PREPARATION AND PROPERTIES OF PLATINUM COATED MAGNETITE NANOPARTICLES

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Abstract: Nanoparticle compositions of noble metals Pt, Au and magnetite Fe_3O_4 were produced by the extractive-pyrolytic method (EPM). The phase composition, the size and the magnetic properties of all samples were investigated by an X-ray diffractometer, a transmission electron microscope and a vibration sample magnetometer, respectively. Formation of the nanocomposite particles was confirmed by the above-mentioned investigations.

1. Introduction

Composite nanoparticles with two or more functional phases in each particle significantly enhance the functions of nanoparticles. Composites containing nanosized particles of noble metals on oxide carriers such as Al_2O_3, MgO, TiO_2, SiO_2, Fe_2O_3 are widely used in heterogeneous catalysis [1]. Synthesis of composite magnetic nanoparticles with noble metal is a promising method to create a new type of material, which can be manipulated by an external magnetic field. Therefore, presently great attention is paid to the preparation and study of catalytic and magnetic properties of such composites [2-7]. The extractive-pyrolytic method (EPM) is a promising new method for the preparation of oxides [8] and composite materials containing nanoparticles of noble metals [9, 10]. The EPM allows quickly and simply (without the use of complex hardware design) to obtain nanoscale metal particles in various media. The aim of this work was to obtain composite Pt/F_3O_4 and Au/F_3O_4 magnetic nanoparticles by the EPM, and investigate the phase composition, morphology and magnetic properties of the composites.

2. Experimental

In order to produce Pt/Fe_3O_4, Au/Fe_3O_4 composites, at the first step a magnetite magnetic fluid (MF) was prepared by the wet chemical method [11] with toluene as a carrier liquid and with oleic acid as a surfactant. A magnetite phase powder specimen was produced by the method of vacuum evaporation of the carrier liquid of MF at 323 K. For the synthesis of noble metal–magnetite nanocomposite, some volume of n-trioctylammonium salt solution in toluene with a certain concentration of noble metal was added to the given mass of MF or nanoparticle powder. Then the mixture was stirred, dried and subjected by pyrolysis by heating from room temperature to the 673 K and cooled at room temperature. To a portion of the 3.8 wt% powder sample Fe_3O_4/Pt a mixture of oleic acid and oleylamine was added. The sample was then placed into a ball mill and subjected to grinding during 170 hours. Afterward the product was transferred to undecane. A stable magnetic fluid MF-1 was produced with the magnetization 7 emu/g and the magnetite mean sizes 18 nm and 8 nm of immobilized

platinum particles on it. Magnetic properties of the colloid and of all powder samples were measured by a vibration sample magnetometer (VSM) (Lake Shore Criotronic Co., model 7404 VSM) in fields up to 1 T. The specific magnetization, the spectrum of particle magnetic moments as well as the magnetic size of nanoparticles were obtained from the magnetization curve of the MF sample. The specific magnetization and coercivity of the solid phase were determinate from the magnetization curves of relative powder specimens. The phase composition of Pt, Au-containing composites was characterized by an X-ray diffraction method using a diffractometer D8 Advance (Bruker Corporation) with CuKα radiation (λ = 1.5418Å). The mean size of platinum and gold crystallites was defined from the (111) peak width by the Scherrer method. The morphology of the composite nanoparticles and sizes of noble metal nanoparticles were observed by a transmission electron microscope (TEM) using the JEOL JEM 2100 operating at 200 kV.

3. Results and discussion

The X-ray image of the magnetic particle powder obtained from the magnetic fluid showed a perfect face-centered crystalline spinel structure. During the pyrolysis reaction with increased temperatures, some ferrous ions oxidized to ferric ones and formed hematite because the reactions were conducted in an open vessel.

Fig. 1 shows the typical XRD spectra of the composite nanoparticles F_3O_4/ Pt 3.8 wt%. In all the patterns with the concentration of noble metal > 1 wt% a significant peak due the definitely metallic phase of noble metal was observed. All curves in the pattern obviously showed two sets of strong diffraction peaks, indicating that the synthesized products were composite materials having good crystallinity and high purity. If the introduced noble metal concentration in the precursor was less than 1 wt%, in the final product after pyrolysis the noble metals were X-ray amorphous. The increasing of the Au content in the composite caused the formation of large metal crystallites (up to 60 nm). When the platinum content increased from 1.1 wt % to 7.4 wt %, the carrier phase composition did not change, and the final product contained basic phase - magnetite and hematite as an admixture. The platinum metal nanoparticles with the mean size less than d < 10 nm were immobilized on magnetite particles.

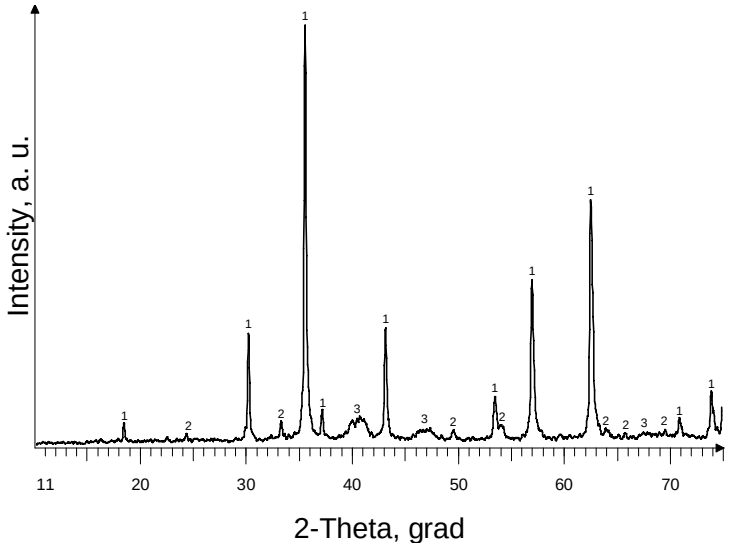
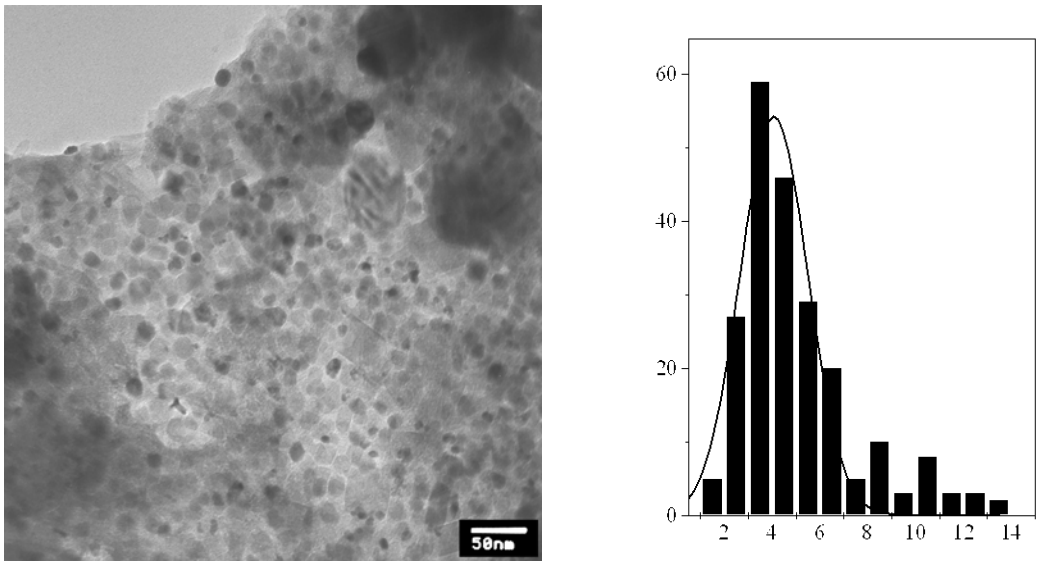


Figure 1: Typical X-ray diffraction pattern of Pt-containing composite nanoparticles: 1 – Fe_3O_4, 2 – α-Fe_2O_3, 3 – Pt.

Fig. 2 (a) displays a typical TEM micrograph of the Fe_3O_4/ Pt 7.4 wt% composite. Smaller particles' images with stronger contrast show platinum metal, indicating their good dispersion on the surface of larger magnetite nanoparticles observed with weaker contrast. Fig. 2 (b) represents the particle size distributions of platinum metal nanoparticles immobilized on magnetite particles.



a) b)

Figure 2: The typical TEM micrograph of composite nanoparticles of Fe_3O_4/Pt 7.4 wt % (a). The size distribution of platinum nanoparticles immobilized on magnetite particles (b).

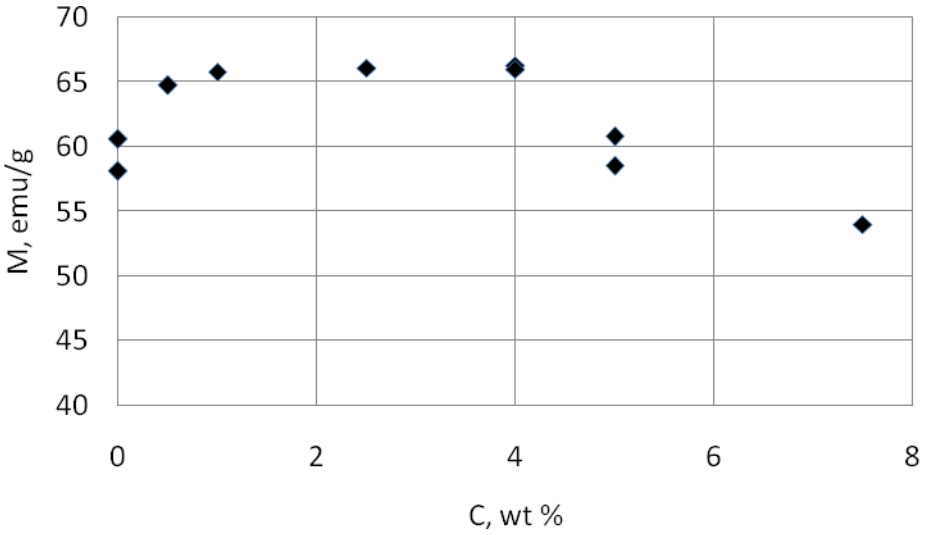


Figure 3: Specific magnetization of the composite nanoparticles.

Fig. 3 shows the dependence of specific magnetization of the composite solid phase on the concentration C of noble metal in the pattern at room temperature. The initial magnetite nanoparticles' magnetization was smaller than that of the bulk phase. This is attributed to an increase in the disorder of the magnetic moment orientation in various sites when the surface/volume ratio increased. With the noble metal concentration increase, the magnetization of the powder samples increased, reached a maximum at 4 wt % and decreased

upon further increasing of the noble metal concentration. The initial increase of magnetization apparently was due to the increasing in nanoparticle sizes after thermal treatment. The further decrease in magnetization with the increasing concentration of noble metal was associated with the decrease in concentration of the magnetic phase in the nanoparticle.The summarized results of all experimental measurements are listed in Table 1.

Table 1.

Sample	Magnetization at max. field, emu/g	Coercivity Oe	Fe_3O_4 crystallite size from XRD, nm	Noble metal crystallite size from XRD, nm	Mean diameter of noble metal particles from TEM, nm
MF	11.2	0	-	-	-
MF-1	7.0	-	18	8	-
Fe_3O_4 powder	58.1	0	11	-	-
Fe_3O_4/Pt 1.1 wt %	65.8	134	39	amorphous	2.46
Fe_3O_4 /Pt 2.4 wt %	64.3	51.1	20, 55 (2 phases)	5.0	-
Fe_3O_4/Pt 3.8 wt %	63.5	100	63	10, 15 (2 phases)	-
Fe_3O_4/Pt 3.6 wt %	63.9	75	68	3	-
Fe_3O_4/Pt 3.8 wt % after grinding	43.4	284	18	~8	-
Fe_3O_4 /Pt 5.0 wt %	55.6	81	60	-	
Fe_3O_4/Pt 7.4 wt %	50	94	58	6, 20 (2 phases)	4.07
Fe_3O_4/Au 0.4 wt %	64.8	140	-	amorphous	3.47
Fe_3O_4/Au 4.9 wt %	-	-	40	60	7.85

3. Conclusions

Magnetic composite nanoparticles were produced by the extractive-pyrolytic method on the base of magnetite and with noble metals Pt and Au as the immobilized part. The formation of the composite nanoparticles was confirmed by XRD. TEM observation revealed that the noble metal nanoparticles were immobilized on the surface of magnetic iron-oxide nanoparticles. The Fe_3O_4/Pt particles dispersion in undecane was achieved by using oleylamine and oleic acid as surfactants. The Fe_3O_4/Pt and Fe_3O_4/Au composite nanoparticles can be manipulated by an external magnetic field, which is a potential for their application in various fields.

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5. References

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