

Preparation and Characterization of Hydrous Zirconium Oxide Formed by Homogeneous Precipitation

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This paper reports on the preparation, characterization and study of the ion exchange behavior of hydrous zirconium oxides formed by homogeneous precipitation from zirconium oxychloride. The precipitants used were obtained by thermal decomposition of urea, sodium nitrite or ammonium carbonate. Seven compounds were prepared and characterized by thermal analysis, X-ray diffractometry and by surface area measurements. Amorphous forms were obtained in each case, a result that agrees with those obtained by conventional gel precipitation methodology. All these materials present surface area values of $>148 \text{ m}^2 \cdot \text{g}^{-1}$, determined after heat treatment at 50°C . The ion exchange behavior of each hydrous zirconium oxide prepared was studied using K^+ as the exchanged species and the results compared with those obtained for hydrous zirconium oxide originally precipitated by the sol gel method.

Keywords: *homogeneous precipitation, ion exchange, cationic exchanger*

1. Introduction

Synthetic and natural inorganic ion exchangers and adsorbents offer definite advantages over well-known and traditionally used organic resins insofar as their chemical properties, radiation and thermal stability, resistance to oxidation and selectivity to certain ions are concerned, as described in the literature¹.

Hydrous oxides based on various polyvalent metal ions have been investigated due to their characteristics of selectivity and simplicity of preparation. They do, however, have a serious disadvantage: a comparison of different studies reveals that they produce inconsistent results owing to the difficulty of reproducing their preparations^{2,3}.

Inoue and Yamazaki⁴ established a method to synthesize a hydrous zirconium oxide ion exchanger, studying its properties of ion exchange and thermal stability behavior. The exchanger was reproducibly synthesized by hydrolysis of a zirconium oxychloride solution at pH 9.3, by the addition of an aqueous ammonia solution, in order to study the cationic exchange mechanism. The distribution coefficients of various cations were measured as functions of the pH and temperature.

Precipitation from a homogeneous solution is a tech-

nique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, relative supersaturation is kept low throughout the precipitation. Homogeneously formed precipitates, both colloidal and crystalline, are usually better suited for analysis than are solids formed by the direct addition of a precipitating reagent⁵.

Santos and coworkers⁶ studied a homogeneous precipitation of aluminum hydroxide from aqueous aluminum sulfate, nitrate and chloride solutions by thermal decomposition of urea, sodium nitrite and ammonium acetate. They observed that the homogeneous precipitation from the aqueous chloride and nitrites solutions were slower than from the sulfate ones. The particles of precipitate were spherical, while all the chloride particles were pseudo-boehmite fibrils or needles; nitrate, urea and ammonium acetate produced fibrils while sodium nitrite produced very thin films. Nevertheless, pseudo-boehmite was formed in every case.

Silva and coworkers⁷ studied a homogeneous precipitation of hydrous niobium oxide from the dissolution of metallic niobium in HNO_3/HF solution by thermal decompo-

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sition of urea. This material presented a higher specific area and ion exchange capacity for Ba^{+2} ions than those observed for hydrous niobium oxide prepared by the conventional gel precipitation method. This product was amorphous and also readily filtered.

In this study, hydrous zirconium oxide ion exchangers were prepared by homogeneous precipitation using an aqueous zirconium oxychloride solution and different precipitating agents, i.e., urea, ammonium carbonate or sodium nitrite. The results were then compared with those obtained by the gel precipitation method. The ion exchange behavior was investigated and the ion exchange capacities of the synthesized products were determined.

2. Materials and Methods

Materials and reagents

All the reagents used here, such as alkaline chlorides, hydroxides and hydrochloric acids, were of analytical grade and were used without purification. The standard aqueous solutions were titrated by the usual procedures.

The $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ used was prepared from an alkaline fusion of a Brazilian zirconite ore (ZrSiO_4) and purified by recrystallization in the Department of Materials of our Institute.

Preparation of hydrous zirconium oxide by homogeneous precipitation

In the first step, 5.0000 g samples of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ dissolved in an aqueous hydrochloric acid solution (0.5 mol.L^{-1}) were added to and mixed with 15.0000 g of urea. The resulting solution was heated to 90°C on an electrical plate to decompose the precipitating agent, leading to the formation of the hydrous oxide. After precipitation, the material was allowed to rest at 90°C for another hour. The white precipitate was filtered and washed repeatedly with deionized water with a pH of 4.5-5.0 for the removal of chloride traces, after which it was dried at room temperature in a desiccator. (See preparation 2A in Table 1).

A total of seven batches of hydrous zirconium oxide were prepared by homogeneous precipitation, to which different amounts of each precipitating agent were added (see preparations 2B, 2C, 3A, 3B, 4A and 4B in Table 1).

Preparation by conventional gel precipitation method

An aqueous solution of ammonia (1:3) was added drop by drop to an aqueous solution of zirconium oxychloride up to a final pH 8, under vigorous stirring. The precipitated gel was then aged in the mother liquor for 24 h. without stirring. After filtration, the gel was washed several times in distilled water for the complete removal of chloride ions (negative silver nitrate test). Finally, the product was dried at 25°C for 18 h (see preparation 1 in Table 1).

Characterization of hydrous zirconium oxides prepared

The hydrous zirconium oxides surface areas, S_{BET} , in $\text{m}^2 \cdot \text{g}^{-1}$, were determined by nitrogen adsorption using the BET method. The samples were previously degassed in the cell at 50°C for 3 h.

Thermal analyses were made using a model TGA-50 Shimadzu thermogravimetric instrument. Around 10.00 mg of material were heated to 600°C at a rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ under a dry nitrogen flow.

X-ray diffractograms were obtained with a Rich Seifert, model Iso-Debyfex 100 diffractometer, using $\text{CuK}\alpha$ radiation and varying 2θ values from 5 to 80° .

Ion exchange behavior

Reversibility of the exchange process

In the titration procedure, 0.0500 g of the hydrous zirconium oxide sample was mixed with 50.00 mL of KCl 0.1000 eq.L^{-1} solution and titrated with $[\text{KCl} 0.05000 + \text{KOH} 0.05000] \text{ eq.L}^{-1}$ to pH 11.0. The reverse reaction – regeneration of the ion exchanger material – was performed similarly, titrating the resulting solution with an aqueous solution of $[\text{HCl} 0.1000 + \text{KCl} 0.01000] \text{ eq.L}^{-1}$ until the pH returned to the initial value. The exchange and regeneration steps were repeated to confirm the reversibility of the process.

Capacity measurements

The samples exchange capacities were determined by pH x OH mEq concentration curves. The curves were obtained by mixing different volumes (different OH^- concentrations) of $[\text{KCl} 0.05000 + \text{KOH} 0.05000] \text{ eq.L}^{-1}$ and a sufficient vol-

Table 1. Experimental conditions and variables used in the preparation of $\text{ZrO}_2 \cdot n \text{ H}_2\text{O}$ by homogeneous precipitation.

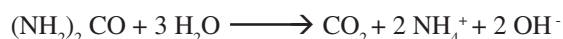
Preparation	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (g)	HCl 0.5 mol.L^{-1} (mL)	Precipitating agents (g)		Precipitation time (min)
2 A	5.0000	100	urea	15.0000	270
2 B	5.0000	60	urea	15.0000	210
2 C	5.0000	60	urea	20.0000	120
3 A	5.0000	60	NaNO_2	15.0000	immediately
3 B	5.0000	60	NaNO_2	20.0000	immediately
4 A	5.0000	60	$(\text{NH}_4)_2\text{CO}_3$	20.0000	60
4 B	5.0000	60	$(\text{NH}_4)_2\text{CO}_3$	40.0000	150

ume of $\text{KCl } 0.1000 \text{ eq.L}^{-1}$ to complete 50.00 mL and 0.0500 g of the exchanger. Thus, the pH changed but the total metallic ion concentration was the same in every sample.

3. Results and Discussion

Synthesis of hydrous zirconium oxides

In this work, the most favorable conditions for precipitation were found to involve precipitation from dilute solutions and gradual addition of the precipitating agent with constant stirring⁵. This *modus operandi* ensures a low degree of supersaturation. Despite these operations, however, an excess of local precipitating reagent is unavoidable when the reagent is added to the sample solution. A process of precipitation from a homogeneous solution should avoid such difficulties. In this technique, the precipitating reagent is generated *in situ* by a chemical reaction that occurs uniformly throughout the solution. The generation of hydroxyl ions for the precipitation of hydrous zirconium oxide is an example of this technique. The precipitating agent may be generated by hydrolysis of urea in an initially acidic solution:



This hydrolytic reaction takes place slowly and occurs at temperatures just below the boiling point of water.

Some hydrous zirconium oxides were prepared by generating precipitant species in the solution, starting from an acid hydrochloric zirconium solution with an excess of generator precipitating agents (urea, sodium nitrite or ammonium carbonate). Slow thermal decomposition of these precipitating reagents generated hydroxyl ions, allowing for the precipitation of hydrous zirconium oxides with different characteristics. Hydrous zirconium oxide precipitates formed by the method of generating reagent in the analyte solution showed a smaller precipitate volume, with precipitates far more easily filtered than those produced using the

external addition of reagent.

Table 1 shows the results obtained from the different preparation runs (gel precipitation method for preparation 1; homogeneous precipitation method for preparations 2A, 2B, 2C, 3A, 3B, 4A and 4B). These results indicate that the rate of formation depends on the initial concentration and on the precipitating agent added.

Characterization of hydrous zirconium oxides

The above-described compounds were characterized by thermal analysis (TG-DTG) in a temperature range of 30 to 600 °C and the experimental results used to determine their chemical composition (see Table 2).

The TG results of the decomposition of the materials prepared by the three different precipitating agents were quite similar, with only one less step, except for product 4A, which presented a two-step decomposition, as reported in Table 2.

Figure 1 shows the thermogravimetric curve obtained for sample 2A. Weight loss occurred in only one step in the

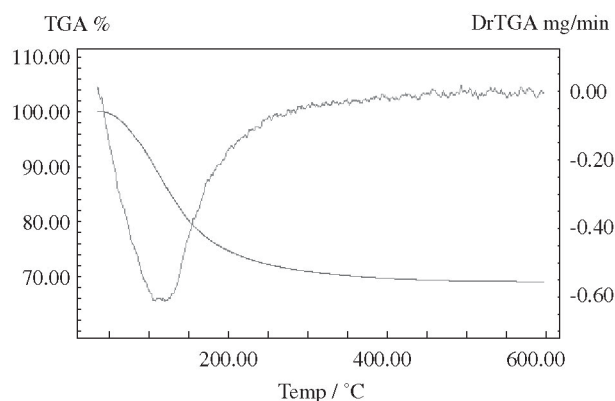


Figure 1. TG curves of hydrous zirconium oxide prepared by homogeneous precipitation of zirconium oxichloride with urea (preparation 2A).

Table 2. Results of the thermal analysis (TG), composition, surface areas and ion exchange capacities (IEC) determined for the hydrous zirconium oxides prepared.

Preparation	Temperature range (°C)	Weight loss (%)	Composition	Surface area (m ² .g ⁻¹)	IEC (meq OH.g ⁻¹)
1	30 - 350	27	ZrO ₂ · 2.2 H ₂ O	231	0.70
2 A	30 - 350	30	ZrO ₂ · 2.5 H ₂ O	210	0.34
2 B	30 - 350	28	ZrO ₂ · 2.3 H ₂ O	249	0.25
2 C	30 - 350	34	ZrO ₂ · 3.0 H ₂ O	317	0.41
3 A	30 - 350	27	ZrO ₂ · 2.1 H ₂ O	259	0.33
3 B	30 - 350	28	ZrO ₂ · 2.2 H ₂ O	263	0.34
4 A	30 - 350	31	ZrO ₂ · 3.1 H ₂ O	148	0.43
	350 - 450	4			
4 B	30 - 350	30	ZrO ₂ · 2.4 H ₂ O	154	0.32

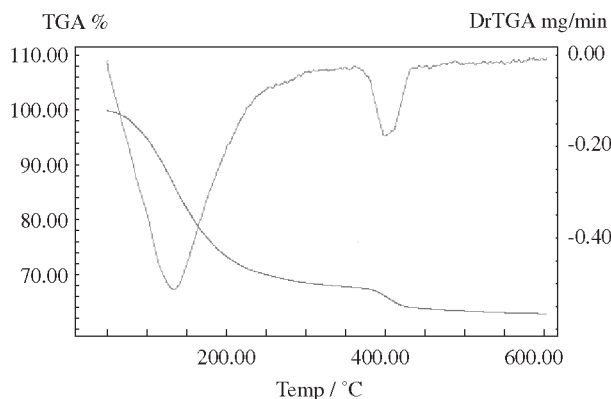


Figure 2. TG curves of hydrous zirconium oxide prepared by homogeneous precipitation of zirconium oxichloride with ammonium carbonate (preparation 4 A).

temperature interval of 30 to 350 °C and was attributed to dehydration of the interstitial water⁸. Similar behavior was observed for the other materials prepared, which were dubbed 2B, 2C, 3A, 3B and 4B. Sample 4A (Fig. 2) showed a 34% weight loss between 30 and 350 °C, which was attributed to dehydration of the interstitial water, while the second weight loss of 4%, which occurred between 350 and 450 °C, may be attributed to residual contamination probably originating from residual carbonate present in the hydrous zirconium oxide. In each case, the weight loss was completed at 600 °C and ranged from 26 to 34% of the sample's initial weight.

The exchanger chemical compositions were established from the thermogravimetric curve results, which indicate the amount of water held in the solid by the following expression:

$$18n = X \cdot (M + 18n) / 100$$

where X is the present mass loss in the respective thermal decomposition, n is the number of external mol of water and M the molar weight of dehydrated compound without the external water molecules.

Taking into account the water content of the different gels, their compositions are given in terms of $ZrO_2 \cdot nH_2O$ (Table 2), where n ranged from 2.1 to 3.1.

The specific surface area, whose calculation was based on the BET method, decreased from 317 to 148 $m^2 \cdot g^{-1}$ (see Table 2). Based on an analysis of preparations 2B, 2C, 3A, 3B, 4A and 4B (see Tables 1 and 2), one can argue that:

(i) high specific areas were obtained using the same HCl concentration for the homogeneous preparations and even different precipitating agents;

(ii) higher specific areas were observed with higher con-

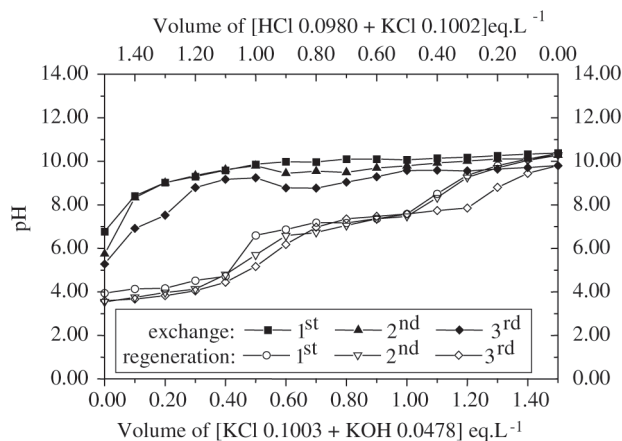


Figure 3. Reversibility study of ion exchange and regeneration curves obtained for K^+ ion exchange with hydrous zirconium oxide (preparation 2A).

centrations of precipitating agent.

Gel preparation 4A presented a lower specific area, probably due to the residual carbonate in the material's micropores.

After drying, none of the gels prepared in this study presented any degree of crystallinity, in accordance with the literature⁹.

Ion exchange behavior

The ion exchange behavior was studied by two different procedures.

In the first procedure, the reversibility of the exchanger was studied by repeating the exchange and regeneration steps; in the second, the ion exchange capacity was determined for K^+ ions with different stirring times.

Figures 3 and 4 show typical results obtained for potassium ions using the first and second procedures, respectively. Figure 3 clearly shows that this material is regenerable.

Table 2 lists the results of ion exchange capacities (IEC) obtained with potassium ions. As can be observed, the ion exchange capacities showed no significant changes for the exchangers prepared by homogeneous precipitation. The values were lower than those observed for hydrous zirconium oxide prepared by the gel precipitation method. The 2C material presented:

- (i) the highest value of water molecules;
- (ii) the best specific area and
- (iii) the highest value of ion exchange capacity for K^+ ions, for the materials obtained from urea. The 3B material obtained from sodium nitrite presented:

- (i) the highest value of water molecules;
- (ii) the highest specific area and

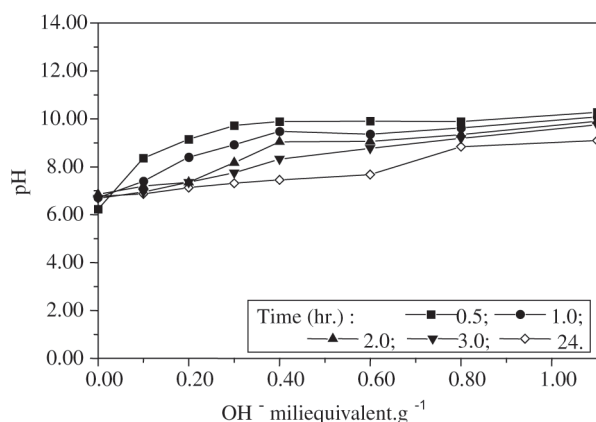


Figure 4. pH x OH miliequivalent curves obtained.

(iii) the highest ion exchange capacity for K⁺ ions.

However, although it presented high water molecule and ion exchange capacity values, the synthesized 4A material showed only 47% of the value found for the specific area of material 2C. These anomalous values were probably due to carbonate ions that remained inside the particles of the material.

4. Conclusions

All the hydrous zirconium oxides proved to be regenerable under the conditions of this study, presenting amorphous forms, relatively high surface areas and similar water contents. These properties of hydrous oxides prepared

by homogeneous solutions render them applicable in ion exchangers. These same products are readily filtered, in contrast to what was observed for hydrous zirconium oxide prepared by the sol gel precipitation method.

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