Journal of Achievements in Materials and Manufacturing Engineering
Volume 63 • Issue 2 • April 2014
International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Hydrothermal synthesis and characterization of double phase magnesium vanadium oxides

G. Celik*, S. Somunkiranoglu, F. Kurtulus
Department of Chemistry, Faculty of Science & Art,
University of Balikesir, 10145 Balikesir, Turkey
* Corresponding e-mail address: gulsahcelik@balikesir.edu.tr

Received 11.01.2014; published in revised form 01.04.2014

ABSTRACT

Purpose: The electronic conductivity of derivatives of $Mg_xV_yO_z$ type compounds is magnitude higher than that of the vanadium oxide without magnesium. Also, magnesium containing compounds exhibit significantly improved kinetic behaviour and rate capability. In this perspective, we aim to synthesis of magnesium vanadium oxide under mild hydrothermal conditions.

Design/methodology/approach: Double phase magnesium vanadium oxides were synthesized by dissolving magnesium nitrate and V_2O_5 in the ultra pure water with in an appropriate molar ratio. The homogeneous solution in the stainless-steel container was put into furnace and heated 3 days (72 hours) at 180ºC. The product was washed by high pure water and ethanol, dried at 70ºC for 2 hours and homogenized in an agate mortar. Then, final product was ready to analyse. Powder X-ray Diffractometer (XRD) was used to determine crystal structure of the product. FTIR spectrum was taken to support the functional groups. Thermo gravimetric-differential thermal analysis (TG/DTA) was carried out to identify thermal character. Morphological properties and semi-quantitative analyse of the sample was performed by Scanning electron microscope/Electron disperse (SEM/EDX). Phase analyse was realized by High Score Plus Program.

Findings: The XRD patterns show that the product is $Mg_{0.01}V_2O_5$ (ICDD:89-0610)-β-$Mg_{1.9}V_3O_8$ (ICDD:23-1232). The result of phase analyse show that the sample contains %27.2 $Mg_{0.01}V_2O_5$ and %72.8 β-$Mg_{1.9}V_3O_8$. The mixture was obtained under mild hydrothermal conditions for the first time as distinct from literature. Characterization studies were mainly based on powder X-ray diffraction technique. Also, thermal behaviour, morphology and percentage of component were determined.

Research limitations/implications: The principal of hydrothermal method is low temperature/high pressure synthesis in water. Sometimes, optimizing of the most convenient condition can be time and chemical consuming. This situation could be a limit to use hydrothermal method. But, this can eliminate with deep background.

Practical implications: The compounds can find many application areas utilizing kinetic behaviour, rate capability and electronic conductivity properties.

Originality/value: We achieved the hydrothermal synthesis of $Mg_{0.01}V_2O_5$ (ICDD:89-0610)-β-$Mg_{1.9}V_3O_8$ (ICDD:23-1232) under mild hydrothermal conditions for the first time as distinct from literature.

Keywords: Powder metallurgy; Hydrothermal synthesis; Magnesium vanadium oxide

Reference to this paper should be given in the following way:

G. Celik, S. Somunkiranoglu, F. Kurtulus, Hydrothermal synthesis and characterization of double phase magnesium vanadium oxides, Journal of Achievements in Materials and Manufacturing Engineering 63/2 (2014) 53-57.

MATERIALS

1. Introduction

Vanadium is a transition element (atomic weight 50.94) with valences -1, 2, 3, 4, and 5. Vanadium acts a big part in human. Minimal amounts of vanadium cause several kinds of effects in body such as binding transferrin, ferritin and iron binding proteins [1]. On the other hand, the electronic conductivity of derivatives of $Mg_xV_yO_z$ type compounds is magnitude higher than that of the vanadium oxide without magnesium. Also, magnesium containing compounds exhibit significantly improved kinetic behaviour and rate capability [2-3].

Magnesium-vanadium oxides are the top catalyst for the oxidative dehydrogenation of alkanes [4]. V_2O_5, a member of acidic oxide family, can react rapidly with the basic MgO resulting magnesium vanadates. Various magnesium vanadates such as magnesium orthovanadate, magnesium pyrovanadate and magnesium metavanadate can be formed in different compositions of vanadium pentaoxide and magnesium oxide [5]. In the past years, magnesium vanadates were synthesized by high temperature calcination method [5], impregnation pathway [6-8], citrate methods [9], absorption of vanadyl compounds [10-11], coprecipitation [6,9,12-15]. Catalytic activity of vanadium containing magnesium oxides is higher than magnesium oxide without vanadium [4]. Solid state methods produce low surface area. So, high temperature calcination methods were avoided to get high surface area [4].

In this perspective, we aim to synthesis of magnesium vanadium oxide, having staggering unusual properties, under mild hydrothermal conditions.

2. Materials and method

2.1. Hydrothermal synthesis of magnesium vanadium oxide

Double phase magnesium vanadium oxides were synthesized by hydrothermal method. After dissolving magnesium nitrate and V_2O_5 in ultra pure water by heat with in an appropriate molar ratio, the resultant homogeneous solution was transferred into stainless-steel container. Stainless-steel teflon autoclave was put into furnace and heated 3 days (72 hours) at 180ºC. The filtered product was washed by high pure water and ethanol, and dried at 70ºC for 2 hours to get rid of volatile component. The dried sample was homogenized in an agate mortar and placed into eppendorf to analyse.

2.2. Analyse of structure

X-ray powder diffraction analysis (XRD) was performed using PANanalytical X'Pert PRO Diffractometer (XRD) with Cu Kα (1.5406 Å, 45 kV and 30 mA) radiation. FTIR spectrum was taken on a Perkin Elmer Spectrum 100 FTIR Spectrometer from 4000 to 650 cm^{-1}. Thermo gravimetric-differential thermal analysis (TG/DTA) was carried out by Perkin Elmer Diamond TG/DTA. Morphological properties and semi-quantitative analyse of the sample were realized by ZEISS Supra 40 VP. Phase analyse was realized by High Score Plus/Rietveld Program 3.0 version (license number:92000029). The Binder ED 53/E2 furnaces for heating process and stainless-steel Teflon autoclave by Parr Instrument Company as a hydrothermal container were used.

3. Results and discussion

The XRD patterns are shown in Figure 1. When we compare the patterns to the standard database, they correspond to two types of magnesium vanadate. The product is determined as double phase containing $Mg_{0.01}V_2O_5$ (ICDD:89-0610)-β-$Mg_{1.9}V_3O_8$ (ICDD:23-1232). The phase analyse was realized by High Score Plus/Rietveld program using XRD patterns. The results show that the sample contains %27.2 $Mg_{0.01}V_2O_5$ and %72.8 β-$Mg_{1.9}V_3O_8$. The double phase was obtained under mild hydrothermal conditions for the first time as distinct from literature.

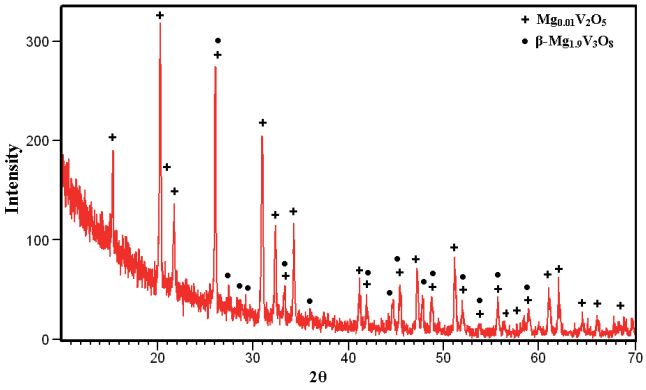

Fig. 1. XRD pattern of the sample

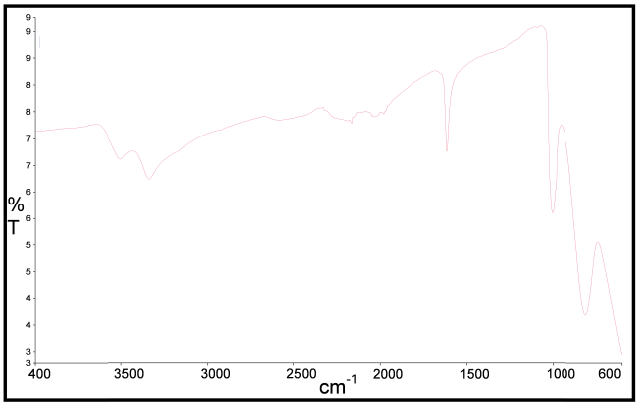

Fig. 2. FTIR spectrum of the sample

FTIR spectra of the product are presented in Figure 2. The peaks in the 790-830 range belong to V-O-V [16], Mg-O, VO_4^{4-} and VO_4^{3-} vibrations [17]. The other peaks can be caused by humidity and carbon dioxide [17].

TG/DTA curves of magnesium vanadium oxide were given in Figure 3. The process was done in the 0-1200ºC range. The material is quite stable, because there is no significant weight loss in the range. The material can be called as heat resistant.

In Figure 4, SEM micrograph of the sample is displayed. In the picture, there are particles in various sizes. In this case, size diversity of the particles demonstrates to being double phase of the sample.

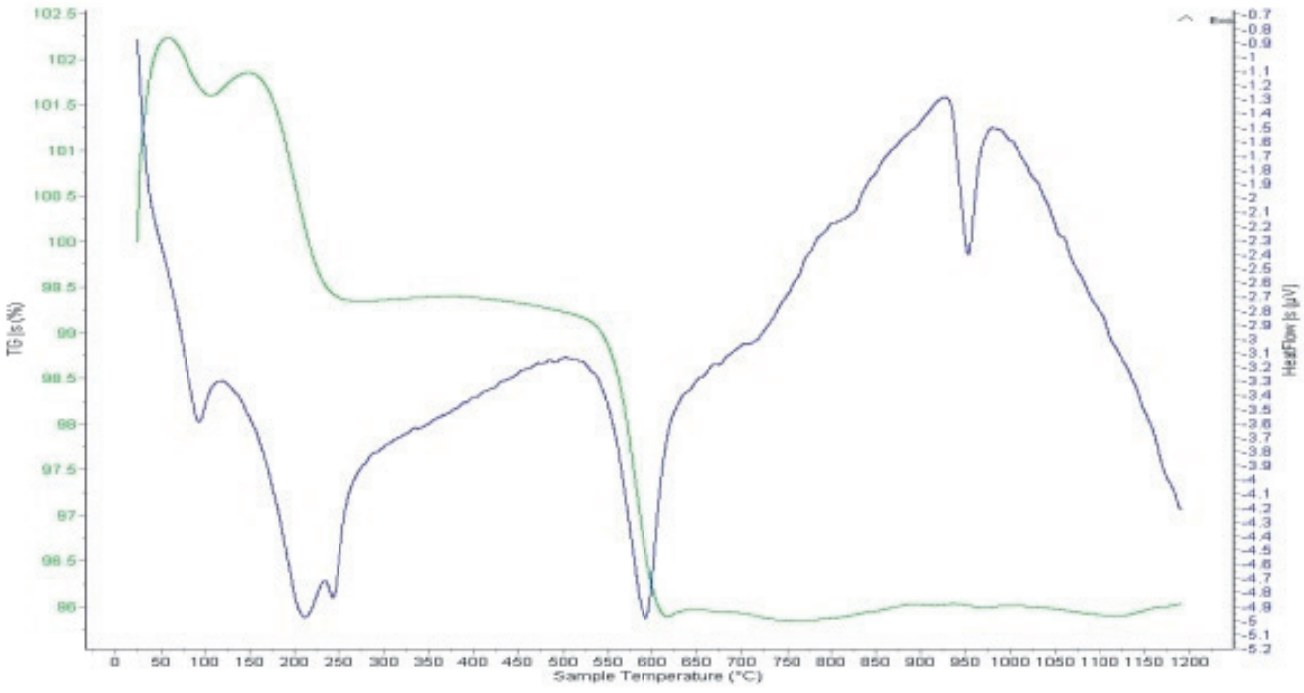

Fig. 3. TG/DTA curves of the sample

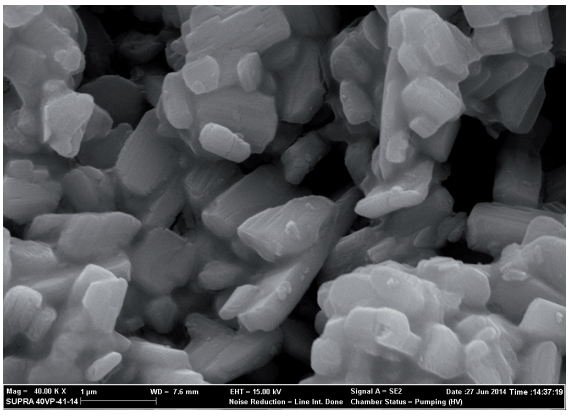

Fig. 4. SEM micrograph of the sample

The results of EDX analyse is exhibited in Figure 5. Green, pink and blue lines correspond with V, O, and Mg, respectively. The small peaks near 25 keV become involved with platinum used covering the sample. The results are taken into account; the calculated combination ratio of the elements is $Mg_2V_{17}O_{32}$. The EDX results are in accordance with XRD data.

4. Conclusions

In brief, we achieved the goal, $Mg_{0.01}V_2O_5$ (ICDD:89-0610)-β-$Mg_{1.9}V_3O_8$ (ICDD:23-1232) was obtained under mild hydrothermal conditions for the first time as distinct from literature. Characterization studies were mainly based on powder X-ray diffraction method. Additionally, thermal behaviour, morphology, EDX analyses and percentage of component were carried out.

Acknowledgements

We thank to TUBITAK BIDEB and BAU-BAP for financial support.

Additional information

This paper will be presented in IMSP'2014.

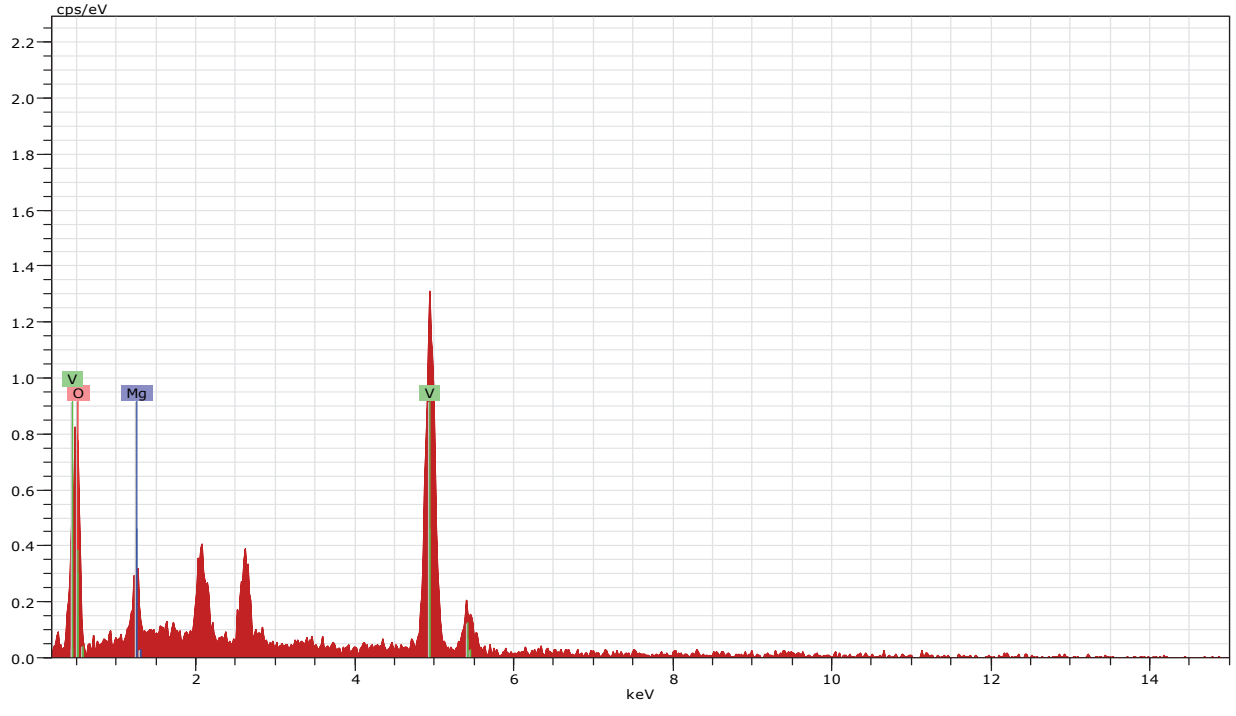

Fig. 5. EDX result of the sample

References

[1] M. Kohlmeier, Vanadium, Nutrient Metabolism, Food Science and Technology A (2003) 762-766.

[2] K.H. Seng, J. Liu, Z.P. Guo, Z.X. Chen, D. Jia, H.K. Liu, Free-standing V_2O_5 electrode for flexible lithium ion batteries, Electrochemistry Communications 13 (2011) 383-386.

[3] M. Eguchi, K. Ozawa, Lithium insertion property of $Li_{22}V_2O_5$•nH_2O, Electrochimica Acta 52 (2007) 2657-2660.

[4] H.H. Kung, M.C. Kung, Oxidative dehydrogenation of alkanes over vanadium-magnesium-oxides, Applied Catalysis A: General 157 (1997) 105-116.

[5] G.M. Clark, R. Morley, A study of the MgO-V_2O_5 system, Journal of Solid State Chemistry 16 (1976) 429-435.

[6] M.A. Chaar, D. Patel, M.C. Kung, H.H. Kung, Selective oxidative dehydrogenation of butane over V-Mg-O catalysts, Journal of Catalysis 105 (1987) 483-498.

[7] D.S.H. Sam, V. Soenen, J.C. Volta, Oxidative dehydrogenation of propane over V-Mg-O catalysts, Journal of Catalysis 123 (1990) 417-435.

[8] A. Corma, J.M. López Nieto, N. Paredes, Influence of preparation methods of V-Mg-O catalyst on their catalytic properties for the oxidative dehydrogenation of propane, Journal of Catalysis 144 (1993) 425-438.

[9] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, Effect of Coexistence of Magnesium Vanadate Phases in the Selective Oxidation of Propane to Propene, Journal of Catalysis 148 (1994) 56-67.

[10] J. Kijenski, A. Baiker, M. Glinsky, P. Dollenmeier, A. Wokaum, Monolayers and double layers of vanadium pentoxide on different carriers: Preparation, characterization and catalytic activities, Journal of Catalysis 101 (1986) 1-11.

[11] W.K. Sharma, A. Wokaum, A. Baiker, ESR characterization of vanadium pentoxide monolayers and double layers supported on various carriers, Journal of Pyhsical Chemistry 90 (1986) 2715-2718.

[12] M. Del Arco, M.J. Holgado, C. Martin, V. Rives, New route for the synthesis of V_2O_5-MgO oxidative dehydrogenation catalysts, Journal of Materials Science Letters 6 (1987) 616-619.

[13] J.M.L. Nieto, A. Dejoz, M.I. Vazquez, W.O. Leary, Oxidative dehydrogenation of n-butane on MgO-supported vanadium oxide catalysts, Journal of Cunningham Catalysis Today 40 (1998) 215-228.

[14] A. Pantazidis, A. Burrows, C.J. Kiely, C. Mirodatos, Direct evidence of active surface reconstruction during oxidative dehydrogenation of propane over V-Mg-O catalyst, Journal of Catalysis 177 (1998) 325-334.

[15] S.R.G. Carrazán, C. Peres, J.P. Bernard, M. Ruwet, P. Ruiz, B. Delmon, Catalytic synergy in the oxidative dehydrogenation of propane over Mg-V-O catalysts, Journal of Catalysis 158 (1996) 452-476.

[16] M.I. Khan, T. Hope, S. Tabassum, Synthesis, reactivity, X-ray structure and thermal study of the mixed- metal oxide hydrate $[Mn(H_2O)_2V_2O_6]$, Solid State Science 1 (1999) 163-178.

[17] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. A Willey-Interscience Publication, John Wiley and Sons, 1986.