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Preparation of γ -Fe₂O₃ from combustion method for sensitivity towards reducing gases

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ABSTRACT

Fine powders of ultrafine γ -Fe₂O₃ particles have been prepared by the combustion synthesis method of the succinate precursor, with an aim to employ it as sensor material. Gas sensor studies have been undertaken on the as prepared γ -Fe₂O₃ and its surface functionalized sample by incorporating fine particles of Palladium, Pd (Pd dispersed γ -Fe₂O₃, hereafter called as PdG sample). The enhancement in the gas sensing behavior of the PdG sample towards test gases like EtOH (ethanol), LPG (Liquefied petroleum gas), CH₄ (methane) and H₂ (hydrogen) is reported. The possible reason for the improved sensing behavior of the PdG sample when compared with the as fine γ -Fe₂O₃ is explained based on the catalytic activity of Pd and also on the affinity for the test gases towards Pd. The sensitivity towards H₂ for the PdG sample shows intensity results. The morphology and spectral characteristics of γ -Fe₂O₃ and PdG sample are also compared.

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KEYWORDS

Combustion synthesis;
 γ -Fe₂O₃;
 Pd dispersion morphology;
 Sensor studies.

INTRODUCTION

Ferrites and other metal oxides demonstrate a new method of selectivity control and sensitivity enhancement, and their surface functionalization is supposed to enhance the activity of these materials for gas sensing^[1,2]. Recently a study of the γ -Fe₂O₃-PPy composite is reported as humidity sensors^[3]. The effect of size of the particles in sensor materials has been proved to play a significant role in enhancing the sensitivity of these materials towards the test gases^[4]. Further synthesis of γ -Fe₂O₃ an important inverse spinel ferrite in finely divided form is being actively pursued^[5-10] for several other Applications (viz., solid adsorbents in pure and surface functionalized forms). The semi conducting oxide ma-

terials and more specifically ferrite based sensors work on the principle of abstraction of electrons from the bulk by adsorbed oxygen to form surface oxygen ions, resulting in the formation of surface states. However, changing a few of the Fe-O linkages by grafting Pd-O linkages can cause a drastic change in the concentration of the adsorbed oxygen species. These results suggest that the ferrite surfaces modified with an inert metal catalyst can dramatically improve the sensitivity and selectivity to hydrogen and other gases^[11-13]. Liquefied petroleum gas (LPG) widely used as a fuel for industrial and domestic purposes, has often proved to be hazardous because of explosions caused by leaks. Similarly, detection of alcohol in monitoring the traffic, detection of toxic and inflammable gases like CH₄, C₃H₈,

H₂, i-C₄H₁₀ etc., in industrial and environmental monitoring are the areas of research in gas sensors for the present day need^[14]. All these only make the development of gas sensors for the detection of toxic and inflammable gases a mandatory scientific effort. The field of materials chemistry has been contributing immensely in understanding chemistry of gas adsorption and for selecting suitable material as gas sensors^[11-12]. Attempts have been made in the past to use different materials viz., ZnO/SnO₂ as hydrocarbon sensors, modified with noble metal additives^[15-16], some perovskites^[17], spinels^[18]. Increasing the sensitivity towards detection of alcohol when Pt is dispersed on a ferrite matrix (γ -Fe₂O₃) matrix has been reported in one of our earlier studies^[19]. The effects of appropriate sensor material and the particle size have an added advantage in the sensing property, when the sensor material is in the ultrafine range, and with proper morphology, an enhanced sensitivity and selectivity is expected^[20-21]. The study of ultra fast dynamics of photo-excited electrons in γ -Fe₂O₃ and γ -Fe₂O₃ is needed to understand the mechanism and band structure, which is essential for modifying the material to be suitable for sensor applications^[22]. In this paper we report on the synthesis of nanosized γ -Fe₂O₃ and its advantages as a gas sensor material towards the test gases like EtOH, LPG, CH₄ and H₂. The advantages of Pd dispersed γ -Fe₂O₃ are also envisioned for the detection of these test gases. The present investigation is also aimed at understanding the chemistry of selectivity of γ -Fe₂O₃ and the Pd dispersed γ -Fe₂O₃ as sensor material.

2. EXPERIMENTAL

Preparation of γ -Fe₂O₃ from ferrous succinate tetrahydrate precursor

The precursor ferrous succinate tetrahydrate was prepared as reported elsewhere^[7]. γ -Fe₂O₃ is synthesized through a self-propagating combustion reaction of this precursor. This involves mixing the precursor with polyethylene glycol in the weight ratio of 1:5 and thereafter heating in order to initiate the self-propagating combustion reaction. The resultant solid is placed in a crucible and heated in air. It is observed that polyethylene glycol first melts, then froths and finally ignites to

convert the precursor into γ -Fe₂O₃. No traces of carbon impurities are observed in the final residue of γ -Fe₂O₃. This reaction that occurs with the evolution of a lot of gases ignites automatically and is called a strong self-propagating combustion reaction^[6-7].

Preparation of Pd incorporated γ -Fe₂O₃ (PdG)

0.2 g of the as prepared γ -Fe₂O₃ is mixed with 0.0033 g of PdCl₂ in a beaker containing 20 ml of deionised water and the mixture is vigorously stirred and dried on a hot plate. Further the powder is subjected to calcinations at 300°C for 3 hours in air, which forms Pd dispersed γ -Fe₂O₃ (1 wt % Pd). The sample is henceforth called as PdG sample.

Preparation of sensor element and the measurement procedure

The as prepared fine powder of γ -Fe₂O₃ are ground to a fine paste with a solvent. The paste is then uniformly coated on the surface of the ceramic cylinder provided with two electrodes for the electrical measurements. This procedure is also followed for PdG sample separately. Schematic representation of the sensor assembly has been described in one of our earlier report^[18]. For gas sensing measurements the sensor element was provided with a heater fixed inside the alumina tube, coated with the sensor material (γ -Fe₂O₃/PdG). The electrical resistance of the element in dry air is measured by means of conventional circuitry in which the element is connected to an external resistor in series and the voltage drop across the external resistor at a circuit voltage of 10V is used to calculate the electrical resistance of the element. The values of the device resistance are obtained by

$$S = \Delta R / R_a = (| R_a - R_g |) / R_a \quad (1)$$

monitoring the output voltage across the load resistor. The electrical resistance of the element was measured in the presence and absence of the test gas. The sensitivity, S is defined as the ratio ΔR , i.e., change in resistance of the sensor (R_g) in air, to the value of the resistance in the presence of the gas (R_a), normalized to the value of sensor resistance in air as given in equation 1.

Characterization of γ -Fe₂O₃ and PdG samples

The as synthesized γ -Fe₂O₃ and the PdG samples are then characterized for their structure by x-ray diffraction and IR spectroscopy and morphology by SEM

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techniques. The XRD patterns were obtained with a Siemens X-ray diffractometer (Japan), and the target was $\text{CuK}\alpha$ ($\lambda 1.54\text{\AA}$). The generator was operated as 30 kV and with a 20 mA current. The scanning range (θ) was selected. A scanning speed of 1° min and a chart speed of 20 mm/min were used for the precise determination of the lattice parameters. High-purity silicon powder was used as an internal standard. The coherently diffracting crystallographic domain size (d_{XRD}) of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was calculated from X-ray diffraction (XRD) line broadening after subtracting the contribution from the $\text{CuK}\alpha$ component (Rachinger correction) and correcting for the instrumental width. The integral line width was used in the Scherrer formula^[23] to calculate d_{XRD} of the (311) plane. The scanning electron micrograph (SEM) images of the samples were obtained with a JSM-840A scanning electron microscope. The scanning electron microscope was operated at 12 kV. The infrared (IR) spectra of the samples were recorded on a Perkin-Elmer FT-IR Spectrum ONE in the range $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} .

RESULT AND DISCUSSIONS

X-ray diffraction

Figure 1(a) shows the XRD pattern of the synthesized $\gamma\text{-Fe}_2\text{O}_3$. The structure was confirmed on comparison with JCPDS file No.04-755. The particle size was found to be 16.4 nm from the line broadening of the 100% peak ((311) peak) using the Scherrer formula^[23]. Figure 1(b) shows the X-ray diffraction pattern of PdG sample. This figure shows the highly crystalline nature of the sample and resembles the earlier pattern of pure $\gamma\text{-Fe}_2\text{O}_3$ (figure 1(a)). There were no specific peaks for Pd in the XRD pattern possibly due to its very low concentration (1%).

Fourier transformation infrared spectroscopy

The IR spectra for $\gamma\text{-Fe}_2\text{O}_3$ and PdG are similar. Hence a representative spectrum is discussed here. Figure 2 shows the infrared spectrum of the PdG sample. The peaks observed at 548 and 458 cm^{-1} are assigned to Fe-O vibrational modes for the inverse spinel compound^[24]. The peak observed at 2344 cm^{-1} may be assigned to some overtone vibrational mode^[8-9]. The IR

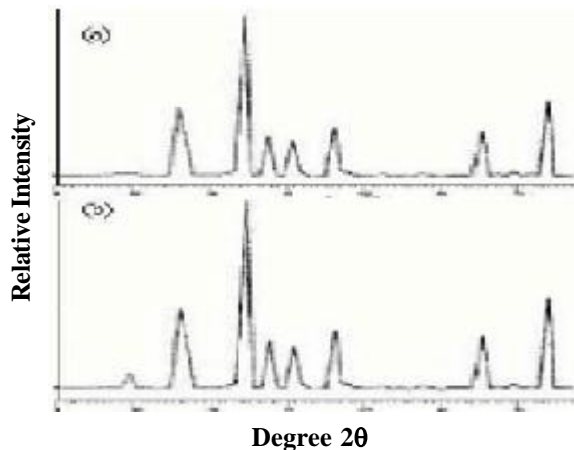


Figure 1: (a) XRD pattern of $\gamma\text{-Fe}_2\text{O}_3$

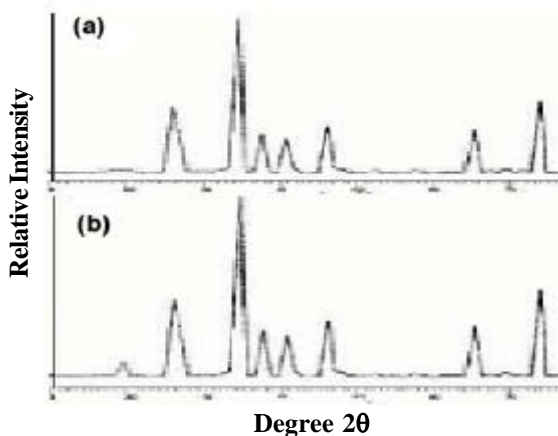


Figure 1: (b) XRD pattern of PdG sample

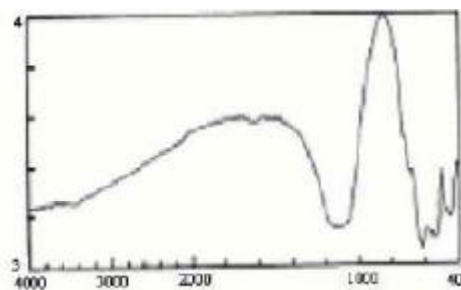


Figure 2: IR Spectrum of PdG sample

spectrum shows the purity of the PdG sample with no other peaks except the cited ones. The possible observation frequency of Pd-O has been possibly masked by the ferrite peaks.

Scanning electron microscopy

Figure 3(a) and (b) are the scanning electron microscopy (SEM) images of the $\gamma\text{-Fe}_2\text{O}_3$ sample under

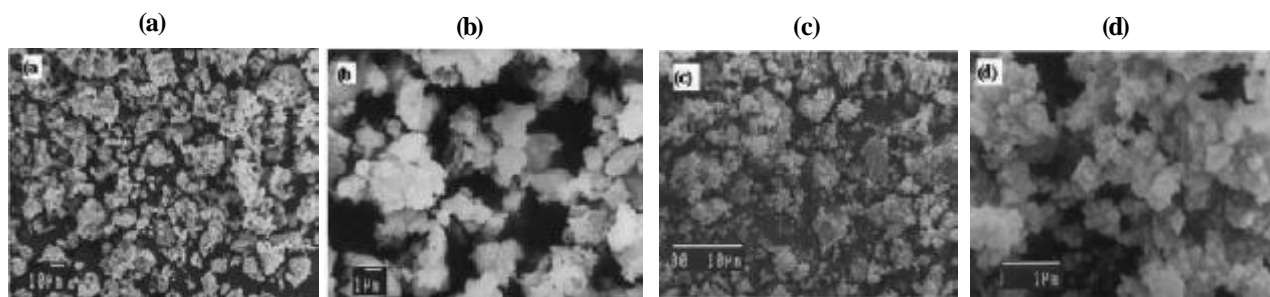


Figure 3: (a) SEM images of γ -Fe₂O₃ sample under low magnification; (b) SEM images of γ -Fe₂O₃ sample under high magnification; (c) SEM images of PdG sample under low magnification; (d) SEM images of PdG sample under high magnification

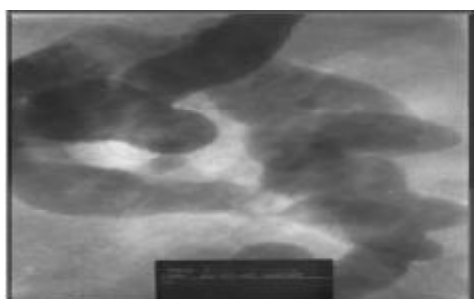


Figure 4: TEM image of γ -Fe₂O₃ sample

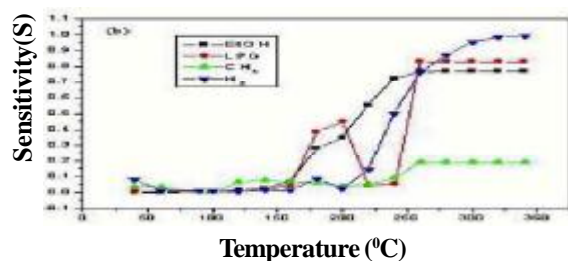
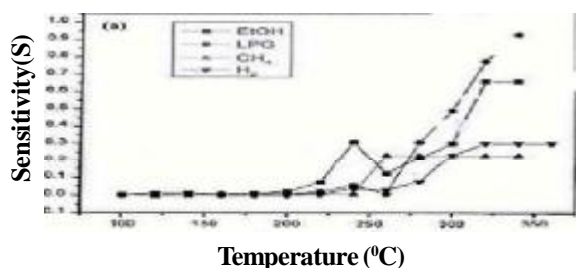


Figure 5: (a) Sensitivity of γ -Fe₂O₃ sample towards the test gases viz., EtOH, LPG, CH₄ and H₂; (b) Sensitivity of PdG sample towards the test gases viz., EtOH, LPG, CH₄ and H₂

high and low magnifications respectively. The images show ultrafine particles with spherical shape and varying sizes. Some agglomerates of sub micron sizes are also observed. Figure 3(c) and (d) are the SEM micrographs of the PdG sample at low and high magnifica-

tions respectively. The figures show ultra fine particles of Pd agglomerated on the surface of γ -Fe₂O₃ particles; in turn γ -Fe₂O₃ particles are closely packed to provide interaction with Pd particles on the surface.

Transmission electron micrograph (TEM)

The nanocrystalline nature of the as prepared γ -Fe₂O₃ is further confirmed by transmission electron micrograph (TEM) images shown in figure 4. TEM photograph provides the information on the microstructure and the particle size and the distribution in the sample. The bright field TEM photograph shows the tabular shaped particles with some aggregated particles with average particle size of less than 40 nm, the individual tabular shaped particles are 20×60 nm in size. These results indicate the formation of nanosized dimension of the γ -Fe₂O₃ and also possibility of agglomerates of these and also possibility of agglomerates of these nanoparticles.

Gas sensing characteristics of γ -Fe₂O₃ and PdG samples

The different test gases (EtOH, LPG, CH₄ and H₂) with fixed volume of 2-5 cc are injected into the specimen chamber through an inlet port. To calculate the sensitivity, the electrical resistance of the element was measured in the presence and absence of the test gases taken in concentrations of 500 ppm in dry air. The details of the procedure are given in our earlier works [18-19]. Figure 5(a) shows the sensitivity Vs temperature plot for γ -Fe₂O₃ for the test gases (a) EtOH, (b) LPG, (c) CH₄ and (d) H₂. It is observed from this figure that the sensitivities for all the gases are quite low up to 250°C, indicating that the nature of gas sensing is similar for these gases for γ -Fe₂O₃ up to 250°C. Above

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this temperature noticeable differences are observed in the sensitivities of these gases. It may be concluded that the sample exhibits a very high degree of selectivity towards LPG and EtOH while comparatively lower degree of selectivity towards CH₄ and H₂ at a temperature of 320°C. It is understood that the sensitivities for gases generally increases around phase transition temperature. We have observed from thermal studies (not shown in the present investigation) that the γ -Fe₂O₃ transition for our sample shows around 300°C, under static air atmosphere. In order to compare the changes in sensitivity and selectivity of the test gases along with operating temperature, the sensor studies employing the same test gases have also been performed on PdG sample. Figure 5(b) shows the sensitivity versus operating temperature plot for the PdG sample. It is seen that the sensitivity reaches very high for all the test gases except for methane at around 260°C. The response of the sensor to all the test gases indicates that the sensitivity for all the gases has increased when compared with the response of the sensor without palladium (pure γ -Fe₂O₃ sample, shown in figure 5(a)) and with a lowering on temperature of around 50°C. In particular the response to hydrogen is higher. In the present case palladium acts as a catalyst^[15] and is responsible for the lowering of the operating temperature, which can be visualized from the above plot. The sensitivity of the sensor to hydrogen gas has increased from about 0.3 to 0.98 along with a decrease by about 50°C of the operating temperature. This significant change could be attributed to the following reasons. Pd is known to have an affinity for hydrogen^[11-13]. This affinity could be responsible for the increased sensitivity. It is also interesting to note that from the above observation that the sensor materials (γ -Fe₂O₃ and PdG) have virtually no effect on CH₄ gas, thereby indicating that these materials may be insensitive towards test for CH₄ gas. The possible reason for this observation may be based on the inert nature of CH₄ (dipole moment =0), making it nonpolarizable towards the sensor materials. Because of this non-polarization, adsorption of CH₄ molecules on the surfaces of γ -Fe₂O₃/PdG samples is very low and hence the low value of sensitivity towards this gas. However, understanding the details regarding the chemistry and physics of adsorption will help in coming to a definite conclusion on this observation.

5. CONCLUSIONS

From this study the following conclusions can be inferred:

1. The paper reports on the successful preparation of γ -Fe₂O₃ from ferrous succinate tetrahydrate precursor.
2. Pd incorporation into the γ -Fe₂O₃ was accomplished by impregnation method.
3. From this study it can be seen that incorporation of Pd has increased the sensitivity and decreased the operating temperature of the sample towards the test gases. This is especially true with reference to H₂ gas which showed 98% S at a temperature of 270°C.
4. Morphology of the parent ferrite and the Pd dispersed ferrite also acts as a contributing factor in their sensitivity towards the test gases.

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