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Characterizations of Fe/Mn binary oxide by nitrogen adsorption

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Characterizations of Fe/Mn binary oxide by nitrogen adsorption

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Abstract. Nanostructure Fe/Mn as a binary oxide with 1:1 molar ratio has successfully synthesized by oxidation raw materials and co-precipitation process. The synthesized Fe/Mn was characterized by N₂ adsorption, Atomic Force Microscope (AFM) and X-Ray Diffraction (XRD). The synthesized Fe/Mn demonstrated poorly crystalline structure as an effective mesopores material with high surface area 403.6165 m²/g and average diameter of particles about 55.66 nm.

Keywords: Fe/Mn binary oxide, co-precipitation, Pore size analysis

1. Introduction

Development new technologies to synthesize nanosized metal oxides (NMOs) with high internal surface area for a variety of applications has attracted the attention of the scientific community. Metal oxide nanoparticles, including nanosized ferric oxides, manganese oxides etc., provide high internal surface area. Iron oxides with poorly crystalline can be synthesized using a well-known protocol “wet chemical methods” [1]. Some of the synthesis techniques include chemical precipitation, sol-gel, hydrothermal, surfactant mediated-precipitation and microwave assisted hydrothermal technique.

These oxides find applications as catalysts, sorbents, flocculants, coatings, and ion exchangers and for lubrication [1] [2] [3] [4] [5]. Iron oxide nanoparticles have many applications in different areas such as magnetic resonance imaging, magnetic recording, magnetic data storage devices, wastewater treatment, bio separation, and medicine [1]. Because of the unique properties of Iron oxide nanoparticles, they can provide economical solution to the most complex and challenging environmental remediation cleanup problems for example soil, groundwater contamination, sediment, or surface water [1] [6] [7] [8]. Adsorption is a low energy technology [9] [10] [11]. Gao sheng *et al.* in 2014 studied porous Fe-Mn binary as adsorbent in water treatment and environmental remediation [12].

The most important properties of adsorbent, which determines its usage, are the specific surface area and the pore structure [13]. N₂ adsorption are the first stage in the characterisation of microporous and mesoporous solids because of its size and it poorly interacts with the adsorbent. The adsorption isotherm of nitrogen gas is always important ‘fingerprint’ and provide a amount of information about BET-area and pore volume. many types of adsorbents such as metal oxides, activated carbons and zeolites have been reported in the literature [14-16].



In this work, a novel Fe/Mn binary oxide sorbent has been successfully synthesized by oxidation and co-precipitation process. The synthesized Fe/Mn was fully characterized by N₂ adsorption, AFM and X-Ray Diffraction (XRD). The synthesized Fe/Mn shows as effective mesopores adsorbent with a smaller particle size, high surface area and porous structure.

2. Experimental Section

2.1. Materials

Nitric acid HNO₃ (PDH, 1%) used to clean all vessels glass of reaction. Iron (II) Sulfate heptahydrate FeSO₄.7H₂O (SCRC China) and Potassium permanganate KMnO₄ panreac spain.

2.2. Synthesis

Nanostructure Fe/Mn binary oxides was synthesized at 1:1 molar ratio. The Fe/Mn as a binary oxide was prepared modified from submission by Zhang et al. with 3:1 mol ratio [17]. So with different parameters in my work that 0.015 mol Potassium permanganate (KMnO₄) and 0.015 mol iron (II) sulfate heptahydrate (FeSO₄.7H₂O) were dissolved in 200 ml of deionized water and under magnetic stirring, the sulfate solution has been added into the permanganate solution with 4 M of NaOH drops solution to remain the solution about range 7 – 8 of pH. After addition, the suspension was formed when stirred it for 1 h, aged for 4 h at room temperature, and then washed with deionized water repeatedly. Filtrated suspension and dried at 65 °C with 24 hours. The dry powder was crushed and keep in a desiccator.

2.3 Characterization methods

X-Ray Diffraction (XRD) data of Fe/Mn binary oxide sample was collected on diffractometer (Cu K α radiation 30 mA and 40 kV). The surface morphology, root-mean-square (r.m.s) roughness and average diameter were analyzed using Atomic Force Microscope (AFM). Nitrogen adsorption/desorption isotherms of Fe/Mn binary oxide sample at -196.15 °C were obtained by Micrometrics Accelerated Surface Area and Porosimetry (ASAP) 2020 analyser, the isotherms' measurement of sample. Equilibration time was set for each data point of isotherms during the analysis. specific surface areas (SSAs) of materials determine Brunauer–Emmett–Teller (BET) method [18]. Langmuir theory was used to study the collected adsorption data in this study [19]. Langmuir model explains the adsorption by assuming a monolayer adsorption where the interaction between the adsorbate (gas) layer and the solid surface is significantly stronger than the one between gas layers.

3. Results and Discussion

XRD of sample in Figure (1) shows the two high broad peaks at 35.51 and 62.72 of d spacing 2.52542 and 1.47460 nm, estimate the average crystallite particle size via using Debye-Scherrer formula and spacing of inter-planar between atoms (d-spacing) is calculated by using Law of Bragg

$$D = k\lambda / (\beta \cos \theta) \quad (1)$$

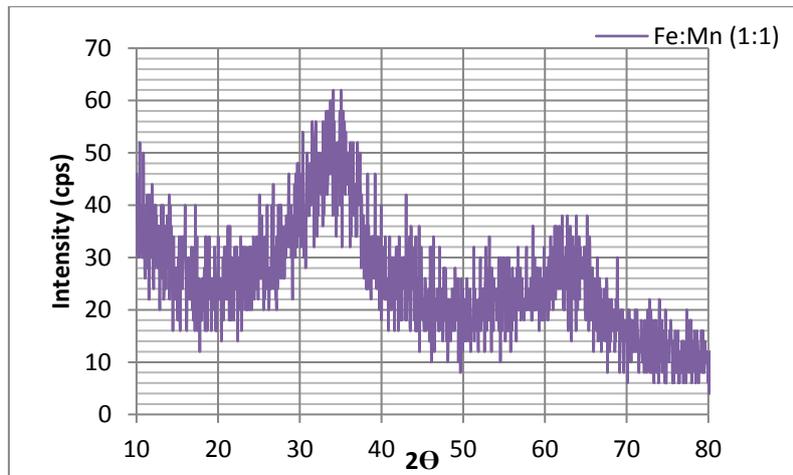


Figure 1. X-Ray Diffraction

D mean the crystallite size in nanometers, the wavelength λ (1.54056 \AA for $\text{CuK}\alpha$ radiation), which is comparable to the size of atom, k is the geometric factor related to crystallite shape equal to 0.9 and D crystallite size by using Debye-Scherrer formula is 2.29 (nm).

Many of broadening in x-ray diffraction lines are done when that particle size is less than 100 nm. The discrete θ dependencies of both effects laid the basis for the separation of size and strain broadening in the analysis of Williamson and Hall. Diffraction pattern showed broadening because of particle size and strain the overall integral breadth of a Bragg peak [20].

2D & 3D view of AFM pictures of surface for Fe/Mn as a binary oxide of nano particle, the general shape is spherical, and quite dispersed, as shown in figure (2) provide more parallel-aligned surface structure, which are suitable for oxygen recognition on cell surfaces and responsible for different color quality. The ferrihydrite morphologies is spherical and does not resemble other iron oxides it occurs only as nano crystals with high specific surface areas [21].

The average grain size, average roughness and (r.m.s) roughness of sample 55.66 nm ,0.57 nm and 0.66nm respectively.

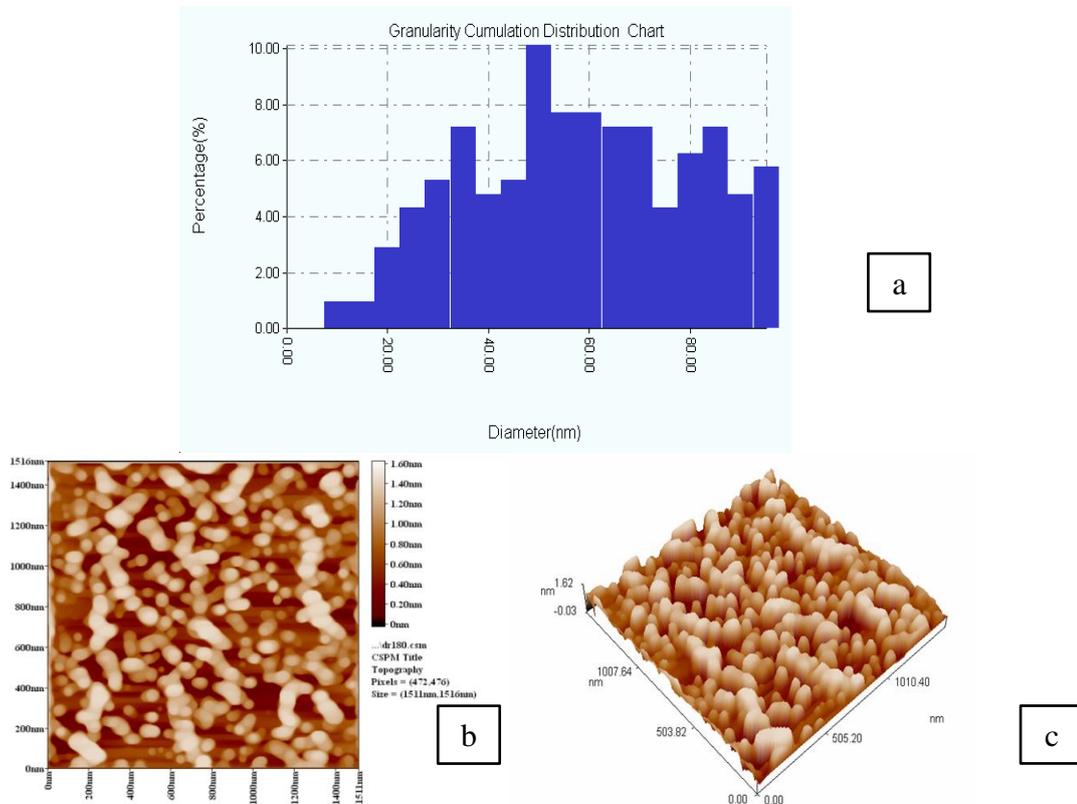


Figure 2. (a,b&c) is (a) average particle size, 2D and 3D view of surface images of sample

Specific surface area (SSA), N_2 adsorption–desorption isotherm by BET method [18], measurement of surface area for Fe-Mn as a binary oxide nanoparticles sample give a good surface area ($314.8 \text{ m}^2/\text{g}$) [22]. The results are recorded in adsorption-desorption isotherms diagrams characteristics with high surface area. The values are a perfect with the specific surface area measurements and the microscopic characteristics.

The adsorption-desorption isotherm of a sample is shown in Figure (3). The formation of a hysteresis loop is visible. This narrow loop can indicate a narrow pore size distribution. Hysteresis loops that discern in the multilayer range of physisorption isotherms related with the stuffing and voiding of mesopores, the desorption branch was favored for mesopore size analysis [23].

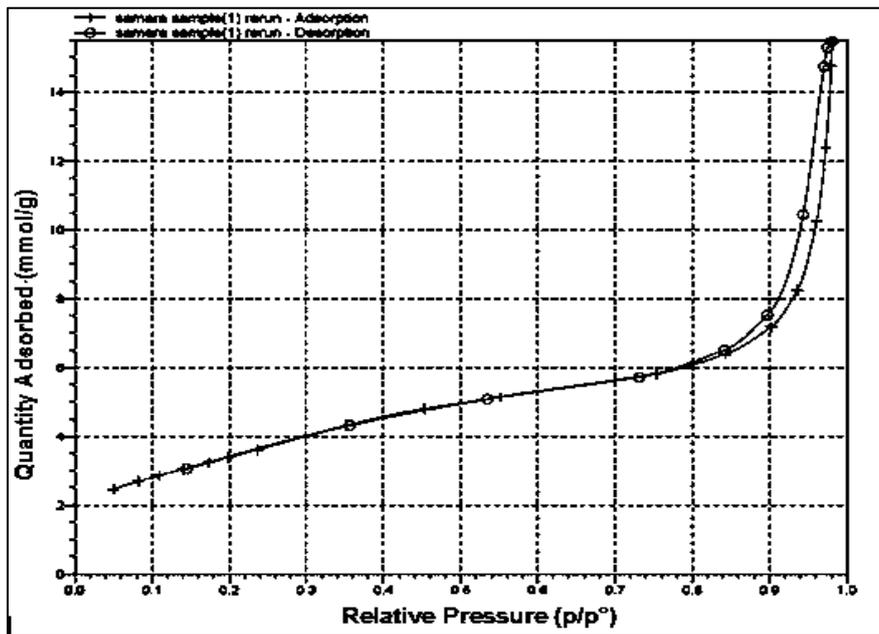


Figure 3. adsorption-desorption isotherms

Langmuir’s prodigious work on monolayer adsorption resulted in repeated interest in the performance of adsorption data, the Langmuir model called ‘ideal localized monolayer adsorption’ the amount adsorbed at the stabilization of a Type one I shown in Figure (4) isotherm identification to full monolayer perfusion [23].

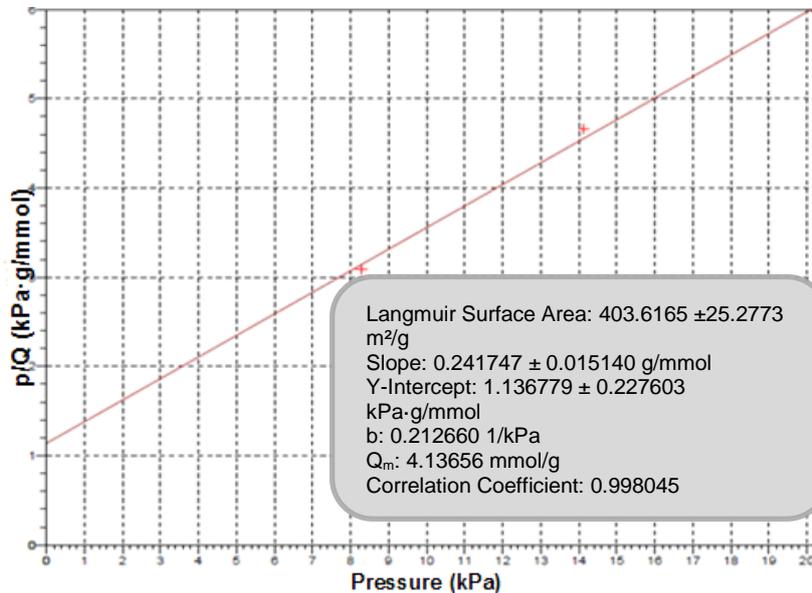
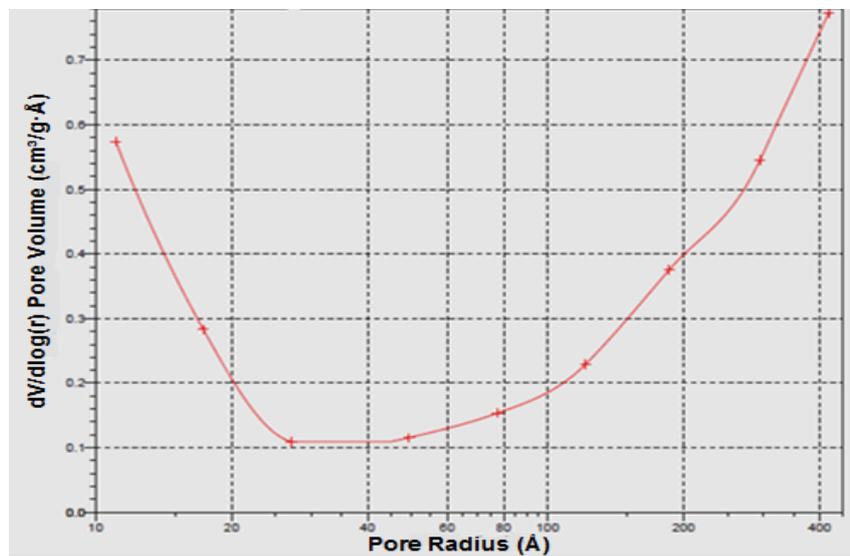


Figure 4. Langmuir Surface Area Plot

From desorption information by using(BJH) Barrett–Joyner–Halenda model, showed (Figure.5,6 and 7), marking that the sample had mesopores in the nanomaterial see table1 for characterization results of physisorption isotherms.

Table 1. Characterization results of physisorption isotherms

Pore volume (cm ³ .g ⁻¹)	
Total pore volume of pores of Single point adsorption less than (489.667 Å) radius at $p/p^\circ = 0.979823370$	0.511475
Total pore volume of pores of Single point desorption less than(401.309 Å) radius at $p/p^\circ = 0.975274888$	0.530074
BJH model of adsorption accumulated volume of pores between (8.500Å) and (1500.000 Å) radius	0.564989
BJH model of desorption accumulated volume of pores between(8.500 Å) and (1500.000 Å) radius	0.562833
Size of Pore (Å)	
Average pore width of adsorption of BET	72.7758
Average pore width of desorption of BET	75.4222
BJH model of Adsorption average pore radius	35.0150

**Figure 5.** BJH Adsorption model (Pore Volume)

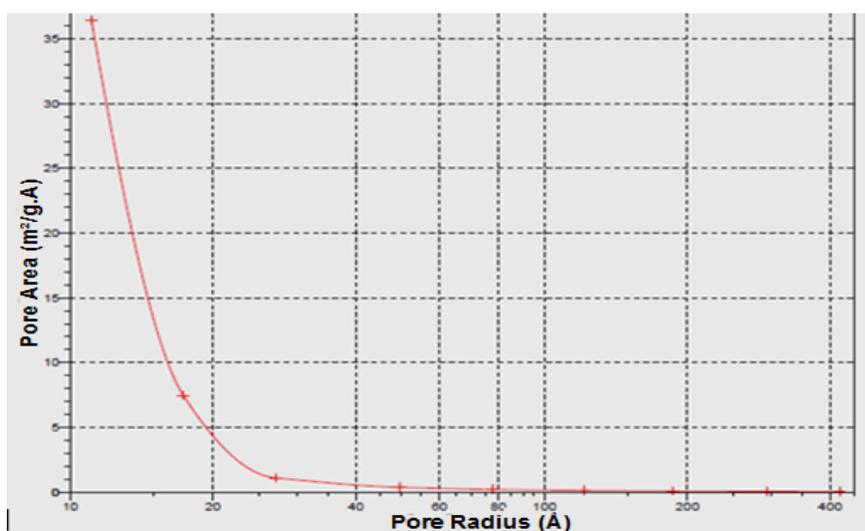


Figure 6. BJH model of adsorption $dA/d\log(r)$ (Pore Area)

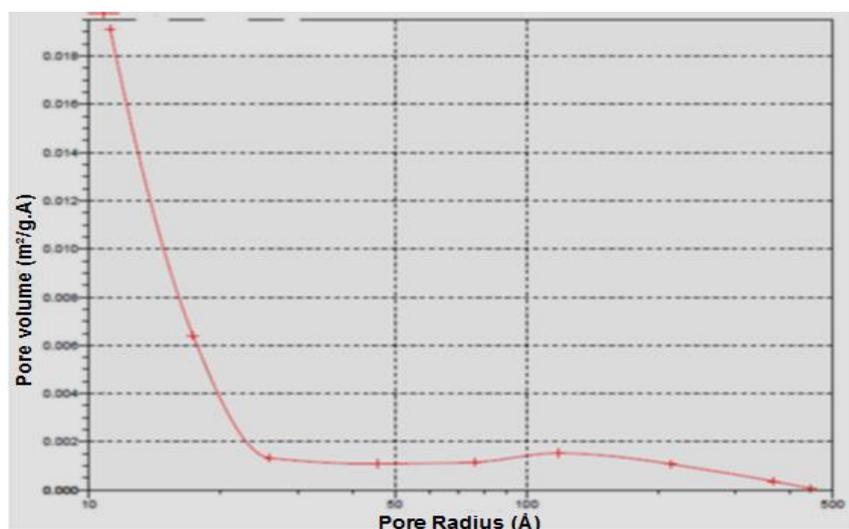


Figure 7. BJH desorption dV/dr (Pore Volume)

4. Conclusions

Porous Fe-Mn binary as adsorbent nanoparticles was synthesized by oxidation and co-precipitation method. Diffraction pattern showed broadening because of particle size and strain in two peaks at 35.51 and 62.72 with d spacing of 2.52542 and 1.47460 nm. The average grain size, average roughness and (r.m.s) roughness of sample 55.66nm, 0.57nm and 0.66nm respectively by using AFM. Adsorption-desorption isotherms, mesoporous material with high surface area 403.6165 m²/g in Langmuir Surface Area for characterization results of physisorption isotherms by nitrogen adsorption measurements at 77 K.

5. References

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