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THE CHARACTERIZATION OF THE IRON OXIDE PARTICLES SYNTHESIZED AT TWO SELECTED TEMPERATURES

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Abstract

The structural, surface and pore properties of synthesized iron oxide samples were studied. The iron oxide samples were prepared by a chemical method at selected temperatures of 20 and 85°C. The changes in the structure were investigated using X-ray diffraction analysis. The scanning and transmission electron microscopy were used to characterize the shape and the size of particles and the pore structure characteristics were obtained from the nitrogen adsorption experiments. It followed from the experiments, that the temperature of synthesis influences the structural parameters of iron oxide particles.

Key words: *synthesized iron oxides, XRD, TEM, SEM analysis, nitrogen adsorption method.*

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1. Introduction

Research in preparation of magnetic particles is of great importance due to their industrial importance: they can be used for example in remediation of oil spill [1], in preparation of magnetic fluids [2], for therapeutic or diagnostic purposes [3]. Magnetic particles can be also used to adsorb contaminants from aqueous or gaseous effluents. In [4] were the magnetic particles used to cover the surface of synthetic zeolite, offering such a separation of the adsorbent from the medium by a single magnetic process. The authors in [5] used the nano-scaled magnetic particles for batch adsorption studies of contaminants from aqueous model solutions.

The aim of this paper is the study of the structural, surface and pore properties of synthesized iron oxide particles. The process of synthesis was investigated at two temperatures – 20 and 85°C. The structural, physical and chemical properties of the samples, involving the crystal and geometrical structure, surface properties, among them the surface area and PSD are the basic quantities specifying the porous structure of the material. The methods of powder X-ray diffraction, scanning (SEM), transmission electron microscopy (TEM) and nitrogen adsorption measurements were used for investigation and analyse of the changes in structure of synthesized samples of iron oxides.

The obtained results can be used for the study of the role of iron oxides precipitated on the surface of natural zeolite as a bearer when following the target of increasing of the sorption properties of zeolite.

2. Experimental

2.1. Materials

The iron oxide was synthesized from the solution of Fe ions prepared from $FeSO_4.7H_2O$ and $FeCl_3$ salts in Fe (II)/(III) ratio of 0.5 under continuous stirring for 30 minutes in nitrogen atmosphere at different selected temperatures 20 and 85°C [6]. The particles were precipitated by NH_4OH solution added drop wise. The final product was decanted, filtrated and dried at the temperature 70°C.

2.2. Characterization

The mineralogical properties of the prepared samples were examined by an X-ray Philips X'PERT powder diffractometer, operating in the reflexion mode with CuKα radiation, equipped with an automatic divergence slit and sample spinner. The range 2-72 deg 2 theta was selected for the data collection. The phase composition was evaluated by catalogue JCPDS (Joint Committee on Powder Diffraction Standards). The average size of synthesized iron oxide particles was estimated using Scherrer's formula. The detailed structural and morphological characterization of iron oxide sample was carried out by transmission electron microscopy (TEM) using the method of replicas and by scanning electron microscopy (SEM). The identification of chemical composition of powder samples was realized by energy-dispersive X-ray analysis (EDX).

The porous properties of iron oxide samples were studied using nitrogen adsorption method realized on the ASAP 2400 (Micrometrics, USA) apparatus at 77K. Before measuring the samples were heated at temperature 300°C and degassed at 3Pa. Specific surface area was calculated from the adsorption isotherms, according to the BET method in a range of relative pressure of saturation and equilibrium from 0.03-0.2 p/p_0. The pore size distribution was determined from the desorption isotherms.

3. Results and discussion

3.1. X-ray diffraction, TEM and SEM analysis

The synthesized iron oxide was investigated by X-ray diffraction. The phase analyse of synthesized iron oxide at both selected temperatures (Fig. 1-2) showed diffraction peaks coincident for maghemite and magnetite reflections. The XRD pattern of both synthesized iron oxide showed crystalline structure. Two expressive peaks appeared for the sample of iron oxide synthesized at 85°C. It followed from Rietveld analyse, that the lattice parameter of crystalline structure a = 0.83574 nm corresponds to γ-Fe_2O_3 crystalline structure.

The mean dimension of crystallites composing the powder samples is related to the X-ray diffraction broadenings and its calculation gives the

following values: for iron oxide synthesized at 20°C the size of crystallites is 17.2nm and for 85°C the size is 19.1nm.

The sample of iron oxide 85°C was observed also by TEM using the method of replicas. By the method of electron diffraction, the six crystallographic planes (221, 420, 432, 321, 310, 521) corresponding only to maghemite γ-Fe_2O_3, were found (Fig. 3). The TEM images of maghemite synthesized at 85°C allowed deducing of the average crystallite size to 20.8nm.

The SEM images (Fig. 4) showed the fine iron oxide particles and confirmed their tendency to form aggregates. This feature is typical for ultrafine powder particles. The EDX spectrum of iron oxide synthesized at 85°C displayed the peaks corresponding to single elements Fe and O occurring in the powder sample, indicating such their concentration in the sample.

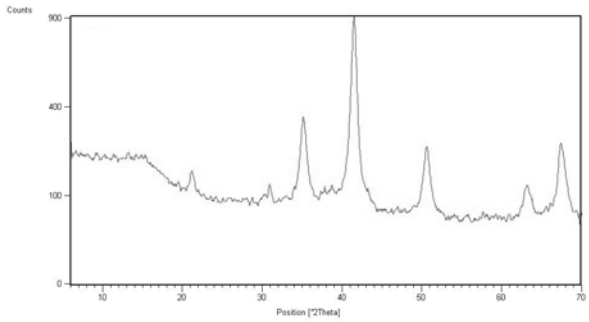

Fig. 1. XRD pattern of iron oxide synthesized at 20°C

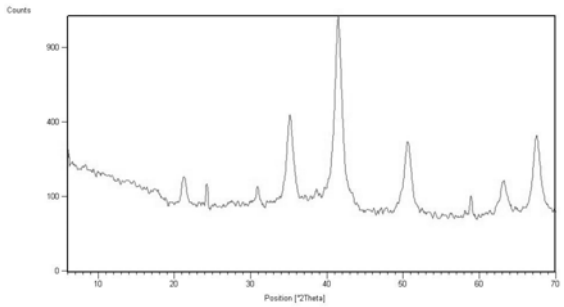

Fig. 2. XRD pattern of iron oxide synthesized 85°C

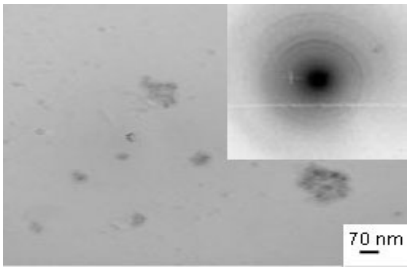

Fig. 3. TEM image of iron 85°C oxide particles and their electron diffraction pattern

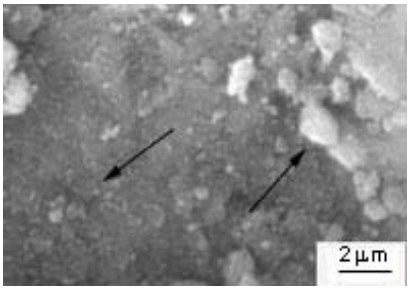

Fig. 4. SEM image of fine iron oxide particles synthesized at 85°C and their aggregates

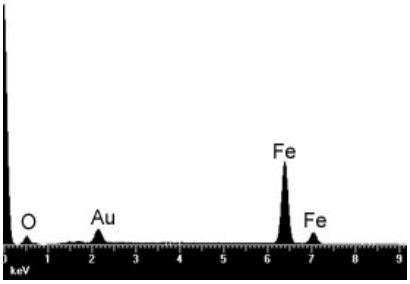

Fig. 5. EDX analyse of iron oxide

3.2. Nitrogen adsorption methods

The total adsorption and desorption isotherms were obtained from the volume of adsorbed and desorbed gas plotted against the relative pressure (Fig 6) for iron oxides synthesized at 20 and 85°C. The hysteresis

loops are typical for the mesopore structure of materials according to the IUPAC (International Union of Pure and Applied Chemistry) report [7].

The values of BET surface area calculated from the adsorption isotherm in the range of relative pressure from 0.03 to 0.2, of external surface and pore volume are included in Table 1. The specific surface area of synthesized iron oxide at 85°C is lower than values corresponding to the iron oxide prepared at 20°C, what is in relation to their average size, calculated using Scherrer's formula. The total pore volume is lower for iron oxide synthesized at 20°C.

Table 1. Structural characteristics of iron oxide samples

Sample	S_{BET} [m^2/g]	V_a [cm^3/g]	V_{mikro} [cm^3/g]	S_t [m^2/g]
Iron oxide 20°C	93.8	0.274	0.003	85.4
Iron oxide 85°C	81.2	0.331	0.004	70.4

The distribution of adsorbed volume on the iron oxide samples was estimated by the Barrett-Joyner-Hallenda (BJH) method from the desorption isotherms. The pore size distribution curve of iron oxide 85°C has one expressive peak, showing its maximum at 18nm. The curve of iron oxide 20°C show peaks between 12 and 14nm, Fig 7. It should be assumed, that the iron oxide synthesized at 20°C has smaller pores due to smaller sizes of particles as calculated according to Scherrer.

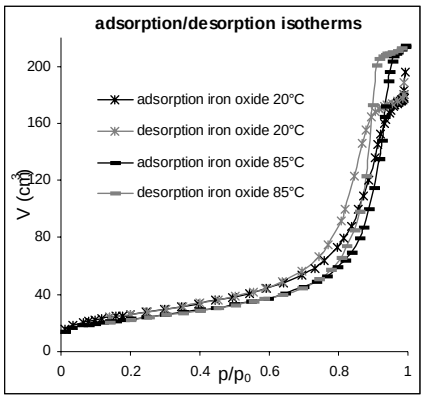

Fig. 6. Adsorption-desorption isotherms of synthesized iron oxide particles

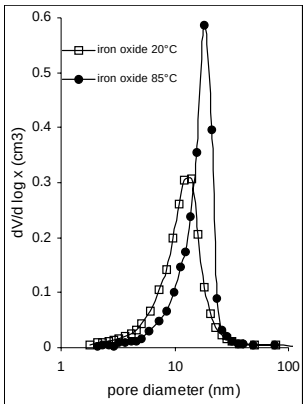

Fig. 7. Pore size distribution of synthesized iron oxide samples

4. Conclusion

The structural characteristics of synthesized iron oxide particles at selected temperatures 20 and 85°C were studied. It followed from the results that the iron oxide synthesized at 85 °C has more crystalline structure. The diffraction peaks of both samples are coincident for maghemite and magnetite reflections. The lattice parameter found by Rietveld analyse corresponds to the crystalline γ -Fe_2O_3. Using the Scherrer's formula the size of crystallites of iron oxide samples synthesized at 20 and 85°C was calculated as follows: 17.2nm and 19.1nm respectively. The TEM electron diffraction method confirmed six crystallographic planes, belonging to maghemite. The behaviour of fine powder particles creating aggregates was observed by SEM. As follows from the Table 1, the BET surface value obtained from nitrogen adsorption measurements for iron oxide synthesized at 85°C is lower than for the sample prepared at 20°C and the total pore volume is higher. From the pore size distribution on Fig. 7 is evident, that the pores are smaller for the sample prepared at lower temperature. That is in accordance with the calculated values of crystallite size.

These results were used in the study of zeolite modification with the aim to enhance its sorption ability. The iron oxide particles precipitated on the bearing zeolite contributed to the changes of structural, pore and surface properties of modified zeolites in dependence on the temperature of iron oxide synthesis [8].

5. Acknowledgements

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6. References

1. J.D. Orbel, L. Godhino, S.W. Bigger, T.M. Nguyen, L.N. Nge, "Oil spill remediation using magnetic particles", J. Chem. Edu, 74, 1446, (1997).
2. S. Jakabsky, M. Lovas, A. Mockovciakova, S. Hredzak, Journal of Radioanalytical and Nuclear Chemistry, 246, 3, 543, (2000).
3. R. Fernandez-Pacheco, M. Arruebo, C. Marquina, R. Inarra, J. Arbiol, J. Santamaria, "Highly magnetic silica-coated nanoparticles prepared by the arc-discharge method", Nanotechnology 17, 1188, (2006).
4. L.C.A. Oliveira, D.I. Petkowicz, A. Smaniotto, S.B.C. Pergher, "Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water", Water Research 38, 3699, (2004).
5. M. Vaclavikova, S. Jakabsky, S. Hredzak, Nanoengineered Nanofibrous Materials, NATO Science Series II. Mathematics, Physics and Chemistry 169, Kluwer Academie Book Publishers, Dordrecht, Netherlands, (2004).
6. M. Matik, M. Vaclavíkova, S. Hredzak, M. Lovas, S. Jakabsky, Acta Montanistica Slovaca, 4, 418, (2004).
7. K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscow, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure and Applied Chemistry, 57, 603, (1985).
8. A. Mockovciakova, Z. Orolinova, M. Matik, "Structural properties of natural zeolite modified by iron oxide nanoparticles", Submitted to Acta Metallurgica, (2006).