Development of Mn_2O_3/SiO_2 nanocomposite by sol-gel route

I. Prakash[1], P. Muralidharan[1], N. Nallamuthu[1], M. Venkateswarlu[2], N. Satyanarayana[1*]

[1] Department of Physics, Pondicherry University, Pondicherry. 605 014, India
HBL power systems Ltd. Hyderabad 500 078, A.P. India

Abstract

Nanocomposite of Mn_2O_3/SiO_2 was prepared through a base catalyst assisted insitu sol-gel process, in which Mn_2O_3 nanocrystals were dispersed in the silica amorphous matrix. The synthesized dried gel, at 373 K, was heat treated at different temperatures and the nanocomposite formation temperature (1023 – 1173 K) was monitored through the XRD study. The size of the dispersed Mn_2O_3 crystallite in the silica matrix was calculated using Scherer's formula and size of the crystallites was found to be 30 nm. The structure and thermal behavior for the formation of nanocomposite was identified through the FTIR and TG-DTA analysis, respectively.

Key words: Sol-gel process; Mn_2O_3/SiO_2 nanocomposite; XRD; FTIR; TG-DTA

1. NTRODUCTION

Recent research has been mainly focused on the manganese oxide nanoparticles and nanocomposite materials because of their extensive applications in the field of catalysis, electrochemistry, ion-exchange materials, magnetite, sensors, batteries, etc. due to their structural flexibility with novel physical and chemical properties [1-2]. In addition, polymorphous Mn_2O_3 was proposed as cheap environmental friendly catalyst for carbon monoxide and organic pollutant oxidation and nitrogen oxide decomposition [3-4]. Various structural, electronic and magnetic properties of manganese based oxides were primarily affected by the different oxidation states and moreover, due to the locations of the manganese ions in the unit cell of the oxides. Nanocrystalline manganese oxides show drastic change in their physical and chemical properties compared with their respective bulk materials [5]. Better controlled size and morphology of the manganese oxide nanocrystalline materials can be obtained by the growth of nanocrystals in polymeric/glassy/ceramic matrices, thereby result in the formation the nanocomposite materials [6,7]. Silica is one the most versatile host matrix available in various forms and easy to prepare. Wide variety of glasses and nanocrystalline ceramic materials were synthesized through sol-gel technique, since it has many advantages such as low temperature synthesis, high homogenous molecular level of mixing, easy to handle and etc. Hence, a base catalyst assisted insitu sol-gel process was used to synthesize uniform dispersed Mn_2O_3 nanocrystals in silica matrix for the formation of Mn_2O_3/SiO_2 nanocomposite and the prepared samples were characterized by XRD, FTIR, TG-DTA.

2. EXPERMENTAL

2.1. Sol-gel process

Nanocomposite of Mn_2O_3/SiO_2 gel sample was prepared

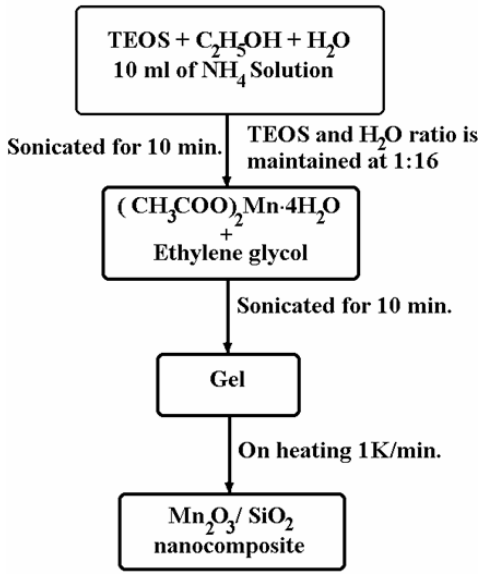

Fig. 1 Flow chart for Mn_2O_3/SiO_2 nanocomposite sample preparation by base catalyst assisted sol-gel process.

through a base catalyst assisted insitu sol-gel process for the composition of 10% Mn_2O_3-90% SiO_2, using analar grade precursor chemicals of tetraethylorthosilicate (TEOS), $Mn(CH_3COO)_2.4H_2O$, ethylene glycol and ammonia solution. The precursor chemicals were mixed according to their respective molecular weight percentages as mentioned above and the synthesis of Mn_2O_3/SiO_2 nanocomposite is described in a schematic diagram, as shown in Fig.1. In a typical synthesis, the required amount

of TEOS was dissolved in ethanol and double distilled water and sonicated for about 10 min. Followed by the addition of 10 ml of ammonia solution, as a base catalyst. The TEOS and water ratio was maintained at 1:16. Manganese acetate dissolved in 10 ml of ethylene glycol was then added to the TEOS solution and further sonicated for 10 min. to form a clear gel. The obtained gel was dried at 373 K. Thus dried gel was heat treated from 373 to 1173 K at heating rate of 1 K per min. The entire heat treatment process was monitored by an XRD, FTIR and TG-DTA techniques.

2.2 XRD, FTIR and TG-DTA measurements

XRD patterns were recorded for the dried gel and heat treated samples using a PANalytical Xpert PRO diffractometer with Cu K_α as the source radiation of wavelength λ=1.4158 Å. The powdered dried gel and different temperatures heat treated samples were mixed with KBr powder each separately in 1:20 ratio and pelletized using a KBr press to form a thin transparent pellet. FTIR spectra were recorded using a Shimadzu FTIR/8300/8700 spectrophotometer in the frequency range of 4000 – 400 cm^{-1} with 2 cm^{-1} resolution for 20 scans. The thermal behavior of the dried gel sample was recorded using a Setaram Labsys TG-DTA instrument. The dried gel sample of 3 mg was placed in the alumina crucible and heated at the rate of 10 K per min. from 333 K to 1173 K under oxygen atmosphere.

3. RESULTS AND DISCUSSION

3.1 XRD

Fig. 2 shows the XRD patterns recorded for the dried gel and the gel sample heat treated at different temperatures from 373 K to 1173 K to form the Mn_2O_3/SiO_2 nanocomposite. From Fig. 2, it is observed that the sample revealed the amorphous nature up to 823 K and further heat treatment result in the growth of Mn_2O_3 nanocrystals and precipitate in the amorphous SiO_2 matrix. The XRD patterns for the samples heated at 1173 K showed a broad reflection centered at 22^o, which is a characteristic of the diffraction peak of amorphous SiO_2 structured matrix. The peaks observed at 32.9^o, 38^o, 42.8^o, 55^o and 65.6^o for sample heated at 1173 K indicate the complete formation of high crystalline Mn_2O_3 dispersed in the amorphous matrix of SiO_2 to form the nanocomposite material and the XRD pattern was compared and confirmed with the JCPDS (# 078-0390) data of the crystalline Mn_2O_3 phases. It is comprehensible that the broad reflection centered at 22^o is retained at 1173 K heat treated sample, which confirmed that the SiO_2 amorphous matrix is retained during the thermal treatment.

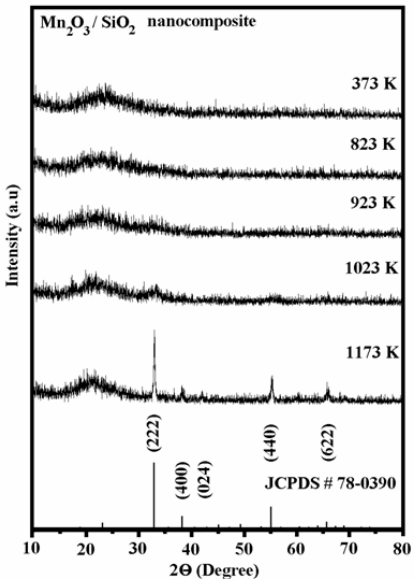

Fig. 2 XRD patterns for Mn_2O_3/SiO_2 nanocomposite heat treated at different temperatures

The formed nanocrystals of Mn_2O_3 in the dispersed SiO_2 amorphous matrix represent the formed nanocomposite. The crystallite size was calculated using Scherer's formula: $D = 0.9\lambda/ (\beta \text{ Cos } \theta)$, where λ is the X-ray wave length (0.15418 nm), β is full width half maximum (FWHM) of the peak. The calculated Mn_2O_3 nanocrystals crystallite size is found to be ~ 30 nm. Thus, it can be concluded from the XRD analysis that the formation of Mn_2O_3/ SiO_2 nanocomposite occurred at 1173 K.

3.2 FTIR

Fig. 3 shows the FTIR spectra recorded for the dried gel and heat treated samples at different temperatures from 373 K to 1173 K. In Fig. 3, the observed major bands are 3405, 1620, 1089, 955, 804, 669 and 468 cm^{-1}. The IR bands at 3405 and 1620 cm^{-1} are respectively, attributed to stretching and bending vibrational modes of O-H of molecular water and Si-OH stretching of surface silanols hydrogen bond to molecular water [7,8]. The FTIR spectra for heat treated samples showed a decrease in the intensity of the bands at 3405 and 1620 cm^{-1}, which is due to the removal of molecular water from the sample. The broad band in the range 1087-800 cm^{-1} is associated with the stretching modes of Si-O- and Si-O-Si [7,8]. The FTIR spectra of the dried gel fired at 1173 K showed the complete removal of the band at 3405 cm^{-1} indicate that the formed nanocomposite is free from the organic residual. The appearance of bands in the range 704-500 cm^{-1} associated with the vibration modes of Mn-O bonds [9]. The band at 462 cm^{-1} corresponds to the deformation mode of Si-O-Si. Thus, the FTIR spectra confirmed that the formation of Mn_2O_3 nanocrystalline structure dispersed in amorphous SiO_2 matrix to form the nanocomposites.

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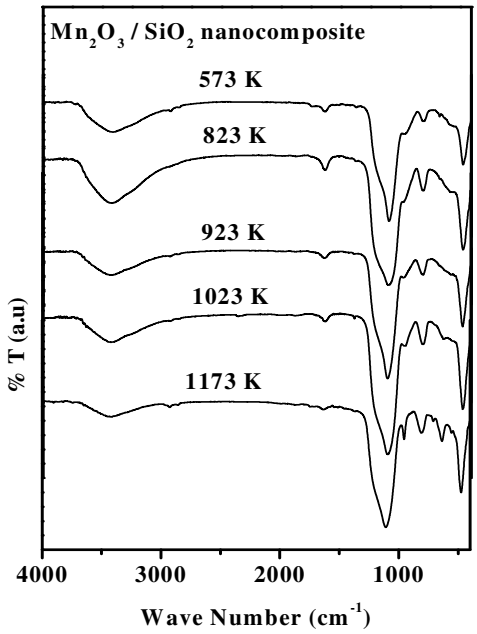

Fig. 3 FTIR spectra for Mn_2O_3/SiO_2 nanocomposite heat treated at different temperatures

3.3 TG-DTA

Fig. 4 shows the TG-DTA thermogram of Mn_2O_3/ SiO_2 nanocomposite. The observed wide endothermic peak between 330 K and 363 K for the dried gel is due to the evaporation of water molecules and other organic residues existing in the sample, which are evidently confirmed from the FTIR analysis. The exothermic peak observed at 560 K is corresponds to the decomposition of ethylene glycol and the corresponding weight loss is observed in the TG curve.

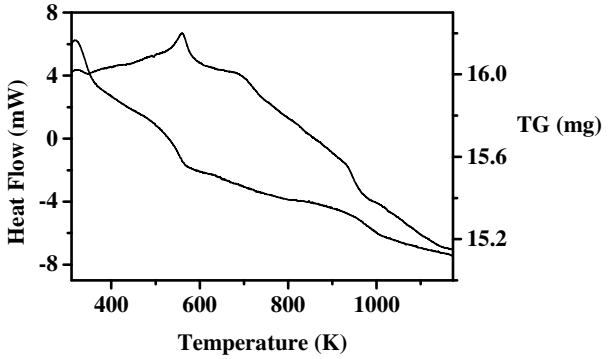

Fig. 4 TG-DTA curve for the Mn_2O_3/SiO_2 sample heated at 333K

The crystallization of Mn_2O_3 is observed in DTA curve at 923 K and the crystallization temperature is obviously confirmed from the XRD analysis.

Conclusion

Nanocomposite of Mn_2O_3/SiO_2 was successfully prepared through a base catalyst assisted insitu sol-gel process. The TG-DTA thermal analysis revealed the crystallization of the sample and the unwanted organic residual removal was confirmed along with the weight loss. The XRD patterns exposed that the Mn_2O_3/SiO_2 gel samples heat treated at different temperatures are found to be amorphous till 823 K Further heat treatment, XRD patterns revealed the formation of crystallite Mn_2O_3 nanoparticles dispersed in the silica amorphous matrix. The calculated crystalline size from the XRD pattern was found to be ~30 nm. The FTIR results confirmed evidently the formation of the Mn_2O_3 structure together with the SiO_2 amorphous matrix.

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References

[1] Y. F. Han, F. Chen, Z. Zhong, K. Ramesh, L. Chen, E. Widjaja, J. Phys. Chem. B, 110, 24450-24456, 2006.

[2] C. Shao, H. Guan, Y. Liu, X. Li, X. Yang, J. Solid State chemistry 177, 2628-2631, 2004.

[3] S. Imamura, M. Shono, N. Okamoto, A. Hamada, S. Ishida, Appl. Catal. A 142, 279-288, 1996.

[4] H.M. Zhang, Y. Teraoka, N. Yamazoe, Catal. Today 6, 155-162,1989.

[5] Z. Gui, R. Fan, X-H. Zen, Y-C. Wu, Inor. Chem. Comm. 4, 294-296, 2001.

[6] L. Li, G. Li, R. L. Smith, H. Inomata, Chem. Mater., 12, 12, 3705-3714, 2000.

[7] I. Prakash, P. Muralidharan, N. Nallamuthu, M. Venkateswarlu, N. Satyanarayana, J. Am. Cer. Soc. 89, 7,2220-2225, 2006.

[8] P. Muralidharan, M. Venkateswarlu, N. Satyanarayana, Solid State Ionics, 166, 27-38, 2004.

[9] B. Gillot, M. E. Guendouzi, M. Laarj, Mater. Chem. and Phys. 70, 54-60, 2001.