Investigation the effect of sol-gel method approach on microstructural of $NiO/MgAl_2O_4$ nanocatalysts applicable for steel industry: modified sol-gel method and sol-gel citrate

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Abstract

Nickel-based catalysts have been widely used in the important reaction for producing hydrogen and synthesis gas from methane reforming processes, which use for producing steel. This study aimed to investigate the effect of the sol-gel method approach on the synthesis of $NiO/MgAl_2O_4$ nanocatalysts through the modified sol-gel and sol-gel citrate methods. Powders are characterized using XRD, SEM-EDS, TEM, and BET-BJH. The results showed that the use of two different sol-gel approaches caused changes in microstructural properties. Nanocatalysts prepared by the modified sol-gel method had smaller crystalline size, smaller particle size, larger porosity, and larger specific surface area than the prepared nanocatalysts by the sol-gel citrate method. The shape of the nanocatalyst particles prepared by the two sol-gel methods was spherical, except that the shape and size of the particles were more homogeneous in the prepared nanocatalyst by the modified sol-gel method.

Keywords: Modified sol-gel method, Sol-gel citrate, Microstructural, Nanocatalyst, $NiO/MgAl_2O_4$.

1. Introduction

Nickel-based catalysts are being widely used in the important reaction for producing hydrogen and synthesis gas from methane reforming processes due to their high intrinsic activity and low cost [1-5]. Synthesis gas is a mixture of hydrogen and carbon monoxide which is used in a petrochemical process such as synthesis of methanol and metallurgical process [6]. One of the important metallurgical processes is the production of steel. A report shows that a Ni-based catalyst has excellent catalytic activity on various supports such as Al_2O_3, MgO, ZrO_2, $MgO\text{-}Al_2O_3$, CeO_2, $Ce_{0.4}Zr_{0.6}O_2$, and $MgAl_2O_4$ [7-10]. It is concluded that the crystallite size of Ni, support of catalyst, and surface area all play an important role in catalytic activity and stability in methane reforming reactions under severe conditions [8, 9]. Undoubtedly, catalytic applications must have appropriate structural properties such as high specific surface area, high porosity, the small crystal size of the active metal, and support. An important, influential factor in the formation of this structural property is the preparation method [5]. Nickel catalyst supported on oxides has been synthesized by different methods, including impregnation [10, 11], precipitation [12], co-precipitation [13, 14], citrate sol-gel [15-17] and classical sol-gel [18-22]. Many researchers reported that the sol-gel method is the best way to synthesize metal catalysts with the high specific surface area, high porosity

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and pore size distribution, small crystal and particle size, high purity, and high stability against formation coke [23, 24]. Besides, the sol-gel synthesis does not release any waste liquid during the whole preparation process, and thus, the sol-gel synthesis is more environmentally friendly than the co-precipitation method [23]. Because of the numerous advantages of this method for synthesis of catalysts such as NiO/Al_2O_3 [25, 26], NiO/MgO [27], Ni/TiO_2 [28], is used. A modified sol-gel method for preparing the metal oxides is the polymerization method (Pechini). The Pechini method involves combining a metal precursor with water, citric acid, and polyhydroxy alcohol, such as ethylene glycol and diethylene glycol monoethyl ether [29]. Some researchers have used this method for preparing nickel-based catalysts, i.e. $NiO–MgO–ZrO_2$ [30] and $Ni/Y_2O_3–ZrO_2$ [31]. They have reported that the Pechini method has a greater homogeneity of the synthesized materials than those made by other synthetic methods such as precipitation, co-precipitation, and impregnation [31, 32]. Besides, the citrate sol-gel method is also used for the preparation of metal oxides nanoparticles as a catalyst, for example, $Ni/MgOZrO_2$, Ni/Al_2O_3-ZrO_2, and Ni/Al_2O_3-ZrO_2-CeO_2 [15-17]. The citrate sol-gel method, which is an effortless, inexpensive, and faster method compared to various sol-gel methods, uses metal nitrate, distilled water, and citric acid to make oxide nanometer powders. In this sol-gel method, citric acid is the gelling agent. Recently, Wang et al.[17] reported that $Ni/Al_2O_3–ZrO_2$ catalysts prepared by the direct citrate sol-gel processing exhibits excellent activity and stability, with 91.9% average conversion of CO_2 and 82.9% of average conversion of CH_4 at 1073 °K in the reforming of methane to synthesis gas. This excellent activity is due to the highly and uniformly dispersed small metallic Ni particles, the reducibility of the Ni oxides, and the interaction between metallic Ni particles and the support. In this work, $NiO/MgAl_2O_4$ nanocrystals are prepared by the sol-gel citrate method and the modified sol-gel method. This investigation focuses on the effect of the preparation method on the physicochemical properties of $NiO/MgAl_2O_4$ nanocatalysts.

2. Experimental

2.1. Materials

The raw materials were nickel nitrate ($Ni(NO_3)_2.6H_2O$, 99%, Merck), magnesium nitrate ($Mg(NO_3)_2.6H_2O$, 99%, Merck), aluminum nitrate ($Al(NO_3)_3.9H_2O$, 98.5%, Merck), anhydrous citric acid ($C_6H_8O_7$, 99%, Merck), diethylene glycol monoethyl ether ($C_6H_{14}O_3$, 98%, Merck) and distilled water. All of the chemicals in our experiment are analytical grade and are used as received without further purification.

2.2. Synthesis of $NiO/MgAl_2O_4$ nanocrystals

2.2.1 The modified sol-gel method

To prepare $NiO/MgAl_2O_4$ powder by the modified sol-gel method, at first, a suitable amount of $Ni(NO_3)_2.6H_2O$ (15Wt.%), magnesium nitrate, aluminum nitrate, and anhydrous citric acid were dissolved in distilled water and mixed and then stirred. After that, a suitable amount of diethylene glycol monoethyl ether (DGME) was slowly added to this solution and stirred at 50°C for one h. Then, the solution was heated for one h at 80°C to remove the residual water as altogether as possible. By increasing in heating of the solution at 110°C for one h, a polymer gel that is known to xerogel is formed by the polyesterification reaction. For fully drying, xerogel was placed at 250°C for one h in an oven. The calcination of powders was performed at 800°C for six h in air.

2.2.2. The citrate sol-gel method

$NiO/MgAl_2O_4$ sample with 15Wt.% content of Ni was prepared by the citrate sol-gel method. To be specific, a suitable amount of $Ni(NO_3)_2.6H_2O$ and anhydrous citric acid was dissolved in distilled water and stirred at 50°C for 15 min. After that, magnesium nitrate and aluminum nitrate dissolved in distilled water and slowly added to the previous solution. The precursor solution was stirred at 50°C for one h to obtain a homogeneous solution. Then, the solution was heated to evaporate the water at 80°C in a water bath on a magnetic stirrer. During heating at 80°C for one h, the solution became more viscose and finally formed a green honey gel. Then the beaker was moved to an oven with a temperature of 150°C and was kept for 1 hour. After grinding of foamy mass, the precursors were heated at 800°C for six h in air. It is worthwhile to note that in all the powders prepared by both methods, Al: Mg and CA, metal ions molar ratio is 2 and 3, respectively.

2.3. Characterization of $NiO/MgAl_2O_4$ nanocrystals

For identifying phase, X-ray diffraction was analyzed by using a Philips Xpert MPD diffractometer and by a rotating anode using Ni-filtered Cu-Kα radiation (λ = 1.5418 Å). The operating voltage was 40 kV, and the current was 35 mA, with a scanning rate of 2°/min and in the range 2θ= 10-90°. Field emission scanning electron microscopy (FESEM) images were obtained by a Hitachi S-4160 equipped with energy-dispersive X-ray spectroscopy (EDS). The samples were coated with gold to enhance contrast. Transmission electron microscopy (TEM) images were obtained by a Philips CM30 with an accelerating 150 kV. The specific BET surface area and pore volume of the materials were determined by measuring nitrogen adsorption at -196°C using a Belsorp mini II instrument. Before the BET analysis, the

samples were outgassed at 250°C for four h to eliminate volatile adsorbates on the surface. Pore size distribution analysis was performed using the Barret–Joyner–Halenda (BJH) method from the adsorption branch data.

3. Results and discussion

3.1 XRD analysis

Fig. 1 shows the X-ray diffraction patterns of both sol-gel methods. Fig. 1 (a) relates to powders prepared by the modified sol-gel method, and Fig. 1(b) refers to powders prepared by the sol-gel citrate method.

The results of phase analysis indicate that in both sol-gel methods, $NiO/MgAl_2O_4$ catalysts are formed, and the presence of NiO (ICSD card # 01-073-1523) and $MgAl_2O_4$ (ICSD card # 01-075-1797) phases at the angles are shown in Fig. 1 are confirmed. The planes of the $MgAl_2O_4$ phase are (111), (220), (222), (400), (422), (511), (440), (533), and (444) which are shown in Fig. 1. The average crystalline size of the NiO phase was calculated using the Scherer equation on planes (220) and (200) for both nanocatalysts. The mean crystalline size of the NiO phase for the modified sol-gel method and the sol-gel citrate method was calculated at about 21.8 and 25 nm, respectively. The reason for the smaller crystalline size of the prepared particles by the modified sol-gel process can be attributed to the presence of DGME in the modified sol-gel process, which acts as a polymerization agent and causes more space inhibition between the metal cations-citrate complexes than the sol-gel citrate method. While in the sol-gel citrate method the spatial inhibition does not exist and after heating at 800°C, the NiO particles arrive together and grow.

3.2. SEM-EDS and TEM-SAED investigations

Fig. 2 shows FESEM images of $NiO/MgAl_2O_4$ powders prepared using two sol-gel methods. In Figs. 2 (a) and (b), the FESEM images are related to powders prepared using the sol-gel citrate method, and in Figs. 2 (c) and (d), the FESEM images are described powders prepared using the modified sol-gel method. The particle size of $NiO/MgAl_2O_4$ in both sol-gel ways is in nanometer dimensions, except that the nanoparticles prepared by the modified sol-gel method are smaller and more homogeneous in shape and size. The shape of the particles in both sol-gel ways is spherical, which due to their small size, the particles are agglomerated together and formed larger particles, namely agglomerates. The agglomerates created by the modified sol-gel method are smaller than the sol-gel citrate method, and fine and spherical particles are well recognizable on their surface. The formation of fine particles in the modified sol-gel process is due to more space barriers, which is due to the fact of the DGME solvent. In other words, in the sol-gel citrate way, the generated gel contains metal-chelating complexes, in the modified sol-gel method, the metal-chelating complex in a polymer network is caused by the DGME solvent. As a result of which the metal cations in this state (modified sol-gel) are taken apart from each other further and thus they have generated much smaller particles. The size range of $NiO/MgAl_2O_4$ nanoparticles was calculated using Image J software. The particle size of powders prepared by the sol-gel citrate method was estimated to be 30-55 nm. Also, the size of the prepared nanoparticles by the modified sol-gel method was measured at 15-30 nm.

The chemical composition of $NiO/MgAl_2O_4$ nanoparticles was investigated by EDX analysis. Fig. 3 shows the elemental analysis of $NiO/MgAl_2O_4$ nanoparticles with a loading nominal Ni of 15Wt. % and an Al: Mg molar ratio of 2. The results of the EDX analysis indicate that there is a good

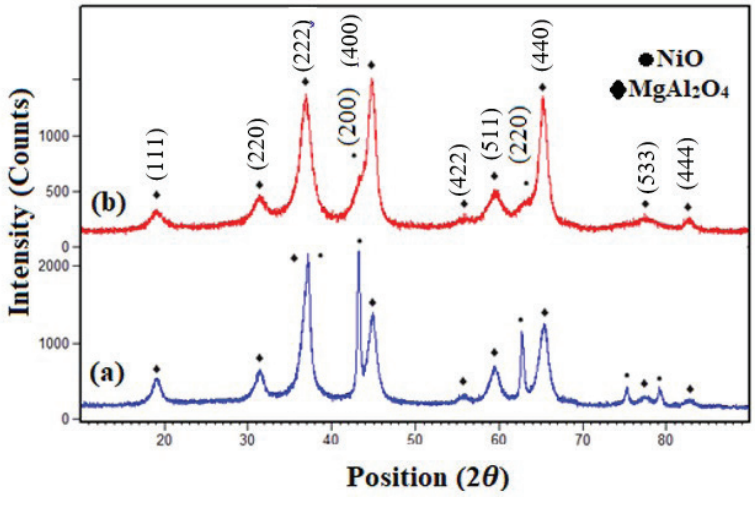

Fig.1. XRD patterns of $NiO/MgAl_2O_4$ powders prepared by (a) the modified sol-gel method and (b) the sol-gel citrate method.

agreement between the nominal amount of the nickel loading and the actual loading amount (from EDX analysis). Also, the ratio of Al to Mg is approximately 2, indicating the formation of the $MgAl_2O_4$ spinel phase.

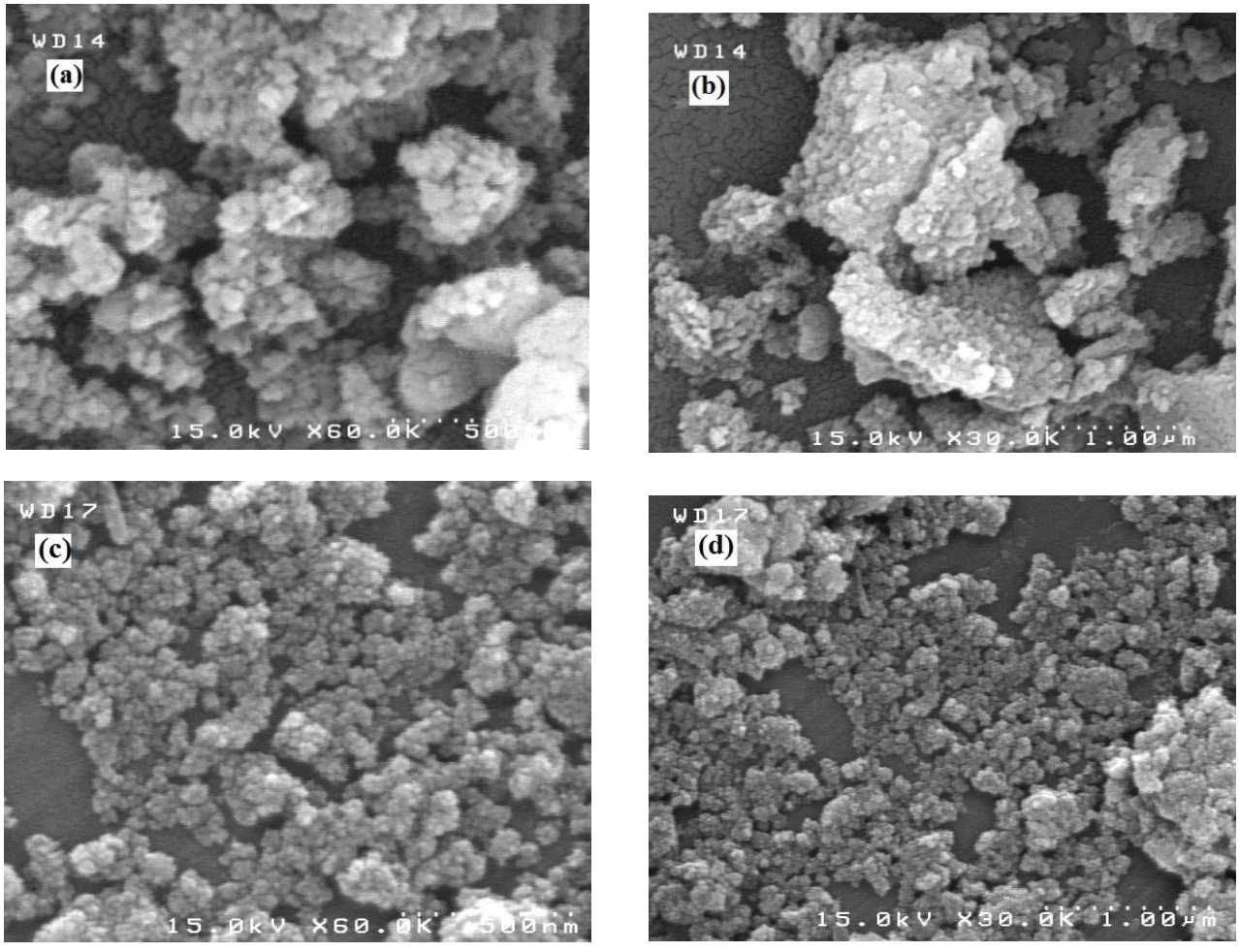

Fig. 2. FESEM images of $NiO/MgAl_2O_4$ powders. (a) and (b) pertaining to powders prepared via the sol-gel citrate method. (c) and (d) related to powders prepared via the modified sol-gel method.

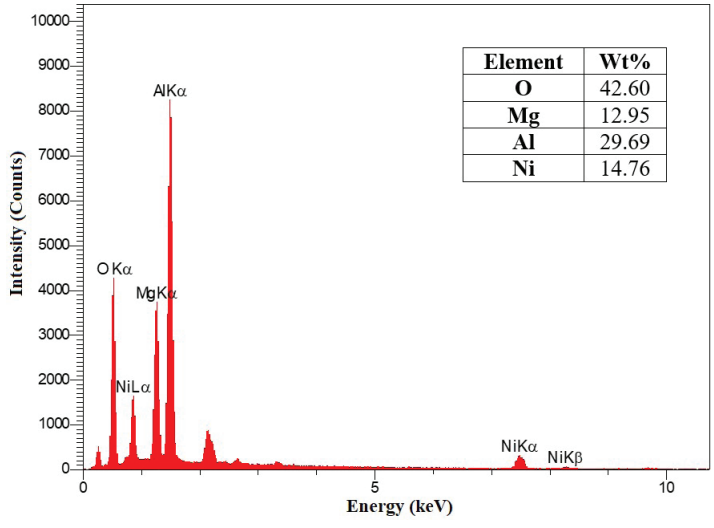

Fig. 3. EDX analysis of $NiO/MgAl_2O_4$ nanoparticles prepared by modified sol-gel method.

TEM images and selected electron scattering patterns (SAED) of $NiO/MgAl_2O_4$ samples prepared using two modified sol-gel and the sol-gel citrate methods are shown in Fig. 4. Figs. 4 (a) and (b) are related to the TEM image and SAED pattern of the sample prepared by the sol-gel citrate method. Figs. (c) and (d) are related to the TEM image and SAED pattern of the sample prepared by the modified sol-gel method. The sample prepared using the sol-gel citrate method in Fig. 1 (a) contains nanometer-sized particles in the form of incomplete spherical particles in the range of 10-22 nm and an average particle size of 15 nm, which are strongly bonded, and large oligomers were created so that the particles are difficult to separate. Fig. 4 (c) shows very fine NiO/ $MgAl_2O_4$ catalyst particles prepared using the modified sol-gel method. The nanometer particles are spherical, very homogeneous with a particle size range of 4-10 nm and an average particle size of 6 nm. It can be said that the prepared sample by the modified sol-gel method has a narrower particle size range and an average smaller particle size. Besides, the adhesion of nanoparticles prepared by the modified sol-gel method is much less, and the particles in this method are well separated from each other and visible. Figs., (b) and (d) are observed the clear rings in the SAED of nanoparticles prepared using two methods of revealing polycrystalline and nanometer structure. Therefore, the $NiO/MgAl_2O_4$ polycrystalline nanoparticles were formed using two modified sol-gel and sol-gel citrate methods.

To investigate the effect of the sol-gel method on the specific surface area, pore-volume, and pore size distribution of $NiO/MgAl_2O_4$ nanocatalyst, N_2 adsorption analysis was performed. Figs. 5 (a) and 5 (b) show the pore size distribution for both types of the sol-gel citrate and the modified sol-gel methods, respectively. As shown in Fig. 5, the pore diameter range of the samples prepared by the modified sol-gel and sol-gel citrate methods is about 2-25 nm and 2-60 nm, respectively. The average pore diameter size calculated of $NiO/MgAl_2O_4$ nanocatalysts prepared by sol-gel citrate and modified sol-gel methods is about 15.442 and 8.2420 nm, respectively, which indicates the presence of mesoporous cavities in the structure of the prepared nanoparticles of both the sol-gel methods. The pore size distribution of the prepared nanoparticles by the modified sol-gel method is narrower, which indicates that the pore size is more homogeneous than the prepared nanoparticles by the sol-gel citrate method.

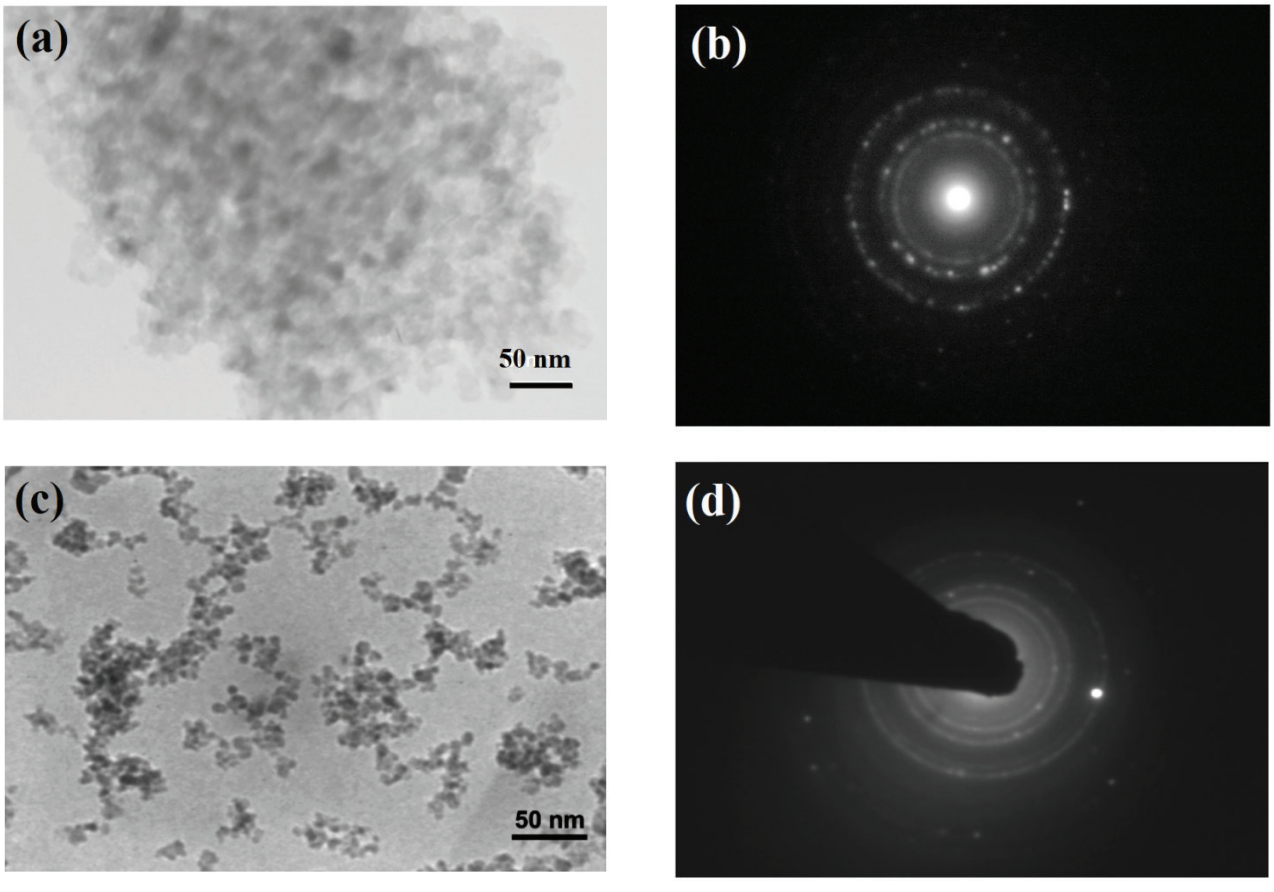

Fig. 4 (a) TEM image and (b) SAED pattern related to the sample prepared by the sol-gel citrate method. (c) TEM image and (d) SAED pattern related to the sample prepared by the modified sol-gel method.

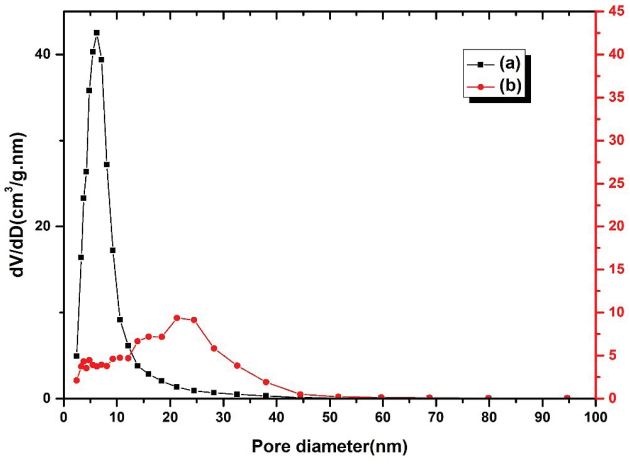

Fig. 5. BJH pore size distribution of $NiO/MgAl_2O_4$ nanoparticles prepared by sol-gel citrate and modified sol-gel.

Fig. 6 shows the N_2 adsorption/desorption diagrams of $NiO/MgAl_2O_4$ nanocatalysts prepared using two methods, (a) sol-gel citrate and (b) modified sol-gel. The specific surface area, pore-volume, and average pore diameter of $NiO/MgAl_2O_4$ nanocatalysts prepared using two modified sol-gel and, sol-gel citrate methods are given in Table 1. The specific surface area and pore volume for nanocatalysts prepared by the sol-gel method were 126.5 $m^2.g^{-1}$ and 0.2697 $cm^3.g^{-1}$, respectively, and for the prepared nanoparticles by the sol-gel citrate method were 57 $m^2.g^{-1}$ and 0.2163. $m^3.g^{-1}$ was obtained, respectively. N_2 adsorption/desorption diagrams of both methods are of type IV in the IUPAC classification of adsorption isotherm with hysteresis loops, which confirms the existence of a mesoporous structure for both nanoparticles. The results of the N_2 adsorption/desorption analysis indicate that the specific surface area and volume of nanoparticle cavities prepared by the modified sol-gel method are higher due to the presence of the DGME solvent. It can be related to creating a more space barrier in the modified sol-gel process, that it can prevent the particles from clumping and prevents the reduction of the surface area after the calcination heat treatment. In other words, it can be said that the DGME solvent creates a vast polymer network with metal-chelate (citric acid) more spaces than if only a complex of metal-chelate (in the sol-gel citrate method) exists. It can be said that it enhances the role of citric acid, which is a mold for the formation of cavities in the sol-gel method and creates more and larger occupied spaces. It is possible that during the calcination heat treatment, these occupied spaces are eliminated, resulting in the formation of nanoparticles with a higher specific surface area. On the other hand, the average particle size and crystalline size of particles prepared by the modified sol-gel method are smaller than the cohesive nanoparticles prepared by the sol-gel citrate method, which can also be a reason for the high specific surface area of nanoparticles prepared sol-gel modified.

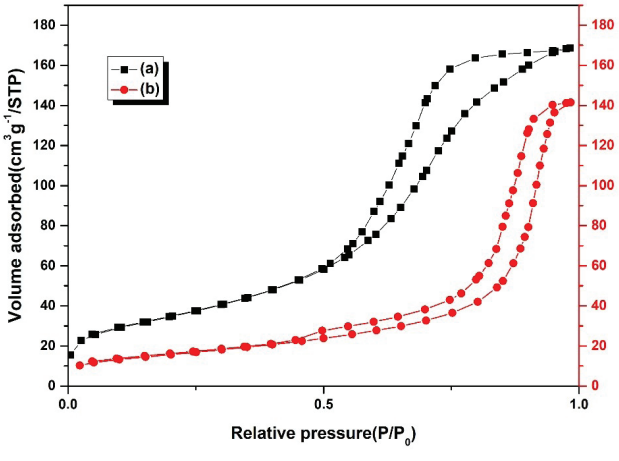

Fig. 6. Comparison of N_2 adsorption/desorption diagrams of $NiO/MgAl_2O_4$ nanoparticles prepared by sol-gel citrate and modified sol-gel.

Table 1. Parameters obtained from BET-BJH analysis of $NiO/MgAl_2O_4$ nanoparticles prepared by two types of sol-gel method.

Method	specific surface area ($m^2.g^{-1}$)	pore volume ($m^3.g^{-1}$)	average size pore diameter (nm)
Modified sol-gel	126.5	0.2697	8.2420
sol-gel citrate	57	0.2163	15.442

4. Conclusions

In this study, two types of sol-gel methods, including the modified sol-gel and sol-gel citrate methods, were utilized to investigate the effect of the sol-gel method approach on the synthesis of $NiO/MgAl_2O_4$ nanocatalysts. The results can be summarized as follows:

- The results indicated that the use of two different sol-gel approaches changed the microstructural of $NiO/MgAl_2O_4$ nanocatalysts.
- Nanocatalysts prepared by the modified sol-gel method had smaller crystalline size, a smaller particle size, higher porosity, and higher specific surface area than the prepared nanocatalysts by the sol-gel citrate method.
- The shape of the nanocatalyst particles prepared by the two sol-gel methods was spherical, with a difference that the shape and size of the particles were more homogeneous in the prepared nanocatalyst by the modified sol-gel method.
- According to the results of this study, the modified sol-gel method proposes a suitable method with more favorable properties for the synthesis of nanocatalysts.

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