

Synthesis and Characterization of Cr₂O₃ Nanoparticles with Triethanolamine in Water under Microwave Irradiation

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Received: 17 May 2011 / Revised: 9 January 2012 / Accepted: 15 January 2012

Abstract

Cr₂O₃ nanoparticles were prepared using Cr(NO₃)₃.9H₂O as starting material, triethanolamine (TEA) as template and water as green solvent under microwave irradiation. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), photoluminescence (PL) and Raman spectroscopy. The size distribution of individual particles were determined to be about 25-70 nm. The catalytic activity of the prepared Cr₂O₃ nanoparticles was found to be more active than the bulk sample in the epoxidation of norbornene with 70% activity and 95% selectivity.

Keywords: Chromium oxide; Nanoparticles; Microwave irradiation; Template; Triethanolamine

Introduction

During the past decade, considerable progress in the synthesis of nanoparticles has been achieved. Nanomaterials, particularly transition-metal oxides play an important role in many areas of chemistry, physics and materials science [1]. In technological applications, metal oxides have traditionally been used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts [1]. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species. Metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites [1,2].

Among metal oxides, special attention has been focused on the formation and properties of chromia (Cr₂O₃) which is important as heterogeneous catalyst [3-5], coating material, wear resistance [6,7], advanced colorant [8], pigment [9] and solar energy collector [10]. Various techniques for the synthesis of Cr₂O₃ nanoparticles such as hydrothermal [11-13], sol-gel [14], combustion [15], precipitation-gelation [8], gel citrate [16], mechanochemical process [17], urea assisted homogeneous precipitation [18,19], gas condensation [20], and microwave plasma have been developed [21]. Both chromium oxide and supported chromium have been used as catalysts in many reactions such as oxidation of toluene [22], ethane dehydrogenation [15], and methanol decomposition [2].

Microwave heating occurs through the interaction of electromagnetic radiation with the dipole moment of the molecules. As required by green chemistry principles,

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water as an inexpensive, non-toxic, non-flammable and abundant material in nature, is a safer and ideal solvent for microwave-activated reactions [23-24]. The direct transformation of the energy into the components present in the reaction vessel not only reduces the synthesis time, but also affords the desired nanoparticles with a narrow particle size distribution, as has been reported in a few studied syntheses [21]. Herein, we report the preparation of Cr_2O_3 nanocrystals under microwave irradiation using TEA as template and water as a green solvent. We have exploited nano-sized Cr_2O_3 sample as catalyst in the epoxidation of norbornene with tert-butyl hydroperoxide (TBHP). Norbornene epoxide has wide applications in polymer synthesis, pharmaceutical intermediates, and organic synthesis [25].

Materials and Methods

Materials and Instruments Details

All chemicals and reagents were of synthetic grade and used without further purification. Powder XRD patterns of samples were recorded on a (SEIFERT), PTS 3003 with CuK_α radiation ($\lambda=1.5406\text{\AA}$). Transmission electron micrograph (TEM) and selected area electron diffraction (SAED) were taken with a Philips CM 200 FEG. Samples for TEM were prepared by dropping a dilute suspension of the sample powders onto a standard carbon film on a copper grid. Fourier transformation infrared spectroscopy (FTIR) was acquired with Bruker, Tensor 27 DTGS spectrometer, using KBr pellets. Raman spectra were obtained with Mediso WI. 53711, Thermo Nicolet corp. Photoluminescence spectra were recorded in a Perkin Elmer LS-55 spectrofluorometer equipped with pulse Xenon lamp, using a triangular quartz cell.

Synthesis of Cr_2O_3 Nanocrystals

In a typical procedure, 25 ml of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.2M) aqueous solution was mixed with appropriate amount of triethanolamine as template (5, 10 and 15 mmol). After stirring for 40 min, the mixture was placed under microwave irradiation for 5 min. The green solid product was filtered and dried in air at room temperature. The solid was then calcined at 200, 500 and 700°C for 2 h.

Results and Discussion

X-ray Diffraction Results (XRD)

Figure 1 shows the XRD pattern of the Cr_2O_3 nanoparticles prepared by $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the chromium source and triethanolamine as template with molar ratio of 2:1 after calcination at 700°C. Based on the XRD pattern, whereas the prepared sample calcined

at 200°C proved to be amorphous, similar nanoparticles were obtained after annealing at 500°C and 700°C. The crystallinity of the sample annealed at 700°C was found to be much better than that calcined at 500°C. Inspection of the results revealed that annealing of Cr_2O_3 at 700°C resulted in the formation of rhombohedral phase (JCPDS no. 38-1479 with $a=4.95876\text{\AA}$, $b=13.594\text{\AA}$ and space group $R\bar{3}c$). The major peaks were indexed as (012), (110), (104), (113), (024), (116), (214), and (300) [17]. The synthesized Cr_2O_3 crystallite sizes was calculated from the diffraction peaks using Eq. (1):

$$D_c = K\lambda / \beta \cos \theta \quad \text{Eq. (1)}$$

In which K is a constant (ca0.9), λ is the X-ray wavelength used in XRD (1.5406\AA), θ is the Bragg angle and β is the pure diffraction broadening peak located at half-height, which is the broadening due to the crystallite dimensions. The calculated average crystal size, using Scherrer formula based on Table 1 was 14.82 nm. Sample lattice constants were evaluated using equation 2:

$$1/d^2 = 4/3 \{ (h^2 + kh + k^2)/a^2 \} + (l^2/c^2) \quad \text{Eq. (2)}$$

The calculated constants from this equation for reflections from (214) and (024) planes are $a = 4.9752\text{\AA}$ and $c = 13.8178\text{\AA}$. It is observed that sample lattice constants coincide with that of hexagonal structure. Diffraction points corresponding to reflections from (214), (012) and (024) planes are shown in diffraction pattern in Figure 2b.

Morphology of Sample

The morphology of the prepared Cr_2O_3 nanoparticles (template/Cr = 2/1) calcined at 700°C was characterized by TEM images as shown in Figure 2. From the TEM image results, we can observe a large quantity of uniform nanoparticles (NPs) with average particle size of 25-70 nm, indicates that our synthesis process is an easy method for the preparation Cr_2O_3 nanoparticles.

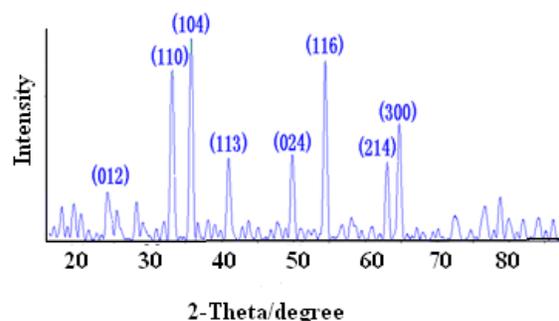


Figure 1. XRD pattern of Cr_2O_3 nanoparticles prepared under microwave irradiation and annealed at 700 °C (TEA / Cr salt =2/1).

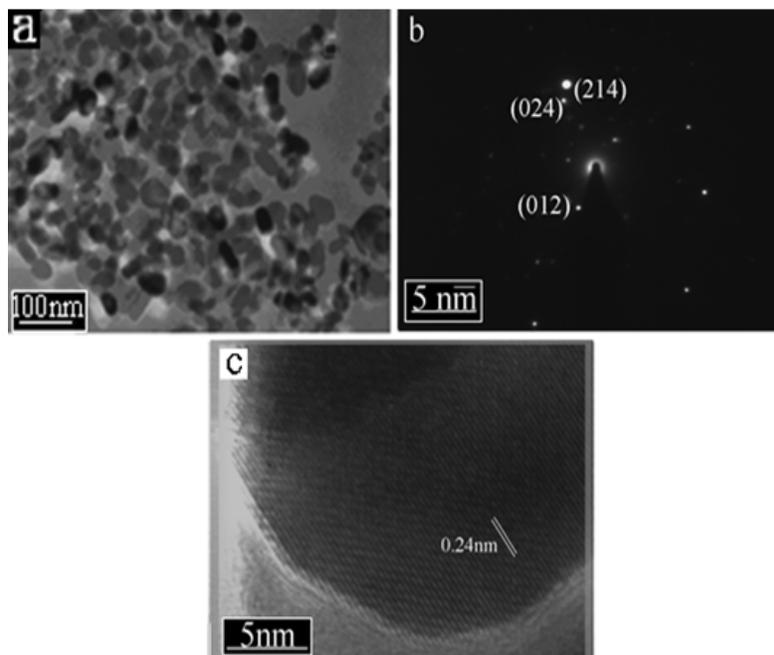


Figure 2. (a) TEM (b) diffraction pattern and (c) HRTEM of Cr₂O₃ nanoparticles obtained by TEA and annealed at 700 °C (Cr salt/ TEA=1/2).

The SAED pattern taken from the selected Cr₂O₃ NPs confirms the XRD pattern (Fig. 2b). The distance between the parallel sheets of Cr₂O₃ NPs is 0.24 nm (Fig. 2c).

The FTIR spectrum of Cr₂O₃ NPs is shown in Figure 3. A broad band at 3420 cm⁻¹ corresponds to the stretching modes of surface OH groups. Metal oxide Cr₂O₃ generally reveal absorption bands below 1000 cm⁻¹ due to inter-atomic vibrations. Two sharp peaks displayed at 652 and 562 cm⁻¹ attributed to Cr-O stretching modes, are clear evidence for the presence of the crystalline Cr₂O₃ [26].

The Raman spectra of bulk and Cr₂O₃ NPs are shown in Figures 4a and 4b respectively. A broad peak centered at 480 cm⁻¹ with a shoulder appearing at 560 cm⁻¹ is due to the bulk sample, whereas the Cr₂O₃ NPs displays an absorption band at 572 cm⁻¹ with a blue shift and relatively sharp peaks due to the active A_{1g} Raman mode. The obtained results are consistent with those that reported before [27]. The PL spectra of Cr₂O₃ NPs and bulk sample are shown in Figure 5. Interestingly, two peaks at 448 and 488 cm⁻¹ region with higher intensity relative to that of bulk one is observed.

Catalytic Activity of the Prepared Cr₂O₃ Nanocrystals

Results obtained for oxidation of norbornene with TBHP in the presence of Cr₂O₃ nanocrystals as catalyst are given in Table 2. The catalytic activity of Cr₂O₃ nanocrystals was found to be 70% with 95% selectivity

toward the formation of the corresponding epoxide. Such result in comparison to that of the bulk sample with 26% conversion is promising. The higher activity of Cr₂O₃ nanocrystals seems to be due to the much larger ratio of surface atoms to the nanoparticle surface.

Table 1. XRD of Cr₂O₃ nanoparticles

Angle JCPDS (2θ)	Observed (2θ)	calculated d(Å)	(hkl)
24.484	24.1158	3.686	(012)
36.181	33.1088	2.702	(110)
33.584	35.7577	2.508	(104)
41.463	40.9711	2.200	(113)
50.199	49.8305	1.828	(024)
54.829	54.4152	1.684	(116)
63.421	63.0217	1.473	(214)
65.078	64.7151	1.439	(300)

Table 2. Effect of catalytic activity of nanoparticles and bulk Cr₂O₃ on the epoxidation of norbornene with TBHP

Catalyst	Conversion (%)	Epoxide (%)	^a TON
Cr ₂ O ₃ (bulk)	26	93	130
Cr ₂ O ₃ (nanoparticle)	70	95	350

Reaction conditions: catalyst (0.2 g), substrate (1.88 g), TBHP (3 ml), acetonitrile, (5 ml), reaction time (6 h). ^aTON= mmol of products/mmol of Cr x 100

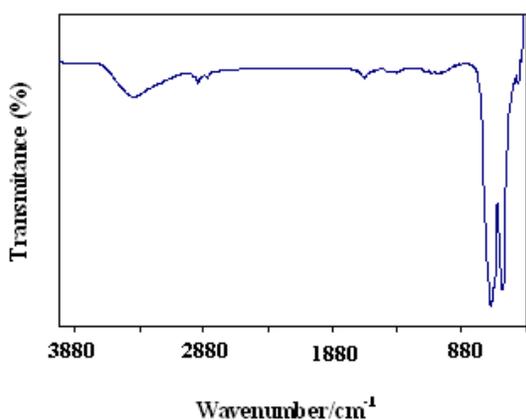


Figure 3. FTIR spectrum of the nano-sized Cr_2O_3 prepared under microwave conditions using TEA with molar ratio of template to metal as 2 to 1.

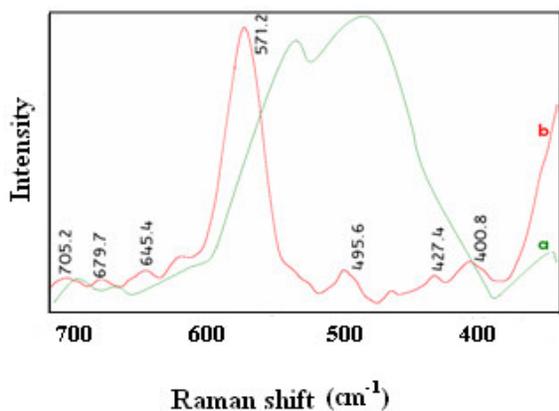


Figure 4. Raman spectra of (a) bulk Cr_2O_3 (b) nano-size Cr_2O_3 .

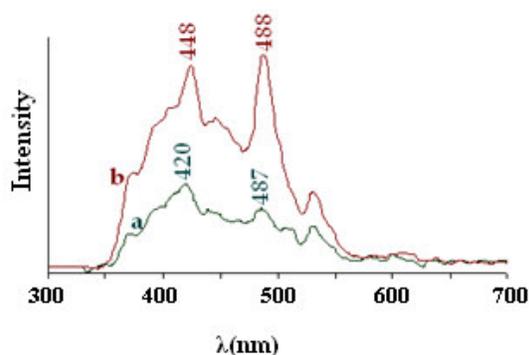


Figure 5. PL spectra of (a) bulk Cr_2O_3 and (b) nano-size Cr_2O_3 .

In summary, we have described the synthesis of Cr_2O_3 NPs under microwave conditions using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as chromium source, water as solvent and triethanol amine as template. The best results were obtained with template to chromium source molar ratio of 2/1. Results obtained in this study clearly indicate the key role of the template on the morphology of Cr_2O_3 , without which no nanoparticles is produced under similar condition. Particularly significant in this research is the enhanced catalytic activity observed for nano-sized Cr_2O_3 in comparison to that of bulk sample in the high selective epoxidation of norbornene with TBHP. Our expedient preparation method proceeding to completion in 5 min, plus the easily controllable conditions with using low cost chromium source is merit to be considered for scaling up by industrial researchers.

Acknowledgements

The financial support from the University of Alzahra is gratefully acknowledged.

References

1. Fernández-Garcia, M. Martinez-Arias, A. Hanson, J.C. and Rodriguez, J.A. Nanostructured oxides in chemistry: characterization and properties. *Chem. Rev.* **104**: 4063-4104 (2004).
2. Tsoncheva, T. Roggenbuck, J. Paneva, D. Dimitrov, M. Mitov, I. and Froba, M. Nanosized Iron and chromium oxides supported on mesoporous CeO_2 and SBA-15 silica: Physicochemical and catalytic study. *Appl. Surf. Sci.* **257**: 523-530 (2010).
3. Rao, T.V.M. Yang, Y. and Sayari A. Ethane dehydrogenation over pore-expanded mesoporous silica supported chromium oxide: 1. Catalysts preparation and characterization. *J. Mol. Catal. A: Chem.* **301**: 152-158 (2009).
4. Rao, T.V.M., Zahidi, E. and Sayari, A., Ethane dehydrogenation over pore-expanded mesoporous silica-supported chromium oxide: 2. Catalytic properties and nature of active sites. *J. Mol. Catal. A: Chem.* **301**: 159-165 (2009).
5. Wang, G. Zhang, L. Deng, J. Dai, H. He, H. and Tong, C. Preparation, characterization and catalytic activity of chromia supported on SBA-15 for the oxidative dehydrogenation of isobutene. *Appl. Catal. A* **355**: 192-201 (2009).
6. Pang, X. Gao, K. Luo, F. Emirov, Y. Levin, A. A. and Volinsky, A.A. Investigation of micro structure and mechanical properties of multi-layer $\text{Cr}/\text{Cr}_2\text{O}_3$ coatings. *Thin Solid Films* **517**: 1922-1927 (2009).
7. Hou, X. and Choy, K.-L. Synthesis of Cr_2O_3 -based nanocomposite coatings within incorporation of inorganic fullerene-like nanoparticles. *Thin Solid Films* **516**: 8620-8624 (2008).
8. Kim, D.-W. Shin, S.-I. Lee, J.-D. and Oh, S.-G.

- Preparation of chromia nanoparticles by precipitation–gelation reaction. *Mater. Lett.* **58**: 1894–1898 (2004).
9. Li, P. Xu, H.-B. Zhang, Y. Li, Z.-H. Zheng, S.-L. and Bai, Y.-L. The effects of Al and Ba on the colour performance of chromic oxide green pigment. *Dyes and Pigments* **80**: 287–291 (2009).
 10. Teixeira, V. Sousa, E. Costa, M. F. Nunes, C. Rosa, L. Carvalho, M. J. Collares-Pereira, M. Roman, E. and Gago, J., Spectrally selective composite coatings of Cr-Cr₂O₃ and Mo-Al₂O for solar energy applications. *Thin Solid Films* **392**: 320–326 (2001).
 11. Pei, Z. Xu, H. and Zhang, Y. Preparation of Cr₂O₃ nanoparticles via C₂H₅OH hydrothermal Reduction. *J. Alloys Compd.* **468**: L5–L8 (2009).
 12. Pei, Z. and Zhang, Y. A novel method to prepare Cr₂O₃ nanoparticles. *Mater. Lett.* **62**: 504–506 (2008).
 13. Sheng, L. Feng-Li, L. Shao-Min, Z., Peng, W. Ke, C. and Zu-Liang, D. Highly sensitive room- temperature gas sensors based on hydrothermal synthesis of Cr₂O₃ hollow nanospheres. *Chinese Physics B*, **18**: 3985–3989 (2009).
 14. El-Sheikh, S. M. Mohamed, R.M. and Fouad O.A. Synthesis and structure screening of nanostructured chromium oxide powders. *J. Alloys Compd.* **482**: 302–307 (2009).
 15. Fu, X.-Z. Luo, X.-X., Luo, J.-L. Chuang, K.T. Sanger, A. R. and Krzywicki, A. Ethane dehydrogenation over nano-Cr₂O₃ anode catalyst in proton ceramic fuel cell reactors to co-produce ethylene and electricity. *J. Power Sources* **196**: 1036–1041 (2011).
 16. Kim, D.-W. Oh, S.-G. Agglomeration behavior of chromia nanoparticle sprepared by amorphous complex method using chelating effect of citric acid. *Mater. Lett.* **59**: 976–980 (2005).
 17. Li, L. Yan, Z. Lu, G. Q. and Zhu, Z. H. Synthesis and structure characterization of chromium oxide prepared by solid thermal decomposition reaction. *J. Phys. Chem. B*, **110**: 178–183 (2006).
 18. Abecassis-Wolfovich, M. Rotter, H. Landau, M. V. Korin E. Erenburg, A. I. Mogilyansky, D. and Gartstein, E. Texture and nanostructure of chromia aerogels prepared by urea-assisted homogeneous precipitation and low-temperature supercritical drying. *J. Non-Cryst. Solids* **318**: 95–111(2003).
 19. Ocana, M. Nanosized Cr₂O₃ hydrate spherical particles prepared by urea method. *J. Eur. Ceram. Soc.* **21**: 931–939 (2001).
 20. Balchandran, U. Siegel, R.W. Liao Y. X. and Askew, T. R. Synthesis, sintering and magnetic properties of nanophase Cr₂O₃. *Nanostruct. Mater.* **5**: 505–512 (1995).
 21. Vollath, D. Szabo, D.V. and Willis, J.O. Magnetic properties of nanocrystalline Cr₂O₃ synthesized in a microwave plasma. *Mater. Lett.* **29**: 271–279 (1996).
 22. Wang, Y. Yuan, X. Liu, X. Ren, J. Tong, W. Wang, Y. and Lu, G. Mesoporous single-crystal Cr₂O₃: Synthesis, characterization, and its activity in toluene removal, *Solid State Sciences* **10**: 1117–1123 (2008).
 23. Dallinger, D. and Kappe, C.O. Microwave-Assisted Synthesis in Water as Solvent. *Chem. Rev.* **107**: 2563–2591 (2007).
 24. Dahl, J. A. Maddux, B. L. S. and Hutchison, J. E., Toward greener nanosynthesis. *Chem. Rev.* **107**: 2228–2269 (2007).
 25. Kala Raj, N. K. Ramaswamy, A.V. and Manikandan, P. Oxidation of norbornene over Vanadium-substituted phosphomolybdic acid catalysts and spectroscopic investigations. *J. Mol. Catal. A: Chem.* **227**: 37–45 (2005).
 26. Henderson, M. A. Photochemistry of methyl bromide on the α-Cr₂O₃ (0001) surface. *Surf. Sci.* **604**: 1800–1807 (2010).
 27. Mougina, J. Le Bihanb, T. Lucazeauc, G. High-pressure study of Cr₂O₃ obtained by high-tempetature oxidation by x-ray diffraction and Raman spectroscopy. *J. Phys. Chem. Solids* **62**: 553–563 (2001).