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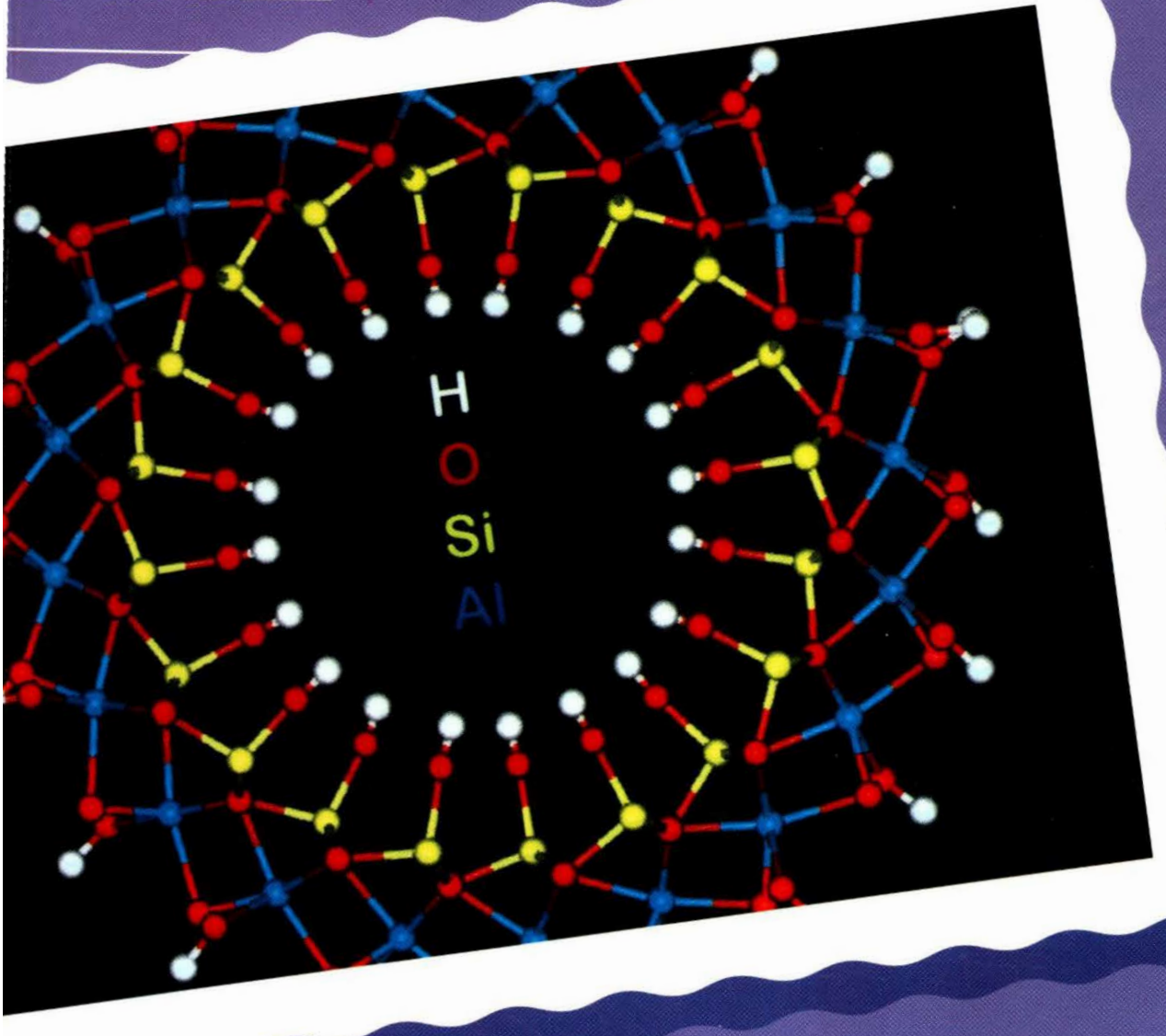

Molecular Model of the Imogolite Structure.

(see p. 4463)

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Controlled Formation of ZrO_2 in the Reaction of $ZrCl_4$ Vapor with Porous Silica and γ-Alumina Surfaces

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The reaction of $ZrCl_4$ vapor at 300, 450, and 600 °C with silica and γ-alumina preheated at 300 and 600 °C was studied by XRD, FTIR, ^1H MAS NMR, and chemical etching with sulfuric acid. NMR and FTIR revealed a consumption of OH groups in the reaction. However, subsequent water vapor treatment brought some of the OH groups of the support back, indicating that part of the surface had been directly chlorinated. The ratio between permanently consumed OH groups and directly chlorinated OH groups depended on the reaction temperature. OH groups were permanently consumed in mono- and bimolecular reactions of $ZrCl_4$, leading to the formation of isolated $M-O-ZrCl_3$ and $(M-O)_2-ZrCl_2$ species (M = Al or Si), respectively. Direct chlorination was associated with the formation of crystalline ZrO_2 agglomerates, as detected by XRD in the samples prepared at 450 and 600 °C. These agglomerates were insoluble in sulfuric acid. Although at the reaction temperature of 300 °C the samples were amorphous in XRD, the reappearance of some OH groups on the original surface after water treatment, together with etching tests, suggested that agglomerates were also formed at that temperature. In addition to agglomeration and exchange reactions with OH groups, on 600 °C alumina $ZrCl_4$ dissociated to (Al–O) pairs. This led to a higher Zr saturation density and Cl/Zr ratio on alumina than on silica. The reactions of the HCl evolved in the main reactions were considered minor. Increasing the preheat and reaction temperatures decreased the Zr concentration on the surface and thus diminished the surface coverage. The surfaces of the $ZrCl_4$-modified and water-treated silica and alumina surfaces consisted of Zr–OH groups formed in the hydrolysis of isolated $ZrCl_x$ species, original OH groups of the supports, and ZrO_2 agglomerates formed in the vicinity of siloxanes and (Al–O) pairs.

Introduction

Zirconia has been studied for use both as a catalyst and as a support for catalytically active species.[1] Our interest is directed to the latter application with the purpose of preparing a high surface area zirconia support with good stability and mechanical strength. The starting point was to use porous, high surface area silica or alumina as a skeleton material and to grow the desired surface oxide phase on this material by the atomic layer epitaxy (ALE) technique with the use of sequential reactions of $ZrCl_4$ and H_2O vapors. Earlier work aimed at dispersing ZrO_2 on silica or alumina supports has concentrated on deposition from the liquid phase using zirconyl chloride or nitrate,[2–4] zirconium nitrate,[5] zirconium ethoxide[5,6] or zirconium *tert*-butoxide[7] as precursor.

ALE is a gas-phase preparation technique which was first introduced in the growth of high quality thin films in the seventies.[8] Somewhat later it was applied to the preparation of catalysts.[9] The technique is based on saturating gas-solid reactions and can be classified as a special mode of chemical vapor deposition techniques.[10] $ZrCl_4$ is a natural choice as source material for growing ZrO_2 because it is the most readily available zirconium compound with suitable vapor pressure and stability. Furthermore, $ZrCl_4$ has been successfully used in the ALE growth of ZrO_2 thin films on soda lime glass by an alternation of $ZrCl_4$ and H_2O vapor sequences at 500 °C.[11]

The reactions of gaseous $TiCl_4$ with silica (ref 12 and references therein) and CCl_4 with alumina (e.g. refs 13–15) have been studied in detail. The reactions of other tetravalent chlorides, such as $ZrCl_4$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and VCl_4, with porous oxides have also been investigated, though less extensively (e.g. refs 16–25). Only through achieving an understanding of the interaction between

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(1) Yamaguchi, T. *Catal. Today* **1994**, *20*, 199.
(2) Luy, J. C.; Yori, J. C.; Castro, A. A.; Parera, J. M. *React. Kinet. Catal. Lett.* **1988**, *36*, 275.
(3) Yamaguchi, T.; Morita, T.; Salama, T. M.; Tanabe, K. *Catal. Lett.* **1990**, *4*, 1.
(4) Dang, Z.; Anderson, B. G.; Amenomiya, Y.; Morrow, B. A. *J. Phys. Chem.* **1995**, *99*, 14437.
(5) Meijers, A. C. Q. M.; de Jong, A. M.; van Gruijthuijsen, L. M. P.; Niemantsverdriet, J. W. *Appl. Catal.* **1991**, *70*, 53.
(6) de Jong, A. M.; Eshelman, L. M.; van IJzendoorn, L. J.; Niemantsverdriet, J. W. *Surf. Interface Anal.* **1992**, *18*, 412.
(7) Márquez-Alvarez, C.; Fierro, J. L. G.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. *J. Colloid Interface Sci.* **1993**, *159*, 454.
(8) Suntola, T.; Antson, A. U.S. Patent 4 058 430, 1970.
(9) Lakomaa, E.-L. *Appl. Surf. Sci.* **1994**, *75*, 185.
(10) Manual on catalyst characterization (Recommendations 1991). *Pure Appl. Chem.* **1991**, *63*, 1227.
(11) Ritala, M.; Leskelä, M. *Appl. Surf. Sci.* **1994**, *75*, 333.
(12) Haukka, S.; Lakomaa, E.-L.; Root, A. *J. Phys. Chem.* **1993**, *97*, 5085 and references therein.
(13) Primet, M.; Basset, J.; Mathieu, M. V.; Prettre, M. *J. Phys. Chem.* **1970**, *74*, 2868.
(14) Hair, M. L.; Hertl, W. *J. Phys. Chem.* **1973**, *77*, 2070.
(15) Podör, B.; Bertóti, I. *Thermochim. Acta* **1982**, *56*, 209.
(16) Peri, J. B. *J. Phys. Chem.* **1966**, *70*, 2937.
(17) Peri, J. B.; Hensley, A. L., Jr. *J. Phys. Chem.* **1968**, *72*, 2926.
(18) Kol'tsov, S. I.; Aleskovskii, V. B. *Zh. Prikl. Khim.* **1969**, *42*, 1950.
(19) Chien, J. C. W. *J. Am. Chem. Soc.* **1971**, *93*, 4675.
(20) Arena, B. J. U.S. Patent 4 459 372, 1972.
(21) Camara, B.; Fink, P.; Pforr, G.; Rackow, B. *Z. Chem.* **1972**, *12*, 451.
(22) Meallier, P.; Bernard, J.-R.; Coste, C.; Knoche, H. *C. R. Acad. Sci. Paris* **1975**, *281*, 103.
(23) Hattori, T.; Itoh, S.; Tagawa, T.; Murukami, Y. *Stud. Surf. Sci. Catal.* **1987**, *31*, 113.
(24) Juszczyk, W.; Marczewski, M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3591.
(25) Haukka, S.; Kytökivi, A.; Lakomaa, E.-L.; Lehtovirta, U.; Lindblad, M.; Lujala, V.; Suntola, T. *Stud. Surf. Sci. Catal.* **1995**, *91*, 957.

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vapor and surface can we determine the possibility of coating a particular surface and identify the bonding sites on the new, modified surface.

It is generally accepted that the hydroxyl groups on silica and alumina react when metal chlorides are brought into contact with them. If these groups are considered the only bonding sites, the simple way to evaluate the reaction mechanism is to determine the Cl/metal ratio on the surface after the reaction. Indeed, this is the approach many researchers have applied in the past, especially with silica, to study the reactions of metal halides used either to modify or to characterize the surface of the oxide.[26] However, use of the Cl/metal ratio to evaluate the reaction mechanism has also been criticized. In a study of the reaction of $TiCl_4$ with SiO_2, Damyanov et al.[27] suggested that the HCl released in the reaction with OH groups may react further with silica to form water, which interferes with the evaluation of the mechanism. The Cl/Ti ratio can thus serve only as a tentative indicator. Haukka et al.,[12,28] moreover, showed that, depending on the reaction temperature, $TiCl_4$ on silica preferably forms either isolated surface species in an exchange reaction with OH groups or else TiO_2 agglomerates. In the former case, the Cl/Ti ratio gives valuable information about the reaction, whereas in the latter case it leads to wrong conclusions. The agglomeration occurs together with direct chlorination of the surface during the interaction of the metal chloride.

In their recent review of characterization and modification of silica surfaces, Vansant et al.[29] did not mention the agglomeration reaction as an alternative for the reaction of $TiCl_4$ with silica but noted the possible reaction of siloxane bridges in addition to OH groups. Thus, according to their review, the possible five reaction routes are the following:

$$\mathrm{Si{-}OH} + \mathrm{TiCl_4} \rightarrow \mathrm{Si{-}O{-}TiCl_3} + \mathrm{HCl} \quad (1)$$

$$\begin{matrix}\mathrm{Si{-}OH}\\ \mathrm{Si{-}OH}\end{matrix} + \mathrm{TiCl_4} \rightarrow \mathrm{(Si{-}O)_2{-}TiCl_2} + 2\mathrm{HCl} \quad (2)$$

$$\begin{matrix}\mathrm{Si{-}OH}\\ \mathrm{Si{-}O{-}TiCl_3}\end{matrix} \rightarrow \mathrm{(Si{-}O)_2{-}TiCl_2} + \mathrm{HCl} \quad (3)$$

$$\mathrm{Si{-}O{-}Si} + \mathrm{TiCl_4} \rightarrow \mathrm{Si{-}Cl} + \mathrm{Si{-}O{-}TiCl_3} \quad (4)$$

$$\begin{matrix}\mathrm{Si{-}O{-}Si}\\ \mathrm{Si{-}O{-}TiCl_3}\end{matrix} \rightarrow \begin{matrix}\mathrm{Si{-}Cl}\\ \mathrm{(Si{-}O)_2{-}TiCl_2}\end{matrix} \quad (5)$$

On alumina, possible adsorption sites are provided not only by OH groups but also by coordinatively unsaturated aluminum and oxygen sites. It has namely been suggested that metal oxychlorides can dissociate to (Al−O) sites[30] and that $ZrCl_4$ can react with exposed oxygen.[24] The dissociation reaction leads to the following surface species:

$$\mathrm{(Al{-}O) + ZrCl_4} \longrightarrow \begin{matrix}\mathrm{Cl}\ \ \mathrm{ZrCl_3}\\ |\quad\ \ |\\ \mathrm{(Al{-}O)}\end{matrix} \quad (6)$$

On alumina, moreover, the reaction of HCl evolved in the reaction of metal chloride with hydroxyl groups cannot be excluded in the evaluation of the mechanism, since HCl can react with OH groups and/or dissociate to (Al−O) sites depending on the reaction conditions.[30,31] These reactions of HCl can be presented as follows:

$$\begin{matrix}\mathrm{H}\\ \mathrm{O}\\ |\end{matrix} \qquad \begin{matrix}\mathrm{Cl}\\ |\end{matrix}$$
$$\mathrm{(Al{-}O) + HCl} \longrightarrow \mathrm{Al} + \mathrm{H_2O} \quad (7)$$

$$\begin{matrix}\mathrm{Cl}\ \ \mathrm{H}\\ |\quad\ \ |\\ \mathrm{(Al{-}O)}\end{matrix}$$
$$\mathrm{(Al{-}O) + HCl} \longrightarrow \quad (8)$$

Furthermore, Hochman and Setinek[32] concluded in their study on reactions of $TiCl_4$ and other chlorides with alumina that reactions with OH groups and direct chlorination of the surface are both possible. Direct chlorination leads to bonding of only the halogen of the metal chloride, and the remaining part of the molecule with a reduced number of halogen atoms is proposed to volatilize and be removed by the carrier gas used in the preparation. Meallier et al.,[22] on the other hand, in a study of the reaction of $SiCl_4$ with alumina, have linked the direct chlorination with the formation of SiO_2.

In this paper, we have concentrated on the reactions occurring on silica and alumina during the first $ZrCl_4$ treatment and the following water treatment. Samples were investigated by FTIR in diffuse reflectance mode and ^{1}H magic angle spinning (MAS) NMR. A later article will deal with the reactions occurring during repeated reaction cycles of $ZrCl_4$ and water, to increase the Zr concentration of the samples and to coat the support with zirconia. Many of the results obtained by Haukka et al.[12,28] for the $TiCl_4/SiO_2$ system can be extended to the $ZrCl_4/SiO_2$ system. On the alumina surface the reaction proceeded through a complex mechanism: the reactions of (Al−O) pairs palyed an important role in addition to the exchange reactions with OH groups and the agglomeration involving direct chlorination.

Table 1. OH Densities of the Preheated Supports

support/preheat temperature (°C)	total amount OH/nm^2	H-bonded OH/nm^2	isolated OH/nm^2
silica/300	5.2	2.6	2.6
silica/600	1.8	0.3	1.5
alumina/300	5.5		
alumina/600	2.0		

Experimental Section

Materials. $ZrCl_4$ was obtained from Fluka. The modified supports were prepared on Grace Davison silica and Akzo 000−1.5 E γ-alumina. The specific surface area of the untreated supports was 300 and 190 m^2/g, and the pore volume was 1.6 and 0.5 cm^3/g for silica and alumina, respectively. The median particle size of silica was 40 μm, and the particle size of alumina was 0.15−0.30 or 0.7−1.0 mm. The OH densities of the silica and alumina supports after heat treatments at 300 and 600 °C, as measured by ^{1}H MAS NMR, are shown in Table 1.

Sample Preparation. The supports (3−6 g) were preheated in air for 16 h at 300 or 600 °C in a muffle furnace. The preheat treatment was continued for 3 h at the same or lower temperature in a fixed-bed flow-type reactor (Microchemistry Ltd.) under pressure of 5−10 kPa in a nitrogen flow. After the pretreatment, $ZrCl_4$ vapor from a heated source was passed downward through the sample at 300, 450, or 600 °C, with nitrogen used as carrier gas. The reaction temperature did not exceed the preheat temperature of the support and was kept higher than the temperature of the source, 270−280 °C. At 279 °C the vapor pressure of $ZrCl_4$ is 133 kPa.[33] The amount of vaporized $ZrCl_4$

(26) Morrow, B. A. *Stud. Surf. Sci. Catal.* **1990**, *57A*, 161.
(27) Damyanov, D.; Velikova, M.; Ivanov, Iv.; Vlaev, L. *J. Non-Cryst. Solids* **1988**, *105*, 107.
(28) Haukka, S.; Lakomaa, E.-L.; Jylhä, O.; Vilhunen, J.; Hornytzkyj, S. *Langmuir* **1993**, *9*, 3497.
(29) Vansant, E. F.; Van Der Voort, P.; Vrancken, K. C. *Stud. Surf. Sci. Catal.* **1995**, *93*, 357.
(30) Damyanov, D.; Vlaev, L. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1841.
(31) Kytökivi, A.; Lindblad, M.; Root, A. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 941.
(32) Hochman, T.; Setínek, K. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1417.
(33) D'ans, J.; Lax, E. *Taschenbuch für Chemiker und Physiker I*, 3rd ed.; Springer: Berlin, 1964; p 1-909.

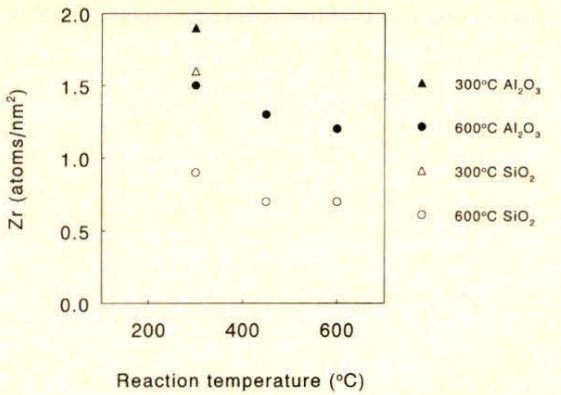

Figure 1. Effect of preheat and reaction temperatures on Zr concentration on silica and on alumina.

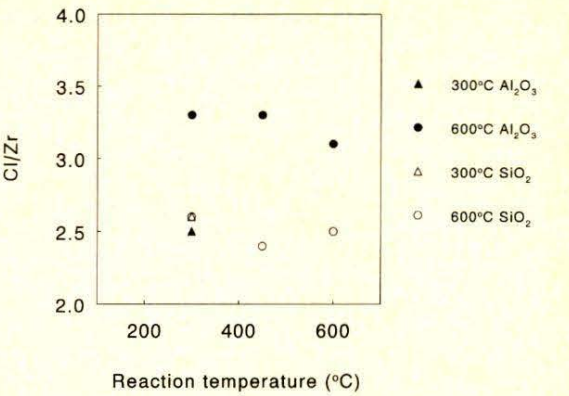

Figure 2. Effect of preheat and reaction temperatures on Cl/Zr ratio on silica and on alumina.

was kept high enough to ensure the saturation of the surface.[9,25] Following the reaction with $ZrCl_4$ the sample was purged with nitrogen at the reaction temperature for at least 2 h. To remove chloride, the $ZrCl_4$-modified surface was treated with water vapor at 300−600 °C. A 2-h purge with nitrogen was also carried out after the water treatment. After the reactor had been cooled to room temperature, the sample was transferred under nitrogen atmosphere to the FTIR and NMR instruments.

Characterization. The zirconium concentration of the samples was determined by X-ray fluorescence (XRF) or instrumental neutron activation analysis (INAA). The chloride concentration was determined by potentiometric titration with $AgNO_3$ after dissolving of Cl from a weighed sample into a 3.5 mol/dm^3 sulfuric acid solution. To prevent release of Cl as gaseous HCl from the sample, the acid was added immediately after the sample was removed from the reactor and weighed. The amount of insoluble zirconia in a sample was determined by INAA after the soluble part of Zr was etched with 2 mol/dm^3 sulfuric acid and the sample was carefully rinsed with water.

X-ray diffraction (XRD) measurements were made with a Siemens Diffrac 500 diffractometer using Cu Kα radiation. A Galaxy Series 6020 or a Nicolet Impact 400D FT-IR spectrometer was used for the diffuse reflectance spectroscopy measurements. The measurements were carried out in an accessory kept in a glovebox under nitrogen atmosphere. Spectra were obtained at 2 cm^{-1} resolution with a signal averaging 1000 scans (Galaxy) or 50 scans (Nicolet). Spectra were presented in diffuse transmittance format.

A JEOL GSX 270-MHz NMR spectrometer was used for ^{1}H MAS NMR measurements. All samples were handled under an atmosphere of nitrogen gas and loaded into 7 mm o.d. zirconia rotors. The samples were rotated at speeds of about 6.5 kHz. The NMR experiments were carried out using a 45° excitation pulse of 2 μs, a 10 s recycle delay, and 100 transients. The small residual ^{1}H background signal, which was obtained from an empty spinning rotor, was subtracted from each spectrum. Spin counting to determine the number of OH groups per square nanometer was done as described previously, using a known reference sample of silica.[12] Spectral deconvolutions were carried out using Gaussian line shapes.[12]

Results

Effect of Preheat and Reaction Temperatures. The starting point in studying the reactions of $ZrCl_4$ was to clarify the influence of the preheat and reaction temperatures on the Zr concentration of silica and alumina samples. As Figure 1 shows, the higher the preheat temperature of the support, the lower was the Zr concentration, with the effect being stronger on silica. An increase in the reaction temperature also reduced the concentration of bound Zr. The average Zr density was lower on silica than on alumina. At a preheat and reaction temperature of 300 °C the values on silica and alumina were 1.5−1.7 and 1.8−2.1 Zr/nm^2, respectively. At a preheat and reaction temperature of 600 °C the values dropped to 0.6−0.7 Zr/nm^2 on silica and to 1.1−1.2 Zr/nm^2 on alumina. In addition to the Zr concentration, the process temperatures also affected the Cl/Zr ratio of the samples, indicating changes in the reaction mechanism (Figure 2). On the 300 °C alumina the ratio was 2.5−2.7, increasing on the 600 °C support to 3 and even above. On silica the values ranged from 2.4 to 2.6.

Table 2. Effect of Preheat and Reaction Temperatures on the Crystallinity of the Samples with Respect to ZrO_2 after $ZrCl_4$ Treatment and no Water Treatment

reaction temperature (°C)	crystallinity on support/preheat temperature of support/(°C)			
	SiO_2/300	SiO_2/600	Al_2O_3/300	Al_2O_3/600
300	amorphous	amorphous	ZrO_2	amorphous
450		ZrO_2		ZrO_2
600		ZrO_2		ZrO_2

XRD Measurements. The possible formation of crystalline agglomerates during $ZrCl_4$ treatment was investigated by XRD. The results in Table 2 reveal the presence of ZrO_2 in all samples prepared at 450 and 600 °C and in the 300 °C alumina sample prepared at a reaction temperature of 300 °C. Other samples prepared at 300 °C were amorphous. Note that Zr concentrations were higher in the amorphous samples than in samples with crystalline ZrO_2, which means that the crystallinity cannot be attributed to increased Zr concentration. The formation of detectable crystalline material seemed to depend mainly on the reaction temperature, although there was some dependence on the preheat temperature as well.

The main crystalline phase in the samples was interpreted as the tetragonal form of ZrO_2. The cubic phase could explain the XRD patterns, but it is a rare form of pure ZrO_2, stable at temperatures over 2000 °C.[1,34] In the sample prepared at 600 °C on 600 °C silica, the monoclinic form was present in small quantities in addition to the tetragonal form. In the casde of other samples, the monoclinic form could be ruled out, although below 1100 °C the normal stable form of pure ZrO_2 is the monoclinic phase. However, the tetragonal form can be stabilized at lower temperatures if the particle size is small enough,[1,34] as it seemed to be here.

Study of Reaction Mechanisms on Silica. The XRD measurements confirmed that agglomeration must be taken into account in considering the reactions between $ZrCl_4$ and the support. The results suggested that the behavior of the $ZrCl_4/SiO_2$ system resembled that of the $TiCl_4/SiO_2$ system described by Haukka et al.[12,28] To determine the suitability of the model of Haukka et al., the reaction mechanism was studied in detail by characterizing part of the samples by IR and ^{1}H MAS NMR

(34) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford Science Publications: Oxford, 1984; p 542.

Table 3. Results of Elemental Determinations, ^{1}H MAS NMR Measurements, and Etching Tests after Reaction of $ZrCl_4$ with Silica

preh and reaction temps (°C/°C)	water temp (°C)	Zr/nm^2	Cl/nm^2	no. of OH groups after reaction				insoluble Zr (%)
				total/nm^2	isol/nm^2	H-bonded/nm^2	Zr−OH/nm^2	
300/300		1.7	4.4	1.3	0.2	1.1		18
300/300	300	1.7	0.2	5.2	1.6	1.7	1.9	
600/300		1.0	2.3	0.3	0.3			48
600/300	300	0.9	0.8	1.6	0.7	0.3	0.6	
600/450		0.6	1.5	0.2	0.2			95
600/600		0.7	1.7	0.05	0.05			94
600/600	600	0.7	<0.1	1.6	1.6			

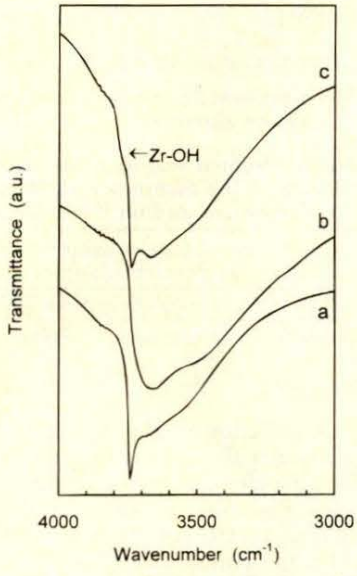

Figure 3. FTIR spectra of (a) 300 °C silica, (b) 300 °C silica reacted with $ZrCl_4$ at 300 °C and (c) 300 °C silica reacted with $ZrCl_4$ at 300 °C and treated with water at 300 °C.

techniques and etching tests. The quantitative results of NMR and the etching tests together with elemental determinations are gathered in Table 3.

IR and ^{1}H MAS NMR Measurements after $ZrCl_4$ Treatment of Silica. According to IR measurements, the consumption of OH groups during the reaction of $ZrCl_4$ occurred at all preheat and reaction temperatures. The reactivity of different types of OH groups could be seen by examining the generally approved assignments for the IR bands.[26,29] At a preheat and reaction temperature of 300 °C, both the sharp band of isolated OH groups at 3743 cm^{-1} and the broad absorption at 3500−3550 cm^{-1} belonging to strongly hydrogen-bonded OH groups disappeared (Figure 3a and b). The band of inaccessible, weakly hydrogen-bonded OH groups at 3650−3670 cm^{-1} was preserved, as expected. According to the ^{1}H NMR measurements, the original amount of 5.2 OH/nm^2 on 300 °C silica decreased to 1.3 OH/nm^2 after the $ZrCl_4$ reaction. The residual band showed more of an H-bonded character than an isolated character (Figure 4a and b and Table 3).

On 600 °C silica the strongly H-bonded OH groups were already removed during the heat treatment,[26] leaving the isolated hydroxyl groups available as principal bonding sites. Most of the weakly H-bonded OH groups also disappeared in the pretreatment. After the reaction at 300 °C, a residual band of the isolated groups at 3745 cm^{-1} could be seen in the IR spectrum. According to ^{1}H NMR, the number of OH groups decreased to 0.3 OH/nm^2. After reactions at 450 and 600 °C on 600 °C silica, only a residual band could be seen at places where the IR bands of isolated and weakly H-bonded OH groups appear. And

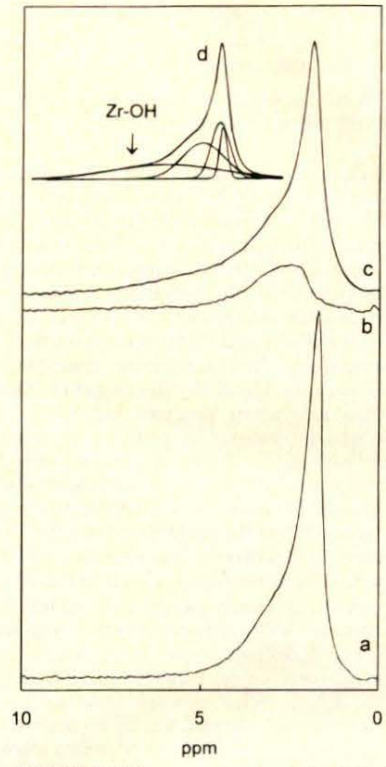

Figure 4. ^{1}H MAS NMR spectra of (a) 300 °C silica, (b) 300 °C silica reacted with $ZrCl_4$ at 300 °C, and (c) 300 °C silica reacted with $ZrCl_4$ at 300 °C and treated with water at 300 °C. Simulation of spectrum c presented in d.

indeed, ^{1}H NMR showed the number of hydroxyl groups left on the surface at 450 and 600 °C to be very small (Table 3).

IR and ^{1}H MAS NMR Measurements after Water Treatment of $ZrCl_4$-Modified Silica Samples. Measuring the consumption of OH groups in the reaction with $ZrCl_4$ does not distinguish the different bonding modes of $ZrCl_4$; for OH groups disappear both when $ZrCl_4$ reacts with OH groups, releasing HCl, and when it chlorinates OH groups directly.[12,15] Differences in the bonding mode should become apparent through water treatment of the samples. If the OH groups are occupied by Cl, the Si−OH groups should reappear. The hydrolysis of $ZrCl_x$ species attached to OH groups, on the other hand, should lead to the formation of Zr−OH groups. Rehydroxylation of silica is not expected to take place in the water treatment: firstly, because the surface is stabilized toward rehydroxylation when the preheat temperature and the reaction temperature of $ZrCl_4$ are the same and, secondly, because when the combination of preheat temperature of 600 °C and water treatment temperature of 300 °C is used, the hydrophobic nature of the dehydroxylated silica should prevent the reaction to a large extent.[26]

According to the IR and NMR spectra (Figures 3c and 4c), water treatment at 300 °C after $ZrCl_4$ reaction at 300

°C on 300 °C silica seemed to restore most of the OH groups of the silica. In addition to the bands of the Si−OH groups, however, a band at 3775−3778 cm^{-1} due to the Zr−OH groups[35-38] was present in the IR spectrum. Similarly, the broad hump at about 5 ppm on the side of the main band of the Si−OH groups in the ^1H NMR spectrum could be assigned to Zr−OH groups.[39,40] The above-mentioned bands do not normally appear alone in the spectra of pure ZrO_2: in IR a second band is usually observed at 3660−3680 cm^{-1},[35-38] and in NMR a shoulder appears between 1.5 and 3.5 ppm.[39,40] In our spectra these bands were obscured by overlapping Si−OH peaks, if existing. The total amount of OH groups on the surface after the water treatment increased to 5.2/nm^2, which, according to the simulations (Figure 4d/Table 3), consisted of about 3.3 Si−OH/nm^2 and 1.9 Zr−OH/nm^2, assuming no Zr−OH resonance under the Si−OH peaks. Evidently the reacted Si−OH groups were occupied both by directly bound Cl and by $ZrCl_x$ species even at the reaction temperature of 300 °C.

On 600 °C silica, the IR spectra of water-treated samples resembled those of untreated 600 °C silica at reaction temperatures of both 300 and 600 °C. No clear Zr−OH bands could be distinguished from the bands of Si−OH. Simulations of the ^1H NMR spectra suggested, however, that, besides Si−OH groups, about 0.6 Zr−OH/nm^2 was formed in the hydrolysis after reaction at 300 °C (Table 3). Once again this indicates that both Zr species and directly bound Cl occupied OH groups. The total number of OH groups after reaction and hydrolysis at 300 °C was 1.6/nm^2, but there was also a residual of 0.8 Cl/nm^2 due to ineffective water treatment. At a reaction temperature of 600 °C on 600 °C silica, hydrolysis restored the number of Si−OH groups to a value of 1.6/nm^2. No Zr−OH groups were detected at this high temperature. This almost complete reappearance of Si−OH groups (the original number was 1.8/nm^2) suggested that the OH groups were mainly consumed by Cl.

On the basis of the above results it was clear that direct chlorination of the surface occurred under all process conditions. At reaction temperatures of 450 and 600 °C on 600 °C silica, the chlorination occurred in conjunction with agglomeration. This could also have been the case at the reaction temperature of 300 °C, but the agglomerates would then have had to be very small crystalline or amorphous ones, or few in number, since no XRD peaks due to ZrO_2 were detected at this reaction temperature.

Etching Tests on Silica Samples. Samples (without water treatment) were etched with sulfuric acid to differentiate the surface forms of Zr[12] (Table 3). At all process temperatures there were both insoluble and soluble Zr attached on the surface. The lower the reaction temperature the greater was the proportion of soluble Zr species. XRD measurement of an etched sample prepared at 600 °C on 600 °C silica revealed crystalline material on the surface. Furthermore, the intensities of the peaks were the same as those in the diffractogram of the original sample. This showed that the soluble Zr was amorphous in character, whereas the Zr left on the surface was in the form of crystalline agglomerates.

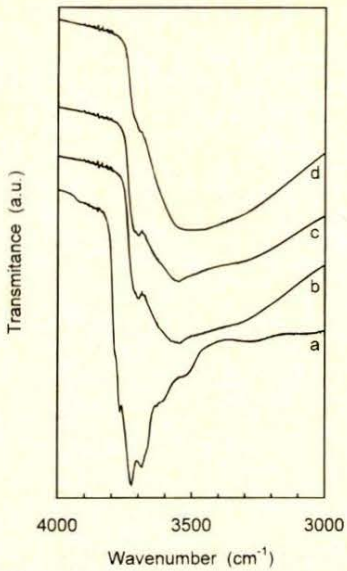

Figure 5. IR spectra of (a) 600 °C alumina, (b) 600 °C alumina reacted with $ZrCl_4$ at 600 °C, (c) 600 °C alumina reacted with $ZrCl_4$ at 450 °C, and (d) 300 °C alumina reacted with $ZrCl_4$ at 300 °C.

Table 4. Results of Elemental Determinations, ^1H MAS NMR Measurements, and Etching Tests after Reaction of $ZrCl_4$ with γ-Alumina

preh and reaction temps (°C/°C)	water temp (°C)	Zr/nm^2	Cl/nm^2	no. of OH groups after reaction/nm^2	insoluble Zr (%)
300/300		1.9	5.3	0.9	34
600/300		1.5	4.9	0.8	40
600/300	300	1.4	0.9	5.1	
600/300	600	1.5	0.2	2.6	
600/450		1.2	4.0		63
600/600		1.1	3.6	0.5	65
600/600	600	1.2	0.1	2.9	

Study of Reaction Mechanisms on γ-Alumina. As with silica, the possible reaction mechanisms on alumina were studied by IR, NMR, and etching. The results of the NMR and etching tests are summarized in Table 4 and discussed below.

IR and ^1H MAS NMR Measurements after $ZrCl_4$ Treatment of Alumina. The consumption of OH groups during the $ZrCl_4$ reaction was clear. At reaction temperatures of 300, 450, and 600 °C on 600 °C alumina, the bands at 3770 and 3790 (sh) cm^{-1} due to isolated basic OH groups[41] disappeared (Figure 5). At the same time, a broad band appeared at about 3550 cm^{-1} in the area of associated hydroxyl groups.[41] The band of isolated OH groups at 3730 cm^{-1} [41] was shifted to lower wavenumbers, appearing at 3700 cm^{-1} with a shoulder at 3715−3720 cm^{-1}. A shoulder at 3700 cm^{-1} could even be seen at a reaction temperature of 300 °C on 300 °C alumina. In all spectra, the band of isolated, more acidic OH groups at 3685−3690 cm^{-1} was overshadowed by the broad band at 3550 cm^{-1}. The changes in the area of associated OH groups appeared smaller at 300 °C on 300 °C alumina due to broad features in the spectrum of original 300 °C alumina (H-bonded OH groups and coordinatively bound water existing on 300 °C alumina[42]).

The disappearance of OH groups could also be seen in the ^1H NMR spectra of 600 °C alumina (Figure 6a−c and

(35) Agron, P. A.; Fuller, E. L., Jr.; Holmes, H. F. *J. Colloid Interface Sci.* **1975**, *52*, 553.
(36) Yamaguchi, T.; Nakano, Y.; Tanabe, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2482.
(37) Bianchi, D.; Gass, J.-L.; Khalfallah, M.; Teichner, S. J. *Appl. Catal., A* **1993**, *101*, 297.
(38) Jacob, K.-H.; Knözinger, E.; Benfer, S. *J. Mater. Chem.* **1993**, *3*, 651.
(39) Mastikhin, V. M.; Zamaraev, K. I. *Appl. Magn. Reson.* **1990**, *1*, 295.
(40) Mastikhin, V. M.; Nosov, A. V.; Filimonova, S. V.; Terskikh, V. V.; Kotsarenko, N. S.; Scmachkova, V. P.; Kim, V. I. *J. Mol. Catal., A* **1995**, *101*, 81.
(41) Knözinger, H.; Ratnasamy, P. *Catal. Rev. Sci. Eng.* **1978**, *17*, 31.
(42) Vlaev, L.; Damyanov, D.; Mohamed, M. M. *Colloids Surf.* **1989**, *36*, 427.

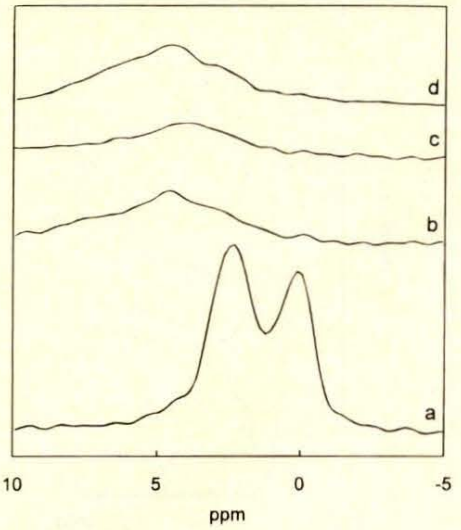

Figure 6. ^{1}H MAS NMR spectra of (a) 600 °C alumina, (b) 600 °C alumina reacted with $ZrCl_4$ at 600 °C, (c) 600 °C alumina reacted with $ZrCl_4$ at 300 °C, and (d) 300 °C alumina reacted with $ZrCl_4$ at 300 °C.

Table 4). Only a broad low peak centered at 4.0−4.5 ppm was left at reaction temperatures of 600 and 300 °C. This residual peak corresponded to values of 0.5 and 0.8 OH/nm^2, respectively, the number of original OH groups being 2 OH/nm^2. The residual peak was at higher frequency than the bands of the original OH groups on alumina. Similar features were found in the spectrum of the sample prepared at 300 °C on 300 °C alumina (Figures 6d and e). There the number of OH groups decreased from 5.5/nm^2 to 0.9 OH/nm^2 (Table 4).

IR and ^{1}H MAS NMR Measurements after Water Treatment of $ZrCl_4$-Modified Alumina Samples. The IR spectrum of the water-treated sample prepared at the preheat and reaction temperature of 600 °C was very similar to the IR spectrum of the original alumina: the isolated basic OH groups at 3770 cm^{-1} seemed to reappear. The band was broadened toward higher wavenumbers, however, compared with the spectrum of the original alumina. The differences between the spectra of water-treated samples and alumina were more distinct in ^{1}H NMR (Figure 7a and b and Table 4). First of all, the total amount of OH groups was 2.9/nm^2, i.e. higher by 0.9 OH/nm^2 than the original number for 600 °C alumina. The band of OH groups was broadened and resonated at higher frequency, while the band at about 0 ppm assigned to basic OH groups[39] did not reappear fully. This implies that the broadened IR band at 3770 cm^{-1} was at least partly due to Zr−OH groups and not entirely to basic Al−OH groups. Indeed, on the basis of the silica results the broadening of the NMR peak could also be assigned to Zr−OH groups. The more acidic OH groups of the original OH groups of alumina, on the other hand, seemed to reappear at 2.5 ppm.

The water treatment at 300 °C carried out on the sample of 600 °C alumina prepared at 300 °C led to an OH density of 5.1 OH/nm^2 (Table 4). The broadening of the ^{1}H NMR spectrum to the left shows the appearance of some Zr−OH groups, but the intensity of the basic groups did not increase to the same level as in the spectrum of 300 °C alumina (Figure 7d and e). Thus, at least part of the basic groups again were consumed by Zr species. It seemed also that at least part of the more acidic groups returned in the hydrolysis of the chlorinated surface. Most of the new OH groups, however, must have formed in the rehydroxylation of the 600 °C alumina surface, so that

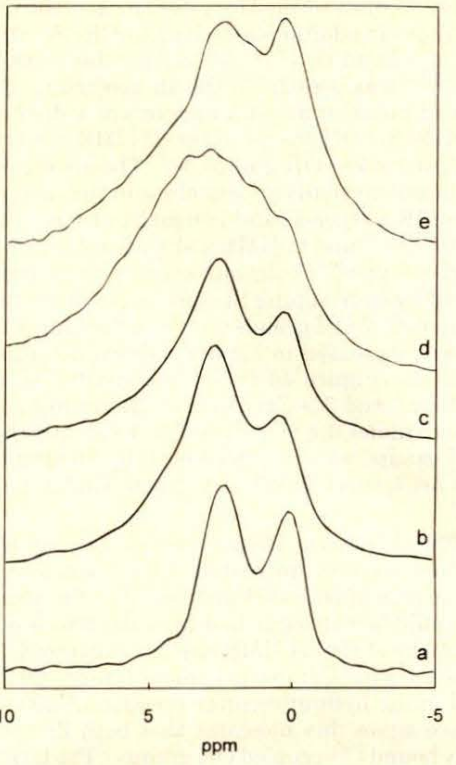

Figure 7. ^{1}H MAS NMR spectra of (a) 600 °C alumina, (b) 600 °C alumina reacted with $ZrCl_4$ at 600 °C and water vapor at 600 °C, (c) 600 °C alumina reacted with $ZrCl_4$ at 300 °C and treated with water at 300−600 °C, (d) 600 °C alumina reacted with $ZrCl_4$ at 300 °C and treated with water at 300 °C, and (e) 300 °C alumina.

the amount of OH groups approached the amount on 300 °C alumina (Figure 7e). When the water treatment of a similar sample to that described above was extended while raising the temperature to 600 °C, the number of OH groups decreased to 2.6/nm^2. The OH groups of the alumina were dehydroxylated upon increasing the temperature. Probably some of the Zr−OH dehydroxylated as well. Hydrolysis of the remaining Cl species decreased the Cl residue from 0.9 Cl/nm^2 to 0.1/nm^2.

Etching Tests on Alumina Samples. Alumina samples were etched with sulfuric acid in a similar way to that used for the silica samples. At the preheat temperature of 600 °C, the lower the reaction temperature, the greater was the soluble portion of Zr (Table 4). The residue of the 600 °C sample gave XRD bands of ZrO_2, allowing a similar interpretation of the results as in the silica case: i.e., the soluble part was attributed to amorphous forms, and the insoluble part, to crystalline ZrO_2. From this it was concluded that agglomerates were formed under all conditions studied. At preheat and reaction temperatures of 300 °C, the amount of insoluble Zr exceeded that for the silica support. This result was consistent with the XRD measurements: XRD peaks of ZrO_2 were recorded for the alumina sample whereas the silica sample was amorphous.

Discussion

Agglomeration. The results showed the $ZrCl_4/SiO_2$ system to behave in a similar way to the $TiCl_4/SiO_2$ system described by Haukka et al.,[12] and a similar model could be adopted as a basis for the alumina system. Essential to this model is that the reaction temperature determines whether $TiCl_4$, or in this case $ZrCl_4$, reacts with the surface to form two-dimensional surface species or three-dimensional agglomerates.

The lowest reaction temperature in our work was 300 °C, which was found to be in the temperature range of agglomeration in both silica and alumina systems. Although XRD measurements on supports reacted at 300 °C revealed crystalline ZrO_2 only on 300 °C alumina, the etching tests showed that all samples reacted at 300 °C contained insoluble crystalline Zr species. Evidently, the amount of crystalline material was too small to be detected in XRD amorphous samples, but as the reaction temperature and the reactivity toward agglomeration increased, the amount of crystalline material became great enough to be discernible.

The observed agglomeration occurred during the reaction of $ZrCl_4$ in conjunction with direct chlorination of the surface. A recent article dealing with the reaction of $ZrCl_4$ with alumina at 400 °C[24] does not present any XRD results and, hence, neither the formation of agglomerates nor the direct chlorination are considered in the paper. Meallier et al.[22] have reported agglomeration in the $SiCl_4/Al_2O_3$ system, and they propose the following straightforward reaction for $SiCl_4$ leading to the formation of bulk oxide and a chlorinated surface:

$$2Al{-}OH + SiCl_4 \rightarrow 2Al{-}Cl + SiO_2 + 2HCl \quad (9)$$

Haukka et al.[28] explain agglomeration and direct chlorination to proceed through the reaction of OH groups and $TiCl_4$ so that a volatile secondary chloride, $Ti(OH)_2Cl_2$, is formed. This unstable compound is not transported away by carrier gas but interacts with silica, forming TiO_2 (and releasing HCl). Thus, the following hypothetical equation could be written for silica, and also alumina, when they react with $ZrCl_4$:

$$2Si{-}OH + ZrCl_4 \rightarrow 2Si{-}Cl + Zr(OH)_2Cl_2 \quad (10)$$

Similarly, the reaction of $ZrCl_4$ could proceed through an oxygen-containing compound:

$$Si{-}OH + ZrCl_4 \rightarrow Si{-}Cl + ZrOCl_2 + HCl \quad (11)$$

Oxygen-containing compounds are reported to form when, for example, CCl_4 reacts with alumina[13-15] or WCl_6[43] or $MoCl_5$[44] reacts with silica, leading to chlorination of the surface at the same time. Furthermore, WCl_6, $MoCl_5$, and CCl_4 may continue to chlorinate the surface until the support oxide of silica or alumina begins to volatilize as $SiCl_4$ or $AlCl_3$.[15,43,44] In the case of $ZrCl_4$, these etching reactions of silica and alumina supports are thermodynamically unfavorable.[45,46]

For titanium the existence of both $TiOCl_2$[47] and $Ti(OH)_2Cl_2$[48] in the vapor phase has been reported, but solid evidence for the existence of similar zirconium compounds is lacking.[49] Still, we propose the formation of such volatile but unstable intermediate species for $ZrCl_4$ as well, to explain the presence of agglomerates. From a practical point of view, however, more important than the actual mechanism was the finding that the number of hydroxyl groups restricts the amount of ZrO_2 formed. This means that the agglomeration reaction stops when the reactive OH groups are consumed; i.e., the reaction is self-limiting and saturation of the surface is achieved. Thus, the reactions are controllable with regard to the Zr concentration on the surface.

The agglomerates themselves did not seem to occupy OH groups on the surface. In the sample prepared at a preheat and reaction temperature of 600 °C the water treatment released practically all the Si−OH groups of the original silica, which shows that the OH groups were instead occupied by independently bound Cl atoms. The agglomerates, for their part, must have been formed on the parts of the surface lacking OH groups, i.e. in the areas of siloxane bridges (or analogously for alumina, in the area of (Al−O) pairs). We can further note that because at lower reaction temperatures not all the OH groups reappeared, the possible additional agglomeration during water treatment leading to release of Si−OH groups[21] must have been insignificant although it cannot be totally excluded.

Amorphous Zr Species. On the basis of the discussion above, we can propose that the soluble and thus amorphous Zr species consuming permanently part of the OH groups was in the form of two-dimensional isolated surface species of the type $-ZrCl_3$ or $=ZrCl_2$. OH reactions were not, however, the only possible mechanism forming two-dimensional species. Similar species may have been formed in dissociative reactions as well.

We consider the OH reactions first. On silica at a low preheat temperature both the strongly H-bonded and isolated OH groups reacted, leaving the weakly H-bonded, inaccessible groups unreacted. At the higher preheat temperature of 600 °C, not all the isolated groups disappeared at 300 °C, but the residual amount of isolated OH groups decreased with an increase in the reaction temperature, leaving only traces of them at 600 °C. As already stated, however, the OH groups were consumed both in exchange reactions and in agglomeration reactions. At preheat and reaction temperatures of 300 °C, no strict correlation could be seen between the type of OH group and the type of reaction, because after water treatment parts of both the H-bonded and the isolated groups had disappeared permanently and parts of both reappeared. At a preheat temperature of 600 °C the amount of H-bonded OH groups was negligible, which led to the consumption of isolated groups in both exchange and agglomeration reactions at 300 °C. An increase in the reaction temperature diminished the amount of isolated OH groups used in the exchange reaction: at 600 °C only 5% of the Zr species was amorphous. Furthermore, arguing from the results for the $TiCl_4/SiO_2$ system,[12] the OH groups of silica could have been used in the monomolecular reaction (eq 1) or the bimolecular reaction (eq 2), with the ratio depending on both reaction and preheat temperature. However, this aspect was not studied in our work.

On alumina at a reaction temperature of 300 °C, amorphous species comprised about 60 or 65% of the total, depending on the preheat temperature. We know that at least part of the basic OH groups were consumed in the exchange reaction, since they did not reappear in the water treatment. The possible consumption of other types of OH groups is difficult to determine: The OH groups seen in the IR and NMR spectra after $ZrCl_4$ reaction could have been either unreacted, originally isolated OH groups of alumina that had been modified by the strong interaction of adsorbed species and thus shifted in the spectra or else new OH groups formed in the dissociation of HCl. In the latter case, the residual OH value could only have been produced if a greater portion of the original OH groups had reacted. It is clear, however, that at least some of the original OH groups of alumina must have been left intact.

(43) Babich, I. V.; Plyuto, Yu. V.; Chuiko, A. A. *Russ. J. Phys. Chem.* **1988**, *62*, 243.
(44) Plyuto, Yu. V.; Gomenyuk, A. A.; Babich, I. V.; Nuiko, A. A. *Kolloidn. Zh.* **1993**, *55*, 85.
(45) Santacesaria, E.; Carrà, S.; Pace, R. C.; Scotti, C. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 496.
(46) *Outokumpu HSC Chemistry for Windows Program*, version 2.03; Outokumpu Research Oy: Pori, Finland, 1994.
(47) Readey, M. J.; Readey, D. W. *J. Am. Ceram. Soc.* **1987**, *70*, C-358.
(48) Gruy, F.; Pijolat, M. *J. Am. Ceram. Soc.* **1992**, *75*, 663.
(49) Readey, M. J.; Readey, D. W. *J. Am. Ceram. Soc.* **1986**, *69*, 580.

The band of isolated OH groups at 3700−3720 cm^{-1} still appeared in the IR spectra, and these groups could not have been formed in the dissociation of HCl because groups so formed would appear in the lower wavenumber area as a result of OH···Cl interaction.[30] The decreasing amount of OH groups left on the surface after reaction at increasing temperature could have been an indication of the increasing reactivity of OH groups (Table 4).

Besides reactions with OH groups, the amorphous species could also have originated from dissociation reactions with siloxanes or (Al−O) pairs, leading to simultaneous chlorination of the surface. The reactivity of siloxanes toward chloride compounds is, however, generally related to strained bridges, which are formed only on highly dehydroxylated surfaces.[26,29,50] More precisely, it has been suggested that such sites form at preheat temperatures over 700 °C,[50] and thus we are inclined to exclude the dissociative reactions with siloxanes under our process conditions, especially as the results can be satisfactorily explained through other mechanisms. The reader is reminded, however, of our suggestion above that the ZrO_2 agglomerates modify parts of the surface consisting of siloxanes.

The higher Cl/Zr ratios on 600 °C alumina than on 600 °C silica suggest the operation of a different mechanism than that identified for silica. Comparing the results for alumina and silica systems at the preheat temperature of 600 °C, we see that, even though the Zr concentration was clearly higher on alumina than on silica at reaction temperatures of both 300 and 600 °C, the amount of consumed OH groups was smaller (Tables 1, 3, and 4) or at least not at a higher level. Thus, the higher Zr concentration could not be due to OH reactions, but some other mechanisms must have been involved. The two feasible alternatives are dissociation to (Al−O) sites and agglomeration. If we assume, however, as in the case of silica, that agglomeration was restricted by the number of consumable OH groups, the only cause of the increase could be dissociation. The dissociation reaction would also explain the increased Cl/Zr ratios on alumina (>3) compared to silica. Furthermore, the greater Zr concentration and higher Cl/Zr ratio at a reaction temperature of 300 °C than those at 600 °C on 600 °C alumina could be attributed to an increased amount of dissociative reactions of $ZrCl_4$, the driving force being the difference between the reaction and preheat temperatures.

Reactions of HCl. HCl was evolved in both the OH reactions and the agglomeration reaction and was available for further reactions. In the silica system, HCl does not react with silica at 300 °C[12] and side reactions can be excluded. However, the reaction of HCl cannot be totally excluded at reaction temperatures of 450 and 600 °C, for HCl has been found to react with 600 °C silica, giving typical surface densities of 0.6−1 Cl/nm^2.[12] We believe, nevertheless, that the HCl reaction contributes to chlorination only a little, if at all, because a much higher number of Si−OH groups (1.6 OH/nm^2) than can be explained by HCl reaction reappear in the water treatment at 600 °C. In view of this, and the availability of an alternative mechanism, namely agglomeration, we conclude that agglomeration is responsible for the direct chlorination. The reactions of HCl on alumina are more probable: alumina has been shown to be reactive toward HCl, for example, at a reaction temperature of 200−600 °C, giving surface densities of 1.5−2.5 Cl/nm^2.[31] We would nevertheless emphasize that $ZrCl_4$ evidently used both the (Al−O) sites and OH groups as bonding sites and, thus, in a competitive situation $ZrCl_4$ is probably the stronger chlorinating party.

We note also that HCl has been suggested to interact with the chlorinated surface, forming surface complexes like $O-ZrCl_4^-H^+$ or $O_2ZrCl_3^-H^+$ in solid super acid systems on alumina.[24] We think that if such species were formed, they would probably be stable only at low temperatures and not after effective purging at temperatures of 300 °C or more.

Water-Treated Surfaces. In the hydrolysis of samples, Zr−OH groups were formed on both supports, especially after $ZrCl_4$ and water reactions at lower temperatures. The Zr−OH IR band at 3775 cm^{-1} observed for one of the water-treated samples is typical for both monoclinic[35,38] and amorphous aerogel ZrO_2[37] but not for tetragonal ZrO_2,[35,38] which, according to XRD, was the phase in our samples. Thus, the Zr−OH groups were most likely associated with the hydrolysis of isolated species of type $=ZrCl_2$ or $-ZrCl_3$ and not to agglomerates of tetragonal ZrO_2. A similar conclusion was reached by Haukka et al.[28] on the basis of combined etching and NMR studies: When the amorphous species were dissolved from the silica surface, the Ti−OH peaks disappeared from the ^1H NMR spectrum.

Finally, we consider the modified surfaces as starting surfaces for growth through repeated $ZrCl_4$ and water cycles. The OH density on the surfaces seemed to be about the same or slightly higher (alumina) after a $ZrCl_4$ and water cycle than before. The notable difference was in the type of these OH groups. Part of the OH groups were permanently consumed by Zr species while new Zr−OH groups became available in the water treatment, at least at low reaction temperatures. Perhaps these groups can serve as new bonding sites for the $ZrCl_4$ vapor or other reagent. At the same time, original OH groups of supports reappeared and became available for the reaction. We can also conclude that, the lower the reaction temperature, the better the Zr coverage of the original surface. Not only was there more Zr but it was better dispersed in the form of isolated species. Of course, the ZrO_2 agglomerates covered part of the original surface as well, especially at high reaction temperatures, but not as effectively as isolated species. On silica this means that the relatively unreactive siloxane bridges were partly covered, whereas, on alumina, probably the most reactive (Al−O) sites were blocked by agglomerates and dissociated Zr species. This furthermore could imply that the catalytic properties of modified alumina are changed more than the properties of modified silica. Many of the properties of the pure support are expected to remain, however, due to the reappearance of OH groups of the original supports.

Summary

We studied the saturating reactions of $ZrCl_4$ vapor at reaction temperatures of 300, 450, and 600 °C on 300 and 600 °C silica and γ-alumina by XRD, FTIR in diffuse reflectance mode, ^1H MAS NMR, and chemical etching. Etching tests and XRD measurements gave more or less parallel results. It was observed that XRD-detectable agglomerates are not soluble in sulfuric acid. The measurements suggested that agglomeration of ZrO_2 occurred at all temperatures studied, although at a reaction temperature of 300 °C the phenomenon was detected only by etching and not by XRD.

The agglomeration mechanism involved simultaneous chlorination of the original surface under all conditions studied. The direct chlorination was revealed in the reappearance of a part of the original OH groups of both the alumina and silica support in the IR and NMR measurements. Part of the original OH groups were,

(50) Wovchko, E. A.; Camp, J. C.; Glass, J. A., Jr.; Yates, J. T., Jr. *Langmuir* **1995**, *11*, 2592.

however, permanently consumed in the exchange reactions leading to the formation of amorphous $-ZrCl_3$ and $=ZrCl_2$ species. FTIR and NMR also revealed the formation of Zr−OH groups in the water vapor treatment in both systems. Higher Cl/Zr ratios and lower reactivity of the original OH groups combined with an increased Zr level, however, were among those results of alumina that suggested differences in the reaction mechanism in the two systems. These differences were explained through a dissociative reaction of $ZrCl_4$ on the (Al−O) sites of alumina.

The level of Zr saturation of the surface depended on the preheat temperature of the porous oxide, i.e. on the OH concentration on the surface. The Zr concentration decreased with increasing preheat temperature. On alumina, the increasing number of (Al−O) sites at high preheat temperature did not overcome the effect attributed to a decrease in the amount of OH groups. The effect of reaction temperature in the process was related to the reaction mechanism. The reaction temperature controlled the ratio between the agglomerated Zr and the Zr that was bound to the surface through OH reactions as isolated surface species. The higher the reaction temperature, the more agglomerated Zr was formed. The agglomeration was responsible for the direct chlorination of the surface on silica. On alumina also the dissociation reaction contributed to chlorination. The reactions of HCl in the chlorination of the surface were considered minor.

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