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New metal alkoxides: Synthesis and hydrolysis-condensation reactions; some adsorption features of the hydrolysis-condensation products

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In this work, (a) hydrolyses of $Ti(OEt)_4$ and $Zr(OPr^n)_4$ with different amounts of water, (b) complexation of the same alkoxides with varying amounts of methacrylic acid, (c) hydrolysis of the complexation products with varying amounts of water, and subsequent polymerization, (d) adsorption capacities of the hydrolysis products (a and c) for aqueous aniline and phenol, were investigated. It was found that condensation reactions which follows the hydrolysis reactions, were alcohol condensations. The products were characterized in detail. Adsorption of aniline and phenol were compared for thermally conditioned powder of the products and some powders coated with 3-glycidyloxypropyltrimethoxysilane. It was observed that the extent of adsorption was influenced significantly by the temperature at which the adsorbents were calcinated by the coating of their surfaces.

1. Introduction

Commercially available metal alkoxides and new products obtained by their modification, have been widely utilized in the synthesis of many substances known as “advanced technological materials”. Sol-gel process, in which the properties and the reactions of metal alkoxides are exploited, is a very important and relatively a new method. In this process, reactions proceed at moderate (e.g. ambient) temperatures with ease [1–4].

Products obtained from metal alkoxides by the sol-gel process lead to the development of new glass and ceramic materials, a wide range of protective coatings, various electrodes as sensors, and some gas adsorbers [5–8].

It is known that metal alkoxides are very reactive, especially towards water. If, on the other hand, they are modified with chelate ligands (such as acetylacetone, allylacetoacetate, diols, and organic acids) they can become quite stable. Hydrolysis of metal alkoxides is the major reaction that converts alkoxides into oxides. Controlled hydrolysis has a significant effect on the oxide formation. By release of either water or alcohol, condensation proceeds rapidly as soon as hydrolysis occurs.

Environmental pollution (especially, air pollution) has been a severe problem nowadays, as an expected result of industrialization. Increasing amount of research has been devoted to environmental cleaning. Synthesis of adsorption catalysts and their use has an important role in cleaning the environment. Continuous absorption of atmospheric contaminants in absorption columns, for instance, can help maintaining a cleaner environment [9]. Formerly, drinking water was purified over charcoal. Later zeolites were used instead [10]. German troops made use of active carbon in gas masks to absorb poisonous gases in Word War I, while US Army employed silicate gels for the same purpose [11]. In one of the studies aimed at preventing environmental pollution, activated kernel shucks of various fruits were used as adsorbents. Adsorption of phenol and aniline in waste water has been realized by using these materials [12]. Utilization of the hydrolysis products

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of metal alkoxides in this respect, has not been attempted yet.

In the first part of this investigation, Titan(IV)-ethoxide [$Ti(OEt)_4$] and Zirconium(IV)-*n*-propoxide [$Zr(OPr^n)_4$], which are very reactive towards water, were complexed with methacrylic acid (having a polimerizable group) to render them stable. The hydrolysis conditions of these methacrylate complexes were examined and their polymerization products were obtained. It was found that methacrylic acid was bonded as a bidentate chelate ligand to metal atoms. In the second part, adsorption of aniline and phenol by the hydrolysis products of both commercially obtained alkoxides and of those modified with methacrylic acid were investigated. The results showed that all these compounds can effectively eliminate aniline and phenol from industrial waste water. Our approach is likely to be applied successfully for a wide range of organic contaminants.

2. Experimental

Titanium(IV)ethoxide, zirconium(IV)-*n*-propoxide (Fluka) and 3-glycidoxypropyl trimethoxysilane (GLYMO) (Fluka) were used as received. Methacrylic acid (MAC) (Aldrich) and methyl ethyl ketone (MEK) (Merck) were stored over molecular sieves (Fluka, 3ÅXL8) for a day before use.

Moisture contents, 0.002% in MAC and 0.0011% in MEK were detected by a Mettler DL18 Model Karl-Fischer Coulometric titrator.

$Ti(OEt)_4$ (0.01 mol) was hydrolyzed in MEK (5 ml) by adding 1–4 mol of water per mole $Ti(OEt)_4$, without using any catalyst. After adding water, the reaction mixture was stirred for 30 min at ambient temperature. The percentage of unreacted water was measured by Karl-Fischer Coulometric titrator, and Beckman 2120 Model Gas Chromatography. The experiment was repeated by substituting $Ti(OEt)_4$ with $Zr(OPr^n)_4$. A colloidal mixture was formed as soon as water was added, and the product changed into a gel as the reaction proceeded. On removal of the solvent and the liberated alcohol under vacuum, a solid product was obtained.

$Zr(OPr^n)_4$ (0.01 mol) was dissolved in MEK (5 ml). After stirring for ten minutes, 1.0, 1.5, 1.8, 2.0, 2.2 and 2.3 mol of MAC was added slowly to the solution, for each mole of $Zr(OPr^n)_4$, respectively. Reactions appeared to be more exothermic as the fraction of MAC increased. The reaction mixture was allowed to react for an hour (required for the completion of the reaction) at ambient temperature, the solvent and the liberated alcohol were removed in vacuum, and a yellow viscous liquid was obtained. This experiment was repeated by substituting $Zr(OPr^n)_4$ with $Ti(OEt)_4$ and then an orange viscous liquid was obtained.

Infrared spectra of the hydrolysis products (using KBr pellets) and methacrylate complex products (dissolved in $CHCl_3$) were taken with a Perkin Elmer 283 Model FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra of methacrylate complex products were recorded on a 60 MHz Perkin Elmer and AM 250 Brucker Spectrometer in $CDCl_3$. UV absorption spectra of complexes dissolved in $CHCl_3$ were recorded on a Philips PU 8715 Model spectrophotometer.

To a large test tube 1 g of titaniumethoxidemethacrylate and 5 ml of toluene were added. Then 0.020 g of benzoyl peroxide was added. The test tube was placed in a beaker filled with water, which was maintained at a temperature of about 90–95 °C. After an hour, the test tube was removed from the beaker and was allowed to cool for 5 min. Then the solution was poured into 100 ml of methanol. A yellow precipitate was collected by decantation, washed with methanol, and dried under vacuum for an hour at room temperature. A similar experiment was carried out for the polymerization of zirconium-*n*-propoxidemethacrylate complex.

Uncatalysed hydrolysis of Ti and Zr-alkoxide-methacrylate complexes were carried out using 1–4 mol of water per mole of alkoxides. The percentage of unreacted water was measured with a Karl-Fischer Coulometric titrator after stirring the solution for 30 min at ambient temperature. The gelation occurred 10–15 min after the addition of water. On removal of the solvent and the liberated alcohol under vacuum, solid products were obtained. All hydrolysis-condensation, complexation and polymerization products were dried in vacuum sterilizer at 40 °C and their thermal analyses were carried out by the Setaram TG-DTA A24 Model thermal analyzer. Elemental analyses were carried out with ICP Perkin Elmer 5500 and Carlo Erba EA 1108 Model elemental analyzers.

Metal-organic adsorbents were obtained by the hydrolysis-condensation products of all compounds. These products were dried in a vacuum sterilizer at 100 °C, then were ground to a fine powder in a grinder and collected through a 175–200 mesh sieve. Powdered materials were calcinated at 150 and 900 °C in a muffel furnace for 60 min. 0.1 g of adsorbents were mixed with solutions of phenol (20 ppm, 10 ml) and aniline (20 ppm, 10 ml) separately, and stirred for 60 min. The solutions were then filtered through a microfilter (0.2 μm). The amounts of phenol and aniline that remained in the filtrate were measured by a Jenway 6105 Model UV/VIS spectrophotometer. GLYMO was hydrolyzed without solvent and catalyst, by adding 1–3 mol of water per mol of GLYMO. The mixture was stirred until it formed a clear and homogeneous solution at ambient temperature and the percentage of unreacted water was measured by the use of the Karl-Fischer Coulometric titrator. The alcohol formed between hydroxyl group of water and methoxy group of GLYMO was removed in vacuum. The product thus obtained was a very viscous liquid. This product was diluted with *n*-propanol (0.01%, w/w) and used as a coating solution. The adsorbents were dipped into the coating solution and the mixture was stirred for an hour. Then it was filtered and dried in a vacuum sterilizer at 120–130 °C. 0.1 g of the coated adsorbents were treated with solutions of phenol and aniline (20 ppm, 10 ml) for 60 min, with stirring. Afterwards, they were filtered (microfilter, 0.2 μm); phenol and aniline amounts in the filtrate were determined by the UV-spectrophotometer.

TABLE I The elemental analysis data of the compounds synthesized

	Found (%)				Calculated (%)			
Compound	C	H	Ti	Zr	C	H	Ti	Zr
$Ti(OEt)_3(MA)$	45.54	7.70	17.78	—	44.79	7.52	17.86	—
$Zr(OPr^n)_3(MA)$	44.07	7.22	—	26.06	44.16	7.41	—	25.80
$Zr(OPr^n)_2(MA)_2$	43.83	6.70	—	23.88	44.30	6.37	—	24.03

3. Results and discussion

The chemical shifts of methacrylate and alkoxide (ethoxide and *n*-propoxide) groups bonded to Ti and Zr atoms are as shown below:

For $Ti(OEt)_x(MA)_y$;

^{1}H NMR (in $CDCl_3$):

Ethoxide group: 1.1 ppm (m, C$\underline{H}_3$–); 4.4 ppm (m, –C$\underline{H}_2$–O–)

Methacrylate group: 1.9 ppm (s, C$\underline{H}_3$–); 5.4 and 6.1 ppm (s, C$\underline{H}_2$ =)

^{13}C NMR (in $CDCl_3$):

Ethoxide group: 25 ppm ($\underline{C}H_3$–); 71 ppm (–$\underline{C}H_2$–O–)

Methacrylate group: 17–19 ppm ($\underline{C}H_3$–); 123–125 ppm ($\underline{C}H_2$ =); 138–141 ppm (CH_2 = $\underline{C}$–); 170–175 ppm (–$\underline{C}$OO)

For $Zr(OPr^n)_x(MA)_y$;

^{1}H NMR (in $CDCl_3$):

n-propoxy group: 0.9–1.0 ppm (m, C$\underline{H}_3$–); 1.7 ppm (m, –C$\underline{H}_2$–); 4.0 ppm (m, –C$\underline{H}_2$–)

Methacrylate group: 1.9–2.0 ppm (s, C$\underline{H}_3$–); 5.4–6.4 ppm (s, –C$\underline{H}_2$ =)

^{13}C NMR (in $CDCl_3$):

n-propoxy group: 10.5 ppm ($\underline{C}H_3$–); 26.2 ppm (–$\underline{C}H_2$–); 66.5 ppm (–$\underline{C}H_2$–O–)

Methacrylate group: 18.3 ppm ($\underline{C}H_3$–); 125 ppm ($\underline{C}H_2$ =); 136.7 ppm (CH_2 = $\underline{C}$–); 167.9 ppm (–$\underline{C}$OO)

According to the gas chromatography measurements, 1.0 mol ethanol and 1.0 mol *n*-propanol were liberated in the complexing reaction of $Zr(OPr^n)_4$ and $Ti(OEt)_4$ with equimolar ratio of MAC (1/1) respectively. UV spectra of all complexes and methacrylic acid were taken in $CHCl_3$. It is well-known that, due to the formation of metal complexes, the absorption band for a π-π^* transition always shifts to longer wavelengths. Absorption maxima for methacrylic acid, titaniumethoxidemethacrylate and zirconium propoxidemethacrylate were observed at 257.5, 261 and 260 nm, respectively.

Complexing ratios above 2/1, the C=O band of unreacted MAC was observed in the FT-IR spectra for the reaction between $Zr(OPr^n)_4$ with different mole ratios of MAC. However, at lower ratios, no unreacted MAC was detected. Hence, the maximum reacting ratio of MAC to $Zr(OPr^n)_4$ is 2/1. The maximum reacting ratio of MAC to $Ti(OEt)_4$ was found as 1.2/1. Thus it is verified that MAC has bonded to Zr and Ti. Moreover, the frequency separations ($\Delta\nu$) which are the difference between $\nu_{(COO)asym}$ and $\nu_{(COO)sym}$ (100 cm^{-1} for zirconiumpropoxidemethacrylate; 110 cm^{-1} for titaniumethoxidemethacrylate) show that MAC was bonded to metal atoms as bidentate chelating ligands [13].

TABLE II Maximum amounts of water consumed and amounts of liberated alcohol in the hydrolysis reactions

Compound	Amounts of water consumed (mol/mol metal)	Amounts of liberated alcohol (mol/mol/metal)
$Ti(OEt)_4$	1.30	2.58
$Zr(OPr^n)_4$	2.00	3.00
$Ti(OEt)_3(MA)$	1.45	2.05
$Zr(OPr^n)_3(MA)$	1.30	1.95
$Zr(OPr^n)_2(MA)_2$	1.00	1.90

TABLE III Amounts of alcohol formed in the condensation reactions

Compound	Amounts of alcohol (mol/mol metal)
$Ti(OEt)_4$	1.28
$Zr(OPr^n)_4$	1.00
$Ti(OEt)_3(MA)$	1.60
$Zr(OPr^n)_3(MA)$	0.65
$Zr(OPr^n)_2(MA)_2$	0.90

These results can be explained by the following complexation reactions:

$$Ti(OEt)_4 + MAC \xrightarrow{MEK} Ti(OEt)_3(MA) + EtOH$$

$$Ti(OEt)_4 + 1.2\ MAC \xrightarrow{MEK} Ti(OEt)_{2.8}(MA)_{1.2} + 1.2EtOH$$

$$Zr(OPr^n)_4 + MAC \xrightarrow{MEK} Zr(OPr^n)_3(MA) + PrOH^n$$

$$Zr(OPr^n)_4 + 2\ MAC \xrightarrow{MEK} Zr(OPr^n)_2(MA)_2 + 2PrOH^n$$

The apparent compositions of the products were also verified by their elemental analyses. The elemental analysis data of $Ti(OEt)_3(MA)$, $Zr(OPr^n)_3(MA)$ and $Zr(OPr^n)_2(MA)_2$ are given in Table I.

According to the Karl-Fischer titrations and GC measurements, maximum amounts of water consumed and the amounts of liberated alcohol in the hydrolysis reactions of all compounds are shown in Table II.

These results show that the amounts of water consumed are less than the amounts of liberated alcohol on the mole basis. This behavior clearly shows that condensation occurs by the interaction of hydroxyl and alkoxyl (no chelating group) groups that are bonded to Ti and Zr. The amounts of the alcohol formed in the condensation reactions are shown in Table III.

According to these results, hydrolysis-condensation reactions of all foregoing compounds can be shown as follows:

$$\begin{tikzcd} \mathrm{Ti(OEt)_4} + 1.3\,\mathrm{H_2O} \arrow[r, "\text{hydr.}"] & \mathrm{Ti(OEt)_{2.7}(OH)_{1.3}} + 1.3\mathrm{EtOH} \arrow[d, "\text{cond.}"] \\ & \mathrm{Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28}} + 1.28\mathrm{EtOH} \end{tikzcd}$$

$$\begin{tikzcd} \mathrm{Zr(OPr^{\mathit{n}})_4} + 2\mathrm{H_2O} \arrow[r, "\text{hydr.}"] & \mathrm{Zr(OPr^{\mathit{n}})_2(OH)_2} + 2\mathrm{PrOH^{\mathit{n}}} \arrow[d, "\text{cond.}"] \\ & \mathrm{Zr(OPr^{\mathit{n}})(OH)(O)} + \mathrm{PrOH^{\mathit{n}}} \end{tikzcd}$$

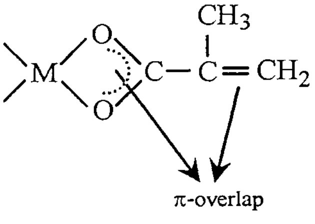
$$\begin{tikzcd} \mathrm{Ti(OEt)_3(MA)} + 1.45\mathrm{H_2O} \arrow[r, "\text{hydr.}"] & \mathrm{Ti(OEt)_{1.55}(MA)(OH)_{1.45}} + 1.45\mathrm{EtOH} \arrow[d, "\text{cond.}"] \\ & \mathrm{Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}} + 0.6\mathrm{EtOH} \end{tikzcd}$$

$$\begin{tikzcd} \mathrm{Zr(OPr^{\mathit{n}})_3(MA)} + 1.3\mathrm{H_2O} \arrow[r, "\text{hydr.}"] & \mathrm{Zr(OPr^{\mathit{n}})_{1.7}(MA)(OH)_{1.3}} + 1.3\mathrm{PrOH^{\mathit{n}}} \arrow[d, "\text{cond.}"] \\ & \mathrm{Zr(OPr^{\mathit{n}})_{1.05}(MA)(OH)_{0.65}(O)_{0.65}} + 0.65\mathrm{PrOH^{\mathit{n}}} \end{tikzcd}$$

$$\begin{tikzcd} \mathrm{Zr(OPr^{\mathit{n}})_2(MA)_2} + \mathrm{H_2O} \arrow[r, "\text{hydr.}"] & \mathrm{Zr(OPr^{\mathit{n}})(MA)_2(OH)} + \mathrm{PrOH^{\mathit{n}}} \arrow[d, "\text{cond.}"] \\ & \mathrm{Zr(OPr^{\mathit{n}})_{0.1}(MA)_2(OH)_{0.1}(O)_{0.9}} + 0.9\mathrm{PrOH^{\mathit{n}}} \end{tikzcd}$$

It is observed that the amount of alcohol liberated in the condensation reaction is much less than that was formed in the hydrolysis. This behavior can be reasoned as follows. The amount of alkoxide bonded to the metal before hydrolysis is greater than that of the hydrolysis product. It seems probable that alcohol released in hydrolysis can form hydrogen bonds with the hydroxide group on the metal and this makes condensation more difficult. It is seen that the amount of water used up in the hydrolysis increases as the alkoxide chain becomes longer and it generally decreases if the group bonded to the metal is both branched and of chelate property, as with methacrylate.

In the case of metal (Ti, Zr)-alkoxide-methacrylate complexes, the chelating bonds are expected to be stronger than that of the alkoxide bonds towards hydrolysis and condensation due to π-overlapping. This is due to the extra stability of the O–M bond resulting from conjugation of the π-bond of C=C to the carboxylate group, i.e., π-overlapping. Conjugation of this type is well known to stabilize carboxylate or β-diketonate modified metal alkoxides [14, 15].



The amount of water consumed and the amount of alcohol released, as a result of hydrolysis and condensation, decreases as the number of methacrylate groups bonded to the metal, increases. Thus the stability of the complex is increased. Therefore, even if excess water is used in the hydrolysis reaction, only the alkoxide (ethoxide, *n*-propoxide) groups undergo substitution and the methacrylate group remains bonded to metal.

FT-IR spectra of the hydrolysis products of methacrylate modified $\mathrm{Ti(OEt)_4}$ and $\mathrm{Zr(OPr^{\mathit{n}})_4}$ recorded even 3 weeks after hydrolysis, show that methacrylate group has not departed from Ti and Zr. C=C and hydroxyl vibration frequencies of the hydrolysis products are observed at 1640–1645 and 3440–3450 $\mathrm{cm^{-1}}$ respectively.

Thermal analysis and elemental analysis data of the hydrolysis-condensation products are given Table IV. The exothermic peaks can be ascribed to the combustion of the organic compounds.

The polymer products of $\mathrm{Ti(OEt)_3(MA)}$, $\mathrm{Zr(OPr^{\mathit{n}})_3}$ (MA) and $\mathrm{Zr(OPr^{\mathit{n}})_2(MA)_2}$ were disrupted approximately at 400–550 °C. According to the TG, the weight loss of polymer products of these complexes were found to be 50.20% (535 °C), 48.47% (524 °C) and 53.65% (538 °C), corresponding to 49.80% for $\mathrm{TiO_2}$, 51.53% and 46.35% for $\mathrm{ZrO_2}$ respectively. The weight losses of these polymers are fairly similar and the effect of the amount of methacrylate groups on thermal stability is not significant. In the differential thermal analysis (DTA) of the polymer product

TABLE IV Thermal and elemental analysis data of the hydrolysis-condensation products of $Ti(OEt)_4$, $Zr(OPr^n)_4$, $Ti(OEt)_3(MA)$, $Zr(OPr^n)_3(MA)$ and $Zr(OPr^n)_2(MA)_2$

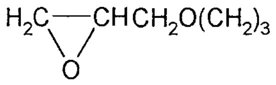
	Thermal analysis		Elemental analysis							
			Calculated (%)				Found (%)			
Compound	DTA Exo. (°C)	TG Weight loss (%)	TiO_2	Ti	ZrO_2	Zr	TiO_2	Ti	ZrO_2	Zr
a	230; 420	24	76	45	—	—	71.9	42.3	—	—
b	330; 450	15.52	—	—	84.48	62.5	—	—	84.9	62.8
c	330; 360; 455	46.97	53.03	31.79	—	—	51.9	31.09	—	—
d	250; 420; 470; 500	46.89	—	—	53.11	39.32	—	—	52.1	38.58
e	320; 480; 560	56.57	—	—	43.43	32.15	—	—	42.87	31.23

a: $Ti(OEt)_{1.42}\ (OH)_{0.02}\ (O)_{1.28}$
b: $Zr(OPr^n)(OH)(O)$
c: $Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$
d: $Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65}$
e: $Zr(OPr^n)_{0.1}(MA)_2(OH)_{0.1}(O)_{0.9}$

of $Ti(OEt)_3(MA)$, the peaks at 98 °C (endo.), 405 and 530 °C (exo.), in the DTA of the polymer products $Zr(OPr^n)_3(MA)/Zr(OPr^n)_2(MA)_2$; the peaks at 91/90 °C (endo.), 400/405 °C (exo.) and 495/515 °C (exo.), can be ascribed to the removal and combustion of the organic contained in the polymer products.

According to the Karl-Fischer titrations, 1.50 mol of water was used up per mole GLYMO. This product was used as coating material for the metal-organic adsorbents. The hydrolysis reaction of GLYMO is shown as follows:

$$R\text{-}Si(OMe)_3 + 3/2H_2O \longrightarrow R\text{-}Si(OMe)_{3/2}(OH)_{3/2} + 3/2MeOH$$

R:


Inorganic acids (e.g. H_2SO_4, HCl) and organic acids (e.g. acetic acid) are used as catalysts in the hydrolysis of alkoxy silanes. A disadvantage of using inorganic acids is the difficulty in their separation from the reaction medium. Drawbacks of using the organic acids, on the other hand, are their insufficiency in increasing the hydrolysis rate and that they may be reactive against alkoxides [8, 16].

Hydrolysis products, calcinated at 150 °C, were first coated with the material that was obtained by a prehydrolysis and then were heated to 120–130 °C to realize both condensation and inorganic polymerization.

The particle size of adsorbents thus obtained were kept in the range of 175–200 mesh. The best adsorption for aniline was observed with the adsorbent which was obtained from $Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$ and coated with GLYMO. Although the phenol adsorption of adsorbents prepared at this temperature is not superior, the uncoated one obtained from $Zr(OPr^n)(OH)(O)$ provided the highest adsorption. The percentages of aniline and phenol adsorption for coated and uncoated adsorbents are shown in Table V.

In addition to these experiments, all hydrolysis-condensation products were calcinated at 900 °C for 1 h. Phenol and aniline adsorption of uncoated and GLYMO-coated adsorbents are given in Table VI.

TABLE V Adsorption results of coated and uncoated adsorbents, prepared at 150 °C

Adsorbent	Aniline adsorption (%)	Phenol adsorption (%)
Uncoated adsorbents:		
$Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28}$	20.40	—
$Zr(OPr^n)(OH)(O)$	54.00	25.70
$Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$	71.15	—
$Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65}$	56.45	—
Coated adsorbents:		
$Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28}$	56.50	—
$Zr(OPr^n)(OH)(O)$	45.25	14.90
$Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$	75.00	—
$Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65}$	41.75	3.70

TABLE VI Adsorption results of coated and uncoated adsorbents, prepared at 900 °C

Adsorbent	Aniline adsorption (%)	Phenol adsorption (%)
Uncoated adsorbents:		
$Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28}$	4.65	20.80
$Zr(OPr^n)(OH)(O)$	8.15	35.45
$Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$	3.60	42.45
$Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65}$	4.65	34.25
Coated adsorbents:		
$Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28}$	75.40	92.00
$Zr(OPr^n)(OH)(O)$	75.40	89.60
$Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$	82.50	89.60
$Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65}$	88.80	88.70

The results given in Table IV show that both aniline and phenol adsorption on all of the GLYMO-coated adsorbents are excellent. This could be attributed to a favorable change in the pore size of the adsorbents after coating with the GLYMO-polycondensation products, which were previously increased due to the high temperature. The relative phenol and aniline capacities of all forms of adsorbents can be given as follows:

Aniline adsorption (for those prepared at 150 °C):

$$\text{GLYMO-coated } Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28} > Ti(OEt)_{1.42}(OH)_{0.02}(O)_{1.28}$$

$$\text{GLYMO-coated } Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6} > Ti(OEt)_{0.95}(MA)(OH)_{0.85}(O)_{0.6}$$

$$\text{GLYMO-coated } Zr(OPr^n)(OH)(O) > Zr(OPr^n)(OH)(O)$$

$$\text{GLYMO-coated } Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65} > Zr(OPr^n)_{1.05}(MA)(OH)_{0.65}(O)_{0.65}$$

Phenol adsorption (prepared at150 $^{\circ}C$): $Zr(OPr^n)(OH)(O)$

For aniline and phenol adsorption (prepared at 900 °C)

GLYMO-coated adsorbents > uncoated adsorbents

4. Conclusion

This work has made the following achievements:

(a) New metal alkoxides that are stable towards hydrolysis were synthesized and fully characterized.

(b) From the hydrolysis-condensation products of these compounds, adsorbents were prepared and tested for aniline and phenol, which are known contaminants in many industrial wastewaters.

(c) This work has also demonstrated that the adsorptive properties of the adsorbents could be improved by coating their surfaces.

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