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OBTAINING ZINC OXIDE FROM AQUEOUS SOLUTIONS OF KOH AND $Zn(CH_3COO)_2$

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Zinc oxide was obtained by precipitation from solutions of KOH and $Zn(CH_3COO)_2$. The effect of excessive presence of one of the reagents and temperature on the physico-chemical properties, structure and size of zinc oxide particles was analysed. The main aim of the study was to establish the optimum conditions of precipitation that would ensure getting the uniform particles of zinc oxide of the minimum diameter. The zinc oxide obtained had particles of nano- and micrometric size. The adsorption/desorption isotherms indicated the mesoporous character of the product. The wettability of ZnO obtained was determined first of all by the morphology and particle size.

key words: ZnO, precipitation, particle size distribution, surface morphology, wettability, adsorptive properties

INTRODUCTION

For the last decade, particular attention has been paid to the techniques for producing nanomaterials with interesting properties. Nanotechnology has been the subject of research at many corrorate and academic research centres (Zhong, 2008; Zhang, 2002; Schmidt-Mende, 2007).

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Besides clay nanomaterials like montmorillonite and carbon nanotubes, of great importance are nanometric metals and their oxides. Nanomolecular ultrafine zinc oxide of particles size from a few to a few ten nanometers are of particular interest. They are many times smaller than those of the standard zinc oxide particles used as an activator in synthetic rubber processing (Wang, 2003, Lu, 2000, Kahn, 2005).

In nature, zinc oxide occurs as the minerals zincite and franklinite in combination with iron oxides and magnesium oxides. It is mainly obtained from zinc ores such as calamine ($ZnCO_3$) or sphalerite (ZnS), and from the post-reaction sludge formed in the processes of reduction of organic compounds with zinc. Making use of the technique of sublimation at high temperature, with careful control of crystal growth and full analytical monitoring, it is possible to obtain ZnO nanocrystals in the shape of combs, rings, helices, spirals, arches, ribbons, strings and cages (Pyskło, 2007).

Particularly promising are ZnO nanopowders, which can be used in many technological processes. They have specific properties including semiconducting, piezoelectric and pyroelectric ones (Duan, 2007). That is why zinc oxide can be used in optoelectronics and laser technology, ceramics, as gas sensors and in production of paints (Wang, 2003; Gao, 2002; Paneva, 1998; Ristić, 2005). As a natural consequence of the progress in nanotechnology, interest in zinc oxide is groving.

EXPERIMENTAL

Precipitation was performed in a reactor 0.5 dm^3 in capacity equipped with a fast-rotating stirrer. The speed of the stirrer rotation was close to 1200 rev/min. A solution of potassium hydroxide was introduced in doses into a solution of zinc acetate (or the reverse) at different temperatures from 20 to 80^oC at a ratio of substrates of 1:1, with excess of KOH (POCh. S.A.), or with excess of $Zn(CH_3COO)_2$ (POCh. S.A). The substrates were dosed with the help of a peristaltic pump PB1B-05A at 1.1; 3.0, 11 and 15 cm^3/min. The zinc oxide obtained was filtered off under reduced pressure. The sediment was washed several times with water. After washing, the sample was dried in a stationary drier at 120°C. A schematic presentation of zinc oxide synthesis is shown in Figure 1.

Particle size distribution, surface morphology and wetability were recorded. Particle size distribution was measured with a Zetasizer Nano ZS using the light backscattering method (NIBS), and a Mastersizer 2000 using laser diffraction (both instruments made by Malvern Instruments Ltd.).

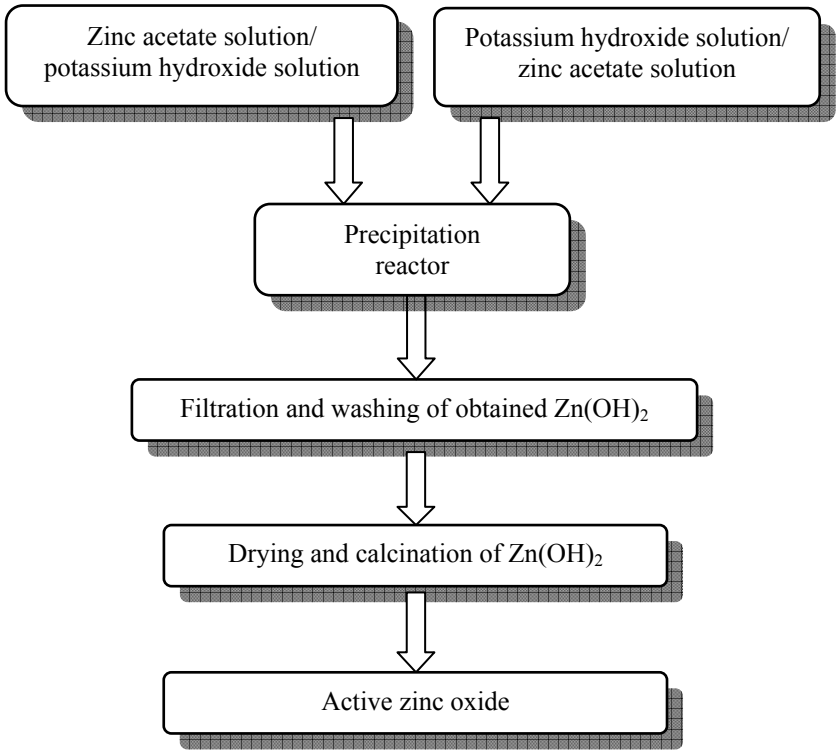


Fig. 1. Schematic presentation of zinc oxide synthesis by precipitation

The degree of dispersion, morphology of the zinc oxide particles and their tendency to agglomeration were assessed using a Zeiss VO40 microscope. Wettability was determined by a Krüss K100 tensiometer on the basis of capillary penetration of water in a sample of ZnO. Isotherms of nitrogen adsorption/desorption on the surface of zinc oxide and surface area were also determined. Measurements were made using Micromeritics ASAP 2020.

RESULTS AND DISCUSSION

At the first stage of the study, synthesis was carried out by introducing a 5% solution of KOH in doses to a 5% solution of $Zn(CH_3COO)_2$ (stoichiometric ratio of reagents). The zinc oxide obtained was characterised by the particle size distribution. The particle size distribution by volume (Fig. 2a) shows one band covering particles 190 to 531 nm in diameter. 27.5% of the total volume represented particles of 295 nm in diameter. The particle size distribution by intensity also shows one band covering the diameters in the range 220 to 459 nm (Fig. 2b). The maximum intensity of 31.4%

corresponds to the particles 295 nm in diameter. The polydispersity index of this sample is 0.682, which indicates a relatively low homogeneity of the particles. This conclusion is confirmed by the data presented in Fig. 3, which shows particle size distributions by volume for the samples of zinc oxide precipitated at the stoichiometric ratio of the reagents, with excess of potassium hydroxide, and with excess of zinc acetate. There was a significant effect of excess of one of the reagents on the sizes of particles of the ZnO solid. The smallest particles were obtained with a 20% excess of zinc acetate solution (Fig. 3).

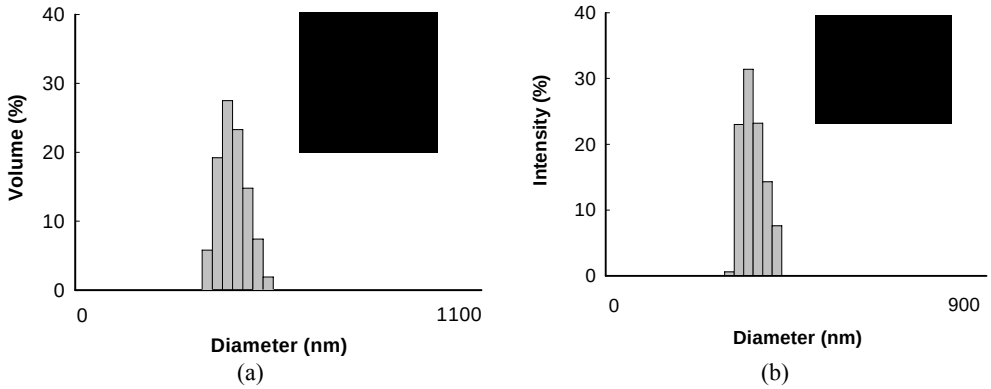


Fig. 2. Particle size distribution of ZnO precipitated by dosing a 5% solution of KOH to 5% solution of $Zn(CH_3COO)_2$ in stoichiometric conditions, by a) volume, b) intensity

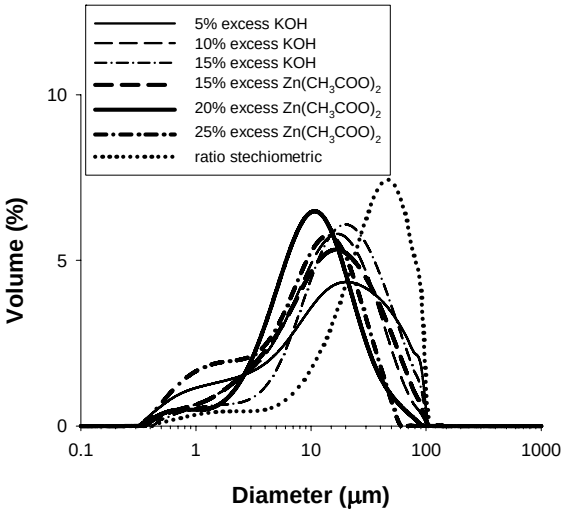


Fig. 3. Comparison of the micrometric particle size distributions versus the volume contribution for ZnO samples precipitated in the presence of excess of KOH or $Zn(CH_3COO)_2$

There were two bands in the particle size distribution by volume of the zinc oxide sample precipitated at the 20% excess of zinc acetate (Fig. 4a) The first was from 43.8 to 58.8 nm, with the maximum volume of 16.7% corresponding to the particles of 50.7 nm in diameter. The second was from 164 to 396 nm, with the maximum volume of 15.8% corresponding to the particles of 220 nm in diameter. There were also two bands in the particle size distribution by intensity for the same sample (Fig. 4b). The first corresponds to particles 50.7 nm in diameter, and the second corresponds to particles between 190 and 342 nm in diameter, with a maximum intensity at 190 nm. Fig. 4c confirms the undesirable contribution of micrometric size particles in the sample precipitated in the presence of 20% excess of zinc acetate. According to the micrometric particles size distribution (Fig. 4c), the sample contains 90% of particles smaller than 30.4 μm in diameter, 50% of particles of 9.61 μm in diameter, and 10% of particles not greater than 2.79 μm in diameter. Fig. 4d shows a SEM image of the sample obtained in the presence of 20% excess of zinc acetate solution confirming the occurrence of nano- and micrometric particles.

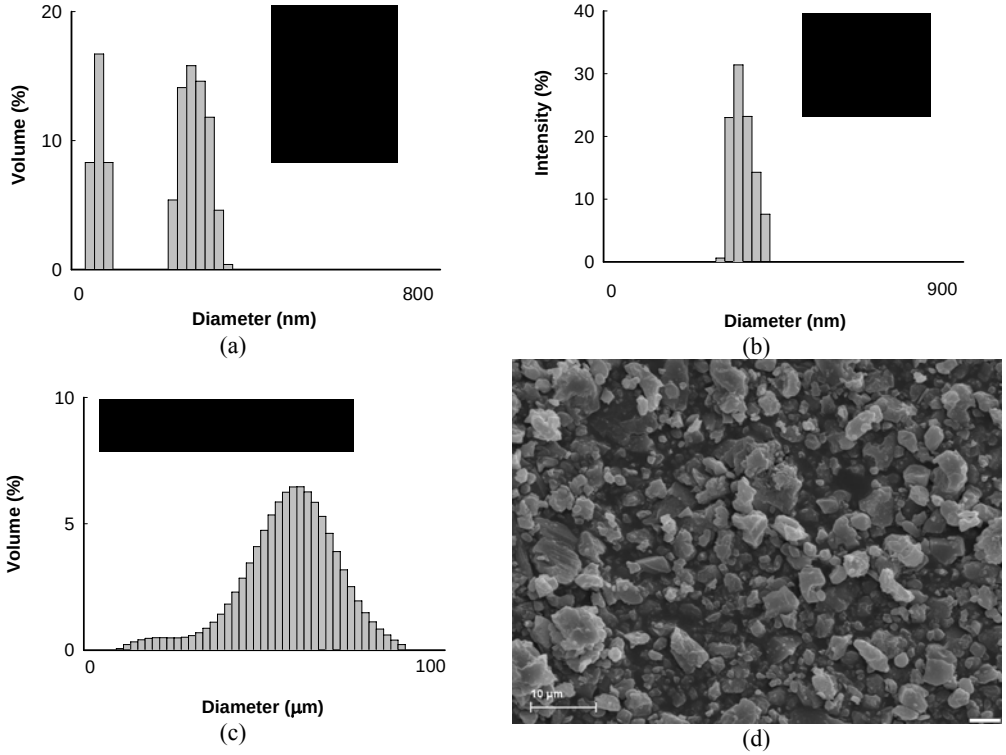


Fig. 4. Particle size distribution of ZnO samples precipitated in the presence of 20% excess of $Zn(CH_3COO)_2$ solution by (a) volume contribution for the particles of diameters from the range 0.6 – 6000 nm, (b) intensity, (c) volume contributions for the particles of diameters from the range 0.02 – 2000 μm, (d) SEM photograph

The effect of temperature on the particle size of zinc oxide precipitated was then analysed. Fig. 5 and Table 1 show the particle size distribution and particle diameters of the zinc oxide sample precipitated in the presence of 20% excess zinc acetate solution at different temperatures from 20 to 80°C. The higher the temperature of precipitation, the greater the size of zinc oxide particles.

Table 1. Analysis of the micrometric particles size of ZnO precipitated at different temperatures

Temperature	Diameter (μm)	Volume (%)	Diameter (μm)		
			d(0.1)	d(0.5)	d(0.9)
20°C	0.36	0.06	2.79	9.62	30.4
	11.5	6.46			
40°C	0.36	0.01	3.06	14.4	53.6
	15.7	5.75			
60°C	0.48	0.08	1.99	9.78	30.1
	15.1	5.49			
80°C	0.36	0.01	2.39	17.1	55.8
	15.1	5.08			

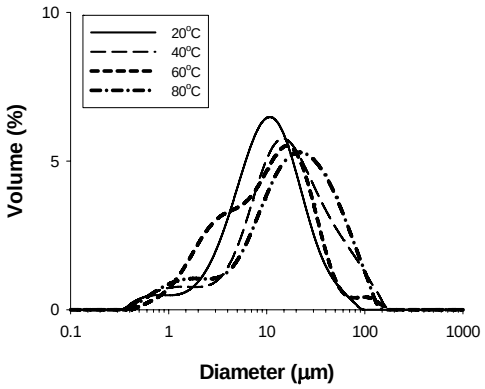


Fig. 5. Comparison of micrometric particle size distributions versus volume contribution for ZnO samples precipitated at different temperatures at a dosing rate of KOH solution to $Zn(CH_3COO)_2$ solution of 15 cm^3 and at the stoichiometric ratio of the reagents

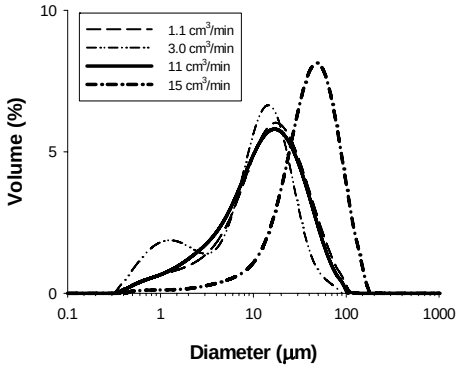
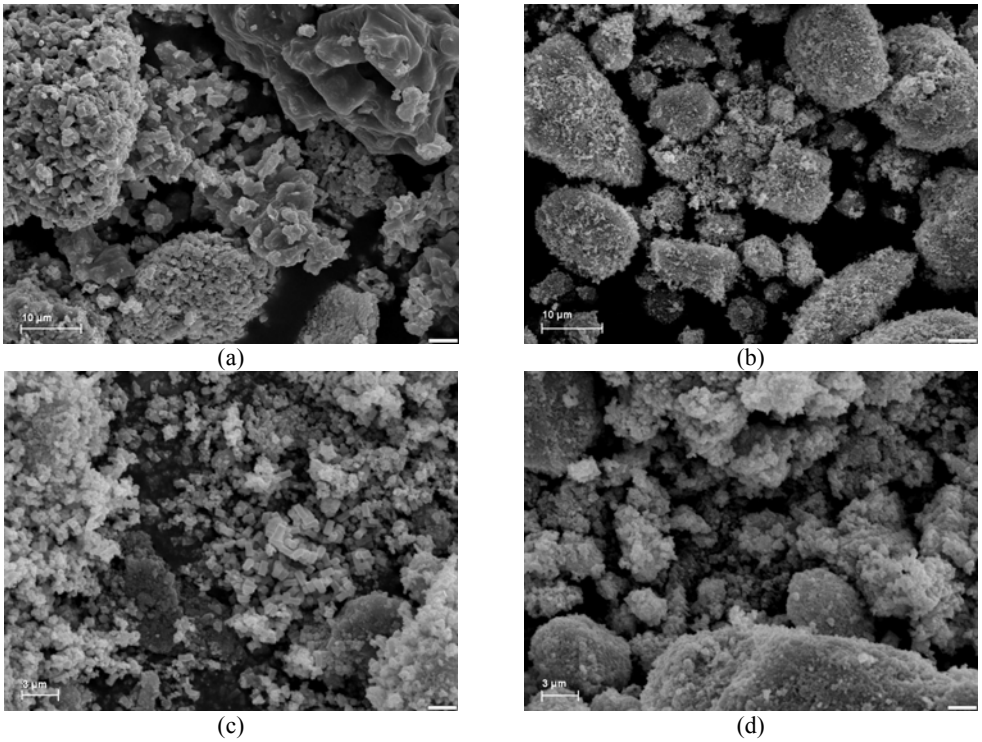


Fig. 6. Comparison of micrometric particles size distributions versus volume contribution for ZnO samples precipitated at different dosing rates of KOH solution to $Zn(CH_3COO)_2$ solution, at 20°C and at the stoichiometric ratio of the reagents

The effect of the rate of dosing on the particle size distribution was also studied. Micrometric particle size distributions obtained for the samples of ZnO synthesised at different rates of dosing of potassium hydroxide to zinc acetate are compared in Figure 6. The optimum rate was 11 cm^3/min. The SEM images presented in Fig. 7 support this conclusion. The ZnO sample precipitated at the rate of KOH dosing to

$Zn(CH_3COO)_2$ of 11 cm^3/min has small almost spherical particles (Fig. 7c) with little tendency to agglomerate. The ZnO samples obtained at the higher or lower rates of dosing show a considerable tendency to agglomerate (Fig. 7a and d).



(a) (b)

(c) (d)

Fig. 7. SEM images of ZnO samples precipitated at different rates of dosing of KOH solution to $Zn(CH_3COO)_2$ solution of (a) 1.1 cm^3/min, (b) 3.0 cm^3/min, (c) 11 cm^3/min, (d) 15 cm^3/min, at 20°C, at the stoichiometric ratio of the reagents

Wettability was lowest in the sample precipitated in the presence of 5% excess of KOH (Fig. 8). For this sample, wetting was completed after 900 s. Wettability was highest in the samples precipitated in the presence of 10% and 15% excess of KOH solution. Wettability of the ZnO obtained is mainly determined by the size and morphology of particles.

Fig. 9 shows the isotherms of nitrogen adsorption/desorption on the surface of the ZnO samples obtained. The character of the curves indicates the mesoporous structure of the samples. The amount of nitrogen adsorbed on all samples increases slowly until the relative pressure reaches 0.9. Above this pressure, the amount of adsorbed nitrogen rapidly increases to reach the highest value of 45 cm^3/g for the samples precipitated at 20°C and 40°C at $p/p_0 = 1$. For zinc oxide precipitated at 60°C, the amount of nitrogen adsorbed is lowest at $p/p_0 = 1$ and reaches 35 cm^3/g. The surface area of the samples

obtained is small and does not exceed 20 m^2/g (Tab. 2). With increasing temperature, the BET surface area of the ZnO samples decreases.

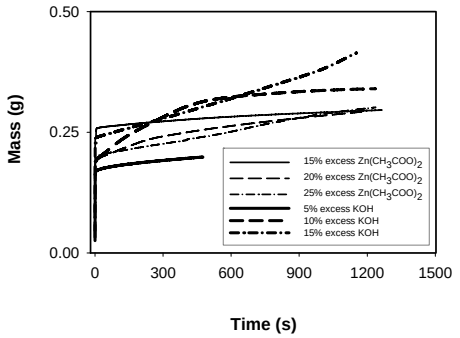


Fig. 8. The wettability curves of ZnO samples precipitated at different temperatures and the other parameters constant

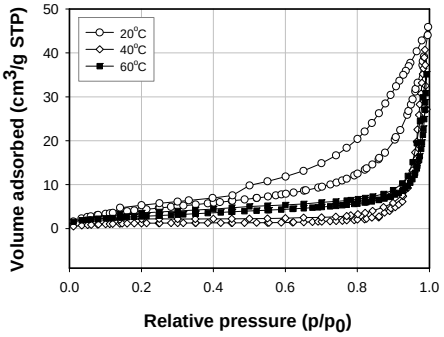


Fig. 9. Isotherms of nitrogen adsorption/desorption for selected samples of ZnO

Table 2. Basic parameters determining the adsorption properties of zinc oxide samples precipitated at different temperatures

Temperature	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
20°C	16.6	0.07	16.4
40°C	4.0	0.06	47.4
60°C	10.0	0.05	14.2

CONCLUSIONS

Zinc oxide obtained by precipitation from water solutions of potassium hydroxide and zinc acetate is characterised by small particles. The sample of the smallest particles was obtained by dosing a 5% solution of KOH to a 5% solution of $Zn(CH_3COO)_2$. The particle size of the samples was found to depend on the excess of the substrates. 20% of zinc acetate gave a sample with very small particles close to 50 nm in diameter. Unfortunately, this sample also contained micrometric size particles, as indicated by the particle size distribution plots and SEM photographs. Based on particle morphology, the optimum rate of dosing of KOH to $Zn(CH_3COOH)_2$ is 11 cm^3/min. Increasing the temperature of precipitation increases the diameters of the ZnO particles obtained. Wettability was lowest in the sample precipitated in the presence of 5% excess of KOH solution, and highest in the samples precipitated in the presence of 10% and 15% exceed of KOH solution. The isotherms of nitrogen adsorption desorption indicate the mesoporous character of ZnO samples obtained.

The sample of ZnO precipitated at 20°C had a BET surface area of 16.6 m^2/g. The higher the temperature of precipitation, the lower the surface area of the samples. This is probably related to the presence of particles of greater diameters.

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Kołodziejczak-Radzimska A., Jesionowski T., Krysztafkiewicz A., *Otrzymanie tlenku cynku wodnych roztworów KOH i $Zn(CH_3COO)_2$,* Physicochemical Problems of Mineral Processing, 44 (2010), 93-102, (w jęz. ang), http://www.minproc.pwr.wroc.pl/journal

Tlenek cynku został otrzymany w wyniku wytrącenia z roztworów KOH i $Zn(CH_3COO)_2$. Analizowano wpływ nadmiarowej objętości jednego z reagentów i temperatury na fizykochemiczne

właściwości otrzymanego materiału. Głównym celem badań było ustalenie optymalnych warunków prowadzenia procesu tak aby otrzymać jednakowe cząstki tlenku cynku o minimalnej średnicy. Otrzymany tlenek cynku miał wymiary cząstek w nano i mikrometrycznej skali. Izotermy adsorpcji i desorpcji wskazują, że produkt ma mesoporowaty charakter. W pierwszym rzędzie została określona zwilżalność otrzymanego tlenku cynku.

słowa kluczowe: ZnO, precypitacja, skład ziarnowy, morfologia powierzchniowa, zwilżalność, własności absorpcyjne