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Spectroscopic Investigation of a Polymerization Catalyst: Tetra(neophyl)zirconium Reacted with Alumina

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Tetra(neophyl)zirconium (TNZ) reacted with alumina, one of a family of high activity, innocuous, and thermally stable polymerization catalysts, was studied using transmission infrared and uv-visible diffuse reflectance spectroscopy (DRS) with the goal of understanding the synthesis of the catalyst and its evolution at the high temperatures of use. (Neophyl is the 2-methyl-2-phenylpropyl group.) Reaction of TNZ with the free hydroxyls present at the surface of alumina to bind the zirconium was observed. Hydrogen bonded hydroxyls were unreactive during synthesis but can serve as catalyst poison at elevated temperatures. High neophyl contents of catalysts prepared with thermally dehydroxylated aluminas imply other modes of TNZ binding are possible on these aluminas. No organic species other than intact neophyl ligands were observed on the untreated catalyst. Heat treatment of the catalyst in vacuum caused loss of neophyl ligands and reduction of the Zr oxidation state. An absorption at 360 nm is seen in the DRS of reduced catalysts. Heat treatment in hydrogen caused hydrogenation of the phenyl group of the ligand, loss of ligands, but no appearance of DRS features characteristic of catalyst reduction. An infrared absorption at 1900 cm^{-1} is produced on hydrogenation of the catalyst and is assigned to a Zr hydride species on the basis of its frequency and response to exposure to air, water, and ethylene. Catalysts containing reduced Zr or Zr hydride sites were active in the polymerization of ethylene. The high temperature activity is suggested to result from the preserved activity of the decomposition products of the original catalyst.

INTRODUCTION

Mineral supported organometallic compounds can be highly active catalysts for olefin polymerization. These catalysts are the basis of new processes that are much more energy efficient than processes based on traditional Ziegler–Natta catalysts.

Activity at high temperatures is characteristic of these catalysts. Silica supported tetra(allyl)zirconium and alumina supported tetra(benzyl)titanium are reported to be active at 470 K (*1*), while tetra(neophyl)zirconium reacted with alumina can be used to produce polyethylene at temperatures as high as 570 K (*2, 3*). Higher production rates and greater recovery of the heat of polymerization result from high temperature operation. In addition, these catalysts are innocuous and noncorrosive when left in the polymer so that catalyst removal and solvent purification steps can be eliminated from the processes.

To best implement these catalysts, it is important that their physical and chemical properties be understood. Complete understanding is not easily achieved because of the large number of potential variables in their synthesis and use. In the area of supported organozirconium catalysts, considerable programs of study have been reported by groups at Imperial Chemical Industries (*4–6*) and at Novosibirsk (*7–14*). These groups looked into allyl and benzyl derivatives reacted with aluminas and silicas using many chemical and physical techniques.

In this paper, we report a study of tetra(neophyl)zirconium (TNZ) reacted with alumina (neophyl = $C_6H_5(CH_3)_2CCH_2$–). This catalyst has proven to be very useful in olefin polymerizations, and it is thought

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that the steric bulk of the neophyl ligands imposes unique properties on this system (*2*). Comparison of the properties of the neophyl zirconium catalyst to those of the previously reported catalysts will clarify the nature of the catalyst.

This catalyst and others exhibit increased activity after hydrogenation, presumably associated with the generation of zirconium hydride species (*1, 2*). Polymerizations are often run with hydrogen present to control molecular weight. Further, at the high temperatures of use, many transformations of the structure of the zirconium center are possible. Characterization of the catalyst, its hydrogenation product, and the transformations induced by thermal treatment are needed to aid understanding of the catalyst. We have used transmission infrared and uv-visible diffuse reflectance spectroscopy to study the effect of alumina drying temperature and Zr loading on the nature of the catalyst, and the changes produced by heat and exposure to hydrogen and ethylene in imitation of the polymerization reactor environment.

Infrared spectroscopy has been demonstrated to be a useful way of examining the surfaces of supported organometallic catalysts. The reaction of surface hydroxyls and the binding of allylic groups were shown in a study of tetra(allyl)zirconium on silica by Candlin and Thomas (*4*). They also saw the formation of polyethylene as ethylene was admitted to the ir cell. Yermakov *et al.* examined tetra(allyl)zirconium and tetra(benzyl)titanium both reacted with silica (*9, 15*). They studied the changes in the spectra of these catalysts with treatment in vacuum or hydrogen at elevated temperatures. New spectral features developed when the catalysts were hydrogenated which they assigned to surface metal hydrides.

Absorption spectra in the uv-visible region of supported organozirconium catalysts have not been investigated. Zr(IV) ions, with no *d* electrons, would not be expected to have any transitions in this region. Zr ions in reduced oxidation states, which have been detected using ESR (*1, 10, 12*), should have detectable transitions between *d* levels. Observation of such transitions is good evidence for reduction of the catalyst.

It was found that synthesis of TNZ/alumina catalyst took place in the manner found for the allyl and benzyl systems, that is, through protolysis of the organic ligand and binding of the Zr by reaction of the catalyst precursor with surface hydroxyl groups. There were no changes in peak positions or relative intensities of absorbances characteristic of the organic ligand as the TNZ to alumina ratio was varied, indicating that the same types of sites were made over a range of synthesis conditions. Diffusional control of the synthesis process can lead to this result (*16*).

It was also found that at least three spectroscopically characterizable types of Zr sites that interact with olefins could be generated under simulated process conditions. In addition to the supported Zr alkyl, Zr hydride and Zr centers in a reduced oxidation state were tentatively identified. This multiplicity of polymerization sites may be a reason for the activity of this catalyst even at high temperatures as the reduced and hydrido Zr species produced by decomposition of Zr alkyls retain activity (*1*).

METHODS

The neophyl zirconium aluminate polymerization catalyst (abbreviated NZA) was prepared by the reaction of tetra(neophyl)zirconium (abbreviated TNZ) in hexane with Degussa C fumed alumina. Measured physical properties of the alumina are 80–100 m^2/g surface area, 0.5 ml/g pore volume by nitrogen adsorption, and 160–270 Å average pore diameter. TNZ was prepared by the reaction of neophyl magnesium chloride with $ZrCl_4$ (*2*). Unless noted otherwise, the alumina was dried at 670 K under flowing nitrogen, and the reaction was allowed to proceed for 2 hr at room temperature with occasional stirring. Powder and wafer samples were rinsed three to five times with hexane after reaction to remove excess TNZ and adsorbed *t*-butylbenzene (the protolysis product of TNZ), and then dried by evacuation.

For infrared measurements, the alumina was first pressed into wafers, dried, and then reacted with TNZ. The wafers were 14 mm in diameter and were pressed in a steel mold at 10^4 kPa. Because this catalyst is nonregenerable and easily poisoned, many wafer samples were prepared and examined. The average weight of 15 undried alumina wafers was 51 mg with a 6 mg standard deviation. The precision of the spectral measurements is largely determined by the reproducibility of sample weights and treatments.

The infrared cell was made of Pyrex with CaF_2 windows attached by O-ring seals. The sample was held between glass rings in the central portion of the cell, which was wrapped with a resistance heater. Temperatures were measured with a Chromel–Alumel thermocouple inserted into a dimple in the cell body near the sample. A rough measure of polymerization activity of the infrared samples was the decrease in ethylene pressure from 90 kPa in 5 min. The volume of the cell, manometer, and vacuum line in these activity measurements was 150 cm^3.

Ultraviolet-visible diffuse reflectance measurements were made on powder samples in a simple cell consisting of a 25-mm-diameter quartz window sealed to a thin vessel with a Teflon fluorocarbon stopcock. This cell was heated by immersion in an oil bath.

Infrared measurements were made either with a Nicolet 7199 Fourier transform spectrometer or a Perkin–Elmer 599 grating instrument. Ultraviolet-visible diffuse reflectance was measured with a Cary 14 spectrophotometer equipped with an integrating sphere.

The organic products of thermolysis of the catalyst were measured by inserting sealed capillaries of the catalysts into the injection port of a GC/MS (held at 520 K) and then breaking the capillaries.

A mercury diffusion pumped glass vacuum line with greased stopcocks was used. Hydrogen and ethylene were purified of oxygen over a Cu catalyst and dried over molecular sieves before use. Because of the hygroscopic nature of dried alumina and the extreme air sensitivity of both TNZ and the supported catalyst, all synthesis and manipulations were done in a Vacuum Atmosphere Dri-Lab glovebox under a nitrogen atmosphere continuously purified of oxygen and water.

RESULTS AND DISCUSSION

Untreated Catalyst

Figure 1a shows the mid-infrared spectrum of the untreated catalyst. Bulk vibrations of the alumina support cause the low frequency cut-off at 1100 cm^{-1}. The catalyst spectrum shows alumina hydroxyl bands and absorptions characteristic of the organic groups bound to the catalyst. Table 1 lists the frequencies of the observed infrared absorptions of the catalyst and assignments of the bands based on group frequency compilations (*17*). Also given in the table are the frequencies of infrared absorptions of two reference compounds, neophyl chloride and *t*-butylbenzene, and of *t*-butylbenzene adsorbed on alumina.

The assignments are useful in distinguishing between catalyst-bound neophyl groups and adsorbed *t*-butylbenzene either leftover from catalyst synthesis or generated by unintentional hydrolysis of the catalyst. As the structure of *t*-butylbenzene is very similar to that of the neophyl group, their infrared spectra are quite similar. There are clear differences in the 2800–3000 and 1400–1600 cm^{-1} regions, and the band assignments show that the differences are in modes associated with the methyl groups of *t*-butylbenzene and the methylene portion of the neophyl group. Comparison of the catalyst spectrum to the reference compound spectra shows that the neophyl

TABLE 1

Infrared Absorption Maxima of Tetra(neophyl)zirconium Reacted with Alumina Polymerization Catalyst and Model Compounds (cm^{-1})[a]

Catalyst		Neophyl Cl (liquid)		*t*-Butyl benzene adsorbed on alumina		*t*-Butyl benzene (liquid)		Assignments
3160	w							
3106	sh	3111	w	3110	sh	3108	w	
3087	m	3090	m	3088	m	3088	m	
3063	m	3061	m	3061	m	3061	m	Aromatic C–H str
3034	m	3035	m	3035	m	3035	m	Aromatic C–H str
3024	m	3026	m	3024	m	3023	m	
2962	s	2973	s	2968	s	2962	s	CH_3 asym str
2928	s	2938	sh	2930	sh			CH_2 in phase str
2910	sh	2915	sh	2910	m	2903	s	
2868	s	2887	m	2873	s	2868	s	CH_3 sym str
		2876	m					CH_2 out of phase str
2805	sh	2817	w			2800	w	
						2777	w	
2750	sh					2749	w	
2730	sh	2735	w			2715	w	
1943	w			1955	w	1940	w	MONO substituted aromatic ring C–H overtone and combination bands
1882	w	1873	w	1885	w	1885	w	
						1868		
1800	w	1802	w	1820	w	1798	w	
1743	w	1748	w			1743	w	
1670	w	1676	w			1670	w	
1600	m	1602	m	1600	m	1600	m	Aromatic skeletal
1580	m	1583	w	1582	w	1583	w	Aromatic skeletal
		1540	w			1535	w	
1496	s	1498	s	1498	s	1497	s	Aromatic skeletal
1470	m	1473	s	1471	m	1469	m	CH_2 def.
		1466	s	1464	sh	1461	m	
1444	s	1448	s	1448	s	1447	s	CH_3 asym. def. and aromatic skeletal
				1444	s			
		1435	sh					
1388	sh	1385	s	1397	m	1393	m	$C(CH_3)_2$ def.
1378	sh							
1364	m	1368	s	1368	s	1366	s	$C(CH_3)_2$ def.
		1334				1309	w	
		1290	s			1288	w	
		1280	sh					
1270	w			1268	s	1269	s	
		1248	sh			1240	w	$C(CH_3)_2$ skeletal
		1234	m					
1188	sh	1201	w	1202	w	1203	m	$C(CH)_2$ skeletal
						1191	m	$C(CH_3)_2$ skeletal
1173	w	1169	w					
1155	sh	1158	w			1157	w	aromatic C–H in plane def.
1115	sh	1100	m			1113	m	

[a] s, Strong; m, medium; w, weak; sh, shoulder.

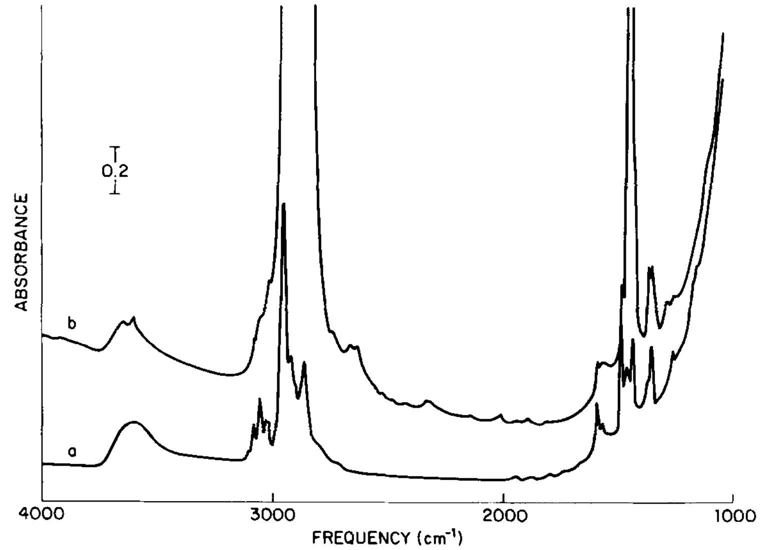


FIG. 1. FT-ir spectra of the NZA catalyst. (a) NZA as prepared, 0.33 mmol TNZ/g of alumina dried at 670 K. (b) Sample (a) after exposure to 90 kPa ethylene for 5 min to form polyethylene.

groups are intact in the fresh catalyst, and that the sample preparation procedure leaves no significant amount of adsorbed solvent or other organic residue.

Changing the amount of TNZ with which the alumina is reacted has no effect on the positions of the infrared bands, only on their intensities. Figure 2 shows the C–H stretching region of the spectra of catalysts of several TNZ to alumina ratios. Figure 3 shows the peak absorbance of the 2960 cm^{-1} methyl C–H stretching mode as a function of TNZ to alumina ratio. The strengths of the neophyl group absorptions seem to saturate at a ratio of about 0.2 mmol TNZ/g of alumina dried at 670 K. Ethylene uptake by untreated catalysts shows a similar dependence on TNZ/alumina ratio (Fig. 4). These observations are evidence that there is no dependence of Zr site structure on TNZ to alumina ratio.

Changes in the alumina hydroxyl stretching absorptions occur on reaction with TNZ. Figure 5 shows the hydroxyl bands of alumina reacted with several amounts of TNZ. The four high-frequency OH bands are attenuated by the reaction with TNZ and the broad hydroxyl band with maxi-

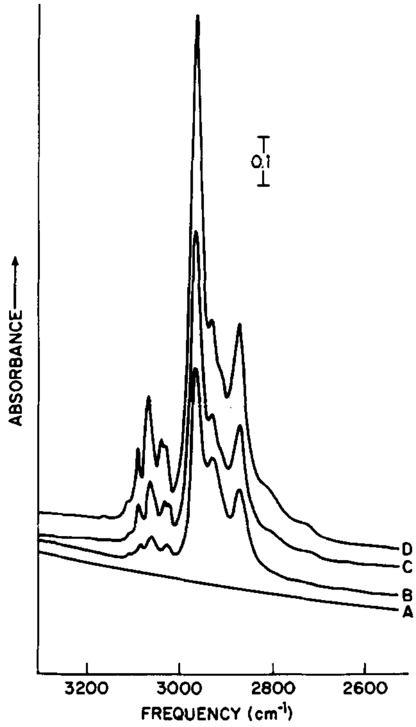


FIG. 2. C–H stretching vibration region of ir spectrum of catalyst. (A) Alumina dried 670 K. (B) NZA 0.06 mmol TNZ/g. (C) 0.11 mmol/g. (D) 0.56 mmol/g.

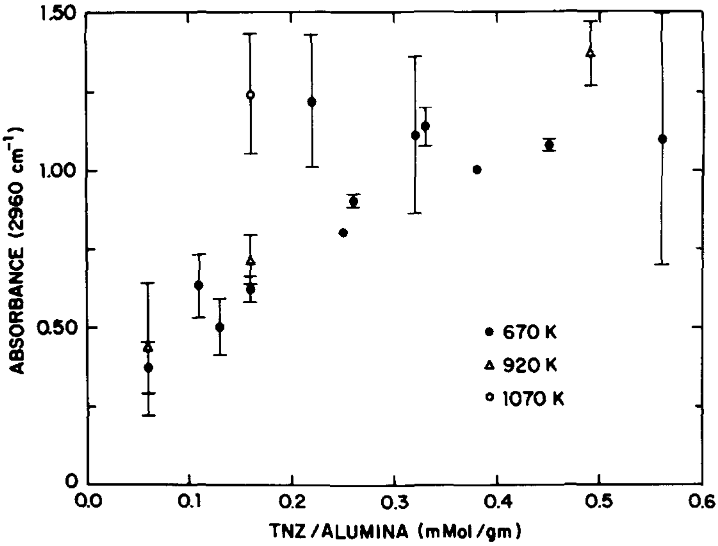


FIG. 3. Strength of 2960 cm^{-1} methyl group absorbance plotted against TNZ/alumina ratio of the catalyst. Aluminas dried at 670, 920, and 1070 K were used. Error bars are one standard deviation of measurements on three to six wafers for each ratio.

mum near 3600 cm^{-1} is left nearly unchanged.

The literature assigns the high frequency bands to free hydroxyls and the 3600 cm^{-1} band to associated or hydrogen bonded hydroxyls (*18, 19*). The associated hydroxyls must be located adjacent to a neighboring oxide or hydroxide ion, presumably preventing the close approach of the bulky TNZ molecule.

The identification of the intact neophyl ligands on the catalyst and the disappearance of the free hydroxyl groups of the alumina confirm that the major form of binding

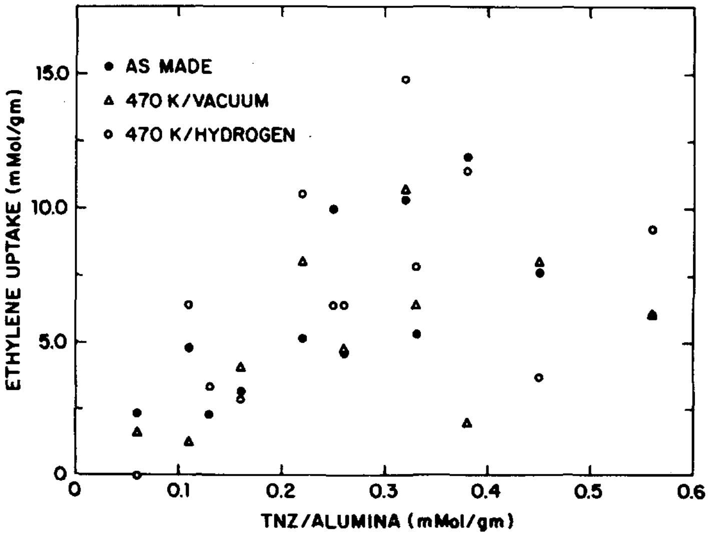


FIG. 4. Ethylene uptake vs TNZ/alumina ratios. Included are data for untreated samples, and samples heated to 470 K in vacuum or hydrogen.

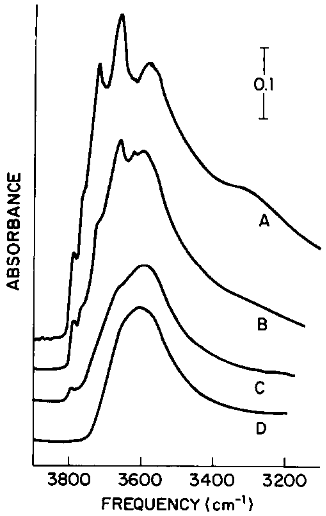
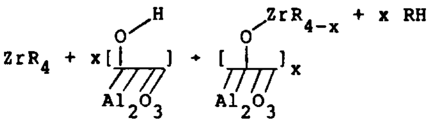


FIG. 5. Alumina hydroxyl stretching region of ir of catalysts prepared with different TNZ/alumina ratios. (A) Alumina dried at 670 K. (B) 0.06 mmol/g. (C) 0.11 mmol/g. (D) 0.56 mmol/g.

of TNZ to the alumina to form the catalyst is:



$$\mathrm{ZrR_4} + x\,[\mathrm{O{-}H}/\mathrm{Al_2O_3}] \rightarrow [\mathrm{O{-}ZrR_{4-x}}/\mathrm{Al_2O_3}]_x + x\,\mathrm{RH} \qquad (1)$$

$$\mathrm{R} = -\mathrm{CH_2C(CH_3)_2C_6H_5}$$

The apparent saturation of Zr loading at high TNZ/alumina ratio implied by Fig. 3 can reflect the saturation of Zr binding sites on the alumina. The infrared spectra of the OH stretching region of many of the catalyst samples show the complete loss of free hydroxyls throughout the catalyst (see Fig. 1a, 5D, or 10a), in agreement with saturation of the surface. However, diffusion control of catalyst synthesis predicts a (TNZ solution concentration)$^{1/2}$ dependence of the uptake, which gives the appearance of saturation and also can explain lack of Zr site structure dependence on TNZ to alumina ratio (*16*).

The total hydroxyl content and the relative strengths of the alumina hydroxyl absorptions depend on the thermal treatment of the alumina (*18, 19*). With treatment at successively higher temperatures, the low-frequency OH bands lose intensity relative to the higher frequency hydroxyl absorptions. Figures 6 and 7 show portions of the infrared spectra of alumina dried at 920 and 1070 K and catalysts produced by reacting those aluminas with 0.16 mmol of TNZ/g of alumina. These catalysts show the same changes from the alumina as the catalyst made with alumina dried at 670 K. Neophyl group absorbances of the same magnitude were found on the catalysts, and the high-frequency alumina hydroxyls were eliminated from the spectra. The obvious difference in the ir spectra of catalysts made with aluminas dried at the higher temperatures is that the broad 3600 cm^{-1} hydroxyl band is decreased in strength in the 920 K catalyst and almost entirely absent in the 1070 K catalyst.

These spectra indicate another mechanism for the attenuation of the free OH stretching bands: a shift to lower frequency caused by association with TNZ or TNZ fragments. Such shifts have been observed during the adsorption of paraffins and aro-

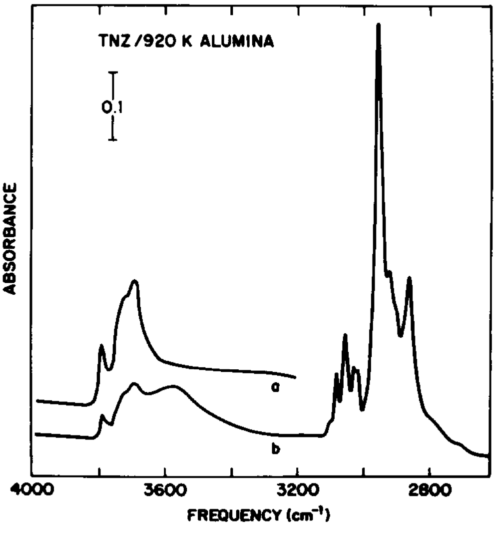


FIG. 6. (a) Hydroxyl stretching region of ir spectrum of alumina dried at 920 K. (b) Portion of the ir spectrum of catalyst prepared with 920 K alumina and 0.16 mmol TNZ/g.

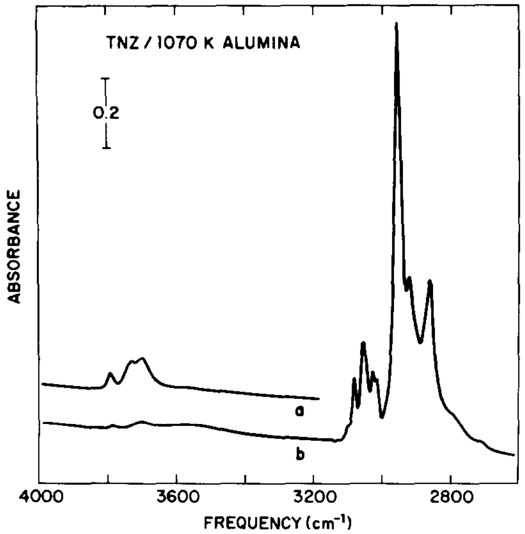


FIG. 7. (a) Hydroxyl stretching region of ir spectrum of alumina dried at 1070 K. (b) Portion of ir spectrum of catalyst prepared with 1070 K alumina and 0.16 mmol TNZ/g.

matic molecules on minerals (*20, 21*). The intense 3600 cm^{-1} band evident at lower alumina drying temperatures would mask the shifted bands. The presence of the 3600 cm^{-1} band after reaction of TNZ with alumina dried at 920 or 1070 K (Figs. 6 and 7) shows that a frequency shift can occur.

The decreased OH content of aluminas dried at high temperatures should affect the amount of TNZ taken up and the value of x in Eq. (1). Increases in the ligand to Zr ratio of catalysts made with increased support drying temperature have been reported for similar catalysts (*1, 4, 8, 12*).

Surprisingly, the strength of the neophyl absorbances is nearly twice as high after reaction of 0.16 mmol of TNZ/g Al_2O_3 with alumina dried at 1070 K as after reaction with alumina dried at lower temperatures (Fig. 3). In view of the small number of OH groups present and the small decrease in OH groups on reaction, some new mode of bonding of TNZ to dehydroxylated alumina surfaces must occur. Alkyl zirconium complexes can form Lewis acid–base adducts with oxygen lone pair containing bases (*5*). If oxygen ions at the alumina surface can serve as sterically accessible Lewis base sites, this form of bonding can explain the infrared results and the reported increases in ligand to Zr ratio with support drying temperature (*1, 4, 8, 12*).

Heating in Vacuum

After heating NZA in vacuum, ir shows a decline in the intensity of all bands attribut-

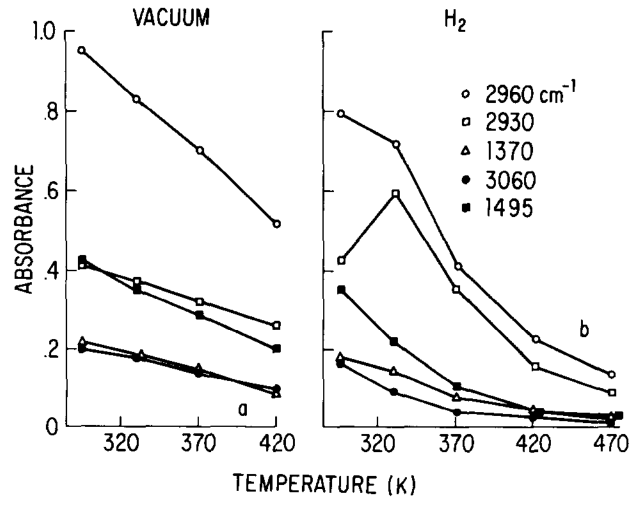


FIG. 8. Absorbances of five strongest bands of ir spectrum of catalyst as catalyst is heated for 15-min periods to successively higher temperatures. (a) In vacuum, (b) in 90 kPa hydrogen. Assignment of bands: 2960, CH_3 stretch; 2930, CH_2 stretch; 1370, CH_3 deformation; 3060, aromatic C–H stretch; 1495, aromatic skeletal mode.

able to the neophyl groups. The changes of intensity of five bands with heating to successively higher temperatures for periods of 15 min are shown in Fig. 8a. The smooth decrease of each of the bands shows that intact neophyl groups are being removed from the catalyst, and only small amounts of rearranged organic residues (if any) are left on the catalyst. In addition to the decrease of the neophyl bands, broad bands of variable intensity occasionally develop on heating. After treatment at 470 K, these new bands fall at 1560–1600, 1390, and 1370 cm^{-1}.

The major organic product of the thermolysis of NZA is *t*-butylbenzene (tBB). Also found are (phenyldimethyl)ethylene and lesser amounts of benzene, propylbenzene, toluene and di(*t*-butyl)benzene. Control experiments, pyrolysis GC/MS of *t*-butylbenzene or dodecane adsorbed on alumina dried at 670 K, showed no fragmentation of either.

One source of the protons added to the neophyl groups to make tBB is the residual hydroxyls present on the catalysts. This was demonstrated in an experiment where NZA was prepared with alumina partially deuteroxylated by heating at 670 K in D_2O vapor before drying at 670 K. Analysis of the tBB generated when portions of the catalyst were heated to temperatures up to 520 K and then hydrolyzed with butanol showed significant d_1-tBB. Figure 9 shows the percentage deuterated tBB vs treatment temperature for two experiments. The only source of deuterium in these experiments is the alumina deuteroxyls. Setterquist *et al.* (*2*) observed that the neophyl group content of NZA catalysts slowly decreased with time. The deuterated tBB produced by the unheated catalyst (Fig. 9) confirms that protolysis by the unreacted hydroxyls is the source of this loss of neophyl groups. The extent of reaction increases with temperature as the deuteroxyls become more mobile. Since species containing acidic protons, such as water or alcohols, are catalyst poisons, the unreacted hydroxyls are a potential limitation on the life and yield of the catalyst.

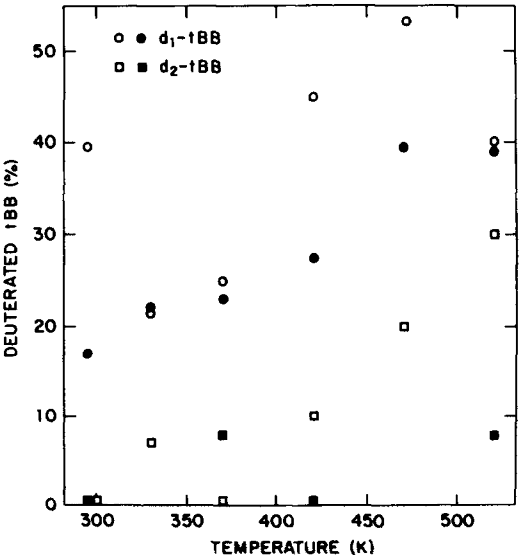


FIG. 9. Deuterium content of *t*-butyl benzene formed after heating, then hydrolysis of catalyst prepared with partially deuteroxylated alumina. The filled and open symbols are from experiments with aluminas of different degrees of deuteroxylation.

Also shown in Fig. 9 are the fractions of d_2-tBB detected. The evolution of d_2-tBB from the deuteroxylated catalyst and the rearranged organic products of thermolysis show that chemistry beyond protolysis is occurring. Either unusual chemistry at the Zr alkyl center or postreactions catalyzed by the alumina may yield these products. The lack of rearrangement of *t*-butylbenzene over alumina in the control experiments and the variety of thermolysis products both point to reactions at the Zr center (*22*). Heat-treated alumina is known to catalyze the exchange of hydrogen isotopes between hydrocarbons and between surface hydroxyls and hydrocarbons (*23*).

NZA catalyst wafers heated as high as 620 K showed polymerization activity in the ir cell at room temperature by both ethylene uptake and ir.

Heating in Hydrogen

Figure 8b shows the intensities of various neophyl ir bands of a catalyst wafer heated to successively higher temperatures in 90 kPa of hydrogen. In contrast to similar heating in vacuum, heating in hydrogen leads to an initial increase in the absorption of a band associated with $-CH_2-$ units (2930 cm^{-1}), and the decrease in the intensities of other bands is more rapid. Significant amounts of *t*-butylcyclohexane, as well as ethyl- and propylcyclohexane are found by GC/MS as product of the hydrogenation of NZA.

Similar heating of NZA in 90 kPa of deuterium gas produced no increase in the 2930 cm^{-1} $-CH_2-$ band, and the rates of decrease in intensity of the neophyl group absorbances were similar to the rates in vacuum. CD stretches near 2100 cm^{-1} were not seen.

The presence of hydrogen facilitates the cleavage of the Zr–C bonds. In addition, the aromatic portion of the neophyl is hydrogenated to a cyclohexyl group while still bound to the catalyst. These infrared spectroscopic observations are consistent with experiments performed on powdered catalysts slurried in mineral oil, where rapid hydrogenation and hydrogenolysis of the ligands at 470 K were also found (*2*). Similar observations were reported by the Russian group for hydrogenation of tetra(allyl)zirconium on silica (*9, 11*). The allyl groups of the catalyst were removed even at room temperature. The product of the hydrogenation was found to be almost quantitatively propane. Twice as many allyl groups were removed by treatment at 470 K in hydrogen as were removed by treatment in vacuum. Similar proportions are seen in Fig. 8.

Whether the mechanism involves hydrogenation of a ligand by a neighboring Zr center or involves self-hydrogenation within one Zr center is not clear. Activation of H_2 and hydrogenation of Zr–C bonds and of aromatic rings are exhibited by this catalyst. Catalytic hydrogenation of olefins by mineral supported organozirconium species under similar conditions have been reported (*5, 24*).

A broad new band centered at 1900 cm^{-1} is seen reproducibly when NZA is heated in hydrogen to temperatures between 420 and 520 K (Fig. 10). It is not seen when NZA is heated in vacuum or in deuterium. Exposure of a catalyst sample which exhibits this ir feature to water or ethylene removes this feature completely. The strength of the

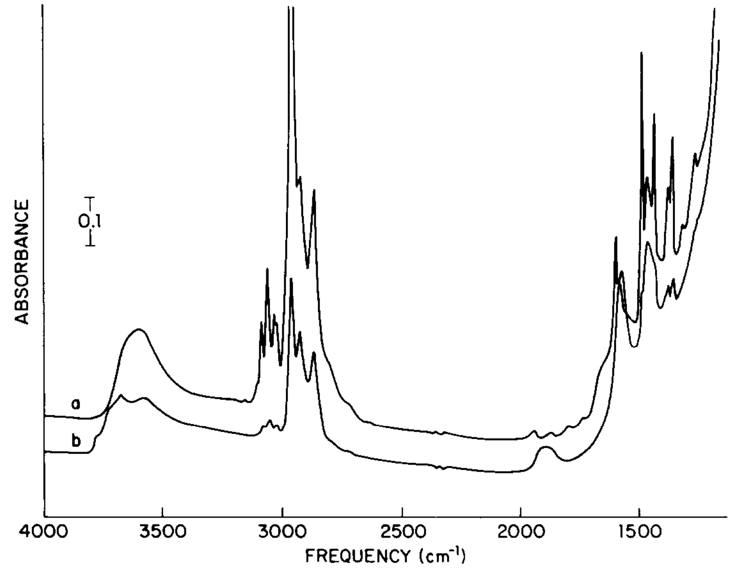


FIG. 10. (a) FT-ir spectrum of catalyst prepared with alumina dried at 670 K and 0.25 mmol TNZ/g alumina. (b) FT-ir of sample (a) after hydrogenation 15 min at 470 K at 90 kPa.

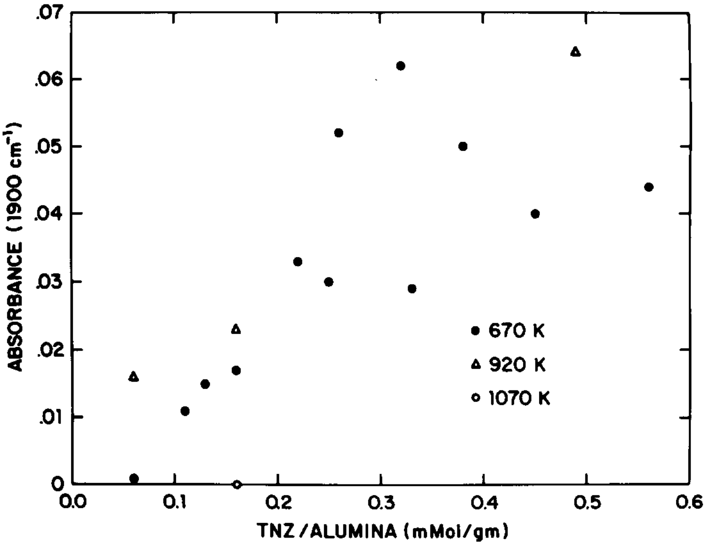


FIG. 11. Absorbances of 1900 cm^{-1} hydride band after heating catalyst 470 K in 90 kPa hydrogen for 15 min vs TNZ/alumina ratio of catalyst.

1900 cm^{-1} band shows the same dependence on TNZ to alumina ratio as the neophyl group absorbance of the catalyst (Fig. 11). This band is assigned to a Zr hydride stretching mode.

The failure of the 1900 cm^{-1} feature to be formed on catalysts heated in deuterium is consistent with its assignment as a metal hydride. The corresponding deuteride feature was not observed, but it would fall in the 1300–1400 cm^{-1} region where interferences from other bands and the decreased transmittance of alumina could hide the weak feature.

The uptake of hydrogen by NZA powder was measured by monitoring the hydrogen pressure drop as the NZA was heated either at a fixed temperature or to steadily increasing temperatures. The total hydrogen uptakes for the fixed temperature experiments are given in Table 2. Hydrogen uptake commences at 360 K. A limiting uptake of 4H_2 per Zr would account for the hydrogenolysis of neophyl groups, formation of Zr hydride species, and hydrogenation of the phenyl to cyclohexyl rings if there was one neophyl per Zr on the original catalyst. The experimental uptakes show that some or all of these processes are incomplete under the conditions of the experiments.

Dudchenko *et al.* found that the increased activity of hydrogenated allyl zirconium catalysts was due to an increased number of growth centers with an unchanged propagation rate (*11*). Formation of zirconium hydride species, a likely intermediate in the polymerization mechanism (*6*), was cited to explain the increased activity. They gave physical and spectroscopic evidence for the existence of these postulated hydrides.

Zakharov *et al.* measured the hydride content of tetra(allyl)zirconium on silica catalysts by measuring the HD generation

TABLE 2

Hydrogenation of NZA Catalyst (90 kPa)

Temperature (K)	H_2 uptake (molecules/Zr)
350	2.5
420	2.8
470	2.9

on hydrolysis with D_2O. They found H/Zr ratios of 1–2 after hydrogenation of the catalyst at 470 K. The activity of catalysts increased with hydride content and the hydride content was found to decrease on exposure to ethylene to an extent similar to the number of polymerization centers measured by radioactive quenching agents (*9*). Similar results were obtained on hydrogenated tetra(benzyl)titanium on silica (*15*).

Vibrational modes of discrete transition metal hydride compounds can be observed in the infrared, although they are commonly weak and broad. Absorptions of zirconium hydrides are found between approximately 2000 and 1200 cm^{-1}, a range too broad for certain identification by a characteristic frequency (*25*).

Zakharov *et al.* reported the infrared spectra of variously hydrogenated or heated tetra(allyl)zirconium on silica (*9*). Bands at 1625 and 2100–2300 cm^{-1} were observed after hydrogenation of the catalyst and assigned to hydride species. The vibrational features assigned by the Russian group to surface hydride species showed chemical behavior consistent with this assignment. On exposure to deuterium, allene, butadiene, ethylene, or heavy water, the infrared spectrum changed in the expected manner (*1*). It is unfortunate that the effects of hydrogenation were seen in portions of the infrared spectrum that coincide with absorptions from the silica support. There are silica bulk vibrational absorptions at 1625 cm^{-1} and between 1800 and 2100 cm^{-1}. Also silicon hydride species on silica surfaces absorb in the range 2150–2300 cm^{-1} (*26*).

The same group looked for evidence of supported Ti hydrides from the hydrogenation of tetra(benzyl)titanium on silica or alumina. With hydrogenation of silica-supported titanium, the same bands at 1630, 2190, and 2260 cm^{-1} were observed that had been assigned to silica-supported zirconium hydride species (*15*). Hydrogenation of alumina-supported tetra(benzyl)titanium produced no new bands. The evidence in the literature supports the existence of hydrides of Zr and Ti in hydrogenated catalysts, but it also suggests the reported infrared features are complicated by changes in the silica support on hydrogenation.

The chemical behavior of the source of the 1900 cm^{-1} band is consistent with a metal hydride. Discrete aluminum hydride compounds have vibrational absorptions in the range 1700–1900 cm^{-1} (*27*), and there is one uncorroborated report of an aluminum-hydride band produced on hydrogenation of γ-alumina at 1910 cm^{-1} (*28*). Hydrogenation of Degussa alumina alone under the conditions that result in the 1900 cm^{-1} absorption has yielded no trace of the band. The intensity of the 1900 cm^{-1} band is roughly proportional to the intensity of the neophyl bands of the catalyst before hydrogenation (Fig. 11), suggesting the band is due to a Zr hydride. There is convincing evidence that the assignment of the 1900 cm^{-1} infrared band to a supported metal hydride is correct, and strong evidence that it is a Zr and not Al hydride (*29*).

The only new infrared bands beside the 1900 cm^{-1} hydride band seen on heating of NZA are at 1370–1390, 1440–1480, and 1580–1600 cm^{-1}. These are occasionally observed after heating the catalyst above 420 K in either hydrogen or vacuum. Very similar bands were reported from alumina heated in toluene at 470–670 K (*30*). Those bands were attributed to carboxylate species produced on oxidation of the toluene by the alumina. The infrared bands seen in the present study may have a similar origin.

Activity for polymerization of ethylene is maintained after treatment in hydrogen (Fig. 4) but lost after hydrogenation at temperatures above 570 K. In NZA samples hydrogenated at above 420 K, polymerization activity is only observed on catalysts which display the 1900 cm^{-1} feature, and polymerization occurs to an extent roughly proportional to the strength of the 1900 cm^{-1} band.

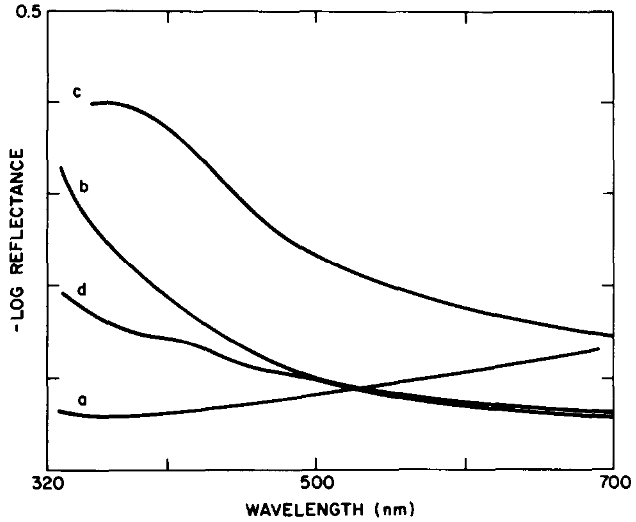


FIG. 12. Ultraviolet-visible DRS of catalyst. (a) Alumina dried 670 K. (b) Catalyst, 0.15 mmol TNZ/g alumina. (c) Catalyst heated 470 K in vacuum, 15 min. (d) Catalyst heated 470 K in hydrogen, 15 min.

Diffuse Reflectance Spectroscopy

Diffuse reflectance spectroscopy (DRS) in the uv-visible region was used to help identify the electronic structure of the NZA catalyst. Reduced Zr species present would have absorptions as a result of transitions between the *d* levels. Organic residues likely to be present do not absorb in this range.

Figure 12 shows DRS spectra for dried alumina, NZA, and NZA heated at 470 K in vacuum or hydrogen. The alumina spectrum is featureless, as expected. The NZA spectrum shows increased absorption at the short wavelength extreme, similar to solution spectra of TNZ. NZA becomes visibly darkened when heated in vacuum, and the DRS of such samples contains a broad maximum at 360 nm. The DRS spectrum of NZA heated in hydrogen is similar to that of untreated catalyst, except that there is decreased absorption at short wavelengths.

Figure 13 compares catalysts of four TNZ/alumina ratios after heating at 470 K in vacuum. There is a substantial increase in the absorption at 360 nm as the TNZ/alumina ratio increases from 0.13 to 0.19 mmol TNZ/g alumina. The correlation of the 360 nm absorption strength with TNZ/alumina ratio associates this feature with the Zr ions of the catalyst.

Figure 14 records the changes in the DRS spectra of 470 K treated catalyst after exposure to ethylene or air. In each case the 360 nm feature is attenuated almost completely. Ethylene uptake and growth of new C–H overtone absorptions at 1730 and 1765 nm show that polymerization of the ethylene occurs. All catalysts which had DRS spectra that exhibited the 360 nm feature showed similar behavior on exposure to ethylene or air.

These observations show that on heating in vacuum, an unknown fraction of the Zr ions of NZA catalyst is reduced from the +4 oxidation state. Reduction does not occur in the presence of hydrogen. The reduced Zr sites are easily reoxidized by exposure to air or ethylene.

Active Sites

A flaw of spectroscopic studies of catalysts such as this one lies in the uncertainty that the spectroscopically characterized

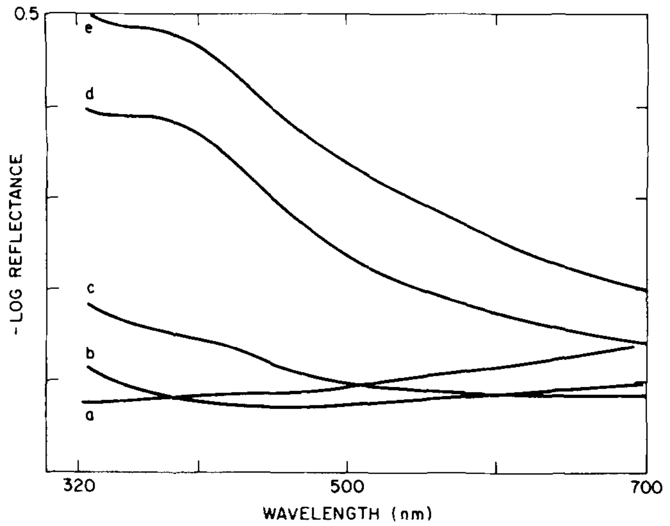


FIG. 13. DRS of catalysts of several TNZ/alumina ratios after heating 470 K in vacuum, 15 min. (a) Alumina dried 670 K. (b) Catalyst 0.06 mmol/g. (c) 0.13 mmol/g. (d) 0.19 mmol/g. (e) 0.31 mmol/g.

species are really involved in the catalytic chemistry. Nonetheless, it remains valuable to compare spectroscopic observations with catalytic properties.

Similar activity for the polymerization of ethylene was observed in three types of samples that differed in treatment and spectroscopic properties: NZA synthesized at room temperature with an infrared spectrum showing only intact neophyl ligands; NZA treated in hydrogen at 420–520 K with neophyl ligand ir absorptions replaced by a 1900 cm^{-1} absorption assigned to Zr–H; and NZA heated above 470 K in vacuum with no infrared absorptions assignable to organic or hydride species but exhibiting

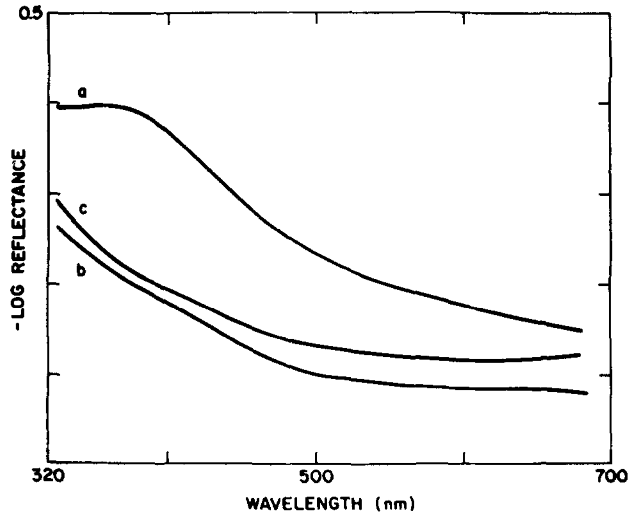


FIG. 14. (a) DRS of catalyst (0.15 mmol/g) heated 470 K in vacuum, 15 min. (b) DRS of catalyst as (a), exposed to 90 kPa ethylene, 5 min at room temperature. (c) DRS of catalyst as (a) exposed to air.

the 360 nm DRS feature. A first rationalization of this fact is that at least three types of Zr species—zirconium alkyl, zirconium hydride, and zirconium in a reduced oxidation state—are active for the polymerization of olefins or can be transformed into the active species (*2*).

The simultaneous presence of several types of polymerization centers in supported zirconium catalysts would lead to a broadened molecular weight distribution in polymers manufactured with these catalysts. Broad molecular weight distributions have been observed (*1*, *2*) although other factors such as mass transfer limitations during polymerization could be responsible.

One of the attractive features of supported organozirconium catalysts is their activity at high temperatures (*1*, *2*, *12*). Activity after treatment at high temperatures has been observed in the present study, but different spectral characteristics were observed following treatment in hydrogen vs vacuum. The retention of activity may be due to the apparent ability of NZA thermolysis products to polymerize ethylene or to interconvert to whatever the catalytic form may be. Interconversion pathways implied by the data are schematically illustrated in Fig. 15. The proposed polymerization mechanism indicates that the alkyl and hydride forms are both active (*1*, *2*, *4*, *5*). Hydride and alkyl species can interconvert by β-hydride abstraction with olefin elimination and the reverse process, olefin insertion into the Zr–H bond. The reduced Zr site can be formed from alkyl species by homolytic cleavage of the Zr–C bond or reductive elimination of ligands. The attenuation of the 360 nm DRS feature of reduced catalyst by ethylene (Fig. 14) evidently proceeds through oxidative addition of the olefin, converting a reduced site into a form of Zr alkyl or hydride site. In the presence of hydrogen, reduced Zr sites may oxidatively add hydrogen also to form Zr–H, as suggested by the featureless DRS of catalysts heated in hydrogen.

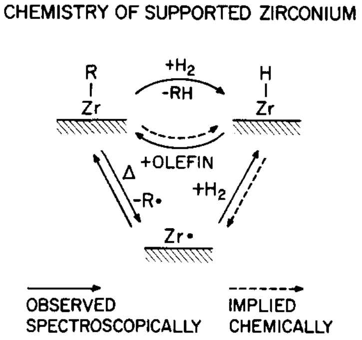


FIG. 15. Transformations of the zirconium site at elevated temperatures that are suggested by spectroscopic and chemical data.

CONCLUSIONS

Several features of the tetra(neophyl)zirconium reacted with alumina olefin polymerization catalyst have been clarified through spectroscopic studies, but many others deserve attention.

As with other supported early transition metal catalysts, TNZ is primarily bound to the alumina surface by reaction with surface hydroxyls and liberation of alkane. Only the free alumina hydroxyls are reactive. Catalysts prepared with aluminas dried at 670 K contain unreacted, hydrogen-bonded hydroxyls. These unreacted hydroxyls are liberated at elevated temperatures, serve as a reservoir of catalyst poison, and are an inherent limitation on the productivity of the catalyst. New sites for binding TNZ, such as oxide ions with Lewis base properties, are present on aluminas treated at high temperatures.

Catalyst samples were treated at high temperatures in attempts to explore the source of their high temperature activity. Spectra of samples heated in vacuum showed loss of neophyl groups and reduction of the Zr oxidation state. Samples heated in hydrogen showed hydrogenation of the phenyl group of the ligand at low temperatures, more extensive loss of ligands at higher temperatures, but no reduction of Zr. A new feature in the infrared spectrum appeared on hydrogenation of the catalyst, which has been assigned as a Zr hydride stretching vibration. Zr hydride species are believed to be important in the chain termination and initiation steps of the polymerization mechanism.

No new organic species were identified on the catalyst after heat treatment except occasional carboxylate species.

Alkyl, reduced, and hydride-zirconium species have been observed on differently treated catalyst samples, and all respond spectroscopically to ethylene exposure with concurrent formation of polyethylene. Whether each serves as a catalytically distinct site for polymerization, or all three interconvert and serve as one polymerization site cannot be deduced from the data. In either case, the activity retained by the thermolysis products of the original catalyst is a likely source of the high temperature activity of these catalysts.

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