SYNTHESIS OF MgO, ZnO AND Al_2O_3 BY SOLID AND SOLUTION COMBUSTION PROCESSES AND STUDY OF THEIR PERFORMANCES IN Co^{2+} UPTAKE

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The study discusses the effect of magnesium, zinc and aluminum oxides prepared by the solid and solution-combustion process. The powders were synthesized by using different urea to metal nitrates ratio and different water concentrations in the solutions. They were characterized by X-ray diffraction, BET surface area and their performance in Co^{2+} uptake from aqueous solutions was studied. Results showed that water addition up to a certain limit during the solution combustion method modified the textural properties of the different oxides and that powders obtained by this process have interesting properties, increase the capacity to uptake Co^{2+} present in water, and increase the surface area of the materials. It was also found that further increments of water in the solutions decreased the Co^{2+} uptake capacity of the obtained solids. Results with Co^{2+} ions indicate that they are readily related to the solids prepared by solution combustion processes. It was found that that solution combustion favors cobalt uptake, depending on the amount of water used in the solution.

INTRODUCTION

Combustion synthesis is a very rapid chemical process based on the principle of explosive decomposition of urea that takes less than 5 minutes to arrive at completion. It involves the exothermic reaction of an organic fuel, in this case, urea, in the furnace chamber, producing metal oxides through the reduction process of metal nitrates [1, 2]. As a result, metal oxides products and gas emission of CO_2, H_2O and nitrogen oxides (NO_2) can be formed directly from the reaction between metal nitrates and urea without the need to get oxygen from outside.

In a previous work [3], solution combustion effects on the combustion preparation of MgO were presented. The obtained materials were characterized through their specific area, morphology, fractal dimension and Co^{2+} adsorption. A liner correlation between the fractal dimension and Co^{2+} adsorption was found.

Cobalt immobilization can occur through retention on several oxides. Several methods have been reported to be effective in generating very fine powders of ceramics that can be used for Co^{2+} uptake from water solutions. During past decades, a variety of contaminants in water has been developed for use as adsorbents [4, 5].

The selection of a specific solid to retain metal ions depends mainly on its capacity and selectivity for the species to be removed from a particular metal ion. Some retention processes are very dependent on the surface charge of these materials, on the form of the chemical species at various pH values, or on the specific surface areas of the solids [6, 7]. However, a clear understanding of all relevant species present in a given solution is of primary interest, because it is widely recognized that the speciation of metal ions can profoundly affect their separation behavior.

The aim of this paper is to explore the use of solid and solution-combustion derived metal oxides, MgO, ZnO and Al_2O_3, and study of their performances in Co^{2+} uptake from aqueous solutions. In particular, the objective is to obtain a better understanding of these two processes, showing whether the solution combustion favors Co^{2+} uptake, depending on the amount of water used in the solution during the synthesis process.

EXPERIMENTAL

Materials

Analytical grade reagents without further purification and distilled water were used in the preparation of solutions. Commercial $Mg(NO_3)_2 \cdot 6H_2O$ A.C.S. reagent 99 wt. % purity, $Zn(NO_3)_2 \cdot 6H_2O$ A.C.S. reagent 99-100 wt. % purity, $Al(NO_3)_3 \cdot 9H_2O$ A.C.S. reagent

98 wt. % purity, and NH_2CONH_2 A.C.S. reagent 99-100 wt. % purity were purchased from Sigma Aldrich. $Co(NO_3)_2\cdot 6H_2O$ A.C.S. reagent 100 wt. % purity was purchased from Baker.

Synthesis by solid-combustion process

For each solid-combustion synthesis, the urea quantities used varied from 0.2 to 0.5 g and the weight of the precursors utilized were 0.2 g of each metal nitrate to prepare four different mixtures with urea to metallic nitrates wt. % ratio of 1:1, 1.5:1, 2:1 and 2.5:1 (Table 1). The mixtures were suspended in 1 ml of distilled water until homogeneous solutions were obtained. They were then heated until most of the water had evaporated with the help of an electric grill, resulting in an integrated solid. Then the resulting pastes were transferred to a 30 ml crucible, which was introduced for five minutes into a muffle furnace, previously heated to 800°C. The entire combustion process was completed in 5 minutes, producing the corresponding metal oxides. In solid state combustion, initial reactants, are all in the solid state.

Table 1. Urea to metal nitrates wt. ratio by solid-combustion process at 800°C for 5 min.

Urea to metal nitrates wt. ratio	Sample labels
1 : 1	MgO (A), ZnO (A), Al_2O_3 (A)
1.5 : 1	MgO (B), ZnO (B), Al_2O_3 (B)
2 : 1	MgO (C), ZnO (C), Al_2O_3 (C)
2.5 : 1	MgO (D), ZnO (D), Al_2O_3 (D)

Synthesis by solution-combustion process

Some samples were prepared by the solution-combustion process, diluting the integrated solid, mentioned in the previous section, with 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ml of distilled water, respectively. These humid mixtures were then transferred directly to 30 ml crucibles to the pastes, just before the 5-minute heating process was performed at 800°C. The essential difference between solid-combustion and solution-combustion methods was that, in the solid-combustion synthesis, the sample introduced into the furnace was dried, whereas in the solution-combustion procedure, it was wet.

Characterization

X-ray powder diffraction patterns were obtained using a Siemens D-5000 powder diffractometer coupled to a copper anode tube. The $K_{\alpha 1}$ radiation ($\alpha = 1.54186$ Å) was selected with a diffracted beam monochromator. The resulting compounds were identified by the corresponding Joint Committee on Powder Diffraction Standards (JCPDS) files. To make sure that no organic radicals due to urea combustion remained, infrared experiments were performed. A spectrophotometer Nicolet 550 was used, and the samples were mixed to KBr in the conventional way.

N_2 adsorption

The N_2 adsorption-desorption isotherms and surface area (BET model) of the samples were determined in a Minisorp II equipment from Bel-Japan, using a multipoint technique. Samples were previously degasified at 60°C for 24 hours in vacuum.

Co^{2+} adsorption

Co^{2+} adsorption on Mg, Zn and Al oxides was carried out in batch mode experiments at room temperature by mixing 0.1 g of each metallic oxide and 10 ml of $Co(NO_3)_2\cdot 6H_2O$, $1\text{x}10^{-2}$ M solution at pH 6.1 in closed vials. The samples were shacked for 2 hours. Solids and liquids were then separated by centrifugation. Thereafter, the amount of Co^{2+} retained (percentage) by the solids at equilibrium were measured in the remaining solutions using a Shimadzu ultraviolet-visible 265 spectrophotometer analyzer at $\lambda = 511$ nm. pH measurements of the solutions after Co^{2+} uptake were made with a pH meter, Cole Parmer model 05669-20. Reference Co^{2+} solutions at the same pH values (10.0 for MgO, 7.3 for ZnO and 6.5 for Al_2O_3) of the final dispersion were also determined._

RESULTS

Metal oxides synthesized by solid-combustion process

Figures 1-3 shows X-ray diffraction (XRD) patterns of the products synthesized by the solid-combustion process utilizing different urea to metal nitrates ratios. The synthesized products were identified by XRD according to the JCPDS files. Those with numbers 045-0946 and 070-8070 corresponded to periclase MgO (Figure 1), and zincite ZnO (Figure 2), respectively. In Figure 1, it is clear that all the sharp and well-defined peaks correspond to the pure phase of MgO, independently of the different urea to metal ratio utilized. There was no other characteristic peak, which could indicate the presence of impurities. In the case of ZnO, X-ray diffraction patterns of the prepared samples shown in Figure 2 evidenced the presence of only one component, zincite. Figure 3 shows the XRD patterns of the Al_2O_3 JCPDS files products 010-0173 and 050-0741 that correspond to two different Al_2O_3 phases, α-alumina (Al_2O_3) and γ-alumina (Al_2O_3) structures, respectively. The sharp and well-defined peaks present in this sample correspond to α-Al_2O_3 phase. The γ-alumina (Al_2O_3) shows the presence of large quantities of amorphous materials, a non-crystalline structure, which was formed by the samples with a urea to $Al(NO_3)_3 \cdot 9H_2O$ wt. % ratio of 1:1, and which is known to have a very high surface area [8].

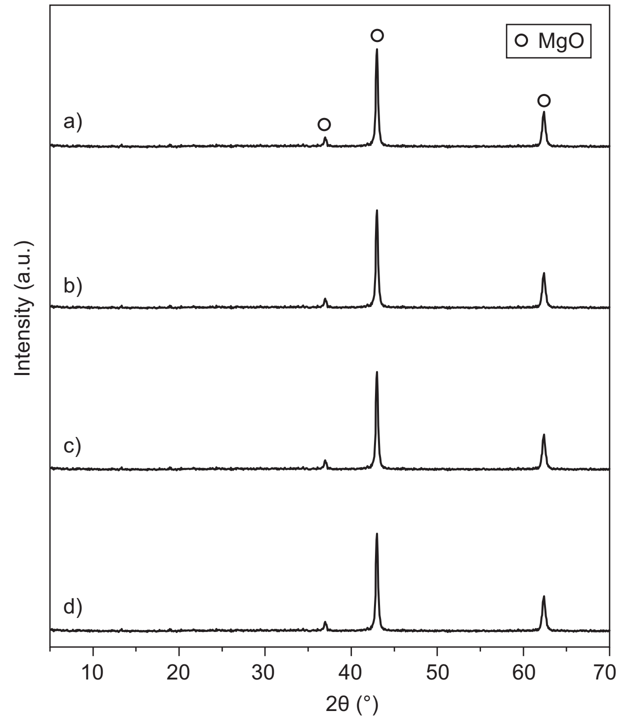

Figure 1. X-ray diffraction patterns of MgO samples prepared by solid-combustion process at 800°C. Urea to metal to nitrate wt. % ratio: a) 1:1, b) 1.5:1, c) 2:1 and d) 2.5:1.

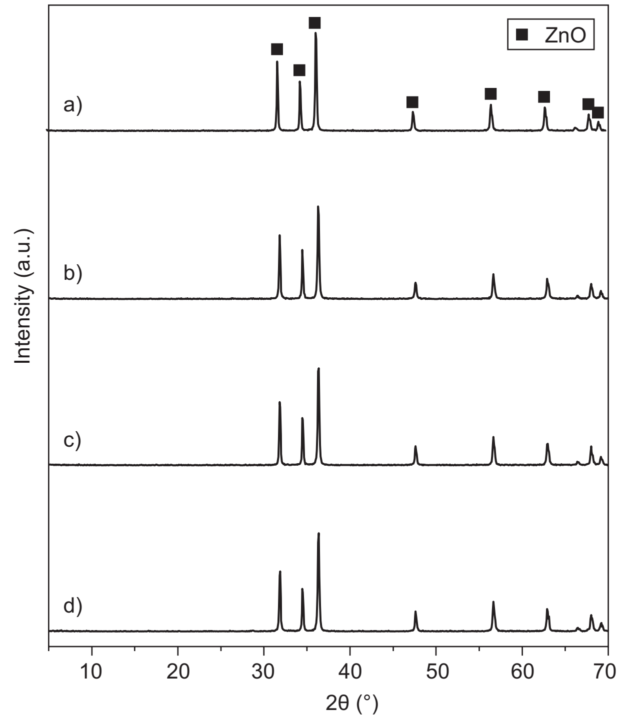

Figure 2. X-ray diffraction patterns of ZnO samples prepared by solid-combustion process at 800°C. Urea to metal nitrate wt. % ratio: a) 1:1, b) 1.5:1, c) 2:1 and d) 2.5:1.

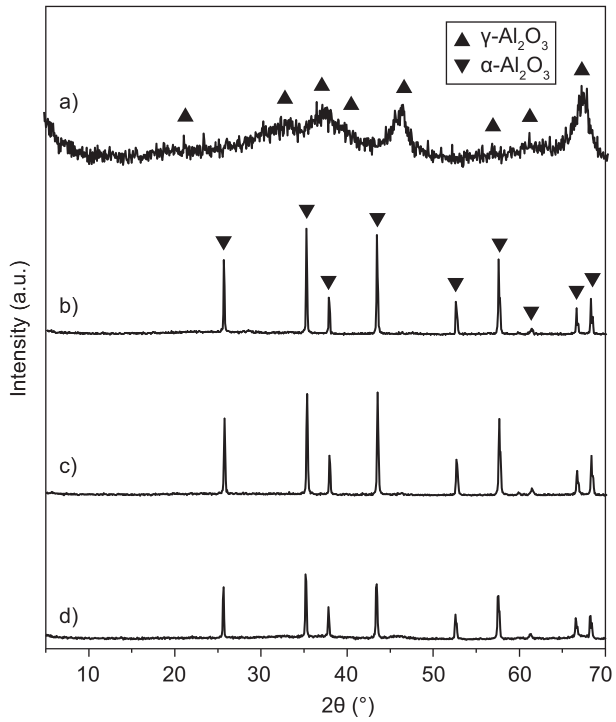

Figure 3. X-ray diffraction patterns of Al_2O_3 samples prepared by solid-combustion process at 800°C. Urea to metal nitrate wt. % ratio: a) 1:1, b) 1.5:1, c) 2:1 and d) 2.5:1.

Co^{2+} uptake on metal oxides prepared by solid-combustion processes

Considering the solid-combustion synthesis of metal oxides, the general procedure was to use the fuel, in this case urea, with the corresponding metal nitrate to be mixed in a proper ratio. The variations of the Co^{2+} uptake capacities (percentages) obtained on each of the three different metal oxides synthesized by solid-combustion process were determined. The final precipitation of cobalt ions in a reference solution at the same pH values (10.0 for MgO, 7.3 for ZnO and 6.5 for Al_2O_3) were also determined. The final precipitations of cobalt ions in the reference solution were found to be 79.45 % for MgO, 9.68 % for ZnO and 7.75 % for Al_2O_3. Figure 4 represents the variations of the Co^{2+} adsorption capacities (percentage) obtained in the residual liquids on each of the three different metal oxides synthesized by solid-combustion process. The maximum Co^{2+} adsorption on the oxides was found to be 8.39 % for MgO and 25.04 % for ZnO. As can be seen in this figure, pH values of the liquids after separation in the final dispersion were also determined. Co^{2+} adsorption was increased on MgO and ZnO oxides as a function of the urea to metal nitrate wt. ratio up to 2:1; at higher values, Co^{2+} adsorption decreased in both cases.

On the other hand, the maximum Co^{2+} adsorption 31.88 % on the Al_2O_3 samples was produced with the sample synthesized with the minimum quantity of urea, which corresponded to the amorphous sample γ-Al_2O_3 (see XRD results). At higher urea content, the product was crystalline with the formation of the stable alpha phase. When the urea content was increased in this case, the Co^{2+} adsorption was decreased.

Co^{2+} adsorption on metal oxides prepared by solution-combustion processes

Those materials prepared by the solid-combustion process with the highest Co^{2+} adsorption capacity (Figure 4) were used to study the samples prepared by the solution-combustion process, which hereinafter are called MgO^h, ZnO^h, and $Al_2O_3{}^h$ (γ-alumina). Figure 5 shows Co^{2+} adsorption on MgO^h, ZnO^h and $Al_2O_3{}^h$ (γ-alumina) samples prepared by solution-combustion process with different distilled water amounts in the synthesis process (0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml). Results demonstrate that in all cases, retained Co^{2+} on these solids increases first with increasing distilled water in the solution, but afterward decrease slightly with further increases in the amount of distilled water. The pH values of the equilibrium solution after Co^{2+} retention are given in Table 2. 1

Table 2. pH of the equilibrium solutions after Co^{2+} uptake on oxides obtained by solution-combustion process utilizing different amounts of water (1.0-2.0 ml) heated at 800°C for 5 min.

Samples	Water	pH
MgO	1.0 ml	10.1
MgO	1.5 ml	9.9
MgO	2.0 ml	9.9
ZnO:	1.0 ml	7.3
ZnO	1.5 ml	7.3
ZnO	2.0 ml	7.3
γ-Al_2O_3	1.5 ml	6.5
γ-Al_2O_3:	2.0 ml	6.5

**pH of the original Co^{2+} solution: 6.1*

Surface areas of the obtained samples were also determined to develop an understanding of the different behavior of retention amounts of Co^{2+} in the solids. Figure 6 shows some examples of the different N_2 adsorption-desorption isotherms obtained for the metal oxides. As can be seen, all presented different isotherm types, according to the IUPAC. ZnO presented an isotherm type III, which corresponds to non-porous materials in which the Co^{2+} retained and the powered obtained interactions are relatively weak and the interactions play an important role. On the other hand, MgO and γ-Al_2O_3 presented isotherms type II and IV, respectively, according to the IUPAC. These isotherms are usually associated to macro- and meso-porous materials, in which unrestricted monolayer-multilayer retention can occur.

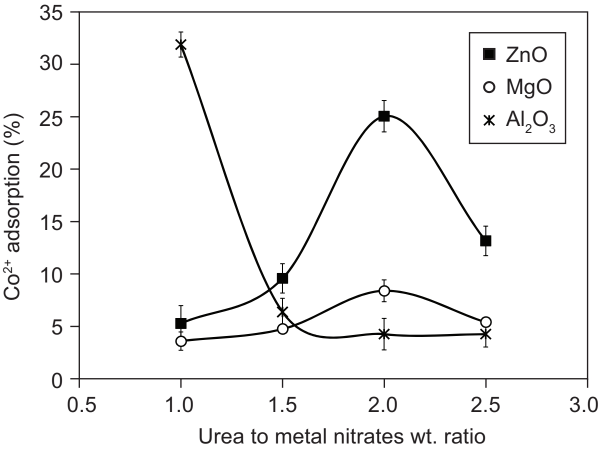

Figure 4. Co^{2+} adsorption on MgO, ZnO and Al_2O_3 samples obtained by solid-combustion process. Urea to metal nitrate wt. % ratio at 1:1, 1.5:1, 2:1 and 2.5:1 respectively.

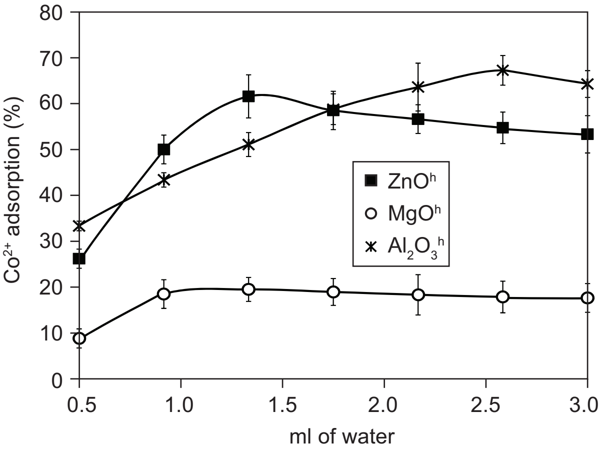

Figure 5. Co^{2+} adsorption on MgO^h, ZnO^h, and $Al_2O_3{}^h$ samples prepared by solution-combustion process with 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of water.

From the isotherms obtained, the surface area (Benauer Emmet Teller (BET) model) and the pore size distribution (BJH model) were determined (Figures 7 and 8). Was found that ZnO samples presented the lowest surfaces areas. Independently of the water addition during the synthesis process, surface areas of ZnO varied between 9 and 18.5 $m^2\,g^{-1}$. MgO presented larger surfaces areas (22.2-37.8 $m^2\,g^{-1}$). The increment observed on the surface areas can be associated with the porous formation. This was confirmed with the porous size distribution graph, in which it can be seen that MgO has some mesoporosity within the range of 2-5 nm. However the amount of adsorbed cobalt ions on MgO shown in Figures 4 and 5 are much lower than the respective cobalt adsorption values on ZnO. Results seem to be contradictory, but during Co^{2+} uptake the solid was transformed and the Co^{2+} solution as well. On the other hand it was found that cobalt adsorption behavior on MgO follows the same trend as those reported for ZnO.

Finally, γ-alumina presented the largest surface areas and pore abundance. The largest surface area was observed on the γ-alumina treated with 2.0 ml of distilled water, 275 m^2 g^{-1} and the pore size distribution was very close to 2.5 nm.

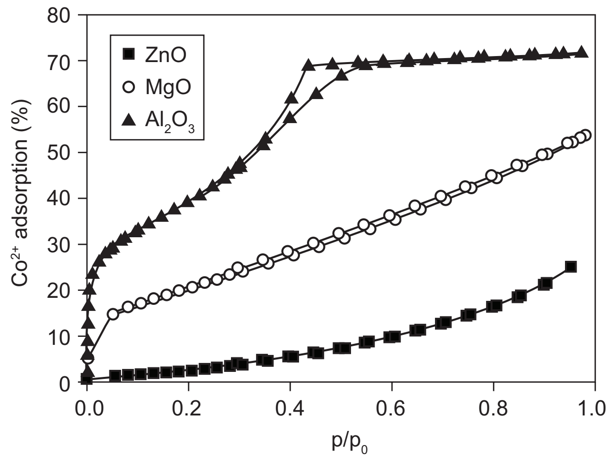

Figure 6. Typical adsorption/desorption isotherms of the three different metal oxides prepared by solution-combustion process; MgO^h, ZnO^h and $Al_2O_3^h$.

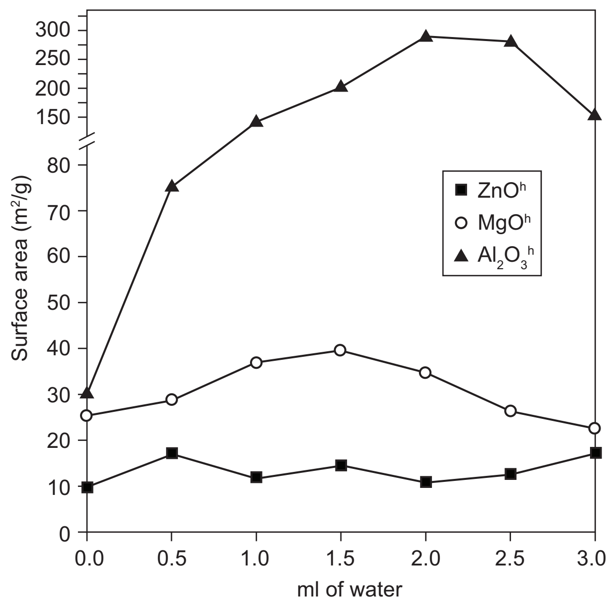

Figure 7. Specific areas of MgO^h, ZnO^h, and $Al_2O_3^h$ samples prepared by solution-combustion process with 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of water.

DISCUSSION

Three different metal oxides, MgO, ZnO and Al_2O_3 were obtained first by solid and then by solution-combustion processes.

Metal oxides synthesized by solid-combustion processes

The plot of the Co^{2+} adsorption on metal oxides, as a function of the urea to metal nitrates ratio of the synthesized materials, depends on the ratio utilized to synthesize them. Figure 4, shows the measured values for Mg and Zn oxides. As noted, the reaction can proceed in two different modes related to the combustion process: 1) increasing Co^{2+} adsorption on the powders obtained when the urea to metal nitrate ratio increases from 1:1 to 2:1. When the urea to metal nitrate ratio is within a proper range, metal oxide products and gases of CO_2, H_2O and NO_2 can be formed directly from the reaction between metal nitrates and urea without the need to get oxygen from outside; and 2) the reaction can also proceed decreasing Co^{2+} adsorption on the powders, when the urea to metal nitrates ratio increases from 2:1 to 2.5:1. In this case, there is excess urea, and the combustion reaction needs oxygen to be supplied externally. Therefore, the reaction is not completed, and the maximum combustion of the fuel is not reached. Co^{2+} adsorption on the solids MgO and ZnO are found to be 8.39 % and 25.04 % respectively, for a urea to metal nitrate ratio of 2:1, which then decreases abruptly to 5.39 % and 13.15 % respectively at a urea to metal nitrate ratio of 2.5:1.

The measured values of cobalt retention on Al_2O_3 samples behave very differently than those obtained on Mg and Zn oxides. Low contents of urea favor the formation of amorphous γ-alumina (Al_2O_3) which is known to have a very high surface area [8], which favors Co^{2+} uptake. At higher urea to metal nitrate ratio amorphous γ-alumina crystallizes in α-alumina, which is a compound with low surface area that consequently has a low Co^{2+} uptake capacity.

Metal oxides prepared by solution-combustion processes

Comparative studies on metal oxides powders prepared by the solution-combustion process have been also carried out, as mentioned above. Thereafter, the analysis of residual Co^{2+} in the water was performed, and the Co^{2+} adsorption capacities (percentage) on metal oxides was established (Figure 5). Co^{2+} uptake on MgO^h, ZnO^h, and $Al_2O_3^h$ (γ-alumina) samples prepared by the solution-combustion process is more efficient than that obtained by the solid-combustion process. As noted, depending on the amount of water utilized during the solution-combustion process, the reaction can proceed first increasing Co^{2+} adsorption capacities from the solution to a maximum of 18.64 % and 58.95 % for MgO and ZnO respectively and then by decreasing it, with further increases in the amount of water added to the mixture during the solution-combustion process.

In the case of $Al_2O_3^h$ (γ-alumina), Co^{2+} adsorption increases constantly from 31.88 % to 64.39 % and then decreases slightly to 61.53 %, when the amount of water in the solution combustion process is increased to 3.0 ml. The decrease of Co^{2+} uptake on the solids observed may be due to the following: A considerable amount of water during the combustion process can cause an increase of evaporation in the solution, carrying away a certain amount of heat through heat loss and resulting in a lower amount of heat for the posterior process. With the additional water added, a fraction of the combustion heat is used to evaporate the excess water.

The effects observed in Figure 5 are related directly to the surface areas of the metal oxides obtained, because the increase of Co^{2+} uptake behaves in a similar way to the surface area of the solids obtained by this process (Figure 7). The surface area values follow the same trend as those reported by Co^{2+} uptake, since the surface of the solution-combustion prepared metallic oxides is larger than that of the solution-combustion prepared samples.

Cobalt ions precipitation on the solid showed an increase, with a pH increase at values around 10. This effect may be explained on the basis of binding sites being protonated, resulting in a competition between H^+ and Co(II) ions for occupancy of the binding sites. As the pH increased and surface functional groups were activated, the Co(II) uptake increased. When the pH value is lower than 7.5, Co(II) is present in the solution mainly in the form of Co(II) ions, according to the chemical equilibrium diagram for Co(II) speciation [9]. The cationic bivalent species corresponded to the octahedral $Co(H_2O)_6^{2+}$, as reported elsewhere [*7,* 10]. The positively charged $Co(OH)_4^{4+}$ and $Co(OH)^+$ hydrolytic products appear in the range of pH 7-12, while the neutral Co(II) hydroxide $Co(OH)_2$ species starts precipitating at higher pH values, 7.5, and becomes predominant at pH 11 (Figure 9). Therefore, it can be concluded that at lower equilibrium pH values, Co(II) is retained from the solution as Co(II) on oxides and that the oxide surface, which is negatively charged in the higher pH region, may contribute to the overall removal process by the adsorption of positively charged hydrolytic chemical species $Co(OH)_4^{4+}$ and $Co(OH)^+$.

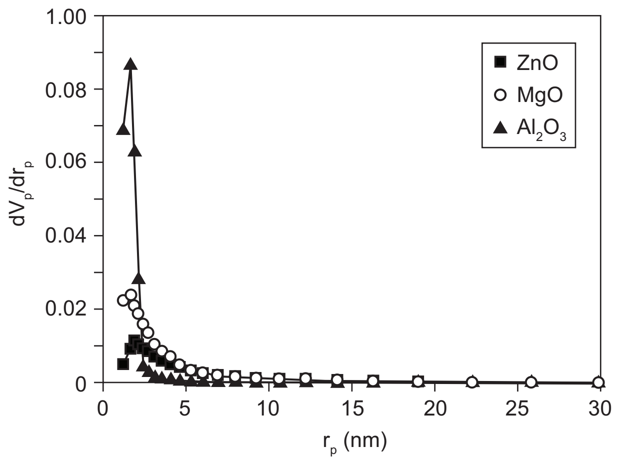

Figure 8. Pore radius of MgO^h, ZnO^h, and $Al_2O_3^h$ samples determined by the BJH model.

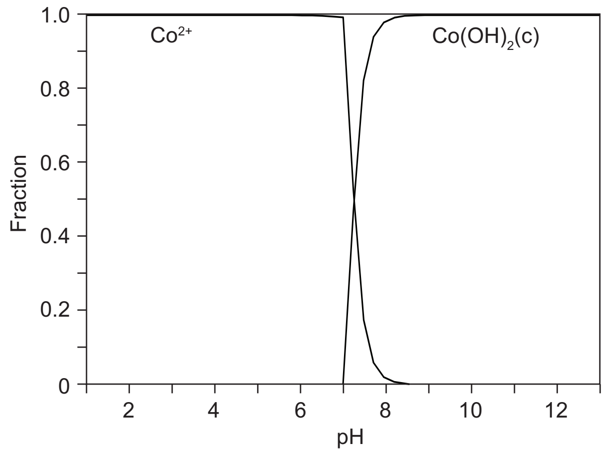

Figure 9. Distribution diagram of hydrolyzed Co^{2+} species, Fraction versus pH.

CONCLUSIONS

MnO, ZnO, and Al_2O_3 can be prepared at 800°C in a very short time. The urea fuel method appears to be well-suited for the preparation of relatively high surface areas. The advantage of the solution-combustion process is that it has great potential in the preparation of these oxides. In this study, an extensive laboratory investigation has been carried out to evaluate the performance of combustion-derived metal oxides as materials to retain Co^{2+} ions. These oxides are found to be very effective in removing Co^{2+} from the aqueous environment. The powders have been prepared by solid- and solution-combustion process. Due to porous nature, large surface area, and fine particle size, metal oxides with good retention characteristics can remove ions that present in water. Solution combustion synthesis appears to meet the demands of solid materials with desired composition. By controlling the amount of water in the solution combustion, it is possible to obtain oxide particles adequate to retain the Co^{2+} present in water. Thus, the combustion method of preparing metallic oxides appears to be a breaking-down process.

Acknowledgments

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