# NANOSIZE NiO/MgO/ZrO$_2$ COMPOSITES PREPARED BY CITRIC ACID/ETHYLENE GLYCOL METHOD

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## บทคัดย่อ

ได้ทำการเตรียมคอมโพสิต NiO/MgO/ZrO$_2$ ด้วยวิธีกรดซิตริก/เอทิลีนไกลคอล ซึ่งมีอนุภาค NiO กระจายตัวอย่างสม่ำเสมอในคอมโพสิต ทำการสังเคราะห์คอมโพสิตโดยใช้โลหะไนเตรทเป็นสารตั้งต้น กรดซิตริกเป็นสารคอมเพล็กซิง พรีเคอเซอร์พอลิเมอร์เกิดขึ้นจากกรดซิตริกและเอทิลีนไกลคอล สัดส่วนโดยโมลของกรดซิตริกต่อเอทิลีนไกลคอลที่ใช้เป็น 1.0-2.0 เจลที่ทำให้แห้งนำมาเผาภายใต้บรรยากาศแก๊สไนโตรเจนและอากาศที่อุณหภูมิต่างๆ ทำการตรวจพิสูจน์เอกลักษณ์ของคอมโพสิตด้วย TG/DTA, XRD, SEM และ BET สารละลายของแข็งของ อยู่ในเฟสลูกบาศก์ที่มีพื้นที่ผิวสูงกว่า (140 ตารางเมตร/กรัม) และมีขนาดอนุภาคที่เล็กกว่า (20 นาโนเมตร) เมื่อเปรียบเทียบกับที่ได้จากวิธีตกตะกอน

## Abstract

A citric acid/ethylene glycol method was used to prepare the NiO/MgO/ZrO$_2$ composite, in which NiO particles uniformly distributed in the composite. The composite was synthesized by using metal nitrates as raw materials, citric acid as complexing agent. A polymeric precursor was formed from citric acid and ethylene glycol. The citric acid/ethylene glycol molar ratio used is 1.0-2.0. The dried gel was calcined under nitrogen atmosphere and air at various temperatures. The composites were characterized by TG/DTA, XRD, SEM and BET. The solid solution of NiO/MgO/ZrO$_2$ exists as cubic phase with higher surface area (140 m$^2$/g) and smaller particle size (20 nm) compared to the coprecipitation method.

**Key words**: composite, nickel, magnesium, zirconium, citric acid, ethylene glycol

## Introduction

One of the outstanding challenges in the field of porous materials is the design and synthesis of chemical structures with high surface areas. Metal oxide nanoparticles comprise one important class of such materials, and have favorable optical, magnetic and electronic properties.

Oxides that form solid solutions show interesting properties as catalyst supports, especially those involving CeO$_2$ and ZrO$_2$. The properties of these oxides can be modified by introduction of cations such as $Ca^{2+}$, $Mg^{2+}$, etc., into their lattice. Coprecipitation method was used for the synthesis of MgO-$ZrO_2$ composite [1] and Ni/$CeO_2$-$ZrO_2$ [2]. The addition of alkaline earth oxides such as MgO and CaO to oxide supports for Ni catalysts has been reported to improve reforming reactions of methane by preventing carbon deposition on the active sites [3]. Ni/MgO is the most preferred catalyst as it exists in the form of solid solution which stabilized nickel against sintering during high temperature steam reforming of methane. Moreover it has the higher activity and selectivity [4, 5]. This can be prepared with sol-gel citrate technique [6] which has been frequently used for the synthesis of single and multi-oxide powders because of cheapness, convenience to set up, and good chemical homogeneity of synthesized powder. This method can prepare homogeneous powders at lower temperatures, the reactant cations are intimately mixed on the atomic scale, so the rate of the reaction will be increased, leading to lower synthesis temperatures and smaller particles. At room temperature pure zirconia exists in monoclinic phase. With increasing of temperature, the monoclinic phase transforms to tetragonal and then to cubic phase[7]. More recently, NiO/$ZrO_2$ composite was synthesized by polymeric complex reaction [8]. First metal-citric acid complexes were formed. The subsequent polymerization of free citric acid and coordinated citric acid in the metal-citric acid complexes with ethylene glycol results in formation of a polymeric resin. This method enables to prepare multicomponent metal oxides with very good homogeneity [9].

In this work, we prepared NiO/MgO/$ZrO_2$ composites by citric acid/ethylene glycol method. The resultant powders have been characterized by various techniques to examine the effect of the preparation method on the surface area and crystal size, and reveal the presence of a new solid state species. The aim of this work is to obtain the NiO/MgO/$ZrO_2$ composites in nano size with high surface area and good morphology.

## Materials and methods

The chemicals used include of magnesium nitrate hexahydrate, $Mg(NO_3)_2.6H_2O$, zirconyl oxynitrate hydrate $ZrO(NO_3)_2.8H_2O$, nickel nitrate hydrate $Ni(NO_3)_2.6H_2O$, ethylene glycol and citric acid. All chemicals were analytical grade (from Fluka) and were used without further purification.

## Synthesis of composite

The procedure is illustrated in Figure 1. $Mg(NO_3)_2.6H_2O$ (12.7 mmol), $ZrO(NO_3)_2.8H_2O$ (12.7 mmol) were dissolved in 50 ml distilled water. Then $Ni(NO_3)_2.6H_2O$ (15.0 wt.% relative to the total weight of the Mg and Zr salts) was added. Citric acid as a chelating agent was added with citric acid/total metal ions molar ratio 2.0, followed by ethylene glycol in different citric acid/ethylene glycol by molar ratios (1.0-2.0). The mixed solution was heated until a highly viscous gel was formed. This was resulted from polymerization between citric acid and ethylene glycol which gives rise to a polymeric chain with sites available to form chelates with the metal ions. The obtained gels were dried in hot air oven at 140 °C for one hour to get a fluffy powder which then was calcined at 800 °C for one hour in nitrogen purge gas and further calcined at 500-950 °C for 6 hours in air to remove carbon.

Coprecipitation method was used for comparison. Same amounts of the above reagents were dissolved in water, and an aqueous solution of KOH (20 % w/w) was added dropwise to the solution at 80 °C. The pH was maintained at 9.5. The precipitates were digested at 80 °C for 72 hours and thoroughly washed with distilled water and dried. The dried mass was ground and calcined in air at 500-950 °C for 6 hours in air.

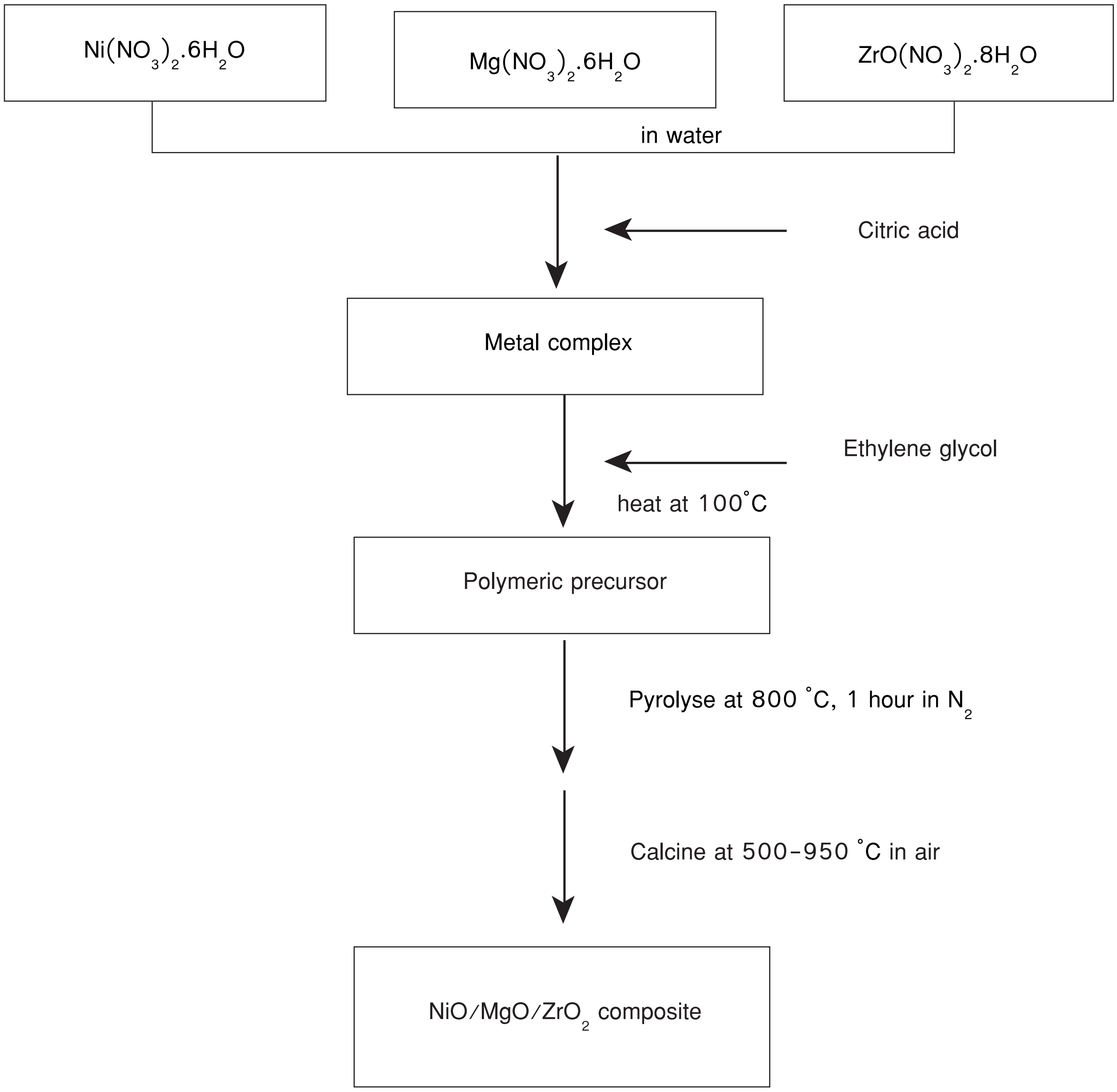


**Figure 1.** Schematic flow of the citric acid/ethylene glycol method.

## Sample characterization

Powder X-ray diffraction (XRD) patterns were measured on a Rigaku DMAX2002/Ultima Plus Powder X-ray diffractometer equipped with a rotating anode using Ni filtered Cu $K_\alpha$ radiation ($\lambda$ = 1.5418 Å). The operating voltage was 40 kV and the current was 40 mA, with a scanning rate of 2°/min. The average crystallite sizes were calculated by the Scherer equation [10].

$$Dhkl = 0.9/\lambda/\beta hkl \cos\theta$$

Dhkl is the crystallite size, $\lambda$ is the wavelength, $\beta$hkl is the peak width at half maximum and $\theta$ is the Bragg diffraction angle.

Thermogravimetric analysis (TGA, a Netzsch STA 409 thermoanalyzer) was performed on the oxides with an incremental heating rate of 20 °C/min, using $\alpha$-$Al_2O_3$ as a reference.

Scanning electron microscopy (SEM) was performed by a JEOL JEM-6400 scanning microscope operating at an accelerating voltage in the 30–35 kV range. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2010F instrument and elemental compositions of TEM specimens were measured by registering the X-ray emissions from specimens with an attached Link ISIS energy dispersive X-ray spectrometer (EDX) from Oxford Instruments Public Company. Samples were coated with gold to enhance contrast.

The specific BET surface area and pore volume of the materials were determined by measuring nitrogen adsorption at 77K using a Quantachrome Corporation Autosorb instrument. Prior to the analysis, the samples were outgassed at 250°C for 4 hours to eliminate volatile adsorbates on the surface. Pore size distribution analysis was performed by using the Barret–Joyner–Halenda (BJH) method from the adsorption branch data.

## Results and discussion

### Thermal analysis

Thermal behavior of the $NiO/MgO/ZrO_2$ composite was studied by thermal analysis. It was shown in Figure 2 as TG/DTA curve.

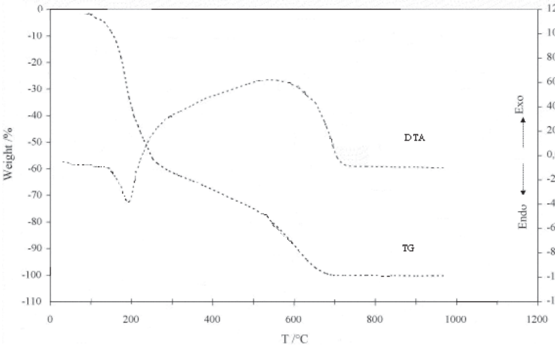


**Figure 2.** TG/DTA curve of the $NiO/MgO/ZrO_2$ composite.

The composite decomposes in three steps. An endothermic peak in the temperature range from 80 °C to 200 °C corresponds to dehydration of gel and evaporation of excessive ethylene glycol. A strong exothermic region in temperature interval of 280-700°C results from the occurring decomposition of metal-citric acid-ethylene glycol complex. It was reported that the metal-citric acid complex is thermally stable at medium temperature (130°C) and could be frozen in a polymer network [11].

## X-ray diffraction

Figure 3 shows the X-ray diffraction (XRD) patterns of composite powder synthesized by two methods, calcined at different temperatures.

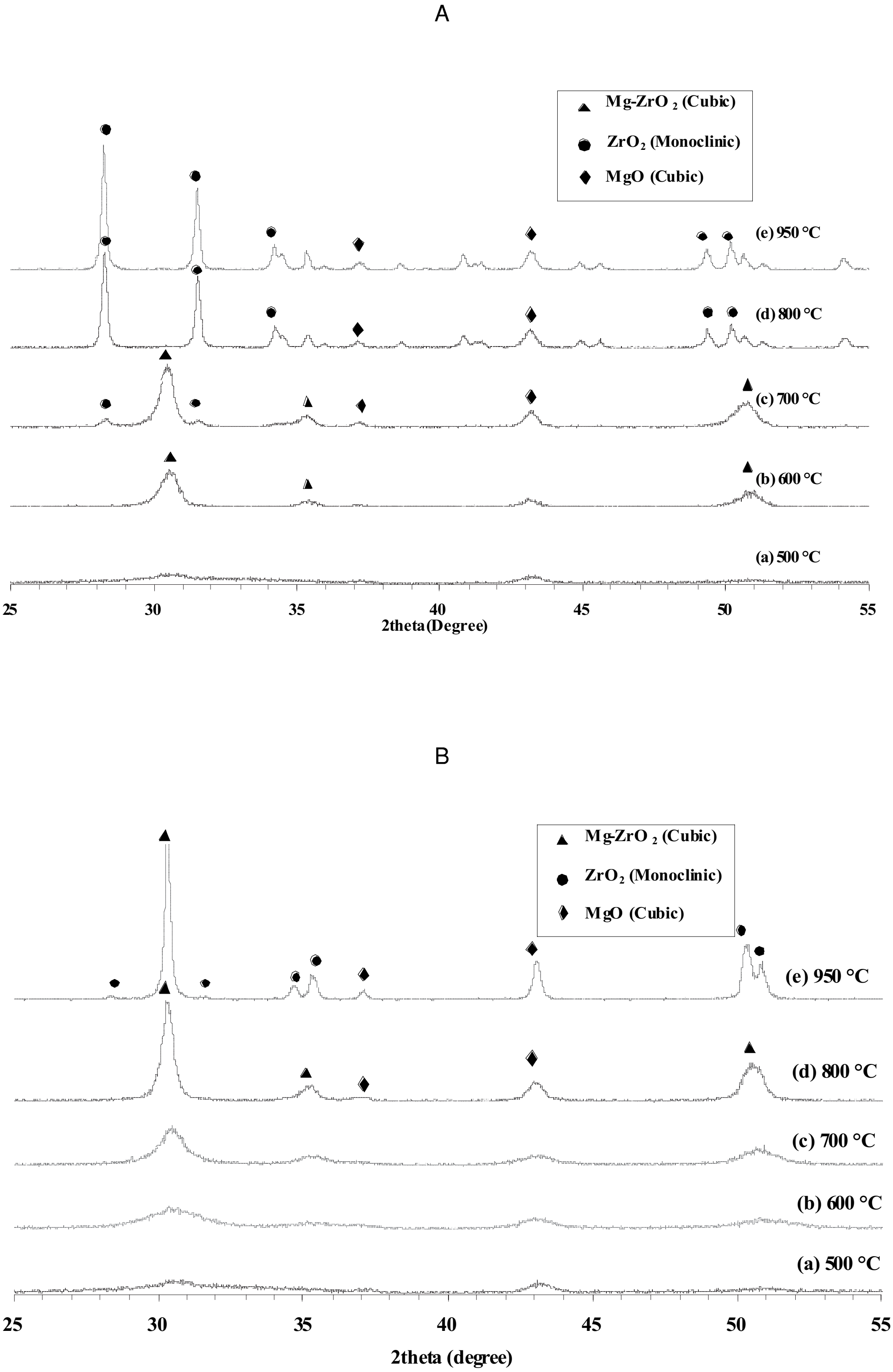


**Figure 3.** XRD patterns of (Å) the mixed oxides prepared by coprecipitation method and (B) the mixed oxides prepared by citric acid/ethylene glycol method.

As it can be observed from Figure 3B, the XRD pattern of the composite synthesized by the citric acid/ethylene glycol method exhibits a cubic phase of NiO/MgO/$ZrO_2$ solid solution (JCPDS: 77-2156 at $2\theta$ = 30.6, 35.4, 50.9 degree) with the lattice parameter of 5.09 Å. At temperature range of 500-700 °C, separated peaks from the single oxides were not detected. This demonstrates that the cubic phase of $ZrO_2$ was stabilized with MgO. A shift of the reflection plane (111) to smaller Bragg angles (from 31.5 to 30.6) shows that the replacement of $Zr^{4+}$ ions by $Mg^{2+}$ ions widens the interplanar distance of the $ZrO_2$ lattice. It can also be seen that at 700 °C the peaks of solid solution from the citric acid/ethylene glycol method become broader and less intense than those from the coprecipitation method, indicating a diminution of the crystallite particle size. The mean crystal size calculated from the (111) reflection peak is 11 nm (compared to 17 nm from the coprecipitation method). The presence of the broad diffraction peaks is coherent with the smaller particle sizes and higher BET areas. At 800 °C, diffraction peaks from MgO (JCPDS: 77-2364 at $2\theta$ = 37.0, 43.0 degree) or NiO, (JCPDS: 65-2901 at $2\theta$ = 37.2 and 43.3 degree) species were found. It was previously indicated that NiO and MgO can form theoretically “ideal” solid solution in any molar ratio [12]. At 950 °C diffraction peaks from monoclinic $ZrO_2$ (JCPDS: 86-1449 at $2\theta$ = 24.2, 28.2, 31.5, 34.4, 49.3, 50.1 degree) were observed together with MgO or NiO. It should be noted that with the coprecipitation method, the presence of extra phases in its XRD (Figure 3A) was found at lower temperature (700 °C) than that in the citric acid/ethylene glycol method (800 °C).

## BET surface areas

**Table 1** summarizes the BET surface areas, pore volumes and average pore sizes of the Ni/MgO/$ZrO_2$ composite samples prepared by citric acid/ethylene glycol method and coprecipitation method. All values of the citric acid/ethylene glycol method are found to be higher.

**Table 1.** Surface areas of Ni/MgO/$ZrO_2$ composites prepared by different methods.

| **Method** | **Citric acid/ ethylene glycol molar ratio** | **Surface area ($m^2$/g)** | **Pore volume ($cm^3$/g)** | **Average pore size (nm)** |
|---|---|---|---|---|
| Coprecipitation | - | 45 | 0.11 | 10.2 |
| Citric acid/ ethylene glycol | 1.0 | 150 | 0.57 | 16.4 |
| | 1.5 | 170 | 0.60 | 13.1 |
| | 2.0 | 156 | 0.60 | 15.1 |

When citric acid/ethylene glycol molar ratio was increased from 1.0 to 1.5, the surface areas and the pore volumes increased, but the pore sizes decreased. In the step of pyrolysis performed under inert $N_2$ atmosphere, carbons were not oxidized. This remaining carbons prevent the complete reaction to metal oxide. After heat treatment in air, the carbons were oxidized and the crystallization of metal oxide is complete. However, when the citric acid/ethylene glycol molar ratio was increased to 2.0, the surface areas decreased while the pore sizes increased.

The BET isotherms of the $Ni/MgO/ZrO_2$ composites are shown in Figure 4. The composite synthesized by the citric acid/ethylene glycol method demonstrated type II pattern indicating both physisorption and chemisorption whereas the isotherm from the coprecipitation method showed type IV pattern.

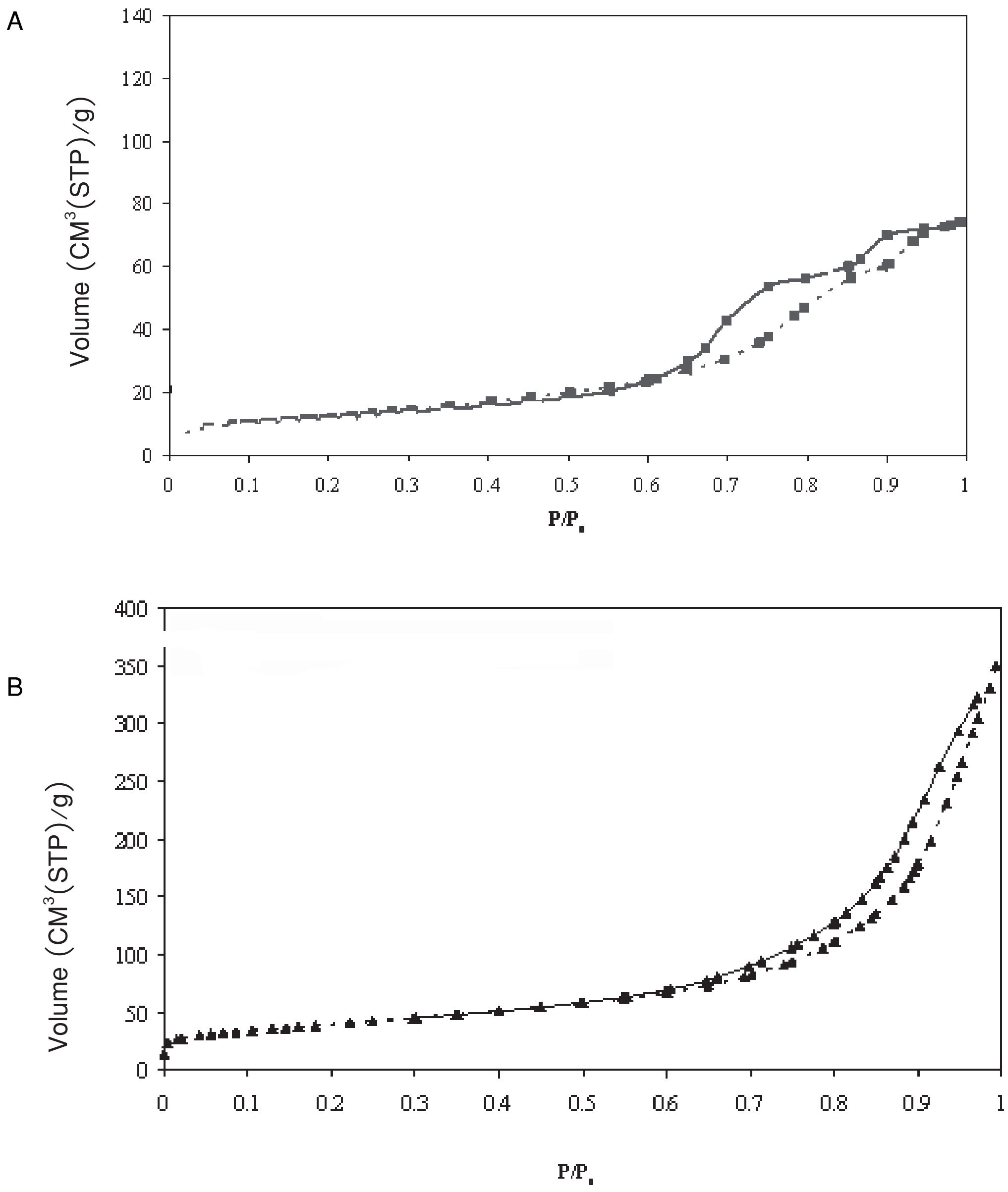
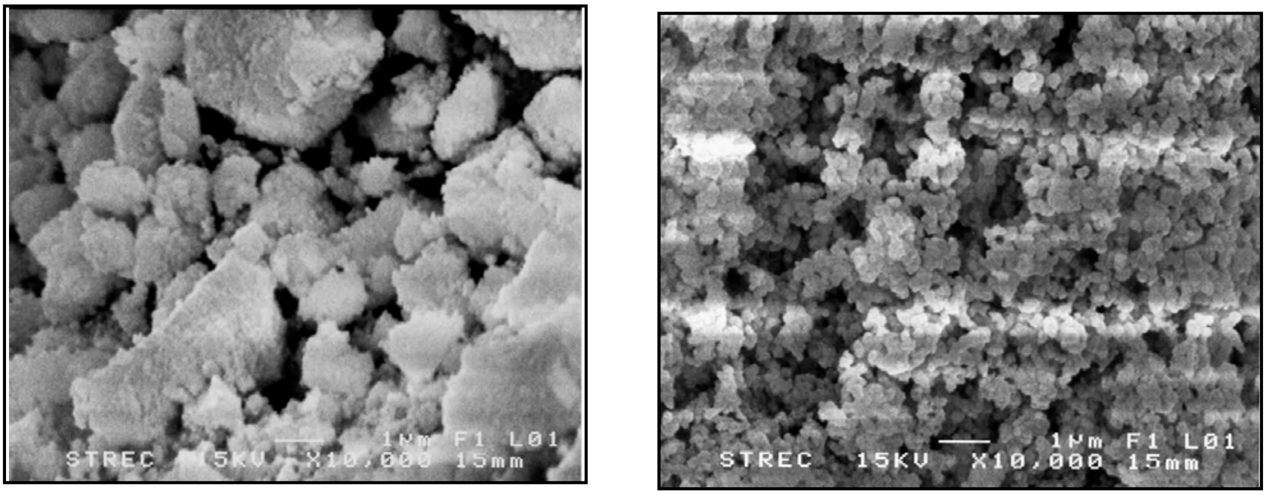


**Figure 4.** Nitrogen adsorption-desorption isotherms of the $Ni/MgO/ZrO_2$ composites synthesized by (A) coprecipitation and (B) citric acid/ethylene glycol methods.

## Scanning electron microscopy (SEM)

Scanning electron micrographs of the composites are depicted in Figure 5. The composite synthesized by the citric acid/ethylene glycol method (Figure 5B) showed smaller crystallites with ~20 nm in size compared to that from the coprecipitation method (Figure 5A). A lot of pores were observed which may be caused by releasing of gases during the combustion process. An analysis of the surface of composite by SEM-EDX revealed 18.80 mol% Ni, 18.87 mol% Mg and 62.34 mol% Zr. This result shows that the metal-citric acid complex could be frozen in a polymer network while preserving the initial stoichiometric ratios of metal ions in the starting solution. The immobilization of metal ions in such a highly branched polymer can prevent the cation mobility during heat treatment which preserves a good dispersion of cations in the composite.



A

B

**Figure 5.** The SEM micrographs of the composites synthesized by (A) coprecipitation and (B) citric acid/ethylene glycol methods.

## Conclusions

Nanosize NiO/MgO/$ZrO_2$ composite with Mg:Zr molar ratio of 1 was synthesized via sol-gel citric acid/ethylene glycol method. The heat treatment in nitrogen atmosphere slowed down the heat generation during the combustion reactions. The suitable calcination temperature is 700 °C. The composite possessed high surface area and good distribution of NiO.

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