Infrared Study of the Surface Species Formed by Sequential Chemical Vapor Deposition of Trimethylaluminum and Methanol on a Hydroxylated Alumina Surface

Vassil Boiadjiev and W. T. Tysoe*

Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53211

Received July 11, 1997. Revised Manuscript Received October 24, 1997⊗

Infrared spectroscopy is used to follow the chemical changes, as a function of temperature, after sequentially adsorbing trimethylaluminum (TMA) and methanol on hydroxylated alumina. Deuterium-labeled methanol is used to distinguish between the chemistry of methyl and methoxy species. To differentiate between methanol adsorbed on TMA-derived sites and on alumina, the adsorption of methanol is studied on alumina alone. The coverage of methanol on alumina alone is only 34 ± 2% of that which adsorbs on a TMA-covered surface. Initial adsorption of methanol on $Al(CH_3)_2$(ads) formed by TMA adsorption, rapidly replaces a methyl by a methoxy species. Further reaction of methanol at ~400 K replaces the second methyl species leading to $Al(CH_3O)_2$(ads). This thermally decomposes on heating to yield primarily dimethyl ether and surface formate species. It is also very reactive with water and rapidly forms adsorbed hydroxylated alumina and methanol.

Introduction

Adsorption of methanol and other alcohols on alumina has been studied by IR spectroscopy for many years[1−4] mainly in relation to their catalytic dehydration (to form dimethyl ether and water). The resulting complex spectra have been carefully analyzed, and a variety of species have been distinguished on the surface in the case of methanol adsorption at room temperature including bridging methoxide species coordinated to two Lewis acid sites, methanol molecules strongly chemisorbed to a Lewis acid site and reversibly adsorbed methanol, hydrogen bonded to the surface hydroxyl groups or to an oxygen basic site from the alumina lattice.[5] Relatively less complicated spectra have been observed[6] when the surface methoxide species are formed by direct reaction of the alumina surface hydroxyl groups with methyl chloride (CH_3Cl), eliminating HCl, where only very little of the reagent weakly physisorbs on the surface.

It is generally believed that the formation of surface methoxide species following adsorption of methanol on alumina does not involve direct esterification of surface hydroxyl groups,[3,5,6] but instead, dissociative adsorption takes place on the surface Lewis acid−base pairs. The methanol-derived species adsorbed on an alumina surface further react to form dimethyl ether, and the results of a more recent catalytic study by Schiffino et al.[7] have shown that dimethyl ether can be formed by the reaction of molecularly adsorbed methanol and methoxy species as well as via methoxy−methoxy reactions.

It is well-known[8] that the hydroxyl groups on alumina surface react with trimethylaluminum (TMA) to such an extent that aluminum oxide thin films can be grown by sequential chemical vapor deposition of TMA and water. Since alcohols can provide similarly active hydrogen by their hydroxyl groups, a similar reaction might provide a convenient method for chemically grafting hydrocarbon chains to an alumina surface. This strategy could potentially find applications, for example, in the areas of corrosion protection, chromatography adsorbent modification, or the preparation of self-assembled monolayers on oxide substrates. A similar approach has yielded good results on silica surfaces using alkylhalogenosilanes or silanols.[9−12] The interest in such chemistry is also driven by the fact that they can be deposited on a variety of oxide substrates, in contrast to the well-developed, but substrate-specific self-assembled monolayers of alkanethiolates on gold.

In this work, methanol is used as the simplest probe molecule to investigate the surface reaction between alcohols and TMA-derived alumina surface (consisting

---

* To whom correspondence should be addressed. Phone: (414) 229-5222. Fax: (414) 229-5530. E-mail: wtt@csd.uwm.edu.

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1997.

(1) Babushkin, A. A.; Uvarov, A. V. *Dokl. Acad. Nauk SSSR* 1956 *110,* 581.

(2) Greenler, R. *J. Chem. Phys.* **1962**, *37,* 2094.

(3) Kagel, R. O. *J. Phys. Chem.* **1967**, *71,* 844.

(4) Travert, J.; Saur, O.; Benaissa, M.; Lamotte, J.; Lavalley, J. C. In *Vibrations at Surfaces*; Caudano, R., Gilles, J. M., Lucas, A. A., Eds.; Plenum Press: New York, 1982.

(5) Busca, G.; Rossi, P. F.; Lorenzelli, V.; Benaissa, M.; Travert, J.; Lavalley, J.-C. *J. Phys. Chem.* **1985**, *89,* 5433.

(6) Beebe, T. P., Jr.; Crowell, J. E.; Yates, J. T., Jr. *J. Phys. Chem.* **1988**, *92,* 1296.

(7) Schiffino, R.; Merrill, R. *J. Phys. Chem.* **1993**, *97,* 6425.

(8) Soto, C.; Wu, R.; Bennett, D. W.; Tysoe, W. T. *Chem. Mater.* **1994**, *6,* 1705.

S0897-4756(97)00496-1 CCC: $15.00 © 1998 American Chemical Society
Published on Web 01/19/1998

of adsorbed $Al(CH_3)_2$ species[8]). The stability of the resulting surface species in aqueous environment is also studied. Reference experiments are conducted by directly adsorbing methanol on prehydroxylated alumina to compare the amount of surface species adsorbed in both cases and to "calibrate" the temperature distribution of the surface species with respect to our experimental conditions since the resulting species for alumina/methanol system are already well characterized. The use of CD_3OD in combination with $(CH_3)_3Al$ allows the formation of the new methoxide species and the displacement of CH_3 groups from TMA to be clearly observed.

Experimental Section

All spectra were taken using a Perkin-Elmer Fourier transform infrared spectrometer at 4 cm^{-1} resolution employing a DTGS detector. They were collected for five cycles (80 scans) which required about 14 min for each spectrum of the alumina pellet and two cycles for the gas phase using a single-beam ratio mode. The background spectrum, taken with the alumina pellet retracted from the infrared beam, is recorded after each evacuation of the infrared cell and is then subtracted from all subsequent spectra of the alumina pellet, as well as from the gas-phase spectra taken after annealing the sample or dosing with the corresponding reagents. Fourier transform smoothing is applied to the stretching regions of all spectra. Multiple point baseline correction is used to level the bending regions of all spectra. Baseline corrected integration is employed to evaluate and compare the relative quantities of $-CH_3$ and $-OCD_3$ surface species.

The glass ampule containing deuterated methanol (CD_3OD, Aldrich Chemical Co., 99.8 at. % D) was opened under nitrogen in a glovebox and transferred in a glass vial using a syringe in order to avoid H−D exchange with the water from the air. Trimethyl aluminum, TMA (Aldrich Chemical Co., 97%) was transferred via syringe into a glass vial, again in glovebox under nitrogen. D_2O used was from Sigma Chemicals, 99.8% purity and distilled water (H_2O) is used for the experiments with CH_3OH. CH_3OH (EM Science, 99.8%) was dried by refluxing over Mg and crystal iodine[13] and freshly distilled. All compounds were additionally purified by at least four freeze−pump−thaw cycles or until no gas bubbles were seen upon thawing, in the case of TMA.

The general pretreatment procedure is illustrated in the spectra of Figure 1 . The pellet, cleaned in O_2 at 800 K (spectrum a) has been exposed to D_2O (~20 Torr, spectrum b), evacuated to 3×10^{-6} Torr (spectrum c), and then heated in vacuo at 400 K (spectrum d) to remove the extra molecular water. This results in a decrease of the −OD stretching intensity at ~2600 cm^{-1} (~3600 cm^{-1} for H_2O) and completely removes the D_2O bending (scissoring) mode at ~1203 cm^{-1} (~1650 cm^{-1} for H_2O) indicating that the alumina surface is free of molecular water and covered by only hydroxyl species.

The alumina pellets were prepared from aluminum oxide powder (Baker Chemical Co.) after thorough grinding using a mortar and pestle and pressing 0.0138 g/cm^2 of the fine powder into a pellet at about 25 500 pounds per square inch (PSI). The pellet is placed in a magnetically coupled, stainless-steal manipulator that can move it back and forth from the infrared beam to the tube oven of the infrared cell as described elsewhere.[8] The removable KBr windows were carefully polished with methanol after every set of experiments. Once in the cell, the pellet is slowly evacuated and heated first to 400 K for 1 h and then to 800 K for about 6−8 h in vacuo. If contamination still persists, the pellet is cleaned twice by adding about 10 mL of oxygen, annealing at 800 K in the closed cell for about 30 min, and evacuating to 3×10^{-6} Torr at that temperature. Despite all this cleaning effort, a small peak still persists at about 1380 cm^{-1} (Figure 1B, spectrum a). This feature, which is also seen in other work (for example, ref 14), was removed completely at temperatures above 873 K during

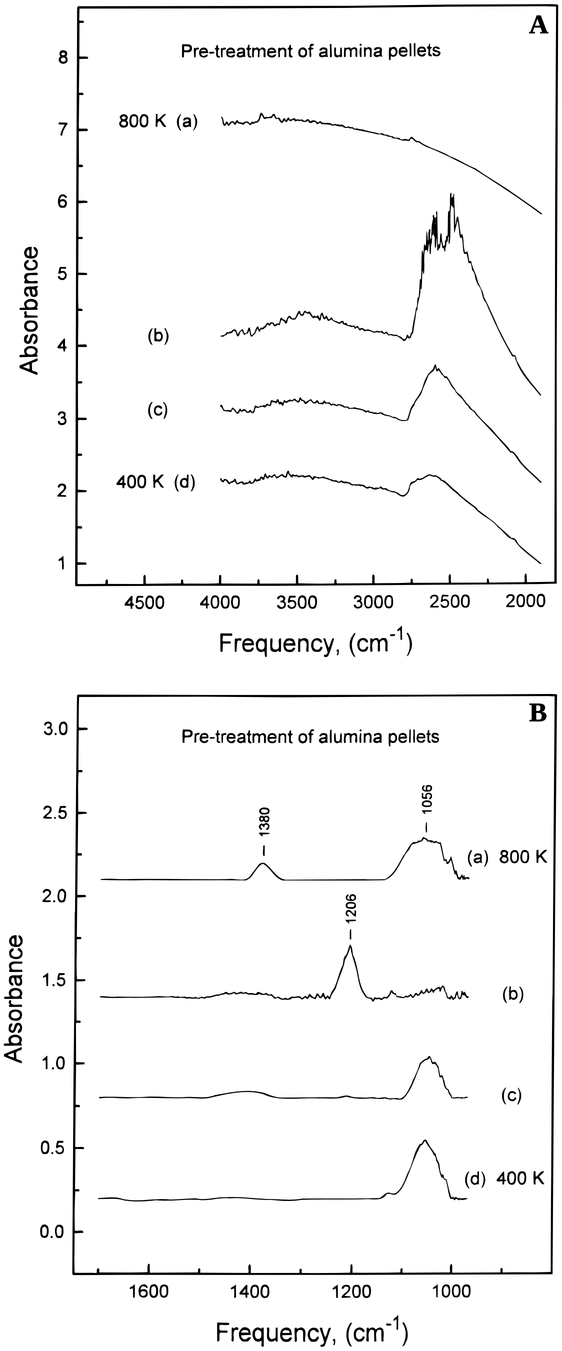


Figure 1. Pretreatment of alumina pellets: (A) Fourier transform smoothed infrared spectra of OH and OD stretching region, (B) baseline-corrected infrared spectra displaying the OH and OD bending region: (a) after cleaning at 800 K in vacuo with addition of oxygen, (b) sample exposed to D_2O at its vapor pressure (~20 Torr), gas phase and pellet, (c) evacuated by diffusion pump to 3×10^{-6} Torr at room temperature and (d) evacuated at 400 K to remove molecular water.

---

(9) Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, 8, 1961.

(10) Parikh, A.; Allara, D.; Azouz, I.; Rondelez, F. *J. Phys. Chem.* **1994**, *98*, 7577.

(11) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

(12) Denoyel, R.; Trens, P. *J. Phys. Chem.* **1995**, *99*, 3711.

(13) Knözinger, H.; Scheglila, A.; Watson, A. M. *J. Phys. Chem.* **1968**, *72*, 2770.

(14) Saniger, J. M. *Mater. Lett.* **1995**, *22*, 109.

preliminary experiments. However, annealing at such a high temperature severely inhibits subsequent alumina rehydroxylation and may significantly change the alumina surface.[15] This peak disappears after water adsorption. The other broad feature seen after activation at 800 K at about 1000−1050 cm^{-1} in Figure 1Ba often appears at the edge of the shoulder of alumina background depending on the particular pellet and the specific pretreatment conditions. Such a band has been assigned to the surface vibrational modes of alumina in ref 15, where its intensity has been shown to increase with increasing activation temperature. This feature is believed to be a result of the thermal dehydroxylation process, and adsorption of water has been reported to decrease its intensity instantaneously.[15] Our results show that this feature is strongly perturbed after methanol adsorption at room temperature and slowly recovers its shape and intensity upon annealing at higher temperatures in vacuo. The overall transparency of the alumina also decreases after adsorption of water and methanol because of extensive hydrogen bonding interactions in agreement with ref 16. This is supported by the observation that conversely TMA, which is known to reduce the concentration of the surface hydroxyls,[8] appears to increase the transparency over the entire studied spectral range.

Alumina pellets are exposed to saturated CD_3OD or CH_3OH vapor (120 ± 10 Torr) for about 2 min and evacuated to 3×10^{-6} Torr at room temperature. In experiments requiring $Al(CH_3)_3$ pretreatment, the alumina surface is first exposed to the organometallic reagent (at its vapor pressure for 2 min at 300 K) and evacuated to 3×10^{-6} Torr. The sample is then held for ~30 min in the closed IR cell under CD_3OD or CH_3OH and evacuated for another 30 min to about 3×10^{-6} Torr *both* at the same temperature as displayed adjacent to each of the spectra. The sample is then allowed to cool to room temperature, and the IR spectrum of the pellet recorded. This procedure is followed up to 398 K with dosing prior to annealing each time in order to ensure that excess methanol is available to react with any remaining CH_3 groups from the TMA. For temperatures above 398 K, the evacuated IR cell is closed at room temperature and the gas products desorbing from the pellet at these temperatures are collected for 30 min. The gas-phase spectrum is recorded, and the cell is evacuated for another 30 min at the same temperature. The sample is then allowed to cool to room temperature and the spectrum of the pellet is recorded.

Results

Adsorption of CD_3OD and CH_3OH Directly on a Prehydroxylated Alumina Surface. Background experiments are carried out by exposing a prehydroxylated alumina surface directly to either CD_3OD or CH_3OH at their equilibrium vapor pressures (120 ± 10 Torr at 298 ± 2 K) for 2 min and then evacuating to 3×10^{-6} Torr without trimethylaluminum (TMA) pretreatment. The temperature dependence of the resulting surface species is also studied, and the results obtained following CD_3OD exposure are displayed in Figure 2. Products desorbed from the surface are also collected after heating the sample in the closed infrared cell at each temperature for 30 min, and their gas-phase spectra recorded.

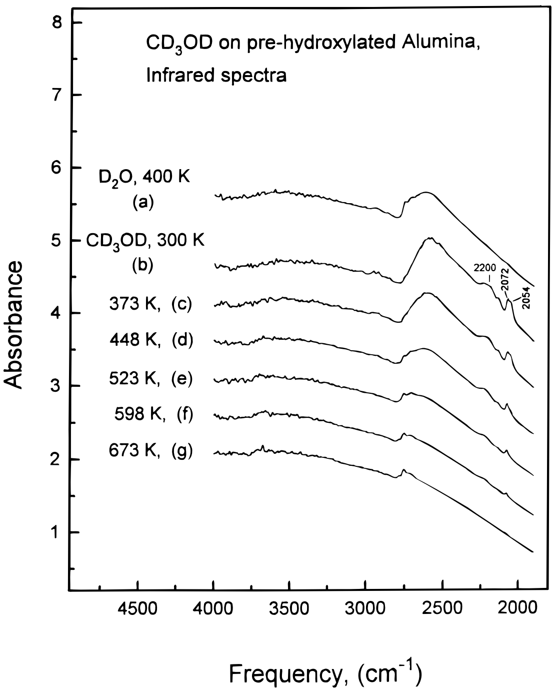


Figure 2. Temperature dependence of the surface species resulting on prehydroxylated alumina after direct exposure to CD_3OD (stretching modes): (a) clean alumina pellet exposed to D_2O and evacuated at 400 K to remove molecular water, (b) sample exposed to vapor pressure of CD_3OD (120 ± 10 Torr) and evacuated at room temperature for 30 min to 3×10^{-6} Torr. Spectra c−g are taken after annealing in vacuo at the temperature displayed adjacent to each spectrum.

Table 1. Assignments of the Infrared Modes Resulting after Methanol Adsorption[a]

mode	alumina/MeOH	alumina/TMA/MeOH
$\nu_{as}(CH_3)$	2966 (2240)	
	2944 (2220)	(2226)
	(2199)	(2179)
combn	2140	2136
$\nu_s(CH_3)$	2844 (2072)	(2079)
	2822 (2054)	(2044)
$\delta_{as}(CH_3)$	1470	1470
$\delta_s(CH_3)$	sh (1138)	1456 (1122)
rock (CH_3)	1190	1192
ν(C−O)	1104 (1058)	1108 (1036)

[a] Frequencies corresponding to CD_3OD adsorption are shown in parentheses and those outside the parentheses correspond to CH_3OH adsorption. The frequencies given for the adsorbed CD_3OD correspond to surface evacuated at room temperature. Since the CH_3- modes at room temperature are obscured by the extensive hydrogen bonding, the frequencies shown for CH_3OH correspond to the surface species after evacuation at 323 K.

Following methanol adsorption and evacuation at room temperature, the characteristic methyl modes of methanol are clearly seen (Figure 2b) and the major peak assignments are given in Table 1 based on the detailed study of Busca et al.[5] Only the stretching region is displayed in Figure 2, and the bending mode frequencies are displayed in Table 1 but not shown. Note that three different types of species have been detected resulting from methanol adsorption on an alumina surface activated at 773 K assigned to a bridging methoxide species coordinated in two alumina Lewis acid sites, methanol molecules strongly chemisorbed to a single Lewis acid site, and methanol molecules hydrogen-bonded to surface hydroxyl groups or surface oxygen ions. All of these species are supposed to be present at this step of our experiment with overlapping bands. The C−H (C−D) stretching modes at 2822 (2054) and 2844 (2072) cm^{-1} (Table 1) represent strongly chemisorbed and hydrogen-bonded methanol. The relatively lower concentration of adsorbed surface species

---

(15) Lavalley, J.-C.; Benaissa, M. *J. Chem. Soc., Chem. Commun.* **1984**, 908.

(16) Knözinger, H.; Stübner, B. *J. Phys. Chem.* **1978**, *82,* 1526.

after evacuation at room temperature in our case (compared also with the spectrum shown in ref 7 where the sample was activated at 723 K) can be explained from the high initial hydroxyl coverage. This is supported by calorimetric measurements on alumina samples where water is both associatively and dissociatively chemisorbed,[17,18] demonstrating that the sites responsible for irreversibly adsorbed methanol are, at least, partially poisoned while adsorbed water may still act as an adsorption site, most probably, for a reversibly hydrogen-bonded methanol overlayer.[5] The intensity of the broad, asymmetric −OD stretching feature near 2600 cm^{-1} increases very drastically (Figure 2, spectrum b) after CD_3OD adsorption and evacuation to 3×10^{-6} Torr at room temperature. After annealing the methanol-covered alumina to 373 K in vacuo, the intensity of −OD stretching region (Figure 2, spectrum c) decreases and reverts to the initial intensity found on the prehydroxylated pellet (spectrum a). All this may indicate the removal of most of the hydrogen-bonded methanol overlayer at about 373 K and recovery of the alumina surface OH groups after this primary methanol desorption. The relatively low intensity of the CD_3 stretching modes at ~2072 and 2054 cm^{-1} compared to ref 7 (see above) indicates a relatively low methanol coverage (spectrum b). A substantial part of the enhancement in intensity of the OD stretches after methanol adsorption on prehydroxylated alumina may be due to the interaction between the surface hydroxyls and adsorbed methanol molecules rather than to interactions within the methanol overlayer. Similar results have been observed in solvents where association effects cause the intensity of the methanol hydroxyl group to be about 8 times as large when dissolved in ether as in carbon tetrachloride due to the different extent of solvent−solute hydrogen-bonding interactions.[19]

The −OH stretching region after exposure to CH_3OH (not shown) is much broader than in the case of deuteromethanol. As suggested earlier,[19] the width of these bands may be due to broadening by combination with a number of low-frequency vibrations, including the deformation frequencies, so that the width of the band generally increases with increasing hydrogen-bond strength while, with deuterium substitution, the breadth of the band is much reduced. This broad and intense −OH absorbance obscures the CH_3 stretching modes as also observed by Busca et al.[5] for an equilibrium vapor pressure of methanol of 5 Torr so that, in our study, they are not clearly seen at temperatures up to 398 K. Such an effect was also discussed in ref.[26] At 398 K, the −OH stretching feature becomes much sharper, which indicates that a significant number of surface hydrogen bonds are broken while most of the hydrogen-bonded methanol overlayer is desorbed.

The baseline-corrected integration of the methyl features between 2370 and 1952 cm^{-1} (Table 4) reveals that the amount of deuterated surface species adsorbed directly on alumina at room temperature is 34 ± 2% of the amount adsorbed on a TMA-pretreated surface at room temperature (see below) and the amount left on the surface after annealing at 373 K in the former case is only 26 ± 2% of the amount present under the same conditions on a TMA-pretreated surface (see below). After increasing the temperature to 373 K, the baseline-corrected, integrated absorbance of the CD_3 stretching modes of methanol adsorbed on alumina decreases together with the intensity of their bending features at ~1138 cm^{-1}. In addition, a significant amount of pure CD_3OD desorbs from the surface. These results indicate mainly desorption of methanol which is hydrogen bonded to the hydroxyl groups of alumina surface.

After evacuation at higher temperatures, the symmetric CD_3 stretching modes shift slightly from 2072 and 2054 cm^{-1} to 2076 and 2060 cm^{-1} (Figure 2c,d,e) corresponding to the formation of bridging methoxide and strongly chemisorbed methanol species.[5] The intensity of both modes decreases significantly with increasing temperature, and at 448 K only a small shoulder remains at ~2060 cm^{-1} (spectrum d). In addition, very small amounts of methanol are seen in the gas phase (ν(C−O) = 980 cm^{-1},[22] Table 2) with the majority of the desorbing species consisting of $(CD_3)_2O$ (ν(C−O) = 1161 cm^{-1}).[23] The intensity of the CD_3 bending mode at ~1132 cm^{-1} (not shown) also decreases together with the C−O stretching feature at 1060 cm^{-1} (not shown) appearing at the same frequency as the surface Al−O−Al mode discussed elsewhere.[15] The shoulder at ~2060 cm^{-1} (Figure 2) is almost lost at 523 K (spectrum e), indicating the removal of strongly chemisorbed methanol and a significant decrease in intensity at 2078 cm^{-1}, representing the bridging methoxide species,[5] is observed while pure ether desorbs into the gas phase. The largest concentration of surface methoxide species is found after annealing the methanol-covered surface to about 373 K. The resulting frequencies and their assignments are presented in Table 2, where a reasonably good agreement with the other studies is seen. Only the stretching modes are displayed in Figure 2, and the bending modes are not shown.

After annealing at 598 K, the symmetric and asymmetric stretching modes of surface $H-COO^-$ ($D-COO^-$) formate species are clearly evident near 1368 (1362) and 1600 (1592) cm^{-1} (Table 3) as reported by Greenler.[2] In the case of CH_3OH adsorption, the C−O stretching mode of the surface methoxide species at ~1100 cm^{-1} (Table 2) disappears on heating to 598 K. This feature is partially obscured by the alumina background mode which appears at ~1000 cm^{-1} referred to above (Figure 1).

Reaction of CD_3OD with TMA-Pretreated Alumina Surface. When the prehydroxylated pellet (Figure 3, spectrum a) is exposed to TMA (at its vapor pressure) for about 2 min at room temperature, a significant amount of methane is detected in the gas-phase together with corresponding decrease of the

---

(17) Knözinger, H.; Ratnasamy, P. *Catal. Rev. Sci. Eng.* **1978**, *17*, 31.

(18) Borello, E.; Della Gatta, G.; Fubini, B.; Morterra, C.; Venturello, G. *J. Catal.* **1974**, *35*, 1.

(19) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958.

(20) Ogawa, T. *Spectrochim* **1968**, *24A*, 15.

(21) Van Thiel, M.; Becker, E. D.; Pimentel, G. C. *J. Chem. Phys.* **1957**, *27*, 95.

(22) Noether, H. D. *J. Chem. Phys.* **1942**, *10*, 693.

(23) Lavalley, J.−C.; Caillod, J.; Travert, J. *J. Phys. Chem.* **1980**, *84*, 2083.

(24) Tench, A. J.; Giles, D.; Kibblewhite, J. F. J. *Trans. Faraday Soc.* **1967**, *67*, 854.

(25) Chen, J. G.; Basu, P.; Ballinger, T. H.; Yates, Jr., J. T. *Langmuir* **1989**, *5*, 352.

(26) El-Ahmadi, A.; Heiba, I.; Landis, P. S. *J. Catal.* **1964**, *3*, 471.

Table 2. Infrared Mode Assignments for Surface Methoxy Species Observed during This Work (First Three Columns) Compared with Other Studies and Gas-Phase Methanol[a]

mode	alumina/ TMA/MeOH (this work)	alumina/ MeOH (this work)	alumina/ TMA/MeOH hydrolyzed (this work)	alumina/ CH_3Cl[6]	alumina/ MeOH[2]	$Al(OCH_3)_3$[2]	MgO/ MeOH[2]	Fe_2O_3/ MeOH[32]	CH_3OH (CD_3OD)[22]
$\nu_{as}(CH_3)$	2954 (2224)	~2950 (2240)	(2234)	2960 (2255)	2950	2940	2920	2920 (2200)	2978 (2227)
	2934 (2180)								
combn	(2140)	(2144)	(2142)						
$\nu_s(CH_3)$	2846 (2076)	2844 (2074)	(2076)	2849 (2089)			2860	2815 (2060)	2845 (2081)
	2818 (2050)	2820 (2058)					2807		
$\delta_{as}(CH_3)$	1470	1470		1475 (1119)					1477
									~1430
$\delta_s(CH_3)$	1456 (1132)	(1132)	(1132)	1420 (1086)				1440	1455 (1121)
rock (CH_3)	1192	1192		1081 (?)					1209
									1240−60
not assigned					1190	1190			
					1100	1100			
					1030	1140			
$\nu(C-O)$	1112 (1060)	1100 (1060)	(1060)	1055 (1067)			1114		P ~ 1010 (969)
							1080		Q 1034 (987)
									R ~ 1058 (1005)

[a] All frequencies given in cm^{-1}. Numbers in parentheses belong to CD_3O- vibrations and those outside correspond to CH_3O- species. The reference number is given as a superscript.

Table 3. Infrared Mode Assignments for Formate Species Observed during This Work at 598 K (First Two Columns) in Comparison with Other Studies[a]

mode	alumina/ TMA/MeOH (this work)	alumina/ MeOH (this work)	alumina/ MeOH[2]	alumina/ $(CF_2H)_2O$[28]	alumina/ HCOOH[33]	HCOONa (s)[34]
$\nu_s(OCO)$	1380 (1360)	1368 (1362)	1377 (1347)	1382	1390	1366
$\delta(CH)$	1395	1395	1394 (1034)	1394	1407 (1029)	1377
$\nu_{as}(OCO)$	1600 (1592)	1600 (1592)	1597 (1587)	1593	1625	1567

[a] All frequencies given in cm^{-1}. Numbers in parentheses belong to $D-COO^-$ vibrations and those outside correspond to $H-COO^-$ species. The reference number is given as a superscript.

surface hydroxyls' stretching mode intensity. Figure 3Ab displays the methyl stretching region where three peaks characteristic of the asymmetric stretch (~2942 cm^{-1}), the symmetric stretch (~2894 cm^{-1}), and the Fermi resonance[8,20] are clearly seen following TMA adsorption.

The bending region of the spectrum of TMA-derived alumina surface (Figure 3B, spectrum b) shows the weak and broad CH_3 asymmetric bending mode (~1433 cm^{-1}) due to both bridging and terminal CH_3 groups[20] as well as the symmetric CH_3 bending mode near 1210 cm^{-1} which consists of two peaks split by ~5 cm^{-1} because of the interaction between the in-phase and out-of-phase symmetrical bending of the two CH_3 groups bound to the same Al atom of the newly formed $-Al(CH_3)_2$ surface species and the terminal CH_3 groups of the TMA dimer.[8] The small, broad feature at ~1264 cm^{-1} is attributed to the symmetric bending mode of the bridging CH_3 groups of the dimer present in a very small amount on the alumina surface after evacuation.[8,20] Predominantly dimethylaluminum species are present on the surface under these conditions.

Figure 3 Ab displays the OH, CH_3, OD, and CD_3 stretching regions of the infrared spectra after initial adsorption of $Al(CH_3)_3$. The very low intensity of −OH stretching features seen between 3500 and 3600 cm^{-1}, together with the intense −OD stretching band at ~2600 cm^{-1} reflect the pretreatment procedure described above.

The TMA-derived surface is then exposed to CD_3OD at room temperature. This causes a significant decrease in the CH_3 stretching intensity, as well as the appearance of new CD_3 stretching modes at ~2226, ~2079, ~2044, and ~2178 cm^{-1} (Figure 3A, spectrum c) in addition to a combination band[5] at ~2136 cm^{-1} (Table 1). Baseline-corrected integration of the CH_3 stretching region between 3050 and 2774 cm^{-1} (Table 4) reveals a decrease in the amount of the CH_3 surface species from TMA by 53 ± 2% due to methanol exposure. In addition, the amount of methane evolved as measured from the intensity of the 3016 cm^{-1} peak in the gas phase, is very close to that formed when a hydroxylated surface is initially exposed to TMA at 300 K. Our results appear to show that CH_3D evolves following the reaction of $Al(CH_3)_2$(ads) with CD_3OD since a characteristic CH_3D peak at ~1477 cm^{-1} is clearly seen when the spectrum is expanded along the absorbance scale. Note, however, that the gas-phase CH_3D spectrum is partially obscured by the excess CD_3OD in the gas mixture. Since predominantly dimethylaluminum species are present on the TMA pretreated alumina surface at room temperature[8] which contains two methyl groups, the first being more reactive than the second, an approximately 50% decrease in the intensity of TMA CH_3 modes is interpreted as a selective replacement of the first CH_3 group in $Al(CH_3)_2$(ads) by a methoxy group from the deuteromethanol.

A clearly noticeable increase in intensity of the broad −OD stretching mode following methanol treatment (Figure 3A, spectrum c) restores it to about the same intensity as that of the pellet D_2O prehydroxylated at 400 K and the whole feature is slightly shifted toward lower frequencies. This is rationalized by an increase of the O−D bond length because of extensive hydrogen

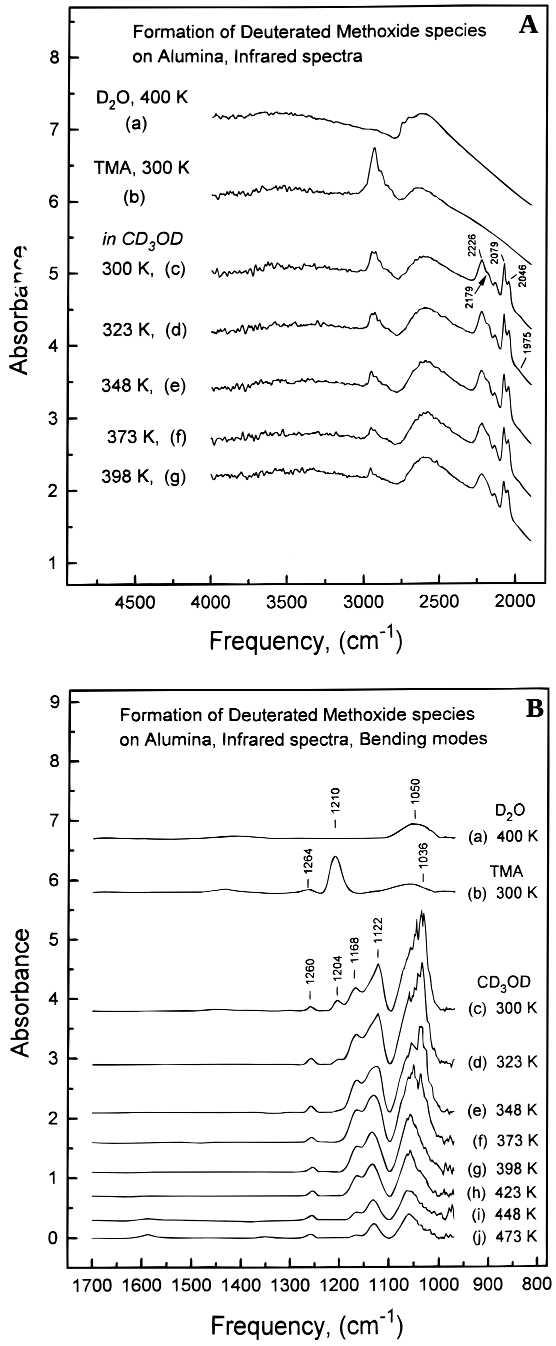


Figure 3. Formation of deuterated methoxide species on prehydroxylated alumina by sequential chemical vapor deposition of trimethylaluminum Al(CH$_3$)$_3$ and CD$_3$OD: (A) O−H, C−H, O−D, and C−D infrared stretching region, (B) bending region of the baseline-corrected infrared spectra. (a) Prehydroxylated alumina pellet, (b) Sample exposed to Al(CH$_3$)$_3$ at room temperature, (c) Exposed to CD$_3$OD vapor (120 ± 10 Torr) and evacuated to 3×10^{-6} Torr at room temperature. Spectra d−g are taken after annealing of the sample under CD$_3$OD vapor at the temperature displayed adjacent to each spectrum and consequent evacuation at the same temperature for 30 min to 3×10^{-6} Torr. Spectra h−j are recorded after annealing in vacuo at the given temperature without CD$_3$OD predosing.

Table 4. Baseline-Corrected Integrated Absorbance (Arbitrary Units) of CH$_3$ Stretching Modes from Preadsorbed TMA and CD$_3$ Stretching Modes Due to Subsequent CD$_3$OD Exposure in the Temperature Range 298−398 K

	alumina/TMA/CD$_3$OD		alumina/CD$_3$OD
temp (K)	ν(CH$_3$) 2370−1952 cm^{-1}	ν(CD$_3$) 2370−1952 cm^{-1}	ν(CD$_3$) 2370−1952 cm^{-1}
TMA/298 K	63		not exposed to TMA
CD$_3$OD 298	29	78	26
323	22	84	
348	16	84	
373	15	82	21
398	9	54	

bonding at the surface. The −OH stretching modes of methanol oligomers and polymers in other experiments[21] have been also observed at lower frequencies compared to the monomer. The first overtone 2ν(C−O) near ~1975 cm^{-1} [5,22] is also seen (Figure 3A, spectra c−e at temperatures up to about 398 K suggesting the existence of hydrogen-bonded methanol[5] with a relatively unperturbed C−O stretching mode at ~987 cm^{-1}. A peak at 981 cm^{-1} is clearly observed in the gas-phase spectrum of thermally desorbed CD$_3$OD with its overtone at ~1974 cm^{-1}, but due to the intense alumina lattice modes below ~1000 cm^{-1}, the fundamental of these relatively unperturbed adsorbed methanol molecules could not be distinguished.[5] All of these observations imply that some molecularly adsorbed methanol is present under these conditions as observed in the case of direct exposure to alumina (see above) as well as surface methoxy species reactively formed by methane elimination. The fact that the intensity of the −OD stretching features increases much less after reaction of the TMA-derived surface with CD$_3$OD at room temperature than in the case of direct alumina/methanol exposure suggests fewer hydrogen-bonding interactions. The −OD stretching modes on the TMA pretreated surface after reaction with CD$_3$OD are much less intense than the CD$_3$ stretching modes than on the alumina directly dosed with methanol where the converse relation is seen. This, again, confirms that most of the surface methoxide species on the TMA pretreated alumina are formed by eliminating methane from the dimethylaluminum surface species rather than by methanol dissociation on Lewis acid−base pairs of sites as happens in the case of direct adsorption.[3,6]

As the temperature is increased in 25 K steps (Figure 3A,B, spectra c−g), the CH$_3$ stretching modes from TMA gradually decrease in intensity (as displayed in Table 4) until they are essentially absent after annealing to about 398 K. It is important to note that almost 30% of the CH$_3$ groups initially present following CD$_3$OD exposure at room temperature remain after heating to 400 K. This may be due not only to the lower reactivity of the second CH$_3$ group[8] but also to the different activity among the alumina adsorption sites as well as to a secondary coordination effect that will be discussed below. The intensity of the broad −OD stretching feature slightly increases at 323 K (Figure 3Ad) most probably because of some additional dissociative methanol adsorption and/or strong molecular chemisorption at Lewis acid sites. The intensity then remains nearly constant up to 373 K (Figure 3Ae−f) with a little sharpening, indicating cleavage of some hydrogen bonds. The baseline-corrected area of the CD$_3$ stretching modes from the deuteromethanol also increases a little at 323 K but then does not change significantly up to about 373 K (see Table 4). The intensity of the CD$_3$ stretching mode at $\sim$2046 cm^{-1} increases relative to that at $\sim$2079 cm^{-1}, and the two peaks become more similar in their intensity like the pair at $\sim$2179 and $\sim$2226 cm^{-1} (Figure 3Ac−g). Considering the assignments of methanol adsorbed on alumina discussed above[5] along with the methane evolution noted in the gas-phase spectra when the alumina/TMA/CD_3OD surface is heated under methanol, it is proposed that the first CH_3 group from the surface dimethylaluminum species reacts with methanol at room temperature forming predominantly bridging methoxide species characterized by the pair of modes near $\sim$2222 and $\sim$2076 cm^{-1}, while the second CH_3 group may react further with molecularly adsorbed methanol, mainly at the higher temperatures, to produce additional methane and nonbridging methoxide species which are characterized by the doublet at $\sim$2180 and $\sim$2050 cm^{-1} (Figure 3A; Table 2). Note that these features almost coincide with the absorption bands of the strongly chemisorbed methanol assigned in ref 5. The lower frequency of the CD_3 stretching mode at 2050 cm^{-1} compared to that at 2058 cm^{-1}, denoting strongly chemisorbed methanol in the case of direct adsorption (Table 2), can also be indicative of a somewhat larger extent of dissociative methoxide formation[23] than when a prehydroxylated surface is exposed to methanol. The proposed nonbridging methoxide species cannot be clearly distinguished from the strongly chemisorbed molecular methanol in our work because they are both "monocoordinated". They may therefore be both present at the same time since the aluminum atom from the dimethylaluminum surface species can itself provide a Lewis acid site and coordinate, not only molecular methanol, but also be a second coordination center for the bridging methoxide species. This would, to some extent, prevent the second methyl group from further reaction with adsorbed methanol by "blocking" the coordination site necessary for methane elimination. This is in good agreement with the stability of the CH_3 groups form TMA remaining after the reaction with methanol at room temperature during this experiment. Coordination of methanol molecule to these "second layer" Lewis acid sites is expected to facilitate methane elimination. This process may account for the additional methane evolved when the TMA pretreated surface is further heated under methanol. Note that this is less than that formed after the initial reaction at room temperature. Such second-layer adsorption may also account for the increase of the intensity of the bands at $\sim$2180 and $\sim$2050 cm^{-1}, representing the resulting nonbridging methoxide species (Table 2, column 1).

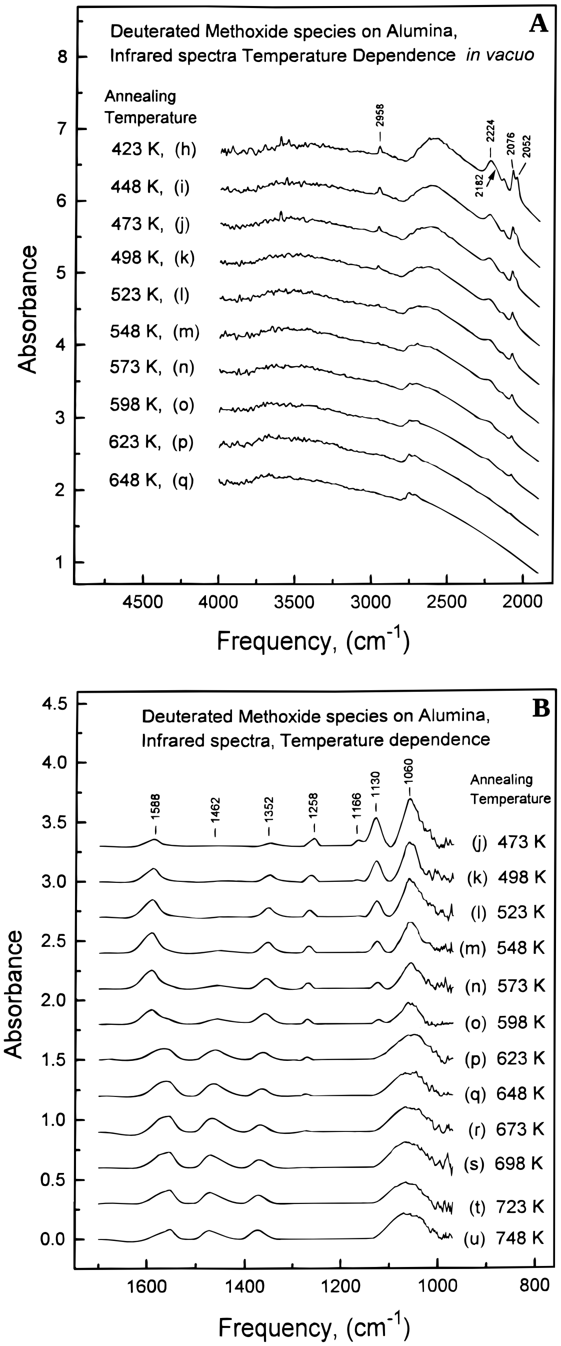


Figure 4. Temperature dependence of the deuterated methoxide species on alumina: (A) O−H, C−H, O−D, and C−D stretching region, (B) bending region of the baseline-corrected IR spectra. All spectra are taken after annealing the sample in vacuo at the temperature displayed adjacent to each spectrum.

Above 373 K (Figure 3A), both the −OD and CD_3 stretching modes begin to decrease in intensity uniformly and this becomes more noticeable at temperatures of 398 K and higher (Figures 3A and 4Ah). At 423 K, deuterated ether ($(CD_3)_2O$) and some methanol are detected in the gas phase, but *no* further methane evolution is observed (up to 498 K when methoxide decomposition begins) even though a small C−H stretching mode is still seen at $\sim$2958 cm^{-1} (Figure 4 A). At higher temperatures, all of these bands continue to decrease in intensity (Figure 4 A) and no further methanol is detected in the gas phase while significant amounts of ether desorbed. The largest concentration of surface methoxide species is observed after heating the surface at 398 K in methanol vapor (Figure 3Ag) since, at higher temperature, these species react evolving dimethyl ether. The major peak assignments for these methoxide species are presented in Table 2.

The bending region of the spectra obtained following the experimental treatment described above is shown on Figure 3B up to 473 K and on Figure 4B up to 748 K. After room-temperature adsorption of CD_3OD, a C−D bending mode appears at $\sim$1122 cm^{-1} (Figure 3Bc), a value very close to its gas-phase frequency (see Tables 1 and 2). A large increase in the infrared absorption intensity in the region near 1050 cm^{-1} is also observed, overlapping the broad Al−O−Al band due to the alumina background (Figure 1B) and giving rise to a new maximum at ~1036 cm^{-1}. This is most likely due to the adsorption of hydrogen-bonded, molecular methanol with a relatively less perturbed ν(C−O) mode compared to the ν(C−O) of the surface methoxide species. This argument is supported by the fact that this ~1036 cm^{-1} feature disappears at 398 K (Figure 3Bg when the hydrogen-bonded methanol overlayer is essentially removed and the methoxide C−O stretching mode becomes evident at ~1060 cm^{-1} (Table 2). Similar behavior of the corresponding mode has been observed on a MgO surface upon removal of the methanol overlayer.[24] The methoxide ν(C−O) mode (~1060 cm^{-1}) persists at higher temperatures up to about 598 K (Figure 4Bo) but overlaps with the surface Al−O−Al mode growing in this region until the methoxide species are essentially completely removed. In the case of CH_3OH adsorption on a TMA-predosed surface, the methoxide C−O stretching mode is also perturbed to some extent by the weakly adsorbed methanol as observed by Travert et al.[4] This mode appears as a broad band centered at ~1108 cm^{-1} at room temperature (Table 1; Figure 5c), becomes much narrower upon annealing at higher temperatures (Figure 5, spectra f, g), and shifts to ~1112 cm^{-1} at 398 K (Table 2) due to the removal of the hydrogen-bonded methanol. Then it shifts to slightly lower frequencies overlapping the growing Al−O−Al surface mode upon decomposition of the surface methoxide species (Figure 5, spectra m−q).

The small peak near 1204 cm^{-1} (Figure 3Bc) can be readily assigned to some unreacted CH_3 groups from the dimethylaluminum surface species since it disappears at about 348 K (Figure 3Be).[8] This mode is obscured by the CH_3 rocking mode at ~1192 cm^{-1} after CH_3OH adsorption (Figure 5, spectrum c).

The intensity of the C−D bending mode at ~1122 cm^{-1} does not change significantly up to 348 K (Figure 3B, spectra c−e), decreases slightly in intensity at 373 K and continues to decrease further at temperatures higher than 398 K (spectra g−j). The frequency also shifts, with some change in shape, to ~1132 cm^{-1}. This frequency appears to characterize a methoxide species after desorption of the hydrogen-bonded molecular methanol (see above). The small feature seen at ~1168 cm^{-1} is detected at lower temperatures up to about 498 K (Figure 3B and 4B) but disappears after hydrolysis at room temperature (Figure 6 Be, see below). This implies that it may be attributed to the deuterated dimethyl ether produced after methanol exposure and weakly adsorbed on the surface since this frequency is very close to the ν(C−O) (1161 cm^{-1}) observed in the gas-phase $(CD_3)_2O$.[25] It is also seen with lower intensity in the spectra taken after direct exposure of prehydroxylated alumina to CD_3OD (not shown). Note that hydrogenated ether ($(CH_3)_2O$) desorbs from a TMA/CH_3OH-treated sample.

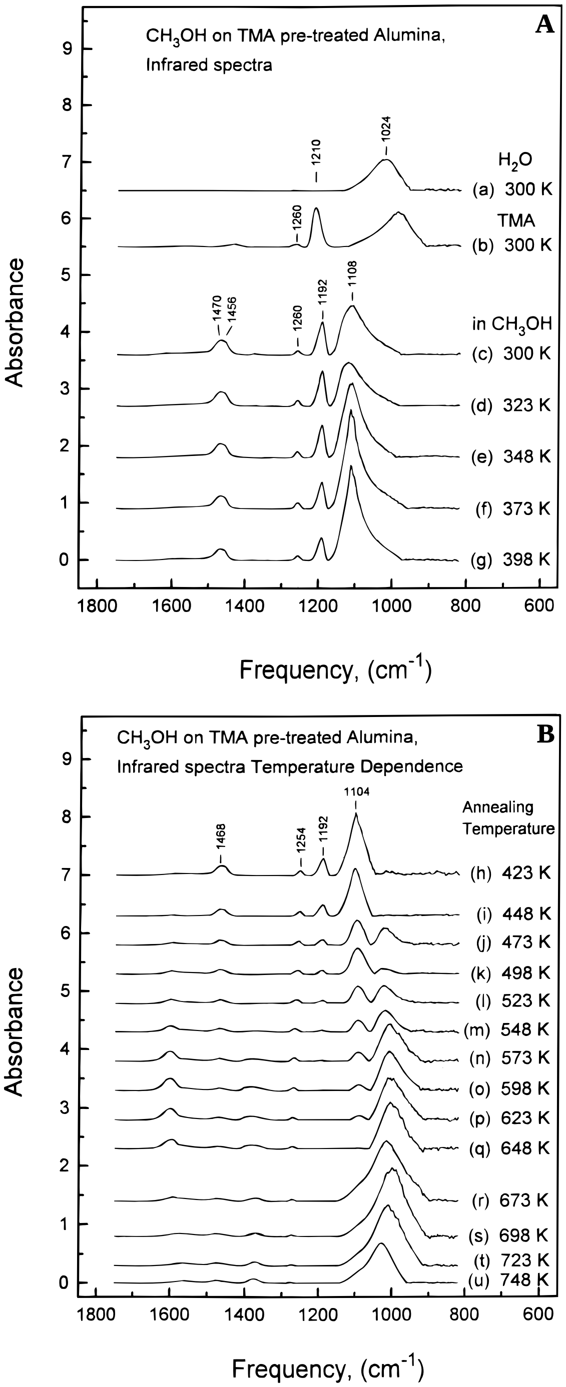


Figure 5. Bending region of baseline-corrected infrared spectra showing the formation and temperature dependence of surface methoxide species resulting from sequential chemical vapor deposition of $Al(CH_3)_3$ and CH_3OH on alumina: (a) clean prehydroxylated alumina, (b) sample exposed to $Al(CH_3)_3$ and evacuated to 3×10^{-6} Torr at 300 K. Spectra c−g are taken after dosing with CH_3OH and annealing in methanol vapor at the temperature shown adjacent to each spectrum and consequent evacuation at the same temperature. Spectra from h−u are recorded after annealing of the sample in vacuo at the temperature shown adjacent to each spectrum.

All modes characteristic of surface methoxide species (Table 2) gradually decrease in intensity upon further annealing at higher temperatures in vacuo and disappear with concomitant ether desorption in the gas phase up to 573 K. This chemistry is also reported for the decomposition of aluminum methoxide.[26] At this temperature, the modes of surface D−COO$^-$ formate species, which start growing at about 473 K (Figure 4Bj) are evident with features at ~1360 and ~1592 cm^{-1} (Table 3, Figure 4B, spectra j−n). Their intensities are much larger than for experiments where the hydroxylated alumina surface is directly treated with

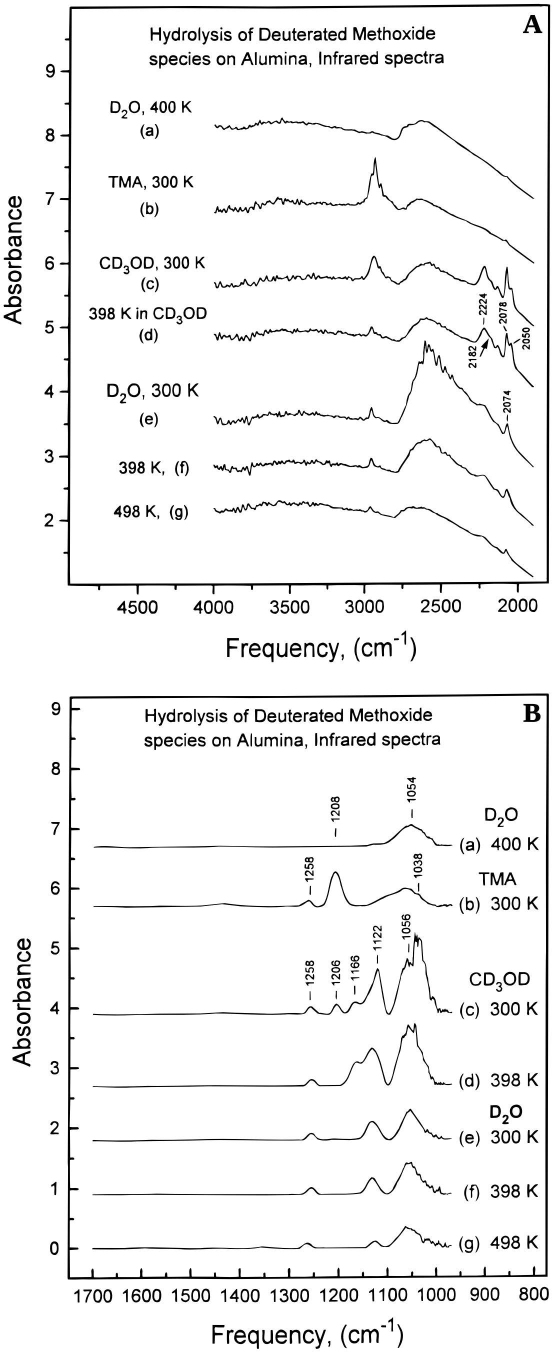


Figure 6. Hydrolysis of deuterated methoxide surface species on alumina with D_2O: (A) O−H, C−H, O−D, and C−D stretching modes, (B) baseline-corrected spectra of the bending infrared region. (a) Prehydroxylated alumina, (b) sample exposed to $Al(CH_3)_3$ at room temperature and evacuated to 3 × 10^{-6} Torr, (c) exposed to CD_3OD and evacuated to 3 × 10^{-6} Torr at 300 K, (d) after annealing at 398 K in CD_3OD vapor and evacuation at the same temperature, and (e) sample exposed to D_2O and evacuated at room temperature. Spectra f and g are taken after annealing at the temperature displayed adjacent to each spectrum in vacuo.

methanol, but a similar temperature-dependent behavior is noted. At higher temperatures, these species also decompose while CO and methane are clearly observed in the gas phase. Note that the methane evolved above ~600 K is at least 2 orders of magnitude lower than that formed by reaction of TMA-covered surface with methanol. These are also found to be the gaseous decomposition products of aluminum methoxide.[26] At temperatures higher than 598 K, a new broad peak grows at ~1462 cm^{-1} (Figure 4B, spectrum o), becoming much more pronounced than in the case of direct methanol adsorption. In addition, the ν_{as}(OCO) mode shifts from ~1592 to ~1560 cm^{-1} (623 K, Figure 4B, spectra o and p) and then to lower frequencies as the temperature increases (spectra q−u). Considering the decreasing splitting between the modes at ~1560 and ~1462 cm^{-1},[27−30] this may be due to a transition to some formate species, with bidentate coordination, to longer chain carboxylate species or to more complicated coke deposits.[31] The surface formate species derived from CH_3OH show similar temperature-dependent behavior (Figure 5, spectra i−r and Table 3).

All of the species seen in the case of direct exposure of the prehydroxylated surface to methanol discussed earlier are observed after TMA pretreatment of alumina. In addition, when alumina is predosed with TMA, the methane observed in the gas phase upon exposure to CD_3OD, the much higher concentration of newly formed deuterated species on the alumina surface, along with the decrease of the CH_3 stretching intensity, confirm that a surface chemical reaction is taking place between TMA-derived surface species and methanol. The very similar temperature dependence of the infrared modes due to the deuterated surface species formed by this reaction, as well as the very similar distribution of their gas-phase products generally corresponds to the assignments given for the species derived by direct exposure to methanol (Table 1 and Table 2).

Hydrolysis of the Surface Species Derived by CD_3OD Adsorption on Prehydroxylated and TMA-Pretreated Alumina Surface. The stability of the methoxide surface species obtained by exposure of prehydroxylated alumina surface to TMA and methanol in a gas-phase aqueous environment is investigated. From the temperature-dependent study discussed above, it is evident that the highest coverage of surface methoxide species is obtained by heating a TMA-precovered sample at 398 K under methanol vapor. After evacuation and cooling to room temperature, a surface prepared in this way is exposed to saturated D_2O vapor (~20 Torr) and the remaining surface species, as well as the gas-phase composition, are characterized by IR spectroscopy.

The infrared data collected during this experiment are shown in Figure 6 displaying the stretching and bending regions of the spectra, respectively. The first three spectra (Figures 6A,B (a−c)) illustrate the sample preparation protocol described above and exactly reproduce those from the temperature dependent study

---

[27] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986.

[28] Basu, P.; Ballinger, T. H.; Yates, Jr., J. T. *Langmuir* **1989**, *5*, 502.

[29] Crowell, J. E.; Chen, J. G.; Yates, Jr., J. T. *J. Chem. Phys.* **1986**, *85*, 3111.

[30] Fu, Y.; Kraus, L.; Knözinger, H. *J. Mol. Catal.* **1989**, *52*, 113.

[31] Datka, J.; Sarbak Z.; Eischens, R. P. *J. Catal.* **1994**, *145*, 544.

[32] Busca, G.; Lorenzelli, V. *J. Catal.* **1980**, *66*, 155.

[33] Noto, Y.; Fukuda, K.; Onishi T.; Tamaru, K. *Trans. Faraday Soc.* **1967**, *63*, 2300.

[34] Ito, K.; Bernstein, H. J. *Can. J. Chem.* **1956**, *34*, 170.

(Figure 3A,B). After exposing to CD_3OD at room temperature and evacuating to 3×10^{-6} Torr, the CH_3 stretching modes from TMA have decreased in intensity by about one-half while their bending modes are still seen at ~1206 cm^{-1}. To further react the remaining methyl aluminum surface species the sample is exposed for 2 min at room temperature to CD_3OD vapor (120 ± 10 Torr), then annealed directly at 398 K in the closed infrared cell for 1 h, evacuated at the same temperature, and allowed to cool to room temperature after which the IR spectrum of the surface is recorded (Figure 6A,B (d). The major peak assignments are again given in Table 2. The frequencies of the resulting peaks are very close to those seen at the same temperature during the temperature dependent study (Figure 3 (A) and (B)), showing that most of the CH_3 species from TMA are removed and new deuterated methoxide species are formed as discussed above.

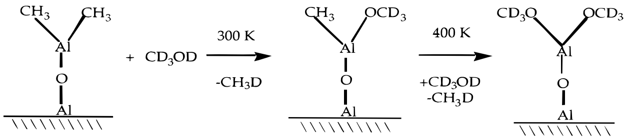
At this point, the pellet is exposed to D_2O at its vapor pressure (~20 Torr) for 2 min and the gas-phase spectra are taken while the infrared cell is kept closed. After about 10 min, the cell is evacuated and spectrum e shown in Figure 6 is recorded at room temperature. The huge increase in the intensity of −OD stretching region and the small, broad feature at ~1203 cm^{-1} due to the O−D scissoring mode of D_2O show that not only are a large amount of surface −OD groups formed by this treatment, but also some molecular D_2O is adsorbed on the surface. The surface CD_3 stretching (Figure 6Ae) and bending modes (Figure 6Be) from the alcohol have decreased to a very low intensity, indicating a very significant removal of the methanol-derived surface species. The peak at ~1166 cm^{-1} is lost as well, indicating that any weakly adsorbed ether is displaced from the surface by D_2O and no more is formed during the room-temperature hydrolysis. Some traces of ether appear again at higher temperatures (Figure 6B, spectrum f). Mainly methanol, a very small amount of D_2O and a little methane are seen in the gas phase after the D_2O exposure at room temperature. The extra adsorbed molecular water and probably some methanol are removed from the alumina surface by annealing at 398 K in vacuo (Figure 6A, spectrum f). After this step, the −OD stretching absorption indeed becomes narrower and sharper but still remains with a significantly higher intensity than the corresponding region of the spectrum taken after the initial annealing at 398 K (Figure 6A, spectrum d) immediately before the D_2O treatment. The results from a baseline-corrected integration of the OD stretching region before and after methoxide hydrolysis (Figure 6Adf) show an increase in intensity by 63 ± 2%. The large amount of methanol with no ether which evolves into the gas phase suggests a hydrolysis reaction rather than ether formation. The baseline-corrected integrated intensity of the features in the region between 2332 and 1960 cm^{-1} of the spectra taken after annealing at 398 K before and after exposing to D_2O (Figure 6Ade) indicates that about 60 ± 2% of the CD_3 stretching intensity is lost as a result of surface methoxide hydrolysis. Most of the surface methoxy species appear to react with D_2O even at room temperature, and those left may occupy stronger (or less accessible) sites, and only a small amount of them react further with the adsorbed water upon heating to 398 K (Figure 6, spectra e and f). Similar argument can be applied to the traces of CH_3 species from TMA on the alumina surface at 398 K and higher temperatures during the temperature dependence study (Figures 3A and 4A) and even after exposing to water (Figure 6A) and annealing to 498 K. The nearly 60% increase in the OD stretching intensity agrees well with the similar decrease in the CD stretching intensity implying a direct and selective substitution of methoxy by a hydroxyl group. This emphasizes the different reactivity of the two methoxy groups.

The CD_3 stretching modes at ~2050 and ~2182 cm^{-1} (Figure 6A, spectra d and e) seem to disappear, and those at ~2074 and ~2224 cm^{-1} significantly decrease in intensity which, in the light of the assignments and discussion above, may mean that the proposed nonbridging methoxide species preferentially react with water at room temperature while some of the bridging methoxide species, which are coordinated to two Lewis acid sites and represented by the higher ν (C−D) frequencies, are much less reactive. This is not surprising since the hydrolysis reaction requires initial coordination of water to the oxygen atom of the surface methoxide. When this is a bridging methoxide bound to two neighboring Lewis acid sites, this oxygen is already electron depleted and will not easily coordinate water molecules. The methanol molecules resulting from bridging methoxide species will be still strongly chemisorbed to the other Lewis acid site and their further desorption would be inhibited. Such species may be responsible for the weak shoulder observed near 2050 cm^{-1} (Figure 6A, spectrum f) after annealing to 398 K since, after room-temperature hydrolysis, no peak or shoulder is seen at this frequency and nonbridging methoxide species are not likely to remain under these conditions.

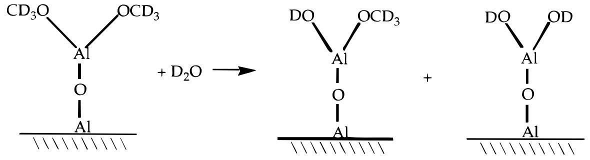
At higher temperatures (498 K, spectrum g), the −OD surface species continue to decrease in intensity significantly and the remaining methoxide species from the deuteromethanol almost disappear.

Conclusions

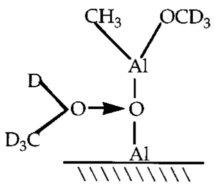
Alumina pellets that have been pretreated with water and evacuated at 400 K have been sequentially exposed to trimethylaluminum and methanol and the temperature dependence of the resulting surface species has been studied by Fourier transform infrared spectroscopy. To observe the CH_3− stretching modes of TMA separately from those of the methanol, deuterated methanol (CD_3OD) has been used, combined with a D_2O-pretreated surface. Reference experiments are carried out by exposing the prehydroxylated alumina surface to methanol directly, and very similar infrared modes are observed in both cases, except that the coverage of surface species is greatly enhanced if the alumina surface has been pretreated with TMA. Isotope experiments show that ~50% of the methyl groups from TMA react with methanol at room temperature, and the remainder are removed only upon annealing at up to 398 K under methanol. The amount of methane eliminated upon exposure to methanol at room temperature is very close to that evolved when the prehydroxylated alumina surface is exposed to TMA. The intensity of the surface CD_3−stretching modes from the alcohol does not change significantly during this annealing process, which confirms that methyl groups from TMA are further replaced by molecularly adsorbed methanol on the surface and not by methanol from the gas phase. Methane evolution is observed in the gas phase, and the modes of the resulting surface species correspond to the methoxide species found in other studies. CD_3H is detected in both steps. Note that it is somewhat difficult to detect since most of its peaks are obscured by the strong methanol features.



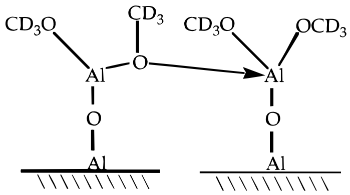
A significant amount of methanol desorbs from both the alumina/methanol- and alumina/TMA/methanol-derived surfaces upon annealing up to 423 K in the preevacuated infrared cell due to removal of molecular methanol overlayer. These surface methoxide species readily hydrolyze to methanol at room temperature upon exposure to water, thus reducing the intensity of the CD_3 stretching features and correspondingly increasing the intensity of the surface OD modes by about 60%. This may imply a direct and selective substitution of hydroxyl for methoxide group:



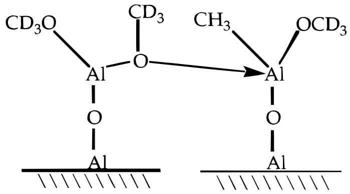
On this basis, it can be proposed that the more reactive of the two methyl groups from the dimethylaluminum species on the TMA-derived alumina surface reacts preferentially with the hydroxyl groups of the methanol at room temperature to form, most probably, aluminum *methyl*methoxide surface coordination intermediate with another adsorbed methanol molecule via Al←:O donor−acceptor interaction:



A larger part of this intermediate decomposes upon further annealing to 398 K evolving methane from the second methyl group and the hydroxyl group of the coordinated alcohol molecule giving aluminum *di*-methoxide surface species with bridging and nonbridging methoxy groups:



This would explain the constant intensity of the surface CD_3− stretching modes from the methanol up to about 373 K when some excess of molecular methanol is present on the surface, as well as the secondary methane evolution. Some of the bridging methoxide species may coordinate to the aluminum atom of the methylmethoxide species which would protect the remaining CH_3 group from further displacement reaction:



This may explain the incomplete removal of the CH_3 groups originating from TMA as well as the relatively lower amount of methane evolved upon annealing from room temperature to 398 K under methanol. The concurrent thermal decomposition of the aluminum methoxide species producing dimethyl ether (CD_3OCD_3) at higher temperatures and up to 573 K can account for the further diminution in CD_3− stretching intensity. $(CH_3)_2O$ is evolved under these conditions from a CH_3OH-derived surface methoxide species. The small amount of methoxide species left on the alumina surface at temperature higher than 573 K is gradually converted to surface formate species as reported by Greenler[2] for methanol directly adsorbed on alumina.

This study shows that the reaction of methanol with TMA-derived alumina does modify the surface but is not very promising for growing dense self-assembled monolayers on alumina because of the following:

(1) Incomplete displacement of the CH_3 groups from the methylmethoxide species at lower temperatures up to 398 K.

(2) Significant reactivity of the resulting methoxide species toward ether formation at temperatures higher than 373 K.

(3) Very high extent of hydrolysis of the surface methoxide species at room temperature producing methanol and surface hydroxyl groups.

The last problem might be partially solved if a dense, well-ordered monolayer of long hydrophobic hydrocarbon chains could be deposited, but once cracked it would spontaneously hydrolyze in any humid environment. Further research of the reaction of thiols with dimethylzinc-derived alumina surface is being undertaken to address these problems.

Acknowledgment. We thank the Laboratory for Surface Studies for partial support of this work.

CM970496S