Microemulsion Synthesis Method for Preparation of Mesoporous Nanocrystalline γ -Al₂O₃ Powders as Catalyst Carrier for Nickel Catalyst in Dry Reforming Reaction

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Abstract

Three large mesoporous alumina powders were prepared by microemulsion (ME) method with different microemulsion structures and compositions (various surfactants and oil phases) and employed as catalyst carrier for preparation of mesoporous nanocrystalline Ni/Al₂O₃ catalysts. The prepared catalysts were used in dry reforming reaction for production of synthesis gas. The samples were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller surface area analysis (BET), temperature programmed reduction (TPR) and scanning electron microscopy (SEM) techniques. The results showed that the prepared γ -Al₂O₃ with different microemulsion compositions possessed mesoporous structure with high surface area from 239.7 to 277.7 m²g⁻¹. In addition, the prepared 10wt.% Ni/ γ -Al₂O₃ catalysts exhibited high activity and stability in dry reforming reaction. The results also revealed that the microemulsion composition have a significant effect on the textural properties and affected the catalytic performance.

Keywords: Mesoporous; Nanocrystalline alumina; Microemulsion; Dry reforming; Syngas

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1. Introduction

Nowadays, much effort is in the synthesis of nanocrystalline metal oxides [1-4]. The porous and mesoporous materials are in attraction because of their pore size, easy handling, green and soft chemistry, good and high specific surface area with stability against mechanical and thermal treatment where some specific features of molecules are in considering [5, 6]. Al_2O_3 has received much attention as catalyst support and it has some advantages compared to SiO_2 because of its adequate nature to use with more different metal species. Furthermore, it is suitable for catalyst preparation. Although the focus of studies were on the siliceous mesoporous materials, alumina materials had less attraction compared to mesostructured silica [7, 8]. Microemulsion was first reported by Schulman and Friend in the 1940s [9]. As far as that time, microemulsions were in the research interests of scientists due to their capability in oil recovery and synthesis of nanoparticles [10, 11]. One of the suitable techniques for preparation of catalyst support is microemulsion method. The microemulsion prepares an excellent environment for combination of precursors and as a result of its ability to create an absolute area in solution; the morphology of nanoparticles with tunable size distribution is at finger tip. Monodisperse colloidal metal particles were firstly prepared by Boutonnet et al. in the early 1980s [12].

Variety of oxides can be prepared in micelles with nano-structural and suitable particle sizes. The utilization of microemulsion droplets as “nanoreactors” to synthesize metal and semiconductor nanoparticles was first reported by Holmes et al. [13] The micelles named as “nanoreactors” establish a suitable environment for controlled nucleation and growth and the surfactant layer prevents the aggregation of nanoparticles [14]. It is clear that in the case of the impregnation technique, the structure of the support, especially the pore size, will influence the sizes of the formed metal particles with a broad size distribution as a result, while in the case of the microemulsion route the sizes of the particles will depend on the

nature of the microemulsion. In this case, a narrow particle size distribution is obtained [15]. Impregnation method is the most conventional method for preparation of metal supported catalysts. With this method, it is possible to prepare small metal particles although it is quite difficult to obtain a narrow particle size distribution. Using impregnation, the morphology of the catalyst support will have some effects on the structure and size of the metal particles. Moreover, it is rather difficult to control the composition of bimetallic particles. Due to the specific structure of a microemulsion, it was expected to be a suitable environment for producing small metal nanoparticles with narrow size distribution as well as bimetallic particles with controlled composition [16].

The co-precipitation and sol-gel method are used to prepare metal oxide or composite metal oxide by chemical reaction. Their advantages lie in the fact of putting the homogeneous mixture of different ingredients into practice. But in their preparation period, an expensive alkoxides must be used as the primary metals and the treatment procedure for the samples is more complicated, which increases the complexity of preparing process and the costs of operation. Thermal decomposition of organic compounds in an organic media is an available method for preparing inorganic material. But this method must be performed under a certain temperature and pressure [17].

CO₂ reforming ($\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$) has several advantageous from both industrial and environmental standpoints. This process uses greenhouse gasses in a lucrative manner, such as: (i) regulate H₂/CO ratio in term of 1:1, which is beneficial for the synthesis of extensive range of viable hydrocarbons if it is combined with partial oxidation or steam-reforming of methane reactions (ii) reduction of two gasses contribute to the global warming and alert them to the fruitful products (iii) better use in the chemical energy transmission [18-24].

The Ni-based catalysts are known as low cost catalysts and exhibit high activity and selectivity during dry reforming reaction [25]. But, the major problem in commercialization of nickel based catalysts for carbon dioxide reforming reaction is the rapid deactivation of nickel catalysts because of carbon deposition. The carbon in dry reforming of methane reaction can be formed by the following reactions [26-30]:

One of the disadvantages of this catalyst is the carbon deposition over the catalysts surface in dry reforming reaction [31, 32]. Due to the endothermic nature of dry reforming reaction, operating at high temperatures with CO_2/CH_4 ratio far above unity is recommended to overcome the problem of carbon formation. However, working at lower temperature with CO_2/CH_4 ratio around one is more favorable from the commercial viewpoints. It is known that the noble metals such as Ni, Pd, Pt, Ru, Rh, and Ir are active catalysts for this reaction and show high activity and low tendency to carbon formation. However, because of low cost and higher availability of nickel, the Ni-based catalysts have received much attention in recent years [28, 31, 33]. The Ni based catalysts have been modified to develop some features of dry reforming reaction such as activity and consistency along time of reaction [34-36]. Recent works are based on the use of mesoporous support, modification of catalyst preparation methods and addition of alkaline earth promoters [37-39].

In this work, three large mesostructured aluminas (LMA) with different starting materials were prepared by microemulsion method. The effects of different microemulsion structures were investigated on the textural properties of the prepared alumina powders. The potential of these prepared samples as support for preparation of nickel catalysts in dry reforming reaction was evaluated.

2. Experimental

2.1. Preparation of Al_2O_3

Three different alumina powders were prepared by microemulsion method. In this process, 3.6 g polyethylene glycol (PEG, MW: 6000, 98% purity, Loba Chemie) as a surfactant was dissolved in 29.2 ml water and 2.5 ml ethanol at room temperature under stirring. n-heptane (99% purity, Samchun) as the organic solvent (oil phase) was then added to the surfactant solution and stirred to form an oil-in-water microemulsion (Microemulsion A).

Another microemulsion was prepared in a similar way using cetyltrimethylammonium bromide (CTAB, 99% purity, Loba Chemie) as a surfactant and n-heptane as an oil phase. The weight ratio of surfactant to oil phase was 0.5 (Microemulsion B).

Last microemulsion was prepared by mixing 2.1 g cetyltrimethylammonium bromide (CTAB) in sufficient water and using ethanol as a co surfactant. After stirring, 5.6 ml cyclohexane (99% purity, Samchun) was added to mixture as an oil phase (Microemulsion C).

After preparation of microemulsion solutions, aluminum triisopropoxide (ATI, 98% purity, Merck) was added to mixtures as an aluminum precursor. The prepared mixtures were covered and stirred at room temperature for 24 h. These as-synthesized materials were washed with distilled water and ethanol to remove any residual surfactant and dried for 12 h at 80°C. Subsequent calcinations were performed at 500°C for 3 h in air at a temperature rate of 5°C/min. Based on microemulsion mixture and their subsequent numbers the prepared aluminas were donated as A, B and C.

2.2. Preparation of $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts

After synthesis of $\gamma\text{-Al}_2\text{O}_3$, the 10 wt. % $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts were prepared via impregnation procedure. The $\gamma\text{-Al}_2\text{O}_3$ was dried and impregnated with adequate amount of

Ni(NO₃)₃·6H₂O aqueous solution under stirring for 4 h at room temperature. The impregnated catalyst was dried at 80°C for 10 h and calcined at 500°C for 3 h.

2.3. Characterization

The structural properties of the samples were investigated by X-ray diffraction (XRD) analysis using an X-ray diffractometer (PANalytical X'Pert-Pro). The surface areas of the prepared catalysts were determined by nitrogen adsorption at -196°C using a Tristar 3020 analyzer (Micromeritics). Prior to analysis the prepared samples were degassed under an inert atmosphere (N₂) for 2 h at 250°C. The pore size distribution of the samples was calculated from the desorption branch of the N₂ adsorption/desorption isotherm by the Barrett, Joyner and Halenda (BJH) method. The reduction behavior of the calcined catalysts was evaluated by the temperature programmed reduction (TPR) technique using a Micrometrics chemisorb 2750 instrument. For this purpose, the calcined catalyst (100 mg) was heated (10°C/min) in a reducing gaseous mixture (20 ml/min, H₂: Ar=10:90). Before the analysis, the catalysts were degassed under an Ar atmosphere at 250°C for 1 h. The amount of H₂ uptake during the reduction process was determined by a thermal conductivity detector (TCD). The carbon formation was evaluated over the spent catalyst using temperature-programmed oxidation (TPO) analysis with a similar apparatus as mentioned for TPR analysis. In this analysis a gas stream (20 mL/min) of a O₂: He (5:95) mixture was passed over 50 mg of spent catalyst, and the temperature was increased with a desired heating rate (10°C/min). Surface morphology of the prepared catalysts was studied by scanning electron microscopy (SEM, Vega@Tescan).

2.4. Catalytic evaluation

Catalytic activity measurements were performed in a quartz tubular fixed-bed reactor (inner diameter = 7 mm) under atmospheric pressure. The reactor was charged with 100 mg

of the calcined catalyst (0.25-0.5 mm). Prior to the reaction, different catalysts were reduced in a H₂ gas flow of 30 mL/min at 700°C for 3 h and cooled to 550°C. The reactant gas feed (CH₄ and CO₂) was introduced into the reactor and the activity tests were performed at different reaction temperatures (550-700°C). The volume percent of reactants and products were determined using a gas chromatograph (Shimadzu 16A) equipped with a TCD and a Carboxen 1000 column.

3. Results and discussion

3.1. Structural properties of the aluminas

Fig. 1 shows the X-ray diffraction patterns of the alumina samples prepared by microemulsion method. Obviously, the samples exhibited similar patterns. From patterns we can understand that the prepared samples have γ -Al₂O₃ crystalline structure. Three peaks with high intensity at $2\theta=37.4^\circ$, 46.07° and 66.9° were appeared in all samples. These peaks were assigned to Al₂O₃ (JCPDS Card 01-1303). The average crystallite size of the samples was estimated using the Debye-Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

In this equation, λ is the wavelength (in nm) of the monochromatic X-ray beam ($\lambda = 0.15406$ nm for Cu-K α radiation), β is the full width at half maximum (in rad) for the diffraction peak under consideration (the inherent broadening of the equipment was ignored in the FWHM measurements) and θ is the diffraction angle in degrees. The crystallite sizes of the samples calculated by Scherrer equation were smaller than 8 nm in the all prepared aluminas.

The textural characteristics of the samples are reported in Table 1. From the results it can be understood that the samples have high specific surface area. Furthermore, the sample

prepared with cyclohexane, CTAB and ethanol had the highest surface area and the smallest pore size.

The nitrogen adsorption/desorption isotherms and pore size distributions of the prepared γ - Al_2O_3 are illustrated in Fig. 2a and 2b, respectively. All samples exhibited IV type isotherm with H2 shaped hysteresis loop. This is the significant feature of “cylindrical-shaped” channels. The formation of hysteresis loops at low relative partial pressures indicated the existence of small pores in these samples as reported in Table 1. The prepared samples also exhibited a narrow single modal pore size distribution in mesopore region with pore size distribution located between 4 and 17.5 nm, Fig. 2b. However, for the Al_2O_3 (B) sample the pore size distribution was shifted to larger size.

3.2. Structural properties of the studied catalysts

The XRD profiles of the nickel catalysts prepared with different supports are shown in Fig. 3. All the samples exhibited similar XRD patterns. In all catalysts the peaks at $2\theta=37.2^\circ$, 46.06° and 66.5° are indexed to the characteristic peaks of alumina phase (JCPDS Card No. 01-1303). As can be seen, no distinct NiO species were observed in X-ray diffraction schemes of the samples due to high dispersion or low concentration of nickel oxide over the catalyst support [40]. The NiAl_2O_4 peaks coincide with Al_2O_3 , so the recognition of this phase could not possible. The Ni species in NiAl_2O_4 are in the spinel-like structure and the diffusion of Ni ions species into support caused the formation of NiAl_2O_4 phase [41].

The structural characteristics of the catalysts are collected in Table 1. From the results, it can be concluded that the impregnating of Ni has a significant effect on the textural properties of the alumina supports. As can be seen, the surface area of catalyst supports decreased after addition of nickel and the produced catalysts exhibited a lower specific surface area than that observed for catalyst support. Moreover, the prepared catalysts showed

a lower pore volume and smaller pore size compared to their catalyst supports. The surface area and pore volume are declined because of the penetration of nickel into the pores of support and partial collapse of alumina pores after impregnation [42, 43]. What is more, the incorporation of Ni induced a slight increase in crystalline sizes.

The N₂ adsorption/desorption isotherms and pore size distributions of the prepared catalysts are depicted in Fig. 4a and 4b, respectively. The samples show IV type isotherm with H2 type hysteresis loop. According to IUPAC classification, this type of hysteresis is assigned to solids consisting of particles crossed by nearly cylindrical channels or made by aggregates (consolidated) or agglomerates (unconsolidated) of spheroidal particles, with non-uniform size or shape [44].

The major fraction of the pore size distributions for the built catalysts is in mesopore region located in the range of 3–17 nm. As shown in Fig. 4b, addition of nickel to prepared supports decreased the pore volume in all three catalysts. Besides, the catalysts exhibited broader pore size distributions compared to catalyst supports.

3.3. Temperature-programmed reduction (TPR)

The reduction behaviors of the calcined catalysts with different supports are shown in Fig. 5. In all reduction profiles two reduction peaks were observed. The first wide reduction peak observed at around 650°C was attributed to NiO located on the surface and surrounded with aluminum ions with strong interaction with support [45]. As can be seen, the T_{max} of the first reduction peak for the 10%Ni/Al₂O₃ (C) was observed at lower temperature compared to other catalysts, indication of higher reducibility of this catalyst. The second peak at 800°C belongs to NiAl₂O₄ species. This phase formed through diffusion of Ni ions into the support [45]. The T_{max} of the first and second reduction peak for the 10%Ni/Al₂O₃ (A) catalyst shifted toward higher temperature, indicating the lower reducibility of this catalyst.

3.4. Catalytic performance

The catalytic performances of the prepared catalysts are shown in Fig. 6. The catalyst powders were pressed, crushed and sieved to obtain the particles in the range 0.25-0.5 mm. It is seen that the catalyst with the highest surface area (10%Ni/Al₂O₃ (C)) showed the highest CH₄ conversion. This behavior of the catalyst supported on the alumina with the highest surface area could be related to higher nickel dispersion. It is seen that the CO₂ conversion was higher than that of methane conversion due to the reverse water-gas shift reaction (CO₂ + H₂ ↔ CO + H₂O), Fig. 6b. This phenomenon takes place parallel for the methane reforming reaction with carbon dioxide. In addition, increasing in reaction temperature increased the methane conversion and reaches the highest value at 700°C due to endothermic nature of dry reforming reaction.

The stability of the reduced catalysts is depicted in Fig. 6c. The results exhibited a relative stability in methane conversion, which remained unchanged during reaction.

Based on the obtained results the γ -Al₂O₃ prepared with water, cyclohexane, CTAB and ethanol exhibited the highest surface area and the catalyst prepared with this support showed the best catalytic performance during the dry reforming of methane. So at final step, the textural properties of this alumina were improved by investigation of the microemulsion composition.

3.5. Different microemulsion compositions for Preparation of Al₂O₃

The partial phase diagram for the system consisting of cyclohexane, ultrapure water, mixed of CTAB and ethanol as surfactant and co-surfactant is shown in Fig. 7. Three different alumina samples were prepared by microemulsion systems shown in this diagram with composition reported in Table 2.

The XRD spectra of these three samples after calcination at 500°C for 3h are shown in Fig. 8. Four peaks at $2\theta=37.2^\circ$, 39.7° , 46.1° and 66.8° were appeared in all samples. These peaks were related to Al_2O_3 (JCPDS Card 01-1303).

The average crystallite sizes of the prepared aluminas computed by the Scherrer equation are presented in Table 3. It is seen that the catalyst supports exhibited a very high specific surface area and pore volume and small crystallite size. Different microemulsion designs seem to influence the surface area of $\gamma\text{-Al}_2\text{O}_3$. The highest surface area and the lowest crystallite size were obtained for composition in R2 point.

For the prepared samples, a typical type-IV isotherm with H2 hysteresis loop was observed (Fig. 9a), indicating that the particles are crossed by nearly cylindrical channels. The distributions of pore size for the samples are in meso region and are located between 3-18 nm.

The conversions of CH_4 and CO_2 are shown in Fig. 10a and 10b, respectively. Increasing the reaction temperature caused both the CH_4 and CO_2 conversions increased due to the endothermic nature of dry reforming of methane reaction. Besides, it is also clear that as far as water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) took place, the conversion of CO_2 is higher than that of CH_4 . As can be seen, the 10%Ni/ Al_2O_3 (2) catalyst prepared with the support with the highest surface area showed the best performance during reaction. This could be related to better dispersion of Ni on support. Short time stability test was carried out on prepared catalysts at 700°C. As can be seen, all these catalysts displayed high stability with a small decrease in CH_4 conversion over the test period of 240 min, Fig. 10c.

The SEM image of Al_2O_3 support sample (2) is shown in Fig. 11. It is seen that particles in alumina support are in nano scale.

4. Conclusions

Mesoporous nanocrystalline gamma alumina powders with high surface area were synthesized by the hydrolysis of aluminum triisopropoxide (ATI) using microemulsion templating method. The sample prepared by microemulsion consisting of water, cyclohexane, CTAB and ethanol showed a high surface area of 277.72 m²/g and total pore volume of 0.58 cm³/g. The catalytic results revealed that the prepared gamma alumina powders have a high potential as support for nickel catalysts in dry reforming. The prepared catalysts possessed a high activity without any decrease in methane conversion. Different microemulsion compositions were applied to investigate the alumina properties. The results revealed that the synthesized alumina in microemulsion containing 11, 27 and 62 wt.% of cyclohexane, CTAB + ethanol and aqueous phase exhibited the highest specific surface area and the catalysts prepared with this support showed the highest catalytic activity in dry reforming reaction.

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Fig. 1. X-ray diffraction (XRD) patterns of the Al_2O_3 samples prepared by microemulsion method.

Fig. 2. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of the samples calcined at 500°C .

Fig. 3. X-ray diffraction (XRD) patterns of the prepared catalysts calcined at 500°C .

Fig. 4. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of the catalysts calcined at 500°C .

Fig. 5. TPR profiles of the catalysts calcined at 500°C .

Fig. 6. (a) CH_4 conversion, (b) CO_2 conversion and (c) Short time stability of catalysts at 700°C , ($\text{CO}_2:\text{CH}_4=1$), $\text{GHSV} = 1.8 \times 10^4 \text{ mL}/(\text{g}_{\text{cat}}\cdot\text{h})$.

Fig. 7. The oil-in-water (O/W) microemulsion systems of oil (O), water (W), and surfactant + co-surfactant (S + C). RX: microemulsion composition X.

Fig. 8. X-ray diffraction (XRD) patterns of the prepared samples calcined at 500°C .

Fig. 9. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of the 10%Ni/ Al_2O_3 (1, 2, 3) catalysts calcined at 500°C .

Fig. 10. (a) CH_4 conversion, (b) CO_2 conversion and (c) Short time stability of the 10%Ni/ Al_2O_3 (1, 2, 3) catalysts at 700°C , ($\text{CO}_2:\text{CH}_4=1$), $\text{GHSV} = 1.8 \times 10^4 \text{ mL}/(\text{g}_{\text{cat}}\cdot\text{h})$.

Fig. 11. (a, b) SEM images of Al_2O_3 support (sample 2).

Table 1. Structural properties of the prepared samples

Alumina support samples	<i>BET surface area (m^2/g)</i>	<i>Pore volume (cm^3/g)</i>	<i>Pore size (nm)</i>	<i>Crystalline size (nm)</i>
Al ₂ O ₃ (A)	239.74	0.57	6.76	3.78
Al ₂ O ₃ (B)	260.33	0.63	7.35	6.94
Al ₂ O ₃ (C)	277.72	0.58	6.34	7.92
10%Ni/Al ₂ O ₃ (A)	210.45	0.46	6.38	8.75
10%Ni/Al ₂ O ₃ (B)	198.05	0.50	7.16	10.82
10%Ni/Al ₂ O ₃ (C)	226.94	0.49	6.20	12.59

Table 2. Different microemulsion compositions at various regions

Microemulsion region	% Cyclohexane	% CTAB + Ethanol	% Aqueous phase
R1	11	11	78
R2	11	27	62
R3	11	39	50

Table 3. Structural properties of the prepared samples

Alumina support samples	<i>BET surface area (m^2/g)</i>	<i>Pore volume (cm^3/g)</i>	<i>Pore size (nm)</i>	<i>Crystalline size (nm)</i>
1	277.72	0.58	6.34	7.92
2	308.0	0.80	7.3	4.8
3	267.95	0.81	9.46	5.35

Figure 1. X-ray diffraction (XRD) patterns of Al_2O_3 samples prepared by microemulsion method.

Figure 2. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of the samples calcined at 500°C.

Figure 3. X-ray diffraction (XRD) patterns of the prepared catalysts calcined at 500°C.

Figure 4. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of the catalysts calcined at 500°C.

Figure 5. TPR profiles of catalysts calcined at 500°C.

Figure 6. (a) CH₄ conversion, (b) CO₂ conversion and (c) Short time stability of catalysts at 700°C, (CO₂:CH₄=1), GHSV = 1.8×10⁴ mL/(g_{cat}.h).

Figure 7. The oil-in-water (O/W) microemulsion systems of oil (O), water (W), and surfactant + co-surfactant (S + C). RX: microemulsion composition X.

Figure 8. X-ray diffraction (XRD) patterns of the prepared samples calcined at 500°C.

Figure 9. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of the 10%Ni/Al₂O₃ (1, 2, 3) catalysts calcined at 500°C.

Figure 10. (a) CH₄ conversion, (b) CO₂ conversion and (c) Short time stability of 10%Ni/Al₂O₃ (1, 2, 3) catalysts at 700°C, (CO₂:CH₄=1), GHSV = 1.8×10⁴ mL/(g_{cat}.h).

Figure 11 (a, b). SEM image of Al₂O₃ support sample (2).

The nickel catalyst support on alumina prepared by microemulsion method exhibited high activity and stability in dry reforming reaction