the linear function. The signal intensities of pure silica and pure oxidized AlN were determined to be 350 and 490, respectively. Dividing the Al and Si signals of samples by these reference signals gave the fraction of the surface that was covered by oxidized AlN and the fraction that was bare SiO_2. The sum of the fractions was close to one, as expected. To correct for small experimental differences, the fractions were further normalized to give a sum of one. Figure 9 shows the results as functions of the total aluminum content of the samples. Oxidized AlN covered about 75% of the substrate in the oxidized 6·AlN/SiO_2 sample. An exponential decay curve fitted to the surface fraction of SiO_2 as a function of the aluminum content of the samples ($y = e^{-0.0888x}$, $R^2 = 0.9929$).

The oxidized 6·AlN/SiO_2 sample was depth-profiled by sputtering. The signal of Al decreased during the sputtering by 40%. At the same time, a small peak of nitrogen appeared, increasing in strength with the sputtering time. This indicates that the surface-nitrogen was easily removed during the oxygen atom treatment, but some type of internal nitrogen that was less reactive with oxygen was also present.

Discussion

Steady growth of AlN-type species was observed on both alumina and silica with the increasing number of reaction cycles. Next, we investigate the trends in the coverage of silica by AlN-type species, the mechanism of the reaction of TMA with the various surface sites of alumina and silica, and the growth mechanism of AlN-type species on the two substrates. Furthermore, the suitability of the AlN-modified surfaces for application as catalyst supports is discussed.

Coverage of Silica by AlN-type Species. The minimum amount of AlN-type species needed to cover the silica surface can be estimated in different ways. One way is to consider the amount of aluminum and nitrogen atoms needed to cover a square nanometer of flat surface with AlN. The densest surface of AlN, with lattice parameter *a* of about 3.11 Å, is the hexagonal (0001) face, and this face consists of about 12 atoms/nm^2, all either aluminum or nitrogen atoms. Another approach is based on the density of bulk AlN, about 3.26 g cm^{-3}.[19] Calculation of the average volume of one AlN unit gives us 20.9 Å^3, which corresponds to about 13 AlN units/nm^2. Yet a third way to estimate the amount is to use the second point in Figure 9. During the first reaction cycle, growth took place in one layer only, and all the attached Al atoms were surface atoms. A straight line connecting the first point (origin) and the second point of the normalized Al peak area should give the monolayer density at its interception with the line $y = 1$. The equation of the line is $y = 0.0776x$ and the value of x at the interception is 12.9 at$_{Al}$ nm^{-2}. Because all three methods of estimation agree gave similar results, we can conclude that a minimum of about 12 at$_{Al}$ nm$^{-2}_{silica}$ is required for total coverage of the silica surface.

Comparison with the Al and N contents given in Figure 1 suggests that, in principle, five reaction cycles of TMA and ammonia might have been enough to obtain full coverage of silica. The LEIS measurements showed that this was not the case, however. The coverage of silica by oxidized AlN increased with each reaction cycle, but the decrease in the normalized surface fraction of SiO_2 was exponential. Straightforward probability calculations can show that the exponential decrease indicates random chemisorption of Al atoms on the substrate in the TMA reaction. Thus, TMA with equal probability reacted with the still-exposed silica and the AlN. Six reaction cycles resulted in coverage of about 75%. We further estimate that nine cycles would be needed for coverage of 90% if growth were to proceed as it did in the fifth and sixth reaction cycles.

Our results differ considerably from those of Bartram et al.,[13] who reported that after just four reaction cycles of TMA and ammonia, aluminum nitride covered the silica fully and silicon was no longer seen in XPS. Because XPS probes several atomic layers (whereas only one atomic layer is probed by LEIS), in their case, deposition of AlN must have occurred far beyond a monolayer. One explanation for these different results may be that Bartram et al.[13] applied TMA at 600 K where it already decomposes thermally.[6,33] Decomposition would result in higher aluminum content on the outermost surface.[6] However, the features attributed to TMA decomposition in IR spectra[6] are not present in the spectra of Bartram et al.,[13] and they concluded that the TMA reaction was self-limiting. The reason for the different findings therefore remains unclear.

Reaction Mechanism of TMA. The carbon contents measured after the TMA reaction support our previous conclusion[4,5] that the saturation of the TMA reaction is defined by the amount of methyl groups always settling to the same value (ca. 5–6 Me nm^{-2}). This value is close to the theoretical maximum density of methyl groups on planar substrates, 7.2 Me nm^{-2},[4] and suggests that the reaction stops when the methyl groups on the substrate surface block the rest of the surface from reacting further. As indicated by SEM–EDS, the whole surface seemed to be covered by AlN-type species. The finding, according to LEIS, that TMA reacts with equal probability with the silica surface and the formed AlN-type species is of interest, for the bonding sites on these surfaces are different. On silica, Si–O–Si bridges and OH groups are present. In our samples the OH groups were consumed in the first reaction cycle, but some NH_x groups attached to silicon were generated by the reac-

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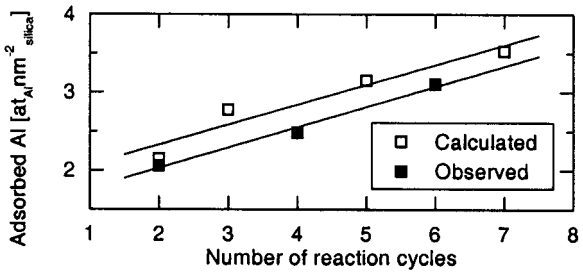

Figure 10. Calculated and measured amounts of aluminum attached in a TMA reaction on AlN-modified silica.

tion of silicon-bonded methyl groups with ammonia. On the AlN layer, Al−N−Al bridges and NH_x groups served as potential reaction sites. Si−O−Al and Si−N−Al bridges were probably present as well. Because, according to the LEIS measurements, TMA reacted with the surface in a random manner, we suggest that, in addition to the OH and NH_x groups and Si−O−Si bridges, Si−O−Al, Si−N−Al, and Al−N−Al bridges also served as reaction sites for TMA. We cannot confirm this with our present results, however, because the amount of hydrogen-containing groups alone is sufficient to explain the amount of aluminum attached to the surface.

The ^{29}Si CPMAS NMR spectrum recorded after TMA reaction in the second reaction cycle revealed that new silicon-bonded methyl groups were formed through the reaction of TMA with siloxane bridges. This differs from the proposal of Bartram et al.[21] that TMA would consume all reactive sites on the silica surface, both OH groups and siloxane bridges, in the first reaction cycle. If all the siloxane bridges were consumed in the first cycle, silicon-bonded methyl groups could not form in the second reaction cycle unless the ammonia reaction regenerated the bridges. This is unlikely. Thus, it seems that the TMA reaction with silica consumes all the OH groups but not all the siloxane bridges. Note, however, that some silicon-bonded methyl groups could form through the reaction of TMA with Si−O−Al or Si−N−Al bridges.

Relation between the Hydrogen Content of the Substrate and the Amount of Aluminum Attached in TMA Reaction. A detailed investigation of the growth of AlN-type species per cycle (Figure 1) reveals a slight increase in the growth with number of reaction cycles. An increase was also seen in the amount of hydrogen present in the AlN-modified samples, although we did not anticipate such growth. The following element balance describes the TMA reaction with hydrogen-containing surfaces:[4,6]

$$[C] = 3[Al] - \Delta[H]. \quad (1)$$

[C] and [Al] denote the amounts of carbon and aluminum attached to the surface, and Δ[H] denotes the amount of hydrogen removed from the surface through methane formation. The [C] is constant at about 5−6 at_C nm^{-2}.[4−6]

For silica, we could calculate the maximum amount of aluminum attached to the surface by assuming that all the hydrogen atoms react and that the carbon content settles to 5 at_C nm^{-2}. Figure 10 shows the calculated maximum amount and the measured amount of attached aluminum atoms. Both increased with the number of reaction cycles, with similar slopes. The absolute values of the calculated and observed amounts of aluminum differed on average by about 0.3 at_{Al} nm^{-2}. This small difference suggests either that there was a constant amount of hydrogen atoms that did not react with TMA or that all the hydrogen reacted but there were systematic errors in the analysis. The presence of residual bands due to NH_x groups in the DRIFT spectra of the 1.5·AlN/Al_2O_3 and 1.5·AlN/SiO_2 samples (Figure 2C,D) favors the first explanation, that is, that not all the hydrogen atoms reacted with TMA. The fraction of unreacted hydrogen was small, however. The nitrogen and hydrogen contents on alumina increased in a way similar to the aluminum and hydrogen contents on silica. Thus, the increasing amount of hydrogen atoms after each cycle probably had an increasing effect on the growth per cycle on alumina just as it did on silica. Six reaction cycles evidently were not sufficient to achieve constant growth conditions; the growth per cycle still seemed to be increasing with each reaction cycle on both substrates. One would expect the growth per cycle to become constant after a certain number of cycles, indicating that the starting surface (i.e., alumina or silica) no longer was affecting the growth.

The amount of hydrogen present in amino groups decreases with increasing reaction temperature of ammonia on TMA-modified alumina.[6] Because there are fewer reactive hydrogen atoms after treatment at higher temperatures, the amount of aluminum atoms attached to the surface in the TMA reaction should be smaller ([Al] = 1/3([C] + Δ[H]), from eq 1). This conclusion is in accord with experimental results: Soto et al.[18] observed a growth per cycle of 3.5 Al and N atoms per nm^2 when ammonia was reacted at 573 K, and we observed a growth of only 2.4 Al and N atoms per nm^2 with ammonia reacted at 823 K.

Growth Mechanism of AlN on Alumina and Silica. The ^{29}Si CPMAS NMR spectra indicate that a considerable amount of Si−N bonds were formed when the number of reaction cycles was increased to six. At the same time, the ^{27}Al MAS NMR measurements indicate that some intermediate aluminum site, probably containing both nitrogen and oxygen around aluminum, forms before the N_4Al sites do. Thus, instead of a sharp interface existing between SiO_2 and AlN, a gradual change from silicon dioxide to aluminum nitride through silicon oxynitride and aluminum oxynitride probably occurs. A corresponding gradual change most likely takes place on alumina, from aluminum oxide to aluminum nitride through intermediate aluminum oxynitride.

The growth per surface area was similar on alumina and silica (Figure 1), which indicates that there were no major differences in the growth mechanisms on the two substrates. There were several minor differences. Residual carbon was present in the samples prepared on silica, and not in those prepared on alumina. This resulted at least in different colors of the samples (yellowish AlN/Al_2O_3 and gray AlN/SiO_2). In addition, the amount of hydrogen that remained on the surface after the ammonia reaction, as determined by ^{1}H MAS NMR, was generally somewhat higher on alumina than

on silica. The types of amino groups were also slightly different on the two substrates, as seen in the different shapes of the ^{1}H MAS NMR spectra. The alumina substrate also fostered greater formation of ^{27}Al MAS NMR-visible N_4Al and $Al-NH_x$ sites than the silica substrate. Although the source of these differences is not clear, most likely they related to the different natures of the substrates, perhaps to the more ionic nature of alumina and the more covalent nature of silica. The substrates thus have an effect on the AlN-type sites and most likely also on the surface properties of the samples.

Suitability of the AlN-Modified Samples as Catalyst Support. Through repeated separate and saturative chemisorptions of TMA and ammonia, AlN-type species were prepared on both alumina and silica. However, full coverage of the substrates with AlN was not obtained in six reaction cycles. This is unfavorable for applications of AlN as a catalyst support, because some substrate surface (~25%) is available for the reagents. On silica, we were able to estimate the probability of compounds reacting with the exposed substrate surface by using the TMA reaction as a probe. TMA is one of the rare components that reacts not only with the OH groups but also with the siloxane bridges. ^{29}Si CPMAS NMR measurements showed that, in the first reaction cycle, O_3SiMe, O_2SiMe_2, and $OSiMe_3$ species were formed when TMA reacted with the siloxane bridges of silica. $OSiMe_3$ species were no longer formed in the second reaction cycle, and the amount of O_2SiMe_2 was considerably reduced. Little change was seen in the ^{29}Si CPMAS NMR spectrum when TMA was reacted after the sixth reaction cycle. Evidently, after six reaction cycles, the coverage of silica by AlN-type species is sufficient to prevent TMA from reacting with the siloxane bridges in considerable quantity. However, up to six reaction cycles, changes occurred in the silica as the amount of Si–N bonding increased. We conclude that the probability of other molecules than TMA reacting with the silica surface of the 6·AlN/SiO_2 sample is small.

In addition to coverage, a relevant consideration for catalyst applications is the nature of the surface layer. The AlN layers consisted of a considerable amount of hydrogen, practically all of which was bound in amino groups. In catalyst applications, where metal atoms are to be deposited on the support, these hydrogen atoms in amino groups could serve as bonding sites similar to the hydrogen atoms in hydroxyl groups of oxides.

One disadvantage of the AlN surface is its easy oxidation in the presence of air. In particular, the humidity of the air may be fatal. It is likely that, even in a very slight air contact, the nitrogen atoms on the outermost surface of the particles will be exchanged with oxygen atoms. This was clearly demonstrated by the LEIS measurements, where a good signal for nitrogen was not obtained. Similarly treated samples did not show loss of amino groups in DRIFT or ^{1}H MAS NMR measurements, however, which indicates that oxidation took place only on the outermost surface of the particles. Prolonged exposure to air would have an effect on the nitrogen atoms present in the internal surface as well, and would have a significant effect in catalysis. Thus, the AlN supports we describe would be used most successfully in applications where water and oxygen are absent.

Acknowledgment. We thank the Analytical Department of Fortum Oil and Gas Oy for the chemical analysis and the nitrogen physisorption, XRD, and SEM–EDS measurements. The Department of Chemistry, University of Joensuu, Finland, is thanked for providing the means for measuring the DRIFT spectra inertly. Financial support was provided by the National Technology Agency of Finland (TEKES) and the Academy of Finland through the Graduate School in Chemical Engineering (GSCE). The European Science Foundation, ALE Network, provided a grant that allowed R.L.P. to be present at Calipso b.v. during the LEIS measurements.

CM011176I